

CERAMICS

Ceramics may be defined as nonmetallic, inorganic solids. By far the most common of terrestrial materials, ceramics in the form of sand and clay have been used for many thousands of years to make brick, pottery, and artware. Modern structural ceramics bear little resemblance to these "traditional" materials; they are made from extremely pure, microscopic powders which are consolidated at high temperatures to yield a dense, durable structure.

The Advanced Structural Ceramics Industry

The world market for advanced structural ceramics in 1983 was only \$250 million.² Of this, the Japanese market made up nearly half. These ceramics were primarily used in heat- and wear-resistant applications. The limited current markets for ceramics do not exert a strong "market pull" on the technology; at present, the situation is characterized by "technology push." In the next 10 to 15 years, however, the market opportunities for structural ceramics are expected to expand rapidly (table 1), such that by the year 2000 U.S. markets are projected variously between \$1 bil-

² B. Kenney and H. K. Bowen, "High Tech Ceramics in Japan: Current and Future Markets," *American Ceramic Society Bulletin* 62(5):590, 1983.

Table 1.—Some Future Applications of Structural Ceramics

Application	Performance advantages	Examples
Wear parts seals bearings valves nozzles	High hardness, low friction	Silicon carbide, alumina
Cutting tools Heat engines diesel components gas turbines	High strength, hot hardness Thermal insulation, high temperature strength, fuel economy	Silicon nitride Zirconia, silicon carbide, silicon nitride
Medical Implants hips teeth joints	Biocompatibility, surface bond to tissue, corrosion resistance	Hydroxylapatite, bioglass, alumina, zirconia
Construction highways bridges buildings	Improved durability, lower overall cost	Advanced cements and concretes

SOURCE: Office of Technology Assessment

lion and \$5 billion.³ This estimate reflects only the value of the ceramic materials and components, and does not include the value of the overall systems in which they are incorporated. When this multiplier effect is taken into account, a recent study has indicated that the country which leads in the development of advanced ceramics will reap large benefits in the form of jobs and economic expansion.⁴

Properties of Ceramics

The properties of some common structural ceramics are compared with those of metals in table 2. In general, ceramics have superior high-temperature strength, higher hardness, lower density, and lower thermal conductivity than metals. The principal disadvantage of ceramics as structural materials is the sensitivity of their strength to extremely small flaws, such as cracks, voids, and inclusions. Flaws as small as 10 to 50 micrometers can reduce the strength of a ceramic structure to a few percent of its theoretical strength. Because of their small sizes, the strength-controlling flaws are usually very difficult to detect and eliminate.

The flaw sensitivity of ceramics illustrates the importance of carefully controlled processing and finishing operations for ceramic components. However, even with the most painstaking efforts, a statistical distribution of flaws of various sizes and locations will always exist in any ceramic structure. Even "identically prepared" ceramic specimens will display a distribution of strengths, rather than a single value. Design with ceramics is therefore a statistical process, rather than a deterministic process, as in the case of metals. The situation is illustrated in figure 2.

The curve on the right of figure 2a represents the distribution of strengths in a batch of identically prepared ceramic components. The curve on the left is the distribution of stresses to which these

³ Greg Fischer, "Strategies Emerge for Advanced Ceramic Business," *American Ceramic Society Bulletin* 65(1):39, 1986.

⁴ Larry R. Johnson, Arvind P.S. Teotia, and Lawrence G. Hill, "A Structural Ceramic Research Program: A Preliminary Economic Analysis," Argonne National Laboratory, ANL/CNSV-38, 1983.

Table 2.—Comparison of Physical and Mechanical Properties of Common Structural Ceramics With Steel and Aluminum Alloys. SiC: silicon carbide; Si₃N₄: silicon nitride; ZrO₂: zirconia

Material	Density ^a (g/cm ³)	Room temperature strength (M Pa)	Strength ^a at 1,095° C (M Pa)	Hard ness ^b (kg/mm ²)	Thermal conductivity 250/1,100° (W/mC)
Various sintered SiC materials	3.2	340-550 (flexure)	340-550 (flexure)	2,500-2,790	85/1 75
Various sintered Si ₃ N ₄ materials . . .	2.7-3.2	205-690 (flexure)	205-690 (flexure)	1,366	17/60
Transformation toughened ZrO ₂	5.8	345-620 (flexure)	—	625-1,125	1.713.5
Steels (4100, 4300, 8600, and 5600 series)	7-8	1,035-1,380 (tensile yield)	useless	450-650	43
Aluminum alloy	2.5	415-895 (tensile yield)	useless	100-500	140-225

NOTE. 1 MPa = 145 psi = 0.102 Kg/mm².

SOURCES: ^aR. Nathan Katz, "Applications of High Performance Ceramics in Heat Engine Design," *Materials Science and Engineering* 71 227-249, 1985.

^bElaine P. Rothman, "Ultimate Properties of Ceramics and Ceramic Matrix Composites," contractor report for OTA, December 1985

components are subjected in service, The overlap between the two curves, in which the stress in service exceeds the strength of the ceramic, determines the probability that the part will fail.

There are several ways to reduce the probability of failure of the ceramic. One is to shift the strength distribution curve to the right by elimination of the larger flaws (figure 2b). A second approach is to use nondestructive testing or proof testing to weed out those components that have major flaws. This leads to a truncation of the strength distribution, as shown in figure 2c. Although proof testing of each individual component is expensive and can introduce flaws in the material which were not there originally, it is widely used in the industry today.

A third approach is to design the microstructure of the ceramic to have some resistance to fracture (increased "toughness"), and hence, some tolerance to defects. Toughness is a measure of the energy required to fracture a material in the presence of flaws. For a ceramic component under stress, the toughness determines the critical flaw size which will lead to catastrophic failure at that stress. In fact, the critical flaw size increases with the square of the toughness parameter; thus, an increase in the material toughness of a factor of 3 leads to a ninefold increase in the flaw size tolerance. Reduction in the flaw sensitivity of ceramics is especially important for applications involving a hostile environment which can introduce strength-degrading defects, and thus negate all efforts to ensure reliability by identifying or eliminating the largest preexisting flaws. Three recent developments have been shown to improve the toughness of ceramics: microstructure design,

transformation toughening, and composite reinforcement.

Microstructure Design

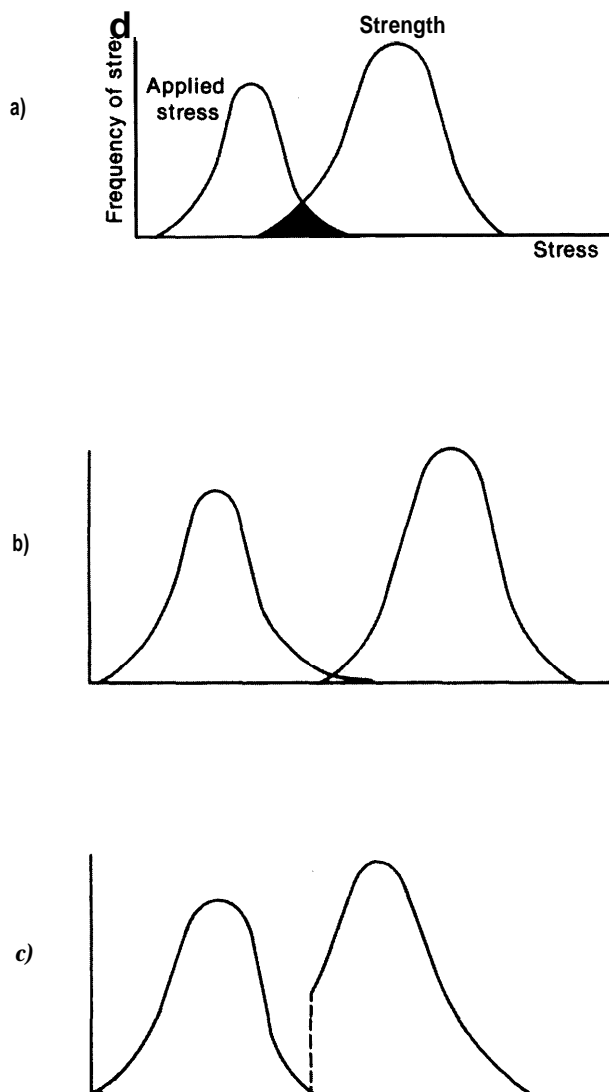
The toughness of monolithic ceramics can be improved considerably by refinement of the polycrystalline grain size and shape. The presence of elongated fibrous grains, especially in ceramics based on silicon nitride, has been shown to increase toughness by as much as a factor of 2 over other monolithic ceramics, such as silicon carbide and aluminum oxide.⁵ Numerous mechanisms have been proposed to account for the observed toughening: crack deflection, microcracking, residual stresses, crack pinning, and crack bridging. It is likely that several of these mechanisms operate simultaneously in these materials. The high toughness is accompanied by high strength, both of which result from the modified microstructure. Commercial activity in the silicon nitride-based materials is projected to expand rapidly by 1990 and many new applications should be established by 1995.

Transformation Toughening

Transformation toughening is a relatively new approach to achieving high toughness and strength in ceramics and has great potential for increasing the use of ceramics in applications requiring wear resistance. The key ceramic material is zirconium oxide (zirconia). Zirconia goes through a phase transformation from the

⁵*Nitrogen Ceramics*, F.L. Riley (ed.) (Boston and The Hague: Martinus Nijhoff Publishers, 1983).

Figure 2.—Probability of Failure of a Ceramic Component



The probability of failure of a ceramic component is the overlap between the applied stress distribution and the material strength distribution, as shown in (a). This probability can be reduced by reducing the flaw size (b), or truncation of the strength distribution through proof testing (c).

SOURCE R. Nathan Katz, "Applications of High Performance Ceramics in Heat Engine Design," *Materials Science and Engineering* 71:227,249, 1985

tetragonal to the monoclinic crystal form while cooling through a temperature of about 1,1500 C (2,102° F). This phase transformation is accompanied by an increase in volume of 3 percent, similar to the volume increase that occurs when water freezes. By control of composition, particle size,

and heat treatment cycle, zirconia can be densified at high temperature and cooled such that the tetragonal phase is maintained down to room temperature. When a load is applied to the zirconia and a crack starts to propagate, the high stresses in the vicinity of the crack tip catalyze the transformation of adjacent tetragonal zirconia grains to the monoclinic form, causing them to expand by 3 percent. This expansion of the grains around the crack tip compresses the crack opening, preventing the crack from propagating. The result is a ceramic that is both tough and strong.

Ceramic Matrix Composites

A variety of ceramic particulate, whiskers (high-strength single crystals with length-to-diameter ratios of 10 or more), and fibers maybe added to the host matrix material to generate a composite with improved fracture toughness. The presence of these additives appears to frustrate the propagation of cracks by at least three mechanisms. First, when the crack tip encounters a particle or fiber which it cannot easily break or get around, it is deflected off in another direction. Thus, the crack is prevented from propagating cleanly through the structure. Second, if the bond between the reinforcement and the matrix is not too strong, crack propagation energy can be absorbed by "pullout" of the fiber from its original location. Finally, fibers can bridge a crack, holding the two faces together, and thus preventing further propagation.

Table 3 presents the fracture toughness and critical flaw sizes (assuming a typical stress of 700 MPa, or about 100,000 psi) of a variety of ceramics and compares them with some common metals. The toughness of monolithic ceramics generally falls in the range 3 to 6 MPa-m^{1/2}, corresponding to a critical flaw size of 18 to 74 micrometers. With transformation toughening or whisker dispersion, the toughness can be increased to 8 to 12 MPa-m^{1/2} (critical flaw size 131 to 294 micrometers); the toughest ceramic matrix composites are continuous fiber-reinforced glasses, at 15 to 25 MPa-m^{1/2}. It is important to note that in the latter composites the strength appears to be independent of preexisting flaw size, and is thus an intrinsic material property. Metals such as steel have toughnesses above 40 MPa-m^{1/2} (some al-

Table 3.—Fracture Toughness and Critical Flaw Sizes of Monolithic and Composite Ceramic Materials Compared With Metals.^a
 A1203: alumina; LAS: lithium aluminosilicate; CVD: chemical vapor deposition

Material	Fracture toughness (MPa·m ^{1/2})	Critical flaw size (micrometers)
Conventional microstructure:		
Al ₂ O ₃	3.5-4.0	25-33
Sintered SiC	3.0-3.5	18-25
Fibrous or interlocked microstructure:		
Hot pressed Si ₃ N ₄	4.0-6.0	33-74
Sintered Si ₃ N ₄	4.0-6.0	33-74
SiA10N	4.0-6.0	33-74
Particulate dispersions:		
Al ₂ O ₃ -TiC	4.2-4.5	36-41
SiC-Ti B ₂		
Si ₃ N ₄ -TiC	4.5	41
Transformation toughening:		
ZrO ₂ -MgO	9-12	165-294
ZrO ₂ -Y ₂ O ₃	6-9	74-165
A1203-zrO2	6.5-15	86-459
Whisker dispersions:		
Al ₂ O ₃ -SiC	8-10	131-204
Fiber reinforcement: ^b		
SiC in borosilicate glass	15-25	
SiC in LAS	15-25	
SiC in CVD SiC	8-15	
Aluminum ^c	33-44	
Steel ^c	44-66	

^aAssumes a stress of 700 MPa (-100,000 psi).

^bThe strength of these composites is independent of preexisting flaw size.

^cThe toughness of some alloys can be much higher.

SOURCES David W. Richerson, "Design, Processing Development, and Manufacturing Requirements of Ceramics and Ceramic Matrix Composites," contractor report for OTA, December 1985, and Elaine P. Rothman, "Ultimate Properties of Ceramics and Ceramic Matrix Composites," contractor report for OTA, December 1985

loys may be much higher), more than 10 times the values of monolithic ceramics.

The critical flaw size gives an indication of the minimum flaw size which must be reliably detected by any nondestructive test in order to ensure reliability of the component. Most NDE methods cannot reliably detect flaws smaller than about 100 micrometers, corresponding to a toughness of about 7 MPa·m^{1/2}. Toughnesses of 10 to 12 MPa·m^{1/2} would be desirable for most components.

