JOURNAL REVIEW

Ceramic Processing: An overview

Processing of ceramics is reviewed from a broad perspective, with emphasis on the predominant powder-based methods, but with considerable attention to other methods. Major stages of the powder process, from preparation, modification, and handling, to sintering or pressure densification (or postdensification) are discussed. Nonpowder-based methods, such as chemical vapor deposition, melt, and polymer pyrolysis processing, are also presented. Processing of ceramic composites is reviewed, noting the shifts in processing technology this entails. Practical aspects, such as part size, shape, volume, and the costs of various processes are also addressed.

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Introduction

Ceramics is inherently an interdisciplinary field and has previously benefited from participants whose training or expertise was in other fields. Because of increased interest in ceramics, the field is in a stage of significant expansion in both size and diversity of participants. Significant interest on the part of major corporations, especially those that are chemically oriented, and on the part of chemistry and chemical engineering organizations, such as university departments and professional societies in the field of ceramics, is testament to this change. This increased interest bodes well for ceramics; it also presents some important challenges of understanding and communication. Therefore, before discussing ceramics processing, it is useful to briefly outline some aspects of the field of ceramics.

A generally accepted modern definition of a ceramic is an inorganic, nonmetallic material. In finished form it is typically a solid material, usually as a bulk three-dimensional body, but various other forms such as coatings or fibers are also important. Typical ceramic products and applications are shown in Figures 1-7and are treated in later discussion. Since most of the processing and much of the use of ceramics in the past has involved high temperatures—as it will in the future—the term ceramics has commonly implied the more narrow, but significant field of refractory ceramics (refractory is not precisely defined, but often refers to temperature capabilities of ≥1,500°C). Composites present an added challenge in adequately defining materials. They are commonly classified by the character of their matrix (at least where there is one clearly interconnected phase that is generally a major or significant constituent of the whole) as organic, metallic, or ceramic matrix composites. Ceramic composites are discussed in this paper.

This field of inorganic, nonmetallic materials known as ceramics is, in part, a branch of inorganic chemistry, but is also much more. It is a branch of physics because of the diversity of physical phenomena and properties involved. It is also very interactive with a variety of disciplines associated with some of its processing and many of its applications; these disciplines include chemical, mechanical, and electrical engineering.

Ceramics has evolved mainly from fabricating silicate-based bodies consisting of a mixture of glass and crystalline oxide phases to fabricating mainly pure glass (at least as fabricated; some glasses are designed for subsequent crystallization) or mainly polycrystalline bodies (frequently with some, generally limited, glass content). While oxides still dominate, materials of nonoxide and mixed chemistries are of increasing interest, as are single crystals. This evolution has left some confusing terminology and opinions. Thus, the term ceramic was previously restricted by some to polycrystalline ceramics, excluding not only glasses but also single crystals. Anachronistic terms are also used, such as glass-ceramic (a partially or fully crystallized glass) and ceram (developing a polycrystalline body from one which is not, generally by crystallization of a glass, although in more recent times by hot working of single crystals). Since most applications are for polycrystalline materials, that will be the focus of the paper, but some aspects of processing pertinent to both glasses and single crystals will be noted.

Interest in ceramics stems from their properties, commonly cited in terms of extremes of, for example, hardness, stiffness (and hence by theoretical implication, strength), dielectric breakdown, and thermal and electrical conductivity. (The recent discovery of high T_c superconductors only reinforces the extreme conductivity ceramics can have, since ceramics have been the major type of superconducting materials discovered in the last 20 or 30 years.) Even more important than single properties is the ability of many ceramics to provide unique combinations of properties. Examples include high electrical resistivity with high thermal conductivity (as found in) BeO and AlN), strong magnetic fields with high electrical resistivity (ferrites), high stiffness and temperature capability combined with high electrical resistivity, and optical transparency (Al_2O_3, $MgAl_2O_4$).

The intent of this overview is to give a view of the breadth of

Figure 1. Large ceramic components.

1. Randome, missile nose tip for radar transmission, up to ~1m in height, >20 cm base dia. wall thickness 0.5–1 cm; typical materials: crystallized cordierite glass or sintered fused SiO_2 particles
2. Hot-pressed B_4C armor breastplate encased in fabric spall shield
3, 11. Glass tube and dome for underwater protection
4. KCL window for high-power CO_2 lasers
5. Typical lightweight refractory brick
6. High-voltage porcelain insulator
7, 8. Assembled lead zirconate titanate sonar transducer rings and larger separate ring
9. Syntactic foam (polymer bonded glass microspheres
10. Large Al_2O_3 insulator

ceramic processing technology, the major trends, and some of the needs and opportunities in the field. In order to do this, considerable, intermediate level discussion is devoted to the traditional processing methods. Information on traditional processing is widely available, and it is important to also give a reasonable discussion of lesser known techniques, especially those that are known or expected to be of increasing importance. It is impossible to address both the technology and the resultant economics in detail, so the former is heavily emphasized, with limited comments on costs. It is also impossible to provide comprehensive referencing for such a review. Instead, the citations comprise a combination of review and representative research papers, books, and conference proceedings. Representative sources include: Wang (1976), Onoda and Hench (1978), Palmour et al. (1978), Richerson (1982), Hench and Ulrich (1984, 1986), Brinker et al. (1984, 1986), Davis et al. (1984), Tressler et al. (1986), Davidge (1986), Messing et al. (1987), Messing and Fuller (1988), Reed (1988).

Ceramic Processing Overview

Fundamental reasons why ceramic processing is extremely challenging include:

1. The high temperatures commonly needed for refractory ceramics of greatest interest, or the clever chemical or physical approaches taken to circumvent their refractory nature.
2. The diversity of processing approaches, which is a major focus of this paper, and of the materials encompassed. Some idea of this diversity is given by Tables 1 and 2, and by Rice (1987).

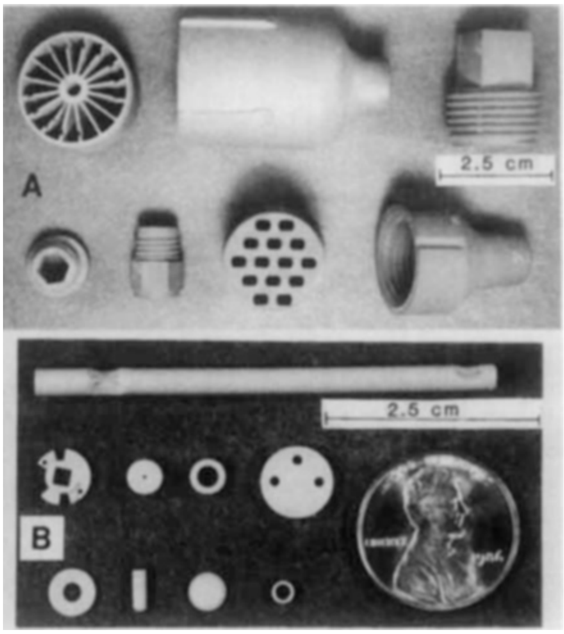

Figure 2. Injection molded ceramics.

A. Medium-size pieces of silicon aluminum oxynitride, SiAlON
B. Finer pieces of Al_2O_3

Many ceramics, indeed, most oxides, while often aided by additives, can sinter relatively well by themselves. Other ceramics, especially nonoxides, such as Si_3N_4 and SiC, are difficult to impossible to sinter without the use of additives. A variety of atmospheric conditions, ranging from air and vacuum to various gases (Ar, N_2, H_2, H_2S) at various pressures, are needed to handle some ceramics. However, what is optimum from the

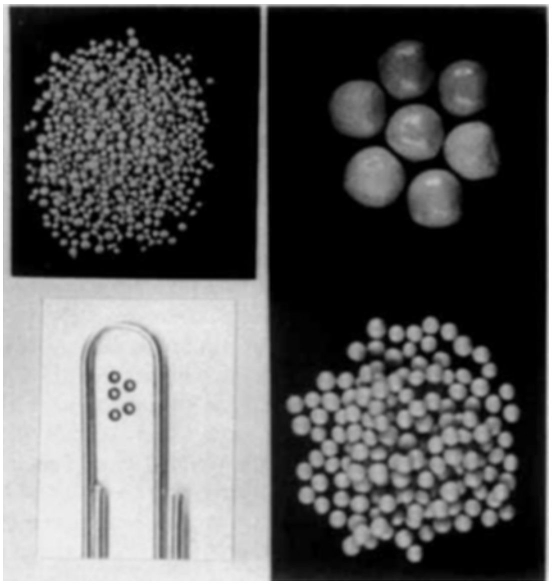

Figure 3. Small ceramic products.

A, B. Two sizes of approximately spherical ceramic pieces used for milling, as in sand or attritor mills; smaller balls are used for propants and for ballpoint pens
C. Early ferrite memory cores made by individual pressings; current cores, made by individual pressings; current cores, made by punching from green tape, are substantially smaller

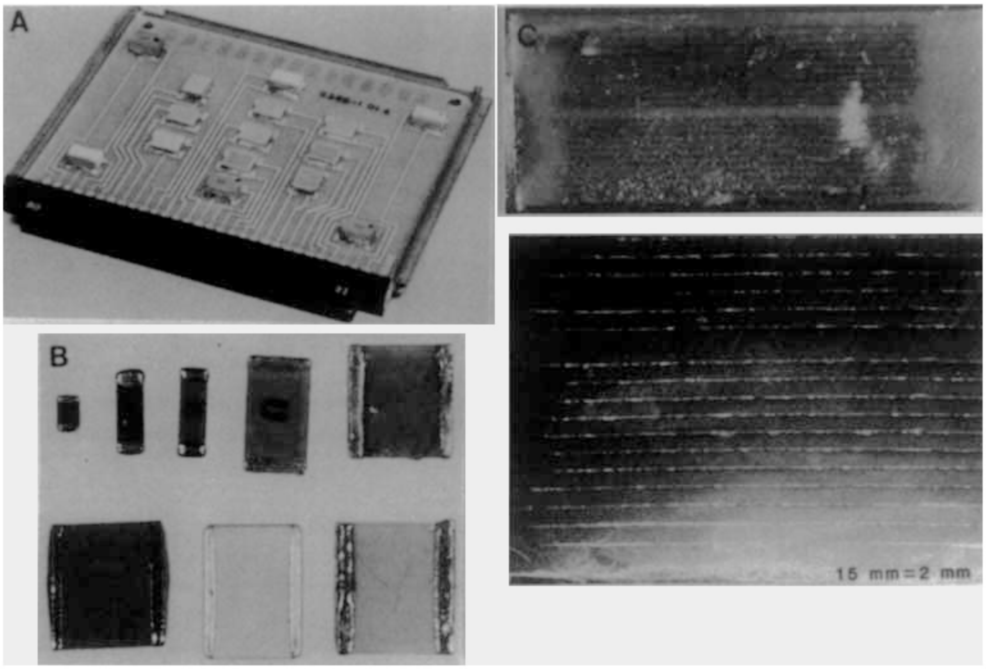

Figure 4. Ceramic layer structures.

A. Circuit board with attached ceramic components, such as multilayer capacitors
B. Various sizes of one style of ceramic multilayer capacitors
C. Simple Al_2O_3 electronic package with attached lead frame
D. Al_2O_3 substrate with screen-printed circuitry and passive circuit elements (resistors)
E, F. Low and high magnifications of complete and partial fracture cross section of a multilayer capacitor

material processing standpoint may not be practical, thus presenting further challenge. A wide variety of melting and vaporization characteristics, must be handled, ranging from those of materials that do not melt normally, to those of materials that substantially change their stoichiometry as a function of both temperature and environment. The broadening diversity of ceramic materials, especially to include more polyatomic compounds and composites, also adds to the processing challenge.

Among the many challenges presented by components to be manufactured by the ceramic process is the variety of sizes, shapes, and forms needed, since there are often both intrinsic and extrinsic limitations or advantages to the size, shape, and character of bodies that can be made by any given process; Table 2 summarizes relevant factors. Besides conventional, dense forms, there is a need for bodies of designed porosity (including ceramic foams), and special forms are needed in which only one or two dimensions are on the macro- as opposed to the microscale; Figures 3–7 show products of these kinds. Special forms include fibers and essentially two-dimensional bodies, ranging from coatings to single- and multilayer structures. These are especially useful in the field of electronics, in such products as capacitors and single- and multilayer component packages. A general challenge is dimensional control, for example, maintaining uniform shrinkage in drying and sintering. The problems include minimizing nonuniformities in powder consolidation, which is related to component size or shape, and maximizing reproducibility.

Finally, one of the biggest challenges in ceramic processing is dealing with microstructure, which has a very important role in virtually every ceramic material and product. Processing techniques commonly determine the microstructures obtained, as indicated in Table 2, and microstructures in turn often play an important role in the resultant physical properties of the material. Thus, the amount and character of porosity, grain size, phase morphology, and distribution, and their interrelations significantly affect a wide range of properties, from the electrical and magnetic to the mechanical. Figure 8 shows the key effects of microstructure on the strength of ceramic material. Many of these, and other, properties and functions of the material are dominated by extremes of the microstructure. This is particularly critical for strength and fracture behavior, not only because they are especially sensitive to the extremes of microstructure, but also because of the necessity of maintaining mechanical integrity for a variety of applications regardless of what the function of the ceramic component or material may be. A single pore or pore cluster, a large grain or a larger grain cluster, or chemical inhomogeneity can be the determining factor in mechanical failure and, hence, mechanical reliability. Figure 9 shows some microstructure-based failures. The commonly dominant role of microstructural extremes has been a major factor in motivating the development of ceramic composites of enhanced toughness for greater mechanical reliability (Rice, 1978, 1984a). However, the processing of composites places additional challenges in achieving the types of microstructures necessary to give improved mechanical properties, and in achieving the homogeneity in a desired microstructure required to ensure that these improvements can be adequately and

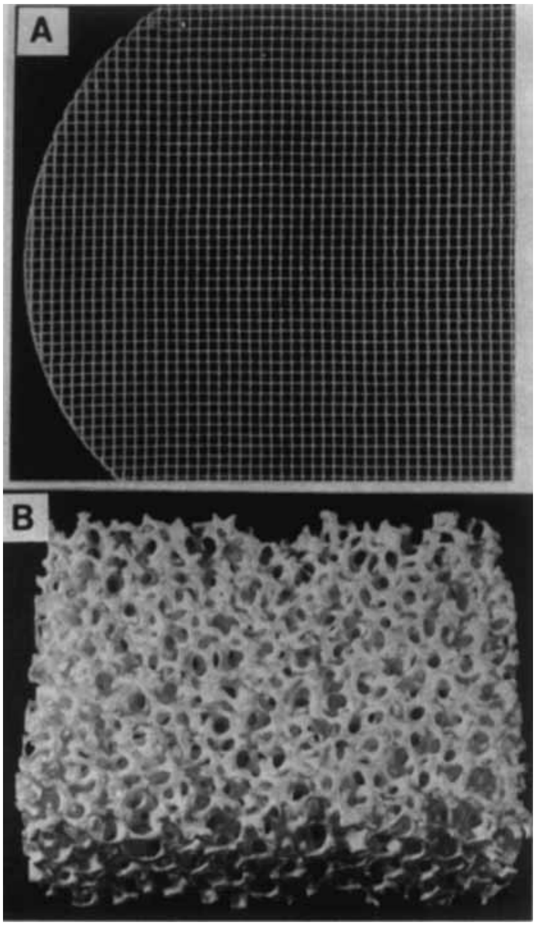

Figure 5. Open structure ceramics.

A. Extruded honeycomb (cordierite) such as used for automotive catalyst exhaust support
B. Reticulated Al_2O_3 foam as used for molten metal filtration

reliably obtained. An overview of ceramic processing needs and opportunities is outlined in Table 1 as a basis for subsequent discussion.

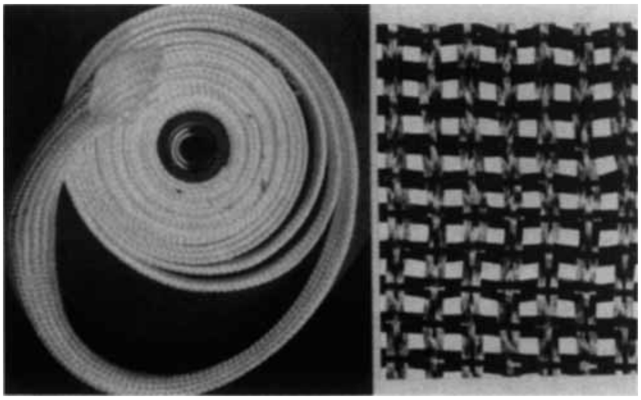

Figure 6. Ceramic fabrics.

Top: Very open weave of SiC based fiber tows; each tow contains a few thousand fibers.
Bottom: Spool of braided oxide fibers

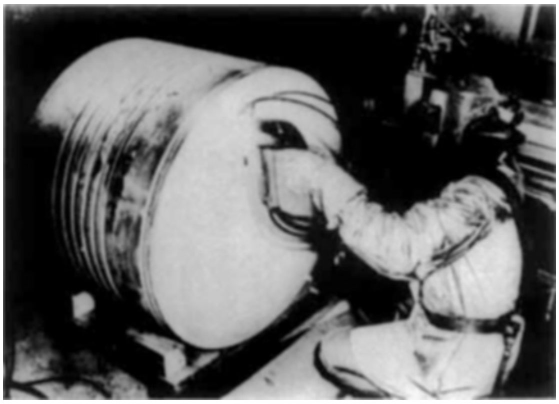

Figure 7. Plasma spraying ceramic coating on the head of a large marine diesel piston.

