Chapter 2

Ceramics

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Ceramics

FINDINGS

The broad class of materials known as ceramics includes all solids that are neither metallic nor organic. Advanced structural ceramics differ from conventional ceramic consumer goods in that they are made from extremely pure, microscopic powders that are consolidated at high temperatures to yield a dense, durable structure. Compared with metals, advanced structural ceramics have superior wear resistance, high-temperature strength, and chemical stability. They generally have lower electrical and thermal conductivity, and lower toughness. The low toughness of ceramics (brittleness) causes them to fail suddenly when the applied stress is sufficient to propagate cracks that originate at flaws in the material. The actual stress level at which this occurs can be very high if the flaw sizes are small. However, unpredictable failure caused by poor control over flaw populations remains a major handicap to the use of structural ceramics in load-bearing applications.

There are several methods that can reduce the sensitivity of ceramics to flaws. Incorporation of ceramic particulate, whiskers, or continuous fibers in a ceramic matrix can produce a composite that absorbs more energy during fracture than the matrix alone, and is therefore tougher. A different approach is the application of a thin ceramic coating to a metal substrate. This yields a component with the surface properties of a ceramic combined with the high toughness of metal in the bulk.

Advanced ceramic components are more expensive than the metal components they would replace. This is primarily due to the high cost of processes that are capable of fabricating ceramics reliably and reproducibly. Finishing and machining operations to form the part to its final shape are expensive due to the extreme hardness of the material. Nondestructive testing to ensure reliability is also a major component of production costs. Therefore, development of processes that can reliably fabricate a component to final net shape is crucial, In many applications, thin coatings of a high-performance ceramic on a metal substrate may offer the best compromise between cost and performance.

Applications and Market Opportunities

Advanced structural ceramics are in production for wear parts, cutting tools, bearings, filters, and coatings. Ceramics are also in limited production (in Japan) in discrete engine components such as turbocharger rotors, glow plugs, and precombustion chambers. Current military applications in the United States include radomes, armor, and infrared windows.

Near-term production (next 10 to 15 years) is expected in advanced bearings, bioceramics, construction applications, heat exchangers, electrochemical devices, discrete components in automobile engines, and military engines. Especially high growth may be seen in bioceramics for dental and orthopedic implants, and chemically bonded ceramics for construction applications.

Far-term applications (beyond 15 years) are those that require solution of major technical and economic problems. These include an advanced automotive turbine engine, an advanced ceramic diesel (although ceramics could be used in military versions of these engines at an earlier date), some electrochemical devices, military components, and heat exchangers. A variety of other turbine engines, especially turbines for aircraft propulsion and for utility-scale power generation, should also be categorized as far-term.

Research and Development Priorities

The following hierarchy of R&D priorities is based on the technical barriers that must be overcome before ceramics can be used in the applications discussed above.

Processing Science

This is the key to understanding how processing variables such as temperature, composition, and particle size distribution are connected to the desired final properties of the ceramic.

Environmental Behavior

In many applications, ceramics are required to withstand high-temperature, corrosive, or erosive environments. Information on the behavior of ceramics in these environments is essential to predict the service life of ceramics in those applications.

Reliability

The reliability of advanced ceramics and ceramic composites is the single most important determinant of success in any application. Progress requires advances in design of brittle materials, process control, nondestructive evaluation, understanding crack growth processes, and life prediction.

Ceramic Composites

These novel materials offer an exciting opportunity to increase the strength and toughness of ceramics.

INTRODUCTION

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

The U.S. market for advanced structural ceramics in 1987 was $171 million.[1] In the next 10 to 15 years, however, the market opportunities for structural ceramics are expected to expand rapidly (table 2-1) such that by the year 2000, the U.S. market alone is projected to be between $1 billion and $5 billion per year.[2]

Properties of Ceramics

The properties of some common structural ceramics are compared with those of metals in table 2-2. In general, ceramics have superior high-temperature strength, higher hardness, lower density, and lower thermal conductivity than metals. The principal disadvantage of using 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

Table 2-1.—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	High strength, hot hardness	Silicon nitride
Heat engines diesel components gas turbines	Thermal insulation, high temperature strength, fuel economy	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 Off Ice of Technology Assessment, 1988

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[1] Up from $112 million in 1985, according to data supplied by Business Communications Co., Inc. of Norwalk, CT. This includes wear parts, cutting tools, heat exchangers, engine components, bioceramics, and aerospace applications.

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

Table 2-2.—Comparison of Physical and Mechanical Properties of Common Structural Ceramics With Steel and Aluminum Alloys. SiC: silicon carbide; Si_3N_4: silicon nitride; ZrO_2: zirconia

Material	Density[a] (g/cm^3)	Room temperature strength (MPa)	Strength[a] at 1,095° C (M Pa)	Hardness[b] (kg/mm^2)	Thermal conductivity 25°/1,100° (W/m° C)
Various sintered SiC materials	3.2	340-550 (flexure)	340-550 (flexure)	2,500-2,790	85/175
Various sintered Si_3N_4 materials	2.7-3.2	205-690 (flexure)	205-690 (flexure)	2,000[c]	17/60
Transformation toughened ZrO_2	5.8	500-1,250 (flexure)[c]	—	1,300-1,635[c]	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/mm^2.

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

[b] Elalne P. Rothman, "Ultimate Properties of Ceramics and Ceramic Matrix Composites," contractor report for OTA, December 1985.

[c] "Ceramic Application and Design," *Ceramic Industry,* February 1988, pp. 29-50.

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, unlike design with metals, is therefore a statistical process, rather than a deterministic process.

Ceramic failure probability is illustrated in figure 2-1. The curve on the right in figure 2-1a represents the distribution of strengths in a batch of identically prepared ceramic components. The curve on the left is the distribution of stresses that these components are subjected to 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, as shown in figure 2-1 b. A second way is to use nondestructive testing or proof testing to weed out those components with major flaws. This leads to a truncation of the strength distribution, as shown in figure 2-1c. Proof testing of each individual component, although widely used in the industry today, is expensive and can introduce flaws in the material that were not there originally.

A third way to reduce failure probability is to design the microstructure of the ceramic so that it has 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 that 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 three 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.[3]

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

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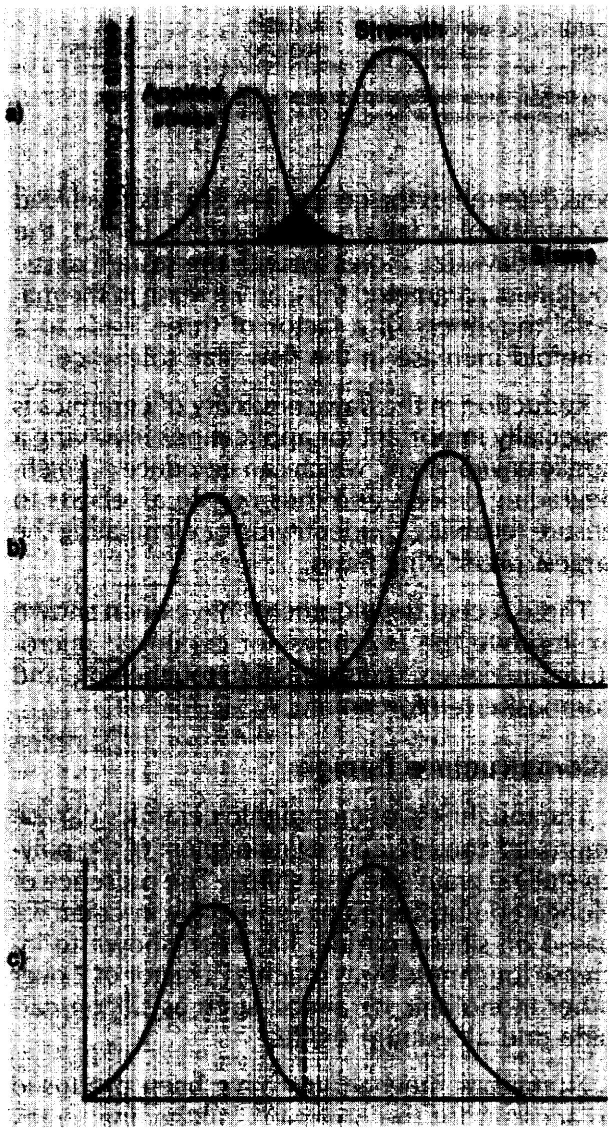
[3] *Nitrogen Ceramics,* F. L. Riley (cd.) (Boston and The Hague: Martinus Nijhoff Publishers, 1983).

in these materials. The high toughness is accompanied by high strength, both of which result from the modified microstructure.

Figure 2-1 .—Probabiiity of Faiiure 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.

Transformation Toughening

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

Zirconia goes through a phase transformation from the tetragonal to the monoclinic crystal form while cooling through a temperature of about 2100° F (1 150° C). 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, thereby preventing the crack from propagating.

Ceramic Matrix Composites

A variety of ceramic particulate, whiskers high-strength single crystals with length/diameter ratios of 10 or more), and fibers may be added to the host matrix material to generate a composite with improved fracture toughness.

The presence of these reinforcements appears to frustrate the propagation of cracks by at least three mechanisms. First, when the crack tip encounters a particle or fiber that 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. Third, fibers can bridge a crack, holding the two faces together, and thus prevent further propagation.