Ceramic Coatings

The operation of machinery in hostile environments (e. g., high temperatures, high mechanical loads, or corrosive chemicals) often results in performance degradation due to excessive wear and

friction, and productivity losses due to shutdowns caused by component failure. Frequently, the component deterioration can be traced to deleterious processes occurring in the surface region of the material. To reduce or eliminate such effects, ceramic coatings have been developed to protect or lubricate a variety of substrate materials, including metals, ceramics, and cermets (ceramic-metal composites).

The coating approach offers several advantages. One is the ability to optimize independently the properties of the surface region and those of the base material for a given application. A second advantage is the ability to maintain close dimensional tolerances of the coated workpiece, since very thin coatings (of the order of a few micrometers) are often sufficient for a given application. Further, cost savings are obtained by using expensive, exotic materials only for thin coatings and not for bulk components. This can contribute to the conservation of strategically critical materials. Finally, it is often cheaper to recoat a worn part than to replace it.

In view of these advantages, it is not surprising that ceramic coatings have found wide industry acceptance. For example, coatings of titanium nitride, titanium carbide, and alumina can enhance the useful life of tungsten carbide or high speed steel cutting tools by a factor of 2 to 5.⁶ In 1983, annual sales of coated cutting tools reached about \$1 billion.⁷ Ceramic coatings are also finding wide applications in heat engines. Low thermal conductivity zirconia coatings are now being tested as a thermal barrier to protect the metal pistons and cylinders of advanced diesel engines. In turbine engines, insulative zirconia coatings improve performance by permitting combustion gas temperatures to be increased by several hundred degrees (F) without increasing air-cooled component metal temperatures or engine complexity.⁸ Ceramic coatings have also been used to provide an oxidation barrier on turbine blades and rings.

⁶David W. Richerson, "Design, Processing Development, and Manufacturing Requirements of Ceramics and Ceramic Matrix Composites," contractor report prepared for the Office of Technology Assessment, December 1985.

⁷U. S. Department of Commerce, Bureau of the Census, Census of Manufacturing, Fuels, and Electric Energy Consumed, 1984.

⁸Tom Strangman, Garrett Corp., personal communication, August 1986.

Progress in the use of ceramic coatings in these and other applications suggest that further research on new coatings and deposition processes is likely to yield a high payoff in the future.

Design, Processing, and Testing of Ceramics

It is in the nature of advanced structural materials that their manufacturing processes are additive rather than subtractive. They are not produced in billets or sheets which are later rolled, cut, or machined to their final shape. Rather, the goal is always to form the material to its final shape in the same step in which the microstructure of the material itself is formed. Because of the severity of joining problems, the designer is always conscious of the need to consolidate as many components as possible together in a single structure. To be sure, these goals are not always realized, and expensive grinding or drilling is often required. However, to a great extent, the promise of the advanced materials lies in the possibility of net shape processing, thereby eliminating expensive finishing and fastening operations.

Ceramics Design

Designing with ceramics and other brittle materials is much different from designing with metals, which are much more tolerant of flaws. In practice, ceramic structures always contain a distribution of flaws, both on the surface and in the bulk. Ceramic designs must avoid local stress concentrations under loading which may propagate cracks originating at the flaws.

Two serious barriers to the use of ceramics are the lack of knowledge among designers of the principles of brittle material design, and the poor characterization of ceramic materials of interest. Greater emphasis needs to be placed on brittle materials in college curricula. Courses at the college level and minicourses for continuing education on design for brittle materials should be offered and publicized. '

The characterization of commercially available ceramics for design purposes is generally poor. The poor quality of the data is due to the fact that mechanical, thermal, and chemical properties of ceramic materials vary with the method of manufacture as well as test method. Both carefully controlled and documented processing procedures and standard test methods will be required to give designers the confidence that consistent properties at a useful level can be obtained at a predictable cost.

Computer-aided design (CAD) techniques have become essential to the design process, particularly in the analysis of mechanical stresses, thermal stresses, and life prediction of the part in service. Sophisticated software to calculate mechanical and thermal stresses is available; however, these programs require detailed data on properties such as thermal expansion coefficient, heat capacity, and elastic modulus, which often are not available. Current techniques for predicting the service life of ceramics are limited by lack of data on the behavior of these materials in various environments of interest. These techniques are especially unreliable in high temperature, high stress regimes where several failure mechanisms are operating simultaneously.¹

It is not particularly unusual that there should be a lack of reliable design data in a field like structural ceramics, which is very new and which is constantly producing new materials. It can even be argued that the imposition of codes and specifications would be premature, given that there is no consensus on the best materials or processes. Although there is a danger in narrowing the field too soon, there is also a danger in keeping it general for too long. It may be appropriate to choose one or two materials which seem most promising and concentrate on producing uniform, high-quality components from these. Silicon carbide and silicon nitride would be two possible candidates, because they have already received a large amount of research funding over the years for heat engine applications. These materials have a broad range of potential uses, but designers cannot compare them or use them without a reliable data-

¹Specific proposals to improve ceramics education are given in the Report of the Research Briefing Panel on Ceramics and Ceramic Composites (Washington, DC: National Academy Press, 1985).

IOR, Nathan Katz, "Applications of High Performance Ceramics in Heat Engine Design," *Materials Science & Engineering* 71 :227-249, 1985.

base on standard compositions having specified properties.

Processing of Ceramics

The production of most ceramics, including traditional and advanced ceramics, consists of the following four basic process steps: powder preparation, forming, densification, and finishing. The most important variations on these steps are given in table 4.

Powder Preparation.—Although the basic ceramic raw materials occur abundantly in nature, they must be extensively refined or processed before they can be used to fabricate structures. The entire group of silicon-based ceramics (other than silica) does not occur naturally. Silicon carbide, silicon nitride, and sialon (an “alloy” of silicon nitride with aluminum oxide in which aluminum and oxygen atoms substitute into silicon and nitrogen lattice positions, respectively) compositions must all be fabricated from gases or other ingredients. Even minerals which occur naturally, such as bauxite, from which alumina is made, and zircon sands, from which zirconia is derived, must be processed before use to control purity, particle size and distribution, and homogeneity.

In recent years, the crucial importance of powder preparation has been recognized. Particle sizes

and size distributions are critical in advanced ceramics to produce uniform green (unfired) densities, so that rearrangement can occur to produce a fully dense, sintered, ceramic part.

Various dopants or sintering aids are added to ceramic powders during processing. Sinterability can be enhanced with dopants, which can control particle rearrangement and diffusivities. These dopants allow sintering at lower temperatures and/or faster rates. Dopants are also used to control grain growth or achieve higher final densities. The use of dopants, while providing many beneficial results, can also influence the material's properties. Segregation of dopants at the crystalline grain boundaries can weaken the final part, and final properties such as conductivity, strength, etc., may differ significantly from those of the “pure” material.

Forming.—Ceramic raw materials must be formed and shaped before firing. The forming process often determines the final ceramic properties. The processing variables in the forming step affect particle shape, particle packing and distribution, phase distribution, location of pores, shrinkage, and dry and fired strength.

Forming processes for ceramics are generally classified as either cold or hot forming. The major cold forming methods include slip casting, extrusion, dry pressing, injection molding, tape casting, and variations. The product of cold forming techniques is called a “green body,” which may be machined before firing. The homogeneity of the cold formed part determines the uniformity of shrinkage during firing.

Hot forming methods combine into one step the forming and sintering operation to produce simple geometric shapes. These techniques include hot pressing and hot isostatic pressing.

Densification.—Sintering is the primary method for converting loosely bonded powder into a dense ceramic body. Sintering involves consolidation of the powder compact by diffusion on an atomic scale. Moisture and organics are first burned out from the green body and then, at the temperature range where the diffusion process occurs, matter is moved from the particles into the void spaces between the particles, causing densification and resulting in shrinkage of the part.

Table 4.—Common Processing Operations for Advanced Ceramics

Operation	Method	Examples
Powder preparation	Synthesis	SiC
	Sizing	Si ₃ N ₄
	Granulating	ZrO ₂
	Blending	
	Solution chemistry	Glasses
Forming	Slip casting	Combustors, stators
	Dry pressing	Cutting tools
	Extrusion	Tubing, honeycomb
	Injection molding	Turbocharger rotors
	Tape casting	Capacitors
	Melting/casting	Glass ceramics
Densification	Sintering	Al ₂ O ₃
	Reaction bonding	Si ₃ N ₄
	Hot pressing	Si ₃ N ₄ , SiC, BN
	Hot isostatic pressing	Si ₃ N ₄ , SiC
Finishing	Mechanical	Diamond grinding
	Chemical	Etching
	Radiation	Laser, electron beam
	Electric	Electric discharge

SOURCE: Office of Technology Assessment

Combined with forming techniques such as slip casting, sintering is an economic method for producing intricate ceramic components. Its drawback lies in the need to use additives and long sintering times to achieve high densities. The complications introduced by the additives have been noted above in the discussion of powders.

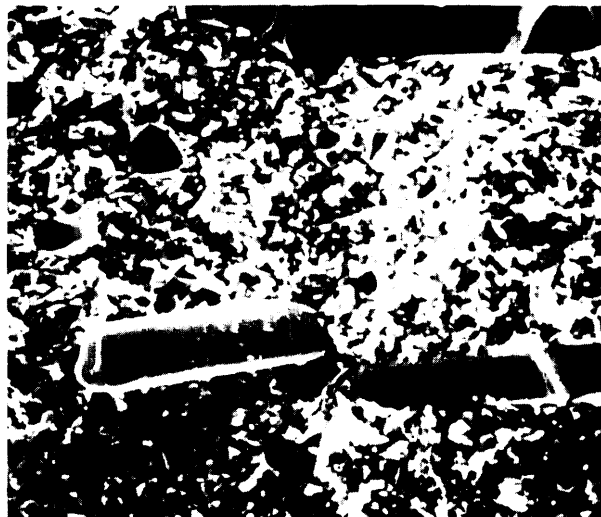
Finishing.—These techniques include grinding and machining with diamond and boron nitride tools, chemical etching, and laser and electric discharge machining. The high hardness and chemical inertness of densified ceramics make the finishing operations some of the most difficult and expensive in the entire process. Grinding alone can account for a large fraction of the cost of the component. In addition, surface cracks are often introduced during machining, which reduce the strength of the part and the yields of the fabrication process.

Near Net Shape Processing (NNSP).—This describes any forming process which gives a final product that requires little or no machining. Typically, ceramics shrink to about two-thirds of their green volume upon sintering. This shrinkage makes it extremely difficult to fabricate ceramics to final net shape. However, if the green ceramic is machined prior to densification, a near net shape part can be obtained. Hot isostatic pressing and ceramic coatings also yield parts which do not require subsequent machining.

Near net shape processes which are currently used for metals include powder metallurgy and advanced casting techniques. Since metals are in direct competition with ceramics in many applications, near net shape processing of ceramics will continue to be a high priority research area which will be critical to their cost competitiveness,

Ceramic Matrix Composites

Ceramic matrix composites may consist of continuous fibers oriented within a ceramic matrix, ceramic whiskers randomly oriented within a ceramic matrix, or dissimilar particles dispersed in a matrix with a controlled microstructure. The potential benefits of ceramic composites include increased fracture toughness, hardness, and improved thermal shock resistance. Processing methods for particulate-reinforced composites are similar to those for monolithic ceramics.



50 μ M

Photo credit: Los Alamos National Laboratory

Fracture surface of a composite formed by hot-pressing silicon nitride powder with 30 percent by volume silicon carbide whiskers.

Whisker Reinforcement.—Ceramic whiskers are typically high-strength single crystals with a length at least 10 times the diameter. Silicon carbide is the most common whisker material. Current dispersed whisker composites are fabricated by uniaxial hot pressing, which substantially limits size and shape capabilities and requires expensive diamond grinding to produce the final

part. Hot isostatic pressing (HIP) has the potential to permit fabrication of complex shapes at moderate cost, but procurement of expensive capital equipment and extensive process development are required.

Continuous Fiber Reinforcement.—The primary fibers which are available for incorporation into a ceramic or glass matrix are carbon, silicon carbide, aluminum borosilicate, and mullite. Currently, glass matrix composites are more developed than their ceramic analogs. These composites are far tougher than unreinforced glasses (tensile strength 100 to 1,300 F (593° to 704° C). Service temperatures up to 2,000 to 2,200 F (1,093 to 1,204 C) may be obtained with “glass-ceramic” matrices which crystallize upon cooling from the process temperature.¹¹ Carbon matrix composites have the highest potential use temperature of any ceramic, exceeding 3,500 F (1,927° C). However, these composites oxidize readily in air at temperatures above about 1,100° F (593 C), and require protective ceramic coatings if they are to be used continuously at high temperature.¹²

¹¹Karl M. Prewo, J. J. Brennan, and G.K. Layden, “Fiber-Reinforced Glasses and Glass-Ceramics for High Performance Applications,” *American Ceramic Society Bulletin* 65(2):305, 1986.

¹²Joel Clark, et al., “Potential of Composite Materials To Replace Chromium, Cobalt, and Manganese in Critical Applications,” contractor report prepared for the Office of Technology Assessment, 1984.



Photo credit: United Technologies Research Center

Tensile fracture surface for
NicalonSiC fiber-reinforced glass-ceramic

Fabrication of continuous fiber ceramic composites is currently of a prototype nature and very expensive. Several approaches are under development:

- The fibers are coated with ceramic or glass powder, laid up in the desired orientation, and hot pressed. Fibers or woven cloth are laid up, then are infiltrated by chemical vapor deposition (CVD) to bond the fibers together and fill in a portion of the pores.
- Fibers are woven into a three-dimensional preform, then infiltrated by CVD.
- A fiber preform is infiltrated with a ceramic-yielding organic precursor, then heat treated to yield a ceramic layer on the fibers. This process is repeated until the pores are minimized.

Considerable research and development will be necessary to optimize fabrication and to decrease the cost to levels acceptable for most commercial applications.

