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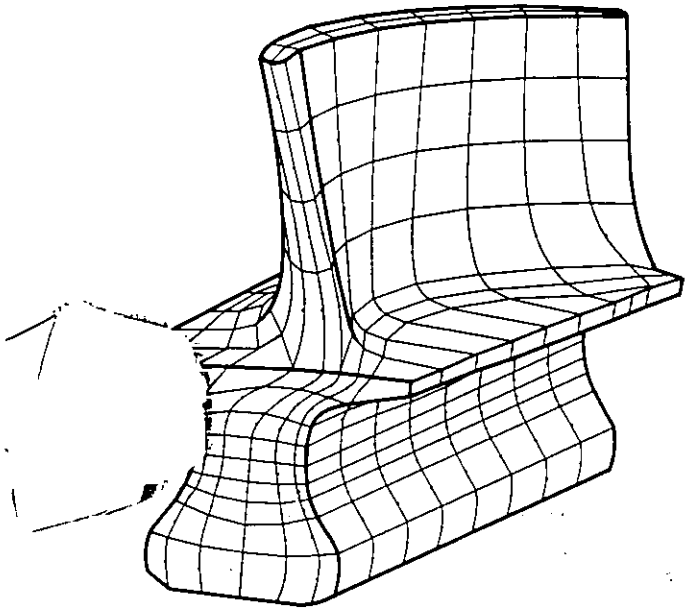
MODERN CERAMIC ENGINEERING

PROPERTIES, PROCESSING, AND USE IN DESIGN

DAVID W. RICHERSON



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II

PROCESSING OF CERAMICS

The relationships among atomic bonding, crystal structure, and properties for ceramics, metals, and polymers were discussed in Part I. It was shown that the theoretical strength is controlled by the strength of bonding, but that in actual ceramic components the theoretical strength is not achieved due to flaws in the fabricated material. The objectives of Part II are to review the fabrication processes used for manufacturing ceramic components, determine where in these processes strength-limiting flaws are likely to occur, and provide the reader with approaches for detecting these flaws and working with the ceramic fabricator to eliminate them.

Most ceramic fabrication processes begin with finely ground powder. Chapter 5 describes the criteria for selection of the starting powder, methods of achieving the proper particle size distribution, and requirements for pretreating the powder before it can be formed into the desired component.

Chapter 6 describes the processes used to form the ceramic powders into the component shapes. Uniaxial and isostatic pressing, slip casting, extrusion, injection molding, tape forming, and green machining are included.

The shapes resulting from the forming processes described in Chap. 6 consist essentially of powder compacts that must be densified by high-temperature processing before they will have adequate strength and other properties. The mechanisms and processes for densification are explored in Chap. 7. Some processes combine forming and densification in a single step. These include hot pressing, chemical vapor deposition, liquid particle spray, and cementicious bonding. These are also discussed in Chap. 7.

Ceramic components requiring close tolerances must be machined after densification. This machining step can be as expensive as all the other process steps together and thus must be thoroughly understood by the engineer. Chapter 8 reviews the mechanisms of material removal during machining, the effects on the strength of the ceramic, and guidelines for selection of a machining method and abrasive material.

Chapter 9 discusses quality control and quality assurance methods for ceramic components. Use of specifications and in-process certification will be described. Nondestructive inspection techniques for both internal and surface flaws are reviewed, including radiography, ultrasonics, image enhancement, penetrants, and some relatively new techniques that look promising.

5

Powder Processing

The nature of the raw material has a major effect on the final properties of a ceramic component. Purity, particle size distribution, reactivity, polymorphic form, availability, and cost must all be considered and carefully controlled. In this chapter we discuss the types and sources of raw materials and the processing required to prepare them into the appropriate purity, particle size distribution, and other conditions necessary to achieve optimum results in later processing steps.

5.1 RAW MATERIALS

Traditional Ceramics

Ceramics have been produced for centuries. The earliest ceramic articles were made from naturally occurring raw materials. Early civilizations found that clay minerals became plastic when water was added and could be molded into shapes. The shape could then be dried in the sun and hardened in a high-temperature fire. The word "ceramic" comes from the Greek word keramos, which translates roughly as "burnt stuff."

Many of the raw materials used by the ancient civilizations are still used today and form the basis of a sizable segment of the ceramic industry [1-3]. These ceramic products are often referred to as traditional ceramics. Important applications of traditional ceramics are listed in Table 5.1. Some of the naturally occurring minerals and their sources and uses are summarized in the following paragraphs.

The clay minerals are hydrated aluminosilicates which have layer structures. There are a variety of clay minerals, including kaolinite [$Al_2(Si_2O_5)(OH)_4$], halloysite [$Al_2(Si_2O_5)(OH)_4 \cdot 2H_2O$], pyrophyllite [$Al_2(Si_2O_5)_2(OH)_2$], and montmorillonite [$Al_{1.67}(Na,Mg)_{0.33}(Si_2O_5)_2(OH)_2$]. All are secondary in origin, having formed by weathering of igneous rocks under the influence of water, dissolved CO_2, and organic acids. The largest deposits were formed when feldspar ($KAlSi_3O_8$) was eroded from rocks such as granite and deposited in lake beds and then altered to a clay.

Table 5.1 Traditional Ceramics

Whitewares	Dishes, plumbing, enamels, tiles
Heavy clay products	Sewer pipe, brick, pottery, sewage treatment, and water purification components
Refractories	Brick, castables, cements, crucibles, molds
Construction	Brick, block, plaster, concrete, tile, glass, fiberglass
Abrasive products	Grinding wheels, abrasives, milling media, sandblast nozzles, sandpaper
Glass	Too numerous to list

The importance of clays in the evolution of traditional ceramic processing cannot be overemphasized. The plasticity developed when water is added provides the bond and workability so important in the fabrication of pottery, innerware, brick, tile, and pipe.

Silica (SiO_2) is a major ingredient in glass, glazes, enamels, refractories, abrasives, and whiteware. Its major sources are in the polymorphic form quartz, which is the primary constituent of sand, sandstone, and quartzite.

Feldspar is also used in glass, pottery, enamel, and other ceramic products. Feldspar minerals range in composition from $KAlSi_3O_8$ to $NaAlSi_3O_8$ to $CaAl_2Si_2O_8$ and act as a flux (reduces the melting temperature) in a composition. Nepheline syenite ($Na_2Al_2Si_2O_8$) is used in a similar fashion.

Other naturally occurring minerals used directly in ceramic compositions include talc [$(Mg_3(Si_2O_5)_2(OH_2]$, asbestos [$(Mg_3Si_2O_5)(OH)_4]$, wollastonite ($CaSiO_3$), and sillimanite (Al_2SiO_5).

Modern Ceramics

During the past 50 years scientists and engineers have acquired a much better understanding of ceramic materials and their processing and have found that naturally occurring minerals could be refined or new compositions synthesized to achieve unique properties. These refined or new ceramics are often referred to as modern ceramics. They typically are of highly controlled composition and structure and have been engineered to fill the needs of applications too demanding for traditional ceramics. Modern ceramics include the oxide ceramics (such as Al_2O_3, ZrO_2, ThO_2, BeO, MgO, and

$MgAl_2O_4$), magnetic ceramics (such as $PbFe_{12}O_{19}$, $ZnFe_2O_4$, and $Y_6Fe_{10}O_{24}$), ferroelectric ceramics (such as $BaTiO_3$), nuclear fuels (such as UO_2 and UN), and nitrides, carbides, and borides (such as Si_3N_4, SiC, B_4C, and TiB_2) [4-6]. Table 5.2 summarizes many of the modern ceramic applications. Emphasis in this book will be on the modern ceramics as they are the ones with which an engineer is most likely to become involved. The following sections describe how some of the modern ceramic starting powders are refined or synthesized.

Aluminum Oxide Powder

Aluminum oxide (Al_2O_3) occurs naturally as the mineral corundum, which is better known to most of us when it is in gem-quality crystals called ruby and sapphire. Ruby and sapphire are precious gems because of their chemical inertness and hardness. Al_2O_3 powder is produced in large quantity from the mineral bauxite by the Bayer process. Bauxite is primarily colloidal aluminum hydroxide intimately mixed with iron hydroxide and other impurities. The Bayer process involves the selective leaching of the alumina by caustic soda and precipitation of the purified aluminum hydroxide. The resulting fine-particle-size aluminum hydroxide can then be thermally converted to Al_2O_3 powder, which is used to manufacture polycrystalline Al_2O_3-based ceramics.

Al_2O_3 powder is used in the manufacture of porcelain, alumina laboratory ware, crucibles and metal casting molds, high-temperature cements,

Table 5.2 Modern Ceramics

Electronics	Heating elements, dielectrics, substrates, semiconductors, insulators, transducers, lasers, hermetic seals, igniters
Aerospace and automotive	Reentry, radomes, turbine components, heat exchangers, emission control
Medical	Prosthetics, controls
High-temperature structural	Kiln furniture, braze fixtures, advanced refractories
Nuclear	Fuels, controls
Technical	Laboratory ware
Miscellaneous	Cutting tools, wear-resistant components, armor, magnets, glass-ceramics, single crystals, fiber optics

wear-resistant parts (sleeves, tiles, seals, etc.), sandblast nozzles, armor, medical components, abrasives, refractories, and a variety of other components. Many hundreds of tons of alumina powder and alumina-based articles are produced each year. It has even been used to make extrusion dies for corn chips and mixing valves for water faucets.

Magnesium Oxide Powder Magnesium oxide occurs naturally as the mineral periclase, but not in adequate quantity or purity for commercial requirements. Most MgO powder is produced from $MgCO_3$ or from seawater. It is extracted from seawater as the hydroxide, which is easily converted to the oxide by heating at the appropriate temperature.

MgO powder is used extensively for high-temperature electrical insulation and in refractory brick.

Silicon Carbide Powder SiC has been found occurring naturally only as small green hexagonal plates in meteoric iron. This same hexagonal polymorph (α-SiC) has been synthesized commercially in large quantities by the Acheson process. This fascinating process appears crude, but is cost effective and simultaneously produces lower-grade SiC for abrasives and high-grade SiC for electrical applications. The Acheson process consists essentially of mixing SiO_2 sand with coke in a large elongated mound and placing large carbon electrodes in opposite ends. An electric current is then passed between the electrodes, resistance-heating the coke in the mound to about 2200°C. In this temperature range the coke reacts exothermally with the SiO_2 to produce SiC plus CO gas. Once the reaction begins, enough heat is produced to keep the reaction going until it is completed in the interior of the mound. After cooling, the mound is broken up and sorted. The core contains intergrown green hexagonal SiC crystals which are low in impurities and suitable for electronic applications. Around the core is a zone of lower purity that is used for abrasives. The outer layer of the mound is a mixture of SiC and unreacted SiO_2 and carbon which is added to silica sand and coke for the next batch.

SiC can be prepared from almost any source of silicon and carbon. For instance, it has been prepared in the laboratory from a mixture of silicon metal powder and sugar. It has also been prepared from rice hulls. It can also be prepared from silicon tetrachloride ($SiCl_4$) and some silanes. In this case, the cubic β-SiC polymorph normally forms.

SiC is used for high-temperature kiln furniture, electrical-resistance heating elements, grinding wheels and abrasives, wear-resistance applications, incinerator lining, and is currently being evaluated for highly stressed components in heat engines.

Silicon Nitride Powder Silicon nitride does not occur naturally. It has been synthesized by several different process. Most of the powder available commercially has been made by the reaction of silicon metal powder with

nitrogen at temperatures in the range 1250 to 1400°C and consists of a mixture of α-Si_3N_4 and β-Si_3N_4 polymorphs. This Si_3N_4 is not a ready-to-use powder when it is removed from the furnace. It is loosely bonded and must be crushed and sized first. The resulting powder is not of high purity, but contains impurities such as Fe, Ca, and Al, which were originally present in the silicon, plus impurities picked up during crushing and grinding.

Higher-purity Si_3N_4 powder has been made by reduction of SiO_2 with carbon in the appropriate nitrogen environment and reaction of $SiCl_4$ or silanes with ammonia. Both of these methods produce very fine particle size powder that does not require further grinding for use. In fact, some of these powders are so fine that they require coarsening by heat treating (calcining) before they are suitable for shape-forming operations.

High-purity Si_3N_4 powder has recently been made in small quantities by laser reaction [7]. A mixture of gaseous silane (SiH_4) and ammonia is exposed to the coherent light output of a CO_2 laser. The silane has high absorption for the wavelengths involved, resulting in the heat required for reaction. The resulting Si_3N_4 is in spherical particles of a uniform size for the given gas flow and laser power conditions. Particles typically in the range 200 to 1000 Å can be produced.

Raw Materials Selection Criteria

The selection criteria for ceramic starting powders are dependent on the properties required in the finished component. Purity, particle size distribution, reactivity, and polymorphic form can all affect the final properties and thus must be considered from the outset.

Purity Purity strongly influences high-temperature properties such as strength, stress rupture life, and oxidation resistance, as discussed in Chaps. 3 and 4. The effect of the impurity is dependent on the chemistry of both the matrix material and the impurity, the distribution of the impurity, and the service conditions of the component (time, temperature, stress, environment). For instance, Ca severely decreases the creep resistance of Si_3N_4 hot-pressed with MgO as a densification (sintering) aid, but appears to have little effect on Si_3N_4 hot pressed with Y_2O_3 as the densification aid [8,9]. In the former case, the Ca is concentrated at the grain boundaries and depresses the softening temperature of the grain boundary glass phase. In the latter case, the Ca is apparently absorbed into solid solution by the crystalline structure and does not significantly reduce the refractoriness of the system.

Impurities present as inclusions do not appreciably affect properties such as creep or oxidation, but do act as flaws that can concentrate stress and decrease component tensile strength. The effect on strength is dependent on the size of the inclusion compared to the grain size of the ceramic and on the relative thermal expansion and elastic properties of the matrix

and inclusion. Tungsten carbide inclusions in Si_3N_4 have little effect on the strength; Fe and Si have a large effect.

Particle Size and Reactivity The effects of impurities are important for mechanical properties, but may be even more important for electrical, magnetic, and optical properties. Electrical, magnetic, and optical properties are usually carefully tailored for a specific application, often by closely controlled addition of a dopant. Slight variations in the concentration or distribution of the dopant severely alters the properties. Similarly, the presence of unwanted impurities can poison the effectiveness of the dopant and cause the device to operate improperly.

Particle size distribution is important, depending on which consolidation or shaping technique is to be used. In most cases the objective of the consolidation step is to achieve "maximum particle packing" and "uniformity" so that "minimum shrinkage" and "retained porosity" will result during densification. A single particle size does not produce good packing. Optimum packing for particles all the same size results in over 30% void space. Adding particles of a size equivalent to the largest voids reduces the void content to 26%. Adding a third, still smaller particle size can reduce the pore volume to 23%. Therefore, to achieve maximum particle packing, a range of particle sizes is required.

A controlled optimum particle size distribution is required to achieve maximum, reproducible strength. The strength is controlled by flaws in the material. A single particle which is significantly larger than the other particles in the distribution can become the critical flaw that limits the strength of the final component. Similarly, a large void resulting from a nonhomogeneous particle size distribution or from particles too close to the same size may not be eliminated during sintering and may become the strength-limiting flaw.

Small particle size is important if high strength is the primary objective. However, there are many applications where strength is not the primary criterion. Refractories are a good example. Most refractories contain either large particles or high porosity as an important constituent in achieving the desired properties.

Another important aspect of starting powder is reactivity. The primary driving force for densification of a compacted powder at high temperature is the change in surface free energy. Very small particles with high surface area have high surface free energy and thus have a strong thermodynamic drive to decrease their surface area by bonding together. Very small particles, approximately 1 μm or less, can be compacted into a porous shape and sintered at high temperature to near-theoretical density. Transparent polycrystalline alumina for sodium vapor lamp envelopes is a good example. To achieve transparency, virtually all the initial pores must be removed during sintering. Highly reactive starting powder with an

average particle size of about 0.3 μm is used as the raw material. Another example is sintered Si_3N_4. Starting powder of approximately 2 μm average particle size only sinters to about 90% of theoretical density. Submicron powder with a surface area roughly greater than 10 m^2/g sinters to greater than 95% of theoretical density.

Particle size distribution and reactivity are also important in determining the temperature and the time at the temperature necessary to achieve sintering. Typically, the finer the powder and the greater its surface area, the lower are the temperature and time at temperature for densification. This can have an important effect on strength. Long times at temperature result in increased grain growth and lower strength. To optimize strength, a powder that can be densified quickly with minimal grain growth is desired.

Polymorphic Form Many ceramics occur in different polymorphic forms, as discussed in Chap. 1. For most applications one polymorph is preferred. For instance, α-Si_3N_4 is superior to β-Si_3N_4 as a starting powder for hot pressing. A similar situation exists for SiC. The stable form at high temperature is the hexagonal α-SiC polymorph. α-SiC starting powder can be densified by either hot pressing or pressureless sintering over a relatively broad temperature range without problems associated with polymorphic transformation. The lower-temperature form, cubic β-SiC, can also be densified, but in a much more limited temperature range.

5.2 POWDER SIZING

Section 5.1 explained the importance of particle size distribution in achieving the optimum properties in the final component. Raw materials are not usually available with the optimum particle size distribution. The ceramic fabricator must further process the raw materials to the specifications. The following techniques are used:

Screening	Hammer milling
Air classification	Precipitation
Elutriation	Freeze drying
Ball milling	Laser
Attrition milling	Plasma
Vibratory milling	Calcining
Fluid energy milling	

The following paragraphs describe briefly each of these approaches and discuss their limitations and how these limitations may alter the properties of the material.

Screening

Screening is a positive method of particle sizing. The powder is poured onto a single screen having the selected size openings or on a series of screens, each subsequently with smaller openings. The particles are separated into size ranges; the particles larger than the screen openings remain on the screen and smaller particles pass through until they reach a screen with holes too small to pass through.