Table 2-3 presents the fracture toughness and critical flaw sizes (assuming a typical stress of 700 megapascals [MPa], or about 100,000 pounds per square inch [psi]) of a variety of ceramics and compares them with some common metals. The toughness of monolithic ceramics generally falls in the range of 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$^{1/2}$ (the critical flaw size is 131 to 294 micrometers); the toughest ceramic matrix composites are continuous fiber-reinforced glasses, at 15 to 25 MPa-m$^{1/2}$. In these glasses, strength appears to be independent of preexisting flaw size and is thus an intrinsic material property. By comparison, metal alloys such as steel have toughnesses of more than 40 MPa-m$^{1/2}$, more than 10 times the values of monolithic ceramics; the toughness of some alloys may be much higher.

Table 2-3.—Fracture Toughness and Critical Flaw Size of Monolithic and Composite Ceramic Materials Compared With Metals.[a]
Al_2O_3: **alumina; LAS: lithium aluminosilicate; CVD: chemical vapor deposition**

Material	Fracture toughness (MPa•m$^{1/2}$)	Critical flaw size (micrometers)
Conventional microstructure:		
Al_2O_3	3.5-4.0	25-33
Sintered SiC	3.0-3.5	18-25
Fibrous or interlocked microstructure:		
Hot pressed Si_3N_4	4.0-6.0	33-74
Sintered Si_3N_4	4.0-6.0	33-74
SiAION	4.0-6.0	33-74
Particulate dispersions:		
Al_2O_3TiC	4.2-4.5	36-41
Si_3N_4-TiC	4.5	41
Transformation toughening:		
ZrO_2-MgO	9-12	165-294
ZrO_2-Y_2O_3	6-9	74-165
Al_2O_3-ZrO_2	6.5-15	86-459
Whisker dispersions:		
Al_2O_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	

[a] Assumes a stress of 700 MPa (-100,000 psi).
[b] The strength of these composites is independent of preexisting flaw size.
[c] The 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

The critical flaw size gives an indication of the minimum flaw size that must be reliably detected in any nondestructive evaluation (N DE) to ensure reliability of the component. Most N DE techniques cannot reliably detect flaws smaller than about 100 micrometers (corresponding to a toughness of about 7 MPa-m$^{1/2}$). Toughnesses of at least 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. First, it is possible to optimize independently the properties of the surface region and those of the base material for a given application. Second, it is possible to maintain close dimensional tolerances of the coated workpiece in that very thin coatings (of the order of a few micrometers) are often sufficient for a given application. Third, there are significant cost savings associated with using expensive, exotic materials only for thin coatings and not for bulk components. Use of coatings can thereby contribute to the conservation of strategically critical materials. Fourth, it is often cheaper to recoat a worn part than to replace it.

These advantages have led to widespread industry acceptance and applications. For instance, coatings of titanium nitride, titanium carbide, and alumina are used to extend the useful life of tungsten carbide or high-speed steel cutting tools by a factor of 2 to 5,[4] In 1983, annual sales of coated cutting tools reached about $1 billions.[5]

Ceramic coatings are also finding wide application in heat engines. Zirconia coatings of low thermal conductivity are being tested as a thermal barrier to protect the metal pistons and cylinders of advanced diesel engines. In turbine engines, insulative zirconia coatings have been found to improve performance by permitting combustion gas temperatures to be increased by several hundred degrees Fahrenheit without increasing the temperature of air-cooled metal components or the complexity of the engine.[6] Ceramic coatings are also being used to provide an oxidation barrier on turbine blades and rings.

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

It is in the nature of advanced structural materials that their manufacturing processes are additive rather than subtractive. Ideally, the materials are not produced in billets or sheets that are later rolled, cut, or machined to their final shape; rather, in each case the material is formed 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 ceramics designer is always conscious of the need to consolidate as many components as possible together in a single structure. Although consolidation cannot always be achieved (expensive grinding or drilling is often required), to a great extent, the promise of 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 very 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.

One serious barrier to the use of ceramics is the lack of knowledge among designers of the principles of brittle material design. 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.[7]

A second serious barrier is the poor characterization of commercially available ceramics for design purposes. The data are inadequate because the mechanical, thermal, and chemical properties of ceramic materials vary with the method of manufacture as well as the test method. Both carefully controlled and documented processing procedures and standard test methods, as discussed in chapter 5, will be required to give designers the confidence that consistent properties at a useful level can be obtained at a predictable cost.

Processing of Ceramics

The production of most ceramics, including both traditional and advanced ceramics, consists of the following four basic process steps: powder preparation, forming, densification, and finishing. The most important processing techniques involved in these steps are identified in table 2-4.

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[4] 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.

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

[6] Tom Strangman, Garrett Turbine Engine Co., personal communication, August 1986.

[7] Specific proposals for improving ceramics education are given in the report of the Research Briefing Panel on Ceramics and Ceramic Composites (Washington, DC: National Academy Press, 1985).

Table 2.4.—Common Processing Operations for Advanced Ceramics

Operation	Process	Examples
Powder preparation	Synthesis	SiC
	Sizing	Si_3N_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_2O_3
	Reaction bonding	Si_3N_4
	Hot pressing	Si_3N_4, SiC, BN
	Hot isostatic pressing	Si_3N_4, SiC
Finishing	Mechanical	Diamond grinding
	Chemical	Etching
	Radiation	Laser, electron beam
	Electric	Electric discharge

SOURCE Office of Technology Assessment 1988

Powder Preparation

Although most of the basic raw materials for ceramics 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. Compositions of 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) must all be fabricated from gases or other ingredients. Even minerals that 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.

The crucial importance of powder preparation has been recognized in recent years. Particle sizes and size distributions are critical in advanced ceramics to produce uniform green (unfired) densities, so that consolidation 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 control particle rearrangement and diffusivities. These dopants permit 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, although providing many beneficial results, can also have a detrimental influence on the material properties. Segregation of dopants at the grain boundaries can weaken the final part, and final properties such as conductivity and strength 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 important variables in the forming step are particle shape, particle packing and distribution, phase distribution, and location of pores.

Forming processes for ceramics are generally classified as either cold forming or hot forming. The major cold forming processes include slip casting, extrusion, dry pressing, injection molding, tape casting, and variations of these. The product of such processes 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 processes combine into one step the forming and sintering operation to produce simple geometric shapes. These processes include hot pressing (in which pressure is applied along one direction) and hot isostatic pressing (HI Ping, in which pressure is applied to the ceramic from all directions at once).

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 at which the diffusion process occurs, matter moves from the particles into the void spaces between the particles, causing densification and resulting in shrinkage of the part. Combined with forming techniques such as slip casting, sintering is a cost-effective means of 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 dopants have been noted above in the discussion of powders.

Finishing

This step involves such processes as 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, and these can reduce the strength of the part and the yields of the fabrication process.

Near-Net-Shape Processing

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

Reaction bonding is a near-net-shape process that has undergone considerable development, particularly for silicon nitride. In this process, green body compacts of finely divided silicon powder are reacted with nitrogen gas to produce silicon nitride. In reaction bonding, the spaces between the silicon powder particles in the green body are filled with silicon nitride reaction product as the reaction proceeds, so no shrinkage occurs. Reaction bonding can also be used to produce ceramic composites with excellent properties because this process avoids damage to reinforcement fibers or whiskers caused by shrinkage during the sintering step.

Near-net-shape processes that are currently used for metals include powder metallurgy and advanced casting techniques. Because metals are in direct competition with ceramics in many applications, near-net-shape processing of ceramics must continue to be a high-priority research area if advanced ceramics are to be cost-competitive.

Ceramic Matrix Composites

Ceramic matrix composites (CMCs) may consist of: randomly oriented ceramic whiskers within a ceramic matrix; continuous fibers 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, high hardness, and improved thermal shock resistance. Processing methods for particulate-reinforced composites are similar to those for monolithic ceramics, and so are not discussed in this section.

Whisker Reinforcement

Ceramic whiskers are typically high-strength single crystals with a length at least 10 times greater than the diameter. Silicon carbide is the most common whisker material. Currently, whisker-reinforced CMCs are fabricated by uniaxial hot pressing, which substantially limits size and shape capabilities and requires expensive diamond grinding to produce the final part. Although hot isostatic pressing has the potential to permit fabrication of complex shapes at moderate cost, this technique requires procurement of expensive capital equipment and extensive process development.

