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CARBON AND GRAPHITE FIBERS
TO
CHLOROCARBONS AND CHLOROHYDROCARBONS-C_1

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CERAMICS

This article was prepared under the editorship of Ronald Loehman.

OVERVIEW

Ceramics may be defined as a class of inorganic, nonmetallic solids that are subjected to high temperature in manufacture or use. Ceramics are distinguished both from metals and metallic alloys and from organic materials such as polymers and plastics, and although syntheses may involve solutions or colloids, the final products are solids. The most common ceramics are oxides, carbides (qv), and nitrides (qv), but silicides, borides, phosphides, sulfides, tellurides, and selenides are ceramics, as well as elemental materials such as carbon (qv) and silicon (see SILICON AND SILICON ALLOYS). Ceramic synthesis and processing generally involve high temperatures and the resulting materials are refractory or heat resistant (see REFRACTORIES). Ceramics are commonly thought to include only polycrystalline materials, but glasses, which are noncrystalline, and single-crystal materials such as ruby lasers, are classified as ceramics (see GLASS; LASERS). Examples of applications of less common ceramics include quartz optical fibers (see FIBER OPTICS) that are revolutionizing telecommunications, the insulating tiles on the space shuttle (see ABLATIVE MATERIALS), silicon nitride turbocharger rotors used in some passenger automobiles, and the corderite multilayer substrates used as chip carriers in the latest generation of supercomputers (see COMPUTER TECHNOLOGY).

Ceramic components are frequently made by sintering of powders. Alternatives such as melt processing are often uneconomical because many ceramics have very high melting temperatures or decompose before melting. Many ceramic melts are also very reactive with container materials, which imposes additional limitations on available processing methods. A rule of thumb in ceramic processing is that the quality of a ceramic part is no better than the quality of the powder from which it is made. Thus, much effort has been directed to improving the properties of ceramic powders. Improvements include higher purity, finer particle size, less agglomeration, and better control of compositions and distributions of dopants.

One of the many possible ways of classifying ceramics is according to use. One group is the bulk or commodity ceramics that have had relatively little processing beyond the constituent raw materials. These are primarily low value-added materials such as brick, tile, pottery, and abrasive grain (see ABRASIVES). At the other extreme are the engineering or fine ceramics that are characterized as low volume, high value-added, highly processed materials having carefully controlled

Table 1. *(Continued)*

Material	CAS Registry Number	Molecular formula
phosphorous pentoxide	[*1314-56-3*]	P_2O_5
potassium niobate	[*12030-85-2*]	$KNbO_3$
rhenium trioxide	[*1314-28-9*]	ReO_3
silica	[*10097-28-6*]	SiO_2
silicon	[*7440-21-3*]	Si
silicon carbide	[*409-21-2*]	SiC
silicon nitride	[*12033-89-5*]	Si_3N_4
sodium chloride	[*7647-14-5*]	NaCl
spinel	[*1302-67-6*]	$MgAl_2O_4$
stannic dioxide	[*18282-10-5*]	SnO_2
strontium hexaferrite		$SrO{\cdot}6Fe_2O_3$
strontium oxide	[*1314-11-0*]	SrO
strontium titanate	[*12060-59-2*]	$SrTiO_3$
tantalum(V) oxide	[*1314-61-0*]	Ta_2O_5
tellurium(IV) oxide	[*7446-07-3*]	TeO_2
thallium calcium barium copper oxide		$Tl_2Ca_2Ba_2Cu_3O_y$
titania	[*13463-67-7*]	TiO_2
titanium dioxide	[*13463-67-7*]	TiO_2
titanium isopropoxide	[*546-68-9*]	$Ti(OC_3H_7)_4$
titanium(IV) oxide	[*1317-80-2*]	TiO_2
triaxial porcelain		$Al_2O_3{\cdot}(K,Na)_2O{\cdot}SiO_2$
triethanolamine	[*102-71-6*]	$(HOCH_2CH_2)_3N$
tungsten(VI) oxide	[*1314-35-8*]	WO_3
vanadium(V) oxide	[*1314-62-1*]	V_2O_5
yttria	[*1314-36-9*]	Y_2O_3
yttrium barium copper oxide	[*107539-20-8*]	$YBa_2Cu_3O_{7-\delta}$
yttrium iron oxide	[*12063-56-8*]	$Y_2O_3{\cdot}Fe_2O_3$
yttrium oxide	[*7440-65-5*]	Y_2O_3
yttrium garnet		$Y_2O_3{\cdot}5Fe_2O_3$
zinc ferrite	[*12063-19-3*]	$ZnFe_2O_4$
zinc oxide	[*1314-13-2*]	ZnO
zirconia	[*1314-23-4*]	ZrO_2
zirconium oxide	[*1314-23-4*]	ZrO_2
zirconium *n*-propoxide	[*23519-77-9*]	$Zr(OC_3H_7)_4$

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CERAMIC PROCESSING

Processing is key to the reproducible manufacture of ceramics. The tolerance of a finished ceramic to defects determines the raw materials selected, and the control that must be exercised during processing. More expensive advanced ceramics require higher quality, more expensive raw materials coupled with more carefully controlled manufacturing processes.

Ceramic processing is complicated both by the number of steps required in manufacture (Fig. 1), and by requirements to optimize the processing in the different steps. These factors are often opposed. For example, a fine particle size provides improved plasticity for forming and a higher thermodynamic driving force for sintering; however, electrostatic attraction and van der Waals forces promote agglomeration, ie, the formation of weakly bound particle clusters, and caking, making mixing and packing difficult. Submicrometer particles can be more easily mixed and packed in liquids, but the finer interparticle pore structure results in higher forming and drying stresses, as well as longer forming and drying times.

Ceramics are basically flaw intolerant materials. Consequently chemical and physical defects can severely degrade properties. Additionally, mistakes are cumulative in ceramic processing and these generally cannot be corrected during sintering and post-sintering processing (as they can be in metals processing, for example). The quality of the product is only as good as the quality of the raw materials used, and the control exercised in each of the process steps.

Raw Materials

Raw materials for ceramic processing range from relatively impure clay materials (see CLAYS) mined from natural mineral deposits, to ultrahigh purity powders prepared by chemical synthesis. Inexpensive raw materials that cost a few cents per kilogram are typically used in manufacturing the traditional, high volume production ceramics shown in Figure 2, whereas synthesized ceramic powders, whiskers, and fibers costing hundreds of dollars per kilogram are used for advanced ceramics (qv). Chemically and physically beneficiated mined raw materials, eg, bauxite [*1318-16-7*] (see ALUMINUM COMPOUNDS), comprise the bulk of the oxide raw materials, eg, Al_2O_3, used in ceramic manufacturing, and make up the middle ground between the two extremes.

Natural. Naturally occurring ceramic raw materials (1–11) such as silica [*7631-86-9*] (qv), SiO_2, sand, quartz [*14808-60-7*], or flint [*7631-86-9*]; silicates eg, talc [*14807-96-6*], $Mg_3Si_4O_{10}{\cdot}OH_2$, wollastonite [*14567-51-2*], and asbestos [*1332-21-4*] (qv); and aluminosilicates, eg, clays, feldspars, pyrophyllite [*12269-78-2*], and sillimanite [*12141-45-6*], are used extensively as raw materials in the manufacture of traditional ceramics (see Fig. 2). Seawater and brine wells provide another source of ceramic raw materials, eg, magnesium oxide [*1309-48-4*], MgO (see CHEMICALS FROM BRINE). The principal advantage of naturally occurring raw materials is the low cost; the disadvantage is chemical impurity.

Naturally occurring raw materials are generally found in large, flat-lying mineral deposits near the earth's surface, and are mined using open-pit methods

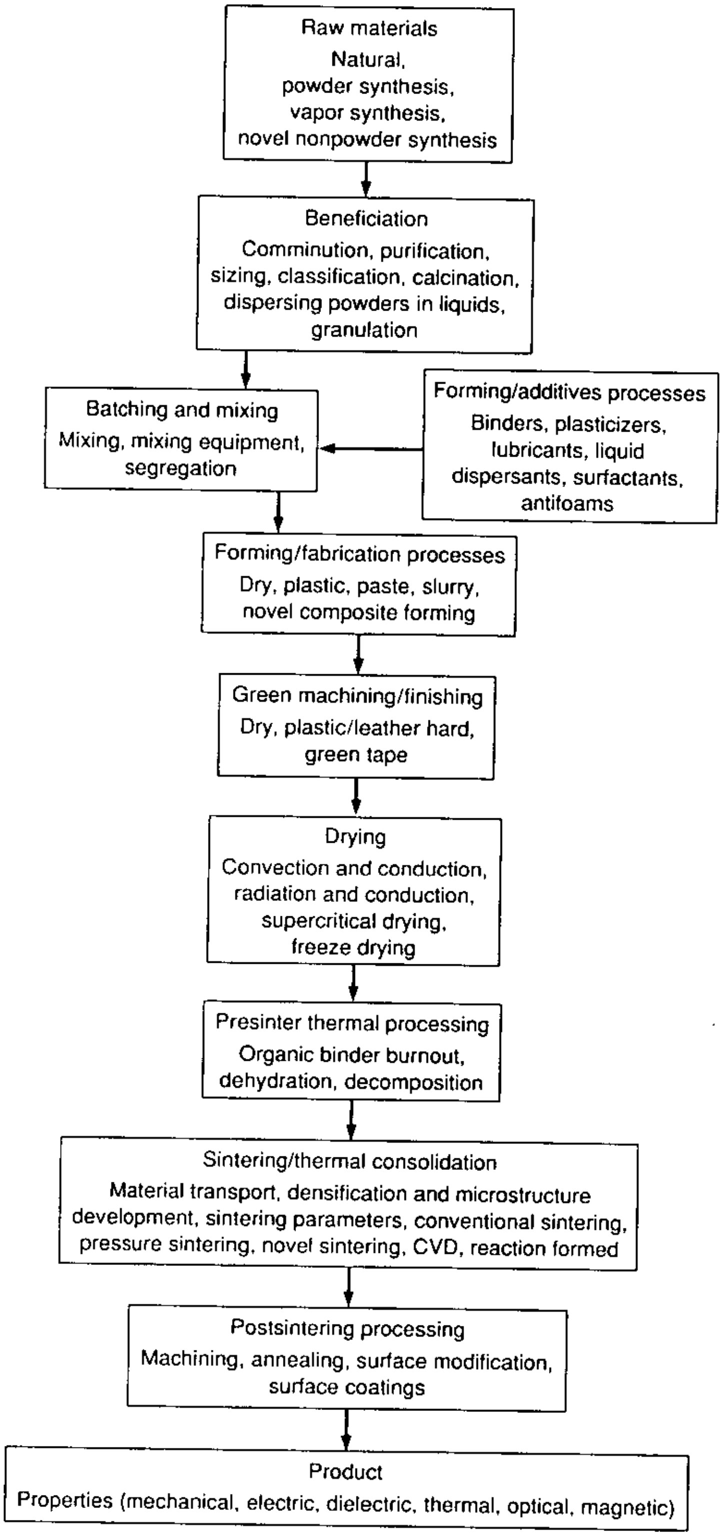

Fig. 1. Flow diagram of the steps and processes involved in manufacturing a ceramic.