However, let us consider first the statistical aspect, and hence the role of homogeneity in ceramic failure. Perspective on the statistical aspects of isolated defects causing failure can be obtained by considering a relatively small ceramic component of nominally 1 cm^3 volume made from 1 μm particles, a common particle size for sintering many ceramic materials. A representative planar flaw size to cause weaker than average failure in a high-performance ceramic would be on the order of 50 μm. The absence of about 1,000 of the 10^{12} 1-μm particles—about one-third to one-half of the particles within one to three particle diameters of an approximately planar region—would dominate the failure characteristics of an otherwise perfect body. The extent of domination of the reduced strength would be a statistical function of the location and orientation of the defect relative to the principle stress(es).

To put this somewhat arbitrary construct in a more specific context, consider that the defect can have a serious effect on a component of almost any size, and can arise from various sources. Sufficiently close spacing of several impurity-containing particles can create a failure-causing region like that described above if the impurity(ies) sufficiently retard sintering (leaving distributed porosity), or accelerate it (resulting in a peripheral void around much of the faster sintering region). Hardened agglomerates of the particles from which the body is formed cause similar problems, whose occurrence and extent depend not only on the agglomerate character and location, that is, on the size and shape of the component, but also on the fabrication process. Pressure is the most common method of powder consolidation. Agglomerates that survive consolidation have different elastic spring-back upon release of the consolidation pressure, which may open a peripheral crack partway around the agglomerate. Whether agglomerates lead to pressing cracks due to greater density, they generally have a higher sintering rate and, hence, result in problems similar to those caused by the presence of impurities enhancing or retarding local sintering.

While agglomerates can be a source of defects, they are extremely important in ceramic processing, since fine powders have very poor flow characteristics and are generally very voluminous. In a production operation this presents significant challenges in controlling the rate and quantity of powder supply as well as its uniformity. Therefore, finer powders are typically processed into larger agglomerates, very often by spray drying. The process is outlined in Figure 10 and described by Lukasiewicz (1989). Variations of temperature, residence times, distribution

Table 1. Ceramic Processing R & D Areas

Processing Area	Goal	Expected Payoff
Materials preparation	Powder Preparation	
	Purer powder	Better composition, control, and properties
	Better particle size control	Finer, more uniform microstructures; easier, better sintering
	Morphological particles	Preferred orientation, better properties
	Particle coating	Better, broader range of composites; better processing
	Whisker/Fiber Preparation	
	Broader range of whiskers	Broader range of composites
	Larger, more uniform whiskers	Safer handling; better composites
	Fibers with better stability	Broader range of more stable composites
	Fiber, whisker coating	Tougher, more stable, broader range of composites
Powder processing	Improved particle size control (e.g., milling)	Finer, more uniform microstructures; easier sintering
	Improved mixing	More homogeneous products
	Improved agglomeration (e.g., spray drying)	Obtain practical powder flowability without hard agglomerates
Consolidation and shaping	Binders for improved forming	More uniform, easier sintered products of broader range of sizes and shapes
	Efficient colloidal consolidation	Finer, more homogeneous microstructures
	Greater control of orientation of particles, whiskers, chopped fibers	Better design, control of properties
Sintering, densification	Additives to aid sintering and/or allow use of lower quality raw materials	Improved properties; lower costs
	Alternate heating methods	More efficient sintering or hot pressing; better outgassing, finer microstructures, more homogeneous sintering
	Better sintering of two-phase systems	Lower costs of composite processing
Nonpowder-based processing	Broader range of ceramic polymeric precursors and understanding of their pyrolysis	Broader range of fibers, coatings, binders, and composite matrices and processing
	Better understanding and control of deposition (e.g., PVD, especially CVD, and melt spray) processes	Improved coatings, bulk bodies, and composites
	Improved manipulation and control of very hot and molten materials	More low/medium-cost fibers; use of eutectic structures; possible higher tech coatings

of additives, and related factors frequently yield some harder agglomerates, which can be important sources of mechanical failure, as shown in Figure 8d. One can similarly recognize the problems of agglomerates of organic matter leaving behind isolated large pores or pore clusters upon being burned out of the body, Figure 8b. Such organic matter may be the binder that bonds the particles together in order to give the powder compact the "green" strength, thus handleability, that is typically necessary in the manufacturing environment before it is finally put in the furnace and sintered. Alternatively, the organic matter may be trapped impurities—dust, lint, dandruff, insects or their feces, and the like—that contaminate the powder during storage or are present in the handling environment and equipment.

There are processing methods that can minimize the occurrence of many of the above defects, but they are often expensive and not necessarily completely effective. There are under development various quality assurance techniques, for example, nondestructive evaluation (NDE), to identify components with unacceptable defects (Rice, 1984). However, such techniques have serious limitations as to the size and shape of components to which they can be applied, the size of defects they can locate, the reliability with which they can locate defects, and cost. We still lack much of the technology required to predict what the failure stress limit of many identified defects will be. This adds to the already significant need for improving reliability by processing.

Powder Preparation and Processing

Preparation

By far the most extensively used methods of preparing ceramics are those based upon powder processing as outlined in Figure 10. Thus, powder preparation is one of the most basic steps for much ceramic processing. The preparation of ceramic powders, which are represented in Figures 11 and 12, has been moving increasingly toward a broader diversity of both powders and preparation processes, with much emphasis on more sophisticated chemical processing. While chemical and phase purity are basic requirements, control of particle size is of increasing importance. Average sizes are $>0.1\ \mu m$, but particles <1 to $3\ \mu m$ are more commonly desired, with limited size range. It is also often desired to have particles consisting of individual rather than multiple crystallites. For a number of applications, particles of individual crystallites having crystallographic shapes (for

Table 2. Ceramic Fabrication Processes, Trends, Capabilities/Results

Process	Shape	Size*	Porosity	Shrinkage	Use of Densification Additives	Residual Stresses	Anisotropy/ Preferred Orientation**
Sintering (pressureless)							
Die-Iso-pressing	Fairly versatile	To <50 cm commonly <10 cm	0.1 to 5%	Commonly 10–20%	Often	Usually limited	0–limited
Extrusion	Versatile	To ~30 cm dia and ≥1 m long					Low—medium
Injection molding	Very versatile	To ~20 cm, commonly ≤6 cm					Low–medium
Slip casting	Very versatile	To 50–100 cm					Low–high
Ramming	Somewhat versatile	≥1 m					0–very limited
Reaction sintering	Same as for various forming operations for sintering		~1 to ≥20%	0–20%	Some	Usually limited	0–limited, but may depend on forming operation
Pressure sintering							
Hot pressing	Fairly limited	To ~70 cm	0.0–0.2%	~0% lateral ~50% axially	Often	Usually limited	0–medium
HIP	Reasonably versatile	To ≤20 cm					0–very limited
Polymer pyrolysis	Very versatile	Thicknesses ≤1 cm, lengths ≤20 cm	15–30%	~5–20%	Generally, No	Can be high	0
Chemical vapor deposition	Fairly versatile	To ≥1 m	0.0–0.2%	~0.5–1%	No	Can be high	Low–very high
Melt (casting)	Somewhat versatile	To ≥1 m	0.0–20%	~2%‡	No	Can be high	Low–very high

*Maximum dimensions commonly reached in only 1 or two directions

**Anisotropy/preferred orientation increase for powder based process tends to vary with the ratio of the particle size to the part lateral dimensions i.e., as t/h increasing crystallographic shape and aspect ratio of the particles, and increasing shear of the process, i.e., is highest for tape casting or extruding thin sheets and especially fine spaghetti. For CVD (and other deposition processes) can be quite material and deposition dependent. For solidication, mainly increases with increasing directionality and decreases with rate of solidification.

orientation during forming, see Table 2) are desired. Examples are shown in Figure 12.

Chemical processing is most advanced with regard to oxide materials. Techniques have moved from primarily refining or mixing natural oxide materials to substantial chemical preparation. The preparation most commonly involves solution chemistry, typically precipitation of a salt that is then calcined to the resultant oxide. A variety of considerations can affect the success of such chemical processing. First, salts that undergo melting during any stage of their heating or decomposition should be avoided in order to maintain fine, unagglomerated particles. Melting or its effects can be avoided in some cases by freeze drying (Real, 1986; Hibbert et al., 1987; Reszka and Reszka, 1987), which can also have other benefits, or by spray pyrolysis. Salts that decompose at moderate temperatures are desired in order to avoid premature sintering and the formation of hard agglomerates or increasing particle size during decomposition. However, calcining at too low a temperature may leave residual gas species detrimental to subsequent densification processes such as hot pressing. Calcining is also widely used to mix or react constituents by solid-state diffusion, for example, $BaO + TiO_2 \rightarrow BaTiO_3$, which becomes an important factor in determining calcining conditions. Resultant characteristics such as particle sizes and distribution and degree of agglomeration

Microstructure	Cost†
Typically medium to coarse grain size tends to be an inverse function of the residual porosity level	Low to medium, depending on volume ↓, complexity ↑, and size ↗
Similar to sintering, but often somewhat finer grain size, but not necessarily finer porosity	Similar to pressureless sintering
Typically finer and more homogeneous than pressureless sintering.	Medium to high, depending most on shape and complexity ↑, some on volume ↘ and size ↓
Mostly very fine (submicron pores and grains) or amorphous, but often with some larger pores	Medium to high, driven mostly by polymer costs
Usually fine to medium, but can be very fine or very coarse; often inverse function of deposition rates	Low to high, driven mainly by volume and materials/deposition costs (e.g., rates)
Usually medium to coarse, often becoming coarser as size increases, but can be quite composition dependent	Generally low with some volume ↘, size ↘, complexity ↗, dependence

†Arrow indicates cost trend with an increase in the factor (e.g., size); 45° arrow indicate lesser trend

‡Strictly due to thermal contraction for processing temperatures, hence more reproducible

can be sensitive to precursor particle (or agglomerate) sizes. Packing density, and batch size and configuration, of precursors in the furnace can also be factors because of their effect on temperature distribution and removal of released gases. The latter is also dependent on furnace atmosphere control. Atmospheres within powder packs and containers significantly affect decomposition rates, grain growth, and sintering during calcining. Residual species left from calcining can also be serious factors during sintering to form the part. For example, small amounts of residual Cl adsorbed on particles can significantly limit sintering (Rith et al., 1976), and CO_2 from carbonate precursors or impurities in new ceramic superconductors can be serious problems. More effective removal of gases can often be achieved by rotary, belt (thin layer), or fluidized bed calciners. Better understanding and control of all these parameters are needed, especially concerning the efficient scaling to larger batch sizes or throughputs.

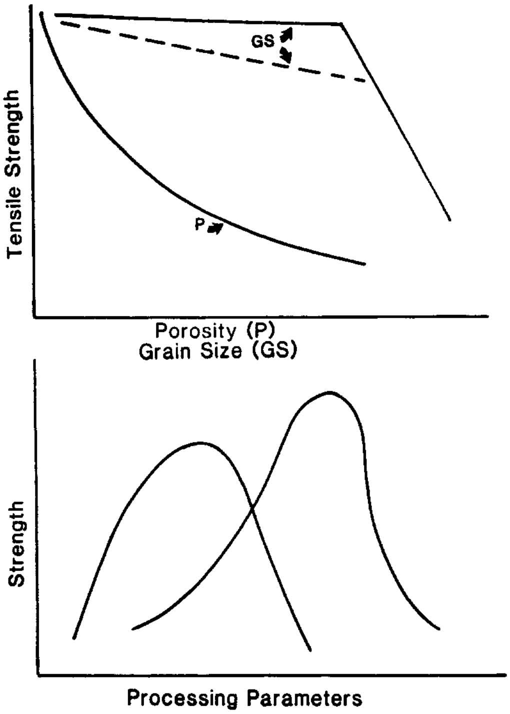

Figure 8. Key microstructural effects on strength.

Top: Grain size and porosity effects on strength.
Bottom: Various sintering conditions lead to different maxima of strength due to grain size increases while porosity decreases in sintering, but at different rates depending on a variety of parameters

Alternate approaches to the solution-precipitation route, in order of increasing newness, and therefore lesser development, are:

1. Spray roasting, also referred to as spray pyrolysis, evaporative decomposition, and mist decomposition, that is, direct calcining of solution droplets by high-temperature spray drying (Roy et al., 1977; Pamplin and Feigelson, 1979; Suyama and Kato, 1982; Chess et al., 1983; Sproson and Messing, 1984; Kagawa et al., 1984; Gardner and Messing, 1984; Ishizawa et al., 1986).
2. Plasma or microwave decomposition (McPherson, 1981; Moiseev et al., 1982; Ono et al., 1985; Palmer et al., 1984).
3. Rapid expansion and pyrolysis of supercritical solutions (Matson et al., 1986).

While spray pyrolysis offers advantages of mixing, the magnitude and uniformity of resultant particle sizes, and their crushability, are issues.

Many refractory nonoxides, especially carbides, nitrides, and borides, have typically been made by carbothermic reduction. Thus, to form a carbide, an oxide and sufficient carbon are mixed and reacted, which not only reduce the oxide but also form the carbide; for example, $SiO_2 + 2C \rightarrow SiC + CO_2$. Similarly, to form a refractory boride, one adds sufficient carbon to a mixture of the oxide, such as TiO_2, and the appropriate amount of B_2O_3 to reduce both oxides such that they will react to

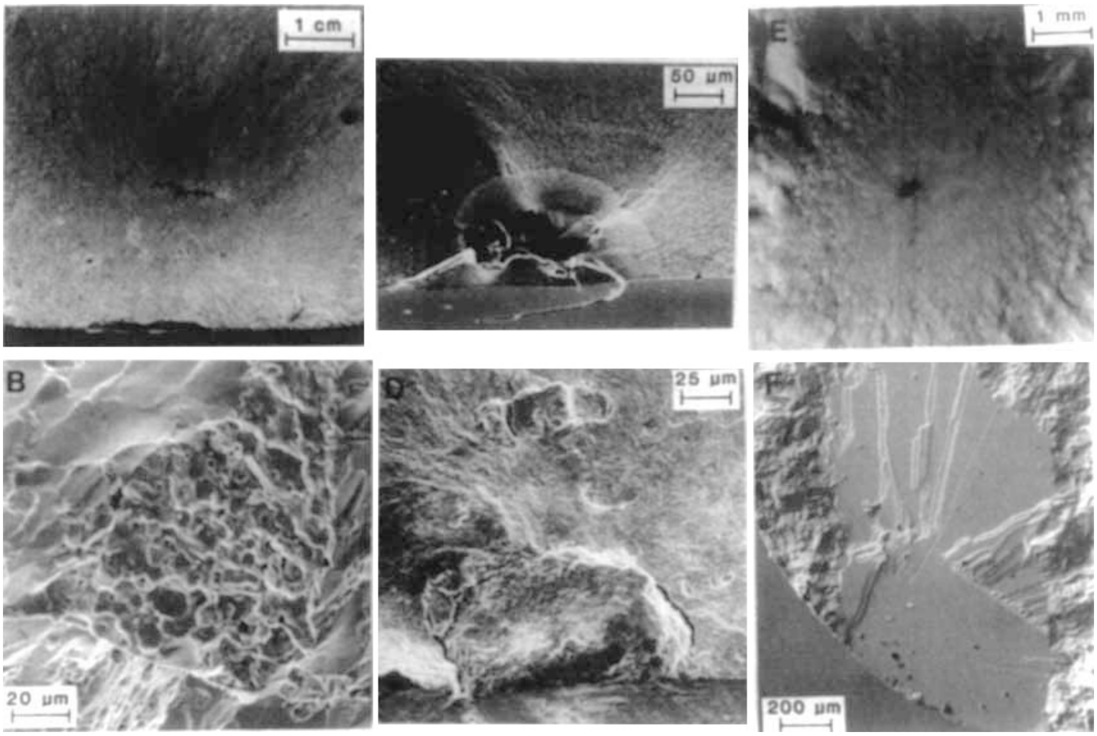

Figure 9. Failure initiation from processing defects.