Screen sizes are classified according to the number of openings per linear inch and are referred to as mesh sizes. A 16 mesh screen has 16 equally spaced openings per linear inch; a 325 mesh screen has 325. Table 5.3 compares the mesh size of standard screens with the actual size of the openings.

Raw and processed ceramic materials are often supplied according to screen size. For instance, a -325-mesh powder has all passed through a 325-mesh screen and should contain no particles larger than 44 μm (0.0018 in.). A powder designated -100 mesh +150 mesh consists of a narrow particle size range that was small enough to pass through a 100-mesh screen but too large to pass through a 150-mesh screen. Powders containing a broad particle size range can also be classified according to screen size, for example:

Size range	Weight (%)
-80 + 100	5
-100 + 150	8
-150 + 220	13
-220 + 280	20
-280 + 325	18
-325	36

Screening can be conducted dry or with the particles suspended in a slurry. Dry screening is used most frequently for larger particles and is a fast and effective approach. It is used in the mining industry and in many phases of the ceramic industry, especially in the sizing of abrasives. For free-flowing particles, dry screening can normally be effective down to about 325 mesh. Below this the particles are so fine that they either tend to agglomerate or clog the screen. Some automatic screen systems use airflow or vibration to aid in screening powders that have a significant portion of particles in the range 325 mesh or smaller.

Table 5.3 ASTM Standard Screen Sizes

"Mesh" sieve designation	Sieve opening	
	mm	in.
4	4.76	0.187
6	3.36	0.132
10	2.00	0.0787
12	1.68	0.0661
16	1.19	0.0469
20	0.84	0.0331
40	0.42	0.0165
80	0.177	0.0070
120	0.125	0.0049
170	0.088	0.0035
200	0.074	0.0029
230	0.063	0.0025
270	0.053	0.0021
325	0.044	0.0017
400	0.037	0.0015

Source: ASTM E11, Annual Book of ASTM Standards, American Society for Testing and Materials, Philadelphia, 1970.

Suspending the particles in a dilute water or other liquid suspension (slurry) also aids in screening fine particles. Slurries can normally be screened easily through at least 500 mesh as long as the solids content in the slurry is low and fluidity is high. For very fine powder, this is a useful method of assuring that no particles larger than an acceptable limit (determined by the screen size selected) are left in the powder. Since isolated large particles in a powder of fine particle size distribution often become the strength-limiting flaw in the final component, wet screening can be used as an in-process quality control step.

Screening does have limitations. As with any process, it is accurate only as long as the equipment is properly maintained. Distorted or broken

screens pass larger particles than specified. Screens of 325 mesh and finer are frequently damaged because of the fragile nature of the thin filaments required to construct the screen. The user tends to get impatient due to the slow feed rate of some powders and tries to force the powder through by brushing or scraping the screen. Once the screen is damaged, particle size control and knowledge of the particle size distribution are lost.

Another limitation of screening is related to the nature of the powder. If the powder tends to compact or agglomerate, groups of particles will act as a single particle and result in inaccurate screening. Similarly, packing or agglomeration can clog the screen and prevent further screening or decrease efficiency.

Air Classification

Air classification (also referred to as air separation) is used to separate coarse and fine fractions of dry ceramic powders. A schematic of an air classifier is shown in Fig. 5.1. Separation is achieved by control of horizontal centrifugal force and vertical air currents within the classifier. Particles enter the equipment along the centerline and are centrifugally accelerated outward. As the coarse particles move radially away from the center into the separating zone, they lose velocity and settle into a collection cone. The finer particles are carried upward and radially by the air currents through selector blades. These selector blades impart an additional centrifugal force to the particles and cause additional coarse particles to settle into the coarse collection cone. The fines are then carried by the airflow to a separate cone for collection.

Air classifiers have been used to separate particles in the approximate range 40 to 400 mesh at rates exceeding 400 tons/hr. They are used extensively in the cement industry for sizing fine particles to close size and surface area specification (range -170 mesh). They are also used to remove undesirable fines in other ceramic industries where a coarse aggregate is required.

Special air classifiers are available for isolating fine powders in the range below 20 μm. Separation can be done with reasonable accuracy down to about 10 μm. However, below 10 μm, it is difficult to obtain a cut that is completely free of larger particles. For instance, if a powder were desired with no particles larger than 5 μm, it could not be guaranteed by air classification.

Air classification is frequently linked directly to milling, crushing, grinding, or other comminution equipment in a closed circuit. Particles from the mill are discharged directly into the air classifier. The fines are separated and the coarse is returned to the mill for further grinding. One type of unit combines size reduction and classification into a single piece of equipment. The coarse powder particles are carried by high-velocity air through two opposing nozzles. Where the two air streams meet, particles

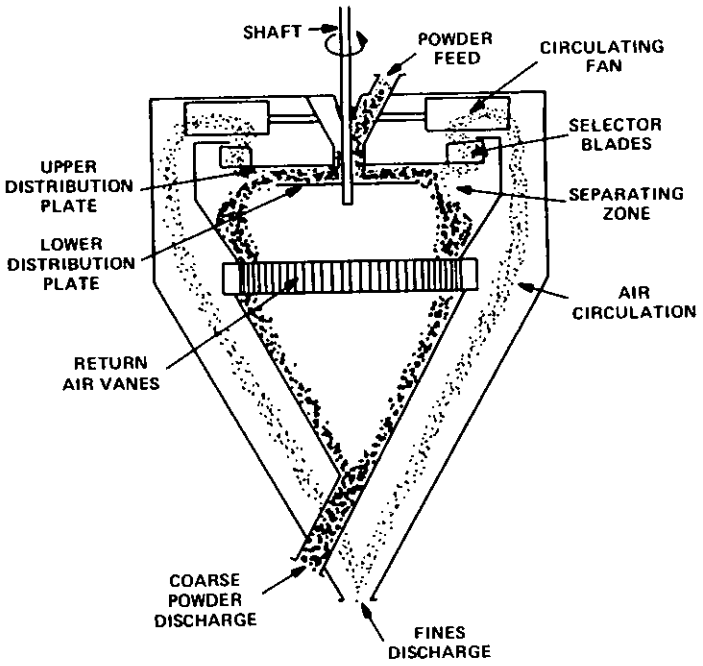

Figure 5.1 Drawing of an air classifier, showing the paths of the coarse and fine particles. (Courtesy of the Sturtevant Mill Company, Boston, Mass.)

strike each other and are shattered into smaller particles. The air carrying the particles flows vertically. Large particles pass through a centrifugal-type air classifier at the top of the unit, where additional controlled sizing is accomplished.

Air classification has its advantages and limitations. It is an efficient and high-volume approach for separating coarse particles from fine particles and producing controlled size ranges roughly from 40 to 400 mesh. However, it is limited in its efficiency and accuracy in producing controlled sizing of particles below 10 μm.

Another concern of the engineer is the presence of contamination. Sliding motion and impact of the ceramic particles against equipment surfaces results in some metallic contamination. The amount of contamination is less than for comminution equipment, but may still cause a problem for some applications. Therefore, the engineer should be aware of the air classification process and its potential for affecting material application specification.

During development, an engineer sometimes needs to have an experimental batch of powder air classified. This can be done on a contract basis with many of the equipment manufacturers at their R&D facilities. Again, though, it should be realized by the engineer that contamination can be picked up, especially since R&D equipment is used on a batch basis with a different material in each batch. Even with careful cleaning (which is not automatically done between batches), foreign particles will remain in the equipment. The best procedure is to insist on careful cleaning, run a sacrificial batch of your powder prior to your study batch, and be aware that contamination may occur that would not occur in production.

Elutriation

Elutriation is a general term that refers to particle size separation based on settling rate; i.e., large or high-specific-gravity particles settle more rapidly from a suspension than do small or low-specific-gravity particles. Air classification is a form of elutriation where the suspending medium is air. For this book the term elutriation is used to describe particle sizing by settling from a liquid suspension.

Elutriation is frequently used in the laboratory for obtaining very fine particle distributions free of large particles. The powder is mixed with water or other liquid and usually with a wetting agent and possibly a deflocculant* to yield a dilute suspension. Stirring or mixing is stopped and settling is allowed to occur for a predetermined time. The time is based on the particle size cut desired. The fluid containing the fine particles is then decanted or siphoned and the remaining fluid and residue discarded or used for some other purpose.

A major problem with elutriation is that the fines must be extracted from the fluid before they can be used. This can be done by evaporating the fluid or by filtration. Both tend to leave the fines compacted or crusted rather than as a free-flowing powder, thus requiring additional process steps before the powder can be used. Also, unless the elutriation and liquid removal are conducted in a closed system, chances for contamination are high.

Ball Milling

The desired particle size distribution usually cannot be achieved simply by screening, classifying, or elutriating the raw material. More typically, a particle size reduction (comminution) step is required. Ball milling is

*The wetting agent and deflocculant help to break up agglomerates.

is one of the most widely used. Ball milling consists of placing the particles to be ground (the "charge") in a closed cylindrical container with grinding media (balls, short cylinders or rods) and rotating the cylinder horizontally on its axis so that the media cascade. The ceramic particles move between the much larger media and between the media and the wall of the mill and are effectively broken into successively smaller particles.

The rate of milling is determined by the relative size, specific gravity, and hardness of the media and the particles. High-specific-gravity media can accomplish a specified size reduction much more quickly than can low-specific-gravity media. The following media are commonly used and are listed in descending order of specific gravity: WC, steel, ZrO_2, Al_2O_3, and SiO_2.

Contamination is a problem in milling. While the particle size is being decreased, the mill walls and media are also wearing. Milling Al_2O_3 powder with porcelain or SiO_2 media can result in about 0.1% contamination per hour. Some Si_3N_4 powder milled in a porcelain-lined mill with porcelain cylinders picked up nearly 6% contamination in 72 hr of milling time. The contamination in the Si_3N_4 resulted in a decrease in the high-temperature strength by a factor of 3 and nearly an order-of-magnitude decrease in creep resistance in the final part.

Contamination can be controlled by careful selection of the mill lining and the media. Polyurethane and various types of rubber are excellent wear-resistant linings and have been used successfully with dry milling and with water as a milling fluid. However, some milling is conducted with organic fluids that may attack rubber or polyurethane. Very hard grinding media can reduce contamination because they wear more slowly. WC is good for some cases because its high hardness reduces wear and its high specific gravity minimizes milling time. If contamination from the media is an especially critical consideration, milling can be conducted with media made of the same composition as the powder being milled. Another approach is to mill with steel media and remove the contamination by acid leaching.

Milling can be conducted either dry or wet. Dry milling has the advantage that the resulting powder does not have to be separated from a liquid. The major concern in dry milling is that the powder does not pack in the corners of the mill and avoid milling. The powder must be kept free flowing. One method of accomplishing this is to use a dry lubricant such as a stearate. In some cases, humidity or moisture in the powder causes packing. This has been resolved through the use of a heated mill.

Wet milling is usually very efficient if the correct ratio of fluid to powder to milling media is used. The ratio varies for different materials and usually has to be optimized experimentally. A slurry of the consistency of syrup or slightly thicker mills effectively.

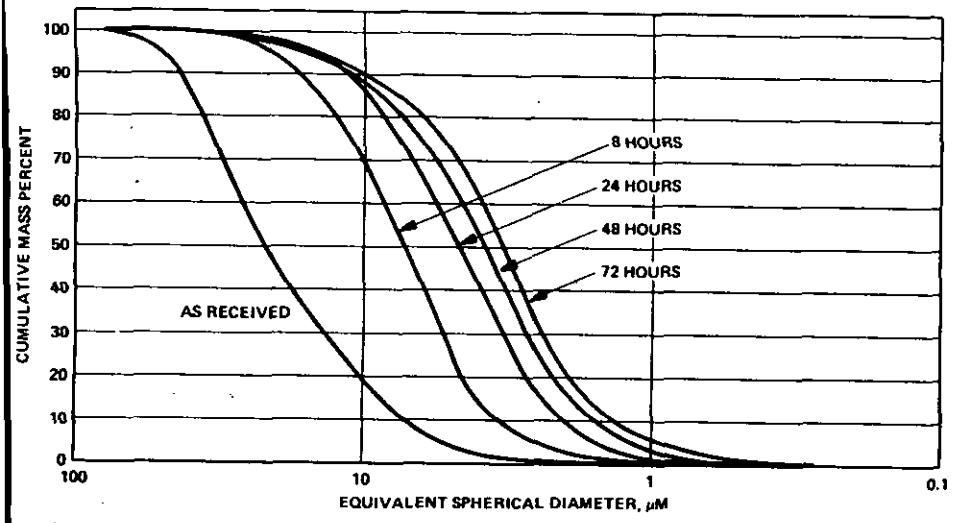

Figure 5.2 Particle size distribution of silicon powder as a function of milling time. (From Ref. 24.)

Milling produces a broad particle size distribution rather than a narrow particle size range as achieved by screening. Milling can readily reduce the average particle size to 5 μm or less. Figure 5.2 shows particle size distribution curves for silicon powder ball-milled for use in the fabrication of reaction-bonded Si_3N_4 parts. Initial particle size reduction was rapid but decreased as the powder became finer.

Besides producing the required particle size distribution, ball milling can also produce a very active powder that is easier to density in later process steps. In some cases, this is achieved by an active surface condition. In other cases it appears to be achieved by increased strain energy in the particle.

At this point, the non-ceramic engineer may wonder why he or she needs to know the details about particle sizing methods, since he or she will probably only be purchasing the final part and will not be involved in the material processing. This is probably true, but it is still the engineer's responsibility to make sure the part works in the particular application. Current engineering requirements of materials are often far more demanding than they used to be and traditional controls and techniques used by ceramic manufacturers may require upgrading. The engineer knows the application requirements better than the supplier does and will thus need extensive liaison with the supplier to achieve the material objectives. It is not unusual for an engineer to request or suggest a process change or modification to the supplier.

Attrition Milling

Figure 5.3 shows a schematic of an attrition mill. It is similar to a ball mill since it is cylindrical and contains balls or grinding media, but rather than the cylinder rotating, the balls are agitated by a series of stirring arms mounted to an axial shaft. Herbell et al. [10] and Claussen and Jahn [11] report that attrition milling is quicker than ball milling, is more efficient at achieving fine particle size, and results in less contamination. Furthermore, attrition milling can easily be conducted dry, wet, or with a vacuum or inert gas atmosphere.

Data from Herbell et al. [10] for dry attrition milling of silicon powder are summarized in Table 5.4. Although the attrition mill was lined with an iron-base alloy, no significant iron or carbon was picked up, even after 18 hr of milling. The oxygen content did increase by interaction with air, as would normally be expected for fine particles of silicon, as the surface area increased.

Even though the average particle size was substantially reduced by dry attrition milling, some particles in the range 40 μm (0.0018 in.) were still present and ultimately controlled the strength of the final component. Evidently, some particles were trapped or packed in regions of the mill where they did not receive adequate milling. This did not occur for wet milling.

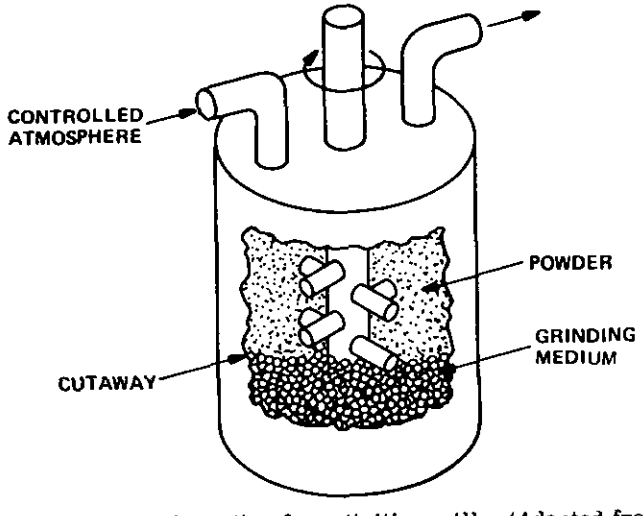

Figure 5.3 Schematic of an attrition mill. (Adapted from T. P. Herbell and T. K. Glasgow, NASA, presented at the DOE Highway Vehicle Systems Contractors Coordination Meeting, Dearborn, Mich., Oct. 17-20, 1978.)

Table 5.4 Changes during Attrition Milling of Silicon Powder

Milling time (hr)	Surface area (m^2/g)	Iron content (wt %)	Carbon content (wt %)	Oxygen content (wt %)
0	3.0	0.62	0.03	0.60
1	11.5	0.59	0.04	2.29
4	14.5	0.58	0.04	2.57
18	23.3	0.55	0.04	3.67

Source: Ref. 10.

Stanley et al. [12] have described a different configuration of attrition mill that has been used primarily for wet milling. It consists of a rotating cylindrical cage of vertical bars surrounded by a stationary cylindrical cage of vertical bars. The material to be ground is mixed with water or other fluid plus sand-size grinding media. Materials such as ZrO_2, Al_2O_3, and SiO_2 have been ground to submicron size in a few hours, compared to 30 hr for vibratory milling and much longer times for ball milling. The primary problem with this attrition milling approach is the amount of contamination and the difficulty of separating the powder from the media. For example, in one case 20 to 30% of the media was ground to -325 mesh (< 44 μm) and was not successfully separated from the 0.1-μm milled powder.

Vibratory Milling

Vibratory milling is substantially different from ball milling or attrition milling. The energy for comminution is supplied through vibration rather than tumbling or mechanical stirring. The powder is placed in the stationary chamber of the mill together with suitable grinding media and a liquid. When the mill is turned on, vibration is transmitted (usually from the bottom center of the mill) through the chamber and into the media and powder. This results in two types of movement. First, it causes a cascading or mixing action of the contents of the milling chamber. Second, it causes local impact and shear fracturing of the powder particles between adjacent grinding media.