Continuous Fiber Reinforcement

The primary fibers 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, but are limited to service temperatures of 11 00° to 1300° F (5930 to 704° C). Service temperatures up to 2000° to 2200° F (1 0930 to 1204° C) may be obtained with glass-ceramic matrices that crystallize upon cooling from the process temperature.[8] Carbon matrix composites have the highest potential use temperature of any ceramic, exceeding 3500° F (1 9270 C). However, they oxi-

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[8] Karl 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.*

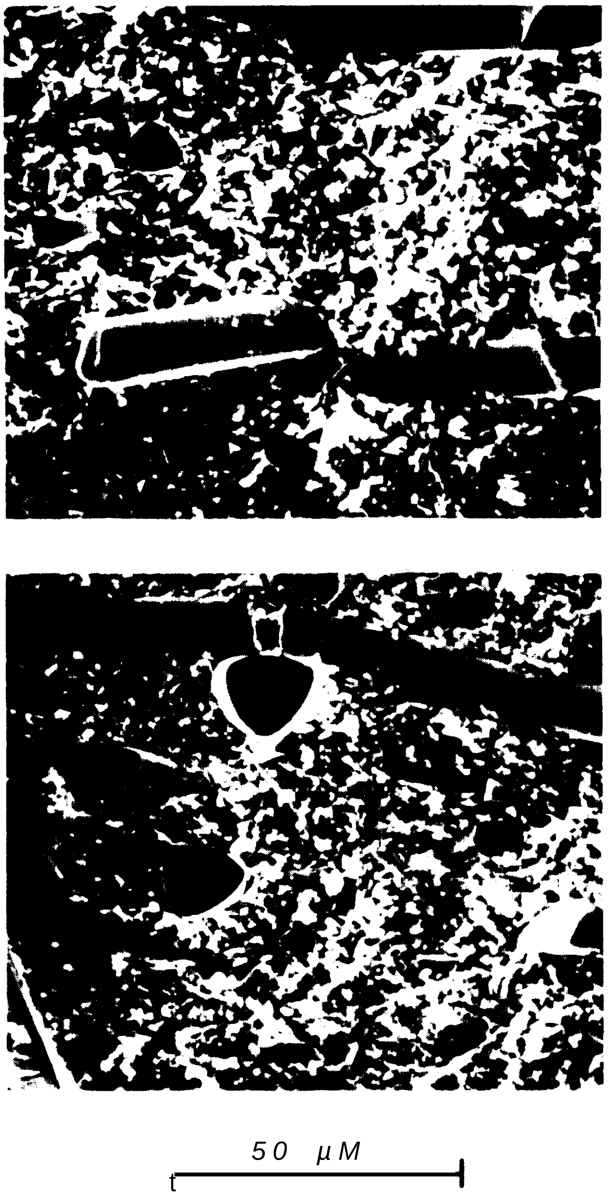

Photo credit: Los Alamos National Laboratory

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

dize readily in air at temperatures above about 1100° F (593° C), and require protective ceramic coatings if they are to be used continuously at high temperature.[9]

Photo credit: United Technologies Research Center

Tensile fracture surface for Nicalon SiC fiber-reinforced glass ceramic.

Fabrication of CMCs reinforced with continuous fiber is currently of a prototype nature and is 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, and are then 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, and are then infiltrated by CVD; and
- a fiber preform is infiltrated with a ceramic-yielding organic precursor, and is then heat-treated to yield a ceramic layer on the fibers. This process is repeated until the pores are minimized.

Considerable R&D will be necessary to optimize fabrication and to decrease the cost to levels acceptable for most commercial applications.

Ceramic Coatings

Many different processes are used in the fabrication of ceramic coatings and in the modification of surfaces of ceramic coatings and mono-

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[9] Joel Clark, et. al., "Potential of Composite Materials To Replace Chromium, Cobalt, and Manganese in Critical Applications," a contractor report prepared for the Office of Technology Assessment, 1984.

lithic ceramics. Table 2-5 lists some of the more important processes.

The choice of a particular deposition process or surface modification process depends on the desired surface properties. Table 2-6 lists some of the coating characteristics and properties that are often considered desirable. Additional considerations that 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 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 prop-

Table 2-5.—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 Flame spraying	Plasma arc 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
Chemical reaction processes	Gaseous anodization processes	Ion nitriding Ion carburizing Plasma oxidation
	Disproportionation processes	Deposition of molecular species Formed in gas phase
Conversion processes	Thermal diffusion	Diffusion of material from surface into bulk of substrate
Etching processes	Chemical etching	Acidic solutions; lye etching
	Ion etching	Sputter process
Mechanical processes	Grinding Peening Polishing	

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

Table 2-6.—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.

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

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. Owing to their low strength (compared with dense ceramics), concrete and other cementitious materials are not normally considered to be advanced materials. 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.

Cements

Cements are chemically active binders that 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; that is, they react with water to form a 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) and of low strength.[10]

Recently, workability of such cements has been improved by using a high-shear processing technique together with pressing or rolling to remove pores from a low-water calcium aluminate cement paste containing 5 to 7 percent (by weight) organic polymers. The dense paste, which is

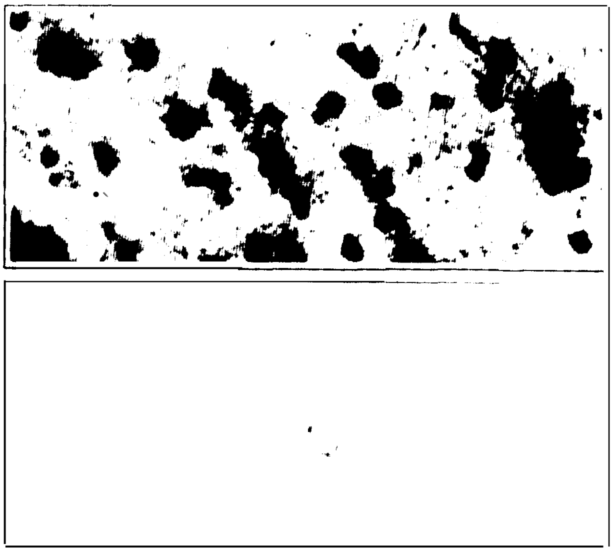

Photo credits: Imperial Chemical Industries PLC

Top photo: Conventional Portland cement paste microstructure, showing large flaws (pores).
Bottom photo: Advanced cement paste microstructure, illustrating the absence of large pores (magnification x 100).

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[10] Richard A. Helmuth, Portland Cement Association, Personal communication, August 1986.

sometimes called macro-defect-free (MDF) cement, has the consistency of cold modeling clay, and can be molded or extruded by techniques similar to those used for plastics.

The hardened cement paste has a compressive strength approaching that of aluminum (table 2-7) and much lower permeability than ordinary portland cement paste.[11] Although MDF cement pastes cost 20 to 30 cents per pound (compared with 3 cents per pound for portland cement paste), they are still significantly cheaper than metals and plastics.

The processing of hydraulic CBCs is very cheap because it involves only adding water, mixing, casting or molding, and permitting 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, it is possible to use any of a wide variety of reinforcing fibers, including metal fibers. However, the presence of organics makes them unsuitable for use above 200° F (93° C). Further work is needed to improve the long-term stability of these materials.

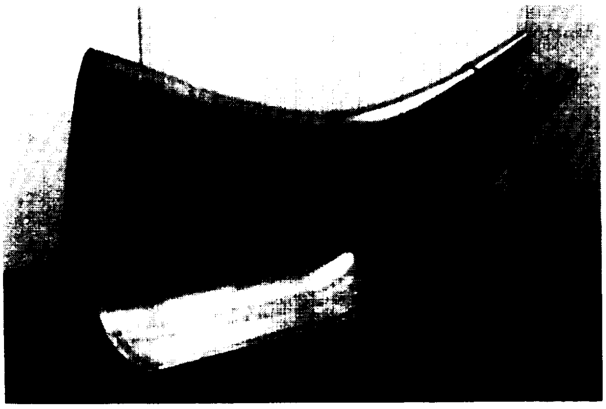

Photo credit: *CEMCOM Research Associates, Inc.*

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

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.[12] 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.[13]

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, and there is no indication that the ultimate strength is being approached.[14] In concrete high-

Table 2-7.—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[b]	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

[a] 1 MPa = 145 psi.

[b] According to information supplied by the Portland Cement Association.

[c] The advanced cement has the following composition: 100 parts high alumina Cement; 7 parts hydrolyzed potyvinylacetate; 10-12 parts water.

SOURCE: Imperial Chemical Industries.

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[11] According to product literature supplied by Imperial Chemical Industries, "New Inorganic Materials."

[12] For a recent review, see Jan Skalny and Lawrence R. Roberts, "High Strength Concrete," *Annual Review of Materials Science* 17:35, 1987.

[13] U.S. Department of Interior, Bureau of Mines, Bulletin 678, "Sulfur Construction Materials," by W.C. McBee, T.A. Sullivan, and H.L. Fike, 1985.

[14] Sidney Mindess, "Relationships Between Strength and Microstructure for Cement-Based Materials: An Overview," *Materials Research Society Symposium Proceedings 42:53,* 1985.

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.[15] Compared with unreinforced materials, fiber reinforcement can increase the flexural strength by a factor of **2.5** and the toughness by a factor of **5** to 10.[16] This reinforcement technology, which dates back to the straw-reinforced brick of the ancient Egyptians, requires fiber concentrations that are sufficiently low (usually 2 to 5 percent by volume) to preserve the flow characteristics of the concrete, plus 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 now being sought.

In recent years, several Japanese firms have developed concretes reinforced with carbon and aramid fibers, and pitch-based carbon fiber-reinforced concrete curtain walls have been used in Tokyo office buildings. Although the carbon fiber concrete panels cost 40 percent more than precast concrete, their light weight permits the use of a lighter weight structural steel frame, resulting in overall construction cost savings.[17]

Nondestructive Evaluation

Nondestructive evaluation (NDE), which is a means of determining properties of a structure without altering it in any way, has long been used for flaw detection in ceramic materials to improve the reliability of the final product. In the future, NDE will be used for defect screening, material characterization, in-process control, and life-cycle monitoring. It will be applied to the starting materials, during the process, and to the final product.