Ceramic Coatings

Many different processes are in use for the fabrication of ceramic coatings and for the modification of surfaces of ceramic coatings and of monolithic ceramics. Table 5 lists some of the more important techniques. The choice of a particular deposition process or surface modification process depends on the desired surface properties. Table 6 lists some of the coating characteristics and properties which are often considered desirable. Additional considerations which can influence the choice of coating process include: the purity, physical state, and toxicity of the material to be deposited; the deposition rate; the maximum temperature which the substrate can reach; the substrate treatment needed to obtain good coating adhesion; and the overall cost.

For most coating processes, the relationships between process parameters and coating properties and performance in various environments are poorly understood. Coating providers tend to rely on experience gained empirically. Work is in progress to establish these relationships for certain processes, e.g. ion beam- or plasma assisted-physical vapor deposition. However, in view of

Table S.—Selected Processes for the Production of Ceramic Coatings and for the Modification of Ceramic Surfaces

Process category	Process class	Process
Ceramic coating processes:		
Low gas pressure ("vacuum") processes	Chemical vapor deposition (CVD)	Pyrolysis Reduction (plasma assisted) Decomposition (plasma assisted) Polymerization (plasma induced)
	Physical vapor deposition (PVD)	Evaporation (reactive, plasma assisted) Sputtering (reactive, plasma assisted) Plasma-arc (random, steered) Ion beam assisted co-deposition
	Low pressure plasma spraying	Plasma discharge spraying
Processes at elevated gas pressures	Plasma spraying	Plasma arc spraying
	Flame spraying	Combustion flame spraying
Liquid phase epitaxy processes	Wetting process	Dip coating (e.g., Sol-Gel) Brush coating
	Spin-on coatings	Reverse-roller coating
Electrochemical processes	Electrolytic deposition	Cation deposition
	Electrophoretic deposition	Charged colloidal particle deposition
	Anodization	Anion oxidation in electrolytes
	Electrostatic deposition	Charged liquid droplet deposition
Processes for the modification of ceramic surfaces:		
Particle implantation processes	Direct particle implantation	Energetic ion or atom implantation in solids
	Recoil particle implantation	Recoil atom (ion) implantation in solids
Densification and glazing processes	Laser beam densification and glazing	CW-laser power deposition Pulsed-laser power deposition
	Electron beam densification and glazing	Energetic electron beam power deposition
	Gaseous anodization processes	Ion nitriding Ion carburizing Plasma oxidation
Chemical reaction processes	Disproportionation processes	Deposition of molecular species Formed in gas phase
	Thermal diffusion	Diffusion of material from surface into bulk of substrate
Conversion processes	Chemical etching	Acidic solutions; lye etching
Etching processes	Ion etching	Sputter process
	Grinding	
Mechanical processes	Peening	
	Polishing	

SOURCE: Manfred Kaminsky Surface Treatment Science International, Hinsdale, IL

the current widespread use of coated machinery components, and projected future requirements for components with advanced coatings, research in processing science for ceramic coatings remains an important priority. In addition, improved deposition processes are required, particularly for the coating of large components or those having a complex shape.

Chemically Bonded Ceramics

Hardened cement pastes and concretes fall in the category of chemically bonded ceramics (CBCs), because they are consolidated through chemical reactions at ambient temperatures rather than through densification at high temperature. Due to their low strength compared with dense

Table 6.—Characteristics and Properties of Ceramic Coatings Often Considered Desirable

Good adhesion
 Precise stoichiometry (negligible contamination)
 Very dense (or very porous) structural morphology
 Thickness uniformity
 High dimensional stability
 High strength
 High fracture toughness
 Internal stresses at acceptable levels
 Controlled density of structural defects
 Low specific density
 High thermal shock resistance
 High thermal insulating properties
 High thermal stability
 Low (or high) coefficient of friction
 High resistance to wear and creep
 High resistance to oxidation and corrosion
 Adequate surface topography

SOURCE Manfred Kaminsky, Surface Treatment Science International, Hinsdale, IL.

ceramics, concrete and other cementitious materials are not normally considered "advanced." However, in recent years, new processing methods have led to significant improvements in the strength of chemically bonded ceramics, and further development will provide additional improvements. In fact, the ultimate limits on tensile and compressive strength have not yet been approached.

Cements.—Cements are chemically active binders which may be mixed with inert fillers such as sand or gravel to form concrete. Cement pastes containing minor additives such as organic polymers can also be used as structural materials. By far the most common cement used in making CBCs is portland cement. Portland and related cements are hydraulic; i.e., they react with water to form an relatively insoluble aggregate. In hydraulic cements, excess water is usually added to improve the working characteristics, but this causes the hardened structures to be porous (the minimum porosity of fully hydrated cements is about **28** percent)¹³ and of low strength. In a recent advance, a high-shear processing technique together with pressing or rolling are used to remove pores from a low-water calcium aluminate cement paste containing 5 to 7 percent by weight organic polymers to improve workability. The dense paste, which is sometimes called macro-defect-free or MDF cement, has the consistency

¹³Richard A. Helmuth, Portland Cement Association, personal communication, August 1986.

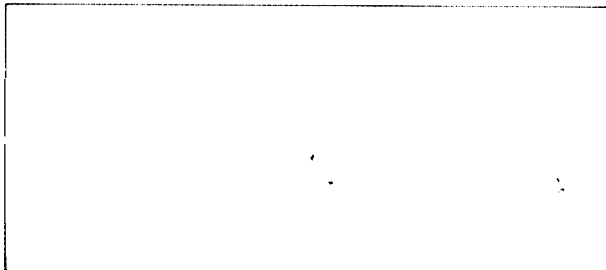
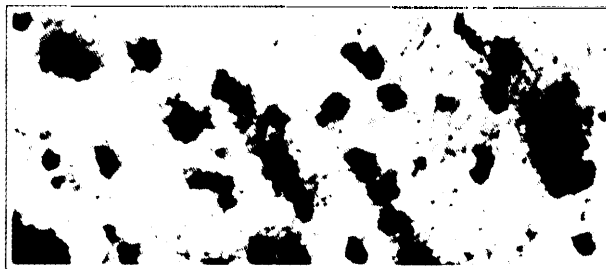


Photo credits" Imperial Chemical Industries PLC

Top photo: Conventional Portland cement paste microstructure, showing large flaws (pores).
 Bottom photo: Advanced cement paste microstructure, illustrating the absence of large pores (magnification x100).

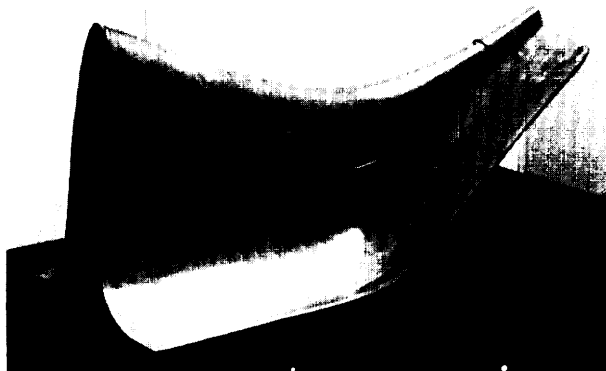


Photo credit" CEMCOM Research Associates, Inc

This tool, made from a cement-based composite, is used for autoclave forming of a fiber-epoxy jet engine component.

of cold modeling clay, and can be molded or extruded by techniques similar to those used for plastics. The hardened cement paste has a strength approaching that of aluminum (table 7) and much lower permeability than ordinary portland cement paste. ¹⁴Although MDF cement pastes cost 20 to

¹⁴According to product literature supplied by Imperial Chemical Industries, "New Inorganic Materials."

Table 7.—Comparison of the Mechanical Properties of Various Cements and Aluminum

Material	Density (g/cm ³)	Flexural strength (psi) ^a	Compressive strength (psi)	Fracture energy (J/m ²)
Portland cement paste	1.6-2.0b	725-1,450	4,000-5,000 ^c	20
Cement/asbestos	2.3	5,075		300
Advanced cements ^c	2.3-2.5	14,500-21,750	22,000-36,000	300-1,000
Aluminum	2.7	21,750-58,000	42,000	10,000

^a1 MPa = 145 psi.

^bAccording to information supplied by the Portland Cement Association

^cThe advanced cement has the following composition. 100 parts high alumina cement; 7 parts hydrolyzed Poly (vinylacetate), 10-12 parts water

SOURCE Imperial Chemical Industries.

30 cents per pound compared with portland cement paste at 3 cents per pound, they are still significantly cheaper than metals and plastics.

Processing of hydraulic CBCs is very cheap, since it involves only adding water, mixing, casting or molding, and allowing the material to set at room temperature or slightly elevated temperature. Very little dimensional change occurs during the set and cure, so that parts can be made to net shape. Due to the low processing temperature, a wide variety of reinforcing fibers can be considered, including metal fibers. Further work is needed to improve the long term stability of these materials, and the presence of organics makes them unsuitable for use above about **2000 F (93° C)**.

Concrete.—As chemical additives, such as organic polymers, have improved the properties of cement pastes, chemical and mineral additives have had a similar effect on concrete. Minerals such as fly ash and microscopic silica particles help to fill in the pores in the concrete and actually improve the bonding in the cementitious portion. This results in greater strength and reduced permeability. In a recently developed concrete, molten sulfur is used as a binder in place of cement. Sulfur concrete has superior corrosion resistance in acidic environments and can be recycled by remelting and recasting without loss of the mechanical properties.

The compressive strength of typical concretes today is around 5,000 psi (34 MPa), although concretes with strengths of 10,000 to 15,000 psi (69 to 103 MPa) are becoming common. Under laboratory conditions, compressive strengths of at least 45,000 psi (310 MPa) have been achieved,

“W. C. McBee, T.A. Sullivan, and H.L. Fike, “Sulfur Construction Materials,” Bulletin 678, U.S. Department of the Interior, Bureau of Mines, 1985.

and there is no indication that the ultimate strength is being approached.¹⁶ In concrete high-rise buildings, the higher compressive strengths permit use of smaller columns, with consequent savings in space and materials.

Two deficiencies in concrete as a structural material are its low tensile strength and low toughness. A typical concrete has a tensile strength below 1,000 psi (7 MPa). Steel reinforcement bars are added to the concrete to provide tensile strength. In prestressed concrete, high strength steel wires under tension are used to keep the concrete in a state of compression. To improve strength and toughness, a variety of reinforcing fibers, including steel, glass, and polymers, have been tried, with varying degrees of success. Fiber reinforcement can increase the flexural strength by a factor of 2.5 and the toughness by a factor of 5 to 10 above unreinforced materials.¹⁸ This technology, which dates back to the straw-reinforced brick of the ancient Egyptians, requires fiber concentrations which are sufficiently low (usually 2 to 5 percent by volume) to preserve the flow characteristics of the concrete, and a chemically stable interface between the fiber and the concrete over time. Asbestos fibers served this function for many years; however, because of the health hazards, new fibers are being sought. A fully satisfactory reinforcing fiber for concrete has yet to be discovered.

Nondestructive Evaluation (NDE) of Ceramics

Nondestructive evaluation refers to techniques for determining properties of interest of a struc-

¹⁶Sidney Mindess, “Relationships Between Strength and Microstructure for Cement-Based Materials: An Overview,” *Materials Research Society Symposium Proceedings*, 42:53, 1985.

¹⁷Ibid.

¹⁸American Concrete Institute, “State-of-the-Art Report on Fiber-Reinforced Concrete,” Report No. ACI 544.11 <-82, 1982.

ture without altering it in any way. NDE has historically been utilized for flaw detection in ceramic materials to improve the reliability of the final product. In the future, NDE will be utilized for defect screening, material characterization, in-process control, and lifecycle monitoring. These techniques will be applied to the starting materials, during the process, and to the final product.

A key goal for the future will be the evolution of NDE techniques amenable to automation and computerization for feedback control. Powder and green body characterization will be critical for materials processed from powders. For in-process characterization, the relation between measurable quantities, obtained through the use of contact or noncontact sensors, and desired properties is crucial. This will require developments in sensor technology as well as theories which can quantitatively relate the measured NDE signal to the properties of interest.

In the past, a great deal of emphasis has been placed on the sensitivity of an NDE technique, i.e., the size of the smallest detectable flaw. A more relevant criterion for reliability purposes is perhaps the size of the largest flaw that can go undetected. There has been very little emphasis on the reliability of NDE techniques, i.e. the probability of detecting flaws of various sizes. Experience has shown that most quality problems result not from minute flaws, but from relatively gross undetected flaws introduced during the fabrication process.¹⁹

¹⁹R Nathan Katz and Alfred L. Broz, "Nondestructive Evaluation Considerations for Ceramics and Ceramic Matrix Composites," contractor report prepared for the Office of Technology Assessment, November 1985.

Cost of production estimates for high performance ceramic components typically cite the inspection costs as approximately 50 percent of the manufacturing cost.²⁰ Successful NDE techniques for ceramic components should meet two major criteria: they should reliably detect gross fabrication flaws to ensure that the material quality of the component is equal to that of test specimens, and they should be able to evaluate the quality of a complex-shaped component in a practical manner. No single NDE technique for ceramics completely satisfies these criteria. However, those which could be cost-effective for production level inspections are described in table 8.

Health Hazards

The most serious health hazard associated with ceramics appears to be associated with ceramic fibers. Studies carried out at the National Cancer Institute have indicated that virtually all durable, mineral fibers having a diameter of less than 1 micrometer are carcinogenic when introduced into the lining of the lung of laboratory rats.²¹ The carcinogenicity drops with increasing diameter, such that fibers having diameters greater than 3 micrometers do not produce tumors. Recent studies on commercially available aluminosilicate fibers suggest that animals exposed to the fibers develop an increased number of lung cancers over time compared with a control group.²² No data on the effects of ceramic fibers on humans are available, and no industry standards for allowable fiber concentrations in the workplace have been estab-

²⁰Ibid.

²¹Mearl F. Stanton, et al., *Journal of the National Cancer Institute* 67:965-975, 1981.