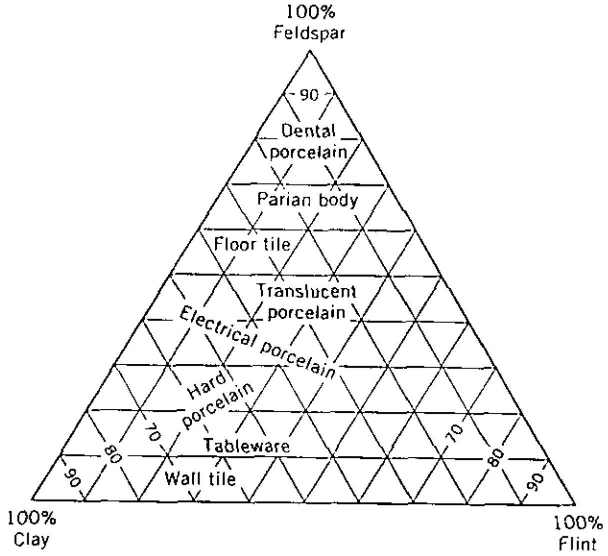

Fig. 2. Examples of traditional ceramics manufactured using traditional ceramic raw materials: clay, flint, SiO_2; and feldspar.

(8–12). Hydraulic mining techniques are also used to mine clays and glass (qv) sands (12) (see MINERAL RECOVERY AND PROCESSING).

Chemically Synthesized Powders. Chemical synthesis provides a means of producing powders for manufacturing advanced ceramics. Disadvantages of chemically synthesized raw materials are expense and difficulties in scale-up and availability. Additionally, ultrafine particle-size powders produced by chemical synthesis pose some unresolved processing problems in the areas of handling and mixing.

Solid State. Ceramic compounds can be formed by reacting constituent oxides and/or thermally decomposed salts at an elevated temperature in a solid-state process described as calcination (2,13–17). For example, spinel [*1302-67-6*], $MgAl_2O_4$, can be formed by reacting magnesia [*1309-48-4*], MgO, and alumina [*1344-28-1*], Al_2O_3. Because solid-state diffusion is inherently slow, fine, well-mixed powders are required to ensure that reactions go to completion and that chemical and structural homogeneity are achieved during calcination. Often multiple calcination, grinding, and mixing steps are performed to ensure homogeneity. Purity of the product is limited by the purity of the constituent raw materials, and by the impurities introduced during grinding. Ceramic powders formed by calcination are typically less expensive (<$1/kg) than those formed by liquid or vapor techniques (~$25–50/kg), but are also typically less pure and larger in size.

Solution Chemistry. Submicrometer particle size, high purity ceramic powders can be produced by precipitation, solvent evaporation, and solvent extraction from liquid solutions. The solid product is typically a salt that can be calcined at low temperatures, followed by light milling to produce reactive particles for sintering. Solution-derived powders have exceptionally high purity and homogeneity and can be extremely fine in size. Additionally, it is relatively easy to form multicomponent compounds and to add and disperse uniformly small concentrations of dopants, eg, sintering aids, by solution processing. However, chemical precursors are typically expensive, solution processes are not well suited to forming nonoxide ceramic powders, and surface contamination and microporosity common in solution-derived powders often make it difficult to produce dense, optical quality, ie, transparent, ceramics.

Precipitation (2,13–17) techniques employ a combination of nucleation and growth induced by adding a chemical precipitant, or by changing the temperature and/or pressure of the solution. Chemical homogeneity is controlled by controlling the rate of precipitation. Heterogeneous precipitation involves the precipitation of a solid of different composition from the solution, and the composition of the precipitate may change as precipitation continues. Coprecipitation involves the simultaneous precipitation of similar size cations in a salt as a solid solution.

Precipitation is commonly performed using water-soluble salts; however, organometallics also provide a good source of high purity reactants for precipitation. Powders can also be formed by mixing reactant oxides in molten salts and precipitating. The calcination step for salt decomposition can be eliminated by precipitating powders in hot, high pressure water, using hydrothermal synthesis (see HYDROTHERMAL PROCESSING).

Solvent evaporation (13–15,17,18) techniques employ rapid drying to produce ceramic powders. Chemical homogeneity can be maintained by rapidly drying isolated, fine (10–100 μm) salt solution droplets produced by atomization, or by microwave or emulsion drying. Aerosol decomposition, also described as spray pyrolysis and evaporative decomposition of solutions, provides a means of enhancing powder production by combining rapid drying, precipitation, and decomposition in a single process similar to spray drying (see EVAPORATION).

Solvent extraction (2,13–15,17) by freeze drying provides another means of maintaining chemical homogeneity in solution-derived powders. Freezing solutions or emulsions prevents chemical segregation and the desired salt is obtained by removing the solvent by sublimation.

Sol-Gel Techniques. Sol-gel powders (2,13,15,17) are produced as a suspension or sol of colloidal particles or polymer molecules mixed with a liquid that polymerizes to form a gel (see COLLOIDS; SOL-GEL TECHNOLOGY). Typically, formation of a sol is followed by hydrolysis, polymerization, nucleation, and growth. Drying, low temperature calcination, and light milling are subsequently required to produce a powder. Sol-gel synthesis yields fine, reactive, pseudo-crystalline powders that can be sintered at temperatures hundreds of degrees below conventionally prepared, crystalline powders.

Vapor-Phase Techniques. Vapor-phase powder synthesis techniques, including vapor condensation, vapor decomposition, and vapor–vapor, vapor–liquid, and vapor–solid reactions, employ reactive vapors or gases to produce high purity, ultrafine, reactive ceramic powders. Many nonoxide powders, eg, nitrides and carbides, for advanced ceramics are prepared by vapor-phase synthesis.

Vapor-condensation (2,14,18) involves vaporizing a solid material at high temperature and precipitating a powder by condensation on cooling. Thermal plasmas that operate at several thousand degrees Kelvin at atmospheric pressure and higher can provide the vaporization energy (see PLASMA TECHNOLOGY). Only a very limited number of ceramic powders can be produced by this technique.

Vapor decomposition (14,15) involves drying, decomposing, and vaporizing a spray of salt precursor solution in a plasma, and subsequently nucleating and growing ceramic particles in the vapor. Silicon carbide [*12504-67-5*], SiC, powder is produced by this method.

Vapor–vapor reactions (14,16,17) are responsible for the majority of ceramic powders produced by vapor-phase synthesis. This process involves heating two or more vapor species which react to form the desired product powder. Reactant gases can be heated in a resistance furnace, in a glow discharge plasma at reduced pressure, or by a laser beam. Titania [*13463-67-7*], TiO_2, silica, silicon carbide, and silicon nitride, Si_3N_4, are among some of the technologically important ceramic powders produced by vapor–vapor reactions.

Vapor–solid reactions (13–17) are also commonly used in the synthesis of specialty ceramic powders. Carbothermic reduction of oxides, in which carbon (qv) black mixed with the appropriate reactant oxide is heated in nitrogen or an inert atmosphere, is a popular means of producing commercial SiC, Si_3N_4, aluminum nitride [*24304-00-5*], AlN, and sialon, ie, silicon aluminum oxynitride, powders.

Nonpowder Synthesis. Many ceramic composites (qv) under investigation utilize reinforcing ceramic whiskers or fibers to achieve toughening (19). Whiskers (17,19,20) are produced by vapor-synthesis techniques. SiC whiskers can be produced by the rice hull or vapor–solid (VS) method whereby rice hulls are pyrolyzed to produce a mixture of carbon, C, and SiO_2, and whiskers are produced by directional growth by vapor deposition. The vapor–liquid solid (VLS) or Los Alamos process uses a liquid catalyzed vapor-deposition process to produce SiC whiskers from reagent-grade gases. Whiskers cost several hundreds of dollars per kilogram.

Fibers (17) can be formed by air drag or blow spinning molten precursors, and extruding or drawing gels through a spinneret. Air drag spinning is one of the oldest techniques for manufacturing fibers and uses air jets to draw a fiber from a melt reservoir and shape it. Blow spinning involves blowing a thin stream of compressed air or steam on a molten liquid as it passes through a small opening in the bottom of a melt reservoir. Al_2O_3–SiO_2 fibers are fabricated by blow spinning.

The extrusion process involves extruding, melt spinning, or drawing a controlled viscosity gel through a spinneret, followed by heating to effect gelation and crystallization. Al_2O_3 and Al_2O_3–ZrO_2 fibers are made this way. Nonoxide ceramic fibers have also been produced from amorphous preceramic polymer precursors by melt spinning. Fibers can also be formed indirectly by infiltrating an organic cloth fiber with a ceramic precursor solution, or by depositing a ceramic coating on a fiber preform using chemical vapor deposition (CVD). The desired ceramic fiber product is subsequently formed upon heating.

Although not as expensive as whiskers, fibers are considerably more expensive than powders. Extrusion processed Al_2O_3 and Al_2O_3–ZrO_2 fibers cost $100–200/kg.

Beneficiation

Beneficiation (2,11,12,21–27) involves a process or series of processes whereby the chemical and/or physical properties and characteristics of raw materials are modified to render the raw material more processible. The extent of beneficiation is determined by a combination of the starting raw materials, the processing scheme, the desired properties of the product, and economics. Powder cost increases with increased beneficiation; consequently, low value-added clay raw materials used to produce inexpensive structural clay products typically undergo a minimum of beneficiation, whereas higher value-added alumina powders undergo more extensive beneficiation.

Chemically synthesized materials also often undergo some form of beneficiation. Beneficiation processes for chemically synthesized ceramics are sometimes incorporated in the forming process such as in aerosol decomposition, where solvent evaporation and salt decomposition occur sequentially in a single operation.

Comminution. Particle size reduction by crushing and grinding/milling, otherwise known as comminution, is used extensively in ceramic processing to liberate impurities, break up aggregates, modify particle morphology, modify particle size distribution, improve processability during the mixing and forming operations, and produce more reactive powders for sintering (12,22,23). Crushing (11,12,21,22) operations are used for coarse grinding; milling (22–25) operations are used for fine grinding.

Primary crushers (11,12,21) are designed to reduce relatively large, up to 0.3 m diameter, mined material down to centimeter size particles. Secondary crushers (11,12,21) employ compression and impact compression to produce millimeter size particles. Natural raw materials processors typically supply material that has been processed through a primary and secondary crusher, and is often sized by screening.

Higher value-added, naturally occurring raw materials are generally ground to micrometer sizes by the raw materials supplier; however, additional grinding may be necessary prior to manufacturing. Micrometer size powders are produced by grinding millimeter and smaller size particles in a ball mill (2,22,23), vibratory mill (2,22), attrition mill (2,22), or fluid energy mill (2,23). Both particle size and size distribution decrease during grinding. In general, wet milling is more efficient than dry milling, producing a finer, typically submicrometer median particle size powder having a narrower size distribution. The practical lower particle size limit that can be achieved by milling is ~1.0 μm.