A key goal 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, it will be essential to determine the relation between measurable quantities, obtained through the use of contact or noncontact sensors, and the desired properties. This will require developments in sensor technology as well as theories that can quantitatively relate the measured NDE signal to the specific properties of interest.

In the past, a great deal of emphasis has been placed on the sensitivity of an NDE technique, that is, the size of the smallest detectable flaw. However, experience has shown that most quality problems result not from minute flaws but from relatively gross undetected flaws introduced during the fabrication process.[18] Therefore, a more relevant criterion for reliability purposes is perhaps the size of the largest flaw that can go undetected. To date, though, there has been very little emphasis on the reliability of NDE techniques, that is, the probability of detecting flaws of various sizes.

Cost-of-production estimates for high-performance ceramic components typically cite inspection costs as accounting for approximately 50 percent of the manufacturing cost.[19] Successful NDE techniques for ceramic components, therefore, should meet two major criteria. First, they should reliably detect gross fabrication flaws to ensure that the material quality of the component is equal to that of test specimens. Second, 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 that could be cost-effective for production-level inspections are identified in table 2-8.

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[15] Ibid

[16] American Concrete Institute, "State-of-the-Art Report on Fiber Reinforced Concrete," Report No. ACI 544.1 R-82, 1982.

[17] Engineering News Record, Aug. 1, 1985, p. 16.

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

[19] Ibid

Table 2.8.—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, 1988.

HEALTH AND SAFETY

The most serious health hazard involved with ceramics appears to stem from use of ceramic fibers and whiskers. 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 lungs of laboratory rats.[20] 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.[21]

No data on the effects of ceramic fibers or whiskers on humans are available, and no industry standards for allowable fiber and whisker concentrations in the workplace have been established. Until such data become available, the animal studies suggest that these fibers should be considered carcinogenic, and they should be treated in a manner similar to asbestos fibers.

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[20] Mearl F. Stanton, et *al., journal of the National Cancer Institute* 67:965-75, 1981.

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

APPLICATIONS OF STRUCTURAL CERAMICS

Figure 2-2 shows an estimated timetable for the introduction of ceramic products in various categories. It shows that some advanced structural ceramics are in production, some have near-term potential for production, and some are far from production.

Current Applications

in the United States, ceramics such as alumina and silicon carbide are already well established in commercial production for many structural applications in the categories of wear parts, cutting tools, bearings, membranes, filters, and coatings. The ceramics portion of these markets is currently small (generally less than **5** percent).[22] However, substantial growth in ceramics production is expected to occur over the next 25 years in response to increasing overall market demand, increase in the ceramics market share, and spin-off applications.

Current U.S. military applications for ceramics include radomes, armor, and infrared windows (see section entitled, *Military Applications and Production).* In Japan, ceramics are in limited production in discrete automotive engine compo-

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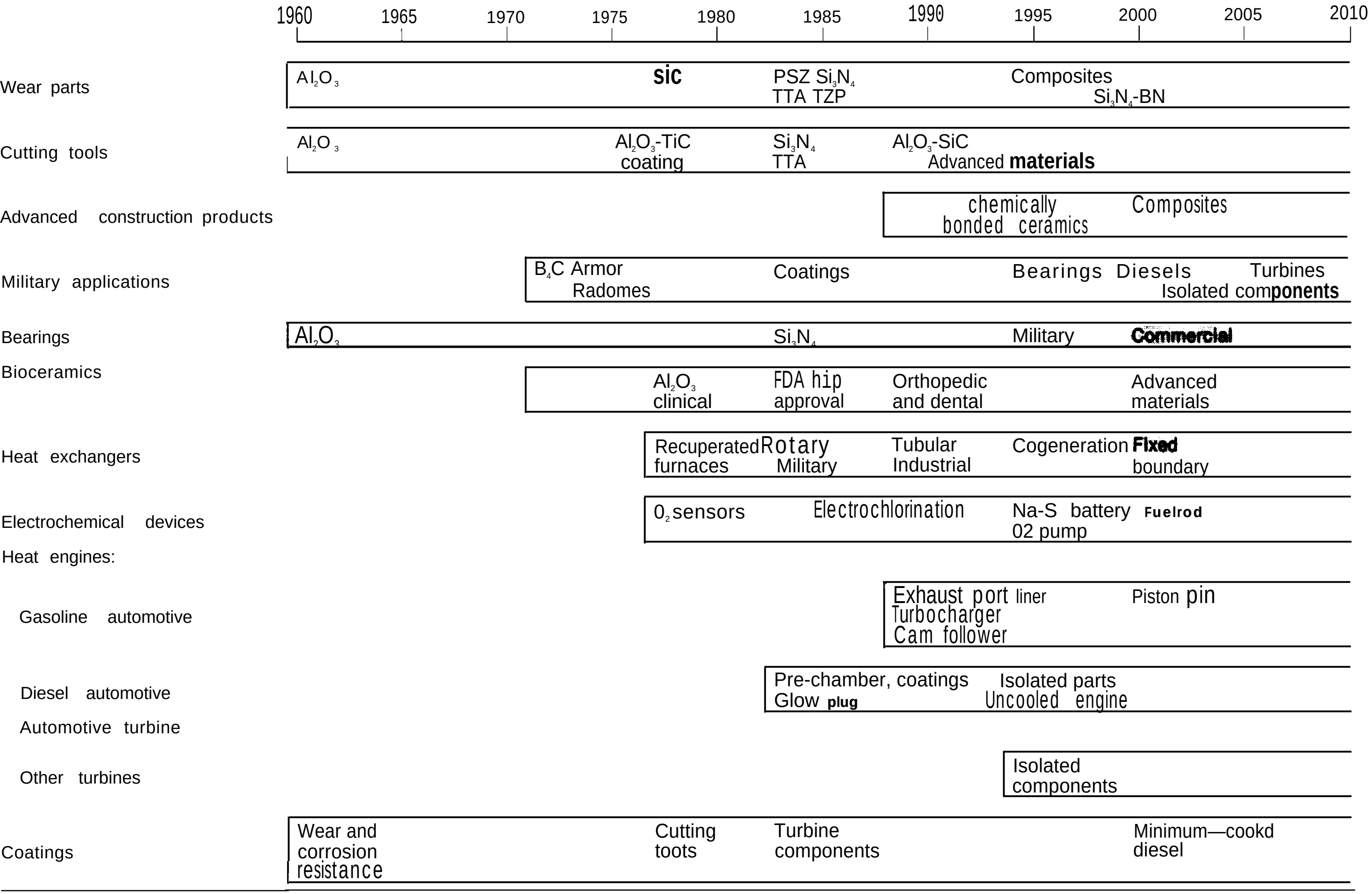
[22] U.S. Department of Commerce, *A Competitive* **Assessment of** *the U.S. Advanced Ceramics Industry* (Washington, DC: U.S. Government Printing Office, March 1984), pp. 38-39.

Figure 2.2.—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.

nents such as turbocharger rotors, glow plugs, and precombustion chambers for diesel engines. In West Germany, the automobile manufacturer Porsche uses ceramic exhaust port liners on one model. To gain experience in fabricating advanced ceramics, Japanese firms use advanced manufacturing techniques to produce such consumer products as ceramic ballpoint pen tips, tools, and scissors. These products also help to promote familiarity with the new materials among the Japanese public.

In the United States, research 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 CMC materials. Key objectives are to achieve improved toughness, higher reliability, and lower 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. Currently, progress is being made in resolving these limitations, and forecasts indicate there will be large increases in the market share for ceramics.

Near-Term Applications

U.S. production in the near term (the next 10 to 15 years) is projected in advanced construction products, bearings, membranes for food processing applications, bioceramics, heat exchangers, electrochemical devices, isolated components for internal combustion engines, and military applications. The technology feasibility for these applications 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; foreign dominance of these markets would adversely affect the U.S. balance of trade.

Far-Term Applications

Some potential applications of ceramics require solution of major technical and economic problems. These high-risk categories are categorized as far-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.

Far-term applications include the automotive gas turbine engine, the advanced diesel, some electrochemical 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 far-term.

Substantial design, material property, and manufacturing advances are necessary to achieve production of applications in the far-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 structural ceramics markets in the year 2000 for several of the categories listed above are shown in figure 2-3.