Vibratory milling is relatively fast and efficient and yields a finer powder than is usually achieved by ball milling. The vibratory mill chamber is typically lined with polyurethane or rubber and minimizes contamination. Vibratory mills are not used exclusively for powder processing. They are used extensively for deburring and cleaning of metal parts.

Fluid Energy Milling

Fluid energy mills achieve particle size reduction by particle-particle impact in a high-velocity fluid [13]. The fluid can be compressed air, nitrogen, carbon dioxide, superheated steam, water, or any other gas or liquid compatible with the specific equipment design. The powder is added to the compressed fluid and accelerated to sonic or near-sonic velocity through jets leading into the grinding chamber. The grinding chamber is designed to maximize particle-particle impact and minimize particle-wall impact.

Fluid energy milling can achieve controlled particle sizing with minimum contamination. Most jet mills have no moving parts and can be easily lined with polyurethane, rubber, wear-resistant steel, and even ceramics. Examples of particle sizing capabilities are shown in Table 5.5 [14]. Output capacity can range from a few grams per hour to thousands of kilograms per hour, depending on the size of the equipment.

The primary problem with fluid energy milling is collecting the powder. Large volumes of gases must be handled. Cyclones are not efficient for micrometer-sized particles and filters clog rapidly.

Hammer

Table 5.5 Typical Grinding Data for Fluid Energy Milling

Material	Mill diameter		Grinding medium	Material feed rate		Average particle size obtained	
	cm	in.		kg/hr	lb/hr	μm	in.
Al_2O_3	20.3	8	Air	6.8	15	3	0.00012
TiO_2	76.2	30	Steam	1020	2250	<1	<0.00004
TiO_2	106.7	42	Steam	1820	4000	<1	<0.00004
MgO	20.3	8	Air	6.8	15	5	0.0002
Coal	50.8	20	Air	450	1000	5–6	~0.00025
Cryolite	76.2	30	Steam	450	1000	3	0.00012
DDT 50%	61.0	24	Air	820	1800	2–3	~0.0001
Dolomite	91.4	36	Steam	1090	2400	<44	<0.0018
Sulfur	61.0	24	Air	590	1300	3–4	~0.00014
Fe_2O_3	76.2	30	Steam	450	1000	2–3	~0.0001

Source: Ref. 14, courtesy of Sturtevant Mill Company, Boston, Mass.

Hammer Milling

Hammer milling is also an impact approach, but the impact is applied by rapidly rotating blades, rather than particle-particle attrition. High levels of energy can be achieved, but particle sizing is difficult to control and contamination from the equipment is generally high. Hammer milling is usually used as an intermediate grinding step following rough crushing with a cone crusher or rolls and preceding ball milling, vibratory milling, or other fine-particle sizing techniques.

Precipitation

Precipitation of soluble salts followed by thermal decomposition to the oxide is a widely used method of both particle sizing and purifying of oxide ceramics [15]. Analogous techniques in controlled atmospheres have also been used to produce nonoxide ceramic powders.

The Bayer process for producing Al_2O_3 from bauxite relies on controlled precipitation. The aluminum hydroxide in bauxite is dissolved with caustic soda and separated from the nonsoluble impurities in the bauxite by filtering. Aluminum trihydrate is then precipitated by changing the pH, controlling the resulting particle size through addition of seed crystals. Table 5.6 lists the characteristics of commercially available Al_2O_3 powders and illustrates the variations in particle size, surface area, and purity that can be achieved in the precipitation process [16]. The very fine reactive alumina powders first became available in 1966 and have led to dramatic improvements in the properties of Al_2O_3 components and an expansion in the number and range of applications.

Freeze Drying

Freeze drying (also known as cryochemical processing) is a relatively new process which was first reported in 1968 by Schnettler et al. [17]. It has potential for producing uniform particle and crystallite sizing of very pure, homogeneous powder.

There are four steps in freeze drying:

1. A mixture of soluble salts containing the desired ratio of metal ions is dissolved in distilled water.
2. The solution is formed into droplets usually 0.1 to 0.5 mm in diameter and rapidly frozen so that no compositional segregation can occur and so that the ice crystals that nucleate are very small.
3. The water is removed in vacuum by sublimation, with care to avoid any liquid phase, thus preventing any chance for segregation.

4. The resulting powder is then calcined (heat-treated) at a temperature that decomposes the crystallized salts and converts them to very fine crystallites of the desired oxide or compound.

Most of the reported freeze drying has been conducted with sulfates. Each frozen droplet contains sheaths of sulfate crystals radiating from the center to the surface. During calcining, the oxide crystallites form in an oriented chainlike fashion along these radial sheaths. The size of the crystallites can be controlled by the time and temperature of calcining. Johnson and Schnettler [18] reported that a 10-hr 1200°C heat treatment of freeze-dried aluminum sulfate resulted in Al_2O_3 crystallites averaging 1500 Å and ranging from 600 to 2600 Å.

Not all compositions can be achieved by freeze drying. The two primary limitations are (1) the nonavailability of soluble salts containing the required metal ions and (2) the reaction of some salt combinations to form a precipitate. For instance, it has been difficult to find soluble salts that will yield lead zirconate titanate. Similarly, a mixture of barium acetate plus ferrous sulfate results in precipitation of insoluble $BaSO_4$.

Rigterink [19] described a laboratory apparatus and potential production approaches for freeze drying. The laboratory apparatus in quite simple and inexpensive and is adequate for making small batches for material processing development. The apparatus consists of a beaker containing hexane which is being mechanically stirred or swirled rapidly. The hexane container is surrounded by a bath of dry ice and acetone. The salt solution is forced through a glass nozzle as uniform drops of the desired size into the swirling hexane. The drops freeze rapidly and settle to the bottom, where they can be removed later by sieve.

Laser

The use of laser energy for synthesizing Si_3N_4 powder was discussed earlier in this chapter. It has also been used successfully to produce controlled particle sizes of silicon and SiC and appears to have potential for synthesizing oxides and other ceramic powders.

Plasma

Plasma spray techniques for applying coatings by depositing plasma-melted particles on a surface are discussed in Chap. 7. Particle sizing can be achieved by spraying the particles into an open space or a quench medium. Any oxide or ceramic composition that melts without decomposing can be handled by this approach. However, plasma spraying is expensive and the resulting powder is not optimum for most ceramic forming processes.

Table 5.6 Range in Powder Characteristics Available for Al_2O_3 Produced by Precipitation Using the Bayer Process

	Type[a]	Percent Na_2O	Average particle size (μm)	Surface area (m^2/g)	Compaction ratio	Final density
Nonreactive, high purity	A-10	0.06	>5	0.2	--	--
	C-75	0.01	2.8	0.49	2.25	2.97[b]
	A-14	0.06	--	0.6	--	--
	RC-122	0.03	2.6	0.35	2.35[c]	3.46[b]
Nonreactive, intermediate purity	A-12	0.24	--	0.5	--	--
	RC-24	0.23	2.9	0.53	2.35[c]	3.50[b]
	C-73	0.2	--	0.34	--	--
Nonreactive, low purity	A-2	0.46	3.25	--	2.21	3.22[b]
	RC-20	0.40	2.7	0.87	2.31[c]	3.37[b]
	C-70	0.50	2.5	0.66	2.28	3.18[b]
	RC-25	0.31	2.6	0.95	2.33[c]	3.52[b]
	A-5	0.35	4.7	--	2.30	3.07[b]
	C-71	0.75	2.2	0.71	2.24	3.33[b]
Reactive, high purity	XA-139	0.008	0.42	6.5	2.00	3.90[d]
	ERC-HP	0.008	0.55	7.4	2.15[e]	3.95[d]
	A-16	0.06	0.6	6.5	--	--
	RC-172	0.04	0.6	4.0	2.21[e]	3.94[d]
Reactive, low purity	A-3	0.36	0.63	9.0	1.79	3.64[b]
	RC-23	0.30	0.6	7.5	1.91[c]	3.86[b]
Reactive, nonreactive mixture	RC-152	0.05	1.5	2.6	2.30[c]	3.46[b]
	A-15	0.07	--	--	--	--

[a] C, Alcan; A, Alcoa; RC, Reynolds.
[b] For 1620°C/1 hr sintering.
[c] 20-g pellet pressed at 4000 psi, 4-hr grind.
[d] For 1510°C/2 hr sintering.
[e] 10-g pellet pressed at 5000 psi, 4-hr grind.
Source: Adapted from Ref. 16.

Other powder synthesis or sizing approaches using plasma equipment technology do exist, but very little information has been published and the specific techniques evidently are proprietary.

Calcining

Calcining is widely used for preparation of precursor ceramic powders for later processing steps and for achieving the optimum particle sizing. It consists essentially of a high-temperature heat treatment selected for each powder and optimized by prior research to achieve a specific objective. In one case, "calcining is used to decompose a salt or a hydrate to the oxide," such as that described earlier for achieving an oxide from a freeze-dried sulfate solution. In another case, "calcining is used to achieve the desired crystal phase and particle size," as described for preparation of Al_2O_3 from the Bayer process.

Calcining is also used for dehydration. The preparation of plaster from gypsum is a good example. Heat treatment at the right temperature partially dehydrates the gypsum ($CaSO_4 \cdot 2H_2O$) to $CaSO_4 \cdot 1/2H_2O$. This hemihydrate is plaster of paris and will rehydrate to form gypsum when water is added. Calcining at too high a temperature removes all the water from the gypsum and produces an anhydrous powder that will not easily rehydrate.

One of the most common uses of calcining is for coarsening, i.e., increasing the particle size of a very fine powder which has poor packing properties to a less-fine powder with improved packing properties. Usually, the coarsening consists of loose bonding of adjacent particles to form aggregates which act like larger particles during later processing steps, such as compaction.

5.3 PRECONSOLIDATION

The sized powders described in Sec. 5.2 are compacted into the desired shapes by techniques such as pressing, slip casting, and injection molding (discussed in Chap. 6) and then strongly bonded or densified (discussed in Chap. 7). To achieve a final component having uniform properties and no distortion requires a uniform particle compact. To achieve the required uniformity, the powder usually requires special treatments or processing prior to compaction. Table 5.7 summarizes some of these special preconsolidation considerations for several compaction or consolidation approaches.

The preconsolidation steps are essential to minimize severe fabrication flaws that can occur in later processing steps. For instance, a powder that is not free flowing can result in poor powder distribution in the pressing die and distortion or density variation in the final part. Similarly, improper viscosity control of a casting slurry can result in incomplete fill of the mold or a variety of other defects during slip casting. Inadequate dearing of

Table 5.7 Preconsolidation Steps for Several Consolidation Approaches

Pressing	Slip casting	Injection molding
Binder addition	Slurry preparation	Thermoplastic addition
Lubricant addition	Binder addition	Plasticizer addition
Sintering aid addition	Deflocculant addition	Wetting agent addition
Preparation of a free-flowing powder by spray drying or granulation	pH control	Lubricant addition
	Viscosity control	Sintering aid addition
	Percent solids control	Deairing
	Deairing	Granulation or pelletizing

either a slurry or an injection molding mix can result in a strength-limiting void in the final slip-cast or injection-molded part. Such fabrication flaws can reduce the strength of a material to a fraction of its normal value.

The following sections describe briefly some of the reasons and techniques of preconsolidation steps. Emphasis will be on preparation of a free-flowing powder suitable for pressing. Preconsolidation considerations for slip casting and injection molding are discussed in Chap. 6 as part of those specific processing steps.

Additives

Additives are required for different reasons, depending on the specific forming process. However, several general comments are relevant to most forming approaches:

1. Binders are added to provide enough strength in the "green" body (unfired compact) to permit handling, "green" machining, or other operations prior to densification.
2. Lubricants are added to decrease particle-particle and particle-tool friction during compaction.
3. Sintering aids are added to activate densification.
4. Deflocculants, plasticizers, wetting agents, and thermoplastics are added to yield the rheological (flow) properties necessary for the specific shape-forming process (discussed in detail in Chap. 6).

Table 5.8 Function of Additives to Ceramics

Additive	Function
Binder	Green strength
Lubricant	Mold release, interparticle sliding
Plasticizer	Rheological aids, improving flexibility of binder films, allowing plastic deformation of granules
Deflocculant	pH control, particle-surface charge control, dispersion, or coagulation
Wetting agent	Reduction of surface tension
Water retention agent	Retain water during pressure application
Antistatic agent	Charge control
Antifoam agent	Prevent foam
Foam stabilizer	Strengthen desired foam
Chelating or sequestering agent	Deactivate undesirable ions
Fungicide and bactericide	Stabilize against degradation with aging
Sintering aid	Aid in densification

Source: Ref. 20.

Table 5.8 further summarizes the function of additives [20].

A wide variety of binders are available, as shown by the partial listing in Table 5.9. Selection depends on a number of variables, including green strength needed, ease of machining, compatibility with the ceramic powder, and nature of the consolidation process. Gums, waxes, thermoplastic resins, and thermosetting resins are not soluble in water* and do not provide a benefit for slip casting, but are excellent for the warm mixing used to prepare a powder for injection molding. Organic binders can be burned off at low temperature and result in minimal contamination, whereas inorganic binders become a part of the composition.

*Emulsions can be used.

Table 5.9 Examples of Binders Used in Ceramic Processing

Organic	Inorganic
Polyvinyl alcohol (PVA)	Clays
Waxes	Bentonites
Celluloses	Mg-Al silicates
Dextrines	Soluble silicates
Thermoplastic resins	Organic silicates
Thermosetting resins	Colloidal silica
Chlorinated hydrocarbons	Colloidal alumina
Alginates	Aluminates
Lignins	Phosphates
Rubbers	Borophosphates
Gums	
Starches	
Flours	
Casein	
Gelatins	
Albumins	
Proteins	
Bitumens	
Acrylics	

Spray Drying

Spray drying is commonly used in ceramic processing to achieve a uniform, free-flowing powder [21-23]. As shown in Fig. 5.4, a spray drier consists of a conical chamber that can either be heated or has an inlet for hot air. The powder to be spray-dried is suspended in a slurry with the appropriate additives. Slurry preparation is most frequently done in a ball mill. The slurry is fed into the top of the spray drier through an atomizer and is swirled around by the hot air circulating in the conical spray drier chamber. The water evaporates and the powder forms into round, soft agglomerates.

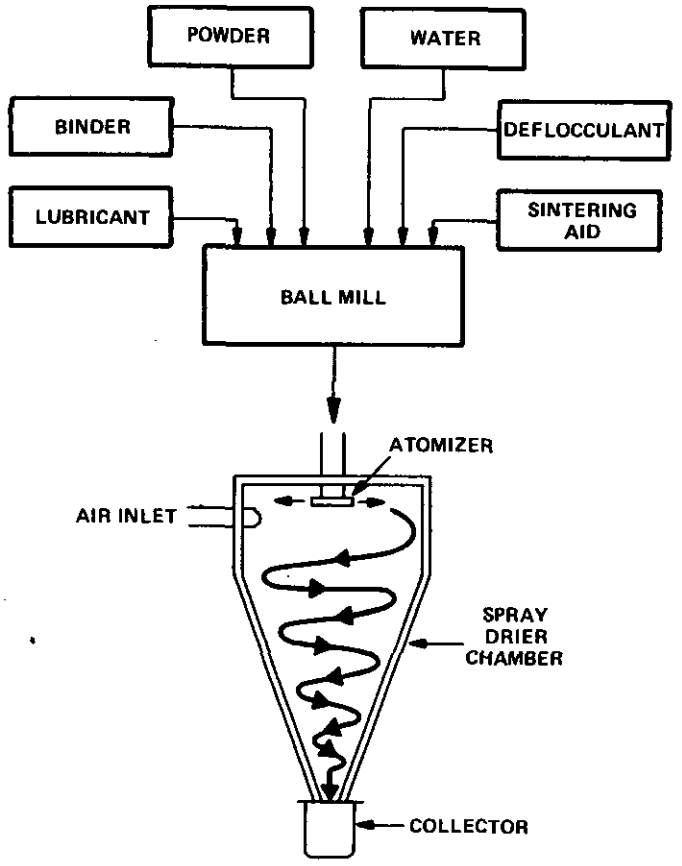

Figure 5.4 Schematic of the spray-drying process for achieving free-flowing spherical powder agglomerates containing a uniform level of additives.

These are less than 1 mm in diameter and are easily crushed during later pressing operations. Because all the particles have a spherical shape, the powder flows almost like a liquid and provides very uniform die fill for automated pressing.

Granulation

Granulation is another approach to achieving better flow properties of a powder. In this case, a slurry is not prepared. Instead, only a damp or plastic mix is prepared, usually with equipment such as a mix muller, a sigma mixer, or any of a variety of other commercially available mixer designs. For laboratory-scale batches, this mixing can be accomplished with a mortar and pestle or even by hand. The damp or plastic material is then forced through orifices of the desired size or screened. The resulting particle agglomerates are usually harder and more dense than spray-dried agglomerates and irregular in shape. They do not flow as readily, but do tend to pack to a lower volume.

The major advantage of granulation is that the powder is prepacked and takes up less volume during pressing, extrusion, or injection molding. In some cases, powders are precompacted at 703 to 1055 kg/cm^2 (10,000 to 15,000 psi) prior to granulation to assure relatively tight packing of the powder in each agglomerate. However, if this pressure is not equaled or exceeded during the shape-forming process, the agglomerates will not be crushed or fused together and the finished part will retain the identity of the agglomerates. This will consist of inhomogeneity in the part and for many applications will require that the part be rejected.

5.4 POWDER PROCESSING SUMMARY

Proper powder selection, sizing, and preconsolidation processing are vital to achieving the final desired shape and properties. Contamination and non-uniformity during powder processing will be carried throughout the rest of the processing and will usually lead to a deficient or rejectable component. This can only be avoided if quality control (QC) procedures are incorporated into each processing step. QC is not only the responsibility of the ceramic manufacturer, but also of the engineer who must use the finished parts or build them into a system. The interactions between QC and processing and the ways an engineer can be involved are discussed in Chap. 9. It might be worthwhile to preread the early sections of Chap. 9 before continuing on to Chap. 6.