Ball milling (2,22,23), also referred to as jar or pebble milling, may be the most popular means of fine grinding ceramic powders. Ball milling can be performed wet or dry and as a batch or continuous process using spherical or cylindrical grinding media. Milling with media that is rod shaped is referred to as rod milling. Approximately 1 wt % grinding aid is generally added to minimize agglomeration during dry milling, and ≤1 wt % of a dispersant can be used to inhibit flocculation during wet milling. Water or alcohol are commonly used as the milling liquid.

Purification. Alumina, Al_2O_3, is produced by the Bayer process (1,9) (see ALUMINUM COMPOUNDS) which involves digestion followed by precipitation and calcination. High purity magnesia is extracted from natural brines and seawater by precipitation and calcination (1,9).

Soluble impurities can be extracted by washing with deionized or distilled water followed by filtration (1,12,26). Powders prepared by wet chemical synthesis are often washed and filtered for purification prior to use. The dewatering (qv) process can be enhanced by pressure filtration. Organic solvents can be used to remove water-insoluble impurities and wash-water sensitive materials.

Chemical leaching (1,12) with acids is used to extract metal contamination. High purity zirconia, ZrO_2, is produced by the caustic fusion of zircon [*14475-73-1*], $ZrSiO_4$, followed by the chemical removal of silica. Chemical leaching is generally followed by washing.

Magnetic separation (12,26) is used to extract magnetic impurities such as iron and iron minerals from raw minerals (see SEPARATION, MAGNETIC). Magnetic separation can be performed on dry powders and fluid slurries passing through an intense magnetic field. Froth flotation (qv) (12,26) can be used to separate intermixed raw materials and to separate the desirable material from the gangue.

Sizing. Sieve sizing (2,12,26,27) utilizes gravitational forces acting on particles translating across a screen (see SEPARATION, SIZE). The process can be enhanced by vibrating the sieves. Dry forced air and sonic sieving are used to size dry powders from 850 to 37 μm in size. Wet sieving eliminates electrostatic particle–particle and particle–sieve attractive forces to size particles down to ~5 μm.

Classification. Classification (2,12,26,28) or elutriation processes separate particles by the differences in how they settle in a liquid or moving gas stream. Classification can be used to eliminate fine or coarse particles, or to produce a narrow particle size distribution powder. Classification by sedimentation involves particle settling in a liquid for a predetermined time to achieve the desired particle size and size distribution or cut. Below ~10 μm, where interparticle forces can be significant, gravitational-induced separation becomes inefficient, and cyclone and centrifugation techniques must be used. Classification also separates particles by density and shape. Raw material separation by differential sedimentation is commonly used in mineral processing.

Calcination. Calcination (1,2,29) involves heat treating a powder or mixture of powders at a temperature well below its melting point to effect decomposition, ie, to liberate unwanted gases and/or chemically bound waste, solid-state reactions, and structural transformations to produce the desired composition and phase product. For example, water is liberated and the crystallographic structure changes when α-$Al_2O_3{\cdot}3H_2O$ is calcined to form α-Al_2O_3.

Calcination or dead burning is used extensively to dehydrate cements (qv) and hygroscopic materials such as MgO, and to produce a less water sensitive product. Calcination is also used to decompose metal salts to base oxides and to produce multicomponent or mixed oxide powders for manufacturing advanced ceramics. For example, barium carbonate, $BaCO_3$, is decomposed to form barium oxide, BaO, and fine particles of $BaCO_3$ and TiO_2 are intermixed and calcined to produce barium titanate [*12047-27-7*], $BaTiO_3$, powder for ceramic capacitors for solid-state electronics.

Calcination can be completed in an inclined rotary calciner, a heated fluidized bed, or by simply heating a static bed of powder in a refractory crucible.

Dispersing Powders in Liquids. The preparation of a slurry by dispersing a solid in a liquid entails (*1*) wetting the solid by the liquid; (*2*) breaking down flocs; and (*3*) stabilizing the system to prevent flocculation (30,31). Dispersing aids such as deflocculants and wetting agents are usually added to the liquid prior to mixing the powder with the liquid.

Slurry processing has a distinct advantage over dry, semi-dry, and plastic forming techniques in that the liquid provides an improved medium for mixing. Additionally, liquids eliminate electrostatic attraction forces between fine particles and particle surface charges and agglomeration can be controlled. The disadvantage is that the liquid has to be removed before firing. This increases the processing time and cost and can create problems with shape distortion and cracking during drying.

Granulation of Powders. To improve flow, handling, packing, and compaction, dry powders are typically granulated (2,32). Agglomerates or granules of controlled size, shape, and strength are formed by directly introducing a liquid/binder solution during powder stirring/mixing, or by spray drying.

Direct mixing (32) by compaction using a tableting die, briquetting rolls, a Muller mixer, extrusion, or spray granulation produces dense, hard, strong granules. An auger extruder or kneader is used to produce more plastic granules. Nearly spherical granules can be formed by spraying a liquid or binder solution into an agitating powder, such as a rotating pan, ribbon, double planetary, or V-cone mixer. The more intense the mixing action and higher the temperature, the smaller the granules.

Spray drying (2,32) provides a means of indirectly forming dense, homogeneous, nearly spherical granules from a slurry. The process involves atomizing a high solids content slurry through a pressure nozzle or rotary atomizer into a conical chamber with a cocurrent or countercurrent stream of heated air that dries the atomized droplets to form >20 μm, free-flowing granules. The product is collected in a container at the base of the spray dryer. Spray drying is widely used to prepare a variety of granulated, free-flowing ceramic powders with excellent compaction behavior for dry powder pressing operations.

Forming Additives/Processing Aids

Forming additives or processing aids (2,33–37) are commonly used to render ceramic powders more processible. Binders and plasticizers (qv) are typically added to improve or aid dry powder and plastic forming, whereas deflocculants, surfactants (qv), and antifoams are commonly used in slurry processing.

Binders. Binders (35,37,38) are used to impart strength to a green or unfired ceramic body for handling and green machining. Binders are polymer molecules or colloids (qv) that adsorb on particle surfaces and promote interparticle bridging or flocculation. Binders are used extensively in dry-pressing operations and are also added to plastic extrusion bodies and pastes. With the exception of tape casting, where a plasticized binder is required to produce flexible green tape, binders are generally avoided in slurry forming operations.

Binder selection depends on the ceramic powder, the size of the part, how it is formed, and the green density and strength required. Binder concentration is determined by these variables and the particle size, size distribution, and surface area of the ceramic powder. Three percent binder, based on dry weight, generally works for dry pressing and extrusion.

Binders such as poly(vinyl alcohol) (PVA) that form hard ceramic granules, produce free-flowing powders that are well-suited for automated pressing operations and yield strong bodies. Plasticizers and or lubricants (see LUBRICATION AND LUBRICANTS) can be added to hard binders to reduce the forming pressure and die wear. Wax binders such as poly(ethylene glycol) (PEG) form soft ceramic granules which yield lower strength, higher green density bodies on forming. Hard and soft binders can be combined to develop binder systems tailored to a given process and product.

Specialty binders may be used in novel or unique forming operations. Cross-linking polymers are used to induce gelation in gelcasting. Thermoplastic resins such as polyethylene and polystyrene often comprise the bonding matrix in injection-molded ceramic parts. Phosphate chemical bonds are used in forming specialty refractories (qv), and chemical hydration is employed in setting hydraulic cements. Preceramic polymers that decompose to a ceramic on heating serve as binders to provide green strength for handling and machining.

Plasticizers. Plasticizers (36–38) are often added to a binder to reduce cross-link density and increase flexibility. Plasticizers improve toughness, springback, and flexibility, but degrade overall green strength. Additionally, plasticizers can increase the sensitivity of a binder system to moisture.

Examples of plasticizers include adsorbed water and ethylene glycol for vinyl binders, stearic acid and oleic acid for wax binders, glycerine and ethylene glycol for clay bodies, and molten oils and waxes for thermoplastic polymers used in injection molding.

Lubricants. Lubricants (36,38) are added to lower frictional forces between particles, and between particles and die surfaces to improve compaction and minimize die wear. Typically ≤ 1 wt % of a lubricant is required for forming, and usually only with hard binders. Stearic and oleic acids are good lubricants for ceramics.

Individual particle surfaces can be lubricated by an adsorbed film that produces a smoother surface and/or decreases interparticle attraction. A plasticized binder may serve this purpose. Forming surfaces can be lubricated by coating with a film of low viscosity liquid such as water or oil. Die surfaces can also be coated with a solution of stearic acid dissolved in a volatile liquid that rapidly evaporates to leave a lubricating film.

Fine particles having a laminar structure and smooth surfaces are effective solid lubricants for rough surfaces and at high pressure. Graphite, boron nitride, BN, and talc are good solid lubricants; however, solid inorganic lubricants do not burn out during sintering and may affect the microstructure and properties of the finished product.

Liquids. Liquids (33) are common forming additives in plastic, paste, and slurry processing. In plastic forming operations, the liquid aids forming and serves as the binder/plasticizer for the system. In pastes and slurries, other additives are also dissolved or dispersed in the liquid/solvent. Water is a good, inexpensive solvent that can be recycled. Organic liquids such as alcohols are used to process water-sensitive materials and to dissolve water-insoluble forming additives, however, at considerably more expense.

Deflocculants. Deflocculants (34), dispersants (qv), or anticoagulants are added to slurries to improve dispersion and dispersion stability. Dispersants break up flocs in a slurry by lowering van der Waals interparticle forces. Deflocculants adsorb on particle surfaces and prevent the approach of particles either by electrostatic or steric stabilization. Deflocculation by electrostatic stabilization is common in clay slurries, as well as with ceramic particles dispersed in polar liquids such as water.

Monovalent cations are good deflocculants for clay–water slips and produce deflocculation by a cation exchange process, eg, Na^+ for Ca^{2+}. Low molecular weight polymer electrolytes and polyelectrolytes such as ammonium salts (see AMMONIUM COMPOUNDS) are also good deflocculants for polar liquids. Acids and bases can be used to control pH, surface charge, and the interparticle forces in most oxide ceramic–water suspensions.

Oleic acid is a good deflocculant for oxide ceramic powders in nonpolar liquids, where a stable dispersion is created primarily by steric stabilization. Tartaric acid, benzoic acid, stearic acid, and trichloroacetic acid are also deflocculants for oxide powders in nonpolar liquids.

Surfactants and Antifoams. Surfactants (33) or wetting agents can also be added to a slurry to improve dispersion. A wetting agent lowers the surface tension of the liquid, lowering the solid–liquid interfacial energy, which favors the liquid coating the solid. Antifoams (36) are added to slurries to remove trapped gas bubbles from the liquid (see DEFOAMERS). Commercial agents include fluorocarbons, dimethylsilicones, stearates, and high molecular weight alcohols and glycols. Typically, less than a few percent of an antifoam agent is required to prevent foaming.