A. Laminar pore *P* in cold-pressed and sintered lead zirconate titanate transducer (Top, Left)
B. Porous region *P* in hot press ZrO_2, apparently from local impurity accumulation (Bottom, Left)
C. SiO_2 inclusion *I* in hot press optical grade MgF_2 IR window (Top, Center)
D. Large agglomerate *A* and associated partial peripheral crack in partially stabilized (toughened) sintered ZrO_2 (Bottom, Center)
E. Graphite inclusion *I* in hot-pressed Al_2O_3 (Top, Right)
F. Large grains in CVD ZnSe for laser windows (Bottom, Right)

form the desired boride, in this case TiB_2. Obvious challenges in this processing are to obtain the proper balance of the reactants on both the macro- and microscales and to avoid excessive agglomeration while maintaining fine particle size. Particle size in particular can be quite sensitive to the starting particle sizes of the reactants, and may be affected by the density of the powder mass that is undergoing the reaction—which can depend significantly on parameters such as batch configuration, size,

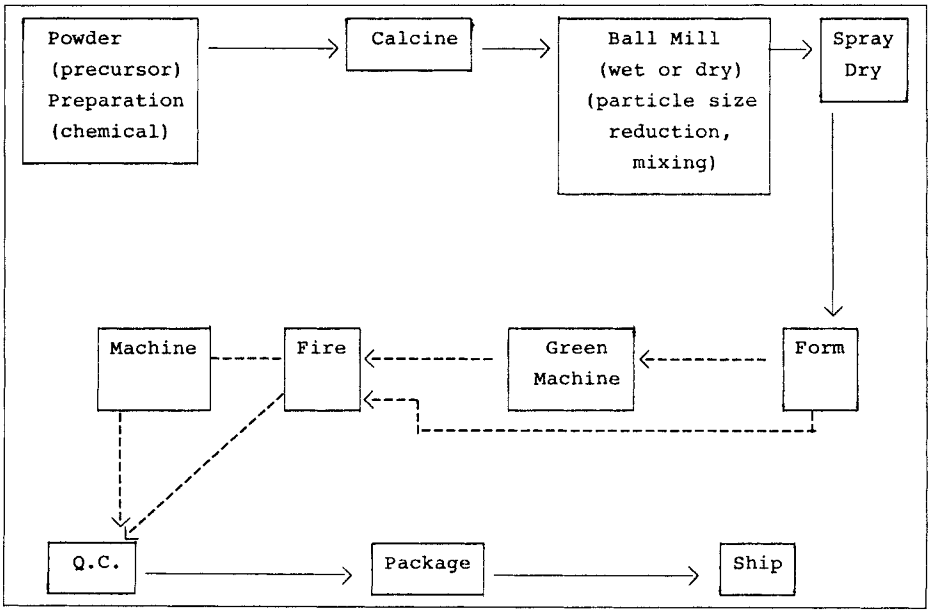

Figure 10. Process outline of conventional (powder/sinter) processing.

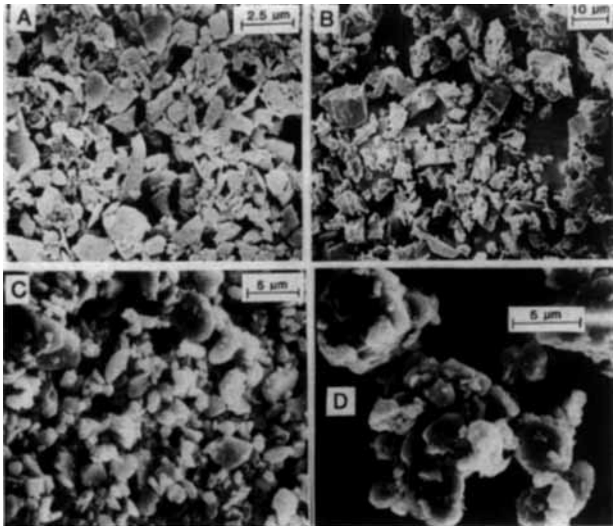

Figure 11. Micrographs of representative ceramic powders.

A. SiO_2, typical particles produced by communication, such as milling
B. Y_2O_3
C. Al_2O_3 powder chemically prepared, followed by calcining and milling
D. AlN powder chemically prepred by carbothermic reduction of Al_2O_3; tenacious agglomerates of finer crystallites are common to many chemical preparation processes

packing density, and uniformity, as well as gas flow. Improved chemical processing is being applied to achieve finer and more homogeneous carbon distribution (Mitomo and Yoshioka, 1987; Durham et al., 1988; Figusch and Licko, 1987; Bolech et al., 1987). An obvious challenge for nonoxides is cost. While they often offer performance advantages over oxides, they are also typically more expensive from the standpoint of materials, Table 3, and processing.

More sophisticated liquid chemical approaches are also being explored, for example, to control particle sizes or morphologies as well as mixing or reaction of constituents (Matijevic, 1986). Particle morphologies can be important—for example, to yield advantageous preferred orientation of single crystal properties in the resultant polycrystalline body, especially for electronic and related uses, Figure 12 (Watanabe et al., 1989). (Polycrystalline bodies with preferred crystallographic orientation may be sought because single crystals are not available, or more commonly, may not be practical in the sizes or shapes needed and do not offer the generally superior mechanical properties of a polycrystalline body. Some processes, as well as parameters, are much more useful in obtaining preferred orientation than are others, as outlined in Table 2). Mixing of constituents is of increasing importance not only for composites, but also for introducing additives or for processing binary and higher order compounds that are of significant and growing importance. Well-established examples of such compounds are $BaTiO_3$, a binary compound of $BaO + TiO_2$, and $PbTiO_3$–$PbZrO_3$ solid solutions for piezoelectric uses. The new ceramic superconductors are ternary compounds, for example, $YBa_2Cu_3O_{7-x}$, derived from Y_2O_3, BaO, and CuO_2. Note that the crystalline phase of one or more of the reactants obtained may be an important factor in forming some compound precursors; for example,

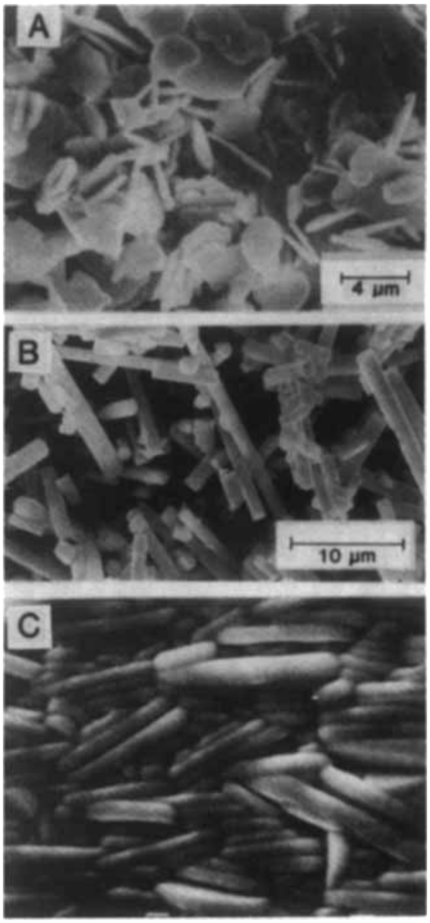

Figure 12. Morphologically shaped powder particles and resultant polycrystalline bodies of preferred orientation.

A. Platelets of $Bi_4Ti_3O_{12}$
B. Rods of lead metaniobate, made in molten salts
C. Example of highly oriented polycrystalline microstructure that can be achieved with such morphologically shaped powder particles

Table 3. Representative Ceramic Powder Costs

Material	Approx. Cost $/lb.
Oxide powders	
Al_2O_3	0.25–2.0
SiO_2	0.5
TiO_2	0.75
ZrO_2	2.0–5.0
Equivalent cost of oxides in sols	
Al_2O_3	5.0
SiO_2	2.0
ZrO_2	15.0
Nonoxide powders	
B_4C	25.0–75.0
BN	25.0
SiC (α)	7.0–12.0
Si_3N_4 (high α)	15.0–25.0
Si_3N_4 (β)	5.0
TiB_2	20.0–35.0
TiC	15.0

$BaTiO_3$ only forms properly from the rutile, not the anatase form of TiO_2.

Sol-gel approaches, especially those using polymeric (for example, alkoxide-derived) gels have received considerable attention for preparing oxides (Mazdiyasni et al. 1965; Mazdiyasni, 1982, 1987; Okamura and Bowen, 1986; Ring, 1987). However, simple crushing of gels to obtain powders can present sintering problems since the crushed gel particles are another manifestation of the agglomerate sintering problem: the crushed particles sinter more slowly than the basic gel particles they contain. Another challenge of gel-based processing is often cost, as indicted in Table 3. Cost is typically quite important for bulk material use, as in structural components, less so for layered applications, for example coatings, and especially electronic circuits, where materials are less, values are higher, or both. While advanced liquid-based chemical approaches are being used most extensively for oxides, they are also being explored, with some commercial use, for nonoxides (Interrante et al., 1986; Hoch and Neir, 1979; White et al., 1987; Brown and Maya, 1988). Examples are:

$$R_3Al + NH_3 \rightarrow R_3Al{:}NH_3 \rightarrow AlN + 3RH \qquad (1)$$

where $R = CH_3, 2H_5, C_4H_9$, and similar compounds, and

$$3SiCl_4 + 18NH_3 \rightarrow 12NH_4Cl + 3Si(NH_2) \rightarrow Si_3N_4 + 2NH_3 \qquad (2)$$

Other important examples of advanced solution processes for preparation of oxide powders are those using a hydrothermal medium (Somiya et al., 1984; Chertov et al., 1986; Vivekanandan et al., 1986; Hirano, 1987; Kutty and Vivekanadan, 1987; Komarneni et al., 1986, 1988; Dawson, 1988) or a molten salt (or metal) medium (Kieffer and Jangg, 1972; Arendt et al., 1979; Kimura et al., 1980; Matveichuk et al., 1980; Nagata and Okazaki, 1985; Nalbandyan et al., 1985; Hayashi et al., 1986a, b; Okamoto and Narumiya, 1986; Watanabe et al., 1987; Kimura et al., 1983; Kimura and Yamaguchi, 1982. Examples of hydrothermal preparation are:

$$Ti + 2H_2O \xrightarrow[100\ MPa,\ 3\ h]{>450°C} TiO_2(rutile) + 2H_2 \qquad (3)$$

$$TiO_2 + Ba(OH)_2 \cdot 2H_2O \xrightarrow[5\ h]{200°C,\ pH\ 7} BaTiO_2 + 3H_2O \qquad (4)$$

$$\alpha - PbF_2 + \beta - BiF_3 \xrightarrow[14\ day,\ 4\ h,\ 100\ MPa]{250\text{–}500°C} Pb_{1-y}Bi_yF2+2 \qquad (5)$$

Examples of molten salt preparation are:

$$BaCO_3 + TiO_2 \xrightarrow[800°C]{NaKCO_3} BaTiO_3 + CO_2 \qquad (6)$$

$$2PbO + ZrO_2 + TiO_2 \xrightarrow[1,000°C]{NaCl\text{–}KCl} PbTiO_3 + PbZrO_3 \qquad (7)$$

Such processes often give desirable sizes and shapes of particles, for example, for preferred orientation, and reduced agglomeration.

Vapor phase processors are also being used or explored for powder, as well as whiskers preparation (Kaito et al., 1976; Suyama et al., 1979; Okabe et al., 1979; Varshney and Beatty, 1982; Hori et al., 1985; Danforth and Haggerty, 1981; Kato et al., 1984). Again, there is a more extensive base of work on the oxides—mainly by flame pyrolysis, for example of chlorides—as commonly used for materials like Al_2O_3 and TiO_2 for a variety of other purposes, such as paint pigments. However, there is considerable activity, including some commercial production, for nonoxides, for example, preparing Si_3N_4 from $SiCl_4 + NH_3$, and vapor phase methods of preparing many other nonoxides are known. Laser-stimulated vapor phase reactions are increasingly being investigated (Cannon et al., 1981; Haggerty, 1984; Kizaki et al., 1985; Suyama, 1985; Cauchetier et al., 1987), as are plasma methods (Phillips and Vogt, 1987). While various challenges such as efficient collection of powders and limiting agglomeration need to be met, vapor phase processes provide useful opportunities. Coating of particles—for example, with binder materials while still in the aerosol state—may be feasible and advantageous. Longer term possibilities may include some particle rejection abilities (based on mass, size, or composition), as demonstrated by dielectrophoresis, for example.

Powder processing

Preparing powders of a desired chemistry, while often the end goal of a chemist, is only the starting point for a ceramist. Commonly, three additional generic steps are needed before the powders are consolidated into a component. The first is particle size adjustment. Good sinterability requires relatively fine particle sizes (a few microns or less), and a controlled, often limited, particle size distribution. In recent years there has been a focus on the effects of particle size distribution on sintering. For example, it is now known that monosized particles sinter much faster than mixed particle sizes. However, monosized particles are not necessarily practical to make or optimum for all consolidation methods; they may lead to defects such as cracks, or larger grains (Chappell et al., 1986, Rice 1987a); and they may give lower green densities, hence higher shrinkage (Yeh and Sacks, 1988). Thus, the broader interest is in identifying optimum particle size distributions for various processes. While most chemical processes, such as precipitation, do not produce crystallites that are too large (many in fact produce crystallites that are very fine), the crystallites often form agglomerates that are much larger. Thus, crystallite, and especially agglomerate, size reduction and control are widely needed. This has traditionally been by dry or, more commonly, wet ball milling, but other methods such as jet and, especially, attritor milling have been used; the later often is more efficient and produces a narrower particle size distribution. Milling often requires additives to prevent sticking of dry powder (approx. 2 w/o polyethyleneglycol) or foaming of slurries (<0.1 w/o silicone emulsion).

The second generic step is the mixing of either ceramic or organic constituents, and often both. Mixing of ceramic constituents is used, for example, to minimize lot-to-lot variations of raw materials, intermix different particle sizes to control shrinkage, and distribute additives to aid in densification, microstructural control, or directly affect properties. In addition to those used to aid milling, organic constituents are added to increase solids contents (~1 w/o surfactants) and as binders to provide the different rheological characteristics needed for various forming operations. An important issue in many cases is the interaction between these additives. While chemical interaction is often the most severe concern in choosing additives, physical interactions can be important. For example, coverage of the particle surfaces by one additive may limit coverage of or interaction with the ceramic particle by a second additive. These factors may also be influenced by the order of additions. Many of the processing-induced fracture origins result from poor mixing of organic constituents, as represented in Figure 9. Thus, improved uniformity and reliability of mixing on the scale of a few particle dimensions is needed.

The third generic step is providing handleability; that is, ensuring the flowability and practical compactibility of powders required by the process, Figure 10. This is most commonly done by spray drying, but other agglomerate generating methods are being explored. The challenge is to form agglomerates that are of sufficiently spherical shape, size (e.g., 50 μm), and integrity for handling and forming, but which will collapse and totally lose their identity when consolidated into a part. Additives, especially organics, and spray drying can have a considerable effect on the ability to achieve this goal. Hard agglomerates—those too hard to totally lose their identity in consolidation—are a frequent and often serious problem. Thus, more uniform and reliable spray drying or cost-effective alternatives are important.

Powder consolidation and component shaping

A major reason for the use of sintering to produce ceramic parts is the versatility of shaping and the attendant cost savings offered by the various powder consolidation and shaping methods available, Table 2. Cost savings are mainly due to avoiding or minimizing machining costs, as detailed in Table 4.

Powder consolidation and shaping methods range from forming from a fluid—colloidal suspension or slurry—to forming of dry powders, Figure 10. The oldest and most widely used fluid method is slip casting. While this has been displaced from many of its earlier applications, it still has substantial industrial use, for example, ceramic sanitary ware. It is quite versatile in the shapes that can be formed and it can be used to make some of the larger ceramic pieces produced. Tape casting, widely used for electronic ceramic applications, such as substrates and multilayer capacitors, is an important derivative of slip casting. This is typically used to make thin sheets (from ≈100 to ≈1,000 μm thick) up to a few feet wide and many feet in length, which may or may not subsequently be laminated, shaped (for instance, to form honeycomb structures as used in fuel cell and other open structure components), or both. The patterning of components (conductors, resistors, capacitors) and ferrites on such sheets by screen printing inks carrying the powder constituents, and more recently by photolithography using photopolymers, is very important in the electronics industry. Slip stability and rheology vs. solids loading and particle sizes are issues of importance, as are homogeneity on both a macro- and microscale—for example, to avoid bubbles and segregation of particles—and retention of integrity: avoiding shrinkage cracking, and having sufficient strength for handleability, often provided by organic binders that hold the ceramic particles together in the unfired, green state.

Pressure casting (Lange and Miller, 1987), a direct derivative of slip casting, may be done by applying pressure on the fluid, vacuum on the mold, or both. This has been applied to the production of some traditional ceramics made by slip casting, and is being considered by some as a solution to the issue of handling fine particles as well as eliminating coarser particles and agglomerators in higher technology ceramics. However, its effectiveness in terms of reproducibility and possible production rates of the small components typical of high technology applications vs. the larger traditional ceramic parts, are not well established. A potential issue is bubbles, which, like a diver's "bends," may occur upon pressure release. Electrophoretic deposition (Krishna Rao and Subbarao, 1979; Olenick and Joseph, 1982; Choudhary et al., 1982; Foissy and Robert, 1982; Heavens, 1986) has been demonstrated for a variety of ceramic systems, and used for some production. Electrostatic deposition, by an aerosol phase, used for deposition of porcelain enamel coating powders, has apparently not been used for making bulk ceramic bodies, but may have some applicability.