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6

Shape-Forming Processes

The properly sized and preconsolidated powders are now ready for forming into the required shapes. Table 6.1 summarizes the major techniques for consolidation of powders and producing shapes. In this chapter we examine the major approaches in terms of the process steps and controls involved, the types of strength-limiting flaws that may result, and the range of shapes that can be produced.

6.1 PRESSING

Pressing is accomplished by placing the powder (premixed with suitable binders and lubricants and preconsolidated so that it is free flowing) into a die and applying pressure to achieve compaction. Typical flow sheets for granulated and spray-dried powders are shown in Fig. 6.1. The following section describes some of the critical factors for individual steps in the processing and some of the common problems encountered.

Binder and Lubricant Selection

Organic materials that provide a temporary bond between the ceramic particles are often required for pressing. These binders provide lubrication during pressing and give the pressed part enough strength and toughness that it can be handled and even machined prior to densification. The amount of binder required is quite low, typically ranging from 0.5 to 5%.

Binder selection is dependent on the type of pressing that will be conducted. Some binders such as waxes and gums are very soft and quite sensitive to temperature variations. These generally do not require moisture or lubricant additions prior to pressing, but must be handled more carefully to avoid changes in granule size that might alter flow characteristics into the pressing die or result in inhomogeneous density distribution. The soft binders also have a tendency to produce flash between the die components, which can cause sticking or reduce the production rate.

Table 6.1 Major Techniques for Powder Consolidation and Shape Forming

Pressing	Plastic forming
Uniaxial pressing	Extrusion
Isostatic pressing	Injection molding
Hot pressing[a]	Transfer molding
Hot isostatic pressing[a]	Compression molding
Casting	Others
Slip casting	Tape forming
Thixotropic casting	Flame spray[a]
Soluble-mold casting	Green machining

[a] These techniques combine consolidation and densification in one step and are discussed in Chap. 7.

Other binders can be classified as hard; i.e., they produce granules that are hard or tough. These granules have the advantage that they are dimensionally stable and free flowing and are therefore excellent for high-volume production with automated presses. However, these are generally not self-lubricating and thus require small additions of lubricant and moisture prior to pressing. They also require higher pressure to assure uniform compacts. If the starting powder agglomerates are not completely broken down into a continuous compact during pressing, artifacts of the approximate size of the agglomerates will persist through the remaining process steps and may act as large flaws, which will limit the strength.

Dextrine, starches, lignins, and acrylates produce relatively hard granules. Polyvinyl alcohol and methyl cellulose result in slightly softer granules. Waxes, wax emulsions, and gums produce soft granules.

Binder selection must also be compatible with the chemistry of the ceramic and the purity requirements of the application. The binder must be removed prior to densification of the ceramic. Organic binders can be removed by thermal decomposition. If reaction between the binder and the ceramic occurs below the binder decomposition temperature or if the ceramic densifies below this temperature, the final part will be contaminated or may even be cracked or bloated. If the temperature is raised too rapidly, the binder may char rather than decompose, leaving carbon.

Lubricants are used to aid in the redistribution of particles during pressing to obtain maximum packing, to improve powder flow into the die, and to minimize die sticking. Paraffin oil is often blended with granulated

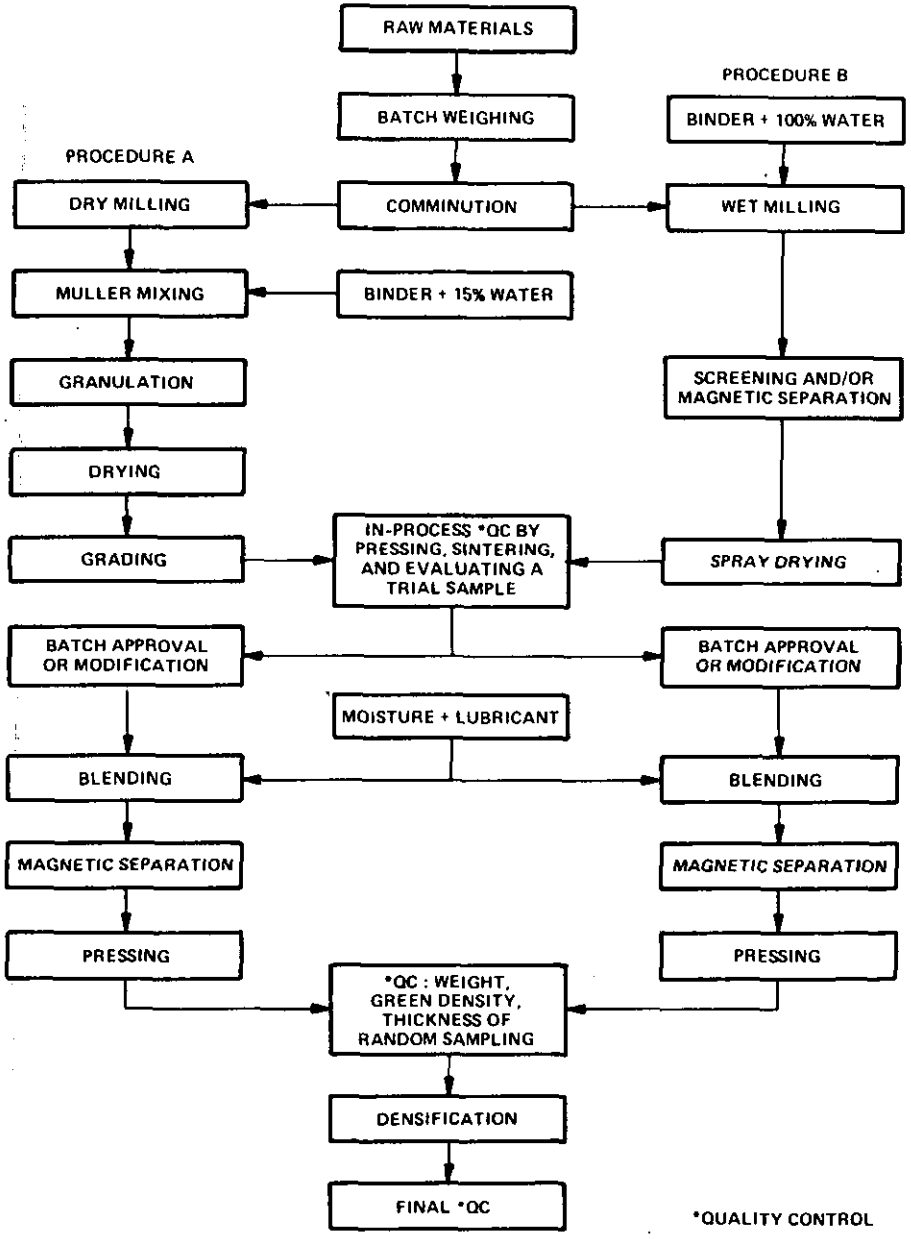


Figure 6.1 Typical flow sheets for fabrication by pressing. [Reprinted from Ceramic Fabrication Processes (W. D. Kingery, ed.), by permission of The MIT Press, Cambridge, Mass. © 1963, The MIT Press.]

or spray-dried powder prior to pressing. This is usually not required if waxes or wax emulsions are used as binders. Dry lubricants such as the stearates are also often used.

Uniaxial Pressing

Uniaxial pressing involves the compaction of powder into a rigid die by applying pressure along a single axial direction through a rigid punch, plunger, or piston. Thurnauer [1] and Whittemore [2] provide introductory descriptions of the approaches and some of the critical considerations of uniaxial pressing, especially automated pressing. The following discussion is derived largely from these two references.

Dry Pressing Most automated pressing is conducted with granulated or spray-dried powder containing 0 to 4% moisture. This is referred to as dry, semidry, or dust pressing. Compaction occurs by crushing of the granules and mechanical redistribution of the particles into a close-packed array. The lubricant and binder usually aid in this redistribution and the binder provides cohesion. *High pressures are normally used for dry pressing* to assure breakdown of the granules and uniform compaction.

High production rates and close tolerances can be achieved with dry pressing. Millions of capacitor dielectrics approximately 0.050 cm (0.020 in.) thick are made to close tolerances and with tightly specified electrical properties. Millions of electrical substrates, packages (thin-walled insulator "boxes" for isolating miniature electronic circuits), and other parts for a wide variety of *applications are made by dry pressing*. Dimensional tolerances to ±1% are normally achieved in routine applications, and closer tolerances have been achieved in special cases.

Wet Pressing Wet pressing involves a feed powder containing 10 to 15% moisture and is often used with clay-containing compositions. This feed powder deforms plastically during pressing and conforms to the contour of *the die cavity. The pressed shape* usually contains flash (thin sheets of material at edges where the material extruded between the die parts) and can deform after pressing if not handled carefully. For these reasons, wet pressing is not well suited to automation. Also, dimensional tolerances are usually only held to ±2%.

Types of Presses Most presses are either mechanical or hydraulic. Mechanical presses typically have a higher production rate. Figure 6.2 shows schematically the pressing sequence of a typical single-stroke mechanical press. The punches preposition in the die body to form a cavity predetermined (based on the compaction ratio of the powder) to contain the correct volume to achieve the required green *dimensions after compactions*. The feed shoe then moves into position and fills the cavity with free-flowing

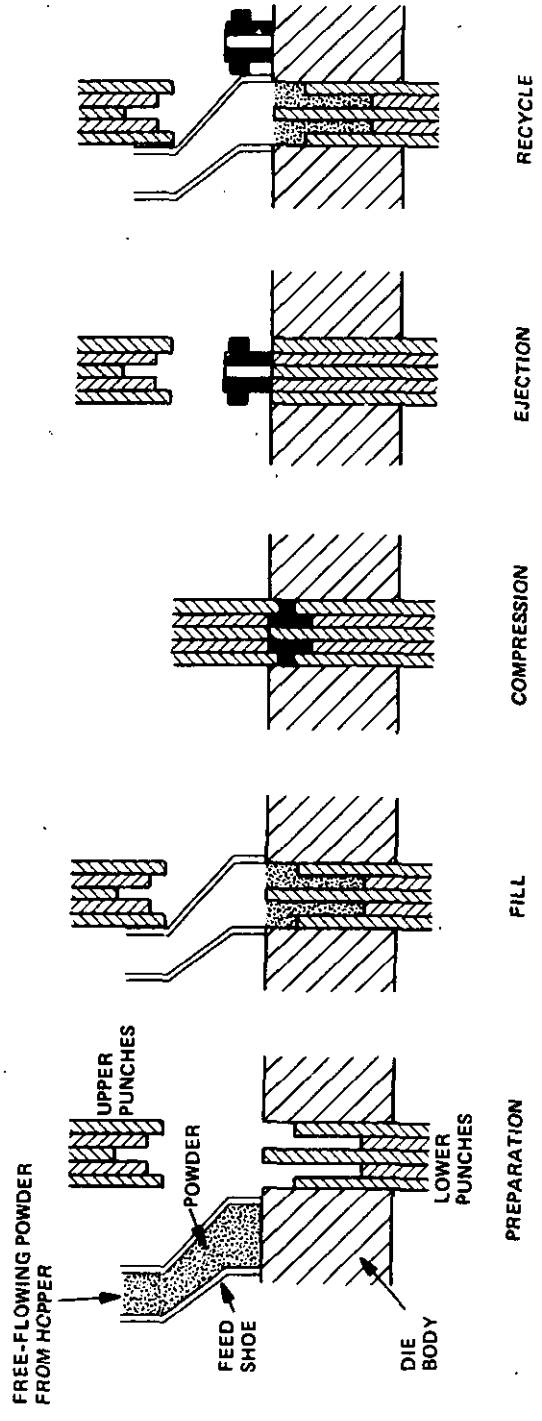


Figure 6.2 Typical single-stroke automated mechanical press cycle. (Adapted from Ref. 1.)

powder containing suitable binders, moisture, and lubricant. The feed shoe retracts, smoothing the powder surface as it passes, and the upper punches move down to precompress the powder. The upper and lower punches then simultaneously compress the powder as they independently move to preset positions. The upper punches retract and the lower punches eject the compact from the die body. The feed shoe then moves into position and pushes the compact away from the punches as the punches reset to accept the correct powder fill. This cycle repeats typically 6 to 100 times per minute, depending on the press and the shape being fabricated. Presses of this type generally have a capacity from 1 to 20 tons, but some operate up to 100 tons.

Another type of mechanical press is the rotary press. Numerous dies are placed on a rotary table. The die punches pass over cams as the table rotates, resulting in a fill, compress, and eject cycle similar to the one described for a single-stroke press. Production rates in the range of 2000 parts per minute can be achieved with a rotary press. Pressure capability is in the range 1 to 100 tons.

Another type of mechanical press is the toggle press. It is commonly used for pressing refractory brick and is capable of exerting pressure up to about 800 tons. The toggle press closes to a set volume so that the final density is controlled largely by the characteristics of the feed.

Hydraulic presses transmit pressure via a fluid against a piston. They are usually operated to a set pressure, so that the size and characteristics of the pressed component are determined by the nature of the feed, the amount of die fill, and the pressure applied. Hydraulic presses can be very large. Whittemore [2] mentions presses that can exert 5000 tons of pressure. Hydraulic presses have a much lower cycle rate than mechanical presses.

Uniaxial Pressing Problems The following are some of the problems that can be encountered with uniaxial pressing:

Improper density or size
Die wear
Cracking
Density variation

The first two are easy to detect by simple measurements on the green compact immediately after pressing. Improper density or size are often associated with off-specification powder batches and are therefore relatively easy to resolve. Die wear shows up as progressive change in dimensions. It should also be routinely handled by the process specification and quality control (see Chap. 9). However, since not all fabrication operations have suitable quality control, off-dimension parts can be delivered, and it then becomes the responsibility of the engineer using the parts to track down the source of the problem and make sure that the problem is resolved.

The source of cracking may be more difficult to locate. It may be due to improper die design, air entrapment, rebound during ejection from the die, die wear, or other causes. Furthermore, cracks may not be readily visible by routine inspection and may not even be detected by dye penetrant or x-ray radiography inspection. Their presence may not become known until the part fails in service. Again, the responsibility for locating a solution to the problem falls in the hands of the engineer in charge of the use of the component. In this case, the engineer must either work closely with the manufacturer to identify the source of cracking or must locate another source of the component.

Perhaps the most important problem to be overcome in uniaxial pressing is nonuniform density. Density variation in the green compact causes warpage, distortion, or cracking during firing. One source of density variation is the friction between the powder and the die wall and between powder particles [3–5]. As shown in Fig. 6.3, a uniaxial pressure applied from one end of a die full of powder will be dissipated by friction so that a substantial portion of the powder will experience much lower than the applied pressure. These areas will compact to a lower density than the areas exposed to higher pressure. The pressure difference increases as the length-to-diameter ratio increases. During firing, the lower-density areas will either not densify completely or will shrink more than surrounding areas. Both will result in flaws that can cause rejection of the part.

Use of suitable binders and lubricants can reduce both die wall and particle-particle friction and thus reduce density variation in the compact. Applying pressure from both ends of the die also helps. But perhaps the most fruitful approach is to work with an experienced die designer who knows the limitations of shape compaction in terms of width-to-thickness variation, shapes and tolerances achievable, and other factors relevant to the specific configuration and application.

Isostatic Pressing

Isostatic pressing (also called hydrostatic pressing or molding) involves application of pressure equally to the powder from all sides. This substantially reduces the problems of nonuniformity due to die wall and powder friction and permits uniform compaction of larger volumes of powder, including shapes with a large length-to-diameter ratio.

A schematic of an isostatic pressing apparatus is illustrated in Fig. 6.4. It consists of a thick-walled steel pressure vessel with either a breach-lock or pressure-seal cover. The powder is enclosed in a liquid-tight rubber mold and immersed in the fluid in the pressure vessel. Glycerine, hydraulic oil, water (with a suitable rust inhibitor), or other essentially noncompressible fluid is used. The fluid is pressurized, transmitting the pressure uniformly to all surfaces of the mold. The rubber deforms as the powder compacts, but springs back after the pressure releases and allows easy removal of the pressed part.

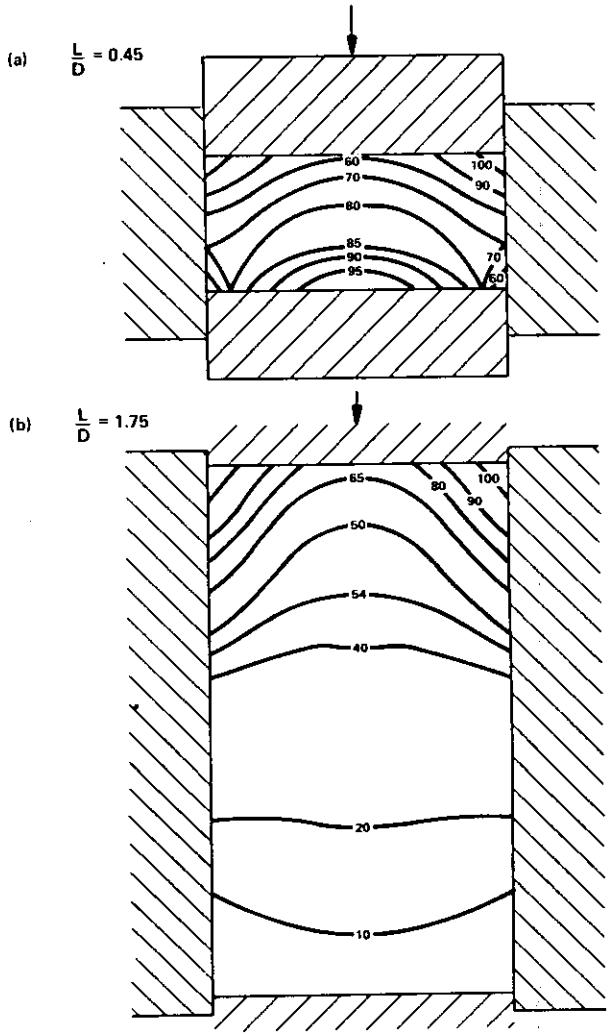


Figure 6.3 Pressure variations in uniaxial pressing due to die wall friction and particle-particle friction, which lead to nonuniform density of the pressed compact. [Adapted from Ceramic Fabrication Processes (W. D. Kingery, ed.), by permission of The MIT Press, Cambridge, Mass. © 1963, The MIT Press.]