Batching and Mixing

Mixing (24,39) is used to combine the constituents of a ceramic body to produce a more chemically and physically homogeneous system for forming (see MIXING AND BLENDING).

Convection, Shear, and Diffusion Mixing. Mixing is accomplished by material transport by convection, shear, and diffusion (39). Feeding devices, stirring, and baffles all produce material flow that contributes to convection. Material flow between surfaces moving at different velocities produces shear stresses that can break down agglomerates and mix viscous materials. Turbulent flow produced by eddy currents, cavitation, impact, and sonic vibration contribute to diffusive mixing, which also breaks down agglomerates.

Segregation. Segregation (24) or separation in mixtures of dissimilar particles can occur during storage and handling, resulting in macroscale heterogeneities in the product. Segregation can be minimized by minimizing size differences, storage and handling after mixing, and individual particle motion during mixing (see POWDERS, HANDLING).

Forming/Fabrication Processes

Ceramic forming involves consolidation and molding of ceramic powders to produce a cohesive body of the desired size and shape. Ceramic forming operations (38,40–66) are conducted with dry powders, plastic bodies, pastes, and slurries.

Dry Forming. Dry powders can be simultaneously compacted and shaped by pressing in a rigid die or flexible mold. Pressing (38,40–42,48–52) is the most widely used forming process in ceramics manufacturing. Microelectronic chip carriers, capacitors, spark plug bodies, cutting tools, and ceramic tiles are manufactured by powder pressing.

Powder pressing involves three general stages including: (*1*) filling the die or mold; (*2*) compacting and shaping the powder; and (*3*) extracting the pressed part from the die. When the pressing pressure is released, the dimensions of the powder compact and die increase or springback. Differential springback between the compact and mold aids extraction of the pressed part; however, excessive differential springback >0.75 linear % can generate catastrophic stresses that create defects or destroy the compact. Pressing defects can be minimized by using granulated powders and appropriate additives, and by controlling the pressing pressure, pressurization rate, and depressurization rate used in forming.

For reproducibility and rapid processing, pressing powders should be free-flowing, have a high bulk density, be comprised of deformable granules, cause minimal die wear, and not stick to die surfaces.

Dry Pressing. Dry or die pressing (38,40–42,45,48–50) which involves compacting a powder between two plungers in a die cavity, is a versatile technique for fabricating relatively uniform thickness and axial symetric powder compacts. Manual dry pressing is used to form limited numbers of cylindrical pellets of single-phase and composite powders for sintering experiments. Automated dry pressing is capable of producing 5000 parts per minute.

Dies are made of hardened steel, specialty steels, and carbides (qv) or other structural ceramics, eg, SiC, Al_2O_3. Single-action, ie, moving top plunger, double-action, ie, moving top and bottom plungers, and floating die, (ie, moving top plunger and die body, pressing assemblies are used. In automated processes, the pressure is typically in the range of 20–100 MPa ($3–15 \times 10^6$ psi); however, manual die pressing operations may be carried out at pressures as high as 200 MPa (29×10^6 psi). Die wear, ejection pressure, and differential springback all increase with pressing pressure.

Nonplastic ceramics are typically dry pressed using ≤4 vol % water. Plastic ceramics can be formed by semidry pressing using 10–15 vol %. Warm dry pressing with heated platens at ≤200°C is used to fabricate multilayer substrates from tape cast green tape for microelectronic packaging.

Isostatic Compaction. Isostatic pressing (38,40–42,45,51,52), which is also known as isopressing, hydrostatic pressing, and cold isostatic pressing (CIP), provides a means of manufacturing complex shapes such as tubes and spark plug bodies, and larger volume parts that are not easily dry pressed. Because the compacting pressure is applied uniformly over a larger free surface area, pressing gradients are typically less severe. Typically, a flexible mold or bag is filled with a granulated powder, sealed, and placed in a gas- or liquid-filled pressure chamber and pressurized to 5–200 MPa ($1–29 \times 10^6$ psi) to compact the powder. Because gas cannot escape during the isopressing operation, molds are typically deaired prior to pressing. Also, to improve the filling density, molds may be filled on a vibratory or tapping table. Both wet and dry bag techniques are employed in isopressing; although only the dry bag technique is suited to automation.

Isopressing molds are typically comprised of synthetic rubber, polyurethane, or silicone rubber with rigid steel fixtures and mandrels. Because of the relatively high springback of flexible mold materials, controlled, slow, depressurization is required below 2 MPa (3 × 10^5 psi) to control mold expansion and to avoid damaging the compact on extraction. Isopressing is typically performed at ambient temperature; however, by heating the pressurizing liquid, warm isostatic pressing (WIP) can be accomplished. WIP is being investigated as an improved technique for laminating multilayers of tape cast green tape to produce microelectronic packages.

Vibratory Compaction. Vibratory compaction (38,53) provides a means of forming irregular shape compacts from ungranulated powders. Under agitation, a powder bed tends to rearrange to a configuration of closest packing. The amplitude and frequency of vibration required for compaction are dependent on the size and size distribution of the particles present, and the size of the compact, and are determined experimentally.

Plastic Forming. A plastic ceramic body deforms inelastically without rupture under a compressive load that produces a shear stress in excess of the shear strength of the body. Plastic forming processes (38,40–42,54–57) involve elastic–plastic behavior, whereby measurable elastic response occurs before and after plastic yielding. At pressures above the shear strength, the body deforms plastically by shear flow.

The cohesive strength required for plastic deformation is provided by capillary pore pressure and flocculation bonding. Plastic clay bodies are typically flocculated by the colloidal clay particles present in the system, whereas nonplastic ceramics can be flocculated with an organic binder. In clay bodies, submicrometer colloidal clay particles coat larger particles, and shear flow occurs between the larger particles in zones of oriented clay and finer nonplastic particles lubricated by interparticle water. In nonclay ceramic bodies plasticized with organic binders, the organic molecules play the role of the colloidal clay particles.

The dimensional tolerances of parts formed by plastic deformation are typically not as good as those in parts formed by dry powder pressing.

Extrusion. Extrusion (38,40–42,54,55) is widely used in manufacturing structural clay products, including sewer pipe, chimney flues, bricks, and tiles. Additionally, refractory tubes and rods, and cordierite catalyst supports for catalytic converters in automobiles having 30–60 openings per square centimeter are formed by extrusion. Clay and talc bodies typically contain 12–20 vol % water, and can be extruded without a lubricant. Nonplastic ceramic powders require a plasticizer for extrusion. The higher the forming pressure, the lower the concentration of liquid required for extrusion, and the shorter the drying time and the lower the drying shrinkage. Extrusion pressures of up to 4 MPa (6 × 10^5 psi) are used to extrude porcelain bodies, whereas pressures up to 15 MPa (2 × 10^6 psi) are used to extrude ceramic powders having organic plasticizers.

Extrusion involves: (*1*) feeding plastic material into a chamber; (*2*) material consolidation and flow into the barrel, through the forming die and the finishing tube; and (*3*) ejection. A typical extruder may have a pug mill for additional mixing, and a vacuum chamber to deair the plastic body prior to extrusion. Dies are specially designed to generate sufficient back pressure to heal defects created during forming.

Both piston and auger type extruders are used in plastic forming. The former provide maximum control of the extrusion pressure and rate and are good for forming large parts. The latter provide a maximum extrusion rate without excess power requirements and are desirable in the continuous production of simple clay ware.

Defects in extruded bodies typically include: insufficient strength or rigidity from too much water or insufficient organic binder; cracks or delaminations because of excess differential springback, hard inclusions, or agglomerates from poor mixing; surface blisters from the expansion of dissolved air; surface delaminations created by slip-stick wall friction; nonuniform flow from improper die design; laminations produced by divided flow as a result of improper die design; gradients in extrudate stiffness; and curling on drying from differential drying.

Jiggering. Jiggering (38,40,54) is one of the most widely used, cost effective, soft plastic forming techniques used in ceramic processing for manufacturing small, simple, axial–symmetrical whiteware ceramics including cookware and fine china, and electrical porcelain. Jiggering involves shaping a plastic clay body on a spinning porous plaster mold using a water-mist or steam-lubricated shaping tool. The shaping tool initially deforms the clay mass to the shape of the mold and subsequently creates a smooth surface finish. The mold and shaped part are then set aside and separation of the mold and part is accomplished by differential drying. Hand molding operations are conducted at 300–400 rpm; 500–1200 rpm are used in automated jiggering processes. Automated, highly mechanized jiggering operations can produce 1000 pieces per hour per line.

Powder Injection Molding. Powder injection molding (PIM) (38,42,45,54, 56,57) provides an economical means of mass producing small, near-net, complex shapes. PIM involves injecting a hot ceramic and polymer binder mixture into a cooler die to form the desired shape, then extracting and deburring the part, and removing the binder. The binder concentrations for PIM range from 30 to 50 vol % and must be high enough for good flow during molding, but low enough to avoid debinding problems and excessive debinding times.

PIM is not cost competitive with die compaction for simple or axial–symmetric shapes. It is limited to small ($\leq$ 10 cm) shapes and is extremely process sensitive. Additionally, PIM tooling is expensive.

Paste Forming. Ceramic pastes (58), often associated with thick-film printing operations, consist of a ceramic powder, a sintering aid such as borosilicate glass, and an organic vehicle comprised of a solvent, dispersant, plasticizer, and high molecular-weight binder. Ceramic thick-film pastes are used for decorating traditional ceramic tableware and to form capacitors and dielectric insulator layers on rigid substrates for microelectronic packaging.

Slurry Forming. Slurries are used in ceramic casting operations (38,40–42,59–66) and slurry formation is perhaps the most important step. A good slurry is well dispersed and free of air bubbles and foaming; it has a high specific gravity; it has good rheological properties for casting; the solid particle settling rate in the slurry is low; and it is chemically stable. Additionally, when dry, the cast should possess sufficient strength for subsequent finishing and handling before firing.

The liquid vehicle in a slurry should: have a low vapor pressure for liquid extraction and drying; be compatible with the solids and casting mold; be inexpensive; and be capable of dissolving and dispersing deflocculants and other additives. Distilled or deionized water is generally used as the liquid vehicle, however, organic liquids must be used for such moisture sensitive oxide powders as CaO and MgO, and for oxidation sensitive nonoxide powders, eg, AlN.

A high solids concentration is desirable to minimize the amount of time and energy required for forming and to minimize drying shrinkage. Using deflocculants, fluid slurries can be made using as little as 15–20 vol % liquid.

Slip Casting. Slip casting (38,40–42,45,59–62), the process in which a cast is formed from a slurry using a porous mold, is used to form sinks and other sanitary ware, figurines, refractory crucibles, porous thermal insulation, fine china, and complex shape structural ceramics such as multivane rotors.