²²Philip J. Landrigan, M.D., The Mount Sinai Medical Center, personal communication, August 1986.

Table 8.—Comparison of Some Possible Production-Level NDE Techniques for Structural Ceramics

NDE technique	Detected flaw type	Sensitivity	Adaptability to complex shapes	Extent of development required for commercialization
Visual (remote)	surface	fair	good	none
Dye penetrant	surface	good	good	none
Radiographic	bulk	1-20/0 of specimen thickness	excellent	none
Ultrasonic	bulk and surface	good	poor	some
Holographic	surface	good	fair	large
Thermographic.	surface	poor	excellent	some
Proof test	any	good, but may introduce flaws	excellent	none

SOURCE: Office of Technology Assessment

lished. Until such data become available, the animal studies suggest that these fibers should be considered carcinogenic, and treated in a manner similar to asbestos fibers.

Applications of Structural Ceramics

Figure 3 shows an estimated timetable for the introduction of ceramic products in various categories. It shows that some advanced structural ceramics are in production, others have near-term potential for production, and some are far away from production.

Current Production

Ceramics such as alumina, silicon nitride, and silicon carbide are already well established in production for many structural applications in the categories of wear parts, cutting tools, bearings, and coatings. The ceramics portion of the market is currently small (generally less than 5 percent).²³ Substantial growth in ceramics production is expected to occur over the next 25 years by growth of the overall markets, by achieving an increase in the market share, and by spin-off applications.

Ceramics are also in limited production (in Japan) in discrete engine components such as turbochargers, glow plugs, and precombustion chambers. Current military applications include radomes, armor, infrared windows, and heat sources.

Funding for known near-term markets is currently being provided by industry. Much of the funding is directed toward development of new or improved ceramic or ceramic matrix composite materials. Key objectives are to achieve improved toughness, higher reliability, and decreased cost. Development of silicon nitride, transformation toughened ceramics, and composites has yielded materials with enhanced toughness and reliability, but costs are still high and reliability remains a problem. Progress in resolving these limitations is occurring, and large increases in the market share for ceramics are projected.

²³U.S. Department of Commerce, *A Competitive Assessment of the U.S. Advanced Ceramics Industry* (Washington, DC: U.S. Government Printing Office, March 1984), pp. 38-39.

The United States is competing with other countries, especially Japan, for the growing markets. Japan has a well-coordinated effort which includes: increasing the quality and availability of the raw materials; conducting material fabrication process optimization; installing the most advanced processing and quality control equipment for prototype and production facilities; and aggressively marketing their evolving materials.

Near-Term Production

Near-term production is projected in advanced construction products, bearings, bioceramics, heat exchangers, electrochemical devices, isolated components for internal combustion engines, and military applications. The technology feasibility has generally been demonstrated, but scale-up, cost reduction, or design optimization are required. Although much of the feasibility demonstration has occurred in the United States, foreign industry and government-industry teams, particularly in Japan, have more aggressive programs to commercialize the near term applications. Large markets are at stake; for example, the world market for all biocompatible materials has been projected to be as much as \$6 billion by the year 1995²⁴; ceramics could capture 25 to 30 percent of this. 25 Foreign dominance of these markets would adversely affect the U.S. balance of trade. Government, industry, and universities need to team together in focused programs to solve the remaining problems and achieve production capability competitive with that of foreign countries.

Long-Term Applications

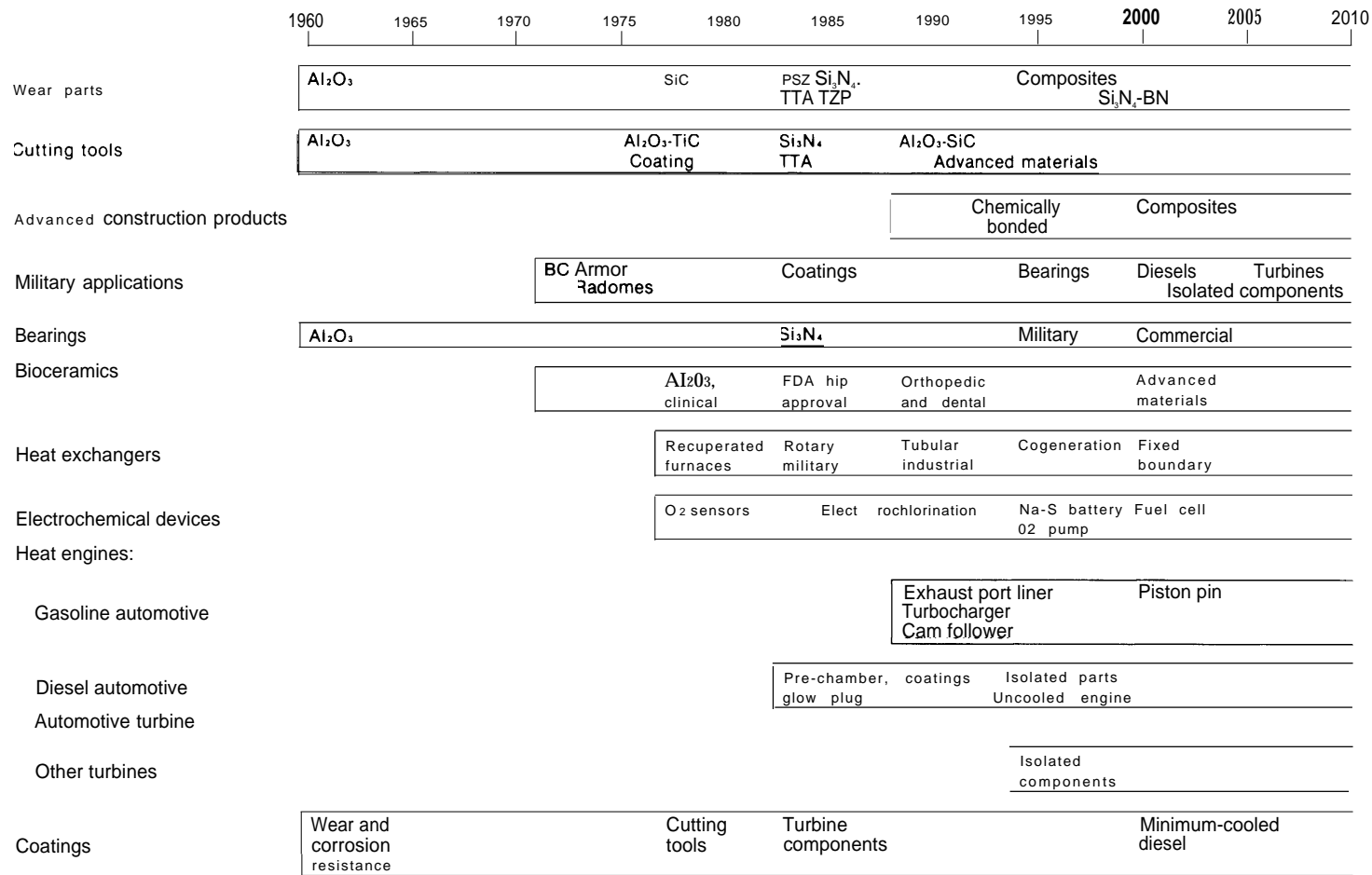
Some potential applications of ceramics require solution of major technical and economic problems. These high risk applications are categorized as long term (greater than 15 years away). The ultimate payoff may be large, but it is not possible to predict confidently that the problems will be overcome to achieve the benefits.

Long-term applications include the automotive gas turbine engine, the advanced diesel, some elec-

²⁴Larry L. Hench and June Wilson, "Biocompatibility of Silicates for Medical Use," *Silicon Biochemistry*, CIBA Foundation Symposium No. 121 (Chichester: John Wiley & Sons, 1986), pp. 231-246.

²⁵Larry L. Hench, University of Florida, personal communication, August 1986.

Figure 3i.—Estimated Scenario for Implementation of Ceramic Components in Structural Application Categories



SOURCE: David W. Richerson, "Design, Processing Development, and Manufacturing Requirements of Ceramics and Ceramic Matrix Composites," contractor report prepared for the Office of Technology Assessment, December 1985.

trochemical devices such as fuel cells, some heat exchangers, and some bearings. A variety of other turbines, especially those for aircraft propulsion and utility scale power generation, should also be categorized as long term.

Substantial design, material property, and manufacturing advances are necessary to achieve production of applications in the long-term category. In general, risk is perceived by industry to be too high and too long range to justify funding the needed developments. Advancement will likely be driven by government funding. In many of these categories, military use will predate commercial use.

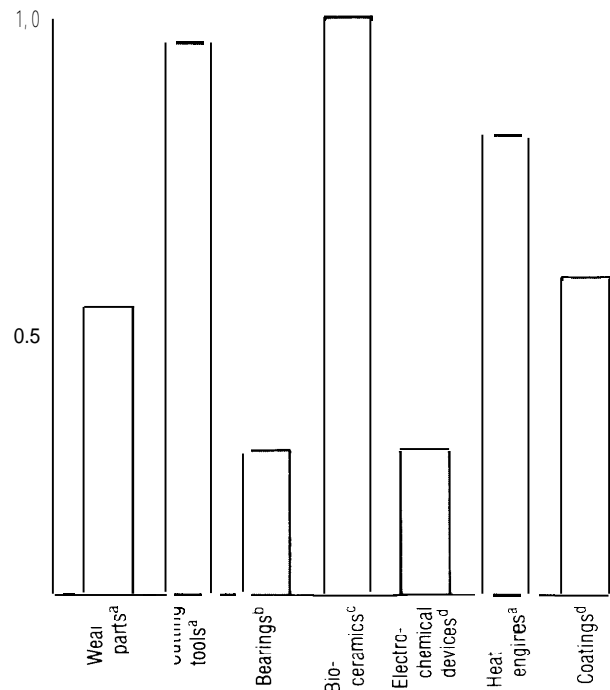
Markets for Advanced Structural Ceramics

Estimated U.S. markets in the year 2000 for several of the categories listed above are shown in figure 4.

Wear Parts.—Wear parts include such applications as seals, valves, nozzles, wear pads, grinding wheels, and liners. The Department of Commerce has estimated that by the year **2000** ceramics could capture roughly **6** percent of the wear parts market, currently dominated by tungsten carbide cermets, and specialty steels. With the total market estimated at \$9 billion, the ceramic portion would be **\$540 million**.²⁶

Cutting Tools .—Ceramics have demonstrated a capability as a cutting tool, especially in competition with tungsten carbide-cobalt cermets (ceramic-metal composites) as inserts for metal turning and milling operations. The advantage of ceramics compared with carbides is retention of high hardness, strength, and chemical inertness to temperatures in excess of 1,000° C (**1,8320** F). This allows use of the ceramics at much higher machining speeds than can be tolerated by carbides. However, the ceramics have lower toughness than the carbide materials, and have only been used successfully in the limited operations of turning and milling. A further impediment to the use of ceramics, especially in the United States,

Figure 4.— Projected U.S. Markets for Structural Ceramics in-the Year 2000 (billions of dollars)



SOURCES aU.S. Department of Commerce, "A Competitive Assessment of the U.S. Advanced Ceramics Industry" (Washington, DC, U S Government Printing Office, March 1984)
^bHigh Technology, March 1986, P. 14.
^cLarry L. Hench and June Wilson, "Biocompatibility of Silicates for Medical Use," CIBA Foundation Symposium 121, pp. 231-246 (Chichester, John Wiley & Sons, Publishers, 1986) Ceramics are assumed to capture 30% of the estimated \$3 billion U S biomaterials market
^dDavid W. Richerson, "Design, Processing Development, and Manufacturing Requirements of Ceramics and Ceramic Matrix Composites," contractor report prepared for the Office of Technology Assessment, December 1985

has been equipment limitations. Much of the production metal machining equipment does not have the rigidity or speed capability to utilize ceramics.

In spite of the current limitations of ceramics and equipment, an assessment by the Department of Commerce estimates steady growth of ceramics for cutting tool applications. It projects a growth of the total U.S. shipments from \$2.2 billion in 1980 to \$8 billion in the year **2000**, with the growth of the ceramics portion from \$45 million (2 percent) to **\$960 million** (12 percent) .²⁷

²⁶U.S. Department of Commerce, Op. cit., March 1984,p.35.

²⁷Ibid.

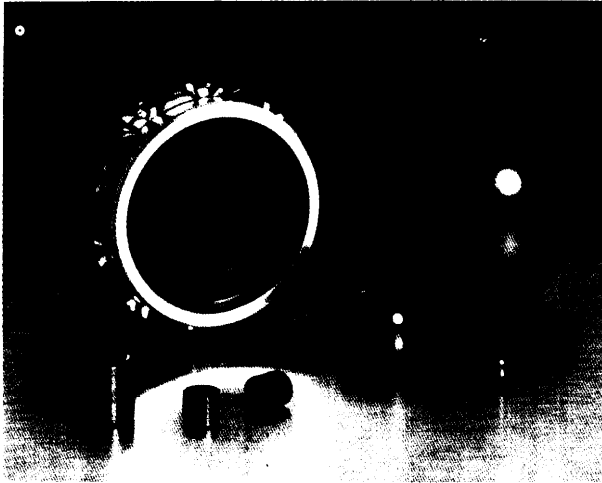


Photo credit: Norton Co

Silicon nitride anti-friction bearing components offer improved wear resistance and fatigue life compared to most bearing steel.

Bearings

High-performance ceramic bearings have been developed for military applications such as missiles. The primary candidate material is hot pressed silicon nitride. Ceramics offer resistance to low temperature corrosion, high temperature stability, low density, and the ability to operate for a moderate length of time with little or no lubrication. Hot isostatic pressing (HIP) is being developed to improve properties and to decrease cost by allowing near-net-shape fabrication.