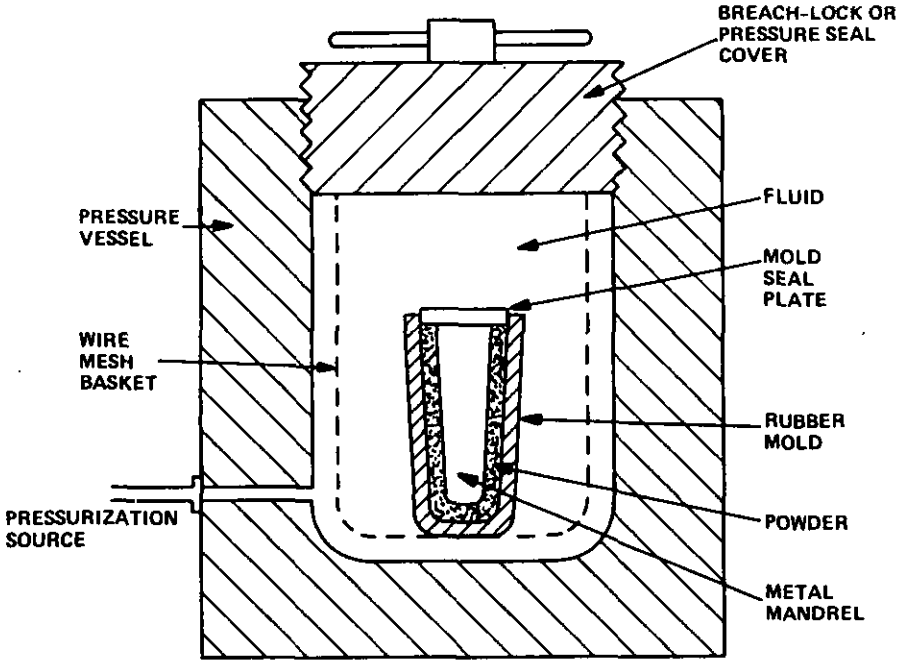


Figure 6.4 Schematic of an isostatic pressing system.

Laboratory isostatic presses have been built with pressure capabilities ranging from 35 to 1380 MPa (5000 to 200,000 psi). However, production units usually operate at 207 MPa (30,000 psi) or less.

A major concern in isostatic pressing is uniform fill of the mold. This is usually achieved by use of vibration plus free-flowing spray-dried or granulated powder. Since higher pressures are usually achieved by isostatic pressing than by uniaxial pressing and since these pressures are applied uniformly, a greater degree of compaction is achieved. This usually results in improved densification characteristics during the subsequent sintering step of processing and a more uniform, defect-free component.

The primary disadvantages of isostatic pressing are a limited production rate and difficulty in achieving close tolerances and good surface finish. Developments in the spark-plug insulator industry demonstrated that these limitations can be overcome. This was achieved by the use of a thick-walled single- or multicomposition rubber mold with controlled fluid passages for pressurization. The rubber material was flexible enough to transmit pressure but not to deform irregularly. The mold could be filled, pressed, and emptied automatically at a rate of 1000 to 1500 cycles per hour [6].

Applications of Pressing

Uniaxial pressing is widely used for compaction of small shapes, especially of insulating, dielectric, and magnetic ceramics for electrical devices. These include simple shapes, such as bushings, spacers, substrates, and capacitor dielectrics, and more complex shapes, such as the bases or sockets for tubes, switches, and transistors. Uniaxial pressing is also used for the fabrication of tiles, bricks, grinding wheels, wear-resistant plates, crucibles, and an endless variety of parts.

Isostatic pressing, typically in conjunction with green machining (which is discussed briefly later in the chapter), is used for configurations that cannot be uniformly pressed uniaxially or that require improved properties. Large components such as radomes, cone classifiers, and cathode-ray-tube envelopes have been fabricated by isostatic pressing. So also have bulky components for the paper industry. Small components with a large length-to-width ratio are also fabricated by isostatic pressing and machining.

Figure 6.5 shows a variety of ceramic parts that have been fabricated by uniaxial and isostatic pressing.

6.2 CASTING

When most engineers hear the term "casting," they automatically think of metal casting where a shape is formed by pouring molten metal into a mold. A limited amount of casting of molten ceramics is done in the preparation of high-density Al_2O_3 and Al_2O_3-ZrO_2 refractories and in preparation of some abrasive materials. In the latter case, casting from a melt into cooled metal plates produces rapid quenching, which results in very fine crystal size that imparts high toughness to the material.

More frequently, the casting of ceramics is done by a room-temperature operation in which ceramic particles suspended in a liquid are cast into a porous mold which removes the liquid and leaves a particulate compact in the mold. There are a number of variations to this process, depending on the viscosity of the ceramic-liquid suspension, the mold, and the procedures used. The most common is referred to as slip casting. The principle and controls for slip casting are similar to those of the other particulate ceramic casting techniques. Slip casting is described in detail, followed by a brief description of less used techniques.

Slip Casting

Most commercial slip casting is conducted with ceramic particles suspended in water and cast into porous plaster molds. Figure 6.6 shows the critical process steps in slip casting and some of the process parameters

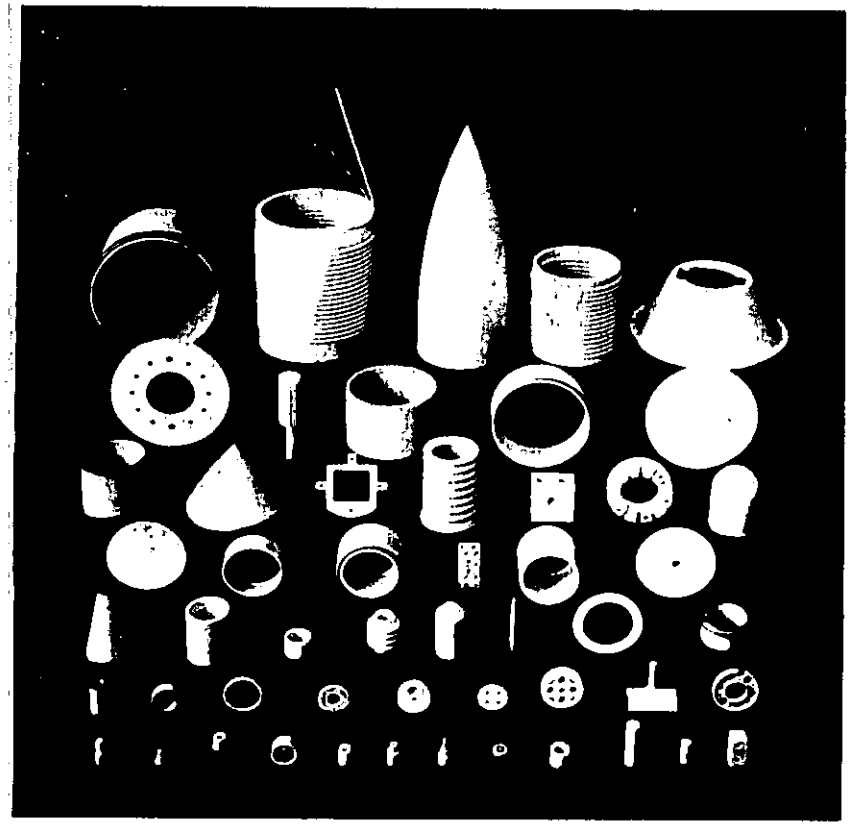


Figure 6.5 Ceramic parts formed by uniaxial and isostatic pressing, some with green machining. (Courtesy of Western Gold and Platinum Company, Belmont, Calif., Subsidiary of GTE Sylvania, Inc.)

that must be carefully controlled to optimize strength or other critical properties.

Raw Materials Selection of the starting powder is dependent on the requirements of the application. Most applications require a fine powder, typically -325 mesh. Applications requiring high strength require even finer powders, averaging under 5 μm, with a substantial portion under 1 μm. Some applications, such as kiln furniture, which must withstand cyclic thermal shock, may require a bimodal particle size with some particles considerably larger than 325 mesh.

The chemical composition is frequently an important consideration in selecting the starting powders and additives. Impurities and second phases can have pronounced effects on high-temperature properties.

Powder Processing As discussed in Chap. 5, powder as received from the supplier does not usually meet all the specifications for the shape-forming process or application and must be processed. Processing for slip casting usually involves particle sizing to achieve a particle size distribution that will yield maximum packing and uniformity during casting. Often, particle sizing is combined in one step with addition of binders, wetting

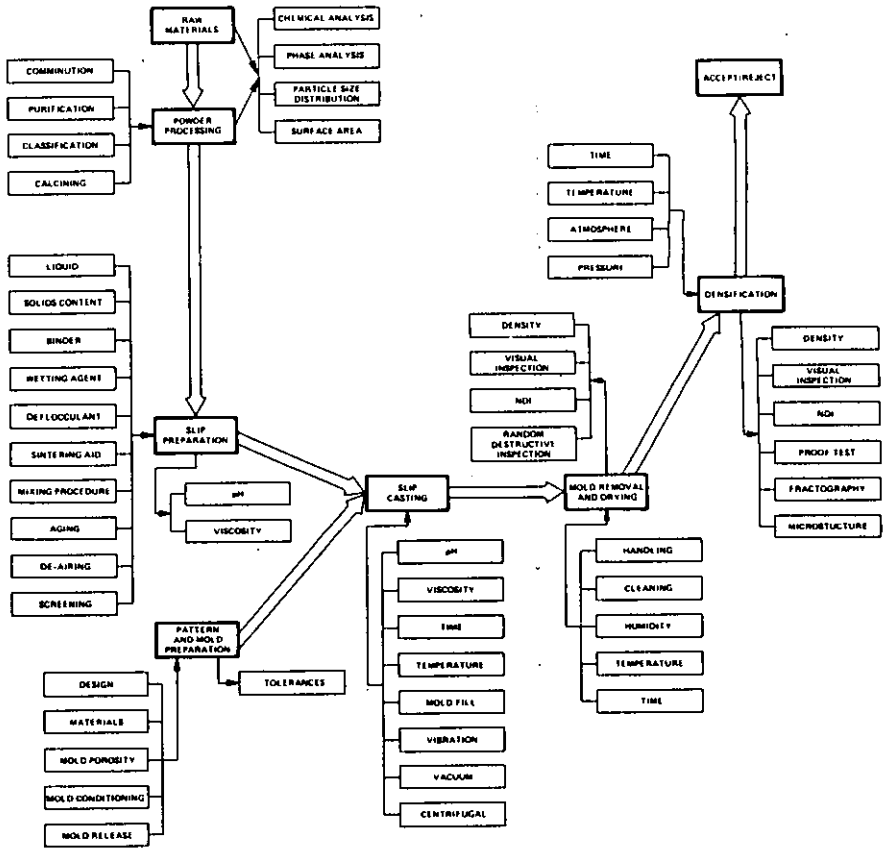


Figure 6.6 Critical process steps in slip casting and some of the process parameters that must be carefully controlled.

agents, deflocculants, and densification aids and with slip preparation. This is usually done by ball milling, but can also be done by vibratory milling or other process that provides wet milling. After milling, the slip is screened and perhaps passed through a magnetic separator to remove iron contamination. Slight adjustment might be required to achieve the desired viscosity and then the slip is ready for aging, deairing, or casting.

Slip Preparation To understand slip preparation considerations one needs to understand a little about rheology. Rheology is the study of flow characteristics of matter, e.g., suspensions of solid particles in a liquid, and is described quantitatively in terms of viscosity η. For low concentrations of spherical particles where no interaction occurs between either the particles or the particles and the liquid, the Einstein relationship applies:

$$\frac{\eta}{\eta_0} = 1 + 2.5V \tag{6.1}$$

where η is the viscosity of the suspension, η_0 the viscosity of the suspending fluid, and V the volume fraction of solid particles. This idealized relationship implies that the resulting viscosity is essentially controlled by the volume fraction of solids. In actual systems, the volume fraction does have a major effect, but so also do particle size, particle surface charges, and particle shape. The following discussion on the nature of these effects is largely derived from Michaels [7].

Decreasing particle size typically results in an increase in viscosity because of increased particle-particle interaction. For a given volume fraction of solids, the smaller the particle size, the closer the particles will be to each other and the greater the chance for interaction. Michaels used the following example assuming 40 vol % spherical particles:

Particle diameter (μm)	Mean distance between particle surfaces (Å)
10	9200
1	920
0.1	92
0.05	20
0.01	9.2

Van der Waals forces of attraction at surfaces are generally strong enough to affect another surface within a range of about 20 Å. It is apparent from the example above that, even in a relatively dilute suspension, considerable particle-particle attraction can occur and that the effect will be increased as the mean particle size decreases or the percent of submicron particles increases. This particle-particle attraction will increase the viscosity by increasing the force required to move one particle past another.

Particle shape is also important. Nonspherical particles, especially rods or plates, approach each other much more closely in a suspension than do spherical particles of an equivalent volume. This consideration is especially relevant in suspensions of clay particles. Clay was traditionally added to a casting slip to provide controlled suspension characteristics. Clays such as kaolinite are made up of thin hexagonal plate-shaped crystals. Michaels [7] used the following example to illustrate the shape effect:

Edge length of plate (μm)	Thickness of plate (μm)	Volume fraction of solid at which mean distance between particle surfaces is 20 Å
10	1	30
1	0.1	30
0.1	0.01	28
0.01	0.001	17

This can be compared to a mean spacing of 20 Å with 0.01-μm-diameter spherical particles at a volume fraction of 40% in the previous example.

For high-solid-content suspensions, particle-particle attraction results in the formation of agglomerates. In some cases these agglomerates can act essentially like roughly spherical particles and result in a decrease in viscosity. In other cases, especially for very high solids content, the agglomerates can interact with each other and further increase the viscosity.

Dispersion and flocculation (agglomeration) of ceramic particles in a fluid are strongly affected by the electrical potential at the particle surface, adsorbed ions, and the distribution of ions in the fluid adjacent to the particle. Thus the chemical and electronic structure of the solid, the pH of the fluid, and the presence of impurities are all critical considerations in the preparation of a slip for casting. Kaolinite clay has been studied extensively and is a good example.

At pH 6 or higher, where low concentrations of sodium or lithium cations are present, kaolinite is well dispersed in water. Under these conditions, each particle has a slight negative charge and the particles repel each other. However, if aluminum or iron salts are present in low concentration ($\sim 10^{-5}$ molar), the net charge on each particle is decreased and flocculation occurs. On the other hand, if the pH is below 6 and a $\sim 10^{-3}$ molar concentration of aluminum or ferric halides is present, the kaolinite will be dispersed. This is because the charge has been reversed under these conditions and the particles again repel each other because they have adequate levels of like charge. A similar situation exists when the pH is below 2 and monovalent anions such as chloride, nitrate, or acetate are present.

Low concentrations (0.005 to 0.3%) of certain organic and inorganic compounds have a strong dispersing effect on kaolinite suspensions. Some of these include sodium silicate, sodium hexametaphosphate (Calgon), sodium oxalate, sodium citrate, and sodium carbonate. These tend to ion exchange with ions such as calcium and aluminum, which prevent surface charge buildup and leave sodium, which allows a residual charge and causes repulsion between particles. Approximately 0.1% addition of sodium silicate reduces the viscosity by a factor of about 1000 [8].

Casting slips can also be formed with ceramics other than clays [9]. Success in casting depends largely on the ability to disperse these nonclay particles and achieve high solids concentrations. For most oxides, dispersion can be controlled by pH using the polar properties of water and the ion concentrations of acids or bases to achieve charged zones around the particles so that they repel each other. For instance, an Al_2O_3 slip with a specific gravity of 2.8 g/cm^3 had a viscosity of 65 cP at a pH of 4.5, but 3000 cP at a pH of 6.5 [10]. The slip at a pH of 4.5 was well dispersed and had good casting properties. It also was not extremely sensitive to changes in the solids content. Reducing the specific gravity to 2.6 g/cm^3 resulted in only a factor of 2 decrease in viscosity. For comparison, decreasing the specific gravity of the pH 6.5 slip to 2.6 g/cm^3 resulted in a tenfold decrease in viscosity.

Proper dispersion of the slip is perhaps the most important parameter in slip casting, warrants a more thorough discussion than some of the other parameters.

The actual physical preparation of the slip can be done by a variety of techniques. Perhaps the most common is wet ball milling or mixing. The ingredients, including the powder, binders, wetting agents, sintering aids, and dispersing agents, are added to the mill with the proper proportion of the selected casting liquid and milled to achieve thorough mixing, wetting, and (usually) particle size reduction. The slip is then allowed to age until its characteristics are relatively constant. It is then ready for final viscosity checking (and adjustment, if necessary), deairing, and casting.

Mold Preparation The mold for slip casting must have controlled porosity so that it can remove the fluid from the slip by capillary action. The mold must also be low in cost. The most common mold material is plaster [11].

Plaster molds are prepared by mixing water with plaster of paris powder, pouring the mix into a pattern mold, and allowing the plaster to set. This produces a smooth-surface mold duplicating the contours of the pattern. For a complex shape, the mold is made in segments, each of which is sized so that it can be removed after slip casting without damaging the delicate casting.