Table 4. Estimated Ceramic Processing Costs*

	Cost, $ (Percent of Total Cost)		
	Headface Plate	Piston Cap	Cylinder Liner
Body	1.55	1.36	7.84
	(1%)	(1%)	(3%)
Forming	2.88	8.08	38.09
	(1%)	(3%)	(15%)
Firing	17.45	12.97	47.48
	(9%)	(5%)	(19%)
Grinding	173.93	259.03	161.32
	(89%)	(91%)	(63%)
Totals	$195.81	$281.44	$254.74
	(100%)	(100%)	(100%)

*Based on making diesel engine ZrO_2 components, but illustrative of many other ceramics and application; source: Bentz (1984), Cummins Engine Company, AMMRC TR 84-24, Report "Ceramics Manufacturing Technology Development for Adiabatic Engine Components" for Contract No. DAAG46-83-C-0002.

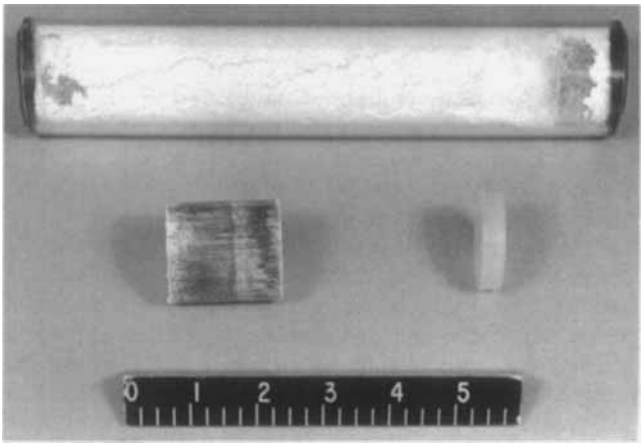

Figure 13. Compaction ratios for submicron MgO powder.

Top: As-received, very fie (~0.1 μm) powder
Lower left: Same powder consolidated under a pressure of ~35 MPa, room temperature
Lower right: Resultant theoretically dense MgO disk hot pressed at ~1,400°C
Such large consolidation ratios of fine powders limit component size and result in extra handling costs.

The most widely used method of forming powder (green) bodies is applying physical pressure; Table 2, Figure 10. In die pressing, the most common method, pressures of 70–200 MPa are applied mechanically by rams extending into the die. While very fine particles are desired for high sinterability, they commonly result in large compaction ratios, Figure 13, and poor flowability, which typically lead to lower and less uniform densities and less efficient processing. Spray drying is often used to form agglomerates for flowability, which, as noted earlier, ideally crush during compaction to completely lose their identity. Failure to achieve adequate crushability is a basic and pervasive problem.

Isostatic pressing, Table 2, is also widely practiced in both laboratory and industry for parts of limited to intermediate size and complexity. Wet bag isopressing (70–200 MPa in production, and up to 700 MPa in the laboratory) entails packing the powder in a plastic or rubber mold or "bag" which is sealed (and evacuated) then placed in a vessel where fluid pressure (at room temperature) is applied directly to the bag. Dry bag isopressing involves loading powder directly into a thicker rubber form mounted in, and readily sealed to the pressure system. This method is more restricted in size, shape, and pressure (35–70 MPa) than wet bag isopressing, but is faster due to fast loading, and fast cycling because of the small volume of fluid used. Roll compaction—feeding powder between rolls—is used for making thin sheets (but usually thicker than by tape casting; $>1{,}000$ μm). Extrusion is widely practiced, with considerable complexity of shape, including forming sheets. Plasticity is achieved by using various combinations of clay, fluid (usually water), and polymers. Finally, compression and injection molding, which force a plastic mix into a mold cavity, are used for forming parts of limited size, but often of considerable complexity. Figure 2 shows injection molded ceramics. Plasticity is typically achieved by the use of substantial organic polymer—really a polymer highly filled with ceramic powder, especially for injection molding. Such high levels of polymer content limit ceramic green densities, hence sinterability, and can present serious problems of removal from the mold. Again, inhomogeneous mixing of these polymers presents serious defect problems. Thus, better polymers, more effective use of them, and better mixing are desired. One potentially important approach to the latter two problems is believed to be polymer coating of individual particles. Use of polymers to pyrolyze to constituents of the final ceramic body is also seen as a possible aid. This technique reduces the amount of organic products to be removed, leaving less porosity.

While the majority of ceramic components are desired in as dense a form as practical, there are diverse needs for bodies of controlled porosity. Uniform or graded porosities can be of interest, with the amount and character of the desired porosity ranging from large volumes of very open pores (reticulated foams) to bodies of more moderate porosity of open, closed, or mixed character. Control of pore sizes can be important in such applications as filtration. Techniques to achieve a wide range of porosities vary from foaming ceramic-polymer mixtures, replicating organic foams, for example, by slips; to incorporation of organic particles, or their *in-situ* formation, for example, by phase separation; to controlled consolidation of controlled particle size powders. Figure 5 shows some open-structure ceramics. More recently, printing of patterns of polymer or other pyrolyzable material to leave voids of precise shape, dimension, and location on ceramic tapes that are laminated to form bodies, has been demonstrated with promising results for significantly enhancing the performance of some electronic ceramics (Kahn and Kovel, 1986).

Considerable machining is done on some parts in the as-consolidated, green, state, as indicated in Figure 10. Conventional machines, such as lathes, are used, usually with carbide tooling. Machining is often used to obtain greater intricacy of shape than can be achieved in forming. It is also used to give more accurate dimensioning, or to remove material that is less or more densely consolidated, perhaps due to die wall friction, in order to obtain better (more uniform) sintering or to avoid residual stresses. It is not uncommon to remove 20–30% of the material volume, nor to recycle material removed by "green machining." Such machining is also often used for making prototypes or limited numbers of production components, usually from isostatically pressed "logs."

Burnout, firing, and sintering

Organic constituents are mainly removed thermally rather than chemically, by solvents, although supercritical processing may increase the use of solvent removal. Thermal removal is often referred to as binder burnout, since in the case of processing oxides, organic constituents may literally be burned out; the organics used for binders constitute the majority of material to be removed. Processing of nonoxides often poses the challenge of finding organic additives that will pyrolyze cleanly in a nonoxidizing environment leaving no carbon residues. The general challenge is to achieve burnout of any binder without disrupting the often delicate character of the body. Disruptions can result from high polymer thermal expansions, which may be five to 20 times the ceramics expansion, from possible condensed-state phase changes, and especially from pyrolysis/combustion gaseous products. Two factors clearly illustrate the scale of the latter problem. First, the volume increase (without combustion) from condensed state to gaseous state is typically on the order of 10^3 to 10^4. Second, the typically 40–50 vol. % porosity of the green body is fine, ranging from less than to greater than the particle sizes, and quite tortuous. Thus, internal gas pressures may be influenced by pore dimensions smaller than the mean free path of the resulting gas species.

Both temperature and atmosphere control to respectively limit the rate of gas generation and aid resultant gas removal are important in burnout. For air firing, sufficient air is needed to remove all organics soon enough, that is, before sintering starts, but excess air that can lead to thermal excursions due to combustion may be detrimental. Clearly, the density and placement of parts relative to gas flow in the furnace can be important. Another challenge of the burnout process is achieving homogeneity, since inhomogeneous burnout can result in distortion or cracking of parts, or both. Homogeneity of burnout is a function not only of component uniformity and geometry, but also of the uniformity of the furnace environment.

Ceramic technology has developed mainly by using available organic materials, for example, from the paint and plastics industries. Thus, there may be considerable room for developing more effective organic additives tailored to ceramic needs. Clearly, binders that decompose in more stages over a broader range of temperatures would be useful. Similarly, binders that decompose to desired constituents of the final body, and hence reduce both the amount of outgassing and the degree of sintering needed could be valuable. Multipurpose organics—that might serve, for example, as binder-surfactant-die lubricant—could also be of interest. Finally, ways of assuring more uniform organic distribution in the ceramic body, and particularly of avoiding organic agglomerates, are needed to reduce defects. As noted earlier, methods of polymer (binder) coating of individual ceramic particles would be the ultimate in uniformity, and would potentially allow use of lower binder levels.

After burnout the next, central, step in typical ceramic processing is firing, which may be done as a continuation of binder burnout or inorganic reaction steps, or separately. On a commercial scale, it is often done separately, especially for parts with high binder contents such as those made by injection molding. Separate burnout and firing operations may be dictated by environmental considerations such as gas flow, and especially by time factors. Binder burnout may take much longer than firing, often days against typically a few hours at firing temperature, so it is not cost effective to tie up more expensive (higher temperature) facilities used for sintering. The main purpose of firing is to sinter the body, that is, to cause it to coalesce into a nearly, or fully, dense body as a result of surface tension forces, as opposed to gross melting. (Solid-state sintering, achieved in the absence of any liquid phase, is commonly done at about two-thirds of the absolute melting temperature.) Firing is usually carried out in a single step, but is sometimes broken into two steps, in which case the lower temperature stage is referred to as bisque firing. A common reason for bisque firing is to obtain an intermediate state at which machining may be more practical than in the green or fully fired states. For example, machining of bisque fired parts may often be done with conventional metal machining equipment with carbide or ceramic tools.

Sintering is commonly the final and major determinant of component microstructure. For parts that receive no, or only partial, subsequent surface finishing or treatment, firing is also a major determinant of the surface character. Thus, sintering plays a central and challenging role. The challenge is accentuated by the generally opposite trends of grain growth and porosity that affect both the sintering process itself and the resultant properties. The overall trends are for both pores and grains to decrease in number. While some aspects of the kinetics of these porosity and grain changes are different, they are also significantly coupled, as shown in Figure 14. Thus, if grain growth is too rapid, such that grain boundaries sweep past pores, entrapping them within the grains, those entrapped pores will not be significantly further reduced. This arises because the mass transport processes needed to eliminate such intragranular pores are far too slow through the individual crystallites to do so in practical times. The necessary transport processes are sufficiently rapid along grain boundaries, so pores must remain attached to a boundary (be intergranular) in order to be eliminated. Since pores tend to inhibit grain growth, one can achieve relatively low porosities (a few percent) with modest grain sizes (a few microns). However, achievement of quite low (<0.5%) porosity typically comes with substantial grain growth, to grain sizes of several tens to a few hundreds of microns. The challenge of sintering that arises from this dichotomy of porosity and grain size is further seen from the opposite effects these parameters have on many aspects of ceramics. Strength, wear resistance, surface smoothness, and optical scattering (in optically transmissive materials), generally increase with decreasing porosity, but decrease with increasing grain size.

Other challenges of sintering result from the shrinkage inherent in the densification typically sought. Failure to shrink uniformly will result in distortion, cracking, less total densification, or any combination of these. The extent and nature of the problems are a function of component size and shape, as well as the uniformity of the components and the furnace environment. While temperature uniformity is usually most important, atmosphere uniformity, which again may depend on furnace loading, can be important. Temperature uniformity is often a more critical problem, especially at higher temperatures commonly required with nonoxide ceramics: 1,600–2,100°C vs. 1,400–1,700°C for oxides. Component size is important not only relative to furnace homogeneity (and hence dimensions), but in an absolute sense due to frictional resistance to shrinkage. Parts are commonly placed on a layer of "setter" powder (typically sufficiently coarse so the particles do not extensively sinter to the body) so as to support the body yet accommodate the shrinkage motion of the part relative to the furnace furniture holding it. However, there are clear limitations to this based on both mass and physical size. Clever methods can extend these limits. For example, large (≥1 m dia.) Al_2O_3 rings (~2.5 x 10 cm cross section, weight ~25 kg) for a Tokomak fusion device were successfully fired accommodating ~16 cm dia. shrinkage. This was accomplished by supporting a ring on separated, pie-shaped pieces of ceramic that in turn were placed on ~3 mm dia. ruby balls glued in place to avoid any movement during loading and early heating (i.e., until the glue burned off) (private communication; M. McLaren and E. Smoke, Rutgers Univ). Physical support during firing is important to prevent creep due to gravitational stresses, or to take advantage of them for simple shaping, a process called slumping. Not only is it important to have limited, uniform shrinkage, it is also important to have it predictable and repeatable. This is so because it is often

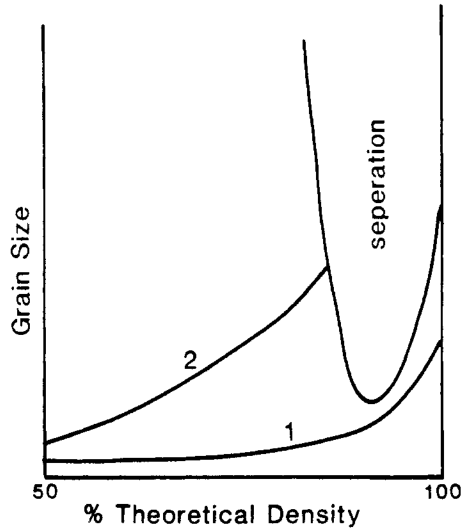

Figure 14. Interrelationship of grain size and density during sintering.

In region labeled *Separation* grain boundaries will break away from pores, entrapping them within grains, so further densification is severely limited. Processing that results in path 1, avoiding such separation, can allow near theoretical density to be achieved; processing that results in path 2 cannot achieve near theoretical density.

necessary to achieve final dimensions or the final location of features such as holes upon firing, which requires that they be determined by green body dimensions and known shrinkage factors. This important role of shrinkage places many demands on processing and green body formation in conjunction with firing.

Traditional (oxide) ceramics are commonly readily sinterable because they have desirable quantities (a few percent) and character (appropriate sollubility of major constituents) of liquid phases, which may come from constituents present in the raw materials or may be added on the basis of empirical evidence. Some higher technology oxides are processed with additives to provide liquid phase sintering; other additives are used to enhance solid-state sintering or to retard grain growth. Many nonoxides, especially the most extensively used, such as SiC and Si_3N_4, can only be sintered with additives. However, despite the importance of sintering aids or additives, their identification has been almost completely empirical, often accidental. Thus, increased understanding of how to select such additives would be of major aid in ceramic processing.

Another challenge that requires further development and understanding is the sintering of more complex compounds, for example, mullite-$3Al_2O_3 \cdot 2SiO_2$, and the high T_c oxide superconductors. Reaction during sintering can lead to complications resulting from changes in volume (positive or negative, and often >10%), diffusion (often substantial reductions), and properties such as surface energies and thermal expansions; each of these can aid or hinder sintering. On the other hand, complete prereaction before sintering often means coarser particle sizes and lower diffusivities, and hence poorer sintering.

Although it might be thought that heating methods for sintering were nearly fully developed, several newer methods are being explored. The most extensively investigated is microwave sintering, but at least three other methods are being explored: inductive plasma, microwave plasma, and glow discharge heating (Johnson et al., 1985; Kemer and Johnson, 1985; Page et al., 1988; Sheppard, 1988). All transfer energy directly to the part, or in some cases apparently to species adsorbed on the particle surfaces. Thus microwave sintering occurs by dielectric absorption or loss in the material, similar to dielectric heating or drying. These newer heating methods all appear to offer rapid part heating and sintering, and hence, finer microstructure, as well as possible energy efficiency. They may also offer the opportunity to have more uniform part heating by direct coupling, instead of depending on diffusion of heat inward from the surface. However, many questions remain to be addressed. These include issues such as better understanding of the basic physics involved and thus the challenges or ease of applying the method, as well as procedures for close process control. In microwave sintering, heating is probably due to nonlinear absorption mechanisms whose power, frequency, and purity dependence is not well understood. Similarly, apparent coupling of inductive plasmas to adsorbed species is not well understood. Further, effects of part size and shape, and interactions of multiple as opposed to single parts under such heating are not well established. Beyond this, there are many practical questions to be answered. Experiments on small, simple parts such as pellets allow high heating rates, but the practical limits of larger, more complex parts are not known for certain. Larger scale is clearly expected to limit heating rates. This, combined with the extent to which multiple parts can be handled, which determines the throughput of such methods, remains a major unknown in their economics. Real efficiencies are also an unknown in the economics, since accurate values for the conversion of power to the form for heating (microwaves) and, in turn, conversion of that to heat in the body, are not well known.

Postfiring or alternate densification methods

An important alternative to sintering of some materials is reaction processing. This is widely used industrially for Si_3N_4, and especially SiC (Washburn and Coblenz, 1988). Processing of Si_3N_4 by this route entails partially sintering Si powder in an inert atmosphere, then firing in an $N_2(+H_2)$ or NH_3 atmosphere. Melting of the Si must be avoided to prevent forming globules of molten Si (due to surface tension and capillarity) that are far too large to fully nitride, even in the several days commonly used for this process. This requires careful control of the reaction since it goes exothermic just below the melting point of Si. Due to vapor transport within the pore structure, this process generally does not disrupt the body despite the large intrinsic volume increase on forming Si_3N_4, if the pore structure of the original Si compact is properly contolled. In fact, dimensional tolerances of ~0.1% can be maintained between the pressed Si compact and the final Si_3N_4 piece. The Si_3N_4 product, referred to as RSSN or RBSN (for reaction-sintered or -bonded Si_3N_4) inherently has residual porosity (~20%) since this is necessary for sufficient N_2 to enter the body for complete nitriding. While this level of porosity limits strength, useful strengths (300 MPa) are commonly achieved. Further, since in contrast to conventional sintering (or hot pressing) of Si_3N_4 no densification aids are needed, the creep resistance of RSSN is much higher than that of sintered Si_3N_4. Recent use of much finer Si (<0.01 μm, produced by laser-stimulated chemical vapor deposition) has yielded less porosity (~15%), finer grain sizes (~0.5 μm), and higher strengths (>500 MPa), (Haggerty et al., 1986).