Slip casting begins by pouring a stable slurry into a porous mold. The capillary suction of the porous mold draws the liquid from the slurry to form a higher solids content, close-packed cast on the inner surface of the mold. Wall thickness increases with the square root of forming time, and with sufficient time a completely solid cast can be formed. After a fixed time the excess slurry is drained from the cast (drain casting). Initial drying occurs in the mold, and the resultant cast shrinkage and strengthening aids in separating the cast from the mold. A mold-release agent, such as an alginate, graphite, a silicate, talc, silicone, or olive oil, can be used to enhance the removal of the cast from the mold. Inexpensive plaster molds comprised of 40–50 vol % porosity are typically used in slip casting.

Casting slips are typically pseudoplastic (<2 Pa·s at a shear rate of 1–10 s^{-1}) for good mold filling and to allow the escape of gas bubbles. Additionally, the concentration of solids must be high enough to minimize settling during casting. Solid casting is generally conducted with slightly higher viscosity and higher solids content slips.

To control the concentration of submicrometer colloidal particles to $\leq 30\%$, clay slips are typically used in the partially deflocculated state. A coagulant can be added to a deflocculated clay slip immediately preceding casting to induce partial flocculation. Slurries for casting oxides, nitrides, and carbides are generally at least partially deflocculated. A fraction of a percent of organic binder increases the pseudoplasticity of the slurry and strength of the cast; too much binder can clog the plaster molds and decrease the rate of casting.

Casting rate can be enhanced through the use of vacuum casting (38,59), ie, by increasing the pressure gradient, or through pressure casting (38,59), ie, by decreasing the slurry viscosity, eg, by heating, or by centrifugal casting. Each enhance the rate of liquid flow from the slurry into the mold and decrease the casting time from hours to minutes, decrease the concentration of water in the cast and the shrinkage on drying from several percent to $\sim 1\%$, and yield higher green density casts that shrink less on firing. Additionally, centrifugal forces created by spinning the mold, and/or vibration can be used to enhance slurry flow and to ensure good filling of complex molds.

Disadvantages of vacuum, pressure, or centrifugal casting include higher costs because of specialty equipment and specialty molds, and density gradients in the casts that result from the higher pressure gradients during forming.

Gelcasting. Gelcasting (63) is a novel method of fabricating particulate bodies from ceramic slurries. Gelcasting employs *in situ* polymerization of organic, eg, acrylamide (qv), monomers to produce a gel structure that binds individual particles together to form a cohesive body. Net and near-net complex shapes such as turbine rotors can be cast in a relatively short period of time, and the high (up to 62 vol %) solids concentrations improve the homogeneity of the cast and contribute to lower and more reproducible shrinkage during drying and sintering. Gelcast parts also have excellent strength for handling and green machining.

Tape Casting. Tape casting (38,45,59,64–66), doctor-blading, or knife coating involves forming a thin film of slurry of controlled thickness by flowing a slurry beneath the knife edge of a doctor blade onto a support surface. Tape casting is an economical means of forming thin (0.02–2.0 mm), uniform thickness, smooth surface, flexible, green ceramic sheet or tape that can subsequently be cut and stacked to form multilayer ceramics for multilayer capacitors and dielectric insulator substrates (see also CERAMICS AS ELECTRICAL MATERIALS).

The thickness of the tape is controlled by the slip characteristics, the height of the doctor blade, the casting rate, and the pressure head of the slip reservoir behind the doctor blade. Slip viscosities in the range of 1–5 Pa·s (10–50 P) are used to cast tapes at 5–100 cm/s. To achieve the desired strength and flexibility in the green tape, tape casting slurries contain more binder than those used in slip casting, as well as a plasticizer to ensure flexibility.

Tape can be cast on a stainless steel table or belt, glass plate, or a Mylar, Teflon, or cellulose acetate film carrier. The tape should adhere to the carrier sufficiently to prevent curling, but should be easily removable. In a continuous casting process, the tape is dried by air flowing 1–2 m/min counter to the casting direction. A typical dry green tape contains approximately 35 vol % organics, 50% ceramic powder, and 15% porosity.

Specialty Casting Techniques. Thixotropic casting (59) processes involve slurries comprised of a gelling, reactive, or hydraulic binder in which yield strength and viscosity increase with time. Thixotropic slurries are used for gunning or troweling castable refractory wall liners, preparing refractory shapes and molds for metal casting operations, obtaining dental impressions and filling cavities, and producing concrete structural materials.

Electrophoretic casting (38,59) is accomplished by inducing controlled migration of charged particles under an applied electric field to deposit on a mandrel. Thin tubular shapes and coatings of limited thickness are formed using this technique. Electrophoretic deposition (EPD) is also used to manufacture thin wall, solid β''-alumina [*12005-16-2*], $NaAl_5O_8$, electrolytes for sodium–sulfur batteries.

Freeze casting (59) is a hybrid of slip casting, gel casting, and freeze drying in which a slurry is poured into a rigid rubber mold, frozen, and the frozen liquid is removed by sublimation, ie, by freeze drying (see CRYOGENICS).

Novel Composite Forming Techniques. Particulates, whiskers, or fibers, can be used to improve the toughness of ceramics (19). Composites (qv) or multicomponent ceramic bodies containing second-phase reinforcing particulates, whiskers, or fibers can be processed by the dry powder, plastic, and slurry forming techniques described, but with considerably more difficulty. Challenges in composite processing include: uniformly dispersing the reinforcing phase; maintaining the desired orientation of the reinforcing phase within the matrix; and uniformly packing the matrix particles about the reinforcing phase.

Particulate Composites. In addition to the geometric obstacles to mixing dissimilar shape and size particles, there are also chemical barriers that must be overcome in processing composites, requiring novel techniques.

Coatings (qv) offer one means of reducing or eliminating the differences in dissimilar materials. For example, a silica coating on alumina allows alumina and silica particles to be dispersed together in water at the same pH. Likewise, oxide-resistant coatings on carbide and nitride powders render them compatible for coprocessing with otherwise incompatible oxide ceramics. Coatings can also be employed to aid the processing of whisker and fiber reinforced composites.

Infiltration (67) provides a unique means of fabricating ceramic composites. A ceramic compact is partially sintered to produce a porous body that is subsequently infiltrated with a low viscosity ceramic precursor solution. Advanced ceramic matrix composites such as alumina dispersed in zirconia [*1314-23-4*], ZrO_2, can be fabricated using this technique. Complete infiltration produces a homogeneous composite; partial infiltration produces a surface modified ceramic composite.

Preceramic polymer precursors (45,68) can be used to make ceramic composites from polymer ceramic mixtures that transform to the desired material when heated. Preceramic polymers have been used to produce oxide ceramics and are of considerable interest in nonoxide ceramic powder processing. Low ceramic yields and incomplete burnout currently limit the use of preceramic polymers in ceramics processing.

Whisker and Short Fiber Composites. Whiskers and short fibers tend to align during forming, leading to anisotropic properties and large flaws in the product. Commercial whisker and fiber reinforced ceramics are formed by dry or isostatic pressing. Slip casting, tape casting, and injection molding processes are under development. Ceramic short fiber mat is manufactured in the dry mat process (42) by blowing a dispersion of 6–25 mm long staple fibers onto a moving belt by a stream of air and reacting it in a heated zone. The mats are resin reinforced and are limited to a thickness of 1–3 mm. The wet mat process (42) employs papermaking technology to fabricate denser, thicker web mat with staple fiber. Fibers and binder dispersed in water are cast, filtered, and dried in ovens (see PAPER).

Continuous Fiber Composites. Textile manufacturing (42) techniques are used to fabricate continuous fiber ceramics and ceramic composites (see TEXTILES). Weaving (42) techniques can be used to manufacture ceramics and ceramic cloths having continuous monofilament fibers (qv) and fiber bundles (yarn). Complex parts can be woven with a high volume fraction of fiber; however, the process is slow and expensive. Complex, three-dimensional structures can be formed by multidirectional winding (42) continuous fiber on a mandrel. Rod, bar, tube, or sheet can be fabricated by pultrusion (42), in which a continuous fiber bundle is drawn through a bath of matrix solution that coats the fibers, through a card screen, and then through a heated die.

Preweave fabric to ceramic fabric (42) uses conventional cloth fiber as a preform of the desired shape that is formed by weaving, and then the weave is impregnated with a precursor solution of the desired ceramic. Zirconia ceramic cloth is formed this way. Impregnation (42) provides a means of fabricating polymer-filled, continuous ceramic fiber composites. Laminates of alumina fibers in a polymer resin matrix have been formed that have a thermal conductivity approaching that of alumina in the in-plane direction, and a dielectric constant approximating that of the polymer in the out-of-plane direction. Such composites have potential application in advanced microelectronic packaging.

Green Finishing/Machining

After forming, green finishing or machining is often required to eliminate rough surfaces, smooth forming seams, trim, and modify the size and shape of the green body in preparation for sintering (38,40,45,58).

Surface Grinding or Turning. Surface grinding and turning (38,40,45,58) on a lathe is used to form contours in ceramic spark plug bodies and high tension porcelain insulators (qv), to machine threads, and to fabricate complex shape bioceramic implants. Typically, the strength of the green part must be >2 MPa (>3 × 10^5 psi), and the tool force for grinding must be carefully controlled to avoid overstressing the relatively weak, green ceramic part during machining.

Blanking, Punching, and Laminating. Blanking, punching, and laminating (45,58,64–66) processes are used to form ceramic multilayers from tape cast green tape. Blanking, coining, or stamping is used to cut or form the desired substrate size and shape, large diameter holes or vias >0.5 mm, and cavities. Smaller vias are punched in a subsequent operation. To form a multilayer ceramic, several layers are stacked together and laminated by uniaxial or biaxial pressing at 3–30 MPa (4–40 × 10^5 psi) between platens at 50–80°C. Warm isostatic pressing can also be used. To compensate for particle alignment and texture in the cast tape, and to minimize shrinkage anisotropy and warping during drying and sintering, alternating layers in the laminate are rotated 90° to the casting direction during stacking. An alignment die can be used to preserve via alignment during lamination. Final shaping and punching can be performed after lamination as necessary.

Drying

For economical reasons, drying (38,41,45,69–73) should be as fast as possible; however, to avoid differential shrinkage that can result in cracking, warping, and shape distortion, drying must be carefully controlled. Generally, larger parts containing more liquid require longer and costlier drying.

Convective And Conduction Drying. *Air Drying.* Air drying is the most common means of drying ceramics (69–73). Circulating hot air supplies heat to the ware to aid evaporation and compensate for evaporative cooling as it removes vapor from the ware surface. The drying rate is determined by two factors: the rate of liquid evaporation and the rate of liquid migration to the drying front.

In a saturated body, drying first occurs at a constant rate by the evaporation of the liquid film surrounding individual paticles at the ware surface. If liquid migration cannot keep pace with evaporation, the drying front moves into the bulk of the ware, where drying continues by evaporation from the menisci of the liquid within the pores. During this later stage, falling rate period, the rate of drying continuously decreases with decreasing liquid content. During initial-stage drying, flowing air lowers the relative humidity and thins the boundary layer to enhance evaporation.

Most shrinkage occurs during initial-stage drying. Drying shrinkage can be reduced by lowering the concentration of liquid, decreasing the film thickness, decreasing the concentration of fines and plastic materials, and by adding nonplastics.