Plaster of paris (hemihydrate) is partially dehydrated gypsum:

$$CaSO_4 \cdot 2H_2O \xrightarrow{180°C} H_2O + CaSO_4 \cdot 1/2H_2O \qquad (6.2)$$

Gypsum Hemihydrate

The reaction is reversible; addition of water to the hemihydrate results in precipitation of very fine needle-shaped crystals of gypsum which intertwine to form the plaster mold. The reaction is satisfied chemically by addition of 18% water, but considerably more water is necessary to provide a mixture with adequate fluidity for mold making. This extra water fills positions between the gypsum crystals during precipitation and results in very fine capillary porosity after the finished plaster mold has been dried. It is this porosity that draws the water out of the slip during slip casting. The amount of porosity can be controlled by the amount of excess water added during fabrication of the plaster mold. For normal slip casting, 70 to 80 wt % water is used.

The setting rate of plaster can be widely varied by impurities.

Casting Once the mold has been fabricated and properly dried and an optimum slip has been prepared, casting can be conducted. Many options are available, depending on the complexity of the component and other factors:

Simple casting into a one-piece mold
Simple casting into a multipiece mold
Drain casting
Solid casting
Vacuum casting
Centrifugal casting
Casting with nonabsorbing pins or mandrels inserted into the mold

Figure 6.7 illustrates schematically drain casting. The slip is poured into the mold and water is sucked out where the slip is in contact with the mold, leaving a close-packed deposition of particles growing into the slip from the mold walls. The slip is left in the mold until the desired thickness is built up, at which time the remaining slip is drained from the mold.

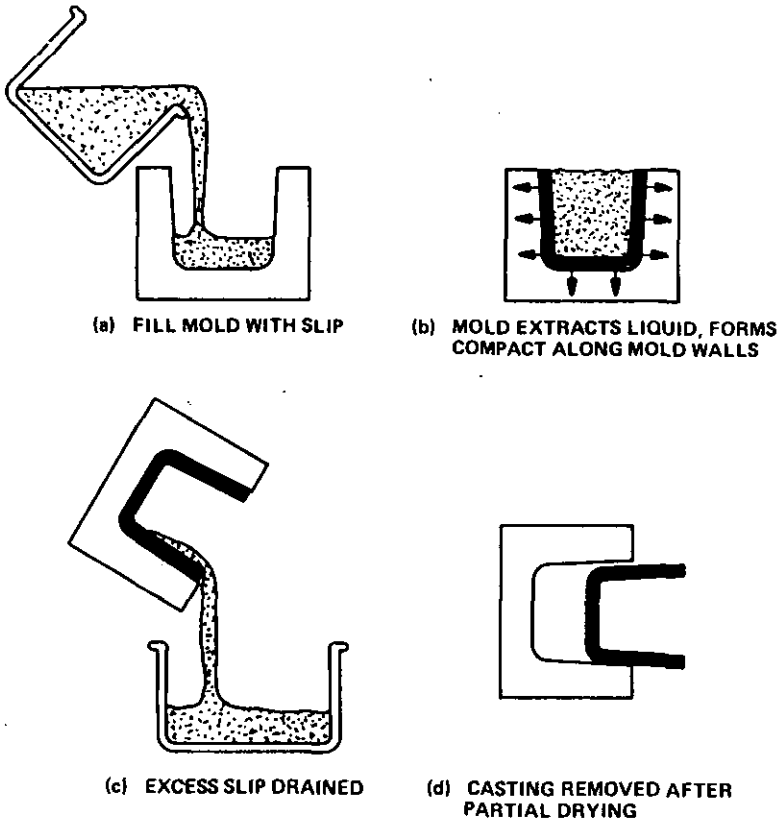


Figure 6.7 Schematic illustrating the drain-casting process.

Drain casting is the most common *slip-casting approach. It is used for* art casting (figurines), sinks and other sanitary ware, crucibles, and a variety of other products.

Solid casting is identical to drain casting except that slip is continually added until a solid casting has been achieved.

Vacuum casting can be conducted either with the drain or solid approach. A vacuum is pulled around the outside of the mold. In some cases this either increases the casting rate or uniformity and improves the economics or quality.

Centrifugal casting involves spinning the mold to apply greater-than-normal gravitational loads to make sure that the slip completely fills the mold. This can be beneficial in the casting of some complex shapes.

Considerable sharpness and complexity of detail can be designed into a *slip-casting* mold. The well-known Hummel figurines are a good example. A more-engineering oriented example is illustrated in Fig. 6.8. It consists of a one-piece annular combustor of SiC fabricated by the Norton Company.

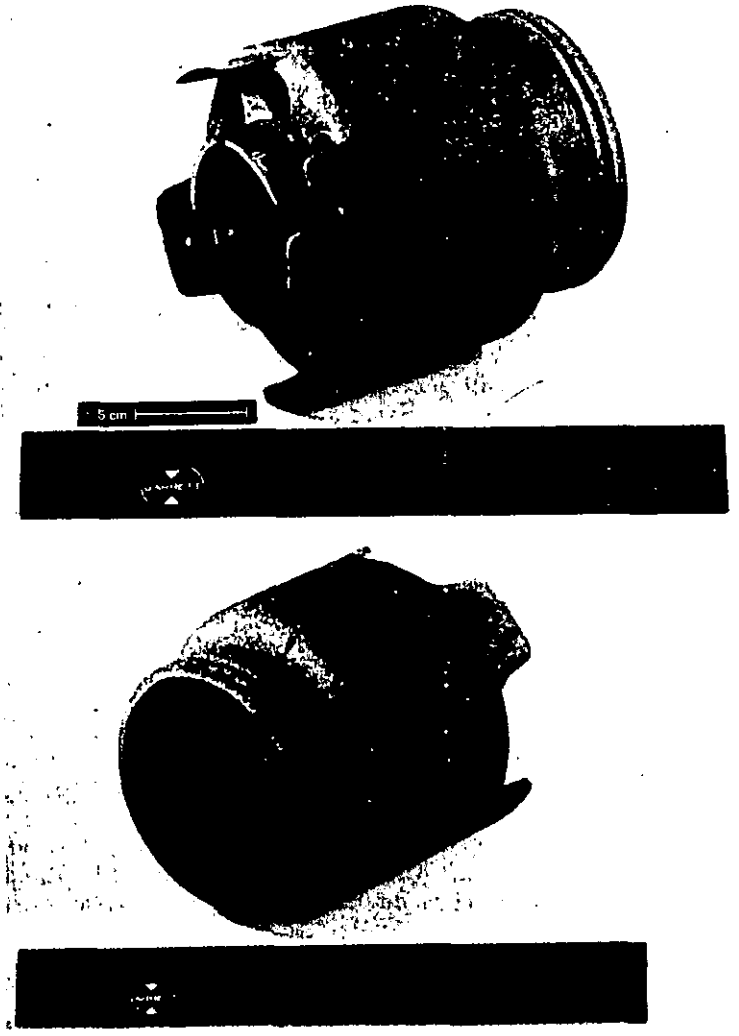


Figure 6.8 Complex annular combustor of SiC for a gas turbine engine fabricated by drain casting. (Courtesy of the Garrett Turbine Engine Company, Phoenix, Ariz., Division of The Garrett Corporation.)

A multipiece mold was required with a segmented plaster outer wall, an inner plaster mandrel, a contoured plaster base block, and nonabsorbing pins (to form the holes). The combustor shape to near-final tolerances was then achieved by drain casting.

Casting Process Control As was illustrated in Fig. 6.6, careful process is necessary in the slip-casting process. St. Pierre [10] lists the following as critical:

Constancy of properties
Viscosity
Settling rate
Freedom from air bubbles
Casting rate
Drain properties
Shrinkage
Release properties
Strength

A detailed working knowledge with suitable specifications and certification procedures of the relative needs of each of the criteria listed above is a requirement for the manufacturer for each component. An awareness of the defects and/or effects on properties are desirable for the engineer in charge of the use of the component or its integration into a system. It usually takes interaction between the user and manufacturer to resolve a quality problem.

Constancy of properties refers to the reproducibility of the casting slip and its stability as a function of time. The slip must be easily reproduced and preferably should not be overly sensitive to slight variations in solids content and chemical composition or to storage time. The viscosity must be low enough to allow complete fill of the mold, yet the solids content must be high enough to achieve a reasonable casting rate. Too-slow casting can result in thickness and density variations due to settling. Too-rapid casting can result in tapered walls (for a drain casting), lack of thickness control, or blockage of narrow passages in the mold.

The slip must be free of entrapped air or chemical reactions that would produce air bubbles during casting. Air bubbles present in the slip will be incorporated in the casting and may be critical defects in the final densified part.

Once casting has been completed, the part begins to dry and shrink away from the mold. This shrinkage is necessary to achieve release of the part from the mold. If the casting sticks to the mold, it will usually be damaged during removal and rejected. Mold release can be aided by coating the walls of the mold with a release agent such as a silicone or olive oil.

However, it should be recognized that the coating may alter the casting rate.

The strength of the casting must be adequate to permit removal from the mold, drying, and handling prior to the firing operation. Usually, a small amount (<1%) of binder is included in the slip. Organic binders such as polyvinyl alcohol work well. With the binder present, strength comparable to or greater than blackboard chalk is achieved. Such strength is adequate for handling and also for green machining if required.

Soluble Mold Casting

Soluble mold casting is a new approach based on the much older technology of investment casting. It is also referred to as fugitive wax slip casting [12-14] and is accomplished in the following steps:

1. A wax pattern of the desired configuration is produced by injection-molding a water-soluble wax.
2. The water-soluble wax pattern is dipped in a non-water-soluble wax to form a thin layer over the pattern.
3. The pattern wax is dissolved in water, leaving the non-water-soluble wax as an accurate mold of the shape.
4. The wax mold is trimmed, attached to a plaster block, and filled with the appropriate casting slip.
5. After the casting is complete, the mold is removed by dissolving in a solvent.
6. The cast shape is dried, green machined as required, and densified at high temperature.

The application of the fugitive wax approach is illustrated in Fig. 6.9 for the fabrication of a complex-shaped stator vane for a gas turbine engine. The injection molding tool on the right produces the water-soluble wax stator vane pattern. The injection molding tool on the left produces the pattern for the reservoir which will hold the slip and guide it through gating channels into the stator vane mold during casting. The reservoir and vane patterns are bonded together by simple wax welding and are shown as the white wax assembly in the center of Fig. 6.9. Below this is the mold produced by dipping and dissolving the pattern. Below the mold is the green casting after dissolving the mold and trimming off any material remaining in the reservoir or gating area.

Very complex shapes can be fabricated by the soluble mold technique. Figure 6.10 shows integral gas turbine stators made by this approach. Individual vanes were injection molded and then welded together to form a pattern such as the one in the upper right of Fig. 6.10a. This was then dipped as a unit to form a one-piece mold.

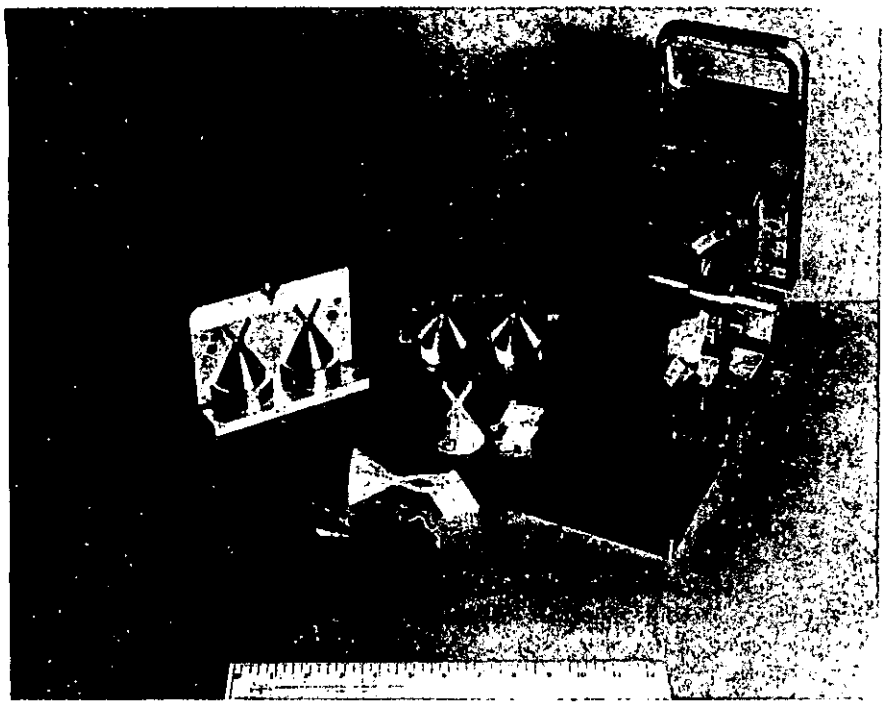
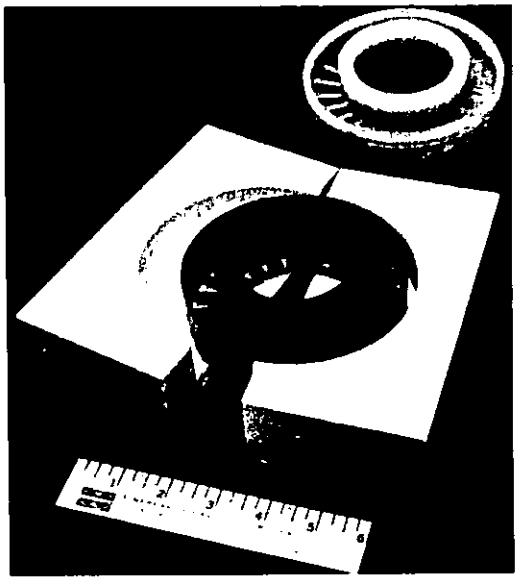


Figure 6.9 Tooling, patterns, mold, and cast part illustrating the fugitive wax slip-casting process as applied to the fabrication of a gas turbine stator vane. (Courtesy of AiResearch Casting Company, Torrance, Calif., Division of The Garrett Corporation.)

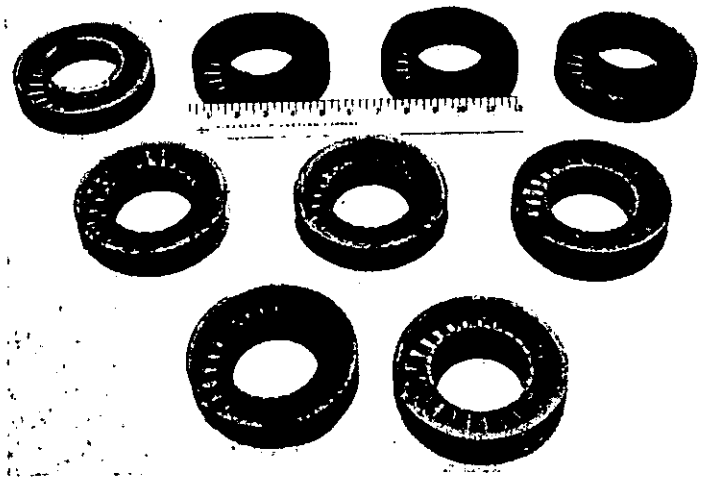
6.3 PLASTIC FORMING

Plastic forming involves producing a shape from a mixture of powder and additives that is deformable under pressure. Such a mixture can be obtained in systems containing clay minerals by addition of water and small amounts of a deflocculant, a wetting agent, and a lubricant. In systems not containing clay, such as pure oxides and carbides and nitrides, an organic material is added in place of water or mixed with water to provide the plasticity. About 25 to 50 vol % organic additive is required to achieve adequate plasticity for forming. Heat normally must be supplied simultaneously to pressure.

A major difficulty in the plastic-forming processes is removing the organic material prior to firing. In the case of a water-clay system,



(a)



(b)

Figure 6.10 Slip casting of an integral gas turbine stator using the fugitive wax process. (a) The water-soluble pattern and the resulting mold interfaced with a plaster block. (b) As-cast stators prior to trimming or machining. (Courtesy AiResearch Casting Company, Torrance, Calif., Division of The Garrett Corporation.)

substantial shrinkage occurs during drying, increasing the risk of shrinkage cracks. In the case of organic additives, the major problems are achieving high enough green density and extraction of the organic. Too rapid extraction causes cracking, bloating, or distortion. Inadequate removal results in cracking, bloating, or contamination during the later high-temperature *densification process.*

Plastic processes are used extensively in the fabrication of traditional ceramics such as pottery and dinnerware. The compositions contain clay and have been made workable by addition of water. Hand forming and jiggering are common fabrication techniques. These operations will not be discussed in this text. Instead, the emphasis will be on either standard techniques applied to demanding shapes or on emerging techniques applicable to modern ceramic applications. Most of the discussion will be on injection molding and extrusion.

Injection Molding

Injection molding is a low-cost, high-volume production technique for making net-shape or near-net-shape parts. A feed material consisting of or containing a thermoplastic polymer or a thermosetting polymer is preheated in the "barrel" of the injection molding machine to a temperature at which the polymer has a low-enough viscosity to allow flow if pressure is applied. A ram or plunger is pressed against the heated material in the barrel by either a hydraulic, pneumatic, or screw mechanism. The viscous material is forced through an orifice into a narrow passageway which leads to the shaped tool cavity. This helps compact the feed material and remove porosity. At the end of the passageway, the strand of viscous material passes through another orifice called the sprue and into the tool cavity. The strand then piles upon itself until the cavity is full and the material has "knit" or fused together under the pressure and temperature to produce a homogeneous part.

Injection molding is used extensively in the plastics industry to make everything from garbage cans to ice cube trays to surprisingly complex constructible toys such as model boats and airplanes. Ceramic parts are made with the same injection molding equipment, but with dies made of harder, more wear-resistant metal alloys. The ceramic powder is essentially added to the plastic as a filler. After injection molding the plastic is then removed by careful thermal treatments.

Injection Molding Parameters Very little has been published on the parameters for injection molding of ceramics. Figure 6.11 lists the general steps in injection molding and some of the controls and inspection procedures that must be considered.