More widely used is reaction processing of SiC, in which a compact of SiC + C powder is infiltrated with molten Si. This leaves a product of mainly SiC with several percent residual Si and C. The ~30% volume shrinkage upon forming SiC from Si and C is accomodated by:

1. Molten Si continuing to wick into the body from the reservoir
2. Deformation of the residual Si
3. The ~5% expansion of Si on solidification

This process allows quite large components (dimensions of 1 m or more) of quite usable mechanical properties to be made.

The above two processes have been extended to several other materials, especially composites. For example, mixtures of SiC and Si are used to produce Si_3N_4–SiC composites, which are used as commercial refractories, and B_4C–SiC–Si–C composites have been produced, for example, for armor. Many other reaction processes are of interest for composites, as discussed later.

A major new type of reaction processing has been developed in the last few years. This is based on the controlled reaction of liquid metals such as the slow oxidation of molten aluminum wicking through the resultant oxide layer (Newkirk et al., 1987). Hot pressing and hot isostatic pressing, Table 2, are two, more modern and effective, methods of densification that can be used in conjunction with, or instead of, sintering. Both are also referred to as pressure sintering, since they involve the application of pressure during sintering. (Conventional sintering is now often referred to as pressureless sintering.) Both methods generally produce substantially superior parts with much less sensitivity to powder and processing parameters than sintering. Limitations of these processes have been part geometry (size, shape, complexity) and environmental conditions.

The older and more widely used of these methods is hot pressing, which entails uniaxially pressing parts in a die, Figures 1, 13. Pressures typically ranging from 7 to 20 MPa for industrial hot pressing and up to about 140 MPa for experimental work are applied on the parts. While these pressures are modest in comparison with those of cold pressing, they are large in comparison with sintering stresses (about 0.7 MPa) derived from surface tension effects. It is this much higher pressure of hot pressing relative to sintering stresses that allows faster consolidation, often at lower temperatures (100–300°C), with resultant finer grain sizes and less sensitivity to powder particle sizes and larger pores or agglomerates in the starting powder compact. Except for very specialized applications, graphite dies and rams are used because of their limited reactivity/bonding with many ceramics, their good strength (especially at high temperatures—graphites typically increase substantially in strength up to ~2,000°C), and low thermal expansion. Most parts shrink more than the die on cooling, an important advantage in removing parts unless holes or cavities are desired, in which case partial or complete hot extraction, which can be a challenging task, is required. Reasonable cost and machinability, as well as availability in large sizes, are also factors heavily favoring graphite. Some dies of refractory metal (mainly Mo or W) and ceramic (Al_2O_3, SiC) have been used (Rice, 1970). Typical hot pressing temperatures are 1,300–2,200°C, with lower temperatures being common for oxides and higher temperatures for nonoxides such as nitrides, carbides, and borides. Times at maximum temperature and pressure are typically 15 to 120 min, with obvious temperature-pressure-time trade-offs. Induction heating of the die directly, or indirectly by a susceptor (which is particularly common, especially industrially), commonly allows heat-up in 30–120 min. Thus, the biggest factor in hot pressing cycles, commonly 4–18 h, is usually cooling. Conventional, resistive-heated furnaces are also used, mainly for moderate-size parts, but are more limited in heating rate. Direct resistive heating of dies, or of rams and parts (even for some oxides) has been demonstrated to achieve high heating rates, and direct heating of parts may give better quality. While vacuum, or controlled environment (Ar, N_2) hot pressing utilizing a chamber is common, mainly in the laboratory, much industrial hot pressing using graphite dies, whether of oxides or nonoxides, is done in air. Normal thermal insulation properly applied limits graphite die oxidation in such air hot pressing, and the internal die atmosphere is inherently reducing due to the CO-CO_2 balance. Parts of substantial size can be hot pressed; part diameters to 30 cm are not too uncommon, and diameters to about 100 cm are feasible.

The major limitation of hot pressing is economics, mainly machining costs and production throughput factors. Because part complexity is quite limited in this process, complex parts made from hot-pressed material must have a considerable part of their complexity achieved by machining, which is expensive, Table 4. Considerable increase in shape versatility has been achieved by using powders as pressure transmitting media. However, this still is less acurate in dimensional tolerances, often requiring some machining, and generally places substantial limits on the number of parts that can be pressed simultaneously. Throughput of complex parts is particularly limited. Where sheet or plate stock is practical, throughput can be good in view of the large sizes achievable and substantial stacking of pieces within the die hot zones (often ~60 cm high). Engineering advances are making it increasingly effective to remove dies (generally with heating coils) from the press and power supply during cooling to increase throughput. Some use of multicavity-multiram dies can also be made. This is best done again with simple sheet/plate shapes where stacking is feasible to minimize effects of variation in powder fill for each part. Further advances in uniformity of powder part loading, for example, by the use of preforms, or schemes to equalize pressure on different rams having some differences in travel can further increase throughput. Advances thus far have led to increased use of hot pressing on a production basis, especially for nonoxides, where differential costs between sintering and hot pressing are less than for oxides, since the cost advantage of lower temperature, air firing of oxides is not feasible.

Other limitations of hot pressing are die–material reactions and incorporation of adsorbed species. As noted earlier, graphite is the dominant die material. However, its direct, contact, reaction with some materials does pose limitations. Considerable relaxation, but not total elimination, of these limitations can be achieved by use of interior die coatings or liners, most commonly BN. Another limitation is indirect reaction in the CO atmosphere, resulting in reduction well beyond the die–specimen contact zone. Thus, for example, some readily reduced oxides, such as some ferrites, cannot be hot pressed in graphite, instead other die materials, usually also made by hot pressing, are used. For example, SiC dies are used for industrial hot pressing ferrites in air. However, alternate dies have serious limitations as to high-temperature strength, size capability, and cost (ten to 100 times more than graphite), as well as thermal expansion and bonding. All these limitations are partly addressable by further engineering developments, such as a wider range of die materials for better thermal expansion and bonding control, and coatings for bonding control.

A final limitation is use of fine powders to reduce hot pressing temperature-pressure-time parameters, obtain fine grain structures, or both. Increasing volumes of finer powders can complicate die fill and compaction, Figure 13. Finer powders also commonly have more adsorbed or residual precursor species, such as OH, H_2O, CO_2, CO_4^{-2}, SO_4^{-2}, and Cl^{-1}, that are a source of volatiles for oxide materials (Rice, 1969). The tenaciousness of these species (especially the last partial monolayers), the high powder surface areas, the tortuosity of pore paths out of the powder compacts (pore dimensions below the gas mean free path), and the more modest temperatures and pressures of hot pressing can lead to retention of such volatile sources. Many of these can be detected in the resultant parts by IR transmission if the part is sufficiently transmissive, Figure 15. Such trapped volatile sources can then volatilize on subsequent high-temperature exposure in the absence of hot-pressing pressure, resulting in clouding, blistering, and bloating, Figures 15, 16.

An extension of hot pressing is press forging or sinter forging, which respectively entail slow compressive deformation, without

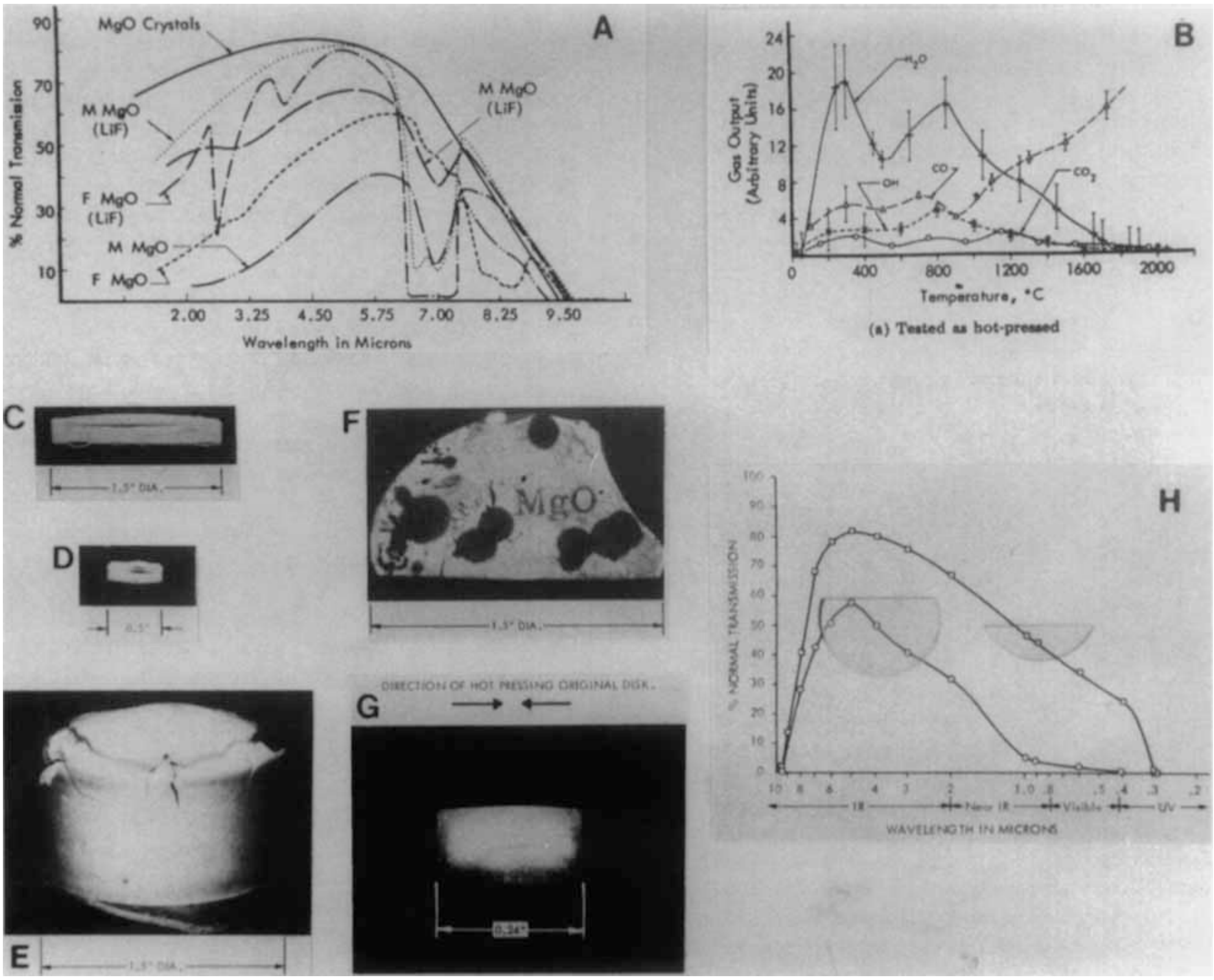

Figure 15. Entrapment of gas producing (anion) impurities in MgO.

A. IR transmission curves of MgO crystal and dense polycrystalline bodies made by hot pressing with/without LiF additions. Note the substantial CO_3 adsorption band at ~7.5 μm in all polycrystalline samples and the 2.75 μm OH adsorption band in one of the materials.
B. High-temperature mass spectrometer gas evolution from some of these hot-pressed pieces
C–G. Various blistering, bloating, and clouding effects of excessive outgassing and/or too rapid heating to remove these impurities
H. Examples of resultant adsorption band free materials properly heat treated to remove included trapped anion impurities; decreasing transmission at shorter wavelengths is due to residual porosity and impurities

lateral constraint, of already dense parts or partially sintered compacts. Press forging (normally of already dense bodies) can yield some shaping, preferred crystallographic orientation of the grains (primarily in materials of noncubic crystal structures), and possible refinement of grain structure (Rice, 1970). The latter is particularly true of single crystals, which can often be recrystallized into a polycrystalline body, for example, for enhanced fracture toughness. Such forging can also be advantageous in converting longer, thinner single crystals into thin plates or dishes, perhaps for windows, of much larger diameters (Becher, 1977; Maguire and Gentilman, 1981). Sinter forging of powder compacts for simultaneous densification and "forging" may yield some shape and orientation effects, but is mainly aimed at enhanced densification rates, resulting from enhanced particle mobility associated with lateral motion as well as the vertical motion of compaction/densification. Press or sinter-forging processes are quite limited in their practical applications since they are commonly limited to processing one part at a time.

The other major postfiring or alternative densification process is hot isostatic pressing (HIP) (Wills et al., 1984; Tsukuma et al., 1981; Larker, 1984). This is analogous to cold isostatic pressing, but is almost always accomplished using a gas instead of a liquid pressure-transmitting medium (some limited work has used powder or glass). Industrial units with pressures to ~200 MPa are common and temperatures to ~2,000°C with reasonable working volumes (20 cm dia. x 50 cm long) are common, and units with orders of magnitude larger working volumes operating at lower temperatures are in industrial use, for example, for metals. HIP is, of course, also more costly than sintering, but since many smaller pieces can be produced by HIP at once, incremental costs for parts can be limited.

HIP for densification requires that the specimen be encased in a gas-impermeable membrane that is compatible with the temperatures and materials of pressing. The original approach, the use of refractory metal cans that were welded closed with an umbilical tube (sealed off after vacuum outgassing of the can

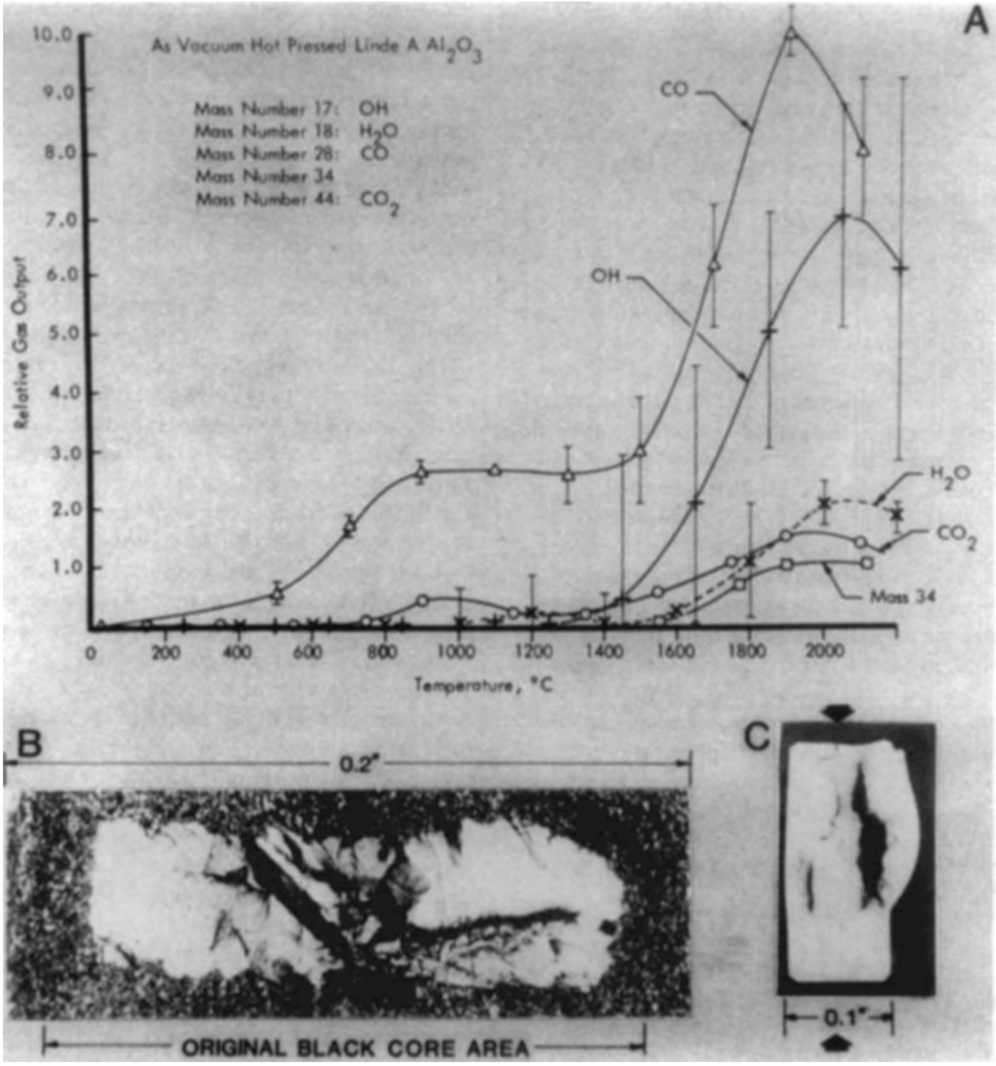

Figure 16. Gas entrapment in a less reactive ceramic (Al_2O_3).