Controlled Humidity Drying. Controlled humidity drying (41,69–71) is used to minimize the moisture gradient and stresses during drying, and to optimize the drying rate. A high humidity atmosphere allows for rapid heating of moist ware without creating catastrophic drying stresses. After initial-stage drying, the humidity is rapidly decreased. Humidity controlled drying can reduce drying times from days to hours.

Air Drying Equipment. Tunnel kiln dryers (70) are long furnaces comprised of several zones of different temperature, humidity, and air flow through which the ware travels on a moving car or belt. These kilns afford continuous processing. Periodic kiln cross-circulation dryers (70) are box furnaces in which ware is stacked on permanent racks or on a car that can be shuttled in and out of the furnace. Fans or jets are used to circulate heat uniformly through the ware. The process is not continuous, but production rates can be enhanced by shuttling multiple cars.

Radiation and Conduction Drying. The rate of drying is often determined by the rate of forming and firing. The rate of drying ceramic ware processed with water can be enhanced by using microwave (69) or infrared (41,70) radiation. Radiation drying techniques can reduce drying times from hours to minutes.

Microwave Drying. Microwave radiation drying (45,64) (see MICROWAVE TECHNOLOGY) is excellent for drying porous molds and porous refractories without shrinkage damage, for drying bulk powders without forming agglomerates, and for uniformly drying large volume bodies. Microwave drying is cost effective at or below 5–10 vol % water, and can be used in combination with conventional controlled humidity forced air drying to be economical at higher water concentrations.

Infrared Drying. Infrared drying (41,70) using 4–8 μm electromagnetic radiation supplied by ir lamps is used to rapidly dry thin ceramic ware, such as china formed by jiggering, tape cast ceramic sheet, ceramic substrates, thick films, and coatings. The water content in a ceramic can be reduced from 25 to 5 vol % within 10–15 minutes, after which drying can be completed using conventional forced air techniques (see INFRARED TECHNOLOGY AND RAMAN SPECTROSCOPY).

Supercritical and Freeze Drying. To eliminate surface tension related drying stresses in fine pore materials such as gels, ware can be heated in an autoclave until the liquid becomes a supercritical fluid, after which drying can be accomplished by isothermal depressurization to remove the fluid (45,69,72) (see SUPERCRITICAL FLUID). In materials that are heat sensitive, the ware can be frozen and the frozen liquid can be removed by sublimation (45,69).

Presinter Thermal Processing

A number of changes can occur on heating a ceramic prior to sintering, including additional drying, burnout of organic additives and impurities, removal of chemically bound water and water of crystallizaton, and decomposition of inorganic precursors or additives (29). These processes may be accomplished by a separate heat treatment well below the sintering temperature, or in a controlled series of ramps and isothermal holds in a single heat treatment process. For traditional clay ceramics, a separate heat treatment termed a bisque firing is often performed prior to glazing and sintering.

Thermal analysis using differential scanning calorimetry (dsc), thermogravimetric analysis (tga), and differential thermal analysis (dta) can provide useful information about organic burnout, dehydration, and decomposition (see THERMAL, GRAVIMETRIC, AND VOLUMETRIC ANALYSIS).

Organic (Binder) Burnout. Organic decomposition (29,42,45,68), which occurs by dissociation or pyrolysis, produces gaseous products that may be hundreds of times the volume of the ceramic part. To preclude the development of catastrophic stresses from gases evolved within the ceramic body, organics must be removed gradually, prior to sintering to high relative density, when the permeability of the body is high. Organics are typically removed at ≤½ the sintering temperature. Incomplete binder burnout can result in residual carbonaceous matter in the finished product that can degrade or alter its properties.

Dehydration. Residual liquid and physisorbed moisture on particle surfaces can be eliminated on heating to ~200°C. Temperatures in excess of 1000°C may be required to eliminate chemisorbed water (29). Kaolin must be heated to 700°C to liberate the water of crystallization and produce the desired dehydrated aluminosilicate. As with binder burnout, rapid gas evolution from rapid dehydration can result in catastrophic stress development within a body.

Decomposition. Decomposition (29,68) processes are primarily accomplished in the beneficiation stage of processing by calcination; however, minor concentrations of sintering aids, which may be added as salt precursors, can be decomposed by heating prior to sintering.

Sintering/Thermal Consolidation

Most ceramics are thermally consolidated by a process described as sintering (29,44,68,73–84), in which thermally activated material transport transforms loosely bound particles and whiskers or fibers into a dense, cohesive body.

Sintering. A ceramic densifies during sintering as the porosity or void space between particles is reduced. Additionally, the cohesiveness of the body increases as interparticle contact or grain boundary area increases. Both processes depend on and are controlled by material transport.

Thermodynamic Driving Force for Material Transport. Under the influence of elevated temperature and/or pressure, atoms move to lower energy, thermodynamically more stable positions within the system to decrease the volume-free energy of the system. In a powder compact, excess volume-free energy is present primarily in the form of excess pore surface or interfacial energy, ie, liquid–vapor and/or solid–vapor interfaces, and the driving force for sintering can be approximated by $dG = \Sigma - \gamma_i dA_i$, where γ_i is the interfacial energy and A_i is the interfacial area. The interfacial area of a powder compact decreases as material transport occurs during sintering.

The primary driving force for material transport comes from the chemical potential difference that exists between surfaces of dissimilar curvature within the system. The greater the curvature, ie, the finer the particle size, the greater the driving force for material transport and sintering.

Material Transport. During sintering, material transport can occur by solid-state, liquid-phase, and vapor-phase mechanisms individually or in combination. The consequences of material transport during sintering, and the different paths of transport are summarized in the two sphere model shown in Figure 3. Initially during sintering, material is transported from higher energy convex particle surfaces to the lower energy, concave grain boundary pore intersections to form necks between adjacent particles. As sintering progresses, interparticle necks grow, grain boundary area increases, interparticle contacts flatten, and the free energy of the system decreases. Densification occurs in a powder compact as the distance between particle centers and the volume of the compact decreases during sintering.

Material transport can also effect coarsening during sintering. Coarsening is the term used to describe material transport that changes the geometry of the system without resulting in densification, ie, the distance between particle centers remains constant. Coarsening decreases the driving force for material transport without affecting densification, and it is often considered to be an undesirable, competing process. Both densification and coarsening mechanism are generally operative at any given time during sintering.

Densification and Microstructure Development. The microstructure both of a sintered ceramic and development during sintering are also controlled by thermodynamics. The material transport that occurs during sintering manifests itself as grain boundary formation, interparticle pore shrinkage and annihilation,

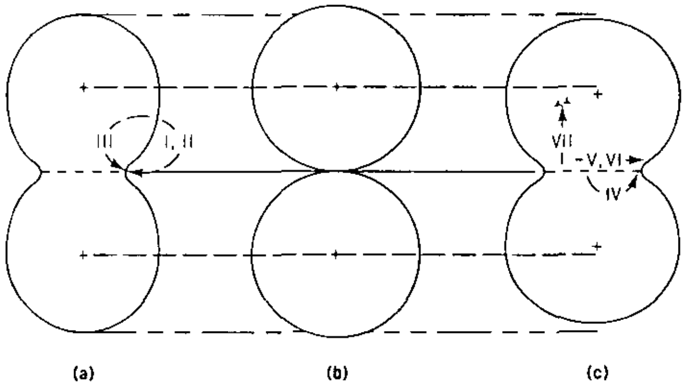

Fig. 3. The two-sphere model illustrating material transport paths I–VII during sintering where (**a**) represents coarsening; (**b**), the two spheres before sintering; and (**c**) densification. The + indicates the center of the sphere.

	Transport path	Atom source	Atom destination	Affect
I	surface diffusion	particle surface	neck	coarsening
II	evaporation–condensation	particle surface	neck	coarsening
III	volume diffusion	particle surface	neck	coarsening
IV	volume diffusion	grain boundary	neck	densification
V	grain boundary diffusion	grain boundary	neck	densification
VI	solution–precipitation	grain boundary	neck	densification
VII	dislocation motion	grain boundary	dislocation	densification

particle compact densification, and grain growth. Initially, interparticle necks and grain boundaries form, creating a three-dimensional array of approximately cylindrical, interconnected, ie, continuous pore channels. These pore channels shrink in diameter during intermediate-stage sintering, and ultimately pinch off to form closed, ie, isolated, approximately spherical pores for final-stage sintering. Additional pore shrinkage and grain growth occur during final-stage sintering.

The primary objective of sintering is to produce a cohesive body of the desired size and shape having a microstructure that optimizes the desired in-use properties. For ceramics, this is usually a theoretically or nearly theoretically dense body comprised of fine (micrometer size), uniform grains.

Physical Characteristics and Property Effects. Powder physical characteristics that can affect sintering include particle size, particle packing, ie, pore size and green density, and particle shape. Particle size has the most pronounced effect on sintering. In general, because material transport occurs faster over shorter distances and less material transport is required to eliminate smaller pores, the finer the particle size, the faster the sintering process, and the lower the sintering temperature. The larger grains grow at the expense of smaller ones, and the smaller pores are preferentially eliminated during sintering. Consequently, as sintering progresses, the average size of the grains and pores in the compact increase and the size distributions become narrower. Densification of large grain and pore size compacts, and compacts comprised of a distribution of grain and pore sizes during sintering, is often limited to $<100\%$ theoretical density. Uncontrolled grain growth during final-stage sintering can result in intragranular porosity that also limits densification.

Particle packing may be the single most important physical characteristic of a powder compact. Improved particle packing increases particle coordination and the relative density of the compact, increasing the number of material transport paths for densification, while decreasing the concentration, size, and size distribution of the pores present in the powder compact. Consequently, densification occurs faster, to higher end point densities, and with less overall volume shrinkage during sintering. Uniform particle packing in a green compact ensures uniform densification and shrinkage. Nonuniform particle packing resulting from the presence of agglomerates, ie, densely packed fine particle clusters, or density gradients is undesirable. Ceramic fabrication processes are usually designed and controlled with the intent of optimizing green density while minimizing density gradients during forming.

Particle shape also affects the sintering of a powder compact. Jagged or irregular shaped particles, which have a high surface area to volume ratio, have a higher driving force for densification and sinter faster than equiaxed particles. High aspect ratio platey particles, whiskers, and fibers, which pack poorly, sinter poorly.

Material properties, including surface energy, diffusion coefficients and fluid viscosity, and bond strength are also important factors in sintering. Surface energy anisotropy, which is common in crystalline ceramics, can lead to differential densification, nonuniform and exaggerated grain growth, and end point densities less than theoretical. Bond strength also affects sintering. Strongly bound covalent materials like SiC, Si_3N_4, and BN are typically difficult to sinter without a sintering aid. Weakly bound ionic materials like NaCl are also difficult to sinter because these tend to dissociate during sintering.