Particle size distribution is important in injection molding to achieve the densest packing and to minimize the amount of organic material. Both

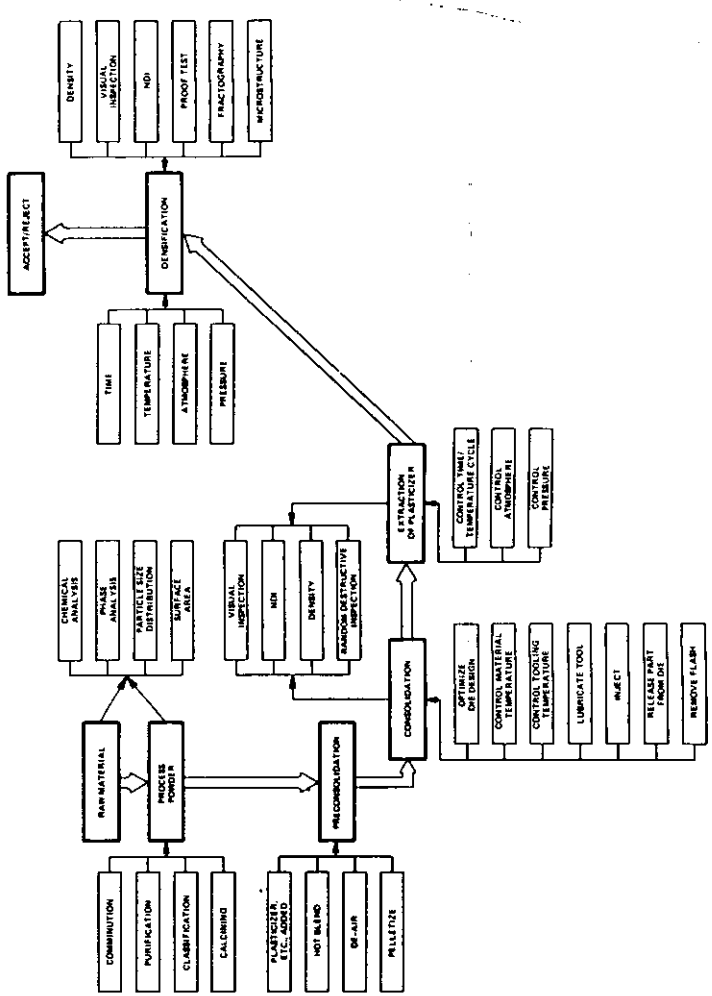


Figure 6.11 Injection molding process flow sheet.

particle packing and sizing affect viscosity. Farris [15] reports that viscosity starts increasing rapidly at about 55 vol % solids for a unimodal suspension of spheres, but that the solids loading can be increased to over 70% before the viscosity starts increasing rapidly for a bimodal distribution containing about 25% fine spheres. By using a graduated particle size distribution, Mangels [16] has successfully injection molded complex shapes of silicon powder having 76.5 vol % solids. His tests were conducted on a plunger-type injection machine at a cylinder pressure of 13.8 MPa (2000 psi) and a temperature 10°C above the melting temperature of the organic binder.

Whalen et al. [17] report injection molding of SiC with a solids content of 52 vol % using a thermosetting resin. They preheated a dry ball milled mixture of the ceramic and organic powder in the barrel of a plunger-type injection molder at 116°C [241°F) for 1 min and then injected the mixture into a mold preheated to 155°C (310°F).

Injection molding can also be conducted using a thermoplastic resin. In this case, though, the mold must be cooler than the temperature of the preheated material.

Injection Molding Defects A variety of defects can occur during the injection molding operation. Table 6.2 summarizes some of these defects and the likely causes.

An incomplete part is usually easy to detect visually and can be rejected immediately after injection molding. Large pores intersecting the surface are also easy to detect and reject. Internal pores require nondestructive inspection (NDI) techniques such as radiography or ultrasonics (described in Chap. 9). However, the capabilities of these NDI techniques are currently limited and some pores may not be detected until they cause failure of the component. Sometimes proof testing (also described in Chap. 9) can be successfully used to reject these defective parts.

Knit lines are areas where the injected material does not properly fuse together. They represent a discontinuity or a weak region in the part. They usually have a laminar or folded appearance. Some can be severe and are easily visible if they intersect the outer surface of the part. Others are very subtle and difficult to detect, even with NDI techniques.

Cracks, like knit lines, can be present in a wide range of severity and visibility. The more severe cases are easy to see visually and can be rejected. Others can be detected by dye penetrant inspection or by inspection at low magnification (up to about 40×) of critical areas.

The application engineer usually does not get involved with defect detection until a part or series of parts have failed in service. It is then vital that he determine the source of failure as soon as possible and develop a solution. Chapter 12 describes powerful techniques for detecting the cause of a failure.

Table 6.2 Injection Molding Defects and Causes

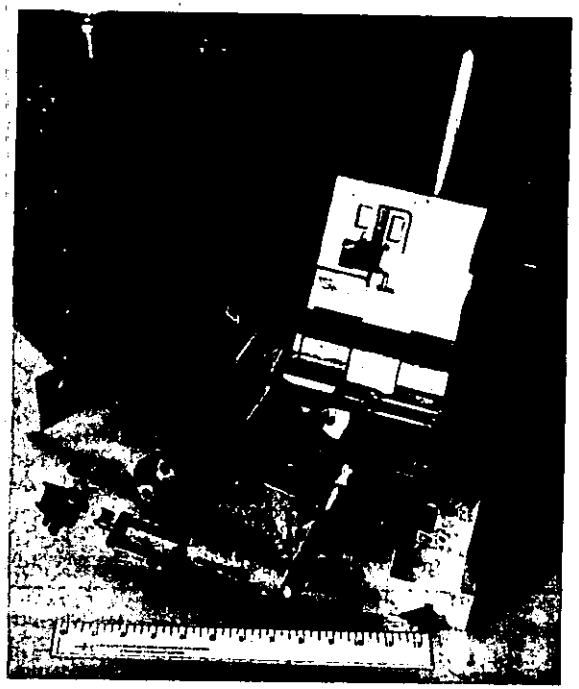
Description of defect	
Incomplete part	Improper feed material, poor tool design, improper material and/or tool temperature, inadequate tool lubrication
Large pores	Entrapped air, improper material flow and consolidation during injection, agglomerates, or large pockets of the organic due to incomplete mixing
Knit lines	Improper tool design or feed material, incorrect temperatures
Cracks	Sticking during removal from tool, improper tool design, improper extraction of the organic

Injection Molding of Complex Shapes Injection molding is currently being developed for net-shape forming of complex aerodynamic rotating and stationary components for prototype gas turbine engines. Figure 6.12 shows a simple injection molding tool for fabricating individual stator vanes [14]. Two strength test bars are injected with each stator vane and accompany that vane through subsequent processing. The strength and microstructure of these bars can then be used for certification purposes to assure the manufacturer and customer that the material meets the required property specification. The other two tabs of material shown in Fig. 6.12 are overflow material. They contain any debris that may have inadvertently been in the tool passages and any excess lubricant.

Figure 6.13 shows larger, more complex prototype gas turbine parts. These were fabricated by the Ford Motor Company [17,18]. The top parts are integral stators made of reaction-bonded Si_3N_4, and the bottom parts are rotor blade rings also made of reaction-bonded Si_3N_4.

Compression Molding

Compression molding, transfer molding, and warm molding are all plastic fabrication processes similar to injection molding. In each case, the ceramic powder is in an organic carrier and is forced into a shaped tool under pressure and temperature. Compression molding also has similarities to pressing, except that a slug of material rather than a free-flowing powder is used for feed. The shape is built into the platens of the press or the faces of the tool and the mix plastically deforms under pressure to fill the cavity.



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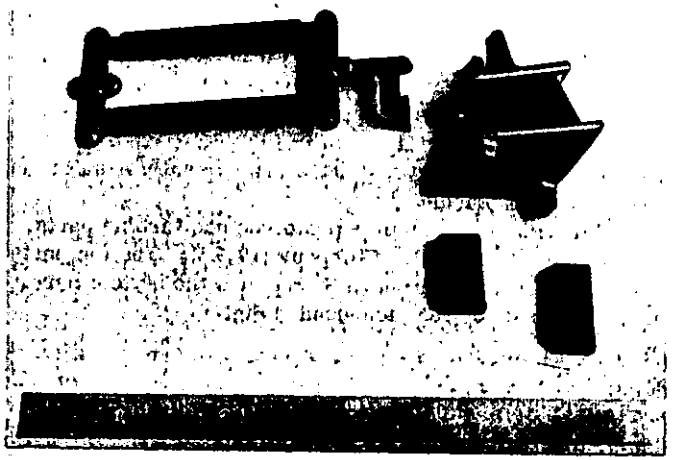


(b)

Figure 6.12 (a) Injection molding tool for fabrication of individual stator vanes for a gas turbine engine. (b) Close-up of the stator vane, test bar gating, and overflow material from a single injection. (Courtesy of AiResearch Casting Company, Torrance, Calif., Division of The Garrett Corporation.)

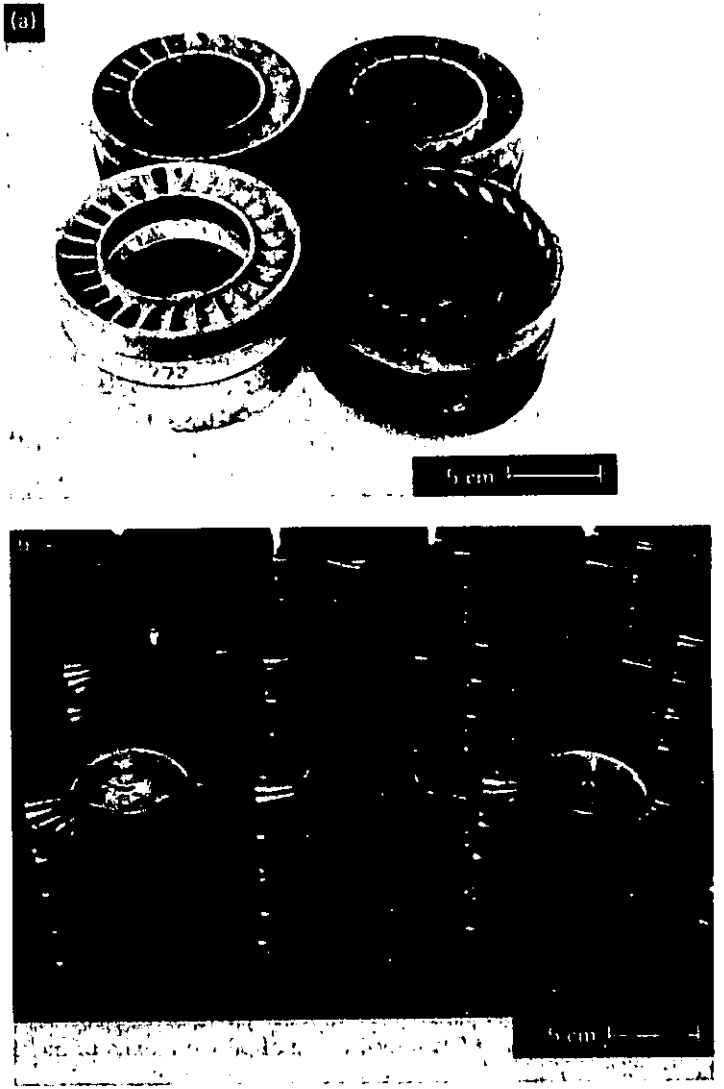


Figure 6.13 Complex shapes made by injection molding. (a) Integral stators. (b) Rotor blade rings. (Courtesy of Ford Motor Company, Dearborn, Mich.)

Extrusion

Extrusion is used extensively for fabrication of brick, tile, tubes, rods, and other elongated shapes that have a constant cross section. A schematic

of an extruder is shown in Fig. 6.14. A plastic mix of the ceramic powder and clay or organic additives is placed in an evacuated cylinder, where it is worked or kneaded to remove air and to achieve uniform consistency. The mix is then typically carried by an auger and forced through a die. As the shaped plastic mix exits from the extruder, it is supported on a suitable flat or shaped surface to prevent distortion and is cut to the required lengths.

Extrusion of compositions containing clay and made plastic by water addition is well developed and has been in common practice for many years. Extrusion of nonclay compositions is less developed and usually requires experimental optimization of each new system. Table 6.3 summarizes examples of extrusion conditions identified by Hyde [19] for several materials.

Very complex cross sections have been extruded. One of the most remarkable is the thin-walled cellular structure shown in Fig. 6.15 fabricated by NGK in Japan. Such honeycomb structures have been fabricated of low-thermal-expansion materials such as lithium aluminum silicate and cordierite (magnesium aluminum silicate) and are being used for heat exchanger and catalyst substrate applications.

6.4 OTHER FORMING PROCESSES

Methods for forming compacted shapes of ceramic powders are limited only by the imagination of the engineer. This is especially true for modifications to current techniques to achieve improved properties, decreased rejections, and decreased cost. It is also true for the development of advanced composites. It would be interesting to speculate on some of the possibilities, but is not within the scope of this text. Discussion in this section will be limited to two important established approaches, tape forming and green machining.

Tape Forming

Some applications such as electrical substrates and plate-fin heat exchangers and exhaust emission control devices require thin strips or structures of ceramics. Tape forming has been developed as an effective means of meeting these needs.

Figure 6.16 illustrates schematically methods of forming a thin sheet or thin-walled ceramic structure by tape forming.

The doctor-blade process [20] is well established for fabrication of electronic ceramics for capacitors, for electrically insulating substrates for thick-film and thin-film circuitry, for ferrite memories, and for catalyst substrates. It consists of casting a slurry onto a moving carrier surface (usually a thin film of cellulose acetate, Teflon, Mylar, or cellophane) and

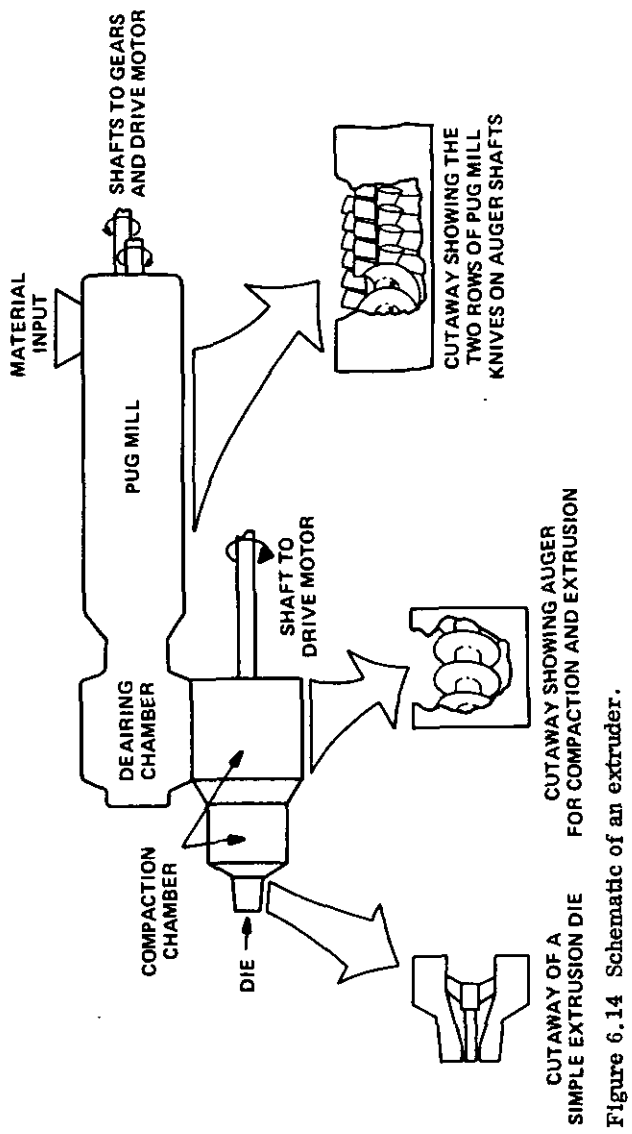


Figure 6.14 Schematic of an extruder.

Table 6.3 Examples of Extrusion of Nonclay Compositions

Composition	Additives	Conditions	Shape
Graphite	50-60 parts phenol formaldehyde emulsion	--	5/8- and 1-in. rods
Petroleum coke	Coal-tar pitch plus heavy oil	90-110°C	--
Al_2O_3-5% Cr_2O_3	Gum ghatti plus mogul starch	--	Round, square, and triangular tubes
30% Si-70% SiC	4% guar gum, 20% water, 3% silicone	--	--
BeO	10-18% mogul starch, 15-18% water-glyceryl mixture	--	Rods, tubes, thin-walled multicell tubes
MgO	30-40% flour paste	--	Vacuum-tube parts

Source: Ref. 19. Reprinted from C. Hyde, in Ceramic Fabrication Processes (W. D. Kingery, ed.), by permission of The MIT Press, Cambridge, Mass. © 1963, The MIT Press.