The military developments will yield a technology base that can be applied to commercial products such as instrumentation bearings, hydraulic and pneumatic activator systems, and ceramic coatings on the foils in gas bearings. Potential ceramic bearing markets have been estimated to be \$300 million per year.²⁸

Coatings

Ceramic coatings provide a variety of benefits, including abrasion resistance, thermal protection, corrosion resistance, and high-temperature lubrication. Applications include ultrahard coatings for cutting tools, thermal insulation and lubricating coatings for adiabatic diesel engines and cooled

gas turbines, and bioactive glass coatings for metal orthopedic implants. The list could be expanded to include other sectors such as mining (e.g., drills), utilities (e.g., turbine-generator sets, heat exchangers), agriculture (e.g., plows and tillers), and aerospace (e.g., bearings, power transfer assemblies, and actuator drive systems).

The availability of advanced ceramic coatings is expected to be a significant benefit to the U.S. economy. The value of the market for ceramic coatings is not easily assessed, because the range of applications is so wide. One estimate is for a \$1 billion market worldwide for all coating materials, about 60 to 70 percent of which is domestic.²⁹ This estimated market includes jet engine, printing, chemical, textile, and tool and die applications. As we have seen, this list could be greatly expanded to include wear parts, bearings, biomaterials, heat exchangers, and automotive components in the future. Ceramic coatings should be considered an extremely important technology for extending the performance of metal components, and, in some cases, coated metal structures may be an excellent alternative to monolithic ceramics.

Advanced Construction Products

Potential applications of advanced cement-based materials include floors, wall panels, and roof tiles, in addition to pipes, electrical fittings, and cabinets. The cements can be laminated with wood or foam to form hard, decorative, and protective surfaces.³⁰ Advanced cement pastes cost 20 to 30 cents per pound compared with 75 cents to 2 dollars for metals and plastics, and could displace them in the future in many common uses.

The development of a cost-effective, durable, high tensile and compressive strength concrete would have dramatic implications for the infrastructure of the United States. It has been estimated that between 1981 and the end of the century the nation will spend about \$400 billion for replacement and repair of pavements, and about \$103 billion to correct bridge deficiencies.³¹ Cost

²⁸Richerson, op.cit., December 1985.

²⁹Imperial Chemical Industries, op. cit.

³¹National Research Council, Transportation Research Board, "America's Highways: Accelerating the Search for Innovation," Special Report 202, 1984.

²⁸High Technology, March 1986, p. 14.

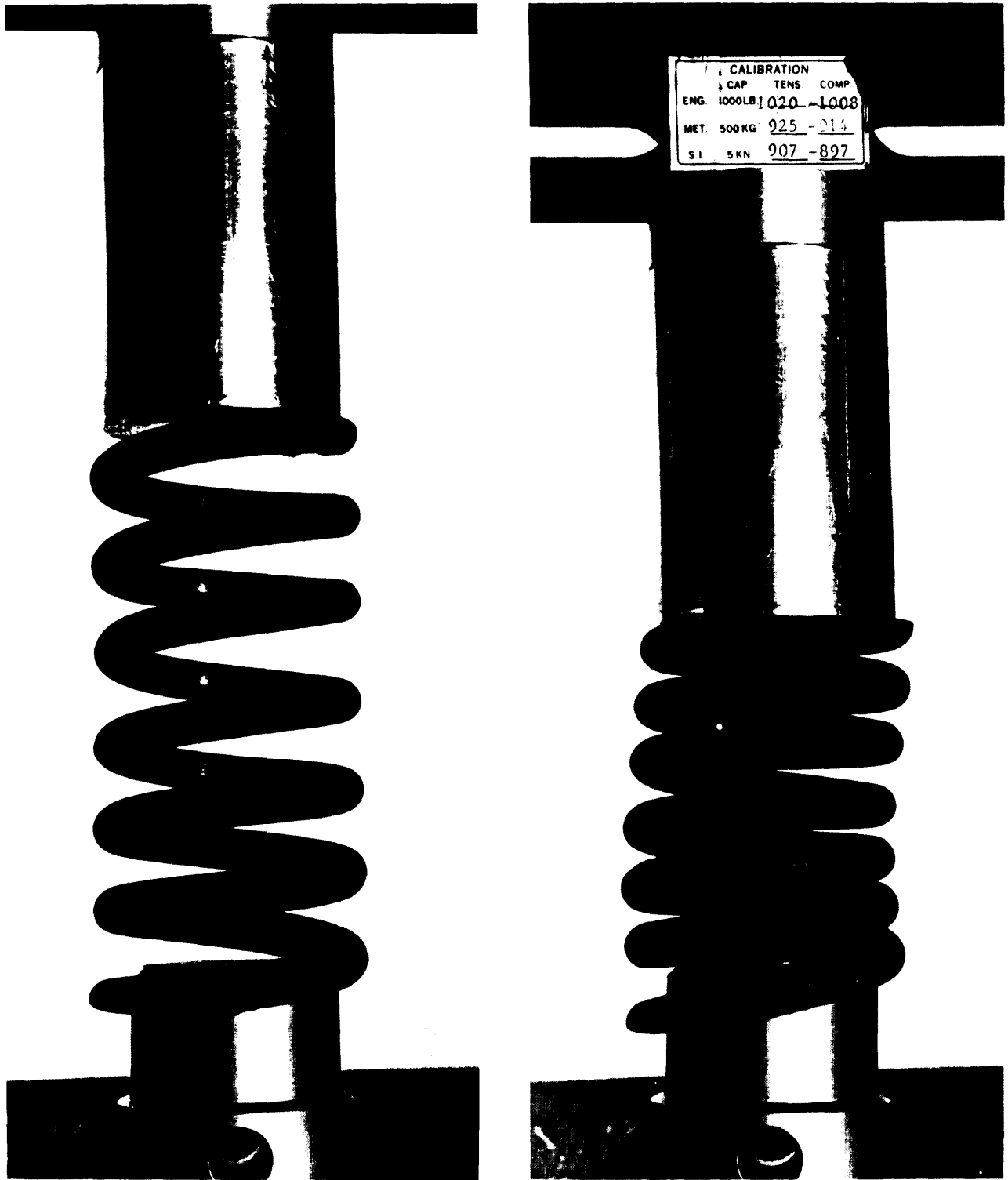


Photo credits" CEMCOM Research Associates, Inc.

A spring made from a high-strength cement, formed by extrusion processing. Left: natural length. Right: compressed. The spring is not intended for any practical use, but demonstrates the versatility and resilience of the material.

savings of about \$600 million per year could result from implementing new technologies.³² In addition to reducing repair and maintenance costs, new materials would provide other benefits. For example, high compressive strength concrete can be used to reduce the number and thickness of concrete bridge girders, significantly reducing the structural weight;³³ in concrete high-rise buildings, its use permits a reduction in the diameter of the columns, thus freeing up additional floor space.

The barriers to the development and implementation of new technologies in the construction industry are high. Some of those most often cited are industry fragmentation (e.g. some 23,000 Federal, State, and local agencies operate the Nation's highway industry), a system which awards contracts to the lowest bidder, and low industry investment in research as a percentage of sales (the steel industry invests 8 times more).³⁴ The low investment is due in part to the fact that the principal benefits of the use of better materials accrue to the owner of the highway or bridge (the taxpayer) rather than to the cement producer.³⁵

Legislation is currently before Congress (the Federal-Aid Highway Act of 1986, S.2405) which would set aside 0.25 percent of Federal-aid highway funds for a 5-year, \$150 million Strategic Highway Research Program. The program, which would be administered by the National Research Council, has targeted six priority research areas for support: asphalt characteristics, \$50 million; long-term pavement performance, \$50 million; maintenance costs, \$20 million; concrete bridge components, \$10 million; cement and concrete, \$12 million; and snow and ice control, \$8 million.

Bioceramics

Bioceramics, or ceramics for medical applications such as dental or orthopedic implants, represent a major market opportunity for ceramics in the future. The overall worldwide market for biocompatible materials is currently about \$3 billion, and this is expected to double or triple in

the next decade.³⁶ Ceramics could account for 25 to 30 percent of this market.³⁷

Bioceramics may be grouped into three categories: nearly inert, surface active, and resorbable.³⁸ Nearly inert ceramics can be implanted in the body without toxic reactions. These materials include silicon nitride-based ceramics, transformation-toughened zirconia and transformation-toughened alumina.

Surface-active ceramics form a chemical bond with surrounding tissue and encourage ingrowth. They allow the implant to be held firmly in place and help prevent rejection due to dislocation or to influx of bacteria. Surface-active ceramics which will bond to bone include dense hydroxy-apatite, surface-active glass, glass-ceramic, and surface-active composites.

The function of resorbable bioceramics is to provide a temporary space filler or scaffold which serves until the body can gradually replace it. Resorbable ceramics have been used to treat maxillofacial defects, for filling periodontal pockets, as artificial tendons, as composite bone plates, and for filling spaces between vertebrae, in bone, above alveolar ridges, or between missing teeth. An early resorbable ceramic was plaster of paris (calcium sulfate), but it has been replaced by trisodium phosphate, calcium phosphate salts, and polylactic acid/carbon composites.³⁹

Any new material intended for use in the body must undergo extensive testing before it is approved. Preclinical testing, clinical studies, and followup may take as long as 5 years to complete.⁴⁰ However, ceramics have been in clinical use for some 15 years, and are gaining acceptance. Industry interest in bioceramics has increased since 1980; however, no data were available on aggregate R&D spending either in industry or the Federal Government. In contrast, France, Germany, and especially Japan have aggressive programs of government support for the commercialization of

³⁶ Hench and Wilson, *op. cit.*, 1986.

³⁷ Larry L. Hench, University of Florida, personal communication, August 1986.

³⁸ J. W. Boretos, "Ceramics in Clinical Care," *American Ceramics Society Bulletin* 64(8):630-636, 1985.

³⁹ *Ibid.*

⁴⁰ Eduardo March, Food and Drug Administration, personal communication, August 1986.

³² *Ibid.*

³³ J. E. Carpenter, "Applications of High Strength Concrete for Highway Bridges," *Public Roads* 44:76, 1980.

³⁴ National Research Council, *op. cit.*, 1984.

³⁵ *Ibid.*



Photo credit' Richards Medical Co

Total hip system including ceramic femoral head and acetabular cup, with metal femoral stem. The system is manufactured in West Germany and marketed by Richards Medical Co.

bioceramics.⁴¹ All researchers interviewed agreed that the Japanese effort in bioceramics is considerably larger than the U.S. effort.

Heat Exchangers

Ceramic heat exchangers are of great interest because they can utilize waste heat to reduce fuel consumption. Heat recovered from the exhaust of a furnace is used to preheat the inlet combustion air, so that additional fuel is not required for this purpose. The higher the operating tempera-

ture, the greater the benefit. Ceramic systems have potential for greater than 60 percent fuel savings.⁴²

Ceramic heat exchangers may be used in a variety of settings, including industrial furnaces, industrial cogeneration, gas turbine engines, and fluidized bed combustion. The size of the unit, manufacturing technique, and material all vary depending upon the specific application. Sintered silicon carbide and various aluminosilicates have been used in low pressure heat exchangers because of their thermal shock resistance; however, the service temperature of these materials is currently limited to under 2,200° F (1,204° C). Silicon carbide is being evaluated for higher temperatures, but considerable design modifications will be necessary.⁴³

Government support has been necessary to accelerate development of the ceramic materials and system technology for heat exchangers, in spite of the design projections of significant fuel savings and short payback time. The material manufacturers, system designers, and end users have all considered the risks too high to invest their own funds in the development and implementation of a system. Specific concerns include: the high installed cost (up to \$500,000 for a 20 MBTU per hour unit), which represents a significant financial risk to the user for a technology that is not well proven; the fact that many potential end users are in segments of industry that presently are depressed; and the fact that designs vary according to each installation, leading the user to want a demonstration relevant to his particular situation.

Many of the ceramic heat exchanger programs were initiated in the 1970s when there was a keen sense of urgency concerning the "energy crisis." In recent years, declining fuel prices have generally reduced this sense of urgency. If the current low fuel prices persist, this could delay the widespread implementation of ceramic heat exchangers for waste heat recovery.

⁴²S.M. Johnson and D.J. Rowcliffe, SRI International Report to EPRI, "Ceramics for Electric Power-Generating Systems," January 1986.

⁴³Richerson, *op. cit.*, December 1985.

⁴¹Richerson, *Op. cit.*, December 1985.

Electrochemical Devices

Though not strictly structural applications of ceramics, devices in this category utilize ceramics for both their electrical and structural properties. Typically, the ceramic, such as zirconia or beta alumina, serves as a solid phase conductor for ions such as oxygen or sodium. Examples include oxygen sensors, oxygen concentration cells, solid oxide fuel cells, the sodium sulfur battery, sodium heat engine, and electrodes for metal winning and electrochlorination cells. As a group, these applications could comprise a market of over \$250 million for ceramics by the year 2000.⁴⁴

Heat Engines

The advantages of using ceramics in advanced heat engines have been widely publicized. These include increased fuel efficiency due to higher engine operating temperatures, more compact designs, and reduction or elimination of the cooling system.⁴⁵ Ceramics are being considered in three general categories: discrete components such as turbochargers in metal reciprocating engines; coatings and monolithic hot-section components in advanced diesel designs; and all-ceramic gas turbine engines.

A number of sources have predicted that components for heat engines will be the largest area of growth for structural ceramics over the next 25 years. Market estimates have varied widely. Kenney and Bowen stated:

The potential demand for ceramic engines could reach \$9 billion in Japan and \$30 billion world wide. If ceramics are used only to partially replace metals as hot parts in the engine, the demand would be from \$1 to \$5 billion.⁴⁶

The Department of Commerce has estimated more conservatively a U.S. market of \$56 million by 1990 and \$840 million by 2000.⁴⁷ A study by Charles River Associates estimates U.S. consumption of ceramic heat engine parts at \$25 to 45 million in 1990 and \$920 million to \$1.3 billion by

2000.⁴⁸ Some structural ceramic components are already in limited production for heat engines. Ceramic precombustion chambers and glow plugs for diesels, and ceramic turbochargers, are now in production in current model Japanese cars. These markets will grow, but not to a level that will account for the projected \$1 billion sales for heat engine components in the year 2000. Growth to this level would require material and design technology breakthroughs, as well as manufacturing scale-up and cost reduction. In view of these technical and economic barriers, the more conservative estimates are likely to be the more accurate.