Phase transformations can also be an important factor in sintering. Volume changes in materials such as quartz and zirconia from polymorphic phase transformations on heating and cooling can generate catastrophic stresses that can destroy a ceramic body. Damage and loss can be minimized by carefully controlling the cooling rate, or by controlling the size and/or concentration of materials that undergo destructive phase transformations during processing. The polymorphic phase transformation in zirconia can be controlled and beneficially utilized to produce toughened ceramics.

Chemical impurities may form a solid solution that alters the rate and/or mechanism of material transport, second-phase precipitates that pin grain boundaries and impede grain growth, or a liquid phase that enhances densification relative to coarsening. Minor additions of appropriate impurities can provide improved control over microstructure development during sintering. MgO-doped Al_2O_3 is the classic example in ceramics. Without MgO, the crystalline anisotropy in the Al_2O_3 system favors the formation of large lathlike grains; however, with as little as a few hundred parts per million MgO, fine, equiaxed, Al_2O_3 grains can be sintered to ~100% theoretical density in ≤ 1 h at ~1500°C. Chemical impurities that are intentionally added to a system to promote sintering and/or control grain growth are referred to as dopants or sintering aids.

Sintering Parameters. For a given material system, densification and microstructure development are primarily controlled by the sintering temperature, time, pressure, and atmosphere. Ceramic sintering is a thermally activated process that follows an Arrhenius-type behavior. Consequently, material transport and sintering occur faster at higher temperatures, but so does coarsening. Typically, ceramics are sintered at 0.50–0.75 of the absolute melting temperature.

Time is another important parameter. If the sintering time is short, a low density, porous ceramic body may be obtained. If the sintering time is long, coarsening mechanisms may take over and produce a coarse grained microstructure. Short to intermediate sintering times are used to manufacture fine grain size, high strength ceramics such as alumina cutting tools, whereas longer times are used to manufacture larger grain size, more creep-resistant ceramics such as Si_3N_4 for advanced heat engines. Extended sintering times (>2 h) are used to manufacture large grain size, high permeability ferrites, and high permittivity ferroelectrics.

In contrast to conventional sintering, which is typically conducted at atmospheric pressure or in vacuum, pressure sintering is conducted using an externally applied pressure. The applied pressure enhances the driving force for material transport during sintering, enhancing the rate of densification and making it possible to densify materials that are difficult to densify by conventional sintering. Oxide ceramics are typically sintered in an oxidizing or inert atmosphere to avoid reducing transition metals and degrading the optical properties and/or aesthetics of the finished product. Depending on the oxygen partial pressure, lead zirconate titanate (PZT) can be densified by solid-state or liquid-phase sintering mechanisms; however, to optimize its piezoelectric properties, precautions must be taken to maintain a PbO overpressure to limit lead loss and maintain stoichiometry during sintering. Si_3N_4 and AlN are typically sintered in a nitrogen atmosphere to prevent nitrogen dissociation and/or oxidation during sintering. SiC must also be sintered in a nonoxidizing atmosphere to avoid oxidation. In processing ferrites (qv), the partial pressure of oxygen must be controlled to optimize magnetic properties. In special cases, such as in processing $YBa_2Cu_3O_7$ ceramic superconductors (qv), it is necessary to control and vary the sintering atmosphere during processing to optimize densification and properties.

Conventional Sintering. Ceramic sintering is usually accomplished by heating a powder compact to ca two-thirds of its melting temperature at ambient pressure and holding for a given time. Densification can occur by solid-state, liquid-phase, or viscous sintering mechanisms.

In solid-state sintering (29,68,78–81) densification occurs by solid-state diffusion-controlled material support. Examples of two technologically important ceramics that density by solid-state sintering are MgO-doped Al_2O_3 and Y_2O_3-stabilized ZrO_2.

In general, material transport occurs faster through a liquid than through a solid. Thus densification generally occurs faster in the presence of a liquid phase as compared to solid-state sintering. The presence of a liquid during sintering can also lower the temperature required for densification. For example, polycrystalline alumina, which requires a sintering temperature of 1500–1600°C, can be densified faster and at temperatures hundreds of degrees lower using 0.5–6 wt % of an additive that forms a liquid phase during sintering (29). It is virtually impossible to densify materials such as SiC and Si_3N_4 without a liquid phase. When sintering with a liquid phase, trapped gases in closed pores often impede and limit densification. Additionally, a residual liquid or glass phase at the grain boundaries can degrade the properties of the finished product.

Liquid-phase sintering (LPS) (68,76,78–80,82) involves sintering with a liquid that is persistent throughout the sintering process. LPS is significantly more complex than solid-state sintering as there are more phases, interfaces, and material transport mechanisms to consider. The requirements for LPS are that the liquid wet the solid particles, that there is sufficient liquid present to wet the particles, and that the solid is soluble in the liquid. In general, the rate of densification increases with decreasing viscosity, increasing solubility, and increasing liquid concentration. Temperature is a critical processing parameter in LPS as the viscosity of the liquid decreases and the concentration and reactivity, ie, the solubility of the solid in the liquid, increase dramatically with increasing temperature above the eutectic temperature.

Reactive LPS (68,76,82) is similar to LPS, but differs by the fact that enhanced diffusion through a chemical reaction or phase transformation promotes faster densification. Examples of reactive liquid-phase sintered ceramics include MgO, Y_2O_3, and/or Al_2O_3 doped Si_3N_4. Transient LPS (76,82) takes advantage of LPS mechanisms and enhances densification in the presence of a liquid during sintering, after which the liquid vaporizes or transforms to a solid solution. Transient LPS produces ceramics devoid of a liquid grain boundary phase; consequently the finished product exhibits improved mechanical properties. LiF-doped MgO is an example of a transient liquid-phase sintered ceramic. Viscous sintering (83), which occurs by surface tension driven viscous flow, is widely used in the processing of glasses and glass-ceramics (qv) for optical and electronic applications. Nonreactive liquid-phase sintering (NLPS) (84) utilizes a combination of LPS and viscous sintering mechanisms to effect densification during sintering. Low temperature sintering ceramic-filled glass, ie, glass matrix, composites for electronic packaging, which typically contain ≥50 vol % glass, densify by NLPS.

Densification and densification rate increase with liquid concentration and temperature during sintering.

Conventional Sintering Equipment. Like drying furnaces, sintering furnaces (29,76,85) can be periodic or continuous in nature. Periodic kilns offer greater flexibility; continuous tunnel kilns are more economical. Advanced ceramics are typically sintered in high purity, controlled atmosphere furnaces by electric resistance heating. Ceramic furnaces used to fire traditional ceramic ware are generally heated with inexpensive natural gas, oil, wood, or coal.

Pressure Sintering. Pressure sintering employs the simultaneous use of pressure and temperature to effect densification during sintering. The externally applied pressure supplements the existing surface tension driving force for material transport during conventional sintering, resulting in an increased driving force and faster densification at the same temperature as conventional sintering, or an equal driving force and densification rate at a lower temperature. Pressure sintering also enhances the rate of densification relative to coarsening, so dense, fine grain size ceramics can be fabricated with little or no sintering aid. The increased driving force for material transport and densification also makes it possible to eliminate larger pores.

Because of higher manufacturing costs relative to conventional sintering, pressure sintering is usually reserved for manufacturing ceramics that are difficult to sinter to high density by conventional sintering, such as nonoxide ceramics, and to produce specialty, pore-free ceramics with improved properties, such as CaF_2 radomes and hard ferrite recording heads.

Hot Pressing. Hot pressing (29,45,68,78–80,86), the oldest and most widely used pressure sintering technique, involves compressing a heated powder in a die between two forming rams. The process is similar to dry pressing, except that the pressing is conducted at the sintering temperature. Hydraulic presses are typically used to apply the pressure, and graphite dies, used to temperatures in excess of 2000°C, but limited to a maximum pressure of ~100 MPa, are commonly used.

Graphite powder impurities, metal oxide reduction, pressing gradients, and preferential grain alignment can be problems in hot pressed ceramics. Additionally, hot pressing is limited to forming simple shapes, and considerable machining may be required to produce the desired finished product.

Hot Isostatic Pressing. Hot isostatic pressing (HIP) (45,68,78,87) is similar to cold isostatic pressing used in green forming with the exceptions that pressing is conducted at the sintering temperature, and the pressing medium is typically a gas. Argon or nitrogen gas is generally used, however, helium, oxygen, and mixtures of argon and oxygen have also been used. HIP allows for net and near-net forming without pressing gradients. Complex shape rotor blades and axial rotors have been formed by HIP which can be conducted at temperatures up to 2000°C and ~300 MPa (3×10^6 atm). Sintered materials with impermeable surfaces can also be subjected to HIP to higher density, a process that has successfully been used to produce improved property $BaTiO_3$ multilayer capacitors and hard ferrites for magnetic recording heads.

Materials to be subjected to HIP must be impermeable to the pressurizing gas. Glasses and refractory metals have been used to "can" ceramics, or ceramics can be presintered to the closed pore stage, ie, ≥92% theoretical density (TD), to produce an impermeable surface for HIP.

Hot Forging. Hot forging (78) takes advantage of the plastic or plasticlike properties of ultrafine grain crystalline ceramic compacts and crystalline ceramic compacts containing a fluid liquid or viscous glass phase at the sintering temperature. Plasticlike flow by grain boundary sliding under the influence of an applied stress at the sintering temperature results in simultaneous deformation and densification. By controlling deformation with forming dies, net and near-net shapes can be formed.

Novel Sintering Methods. Novel sintering methods employ combinations of radiation and conduction heating to directly heat ceramic parts rapidly in low mass furnaces. Rapid heating often promotes faster densification relative to coarsening, resulting in densification to high relative densities faster, with less grain growth. Additionally, direct sample heating minimizes the energy wasted heating the surrounding furnace and reduces the time required for heating and cooling.

Plasma Sintering. Plasma sintering (88) offers an economical means of rapidly sintering ceramics using rapid heating rates of up to 100°C/s to temperatures up to 10,000°C. Sintering times, on the order of tens of seconds, produce up to 99.5% dense, fine grain size microstructures with improved mechanical properties. Rapidly heating, sintering, and cooling by plasma sintering also offers the possibility of producing unique microstructures comprised of metastable phases.

Microwave Sintering. Microwave sintering (89) offers the potential of uniformly processing large volume parts both rapidly and economically. Rapid heating at up to 600°C/min to temperatures up to 2000°C can be achieved by microwave heating. Microwave sintering is faster than conventional sintering and may favor densification at lower temperatures.

Rapid Thermal Processing (IR Sintering). Selective and preferential heating using ir radiation provides the potential for faster heating, shorter soak times, and faster cooling. Ir sintering can be 2–3 times faster than conventional sintering, and offers improved control over microstructure development and the benefit of simultaneously processing dissimilar materials.