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, which is currently dominated by tungsten carbide, cermets, and specialty steels. With the total market estimated at $9 billion, the ceramic portion would be $540 million.[23]

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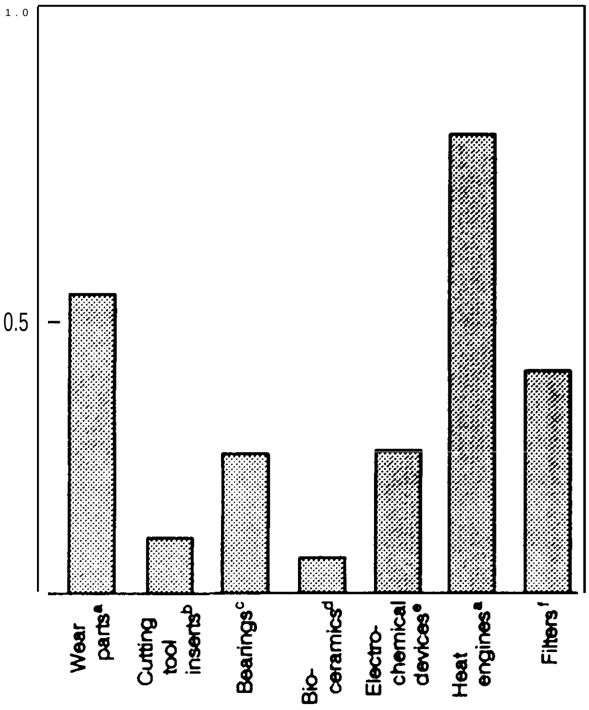
[23] Ibid., p. 35,

Figure 2-3.—Projected U.S. Markets for Structural 'Ceramics in the Year 2000 (billions of dollars)



SOURCES: [a]U.S. Department of Commerce, "A Competitive Assessment of the U.S. Advanced Ceramics Industry" (Washington, DC, U.S. Government Printing Office, March 1984)
[b]E.P. Rothman, J. Clark, and H.K. Bowen, "Ceramic Cutting Tools: A Production Cost Model and an Analysis of Potential Demand," *Advanced Ceramic Materials,* American Ceramics Society, Vol 1, No. 4, October, 1986, pp 325-331.
[c]High Technology, March, 1988, p. 14.
[d]Business Communications Co., Inc., as reported in Ceramic Industry, Jan 1988, p. 10.
[e]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
[f]Assumes a doubling from 1986. Paul Hurley, "New Filters Can Clean Up in New Markets," High Technology, August 1987

Cutting Tools

Ceramics have demonstrated capability as cutting tools, especially in competition with tungsten carbide-cobalt cermets 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 1000° C (18320 F). This permits 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, has been equipment limitations; much of the production metal machining equipment does not have the rigidity or speed capability to use ceramics.

A 1986 projection for ceramic and ceramic-coated cutting tools (the largest portion of which are inserts) places the growth rate at about 6 percent per year from a present market of $600 million to a market of over $1 billion by *1995.*[24] The vast majority of this market is coated carbide tooling. A second projection, for only the solid ceramic insert cutting tool market, is $128 million overall market by the year 2000. [25]

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 is being developed to improve properties and to decrease cost by permitting 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.[26]

Membranes

Membrane filters are used in a wide variety of separation and purification processes, and markets are projected to increase from $500 million in 1986 to $2 billion by 1995. Some of the fastest growing segments are expected to be food and

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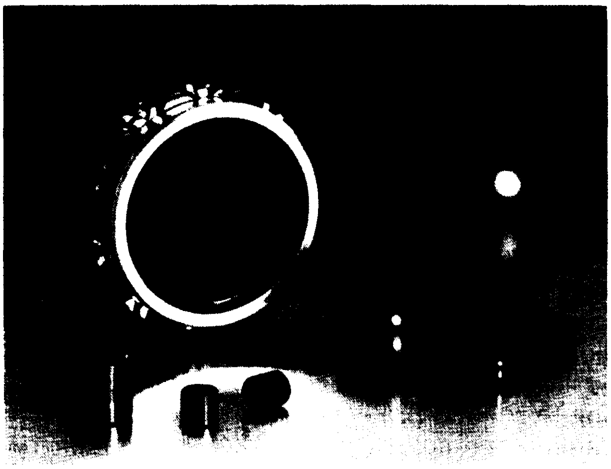
[24] G. Shroff, SRI International, "Business Opportunities in Advanced Structural Ceramics and Ceramic Coatings, excerpted in *Advanced Ceramic Materials* 1(4):294, October 1986.

[25] Elaine P. Roth ma n, Joel Clark, and H. Kent Bowen, "Ceramic Cutting Tools: A Production Cost Model and an Analysis of Potential Demand, " *Advanced Ceramic Materials,* American Ceramic Society 1(4):325-331, October 1986.

[26] High Technology/, March 1986 p. 14.



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beverage processing, aqueous waste processing, diesel engine exhaust filters, and gas separation. Although ceramic membranes cost more than the more well-established polymer membranes, ceramics offer a number of performance advantages, including resistance to high temperatures, chemical and mechanical stability, and ease of cleaning. In 1986, markets for ceramic membranes were estimated at $200 million, and growth rates of up to 30 percent are projected into the 1990s.[27]

Coatings

Ceramic coatings should be considered an extremely important technology for extending the performance of metal components, and, in some cases, they may be an excellent alternative to monolithic ceramics. They 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. In 1985, markets for ceramic coating materials were estimated at $1 billion worldwide, of which about 60 to 70 percent was domestic.[28] This estimated market includes jet engine, printing, chemical, textile, and tool and die applications. This list could be greatly expanded in the future to include wear parts, bearings, biomaterials, heat exchangers, and automotive components.

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.[29] Advanced cement pastes cost $0.20 to $0.30 per pound (compared with $0.75 to $2 per pound for metals and plastics), and they could displace these materials in the future in many common uses.

The development of a cost-effective, durable, high-tensile, and high-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 on replacement and repair of pavements and about $103 billion to correct bridge deficiencies.[30] Cost savings of about $600 million per year could result from implementing new technologies.[31]

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[27] Paul Hudey, "New Filters Clean Up in New Markets," High *Technology,* August 1987.

[28] Julie M. Schoenung, Elaine P. Rothman, and Joel P. Clark, "properties, Costs, and Applications of Ceramics and Ceramic Matrix Composites," a contractor report prepared for the Office of Technology Assessment, December 1985.

[29] Imperial Chemical Industries, "New Inorganic Materials" (product literature).

[30] National Research Council, Transportation Research Board, *America's Highways: Accelerating the Search for Innovation,* special report No. 202, 1984.

[31] Ibid.

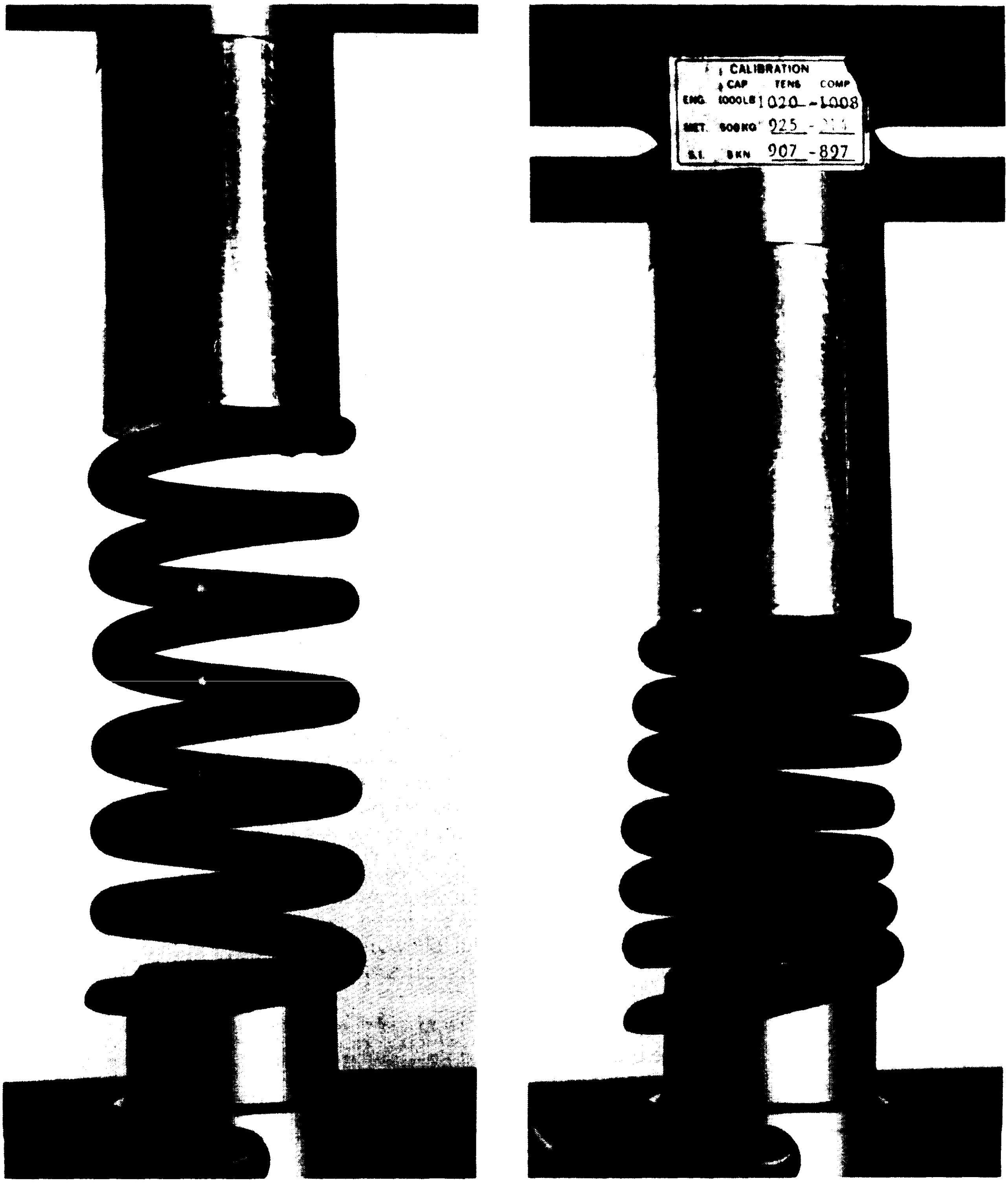

Photo credits: CEMCOM Research Assiciates, Inc.