Gasoline Engines.—The automotive internal combustion engine offers a vast market for materials. Total sales for 1985 of cars and trucks in the free world have been estimated at 38.7 million units.⁴⁹ Any part replacement or new part would represent a volume market with substantial sales, even if the unit price were small. However, the current engine designs are considered by automotive companies to be mature, reliable, and cost-effective. Very few incentives for change exist. Cost reduction remains a significant incentive, but this is extremely difficult to satisfy for a new material, whose introduction may require redesign of adjacent parts, retooling, and modification of the production line.

Another incentive is to develop new technology which may be applicable to advanced designs. This consists of both generic and directed R&D with the primary objective of maintaining a competitive position. Ceramics within this category which have potential for production include exhaust port liners, cam followers, and turbocharger components. To date, U.S. firms have not introduced these products, although R&D programs continue. Ceramic turbocharger rotors, glow plugs, precombustion chambers, and rocker arm wear pads are currently in limited production in Japan.

The United States is well behind Japan in procuring the advanced production equipment to

⁴⁴Ibid.

⁴⁵Katz, *op. cit.*, 1985.

⁴⁶Kenney and Bowen, *Op. cit.*, 1983.

⁴⁷U.S. Department of Commerce, *op. cit.*, March 1984.

⁴⁸Charles River Associates report prepared for the National Bureau of Standards, "Technological and Economic Assessment of Advanced Ceramic Materials, Vol. 2: A Case Study of Ceramics in Heat Engine Applications," NBS-GCR 84-4760-2, August 1984.

⁴⁹Richerson, *op. cit.*, December 1985.

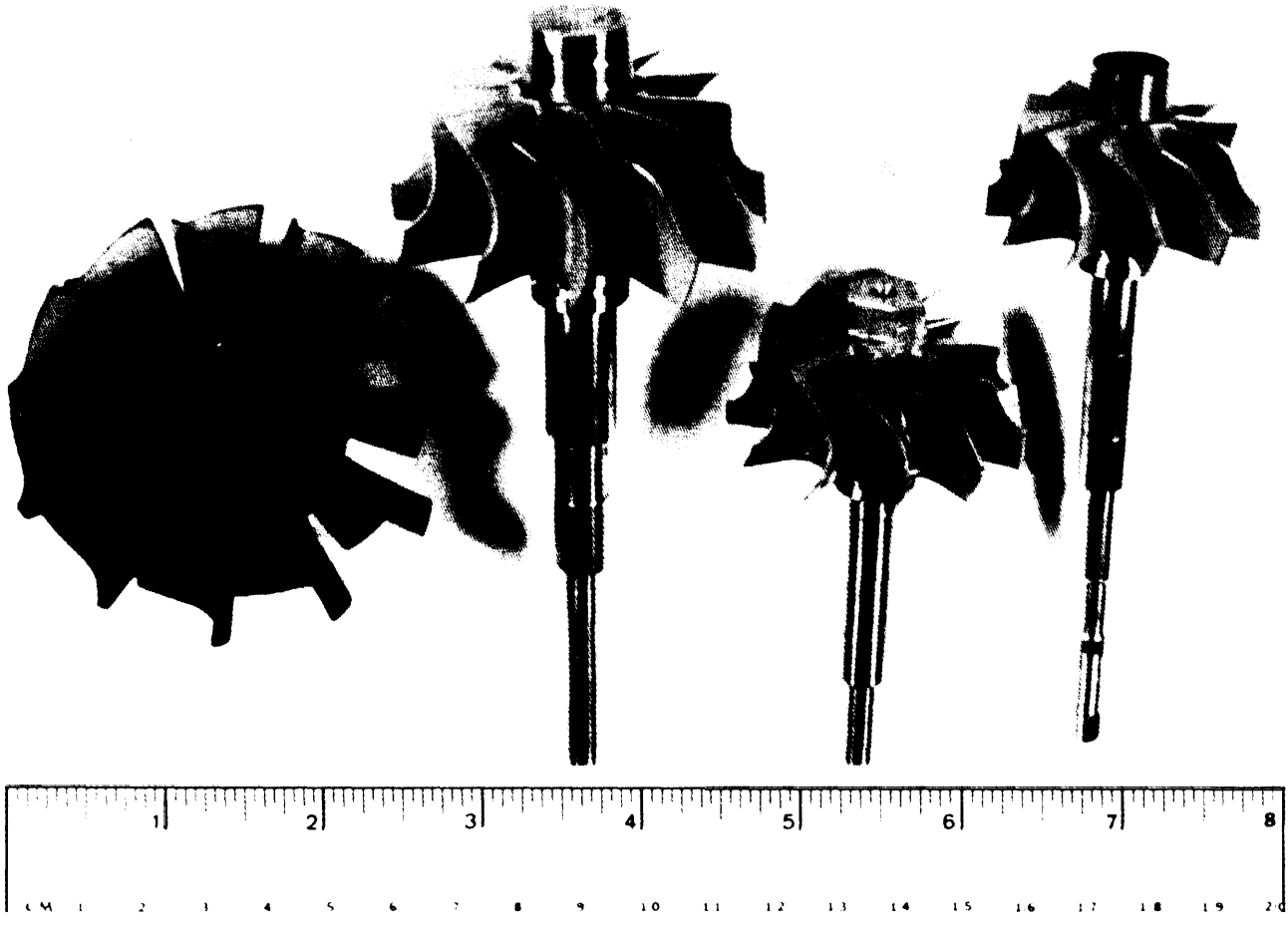


Photo credit The Garrett Corp

Ceramic turbocharger turbine rotors

produce ceramic turbocharger rotors. U.S. automotive companies do not appear to have the same level of confidence as the Japanese that a ceramic turbocharger market will develop. This is an institutional barrier based on perceived risk. In spite of this, U.S. industry is still funding considerable R&D on ceramic turbocharger rotors. One study has estimated that if a ceramic rotor price of \$15 can be reached, and if performance and reliability are acceptable, a worldwide market of \$60 million could be generated for ceramic turbocharger rotors by the year 2000.⁵⁰

⁵⁰Elaine P. Rothman, "Advanced Structural Ceramics: Technical Economic Process Modeling of Production and a Demand Analysis for Cutting Tools and Turbochargers," Materials Systems Laboratory, Massachusetts Institute of Technology, August 1985.

The ceramic turbocharger has a significance far beyond its contribution to the performance of the engine. It is regarded as a forerunner technology to far more ambitious ceramic engines, such as the advanced gas turbine. Design, fabrication, and testing methods developed for the turbocharger are expected to serve as a pattern for subsequent ceramic engine technology efforts.

Diesel Engines.—There are several levels at which ceramics could be incorporated in diesel engines, as shown in table 9. The first level involves a baseline diesel containing a ceramic turbocharger and discrete ceramic components. The second level adds a ceramic cylinder and piston, and eliminates the cooling system. The ceramic used at this level would provide high-temperature

Table 9.—Future Diesel Engine Technology Development Scenario

Technology level	Engine configuration	Potential ceramic components	Potential payoffs
1	State-of-the-art engine, turbocharged	Turbocharger Valve train components Prechamber, glow plugs	Improved performance Reduced cost? Early manufacturing experience
2	Uncooled, non-adiabatic (no water or air cooling) (no turbo-compounding)	Turbocharger Valve train components Piston, cap Cylinders, liners	Reduced weight - efficiency gain Gives option to improve aerodynamics - efficiency gain Reduced maintenance Reduced engine systems cost? Flexibility of engine placement
3	Adiabatic turbo-compound	Turbocharger Turbo-compound wheel Valve train components Piston, cap Cylinders, liners Exhaust train insulation	Very significant reduction in specific fuel consumption Improved aerodynamics Reduced maintenance
	Minimum friction technology (could be combined with 1, 2 or 3)	Air bearings High-temperature rings High-temperature bearings Nongalling wear surfaces Low friction liquid, lubricant-free bearings	Lower specific fuel consumption

SOURCE R Nathan Katz, "Applications of High Performance Ceramics in Heat Engine Design," *Material Science and Engineering* 71227.249, 1985

strength, rather than thermal insulation. The third level would utilize ceramics for thermal insulation in the hot section as well as in the exhaust train. Turbocompounding would be used to recycle energy from the hot exhaust gases to the drive train. The fourth level would use advanced minimum friction technology to improve the performance of the engine. Appropriate aspects of this could be utilized at levels one, two, or three,

The four levels listed above place different demands on the ceramic materials. Levels one and two require a low-cost, high-strength material, but without insulating properties; sintered silicon nitride or silicon carbide would be possibilities here. It has been suggested that level two represents the best compromise for light duty ceramic diesels such as those in automobiles.⁵¹ Level three would require an insulating ceramic, probably zirconia or a zirconia-based composite. This is the level where the most significant improvements in fuel efficiency would be realized. The current zirconia and alumina-zirconia transformation toughened ceramics are not reliable at the high stress of the piston cap and do not have a low enough coefficient of friction to withstand the sliding contact stress of the rings against the cylinder liner.

⁵¹Katz, *op. cit.*, 1985.

These materials do seem to have adequate properties, however, for other components such as the head plate, valve seats, and valve guides.⁵²

Emission requirements will likely affect the size of the diesel market for passenger cars and trucks. Diesel engines generally produce a high level of particulate emissions. The higher operating temperatures of the adiabatic diesel could reduce emissions or allow emission control devices to operate more efficiently. The market for ceramics could also be affected in another way: a major candidate for diesel emission control is a ceramic particle trap. However, such a trap is likely to be expensive, and could raise the price of the automobile to an unacceptable level.

Ceramic coatings may be an alternative to monolithic ceramics in diesel applications. Zirconia coatings can be plasma-sprayed onto metal cylinders to provide thermal insulation. In a joint program between the United States Army Tank Automotive Command and Cummins Engine Co., the combustion zone of a commercial Cummins NH diesel engine was coated with a zirconia-based ceramic and installed in a 5 ton Army truck, minus the cooling system. The engine accumu-

⁵²Richerson, *op. cit.*, December 1985.

lated over 15,000 km of *successful* road testing.⁵³ The current state-of-the-art thickness of zirconia coatings is 30 to 50 thousandths of an inch. It is estimated that thicknesses of 125 thousandths will be required to provide thermal insulation comparable to monolithic zirconia.⁵⁴ The coating is not as impermeable nor as resistant to thermal shock as the monolithic zirconia. However, the coated metal part has higher strength and toughness than the all-ceramic part.

In the past, confusion has arisen because identical configurations of ceramic and metal engines have not been compared. It is important to separate out the configuration options, such as turbocharging, turbocompounding, heat recovery, cooling, etc., from the material options in order to isolate the benefits of the use of ceramics. Failure to do this has led to overestimation of the benefits of ceramics. For example, a recent study of a ceramic diesel design funded by DOE indicates that "a practical zirconia-coated configuration with a cooled metal liner, intercooled, with combined turbocompounding and Rankine cycle exhaust heat recovery, provides a 26 percent increase in thermal efficiency over a metallic, cooled, turbocharged, intercooled, baseline engine."⁵⁵ The bulk of the performance improvement was attributed to the turbocompounding and the Rankine cycle exhaust heat recovery. Only 5.1 percent was attributed to the improved thermal insulation.

A recent study by Charles River Associates predicts that the uncooled ceramic diesel engine system will be the first to be commercialized.⁵⁶ It projects that the initial introduction will be in the late 1980s to early 1990s, and could account for 5 percent of new engines manufactured in 1995. This projection is more optimistic than the above discussion would imply. Zirconia materials do not yet exist which can be used for level three technology, where the greatest fuel efficiencies are expected. It remains to be seen whether the elimi-

nation of the cooling system will provide sufficient incentives to U.S. automakers to commercialize level two ceramic technology. However, Japan in particular has very active programs both in material and diesel engine development. The Japanese company Isuzu has reported greater than 300 miles of road testing and is projecting 1990 production. "

Automotive Gas Turbines.—The major incentive for the use of ceramics in turbines is the possibility of operating the engine at turbine inlet temperatures up to about **2,500° F** (1,3710 C), compared with superalloy designs, which are limited to about 1,900° F (1,038° C) without cooling. This temperature difference translates into an increased thermal efficiency from around 40 percent to nearly 50 percent. 'g Power increases of 40 percent and fuel savings of around 10 percent have been demonstrated in research engines containing ceramic components.⁵⁹ Other potential advantages include reduced engine size and weight, reduced exhaust emissions, and the capability to burn alternative fuels, such as powdered coal.

Structural ceramics are an "enabling technology" for the automotive gas turbine; i.e., without the use of ceramics, an automotive turbine cannot be designed and manufactured that can compete in cost or performance with current gasoline and diesel engines. Extensive design, materials, and engine efforts have been made over the past 15 years in the United States, Europe, and Japan. These efforts have resulted in significant progress in design methods for brittle materials, the properties of silicon nitride and silicon carbide materials, fabrication technology for larger and more complex ceramic components, NDE and proof testing, and engine assembly and testing.

Ceramic components have been operated in prototype turbine engines in Germany, Sweden, Japan, and the United States. The tests in the United States have been highly instrumented development engines in test cells.⁶⁰ Current pro-

⁵³Katz, op. cit., 1985.

⁵⁴Bill Mandler Cummins Engine Co., personal communication, August 1986.

⁵⁵T Morel et al., "Analysis of Low Heat Rejection Engine Concepts," Proceedings of the 23rd Automotive Technology Development Contractors Coordination Meeting, to be published by the Society of Automotive Engineers in 1986.

⁵⁶Charles Rivers Associates, op. cit., August 1984.

⁵⁷Richerson, op. cit., December 1985.

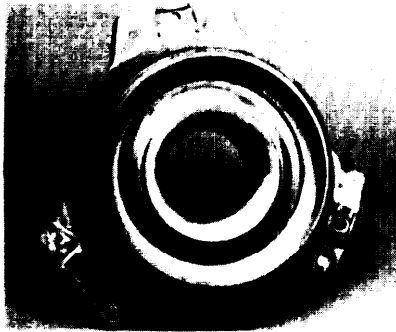
⁵⁸John Mason, Garrett Corp., presentation at the Society of Automotive Engineers International Congress and Exposition, February 1986.