A. Knudsen cell gas evolution from theoretically dense, hot-pressed Al_2O_3

B, C. Cross sections of dense samples heat treated in air to ~1,800°C, showing extreme cases of internal grain growth and bloating

and specimen in a separate furnace prior to HIP, was clearly restricted to research or highly specialized components. More recently, much more practical canning techniques based on the use of silicate-base glass encapsulants have been developed. Components can be sealed in glass tubes or by applying a glass powder coating. Proper sintering of the glass powder results in a sealed can, ideally with the compact outgassing prior to the glass sealing it in. (Some HIP units now allow the chamber to be operated at modest vacuum, 700 microns, and to temperatures on the order of 1,500°C before switching to the gas pressure.) The glass can is subsequently removed, for example, by acid leaching. Production of complex shapes, such as ceramic turbocharger rotors, has been demonstrated using glass encapsulants. Coating powder compacts with polymers that pyrolyze to carbon also may be a possible, practical canning technique, with subsequent removal by oxidation.

The other basic method of canning is self-canning—sintering the parts to closed porosity so their own surfaces become the impermeable layer, the can. This method is thus really a postsintering method rather than an alternate densification method, and is in fact the dominant mode of using HIP. Such HIP of sintered parts is often quite practical, especially for small parts since many can be processed at once. While there are limitations on the size of isolated pores or pore clusters that can be closed by HIP of ceramics (Kwon and Messing, 1984), very substantial improvements in properties can be achieved (20–100% higher strengths than by sintering alone). HIP typically produces somewhat more superior parts than hot pressing. A particularly successful, and substantial, application of postsintering HIP is of cobalt-bonded WC components such as for drilling bits. It reduces or eliminates isolated voids and void clusters so as to substantially reduce infancy failures of components, which are due mainly to such voids (Lardner, 1975).

Recent extensions of these processes are coating or burying component preforms in glass or other ceramic powder, heating, then rapidly transferring to a steel die, in which they are subjected to high pressures (1 GPa) (Pyzik and Pechenik, 1988; Kelto et al., 1989). The glass or powder serves as both insulation and pressure-transmitting medium, yielding an approximate isostatic pressure.

Nonpowder-based Processing and Coating

Several methods for making ceramics either use no powders at all, or do not directly make the ceramic from powder, Table 1. The most extensive of these are the various melt processing methods, of which melt casting produces by far the largest volumes and individual sizes (up to a few tons in weight). Arc melting using graphite electrodes predominates, but some induction melting is used, directly coupling to the ceramic to be melted, usually after heating part of the mass by other means to about 1,000°C for sufficient coupling. One application of this method is to grow cubic ZrO_2 crystals for the jewelry trade (Nassau, 1981). In either case, the method is predominantly skull melting, in which the melt is contained within a layer of the same ceramic that is kept unmelted, for example by a water-cooled shell). Nonoxide materials that melt (several do not melt without high overpressures) can be processed by melting—achieved, for example, by arc or electron beam—however, melting is predominantly applied to oxides, such as Al_2O_3 and ZrO_2 (Klaussen et al., 1983). Figure 17 shows some characteristics of cast Al_2O_3. *In-situ* solidification of a skull melt to form an ingot which is crushed into grain, for example, for the manufacture of refractories, or into powder for plasma spraying. The advantage of melt-derived powders for plasma spraying lies in multiconstituent powders such as $MgAl_2O_4$, $3Al_2O_3 \cdot SiO_2$ (mullite), and ZrO_2–Y_2O_3, since better homogeneity is achieved by melt preparation than by chemical preparation of the powders (Chuanxian et al., 1984).

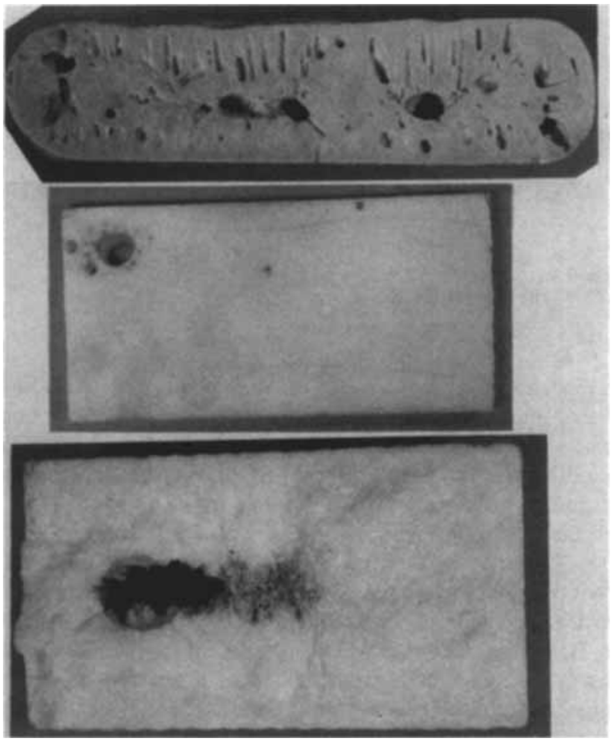

Figure 17. Porosity in fused Al_2O_3-based ceramics.

Left: Cross section of fused cast brick showing desired internal entrapment of large void mainly from liquid to solid volume shrinkage
Middle: Distributed voids, most too fine to see in photo; a few undesirably large voids
Right: Approximately homogeneous but generally undesired distribution of larger voids.

Ceramic components cast from the melt, usually into graphite molds, typically have much (10–1,000-fold) larger grains and substantial porosity (10–20%) compared to sintered ceramics. Grain sizes on the surface of such cast pieces will typically be finer than in the interior due to rapid surface chilling, especially in single-phase materials. However, even the surface grain size will typically be at least an order of magnitude or greater than typical sintered grain sizes. While some porosity can arise due to extrinsic entrapped gases, as well as exsolution of some dissolved gases during solidification, much of it arises intrinsically from the substantial (10–25 vol. %) smaller volume of the solidified material relative to its melt for oxide materials (Rasmussen, 1972). The intrinsic porosity, as well as much of the extrinsic porosity, forms at the solid/liquid interface. Directional solidification, as used in growing single crystals, can eliminate entrapment of any of the intrinsic porosity, and be used to give potentially beneficial eutectic structures (Dauchier et al., 1982). (To minimize problems due to extrinsic porosity from trapped volatile species most single crystals are grown from material that has previously been melted at least once, and commonly twice.) Most ceramic castings are designed to result in a solidification front that in term results in the solidification porosity being located in regions where it is less detrimental to the component's performance.

Melt processing is also one of the most widely used methods for making ceramic coatings (Fairbanks, 1984), and can be done over sizable areas, Figure 7. This is most commonly done by feeding appropriate size powders, for example, spray dried agglomerates a few tens of microns in diameter, into a chemically (e.g., oxyacetylene) or electrically (e.g., plasma) derived flame. Such melt spray coatings, although used considerably in the past, have often suffered from variable quality and too much porosity. While some porosity is intrinsic in the process (and increases with subsequent heat treatment in materials such as Al_2O_3 that are quenched in unstable, lower density phases), denser coatings have been obtained in recent years by using chambers for spraying at reduced pressure for higher particle velocities. Chamber spraying also allows cleaner, more reliable surfaces to be obtained, for example, by sputtering, for better, more reliable adhesion. Computer control of spray parameters is leading to significant improvements in reproducibility. Melt spraying has also seen some application for fabrication of freestanding ceramic parts. Recent developments that enhance the rate of deposition, help cut costs, and increase microstructural control and reproducibility all suggest increased opportunities for such processing. Potential wide shape capabilities that can be obtained by spraying onto appropriate mandrels, especially low-cost removable mandrels, could greatly expand the applicability of this method to freestanding parts if appropriate engineering can be developed to effectively carry this out.

Another nonpowder-base method is that of chemical vapor deposition (CVD) (Pierson, 1981; Niihara, 1984; Stinton et al., 1987). While used for making ceramic powders, this method is also used quite extensively for making ceramic coatings (and some reinforcing filaments) and even more extensively for making freestanding parts (Goela and Taylor, 1988). Typically, inorganic and related precursors, which are substantially less expensive, are utilized for bulk, as in structural bodies, with processing temperatures commonly in the 1,000–1,500°C range. Organometallic precursors, typically much more expensive, can be used, for example, for coatings for electronics, with deposi-

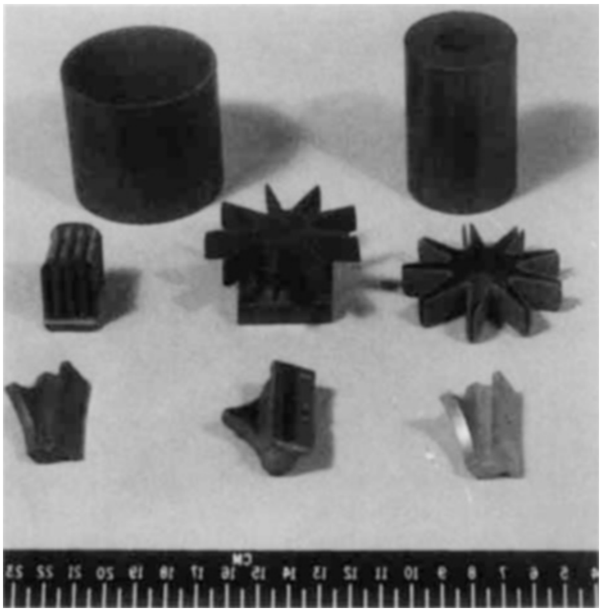

Figure 18. Freestanding SiC produced by CVD.

Top: Thick and thin wall tube sections.
Middle, left to right: carbon form for simple paddle wheel, resultant SiC paddle wheel, miniature SiC CVD heat exchanger
Bottom, left to right: metal model, resultant carbon mold, resultant CVD SiC part
Samples courtesy of R. Ingdahl, Synterials, Herndon, VA

tions at temperatures from a few to several hundred degrees C. CVD has played a key role in the development of fiber optics by producing high-purity boules, from which the fibers are drawn (Ketron, 1987).

Potentially important advantages of CVD include costs, shape and size, and not requiring additives, Table 2. Many precursors are relatively inexpensive; for example, the cost of methyltrichlorosilane for directly producing SiC is competitive with costs of conventionally produced SiC abrasive material. The considerable potential for near, or true, net shape capability of CVD minimizes expensive machining; Figure 18 shows some applications of CVD. Also, under appropriate conditions quite high deposition rates (as high as tens of microns/min) can be achieved for moderate process costs. CVD can produce some of the largest pieces of technical ceramics. Another important advantage of CVD is that it can fairly readily produce a variety of quite important nonoxide materials, such as SiC, Si_3N_4, B_4C, and BN, which otherwise require very high temperatures to produce and typically can only be produced from powder by using additives that may limit performance of the resultant body, especially at high temperatures. For example, chemical vapor deposited SiC or Si_3N_4 have substantially higher (an order of magnitude or more) creep resistance at elevated temperatures than do bodies made by densifying powders that require additives.

The challenges of CVD are mainly control of microstructure and residual stresses; Figure 19 presents some examples. CVD commonly results in substantial grain sizes (from a few tens to a few hundreds of microns), development of growth cones (colonies of similarly oriented grains) usually growing at a much higher rate perpendicular to the growth surface rather than parallel with it, or both. Large grains typically result in weaker mechanical properties, and can have other disadvantages, such as rough as-deposited surfaces that require more machining and may limit the surface finish quality. Growth cones typically result in much greater surface roughness than do large grains and often limit strengths, similar to large grains. This last occurs because the boundaries between growth cones frequently are locations of porosity (due to inadequate lateral vs. aerial cone growth rates) and concentration of impurities.

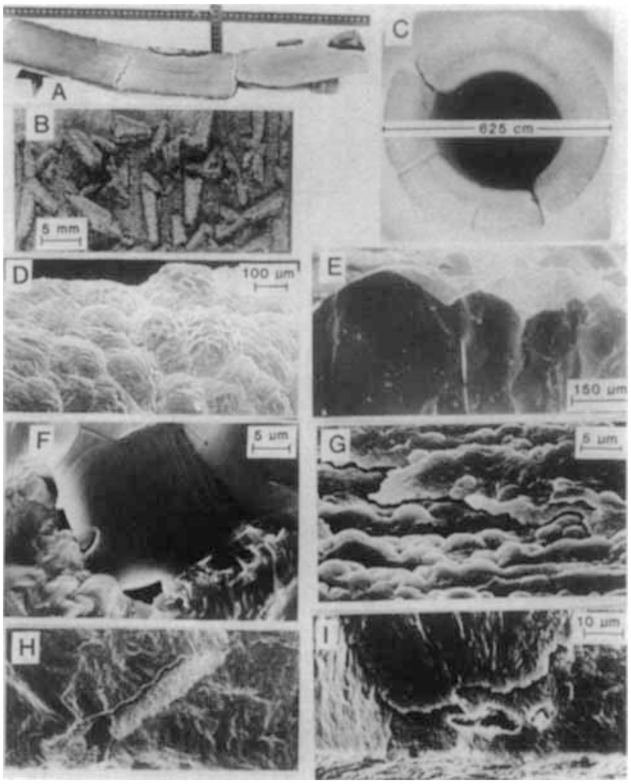

Figure 19. Outline of issues for CVD: problems from work on Si_3N_4 and SiC.

A–C. Residual stress manifested by bowing and cracking of large place meant to be flat, curling of thin Si_3N_4, and splitting of thick SiC tube section during deposition
D, E. Rough as-deposited surfaces due, respectively, to growth cones and large grains.
E, F. Large grains
F, I. Pores of various shapes and sources
G. Pores between interrupted deposition

Residual stresses can be a very serious problem for CVD, as for any deposition process. Some stresses arise due to differential expansion between the material being deposited and the substrate—usually graphite for producing freestanding bodies, since it is easily removed, is relatively modest in cost, and allows a fair range of accommodation of thermal expansion. However, the major sources of residual stresses are apparently variations in stoichiometry and resultant lattice strains, since some stresses can actually substantially distort or destroy a component at deposition temperature, where there is little or no strain differential between the component and the surface onto which it is being deposited. Control of both residual stress and microstructure is a common reason for CVD being conducted at relatively modest deposition rates, that is, reduced temperatures, pressures, and flow rates. However, the issue appears in part to be one of controlling appropriate nucleation, which should be

Table 5. Possible use of Ceramic Oxides with Anisotropic Thermal Expansion as Coatings on Metals

Material	Melting Temp °C	Thermal Expansion Coefficient × 10^{-6}°C^{-1}*		
		αa	αb	αc
Al_2O_3	2,050	8.6	8.6	9.5
TiO_2	1,825	8.3	8.3	10.2
Cr_2O_3	2,260	8.1	8.1	6.1
SiO_2 (α quartz)	1,720	22.0	22.0	12.0
$MgTiO_3$	1,630	9.4	9.4	12.4
$LiNbO_3$	1,410	21.2	21.2	0.1
$CaWO_4$	1,580	13.7	13.7	21.5

*Al_2O_3, TiO_2, Cr_2O_3, three commonly used ceramics, are shown for comparison. For reference, compare the two identical expansions of each material with that of typical Fe- and Ni-based alloys ($\alpha \sim 15 \times 10^{-6}$°C^{-1}), and Al-based alloys (20–25 × 10^{-6}°C^{-1}).

addressable more fundamentally by chemical and physical means. There appears to be no intrinsic reason why one cannot utilize the cost advantages of high deposition rates while achieving acceptable microstructures and residual stresses. This should be in an area for important research and development.

Various methods of physical vapor deposition (PVD) are also used. These include evaporation (e.g., electron beam), sputtering, and reaction process (e.g., reactive sputtering). Since the deposition rates are quite low, such processes are restricted to thin coatings. Coatings for wear applications, especially for many cutting and related tools—for example, with TiN by reactive deposition—are now widely done on an industrial scale. An important opportunity presented by PVD, as well as CVD and probably some other deposition processes, is to learn to control preferred orientations in coatings. If one can obtain coatings with proper preferred orientation of some anisotropic ceramics, much better matching of ceramic coating and substrate thermal expansions can be achieved. The coefficients of expansion are ~15 × 10^{-6}°C^{-1} for Fe- and Ni-based alloys and ~25 × 10^{-6}°C^{-1} for Al-based alloys. Table 5 presents a comparison of coating materials.

A number of ceramics can also be deposited by electrochemical means which, in principle, could be used for producing freestanding components as well as coatings as with CVD. However, there has been only limited investigation of this technique for coating purposes (Anthony and Welch, 1969; Finn et al., 1979; Zubeck et al., 1976; Elwell et al., 1982; Stern and Gadomski, 1983; Switzer, 1987). The most extensive development has been with TiB_2, but the feasibility of several other coating materials, such as WC and SiC, has been demonstrated. Typically, the vehicle for deposition is molten salts, which in themselves present a substantial challenge of temperature and corrosion, as does the problem of small pockets of the bath being incorporated in the coating, limiting coating quality. Much more development of the process is needed, ranging from basic chemistry to control of factors such as microstructure.