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.

In addition to reducing repair and maintenance costs, new materials would provide other benefits. For instance, high compressive strength concrete can be used to reduce the number and thickness of concrete bridge girders, significantly reducing the structural weight.[32] In concrete high-rise buildings, the use of such materials permits a reduction in the diameter of the columns, thus freeing up additional floor space.

There are major barriers to the development and implementation of new technologies in the construction industry. Some of those most often cited are industry fragmentation (e.g., some 23,000 Federal, State, and local agencies operate the Nation's highway system); an arrangement that awards contracts to the lowest bidder; and low industry investment in research as a percentage of sales (the steel industry, by contrast, invests eight times more).[33] 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.[34]

The Surface Transportation Assistance Act of 1986 (Public Law 100-1 7) sets aside 0.25 percent of Federal aid highway funds **for the** 5-year, $150 million Strategic Highway Research Program. The program, which is 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 cost-effectiveness, $20 million; concrete bridge components, $10 million; cement and concrete, $12 million; and snow and ice control, $8 million.[35]

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] However, not all estimates are so optimistic. One projection places the U.S. bioceramics market at $8 million in 1987, increasing to $60 million by 2000.[38]

Bioceramics may be grouped into three categories: nearly inert, surface-active, and resorbable.[39] 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 permit the implant to be held firmly in place and help prevent rejection due to dislocation or to influx of bacteria. Surface-active ceramics that will bond to bone include dense hydroxyapatite, surface-active glass, glass-ceramic, and surface-active composites. The function of resorbable bioceramics is to provide a temporary space filler or scaffold that will serve until the body can gradually replace it.

Resorbable ceramics are 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.[40]

Any new material intended for use in the human body must undergo extensive testing before it is approved. Preclinical testing, clinical studies, and followup generally take a minimum of 5 years to complete.[41] However, ceramics have been in

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[32] J. E. Carpenter, "Applications of High Strength Concrete for Highway Bridges," *Public Roads* 44(76), 1980.

[33] National Research Council, op. cit., 1984.

[34] Ibid.

[35] "Construction and Materials Research and Development for the Nation's Public Works," OTA staff paper, June 1987.

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

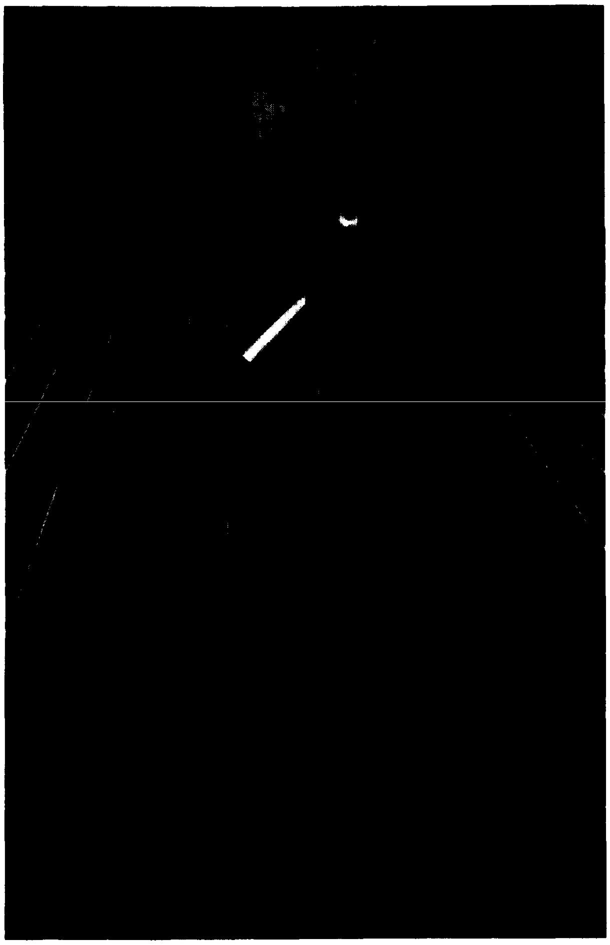
[37] Larry L. Hench, University of Florida, personal communication, August 1986.

[38] According to Business Communications Co., Inc., as reported in *Ceramic Industry,* January 1988, p. 10.

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

[40] Ibid.

[41] Edwardo March, Food and Drug Administration, personal communication, August 1986.



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Heat Exchangers

Ceramic heat exchangers are cost-effective because they can use 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 temperature, the greater the benefit. Ceramic systems have the potential to reduce fuel consumption by more than 60 percent.[43]

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 on 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 *2200°* F (1204° **C).** Silicon carbide is being evaluated for higher temperatures, but considerable design modifications will be necessary .44

Federal 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.

Three of their specific concerns are: 1) the high installed cost (up to $500,000 for a unit that delivers **20 million British thermal units** per hour), which represents a significant financial risk to the user for a technology that is not well proven; 2) many potential end users are in segments of industry that presently are depressed; and 3) designs vary according to each installation, leading the user to want a demonstration relevant to his particular situation.

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42 *Richerson,* op. cit., footnote 4

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

[44] Richerson, op. cit., footnote 4.

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

Electrochemical Devices

Although not strictly structural applications of ceramics, devices in this category use 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.[45]

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.[46] Ceramics are being considered in three general categories: 1) discrete components such as turbocharger rotors in metal reciprocating engines; 2) coatings and monolithic hot-section components in advanced diesel designs; and 3) all-ceramic gas turbine engines.

Some analysts have predicted that components for heat engines will be the largest area of growth for structural ceramics over the next 25 years. projected market estimates vary widely. Earlier estimates tended to be more optimistic, with several analysts projecting U.S. ceramic heat engine markets around $5 billion by the year 2000. The Department of Commerce has conservatively estimated 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 in automobile engines. Ceramic precombustion chambers and glow plugs for diesels, as well as ceramic turbocharger rotors, are now in production in current model Japanese cars.

Ceramic engine components 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 gasoline 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, current engine designs are considered by automotive companies to be mature, reliable, and cost-effective.

Very few incentives for change exist. Cost reduction does remain a significant incentive, but this goal 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 a new technology that may be applicable to advanced designs. This would involve both generic and directed R&D, with the primary objective of maintaining a competitive position. Ceramics within this category that have potential for production in-

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[45] Ibid.

[46] R. Nathan Katz, "Applications of High Performance Ceramics in Heat Engine Design, " *Materials Science and Engineering 71 ;227-249, 1985.*

[47] U.S. Department of Commerce, op. cit., footnote 22.

[48] Charles 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.

[49] Richerson, op. cit., footnote 4.

Photo *credit: The Garrett Corp*

Ceramic turbocharger turbine rotors

elude exhaust port liners, cam followers, and turbocharger components. To date, U.S. firms have not introduced these products, although R&D programs continue.

The United States remains behind Japan in procuring the advanced production equipment needed to 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 rotor market will develop. 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]

The ceramic turbocharger rotor 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 rotor are expected to serve as a pattern for subsequent ceramic engine technology efforts.

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[50] Elaine P. Roth man, "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.

Diesel Engines

There are several levels at which ceramics could be incorporated in diesel engines, as shown in table 2-9. The first level involves a baseline diesel containing a ceramic turbocharger rotor 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 strength, rather than thermal insulation.

The third level would use 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 technology also could be used at levels one, two, or three.

The four levels 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. Level three is the level at which the most significant improvements in fuel efficiency would be realized. However, 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. 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 permit emission control devices to operate more efficiently. The market for ceramics could also be affected by the fact that one major candidate for diesel emission control is a ceramic particle trap. However, such a trap is likely to be expensive.

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[51] Katz, op. Cit. , footnote 46.

[52] Richerson, op. cit., footnote 4.

Table 2-9.—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
	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," *Materials Science and Engineering 71:227-249, 1985,* 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 U.S. 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 accumulated over 9,375 miles (15,000 kilometers) of successful road testing.[53] The current state-of-the-art thickness of zirconia coatings is 0.03 to 0.05 inch (0.762 to 1.27 millimeter). It is estimated that thicknesses of 0.125 inch (3.175 millimeter) will be required to provide thermal insulation comparable to monolithic zirconia.[54] The coating is not as impermeable or as resistant to thermal shock as the monolithic zirconia. However, the coated metal part has greater 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 to isolate the benefits of the use of ceramics. Failure to do this has led to overestimation of the benefits of ceramics. For instance, a recent study of a ceramic diesel design funded by the Department of Energy 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]

However, 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. Recent work at Ford Motor Co. also showed a 5- to 9-percent increase in fuel efficiency in an uncooled test engine fitted with ceramic inserts, compared to the baseline water-cooled design.[56]

Charles River Associates predicts that the uncooled ceramic diesel engine system will be the first to be commercialized.[57] 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 that can be used for level three technology, wherein the greatest fuel efficiencies are expected. It remains to be seen whether the elimination of the cooling system will provide sufficient incentives to U.S. automakers to commercialize level two ceramic technology.