⁵⁹David W. Richerson and K.M. Johansen, "Ceramic Gas Turbine Engine Demonstration Program," Final Report, DARPA Navy contract N00024-76-C-5352, May 1982.

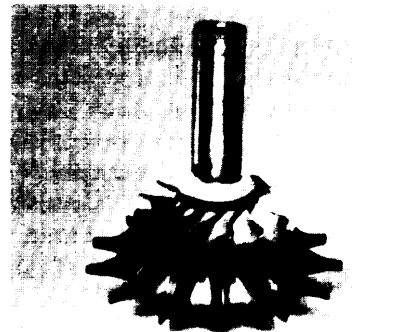
⁶⁰D.W. Richerson, "Evolution in the U.S. of Ceramic Technology for Turbine Engines," *American Ceramics Society Bulletin* 64(2):282-286, 1985.



1. Flow Separator Housing



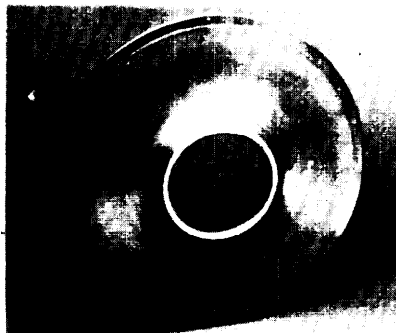
2. Turbine Shroud



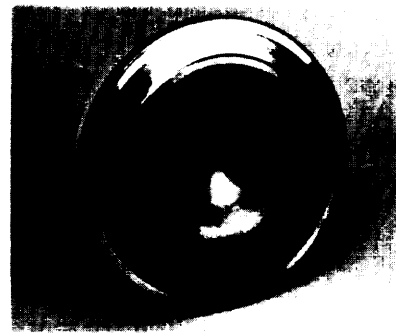
3. Turbine Rotor



4. Inner Diffuser HSG



5. Outer Diffuser HSG



6. Turbine Backshroud



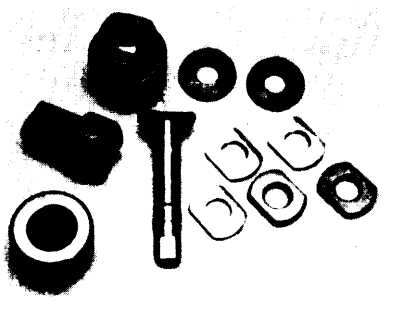
7. Stator Vane Segments



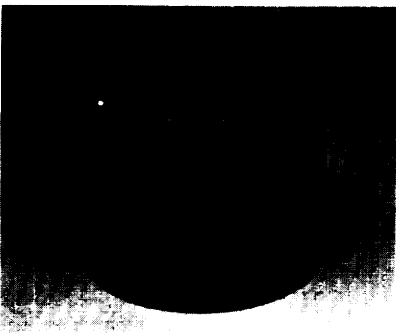
8. Turbine Transition Liner



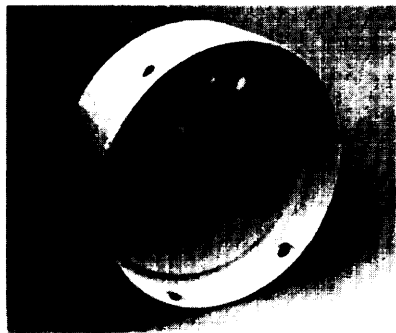
9. Combustor Baffle



10. Bolts



11. Regenerator Shield



12. Alumina-Silica Insulation

Photo credit The Garrett Corp

Prototype ceramic gas turbine engine components

grams have achieved over 100 hours of operation at temperatures above 2,000 F (1,093 C).⁶¹ These achievements, while impressive, are still far from the performance required of a practical gas turbine engine, which will involve continuous operation above 2,500 F (1,371 C). The limiting component in these engines appears to be the rotor, which must spin at about 100,000 rpm at these temperatures. The best rotors available today are Japanese. The target automotive gas turbine engine is designed to provide about 100 horsepower with fuel efficiencies of about 43 mpg for a 3,000 lb. automobile.⁶³

The automotive gas turbine would be a more revolutionary application of ceramics than the diesel. The diesel engine is a familiar technology and incorporation of ceramics can occur in stages, consistent with an evolutionary design. The gas turbine, on the other hand, represents a completely new design requiring completely new tooling and equipment for manufacture. Because of the remaining technical barriers to ceramic gas turbines and the fact that they represent a complete departure from current designs, it is unlikely that a ceramic gas turbine passenger car could be produced commercially before 2010.⁶⁴ In view of this long development time, it appears possible that this propulsion system could be overtaken by other technologies, including the ceramic diesel. One factor which would favor the turbine engine would be dramatically increased fuel costs. In the case that traditional fuels became scarce or expensive, the turbine's capability to burn alternative fuels could make it the power plant of choice in the future.

In summary, the outlook for ceramic heat engines for automobiles appears to be highly uncertain. The performance advantages of ceramic engines are more apparent in the larger, more heavily loaded engines in trucks or tanks than they are in automobiles. Ceramic gas turbines and adiabatic diesel designs do not scale down in size

as efficiently as reciprocating gasoline engines.⁶⁵ Thus, if the trend toward smaller automobiles continues, reciprocating gasoline engines are likely to be favored over advanced ceramic designs.

The prevailing approach of U.S. automakers is to wait and see if a clear market niche for ceramics develops before investing heavily in the technology. This is likely to mean that previous forecasts of the U.S. ceramics heat engine market, which cluster in the \$1 to \$5 billion range by the year 2000, are too optimistic. On the other hand, the Japanese approach, in which ceramics are steadily being incorporated in engines on a more experimental basis, reflects greater faith in the future of the technology. If a substantial automotive market for ceramics does develop, heat engine applications for ceramics would be one of the most highly leveraged in terms of economic benefits and jobs.^{66 67}

Military

Production of ceramics for military applications is projected to expand substantially during the next 25 years.⁶⁸ Near-term growth is expected for armor, radomes and infrared windows, bearings for missiles, and rocket nozzles (carbon-carbon composites and ceramic-coated carbon-carbon composites). New applications are likely to be laser mirrors, gun barrel liners, rail gun components, and turbine and diesel engine components. Ceramics and ceramic composites in many cases offer an "enabling" capacity which will allow applications or performance that could not otherwise be achieved. Some of the resulting technology will be suitable for commercial spinoff if acceptable levels of fabrication cost and quality control cost can be attained.

Diesels.—In military diesels, ceramics provide much the same benefits as in commercial diesels. Of particular interest to the military is the elimination of the cooling system to achieve smaller packaging volume and greater reliability, Con-

⁶¹Mason, op. cit., January 1986.

⁶²Richard Helms, General Motors Corp., presentation at the Society of Automotive Engineers International Congress and Exposition, Detroit, MI, February 1986.

⁶³Katz, op. cit., 1985.

⁶⁴Richerson, op. cit., December 1985.

⁶⁵US Congress, Office of Technology Assessment, *Increased Automobile Fuel Efficiency and Synthetic Fuels: Alternatives for Reducing Oil Imports, OTA-E-185* (Washington, DC: U.S. Government Printing Office, September 1982), p. 145.

⁶⁶Johnson, Teotia, and Hill, op. cit., 1983.

⁶⁷Charles River Associates, op. cit., August 1984.

⁶⁸Richerson, op. cit., December 1985.

siderable progress has been made through the use of ceramic coatings, Monolithic ceramics have also been tried, but have only been successful in a few components, and require further development. A military diesel with minimum cooling achieved primarily with ceramic coatings could be produced within 5 years. Engines containing more extensive ceramic components are not likely to appear before 1995 to 2000. 69

Turbines.—Turbine engines are in widespread use in the military for aircraft propulsion, auxiliary power units, and other applications. They are being considered for propulsion of tanks, transports, and other military vehicles. Ceramics have the potential to enable advanced turbines to achieve a large increase in performance: as much as 40 percent more power, and 30 to 60 percent fuel savings.⁷⁰ In addition, they offer lower weight, longer range, decreased critical cross section, and decreased detectability.

Design and material technologies are available in the United States to produce high-performance, ceramic-based turbine engines for short life applications such as missiles and drones. Furthermore, it appears that these engines have potential for lower cost than current superalloy-based short life engines.⁷¹ Longer life engines will require considerable development to demonstrate adequate reliability. This development must address both design and materials in an iterative fashion. While the use of ceramic thermal barrier coatings in metal turbines is well underway, new turbines designed specifically for ceramics are not likely to be available before the year 2000.

Future Trends in Ceramics

Ceramic Matrix Composites

Dramatic improvements in the fracture properties of ceramics have been obtained by reinforcing with continuous, high-strength fibers. Optimum microstructure result in composites that do not fail catastrophically, and therefore have mechanical properties that are very different from

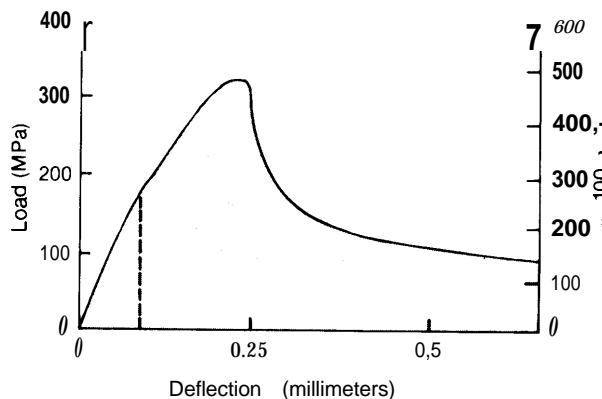
those of monolithic ceramics, as shown in figure 5. The most developed composites to date are silicon carbide fiber-reinforced glass/ceramic matrices.

Recent analysis suggests that fibers resist the opening of a matrix crack by frictional forces at the matrix-fiber interface.⁷² One of the important results is that the strength of the composite becomes independent of preexisting flaw size. This means that strength becomes a well-defined property of the material, rather than a statistical distribution of values based on the flaw populations,

Ceramic matrix composites present an opportunity to design composites for specific engineering applications. This will require a detailed understanding of the micromechanics of failure and explicit quantitative relations between mechanical properties and microstructural characteristics. The most important breakthrough in ceramic composites will come with the development of new high-temperature fibers that can be processed with a wider range of matrix materials. New chemical methods to form fibers and matrices together could yield even more revolutionary advances.

⁷²D. B. Marshall and A.G. Evans, "The Mechanics of Matrix Cracking in Brittle-Matrix Fiber Composites," *Acta Metall.* 33(11): 2013-2014, 1985.

Figure 5.— Load-Deflection Curve for a SiC/Glass-Ceramic Composite



Dotted line indicates deflection at which a single crack has passed completely through the matrix, but remains bridged by intact fibers,

SOURCE: D.B. Marshall and A.G. Evans, "The Mechanics of Matrix Cracking in Brittle-Matrix Fiber Composites," *Acta Metall.* 33(11):2013-2021, 1985

⁶⁹Ibid.

⁷⁰Ibid.

⁷¹Ibid.

Chemical Processing of Ceramics

In the future, chemical approaches to the fabrication of ceramics will probably be preferred to the traditional methods of grinding and pressing of powders. Chemical methods, such as sol-gel processing,⁷³ are already used extensively in the production of electronic ceramics, and will become increasingly important in structural ceramics as well. These techniques afford greater control over the purity of the ceramic and over its microstructure. It has been estimated that by the year 2010, 50 percent of structural ceramics will be processed chemically.⁷⁴

Ceramics Factory of the Future

Because of the extreme reliability and reproducibility problems of ceramics, production processes in the future must be highly automated. Processing equipment will be microprocessor controlled, including automatic load/unload devices and numerically controlled grinding and finishing machines.

Computer-process control of critical steps combined with nondestructive, in-line test methods such as acoustic flaw detection and radiography will form the heart of the manufacturing operation. In the near term, off-line proof testing of critical components will be required.

Quality assurance will be integrated into the process and will range from incoming raw materials inspection to automated dimensional inspection techniques such as computer controlled coordinate measuring machines of either a contact or noncontact (optical) configuration. Great emphasis will be placed on the characteristics of the starting powders, and use of clean rooms will be the rule in the initial forming steps.

Perhaps the most important processing goal in the future will be forming to net shape. This will reduce the costs of ceramics by eliminating costly grinding steps, and by making more efficient use of the material. Moreover, it will increase the

reliability and yields, by eliminating flaws which are introduced in the finishing operations.

Biotechnology

Structural ceramics could have a significant interaction with the developing field of biotechnology in the future. Ceramics could be used extensively in fermenters, and are likely to be important in a broad range of product separation technologies.

Fermenters .—Most current fermenters are made of 316 grade stainless steel.⁷⁵ Steel fermenters suffer from several disadvantages, including contamination of the cultures with metal ions, corrosion caused by cell metabolites or reagents, and leaks around gaskets and seals during sterilization and temperature cycling. Glass-lined steel bowls are sometimes used, especially for cell cultures, which are more sensitive to contamination than bacterial cultures. However, the thermal expansion mismatch between the glass lining and the metal causes problems during steam sterilization. Ceramics offer a solution to these problems, because of their chemical stability and low thermal expansion. Ceramics could be used in the bowl and agitator as well as in the peripheral plumbing joints and agitator shaft seal to prevent leaking.

Separation Technology .—Separation and purification of the products of cell and bacterial cultures is a key aspect of biotechnology. In general, the separation techniques are based less on filtration than on active interactions between a solid phase and the liquid mixture, as in chromatography. For example, biologically produced insulin is now being purified with a chromatographic process based on a modified silica material,⁷⁶ Silica or alumina particles can also be used as a solid support for attaching monoclonal antibodies, which bind to specific proteins and effect a separation by affinity chromatography.⁷⁷ The strength and hardness of the ceramics are key to the avoidance of deformation of the ceramic particles under conditions of high throughput.⁷⁸ In

⁷³See for example: David W. Johnson, Jr., "Sol-Gel Processing of Ceramics and Glass," *American Ceramic Society Bulletin* 64(12):1597-1602, 1985.