One of the newest nonpowder-based methods of preparing ceramics or ceramic coatings is polymer pyrolysis (Yajima et al., 1978; Rice, 1983; Wynne and Rice, 1984). Here, one obtains a ceramic by the pyrolysis of an appropriate metal organic polymer, in direct analogy with the fabrication of glassy carbon or graphite fibers by pyrolysis of appropriate organic polymers. Example products are shown in Figure 20. While this method is applicable to some oxides, mainly to obtain SiO_2 from silicones, it is predominantly for nonoxides. The preparation of SiC from Si-C-based polymers and Si_3N_4 from Si-N-based polymers has been demonstrated and progress has been made toward obtaining B_4C and BN-based ceramics (Narula et al., 1986) from appropriate polymeric precursors. The term "based" is used to denote the fact that one typically does not obtain exact stoichiometry of the desired ceramic or the precursor polymer. Instead, an excess of one constituent or a mixture of products is generally obtained. For example, it is common to obtain mixtures of Si_3N_4 and SiC, or to produce Si_3N_4 with excess Si (which can be converted to Si_3N_4 by pyrolyzing in a nitrogen producing atmosphere, such as N_2 or NH_3). The weight yield of the resultant ceramic from the polymer must typically be in the range of 50–80% for a practical process. However, for some

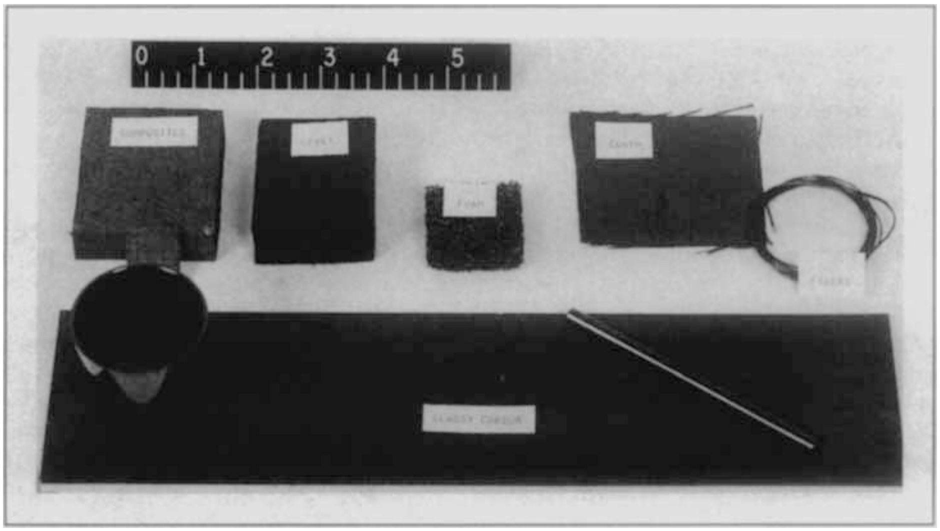

Figure 20. Carbon products from polymer pyrolysis.

Top, left to right: carbon-carbon composite, graphite felt, reticulated glassy carbon foam, carbon cloth, carbon fiber tows
Bottom: Glassy carbon crucible, plate, rod

systems yields as high as 90% have been calculated theoretically and approached very closely experimentally with the appropriate precursor, one that results in essentially exclusive loss of hydrogen in the forming of the final ceramic product. Substantial shrinkage and/or cracking, as well as porosity, are the typical mechanisms by which the substantial differences in densities between the starting polymer and the resultant ceramic composition are accommodated. A basic limitation of polymer pyrolysis is that it cannot produce fully dense ceramic materials unless at least one dimension is small, on the order of microns. Typical resultant porosities of bulk bodies from pyrolysis are in the range of 20–40%, at least for pieces a few mm thick; thicker pieces (≥ 1 cm) may have more porosity, and are generally not made. Also, because of the large shrinkages involved, the macroscopic dimensions that can be achieved may be limited, but glassy carbon parts at least 30 cm long are produced. The process is potentially most widely applicable for fabrication of coatings or fibers, for which it is already in commercial production, as well as composites.

Sol-gel processing can, in many respects, be similar to polymer pyrolysis, but for oxides. It generally involves lower yields, owing to greater shrinkage or porosity, and produces *in-situ* particles that must be sintered. It is particularly useful for fibers and coatings, for which there is commercial production. However, bulk, dense pieces of limited sizes have been produced directly from gels (Becher et al., 1978; Hench, 1986), most extensively for glasses. On an industrial scale, sol-gel processing has made important inroads in the processing of oxide abrasive particles. Sol-gel processing is also of interest for composites.

Melt processing is used extensively for producing oxide fibers. Industrially, this includes fibers for fiber optics, reinforcement (fiber-glass composites), and insulation fibers for products ranging from home to high-temperature furnace applications. Insulation fibers are typically formed by blowing molten streams, while optical and reinforcement fibers are drawn. Previously, only quite viscous melts, such as silicate, could be used, otherwise surface tensions would result in droplet formation. However, the development of inviscid melt spinning (Dunn et al., 1972; Cunningham et al., 1978) has relaxed this limitation. This is accomplished by extruding the molten fiber into a chamber where the hot fiber acts as a substrate for CVD (commonly of graphite, from CH_4, for example) such that sufficiently rapid CVD coating onto the fiber prevents its breakup into droplets. New glass compositions for fibers are of interest, including halides for low-loss IR fibers, and oxynitride or oxycarbide compositions for higher stiffness (Videau and Portier, 1985; Messier and Gleisner, 1988; Unuma et al., 1988; Homeny and Nelson, 1988).

Processing of Ceramic Composites

Substantial interest has arisen in recent years in fabricating ceramic composites (Rice, 1983b, 1984b, 1990; Newnham, 1986). While there is considerable interest in composites with one or more nonceramic constituents, the greatest attention, and the focus of this section, is on composites in which all constituents are ceramic. These typically comprise two ceramic constituents: a continuous matrix, and a dispersed phase of ceramic particles, whiskers, or short (chopped) or continuous ceramic fibers. The processing challenge is to obtain a homogeneous distribution of the dispersed particle or fiber phase, which is typically of at least 10 vol. % and more commonly in the 30–60 vol. % range. Meeting this challenge shifts the emphasis from some of the processing methods most common for traditional ceramics to less traditional methods.

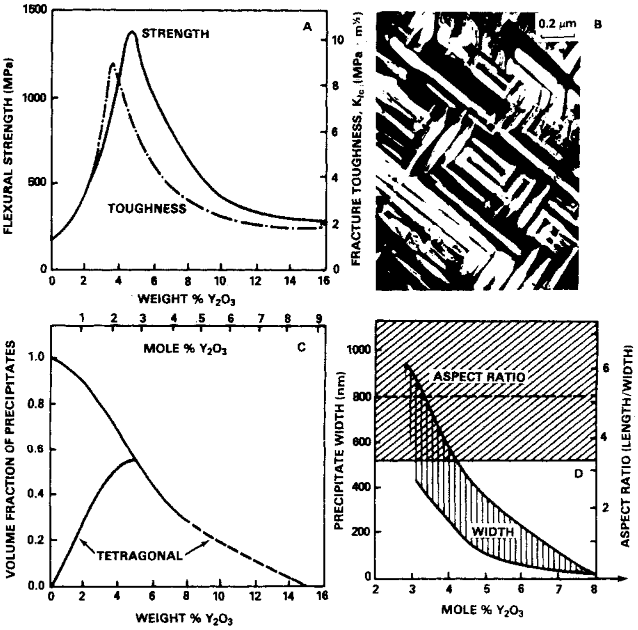

Figure 21. Toughening of ZrO_2 single crystals partially stabilized with Y_2O_3.

A. Strength and toughness as a function of Y_2O_3 content

B. Transmission electron micrograph of resultant blade/rod precipitate structure

C. Volume fraction of precipitates in either tetragonal or monoclinic structure as a function of Y_2O_3 content

D. Precipitate width and aspect ratio as a function of Y_2O_3 content

Consider first processing of particulate composites. The particulate phase of greatest interest is tetragonal zirconia because of the toughening that can be achieved from the transformation from the metastable tetragonal to the monoclinic crystalline phase. This is shown in Figure 21 and covered in detail in Heuer and Hobbs (1981). However, there is also substantial interest in dispersion of hard, nonoxide phases such as SiC, TiB_2, TiC, and B_4C in other matrices, most commonly oxide matrices like Al_2O_3 and mullite ($3Al_2O_3 \cdot 2SiO_2$). There is interest too in incorporating other ceramic particulates, especially those of highly anistropic thermal expansion, for example, Al_2TiO_5, graphite, and especially BN (Rice et al., 1981; Rice, 1990).

In processing particulate composites, the issue is not only homogeneity of the size and spatial distribution of the dispersed and matrix phases, but also control of the matrix grain size. However, there is some built-in self-control due to inhibition of matrix grain growth by the dispersed phase. Particulate composites, though generally of increased resistance to damage, failure, or both, are still quite sensitive to inhomogeneities of composition as well as other processing defects such as pores; thus they need good processing to be effective. Particulate composites have been made on a commercial basis by simplying mixing powders of the two constituents. Although this approach is inherently limited in the homogeneity that can be achieved, it is the most readily adaptable for existing ceramic production technology. However, other approaches are of interest. From the technological standpoint, a particularly desirable approach to fabricating particulate composites is to coat the matrix or its precursor onto fine particles of the dispersed phase with good control of the starting dispersed particle size and the resultant matrix coating thickness. One should in principle be able to achieve the ultimate in homogeneity of distribution and thereby optimize composite performance. This can also have other ramifications, such as allowing more useful composite performance to be achieved in a body having porosity, which might be desired for other factors, such as limiting thermal conductivity. Only limited work has, however, been done on such particle coating (Kratohvil and Matijevic, 1987).

Toughened ZrO_2 is made mainly be sintering either:

1. fine (submicron) chemically (e.g., oxychloride) derived powders in the two-phase region (at ~1,400°C) with sufficient stabilizer (usually Y_2O_3) to yield a fine grain body of mainly tetragonal ZrO_2, or
2. more traditional powders in the single-phase region to produce a dense, single solid solution body of cubic ZrO_2 and stabilizer (e.g., MgO), then heat treated to produce a large population of tetragonal precipitates in the cubic ZrO_2 matrix, similar to Figure 21.

There is some processing using melt-derived powders, or direct solidification from the melt, Figure 22. Al_2O_3–ZrO_2 composites are the next most popular form of zirconia-toughened material after dispersion of tetragonal zirconia in a cubic zirconia matrix. Such composites having a common anion have been successfully made from a zirconia sol and alumina sol (Becher, 1981). However, since sols are more expensive ingredients, such processing is less favored for industrial applications. Combinations of sol and conventional processing are also feasible: for example, using a sol as a source of ZrO_2, as well as an important asset in homogeneous mixing with a more conventionally derived alumina powder. Chemical vapor preparation of powders, again generally requiring a common anion of the constituents, has also been demonstrated, at least for the Al_2O_3–ZrO_2 system, wherein mixtures of $AlCl_3$ and $ZrCl_4$ are oxidized at high temperatures with H_2O (Hori et al., 1984, 1985). All of these approaches produce dispersions of finer ZrO_2 particles in between somewhat larger Al_2O_3 grains, Figure 21a. Again there is investigation of melt-derived powders (Claussen et al., 1983), direct melt casting, or directional solidification especially of eutectics (Dauchier, 1982). In either case, an important goal is to take advantage of the desirable homogeneous mixing of the eutectic structure, Figure 22.

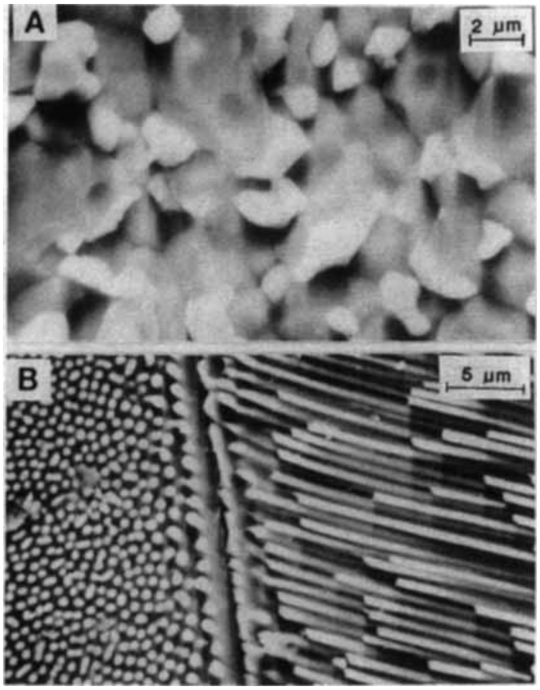

Figure 22. Al_2O_3–ZrO_2 microstructures.

A. Typical microstructure achieved by mixing powders, resulting in ZrO_2 particles along boundaries between larger Al_2O_3 grains
B. Eutectic structure resulting from melting: left, section perpendicular to ZrO_2 rod structure; right, section almost parallel to rod structure

Another approach to making particulate composites that is of increasing interest is reaction processing (DiRupo et al., 1979; Claussen and Jahn, 1980; Anseau et al., 1983; Cambier et al., 1984; Rice, 1989). Reactions that occur only upon heating the reactant compact to high temperature are common, for example:

$$2ZrSiO_4 + 3Al_2O_3 \rightarrow 3Al_2O_3 \cdot 2SiO_2 + 2ZrO_2 \qquad (8)$$

where zircon, the lowest cost source of ZrO_2, is used to react with alumina to produce *in situ* a mullite-plus-zirconia toughened composite. Another example (Rice, 1984) is:

$$B_2O_3 + Si_3N_4 + Al_2O_3 \rightarrow 3Al_2O_3 \cdot 2SiO_2 + BN \qquad (9)$$

Note here that lower grades of Si_3N_4 having potential costs of a few dollars per pound should be usable, since it is effectively being used as a low-cost source of nitrogen but can clearly tolerate substantial oxygen contamination (the reduction of which is a major cost factor in higher quality Si_3N_4 powders) and uses a very low cost boron source, thus avoiding the very high costs of the end BN (typically $25 or more per pound). This reaction uses materials averaging on the order of $1 or less per pound to produce a product that if made directly from the final constituents would be an order of magnitude higher in cost. With proper selection of reactant and processing parameters, some of these reactions such as no. 8, can be densified by sintering, then reached *in situ*. Other reactions, such as no. 9, commonly require hot pressing for densification.

Another class of reactions of interest comprises highly exothermic reactions in which a high-temperature reaction front will commonly propagate through a compact of the powder reactants if it is ignited at one point, as with a thermite reaction, to which these reactions are closely related (Munir, 1988; Ambramovici, 1984; Richardson et al., 1986; Rice et al., 1986a,b). An example is:

$$10Al + 3B_2O_3 + 3TiO_2 \rightarrow 5Al_2O_3 + 3TiB_2 \qquad (10)$$

Again, a composite of mixed anion content is produced *in situ*, one that has a high hardness and stiffness (of interest for wear and possibly armor applications) from raw materials whose costs are a fraction of that of the resultant constituents, if they had been produced as separate individual products and then mixed. Note that the issue of producing particles that consist of one constituent in the center coated with one or two of the reactants in progressive outer layers has the potential not only for enhancing homogeneity, but also for controlling the kinetics and possibly the proportions of reacted constituents. Thus, for example, if one reacts the elements Ti + B + C in a finely divided mixture, they will upon ignition and resultant reaction proceed according to the following equation:

$$2Ti + 2B + C \rightarrow TiB_2 + TiC \qquad (11)$$

However, if, for example, the Ti and C particles were coated with B, it is expected that the yield of the above reaction products would be reduced and partially replaced by products such as TiB and B_4C, with the relative proportions being a function of the particle sizes as well as the proportion of the elemental reaction ingredients. Such reactions can, of course, be used to produce single-phase ceramics. However, other than for producing powders, this process is generally not particularly practical for directly producing such bodies (Rice, 1989).

An important issue in processing particulate composites is densification. A few particulate composites, primarily those using dispersed ZrO_2 particles for toughening, can be sintered as well as, or in some cases possibly slightly better than, the matrix by itself. However, in most cases, sintering of composites is intrinsically more difficult, since by definition one wants to maintain separate identities of the dispersed phase and the matrix phase such that there is little or no interdiffusion between the two. Thus material transport paths for densification are inherently disrupted in such composites. Further, the diffusion kinetics for the two different phases often are mismatched; for example, most of the nonoxide phases require much higher temperatures for comparable levels of diffusion than do the oxides. This typically results in greater difficulty in sintering and requires higher sintering temperatures. These can, in some cases, be tolerated, since the second phase limits the grain growth of the matrix that would normally result from such higher sintering temperatures. However, the combination of higher temperatures and typically the use of nonoxidizing atmospheres required for such composites reduces the cost advantage that commonly exists for sintering over hot pressing. Further, since residual processing defects, such as residual porosity, in the resultant composites compromise the enhanced performance sought from the composite character, one is much more frequently driven to hot pressing such composites because of the resultant higher density, greater homogeneity, and finer, more uniform microstructure. Thus, for example, most Al_2O_3 + TiC composites, which are probably the most extensively commercially produced ceramic composites (for such applications as cutting tools and hard wear surfaces) are processed primarily by hot pressing or sintering and HIP, as opposed to sintering alone. Similarly, many of the other composite materials, even those that can be reasonably sintered (e.g., Al_2O_3–ZrO_2), have frequently been hot pressed or HIPed (Hori et al., 1986) and a number of other composites (e.g., mullite + BN) have been produced only by hot pressing. The driving force for hot pressing becomes even greater as one goes to larger volume fractions of the second phase, since this exacerbates the sintering problems discussed above.