Japan in particular has very active research programs both in material and diesel engine development. Isuzu, the strongest ceramic engine advocate of all of the Japanese auto companies, has reported more than 300 miles (480 kilometers) of road testing and is projecting 1990 production,[58] Toyota has plans to produce an all ceramic diesel, using injection molded and sintered silicon nitride by 1992. Every part will be proof tested. The largest Japanese automakers all maintain extensive research activities in the area of ceramic engines.[59]

Automotive Gas Turbines

The major incentive for using ceramics in turbines is the possibility of operating the engine at turbine inlet temperatures up to about 2500° F (1371° C), compared with superalloy designs, that are limited to about 1900° F (1038° C) without cooling. This temperature difference translates into an increased thermal efficiency from around

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[53] Katz, op. cit., footnote 46.

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

[55] T. Morel, et al., "Methods for Heat Transfer and Thermal Analysis of Insulated Diesels," *Proceedings of the 23rd Automotive Technology Development Contractors Coordination Meeting* (Dearborn, MI Society of ,Automotive Engineers, March 1986).

[56] Arthur F. McLean, "Materials Approach to Engine/Component Design," *Ceramic Materials and Components for Engines*, W. Burk and H. Hausner (eds.) (Bad Honnef, FRG: Verlag Deutsche Keramische Gesellschaft, 1986), p. 1023.

[57] Charles Rivers Associates, op. cit., footnote 48.

[58] Richerson, op. cit., footnote 4.

[59] Robert J. Gottschall, "Basic Research in Ceramic and Semiconductor Science at Selected Japanese Laboratories," DOE/ER-0314, a Department of Energy report available from the National Technical Information Service, March 1987, p. 39.

40 percent to nearly 50 percent.[60] Power increases of 40 percent and fuel savings of around 10 percent have been demonstrated in research engines containing ceramic components.[61] 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 represent an enabling technology for the automotive gas turbine; i.e., ceramics are the key to designing and manufacturing an automotive turbine 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, 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 West Germany, Sweden, Japan, and the United States. The tests in the United States have involved highly instrumented development engines in test cells.[62] Current programs have achieved over 100 hours of operation at temperatures above 2000° F (1093° C).[63] These achievements, although impressive, are still far from the performance required of a practical gas turbine engine, which will involve continuous operation above 2500° F (1 3710 C). The limiting component in these engines appears to be the rotor, which must spin at about 100,000 rpm at these temperatures. The most reliable rotors available have generally been manufactured in Japan.[64] The target automotive gas turbine engine is designed to provide about 100 horsepower with fuel efficiencies of about 43 miles per gallon for a 3,000-pound automobile.[65]

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.[66] 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 that 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 powerplant 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.[67] 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–that of waiting to see if a clear market niche for ceramics develops before investing heavily in the technology—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

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[60] John Mason, Garrett Corp., presentation at the Society of Automotive Engineers International Congress and Exposition, Detroit, MI, February 1986.

[61] David W. Richerson and K.M. Johansen, "Ceramic Gas Turbine Engine Demonstration Program, " final report, DARPA/Navy contract N00024-76-C-5352, May 1982,

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

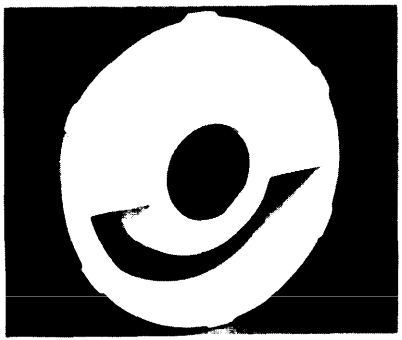
[63] Mason, op. cit.

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

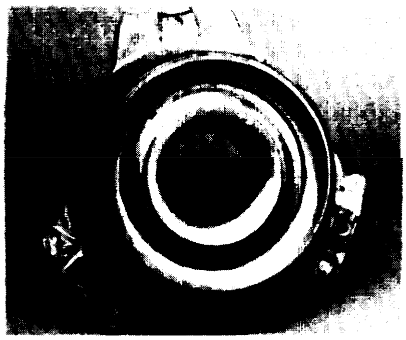
[65] Katz, op. cit., footnote 46.

[66] Richerson, op. cit., footnote 4.

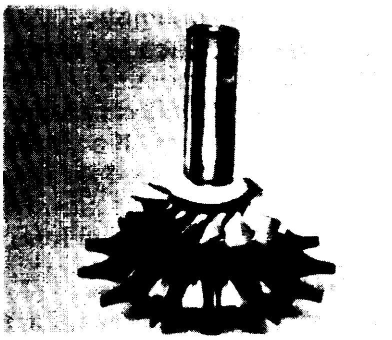
[67] U.S. Congress, Office of Technology Assessment, *Increased Automobile Fuel Efficiency and Synthetic Fuels: Alternatives for Reducing Oil Imports, OTA-E-185* (Washington, DC: U.S. Government Printing Office, September 1982), p. 145.



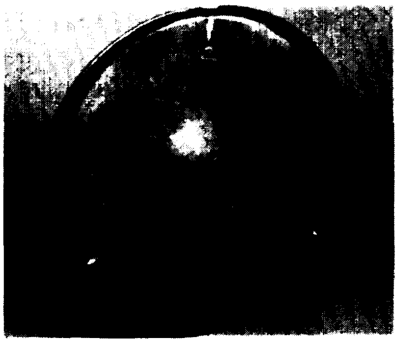
1. Flow Separator Housing



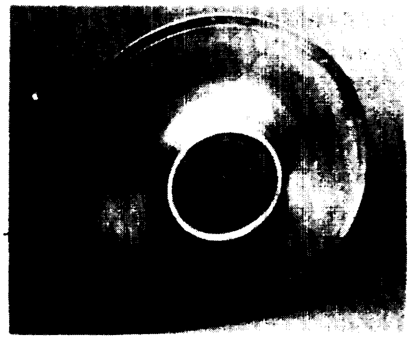
2. Turbine Shroud



3. Turbine Rotor



4. Inner Diffuser HSG



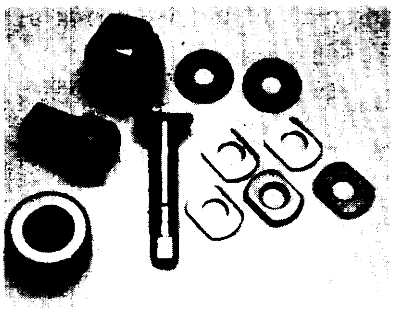
5. Outer Diffuser HSG

6. Turbine Backshroud

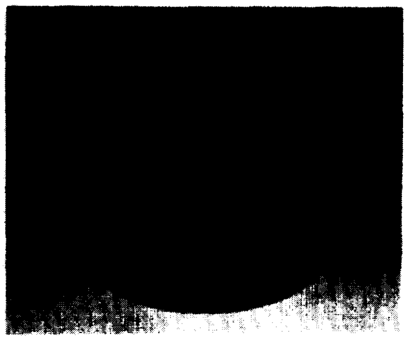
7. Stator Vane Segments

8. Turbine Transition Liner

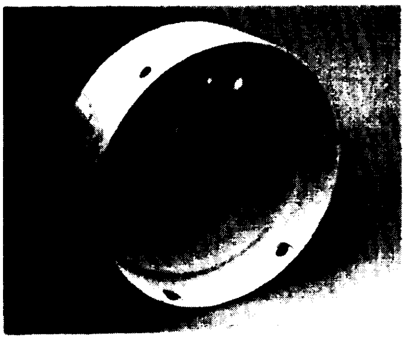
9. Combustor Baffle



10. Bolts



11. Regenerator Shield



12. Alumina-Silica Insulation

Photo credit: The Garrett Corp.

Prototype ceramic gas turbine engine components 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.[68] [69]

Military Applications and Production

Production of ceramics for military applications is projected to expand substantially during the next 25 years.[70] 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 that will lead to applications or performance that could not otherwise be achieved. Some of the resulting technology will be suitable for commercial spinoffs 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. Considerable progress has been made through the use of ceramic coatings. Monolithic ceramics have also been tried, but have been successful only in a few components and still require further development. A military diesel with minimal cooling achieved primarily with ceramic coatings could be produced by 1991. Engines containing more extensive ceramic components are not likely to appear before about 1995 to 2000.[71]

Turbines

Turbine engines are in widespread military use 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 major improvements in performance: as much as 40 percent more power, and fuel savings of 30 to 60 percent.[72] 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.[73]

Longer-life engines will require considerable development to demonstrate adequate reliability. This development must address both design and materials in an iterative fashion. Although the use of ceramic thermal barrier coatings in metal turbines is well under way, new turbines designed specifically for ceramics are not likely to be available before the year 2000,

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

[69] Charles River Associates, op. cit., footnote 48.

[70] Richerson, op. Cit., footnote 4.

[71] Ibid.

[72] Ibid.

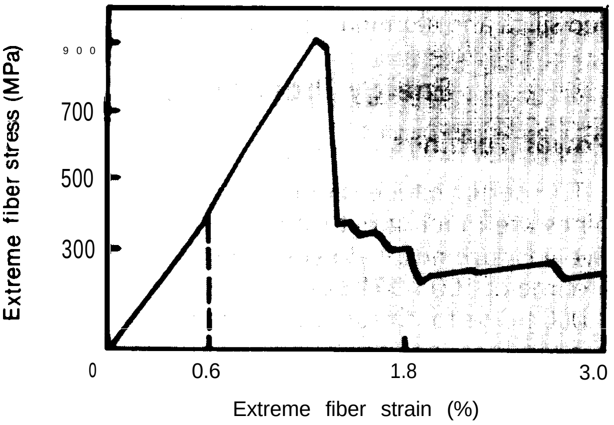
[73] Ibid.