⁷⁴R. Nathan Katz, in presentation at the Society of Automotive Engineers International Congress and Exposition, Detroit, MI, February 1986.

⁷⁵Richard F. Geoghegan, E.I. du Pont de Nemours & Co., Inc., personal communication, August 1986.

⁷⁶Joseph J. Kirkland, E.I. du Pont de Nemours & Co., Inc., personal communication, August 1986.

⁷⁷George Whitesides, Department of Chemistry, Harvard University, personal communication, August 1986.

⁷⁸Ibid.

the future, the most efficient processes could be hybrids based on both filtration and chromatography.⁷⁹ As these processes are scaled up to production units, a large increase in the demand for specially modified silica and alumina column packing materials can be anticipated.

Energy Production

Power Turbines.—The performance requirements for power turbines are much greater than those for automotive gas turbines.⁸⁰ Power turbines must have a lifetime of 100,000 hours, compared with about 3,000 hours for the auto turbine. In addition, the consequences of power turbine failure are much greater. In light of these facts, a recent report has concluded that power turbines will be commercialized after automotive gas turbines.⁸¹ While some of the processing technology developed for the auto turbine may be applicable to power turbines, the scale-up from a rotor having a 6 inch diameter to one having a much larger diameter may require completely new fabrication techniques. The larger ceramic structures may also require different NDE techniques to ensure reliability. Thus, use of mono-

⁷⁹Michelle Betrido, Celanese Research Corp., personal communication, August 1986.

⁸⁰Johnson and Rowcliffe, op. cit., January 1986.

⁸¹Ibid.

lithic ceramics in the critical hot section components of power turbines is not anticipated in the next 25 years. However, ceramics may find applications in less critical structures, such as combustor linings, and ceramic coatings could be used to augment the high-temperature resistance of cooled superalloy rotor blades.⁸²

Research and Development Priorities for Ceramics

In 1986, the U.S. Government spent about \$60 million on structural ceramics research and development (table 10). R&D expenditures in private industry may be roughly comparable.⁸³ The Departments of Energy and Defense spent the largest fractions, at 47 percent and 36 percent, respectively. Funding for fiscal year 1987 is expected to decrease by over 20 percent, with 50 percent reductions in the DARPA program and in the DOE vehicle propulsion program. The following hierarchy of R&D priorities is based on the opportunities identified above. These are then correlated with the actual spending on structural ceramics R&D in fiscal year 1985.

⁸²Ibid.

⁸³Charles River Associates, op. cit., August 1984, p. 38.

Table 10.—Structural Ceramic Technology: Federal Government Funded R&D (in millions of dollars)

	FY 1983	FY 1984	FY 1985	FY 1986	Estimated FY 1987
Department of Energy:					
Conservation and renewable energy:					
Vehicle propulsion	11.4	12.7	11.9	10.0	5.2
Advanced materials	3.2	5.1	6.0	8.7	6.5
Industrial programs	1.0	2.3	1.7	1.5	0.8
Energy utilization research	0.5	1.5	1.8	1.8	1.0
Fossil energy:					
Advanced research and technology development	1.0	1.1	1.5	1.2	0.9
Energy research:					
Basic energy science	3.0	4.4	4.6	4.5	4.5
NASA:					
Lewis Research Center	3.0	2.5	5.4	4.5 ^a	4.6 ^a
National Science Foundation	2.9	3.3	3.6	3.6	3.7
National Bureau of Standards				2.2	3.0
Department of Defense:					
Defense ARPA	7.7	8.2	9.4	10.0	5.0
U.S. Air Force	3.0	3.4	4.7	4.7	5.0
U.S. Army	4.7	6.0	2.5	4.4^b	4.7 ^b
U.S. Navy	1.2	1.3	1.4	2.3	2.3
Total	42.6	51.8	54.5	59.4	47.2

^aIncludes \$1.6 for Manpower Salaries.

^bIncludes \$4.0 for TACOM Diesel.

SOURCE: Robert B. Schulz, Department of Energy

Very Important

Processing Science.—There is a great need for generic research to support the development of practical manufacturing technologies within industry. The agenda for such research is long, but includes such topics as:

- development of near-net-shape processes;
- development of pure, reproducible powders, whiskers, and fibers which can be formed and densified with a minimum of intermediate steps; role of solution chemistry in powder preparation and control of interface properties in composites;
- development of practical in-process inspection devices to identify problems at the earliest possible stage in the process;
- iterative development of new equipment such as hot isostatic presses (HIP) and multi-stage processes such as sinter-HIP, with emphasis on scaling up to commercially viable size; and
- understanding the relationships between coating process variables and final properties and performance of ceramic coatings.

Environmental Behavior.—Many of the applications for ceramics mentioned above require long-term performance in severe environments. In order to develop higher temperature, corrosion resistant materials, it is necessary to understand the long-term behavior of candidate ceramic materials in the anticipated environments.

- For heat engine applications, the general requirement is to understand the mechanical and chemical behavior of advanced ceramics such as silicon nitride, silicon carbide, zirconia, and composites based on these materials in environments of 1,000 to 1,400 C (1,832 to 2,552 F) in air, carbon monoxide, or carbon dioxide.
- In ceramic wear parts, it will be necessary to understand the relationship between wear, erosion, and toughness in the presence of lubricating fluids and gases. Generally, wear parts include hard materials like tungsten carbide, titanium boride, and materials which have good lubrication characteristics, like silicon nitride.

- Since heat exchangers generally fail as a result of long-term corrosion at high temperatures, it is important to understand the chemical processes of corrosion in environments like salts of sodium, potassium, magnesium, calcium, vanadium, and mixed metals. In addition to existing materials (e.g. silicon carbide, cordierite, and zirconium silicate), newer materials, including silicon nitride and composites, should be investigated. Corrosion-resistant ceramic coatings may become important here.
- Considering the large size of the potential markets in bioceramics, it will be critical to understand the long-term effects of body fluids on chemical structure and mechanical properties. In view of the many years which ceramic implants must serve without failure, the interaction between slow crack growth and the body environment should be investigated.
- The long-term environmental stability of advanced chemically bonded ceramics will be crucial to their effectiveness in construction and other applications. The deterioration of the properties of some advanced cements in the presence of moisture remains a problem, and the chemical degradation of the fiber interface in reinforced cements and concretes have limited the structural uses of these materials.

Reliability. -No factor is more important to the success of ceramics in all of the applications discussed than reliability. Since the performance specifications and environment of each application are different, it will be necessary to establish the most appropriate and cost-effective non-destructive testing methods for each one.

In order to facilitate design, models need to be developed for predicting the service lifetime of ceramic parts containing various kinds of flaws. Such models must depend heavily on information derived from the categories of environmental behavior of ceramics and composite failure mechanisms discussed above. Beyond a dependence on intrinsic flaws in the material, however, lifetime also depends on the location and nature of the flaw relative to the structure itself. It is not suffi-

cient to characterize the behavior of a coupon of the material from which a structure is made; either the structure itself must be tested, or additional models must be available to predict the effects of a particular flaw on a particular structure.

Interphase in Composites.—The interphase between ceramic fiber and matrix is crucial to the static strength, toughness, and long-term stability of the composite. Very little is known about the relationship between the properties of the interphase and these overall composite properties. The capability to modify the surface chemistry of ceramic fibers and whiskers to provide optimum compatibility between reinforcement and matrix could yield remarkable improvements in ceramic performance and reliability,

Important

Joining of Ceramics. -In most applications, ceramics are not used alone; rather, ceramic components are part of larger assemblies. Therefore, the ceramic must be joined to more conventional materials in the assembly to function properly. Broad research in joining of ceramics to metals, glasses, and other ceramics could have a decisive impact on a future use of monolithic ceramics, coatings, and composites. The key to joining is an understanding of the surface properties of the two materials and of the interface between them. In general, the interface is a critical point of weakness in discrete ceramic components such as those in heat engines, in ceramic coatings on metal substrates, and in ceramic fibers in composites. Principal needs in this area are in the strengthening and toughening of joints, an understanding of their high-temperature chemistry, and improved resistance to corrosion in the environments of interest. As with solution methods in powder preparation, chemistry will make a crucial contribution to this field.

Tribology of Ceramics.—Tribology, the study of friction, wear, and lubrication of contiguous surfaces in relative motion, is a field of key importance to ceramic wear parts and heat engine components. Lubrication is a particularly serious problem in ceramic engines because of their high operating temperatures. Ordinary engine oils cannot be used above about 3500 F (177° C). For

operating temperatures of 500° to 7000 F (2600 to 371° C), synthetic liquids such as polyol esters are available, but are extremely expensive and require further development. In a low-heat rejection (“adiabatic”) ceramic engine, cylinder liner temperatures may reach 1,000° to 1,700° F (5380 to 927° C), depending on the insulating effectiveness of major engine components. For this elevated temperature regime, synthetic lubricants cannot be used effectively. One approach is to use solid lubricants which would become liquid at elevated temperatures; however, no such lubricants exist for use in the environments envisioned (high temperature, corrosive gases). Moreover, the distribution of solid lubricant around the engine is a persistent problem.⁸⁴

A second approach involves modifications of the surface of the component to produce “self-Lubrication.” The lubricant can be introduced through ion implantation directly into the surface (to a depth of several micrometers) of the component; it then diffuses to the surface to reduce friction. Some metal or boron oxides show promise as lubricants. Another alternative is to use surface coatings of extremely hard ceramics such as the carbides and nitrides of zirconium, titanium, or hafnium, without any lubrication. At present, these techniques all lead to sliding friction coefficients which are roughly four times higher than those achieved at low temperatures with engine oils.⁸⁵ Further research is needed to improve this situation.

Failure Mechanisms in Composites.—Ceramic matrix composites offer the best solution to the problem of the brittleness of ceramics. However, this field is still in its infancy, and research is characterized by a very empirical approach to mixing, forming, densification, and characterization of fiber-powder combinations. Fundamental understanding of the failure mechanisms in composites would provide guidance for development of new, tougher ceramics. This would include an investigation of: multiple toughening techniques, such as transformation toughening and whisker reinforcement; the role of interphase properties

⁸⁴Manfred Kaminsky, Surface Treatment Science International, personal communication, August 1986.

⁸⁵Ibid.

in fracture; and failure mechanisms in continuous fiber composites.

Standardization and Testing.—Standardized tests and methods of reporting test data are fundamental to the use of any engineering material; however, a consensus on even these basic principles has eluded the ceramics community. It is not surprising that in a new field like structural ceramics, which is constantly inventing new materials and processes, there should be a lag in the development of standards and test methods. Standardization of materials must inevitably follow the formation of a consensus that certain materials are worth pursuing. While there is a danger in prematurely narrowing the possibilities, there may also be a danger in not developing the materials we already have. This is particularly true of the relatively well-studied materials: silicon nitride, silicon carbide, and zirconia.

In the case of ceramic composites, the specification of standard tests is more difficult, because the relationship between the micromechanics of the fibers and matrix and the macroscopic composite behavior is not well understood. In continuously reinforced composites, for example, which display progressive rather than catastrophic failure behavior, the stress at which the composite “fails” is ambiguous.

There is a growing interest, both nationally and internationally, in the development of standards for ceramics.⁸⁷ Areas which could benefit from standards include: statistical process control, non-destructive testing, analytical procedures, mechanical properties, performance characteristics in various environments, design procedures and terminology.⁸⁷ Standards are essential for the generation of design data, and for reliability specifications for ceramic materials sold domestically or abroad,

⁸⁷Concerned organizations include the American Ceramic Society, the U. S. Advanced Ceramic Association (USACA), the American Society for Testing and Materials (ASTM), the Versailles Project on Advanced Materials and Standards (VAMAS), and the National Bureau of Standards.

⁸⁸Proposal developed by S. J. Schneider, as described in the Ceramic Technology Newsletter, Oak Ridge National Laboratory, No. 10, February-April 1986.

Desirable

Chemically Bonded Ceramics.—Chemically bonded ceramics offer great promise for low-cost, net shape fabrication of structures in such applications as wear parts and construction. Recent improvements in the tensile strength of CBCs suggest that the limits of this key engineering property are far from being realized. Further research is required in flaw size reduction, long-term stability in various environments, and the properties of the interphase in fiber-reinforced cements and concretes.

Table 11 shows that the actual structural ceramics R&D spending in fiscal 1985 for all government agencies corresponds roughly with the priority categories recommended above, although specific projects differ. Processing research accounted for the lion's share, with 76 percent. No separate estimate was available of research on the interphase in composites; no doubt a portion of this work was included under composite fabrication, listed in table 11 as a subcategory of processing. Also, no separate figure was obtained for

Table 11.—Breakout of the Fiscal Year 1985 Structural Ceramic Budget According to the R&D Priorities Cited in the Text

Research area	FY 1985 budget percentage
Processing:	
Powder synthesis	4
Monolithic fabrication	32
Composite fabrication	32
Component design and testing	4
Coatings	4
Machining	<1
Subtotal	76
Environmental behavior	4
Reliability:	
Modeling	2
Time dependent behavior	1
Nondestructive evaluation	3
Microstructure evaluation	4
Subtotal	10
Interphase in composites	no separate figure
Tribology	2
Joining	3
Fracture	5
Standards	<1
Total	100 %/0

SOURCE S J Dapkunas, Department of Energy

Federal expenditures on new cements and concretes. In 1983, however, total U.S. Government and industry funding of cement research was estimated at only \$1 million, compared with a portland cement sales volume over \$1 billion.⁸⁸ As-

⁸⁸National Research Council, Transportation Research Board, op. cit., 1984.

suming that the current breakdown of Federal ceramics research is similar to that in fiscal 1985, a comparison of table 11 with the priorities above suggest that greater emphasis should be placed on standards development, joining, tribology, and cement-based materials.