Even in many of the reaction processed composites, hot pressing is of value or is necessary for either or both of two reasons. First, the reactions may in fact reduce the driving force for sintering, for example, through coarsening of the microstructure or changing the location or configuration of grain boundaries. Second, there are frequently intrinsic volume changes that generate porosity due to the denser character of many of the resultant reaction products in comparison with the reaction constituents (Rice and McDonough, 1985). Also, in some of the very exothermic reactions there can be extrinsic problems due to vaporization of either a reaction species or an adsorbed species due to the transient very high reaction temperatures (≥2,000°C), all of which are a driving force, again, for hot pressing.

There can be some processing of particular composites by CVD. Direct processing of Si_3N_4 based composites have been reported (Hirai and Hayashi, 1982; Hirai et al., 1984). Preparation of Al_2O_3–ZrO_2 powders by CVD has been shown to be promising (Hori et al., 1984).

Turning to whisker or short-fiber composites (Homeny and Vaughn, 1987; Rice, 1990), the problems noted above for particulate composites are exacerbated, as mixing whiskers with an appropriate ceramic matrix powder is considerably more challenging than simply mixing two powder constituents for particulate composites. This challenge becomes particularly serious as one goes beyond about 10 vol. % whiskers (typically at least 20 to 40 vol. % is desired for greater toughening effects) because of the increasing entanglement of whiskers or short fibers. Clearly, controlling the organization of the whiskers for example, their orientation can be important to achieve higher volume loadings and may have other advantages in terms of performance of the resultant composite. Also, the feasibility of coating some or all of the matrix or its precursor onto the whiskers prior to consolidation may have a considerable advantage in terms of resultant quality and performance.

The challenge of sintering whisker or short-fiber composites is much greater than that of sintering particulate composites. The higher temperatures needed to partially compensate for density limitations with increasing whisker or short fiber contents are substantially more severe. Again, some progress can be made by the introduction of additives to provide liquid-phase sintering. However, these provide serious dangers of chemical attack on the fibers or whiskers, and thus of composite degradation, although in some cases this can in part be mitigated by appropriate coating of fibers or whiskers. Chemical attack also may compromise the performance of the composite, especially at high temperatures, due to the enhanced diffusion provided by the additive phases. Thus it is not surprising that almost all whisker composites have been hot pressed and, in fact, all of those that are currently in commercial production (mainly for cutting tools) are produced by this method because of its much greater driving force for densification.

Because of these challenges in mixing and densification, alternate methods of processing are being sought. Thus, in addition to the issue of whisker coating or surface treatments, which is of increasing interest, there is interest in applying to whisker composites some of the processing technologies for continuous fiber composites. There is also interest in possibly processing whisker composites by *in-situ* development of whiskers. This may be accomplished in some cases by precipitation from solid solutions, and there are indications that it may be accomplished by appropriate control of some reaction processes (Hori et al., 1987). Besides processing advantages, such approaches should help reduce costs, which currently restrict application to high value added applications such as cutting tools.

Continuous-fiber composites provide the most outstanding change in mechanical performance of any ceramic composites (Prewo et al., 1986; Rice and Lewis, 1989; Rice, 1990). They are the only ones to have thus far clearly demonstrated non-catastrophic failure. In this they are essentially identical to fiberglass-type composites, in contrast to the totally catastrophic failure of traditional ceramics and other ceramic composites. Continuous-fiber ceramic composites are also the most challenging from the processing standpoint. First, they require fiber handling technologies—such as working with cloth, random fiber mats, filament winding, and the like—that are similar to other composite technologies, which in themselves are a significant departure from traditional ceramic processing. Second, they provide considerable challenges in terms of infiltrating ceramic matrices or matrix precursors among the fibers in a reasonably uniform fashion. One typically wants to use fibers that are quite fine, a few to ten microns in diameter, typically available in tows—bundles usually containing a few hundred to a few thousand fibers. Proper infiltration is especially a problem in cloth, where separation of the individual fibers is constrained where tows cross in the weave. Third, continuous ceramic fiber composites represent the ultimate in limitations on sintering. While part of the limitations may be extrinsic (due to issues of homogeneity, and so on), they are in general intrinsic, arising because the sintering process typically requires shrinkage in order to reduce porosity. However, with continuous-fiber composites, there is an inherent continuous, nonshrinking phase (i.e., the fiber). There is thus a fundamental incompatibility in shrinkage, the extent and nature of which depends upon the fiber architecture, becoming increasingly greater as one goes from a one-dimensional to a two-, three-, or multidimensional fiber composite. A few demonstrations of sintering to useful mechanical strengths have been made in small test specimens of unidirectionally aligned fiber composites, but the properties that can be achieved are inherently limited and become progressively more so as one goes to larger sized components and, especially, to more sophisticated and practical fiber architectures. Thus, it is not surprising that the predominant method of processing ceramic fiber composites to date has been hot pressing. This has been most extensively applied to composites utilizing silicate-based glass matrices, which are in fact the most extensive type of composites developed to date (Prewo et al., 1986). However, there has been increasing development of ceramic composites using nonglass-based oxide matrices (Rice and Lewis, 1989). These have also been made predominantly by hot pressing.

The basic approach to preparing a ceramic fiber composite for hot pressing (or sintering) is to infiltrate the fiber tows with a matrix or matrix precursor. Ceramic slips have been extensively used in which fine particles of the matrix have been put in a reasonably stable suspension through which the fiber tows (with sizing removed, often by pyrolysis, and with some fluffing of the tows, as by an air blast) are pulled, quite analogous to filament winding. Thus, the appropriately wetted fiber tow (possibly using surfactants to control wetting) is wound onto a drum to form a uniaxial tape which then may be cross-plied. Similarly, one can use sols as a matrix precursor in a bath process. In either case, the challenge is to get appropriate levels of matrix precursor in between the individual fibers as well as between the tows. The importance of controlled wetting is shown in Figure 23. Alternatively, one can make a fiber perform—for example, by papermaking techniques, which can also be used for whisker and short fibers—and infiltrate this with either a slip or a sol. However, there are commonly two concerns with the papermaking approach. One is that it is often difficult to get an adequate fiber volume fraction in such a preform (most papermaking techniques typically give only 5–15 vol. % fibers). The other concern is that the fiber preform may tend to act as a filter, leading to serious gradients in infiltrating the matrix or its precursor into the preform.

Figure 23. Fracture of ceramic fiber composite with poor distribution of fibers.

Reasonable strength and toughness were achieved, but substantially better performance would have been obtained with a much more uniform distribution of matrix among the fibers; major inhomogeneities resulted from too much matrix slurry between the fiber tows.

While hot pressing is by far the most extensive method of processing continuous-fiber composites today, a variety of alternate methods of processing are being used or evaluated. The driving forces for developing alternate processing methods are the need for reduced fiber–matrix interactions, enhanced size and shape capabilities, and reduced costs. The leading alternate method has been CVD, often referred to for composite processing as CVI, chemical vapor infiltration (Warren, 1985; Lamicq et al., 1986; Caputo et al., 1987). CVI can typically be carried out at lower temperatures than hot pressing, thus reducing thermal degradation of fibers (but chemical degradation may be a problem), and offers substantial size and shape versatility, such as producing composite tubes nearly 6 ft long. There is also a synergism in CVI: vapor deposition occurs throughout the fiber preform on the individual fibers. Thus even if deposition rates on individual fibers are lower—for example, to keep deposition temperatures low—the fact that one is simultaneously depositing throughout much, or all, of the composite means that reasonable deposition times can be achieved. This is enhanced by the fact that typically there will be on the order of 50 vol. % fibers, so one only needs to deposit half as much material to achieve an end component, which lease to much more practical deposition times. Similarly, because one is depositing on individual fibers and hence has a large number of sources of nucleation, the matrix microstructure will be controlled by impinging growth from adjacent fibers, which may also limit residual stresses.

The basic limitation of CVI stems from the matrix deposit forming predominantly concentrically on the fibers, so that the interstices between the fibers become closed off, to remain as pores. As a result, this method is limited in the densities that can be achieved, typically to about 15% porosities. In fact, surface sealing of the entire body can be a problem, and may require machining off the sealed surface and reinfiltrating, possibly several times. However, the concentric forming of the matrix on the fiber may also provide more environmental protection, since high-temperature environmental effects appear to be the pacing issue in the temperature performance of ceramic fiber composites. This may become an important factor and, in fact, limited data to date suggest possibly better temperature performance of composites made by CVI.

The second, but less explored, alternative method of fabricating ceramic composites is by polymer pyrolysis (Jamet et al., 1984). It has been demonstrated that one can make a composite using a polymeric precursor as the matrix around ceramic fibers; the processing is essentially identical to that of making a fiberglass composite. However, upon *in-situ* pyrolysis one converts the composite to an all-ceramic composite. Again, there is some potential synergism, in that the significant volume fraction of fibers, typically 50%, reduces the volume and hence the cost of the organometallic polymer precursor for the ceramic matrix. In addition, the presence of the fibers significantly limits shrinkage and cracking. Quite acceptable composites have been demonstrated by this process. In principle, other related approaches might be utilized, for example, sol-gel techniques. However, the substantially greater weight losses and shrinkages of most other precursors tend to limit the opportunities.

A major factor in ceramic fiber composites, and also one increasingly being recognized in whisker composites, is control of fiber–matrix interface chemistry, in particular to severely limit or prevent any chemical bonding at the interface (Rice et al., 1984c; Rice, 1987; Bender et al., 1986). This may appear counterintuitive to some who have dealt with other types of composites. However, consider:

1. There is much less disparity in properties between ceramic matrices and ceramic fibers. Fiber–matrix Young's modulus ratios are commonly only in the range of 1–2, in contrast to somewhat higher ratios in metal–matrix composites and very substantially (an order of magnitude) higher ratios in polymeric matrix composites.
2. In ceramic matrix composites the fibers have greater strain to failure so the matrix begins to fail before the fibers, in contrast to exactly the opposite occurring in polymeric and metal–matrix composites.
3. The need in ceramic composites is mainly toughening, not stiffening or enhanced deformation resistance.
4. With close conformity of the matrix around the fibers one can typically have sufficient mechanical transfer of load, similar to load transfer between fibers in a rope.

Much attention is now being focused on controlling bonding between fiber and matrix in ceramic fiber composites. Dramatic benefits have been demonstrated by coating fibers with an appropriate material such as BN. This has been most extensively done by chemical vapor deposition; examples are shown in Figure 24. However, sputtering has also been used with certain boron-containing fibers, and reaction in a reactive nitrogen atmosphere, for example, ammonia, has also been utilized.

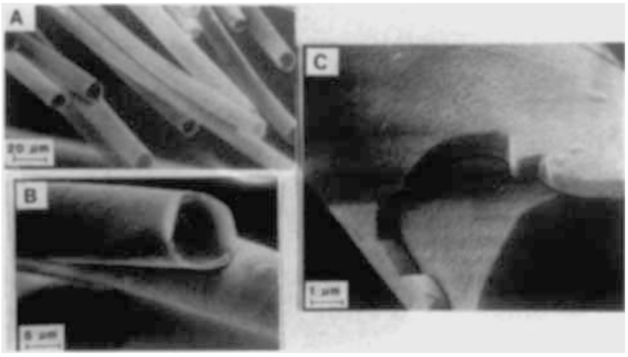

Figure 24. BN-coated SiC-based fibers.

A. Fibers successfully coated with BN by CVD
B. Fibers fairly successfully coated, but some cracking in coating
C. Fibers with poor coating; note cracking and spalling

There are also some opportunities to utilize melt processing for fabrication of ceramic, particulate, whisker and short-fiber, and continuous-fiber composites. Clearly, both particulate and whisker composites are conceivable by solid-state precipitation after solidification of the melt; this can also be obtained in some cases by sintering, as for precipitation-toughened, partially stabilized zirconia. Similarly, it is known that one can directionally solidify ceramic eutectic mixtures and hence obtain uniaxially aligned fiber composites. Such composite processing has typically been limited to very simple shapes and thus suffers from serious economic problems due to high machining costs. There are possibilities of combining this technique with methods of versatilely shaping single crystals in the growth process to produce useful aligned fiber composites directly from the melt (Surek et al., 1980; Bergin, 1980). Note also that use of a eutectic mixture, for example the Al_2O_3–ZrO_2 eutectic structure, in principle gives a more homogeneous and potentially more useful distribution of ZrO_2 than would normal solid-state processing. Clearly, there are possibilities of using melt casting for many of these approaches. Potentially even more desirable is using melt-derived particles. In this method, quenching is done in a solid solution or in a fine eutectic structure, in which the particles are then processed by more typical ceramic powder processing methods into a useful body. There have also been preliminary attempts to use melt spraying as a means of forming composites by introducing the dispersed particulate, whisker, or fiber phase in conjunction with the melt spraying process.

Besides many process improvements, the first of two major needs for fiber composites is lower fiber costs. Current costs are typically a few hundred to several hundred dollars per pound, equal to or greater than whisker costs. Costs in the \$50–\$100/lb range would usefully expand applications, and costs of \$10–\$20/lb should substantially expand them. The second major need is fiber compositions or coatings, or composite processing, to reduce degradation that results from high-temperature composite exposure under oxidizing conditions.

Conclusions

Ceramics are in a very dynamic stage of development because of the already, and significantly increasing, diverse nature of ceramic needs and opportunities. This places a variety of demands on ceramic processing: for improved properties, greater uniformity and reproducibility (hence reliability), and larger scale, more efficient production. All facets of these can benefit from further development in both the basic science and the engineering aspects of the field. This paper has reviewed present and developing processing technology as well as R&D needs and opportunities directly pertinent of improved properties and reliability, Table 1. Larger and more efficient production has been only partly addressed, mainly in terms of the underlying technology. This has been done from a materials standpoint. However, there is also a variety of forming and manufacturing opportunities that could result from new or improved machinery.

Turning specifically to the technology, powder processing—the past and continuing dominant mode of processing—is expanding in its scope and diversity of application. Incremental improvements in traditional methods are important, as are newer, more sophisticated methods. The latter include better chemical preparation of powders for higher purity, more complex compositions, and better particle size control. Other methods of powder preparation, melt derivation and especially chemical vapor deposition, are also being used. Improved methods of processing powders, ranging from colloidal processing methods to coating particles with other ceramic or organic constituents, or both, are also increasing. Forming processes for powders, Table 2, are a critical step, one that is highly interactive with both powder processing, as in mixing of organic binders, and subsequent sintering.

Densification of consolidated powder bodies continues to be achieved predominantly by (pressureless) sintering. However, the use of pressure sintering by hot pressing is increasing, especially for nonoxides and parts of simple shapes where higher quality (mainly microstructural homogeneity) is needed, and larger size or multiple parts per pressing can be an advantage. Hot isostatic pressing is also increasing, especially following sintering to closed porosity, and where quality and complexity of shape justify the cost. Alternatively, HIP is used for many small parts over which the costs can be more readily distributed. The use of additives to aid densification or otherwise improve resultant properties is of increasing importance for both sintering and hot pressing, and to a lesser extent HIP. There are also important opportunities to make quality ceramic products using lower cost ingredients, again mainly by sintering or hot pressing, for example, by reaction processing. With further developments, other methods, such as melt processing, polymer pyrolysis, and CVD (also of interest for coatings) hold increasing promise for bulk components.

The increasing interest in composites adds new complexity in powder preparation for particulate composites. Not only are improved chemical (e.g., sol-gel and particle coating) methods of interest, but there is increasing interest in CVD and melt preparation of composite powders. Both whisker and fiber composites clearly require new methods of fabrication to achieve desired architectures and can benefit from coating processes. Composites are making much greater shifts in densification processes because the applicability of (pressureless) sintering ranges from mixed, for particulate composites, to limited, and very limited for, respectively, short-fiber (or whisker) and continuous-fiber composites. Pressure sintering, mainly hot pressing, has been the dominant method of densification. However, CVI has seen considerable use, polymer pyrolysis shows promise, and melt processing may have some applicability.

The increasing use and diversity of specialty forms of ceramics also adds to the diversity of process technologies to be used. Thus, reinforcing fibers and filaments are mainly made by polymer, sol-gel, or CVD processes, but melt processing also has applicability. The most widely used specialty form is layered structures, with tape casting for electronic substrates and packages being preeminent. Photolithography is of increasing interest for precise patterning of conductors and other components for such packaging. Tape casting or forming processes are also of increasing interest for other applications, ranging from open structures such as fuel cells to ceramic composites. The other major layer structure is coating, where melt spraying is very important, but chemical and physical vapor deposition and chemical (e.g., sol-gel and polymer pyrolysis) methods are all seeing increased use. Besides open structures from formed tape, extruded structures, such as honeycomb catalyst supports, and highly porous structures, including various foams, for example, reticulated foam, are of increasing use.

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