FUTURE TRENDS IN CERAMICS

Ceramic Matrix Composites

Major improvements in the fracture properties of ceramics have been obtained by reinforcing matrices 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 2-4. The most developed composites to

Figure 2-4.–Load-Deflection Curve for a Nicalon Fiber-Reinforced Silicon Nitride Composite



Dotted line indicates point at which fracture would occur without fiber reinforcement.

SOURCE: Joseph N. Panzarino, Norton Co., Personal communication, Sept. 3, 1987.

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.[74] 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.

CMCs 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 Processes for Ceramics

Several forming and sintering techniques may offer the potential for significant improvements in the microstructure of ceramics produced from powders. These include advanced casting methods, such as open casting and centrifugal casting; and such new heating methods as microwave and plasma sistering.[75]

In the future, however, chemical approaches to the fabrication of ceramics will probably be preferred to the traditional methods of grinding and pressing powders. Chemical routes to ceramics include such techniques as sol-gel processing, chemical vapor infiltration of ceramic fiber preforms, and in-situ formation of metal-ceramic composites by reactions between liquid metals and appropriate gases.[76] [77] These techniques afford greater control over the purity of the ceramic and over its microstructure. it has been estimated that 50 percent of structural ceramics will be processed chemically by the year 2010.78

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 they are likely to be important in a broad range of product separation technologies.

Fermenters

Most current fermenters are made of316 grade stainless steel .79 Steel fermenters suffer from several disadvantages, including contamination of the cultures with metal ions, corrosion caused by cell metabolizes 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 be-

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[74] D.B. Marshall and A.G. Evans, "The Mechanics of Matrix Cracking in Brittle-Matrix Fiber Composites," *Acta Metallurgica* 33(1 1):2013-2014, *1985.*

[75] Richard Pober, Ceramics Processing Research Laboratory, MIT, personal communication, April 1987.

[76] See for example David W. Johnson, Jr., "Sol-Gel Processing of Ceramics and Glass," *American Ceramic Society Bulletin* 64(1 2): 1597-1602, 1985.

[77] Commonly called the Lanxide process, this technique has recently been extended to permit the fabrication of ceramic fiber-reinforced composites, See *Materials and Processing Report*, MIT Press, vol. 2, June 1987.

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

[79] Richard F. Geoghegan, E.1. du Pent de Nemours & Co., personal communication, August 1986.

tween 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 instance, biologically produced insulin is now being purified with a chromatographic process based on a modified silica material.[80] 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.[81]

The strength and hardness of the ceramics are key to the avoidance of deformation of the ceramic particles under conditions of high throughput.[82] In the future, the most efficient processes could be hybrids based on both filtration and chromatography.[83] As these processes are scaled up to production units, there will probably be a large increase in the demand for specially modified silica and alumina column packing materials.

Energy Production

Power Turbines

The performance requirements for power turbines are much greater than those for automotive gas turbines.[84] 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.[85]

Although 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 monolithic 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. in addition, ceramic coatings could be used to augment the high-temperature resistance of cooled superalloy rotor blades,[86]

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[80] Joseph J. Kirkland, El. du Pent de Nemours & CO., personal communication, August 1986.

[81] George WhiteSides, Department of Chemistry, Harvard University, personal communication, August 1986.

[82] Ibid.

[83] MichelleBetrido, Celanese Research Corp., personal communication, August 1986.

[84] Johnson and Rowcliffe, op. cit., footnote 43.

[85] Ibid.

[86] Ibid.

RESEARCH AND DEVELOPMENT PRIORITIES

In fiscal year 1987, the U.S. Government spent about $65 million on structural ceramics R&D (table 2-10). R&D expenditures in private industry may be roughly comparable.[87] [88] DOE and DoD spent the largest proportions, at 55 and 28 percent, respectively. The following hierarchy of R&D priorities are based on the opportunities identified above. These are then correlated with the actual spending on structural ceramics R&D in fiscal year 1985.

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[87] Charles River Associates, op. cit., footnote 48, p. 38.

[88] A recently completed survey by the United States Advanced Ceramics Association places the private industry R&D investments in all advanced ceramics, including structural and electronic ceramics, at $153 million in 1986, somewhat greater than the total government expenditure of $100 to $125 million.

Table 2-10.—Structural Ceramic Technology: Federal Government Funded R&D (in millions of dollars)

	FY 1983	FY 1984	FY1985	FY1986	FY1987
Department of Energy:					
Conservation and renewable energy:					
Vehicle propulsion	11.4	12.7	11.9	10,0	12.0
Advanced materials	3.2	5.1	6.0	8.7	14.0
Industrial programs	1.0	2.3	1.7	1.5	1.9
Energy utilization research	0.5	1.5	1.8	1.8	2.0
Fossil energy:					
Advanced research and technology development	1.0	1.1	1.5	1.2	1.9
Energy research:					
Basic energy science	3.0	4.4	4.6	4.5	4.2
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	7,3
U. S. Air Force	3.0	3.4	4.7	4.7	5.1
U.S. Army	4.7	6.0	2.5	4.4[b]	3.6[c]
U.S. Navy	1.2	1.3	1.4	2.3	1.9
Total	42.6	51.8	54.5	59.4	65.2

a Includes $1 6 million for Manpower Salaries.
b Includes $40 million for TACOM Diesel
c Includes $20 million 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 that can be formed and densified with a minimum of intermediate steps; role of solution chemistry in powder preparation and control of interface properties in CMCs;
- development of practical in-process inspection devices and techniques to identify problems at the earliest possible stage in the process;
- iterative development of new equipment such as hot isostatic presses (HIPs) and multistage processes such as sinter-HIP, with emphasis on scaling up to commercially viable size; and
- understanding of 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. 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 CMCs based on these materials in environments of 1000° to 1400° C (1 8320 to 2552° F) in air, carbon monoxide, and carbon dioxide.
- In ceramic wear parts, it is necessary to understand the interrelationships of wear, erosion, and toughness in the presence of lubricating fluids and gases. Generally, wear parts include hard materials such as tungsten carbide, titanium diboride, and materials that have good lubrication characteristics, such as silicon nitride.
- Because heat exchangers generally fail as a result of slow corrosion at high temperatures, it is important to understand the chemical

processes of corrosion in such environments as 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 CMCs, should be investigated. Corrosion-resistant ceramic coatings may become important here.

- Considering the large size of the potential markets in bioceramics, it is critical to understand the long-term effects of body fluids on chemical structure and mechanical properties. In view of the many years that 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 is 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 has 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. Because the performance specifications and environment of each application are different, it is necessary to establish the most appropriate and cost-effective NDE methods for each one.

To distinguish between critical flaws and harmless flaws, models need to be developed for predicting the service life 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 CMC failure mechanisms discussed above. Beyond a dependence on intrinsic flaws in the material, however, service life also depends on the location and nature of the flaw within the structure itself. it is not sufficient 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 CMCs

The interphase between ceramic fiber and matrix is critical to the static strength, toughness, and long-term stability of the CMC. Very little is known about the relationship between the properties of the interphase and these overall CMC 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 on joining of ceramics to metals, glasses, and other ceramics could have a decisive impact on future use of monolithic ceramics, coatings, and CMCs.

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 CMCs.

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 various environments of interest. As with solution methods in powder preparation, chemistry will make a crucial contribution in this area.

Tribology of Ceramics

Tribology, the study of friction, wear, and lubrication of contiguous surfaces in relative motion, is of key importance in terms of 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 350°F (177°C). For operating temperatures of 500° to 700°F (260° 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 1000° to 1700° F (538° 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 to this problem is to use solid lubricants that 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 .[89]

A second method 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. Alternatively it is possible 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 that are roughly four times higher than those achieved at low temperatures with engine oils.[90] Further research is clearly needed.

Failure Mechanisms in CMCs

CMCs 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 CMCs would provide guidance for development of new, tougher ceramics. This would include investigation of: multiple toughening techniques, such as transformation toughening and whisker reinforcement; the role of interphase properties in fracture; and failure mechanisms in continuous-fiber CMCs.

Desirable

Chemically Bonded Ceramics

Chemically bonded ceramics (CBCs) 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 reduction of flaw size, long-term stability in various environments, and the properties of the interphase in fiber-reinforced cements and concretes.

* * *

Table 2-11 shows that the actual structural ceramics R&D spending in fiscal year 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 CMCs; a portion of this work is included under CMC fabrication, listed here as a subcategory of processing. Also, no separate figure was obtained for Federal expenditures on advanced cements and concretes. In fiscal year 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. [91] Assuming that the current breakdown of Federal ceramics research is similar to that in fiscal year 1985, a comparison of table 2-11 with the priorities listed above suggests that greater emphasis should be placed on joining, tribology, and cement-based materials.

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[89] Manfred Kaminsky, Surface Treatment Science International, personal communication, August 1986.

[90] Ibid.

[91] National Research Council, Transportation Research Board, op. cit., footnote 30.

Table 2-11.–Breakout of the Fiscal Year 1985 Structural Ceramics 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%

SOURCE: S.J. Dapkunas, National Bureau of Standards, unpublished survey, 1985