Chemical Vapor Deposition. Chemical vapor deposition (CVD) (45,68,78,90) is a means of fabricating bulk ceramics, or depositing ceramic coatings (qv) on solid surfaces utilizing a homogeneous or heterogeneous surface vapor chemical reaction. CVD can be used to deposit high purity, fine grain size, controlled morphology ceramic films or monoliths at relatively low temperatures. CVD is used in advanced electronics to form dielectrics in metal oxide semiconductors (MOS), transistors and capacitors, insulators, and diffusion barriers. Additionally, in a process in which a ceramic is deposited on a mandrel, CVD is used to manufacture dense, high purity cubic boron nitride, BN, specialty refractories (qv).

Reaction Formed Ceramics. A variety of specialty ceramics are produced by a combination of a chemical reaction and growth, or by simultaneous chemical reaction and consolidation using relatively novel ceramic reaction forming and thermal consolidation processes. Reaction forming processes provide the potential of producing unique ceramics and ceramic composites and high purity ceramics for specialty applications.

Directed Oxidation of a Molten Metal. Directed oxidation of a molten metal or the Lanxide process (45,68,91) involves the reaction of a molten metal with a gaseous oxidant, eg, Al with O_2 in air, to form a porous three-dimensional oxide that grows outward from the metal/ceramic surface. The process proceeds via capillary action as the molten metal wicks into open pore channels in the oxide scale growth. Reinforced ceramic matrix composites can be formed by positioning inert filler materials, eg, fibers, whiskers, and/or particulates, in the path of the oxide scale growth. The resultant composite is comprised of both interconnected metal and ceramic. Typically 5–30 vol % metal remains after processing. The composite product maintains many of the desirable properties of a ceramic; however, the presence of the metal serves to increase the fracture toughness of the composite.

Self-Propagating High Temperature Synthesis. Self-propagating high temperature synthesis (SHS) (45,78,92) offers the potential for simultaneous synthesis and densification. Combustion front temperatures range from ~2200–2700°C and the combustion wave propagates at 0.1–100 cm/s. Sintered parts tend to be porous; however, higher densities can be achieved by applying pressure during the combustion process or by melt casting. SHS has been used successfully to produce corrosion-resistant coatings on pipes.

Vapor and Reactive Liquid Infiltration. Chemical vapor infiltration (CVI) (45,90,93,94) is a modified version of CVD whereby a matrix is chemically deposited within a porous preform by a solid–vapor chemical reaction. CVI provides a means of making fiber-reinforced ceramic matrix composites without chemically, thermally, or mechanically damaging the fragile fibers. Particulate composites are also formed by CVI which involves vapor-phase mass transport over distances corresponding to the size of the preform. The mass of the preform increases with time as the vapor deposits and reacts on free surfaces within the preform. CVI requires a porous preform and the reaction proceeds until the pore channels plug or close off at ~90% TD and the reacting gas can no longer infiltrate the preform. CVI is a time-intensive process taking days to weeks to complete; however, an extremely high purity, fine grain matrix devoid of sintering aids or residual glassy phases is produced. Products manufactured by CVI include reaction bonded silicon nitride (RBSN) and reaction bonded silicon oxynitride that have good corrosion resistance to fluorides and chlorides. Additional products include carbon and silicon carbide fiber and matrix composites for aerospace applications and heat exchangers (see ABLATIVE MATERIALS; HEAT EXCHANGE TECHNOLOGY).

Reactive liquid infiltration (45,68,90,93,94) is similar to the CVI process used to make RBSN. Driven by capillarity, a reactive liquid infiltrates a porous preform and reacts on free surfaces. Reactive liquid infiltration is used to make reaction bonded silicon carbide (RBSC), which is used in advanced heat engines and as diffusion furnace components for semiconductor wafer processing.

Postsintering Processes

Traditional ceramic processing is generally complete after forming and firing. In contrast, advanced ceramics used in engineering applications may require postsintering processing (95,96). Machining may be required to meet dimensional tolerances and surface finish requirements, thermal annealing may be required to optimize properties, or a surface coating or modification may be required to alter the properties of a ceramic surface for a given application.

Machining. Ceramics can be machined using mechanical, thermal, and chemical action. Techniques employed in machining ceramics include abrasive grinding, chemical polishing, electrical discharge machining, and laser machining (95,96).

Annealing. Oxygen sensitive ceramics often require a postsintering thermal anneal in a controlled partial pressure oxygen atmosphere to achieve the stoichiometry that optimizes properties (76). For example, the magnetic permeability of manganese zinc ferrite, $MnO_{0.5}ZnO_{0.5}Fe_2O_4$, and the electrical properties of $YBa_2Cu_3O_7$ ceramic superconductors are strongly dependent on oxygen concentration. Additionally, insulating metal oxides can be reduced in an oxygen deficient atmosphere to become electrical conductors, and electrically conducting metals in metal and ceramic co-fire microelectronic packaging systems can oxidize in an oxygen-rich atmosphere to become electrical insulators during sintering. Sometimes the oxygen partial pressure that favors a high sintered density is different from the one that yields optimum properties. In such cases sintering is initially conducted in one atmosphere and the properties are optimized by subsequently thermal annealing in another.

Surface Coatings. The surface properties and characteristics of a ceramic can be modified with coatings (58,68,78,97). Coatings are applied to traditional clay ware to create a stronger, impermeable surface, and for decoration. Coatings may be applied to advanced structural ceramics and ceramics used in corrosive environments to improve strength, abrasion resistance, ie, wear or erosion, and corrosion resistance. Coatings can be applied dry, as slurries, by spraying, or by vapor deposition.

Glaze coatings (58) are applied to dry or bisque-fired clay ceramics to form a strong, impermeable surface that is aesthetically pleasing. Protective ceramic coatings can also be deposited by CVD (68,90). Plasma activated CVD has been used extensively to produce diamond and diamondlike films. Diamond films can also be used to make optical coatings with a tailored refractive index.

Sol-gel coatings (97,98), which are used to produce reflective, colored, and anti-reflective coatings for glass, can also be used in optoelectronic and integrated optic applications as modulators and switches, eg, sol-gel polycrystalline ferroelectric ceramic films. Sol-gel coatings can also be used to form films of dielectric insulators (qv), high temperature superconductors, capacitors, and piezoelectrics (qv) for advanced microelectronic packaging. Common methods of applying sol-gel coatings include dipping and spin coating.

Plasma or flame spray coatings (76,95) are applied like spray glaze coatings except that on passing through the spray gun, the powder feed is superheated by a plasma or flame to produce molten droplets. Upon impinging the object surface, the molten droplets spread to form a continuous coating and are rapidly quenched and solidified. The rapid cooling of the droplets on the ware surface can lead to the formation of nonequilibrium phases with unique properties. Plasma spray coatings are used to form conductive, refractory, and erosion- and corrosion-resistant coatings.

Thin coatings can be formed by ion deposition or sputtering (95), whereby an electron beam strikes a target to produce ions that condense on the object surface. This process is used to alter the electrical properties of a surface by depositing either a conducting or insulating layer. Ion beam deposition is limited to forming thin coatings in a vacuum.

Surface Modification Techniques. Other means of modifying the surface of a ceramic include ion implantation (qv), ion exchange, and quenching. Ion implantation (95) is accomplished by physically bombarding and stuffing the surface of a ceramic with ions. Ion exchange involves the chemical exchange of a larger cation for a smaller one of equal valence in the surface. Thermal quenching by rapid cooling results in differential cooling between the surface and the bulk, freezing in a less ordered, higher volume structure at the surface relative to the bulk such as in tempered glass.

Processing–Microstructure–Properties

The processes employed in manufacturing a ceramic are defined and controlled to produce a product with properties suited to a specific application. Processing–microstructure–property relationships are determined by characterizing the ceramic raw materials, mixes, and the formed ceramic body intermittently during processing and after final thermal consolidation. It is possible to modify and optimize processes to optimize properties and to identify and correct processing deficiencies when less than optimal properties are obtained. Examples of some process–microstructure–property relations in advanced ceramics are outlined in Figure 4.

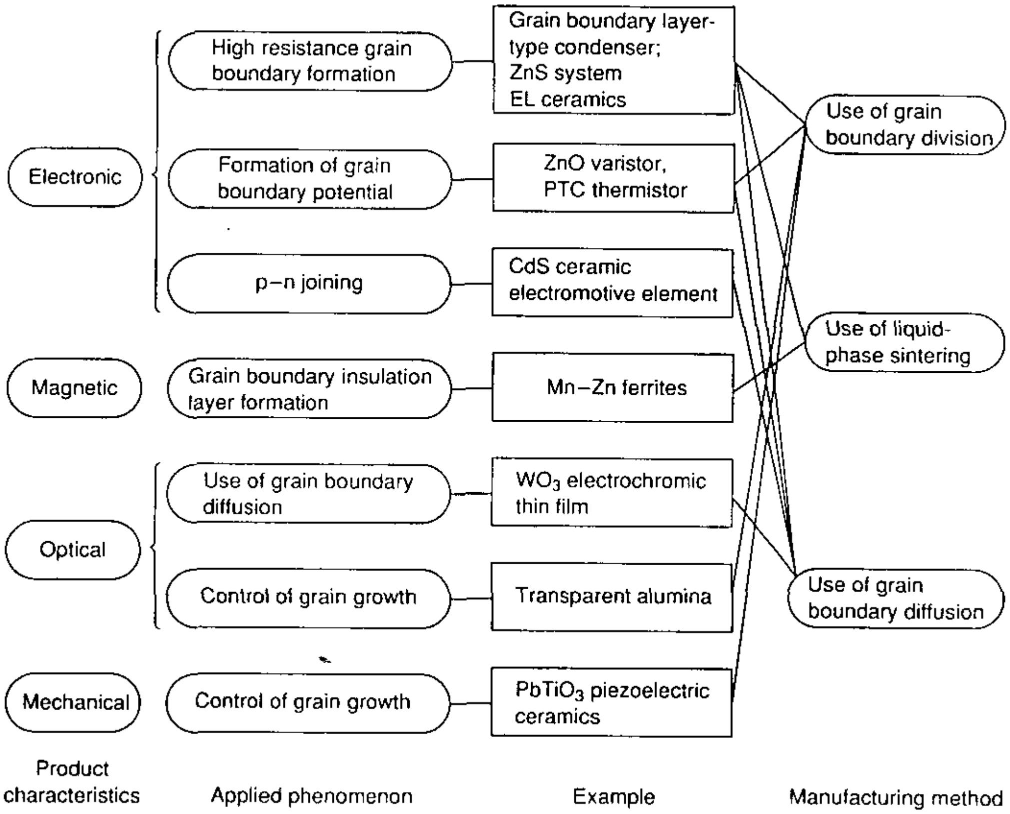

Fig. 4. Process–microstructure–property relationships in advanced ceramics (99).

Characterization. Ceramic bodies are characterized by density, mass, and physical dimensions. Other common techniques employed in characterizing include x-ray diffraction (XRD) and electron or petrographic microscopy to determine crystal species, structure, and size (100). Microscopy (qv) can be used to determine chemical constitution, crystal morphology, and pore size and morphology as well. Mercury porosimetry and gas adsorption are used to characterize pore size, pore size distribution, and surface area (100). A variety of techniques can be employed to characterize bulk chemical composition and the physical characteristics of a powder (100,101).

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