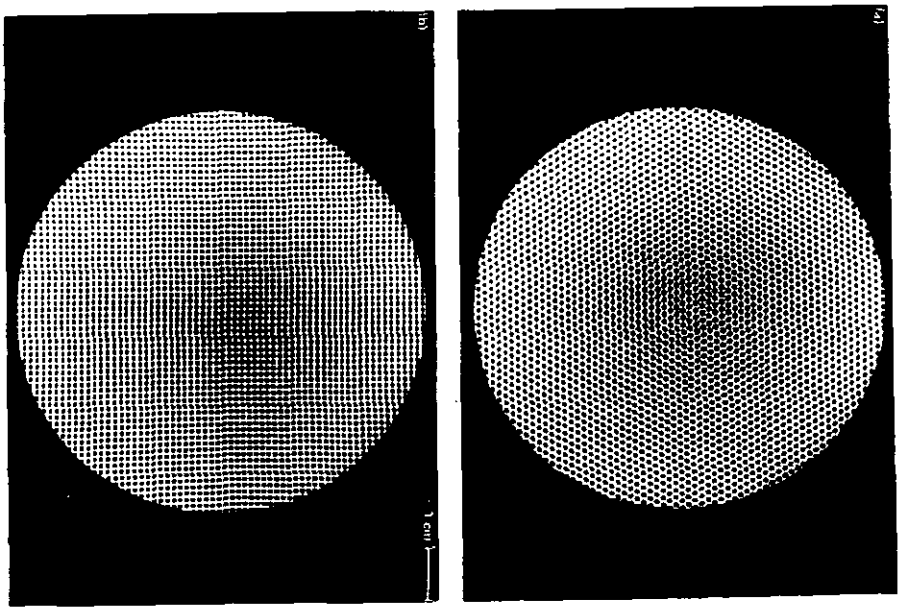


Figure 6.15 Extruded honeycomb structures for heat exchanger and emission control applications. (Courtesy of NGK Insulators, Nagoya, Japan.)

spreading the slurry to a controlled thickness with the knife edge of a blade. The slurry is then carefully dried, resulting in a thin, flexible tape that can be cut or stamped to the desired configuration prior to firing.

The doctor-blade process sounds simple, but actually requires very careful controls to avoid warpage, out-of-tolerance thickness, and other defects. This is illustrated in Table 6.4 by listing the additives required in the Western Electric Company process for making Al_2O_3 substrates [21]. Williams [20] lists a variety of other additives for both nonaqueous and aqueous doctor-blade systems.

The paper-casting process is similar to the doctor-blade process. A controlled thickness of slurry is deposited on a moving carrier. In this case the carrier is a low-ash paper that can be burned off in a later process step. The paper-casting process has been used in the manufacture of catalyst substrates and rotary regenerator heat exchangers [22].

The roll process produces a tape by mechanically reducing the thickness of a ceramic powder/organic polymer mixture. It is also used for fabrication of catalyst substrates and rotary regenerator heat exchangers.

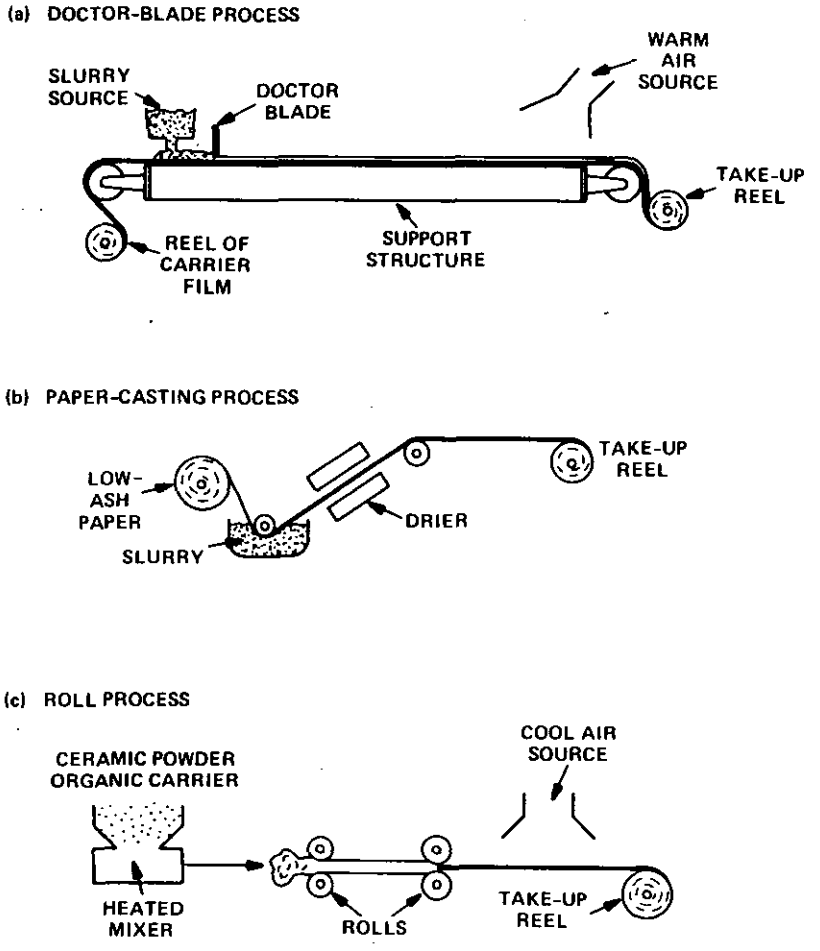


Figure 6.16 Schematics of tape-forming processes. (Adapted from Ref. 22.)

Table 6.4 Additives to Al_2O_3 for the Western Electric Company ERC-105 Doctor-Blade Process

Material	Function
MgO	Grain-growth inhibitor
Menhaden fish oil	Deflocculant
Trichloroethylene	Solvent
Ethyl alcohol	Solvent
Polyvinyl butyral	Binder
Polyethylene glycol	Plasticizer
Octylphthalate	Plasticizer

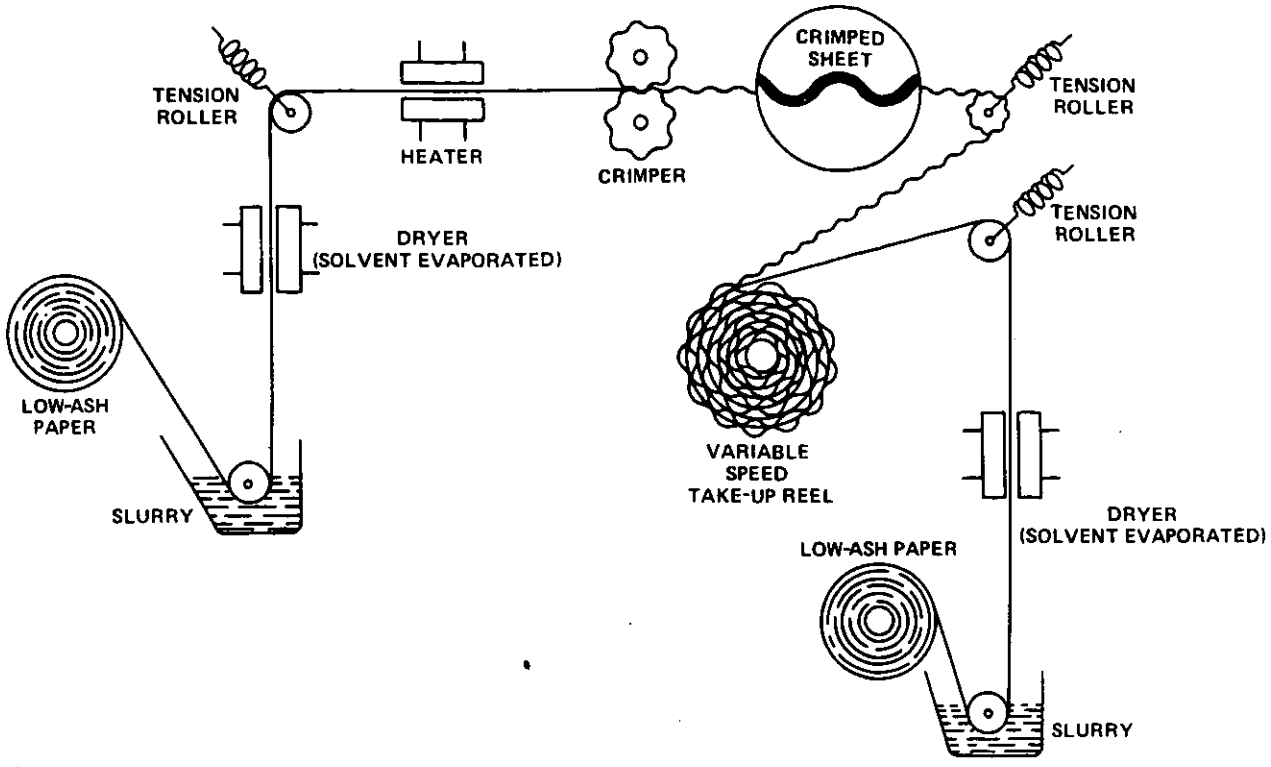
Source: Ref. 21.

Figure 6.17 illustrates how a rotary heat exchanger is fabricated by the paper-casting and roll-forming processes [22].

Green Machining

Green machining refers to machining of a ceramic part prior to final densification while the material consists of compacted, loosely bonded powder. Such material is much softer than the ceramic in its final densified condition and can be machined much more economically since diamond tooling is not required. However, the material is relatively fragile, and great care is necessary in the design and fabrication of the tooling and fixturing so that the parts can be accurately and uniformly held during the various shaping operations. In addition, the machining parameters must be carefully controlled to avoid overstressing the fragile material and producing chips, cracks, breakage, or poor surface.

Holding of the compact for machining is typically accomplished with a combination of bee's wax and precision metal fixtures. The part must be held rigidly, but with no distortion or stress concentration. Metal fixturing should normally be located either on the outer diameter or the face of the part. This is to avoid expansion of the metal fixture into the ceramic, causing breakage when heat is applied to soften the wax during removal of the machined part from the fixture. If there is no way to locate the part except on the inside diameter, special care must be taken to heat the ceramic rapidly while keeping the metal cool.



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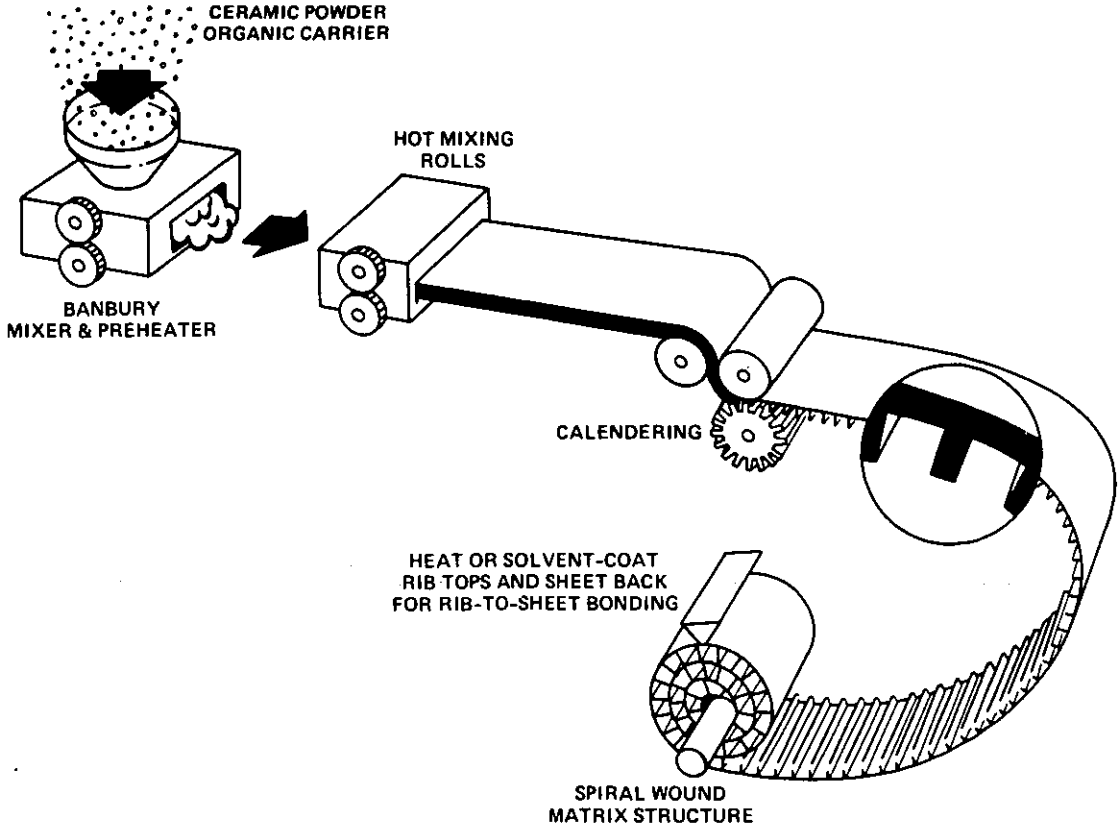


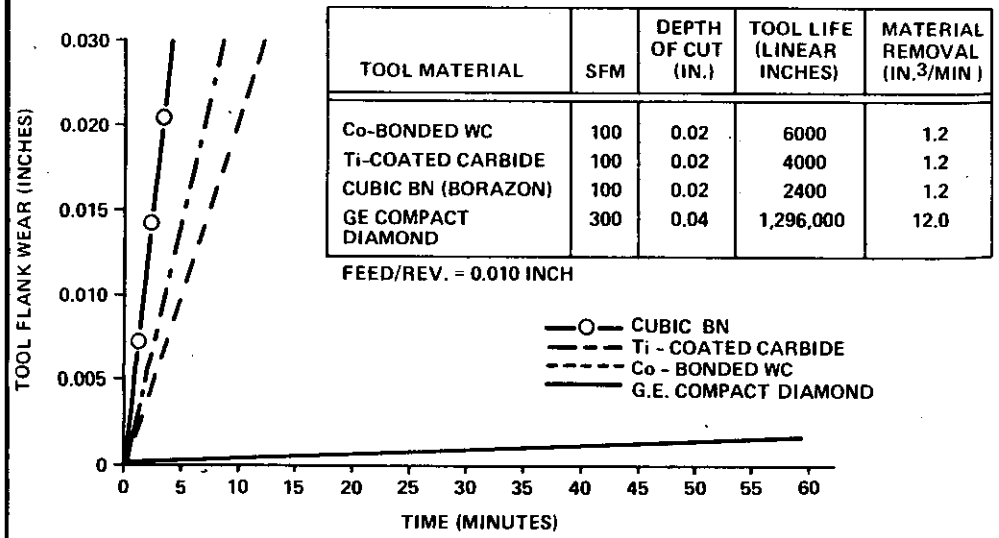
(b)

Figure 6.17 Fabrication of a rotary regenerator heat exchanger structure using tape-forming processes. (a) Paper-casting process. (b) Roll-forming process. (From Ref. 22.)

Once a ceramic part has been secured rigidly in a fixture, machining can be conducted by a variety of methods—turning, milling, drilling, form wheel grinding, and profile grinding. Machining can be either dry or wet. In either case, the compact is abrasive and results in tool wear. A wear land on the cutting edge as little as 0.005 in. wide will result in a buildup of the cutting pressure and damage to the ceramic.

It is possible to machine compacts with high-speed steel or cemented carbide cutting tools, but this is not recommended for all components or all green materials. In some cases, the tool dulls so rapidly that extreme care is necessary to avoid damage to the workpiece. Figure 6.18 summarizes a study [23] of other cutting tool materials using a 5° positive rake and 10° clearance angle. The GE compact diamond cost about 10 times as much as the tungsten carbide, but resulted in a significant cost saving in terms of increased life, less time changing inserts, and reduced risk of damage to the workpiece from a dull tool. The study was conducted with single-point turning on an engine lathe. Milling with a two-flute end mill at 200 surface feet per minute (sfm) with GE compact diamond inserts showed the same life characteristics.

Green machining can also be conducted with grinding wheels containing multiple abrasive particles bonded in a resin or metal matrix. Higher



TOOL MATERIAL	SFM	DEPTH OF CUT (IN.)	TOOL LIFE (LINEAR INCHES)	MATERIAL REMOVAL ($IN.^3$/MIN)
Co-BONDED WC	100	0.02	6000	1.2
Ti-COATED CARBIDE	100	0.02	4000	1.2
CUBIC BN (BORAZON)	100	0.02	2400	1.2
GE COMPACT DIAMOND	300	0.04	1,296,000	12.0

FEED/REV. = 0.010 INCH

Figure 6.18 Tool wear for different tool insert materials for green machining of a presintered silicon compact in the fabrication of reaction-bonded Si_3N_4. (From Ref. 23.)

surface speed, broader contact, and decreased depth of cut are characteristic of this technique, resulting usually in a better surface and less chance of damage. Excellent tool life can be achieved, especially if diamond abrasive is used. Furthermore, coarse abrasive can be used for roughing passes and fine abrasive for finishing. Formed wheels can also be used to produce a controlled and reproducible contour.

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7

Densification

In Chaps. 5 and 6 we discussed the criteria and techniques for selecting and processing ceramic powders and for forming these powders into shaped particulate compacts. In this chapter we explore the processes for densifying these particulate compacts into strong, useful ceramic components.

7.1 THEORY OF SINTERING

The densification of a particulate ceramic compact is technically referred to as sintering. Sintering is essentially a removal of the pores between the starting particles (accompanied by shrinkage of the component), combined with growth together and strong bonding between adjacent particles. The following criteria must be met before sintering can occur:

1. A mechanism for material transport must be present.
2. A source of energy to activate and sustain this material transport must be present.

The primary mechanisms for transport are diffusion and viscous flow. Heat is the primary source of energy, in conjunction with energy gradients due to particle-particle contact and surface tension.

Although ceramic materials have been used and densified for centuries, scientific understanding and control of sintering has only developed during the past 40 to 50 years. Early controlled experiments were conducted by Muller in 1935 [1]. He sintered compacts of NaCl powder for a variety of times at several temperatures and evaluated the degree of sintering by measuring the fracture strength.

Much progress in our understanding of densification has been achieved since 1935. Now sintering is studied by plotting density or shrinkage data as a function of time and by actual examination of the microstructure at various stages of sintering using scanning electron microscopy, transmission electron microscopy, and lattice imaging.

Sintering can occur by a variety of mechanisms, as summarized in Table 7.1. Each mechanism can work alone or in combination with other mechanisms to achieve densification.

Vapor-Phase Sintering

Vapor-phase sintering is important in only a few material systems and is discussed only briefly. The driving energy is the difference in vapor pressure as a function of surface curvature. As illustrated in Fig. 7.1., material is transported from the surface of the particles, which have a positive radius of curvature and a relatively high vapor pressure to the contact region between particles, which has a negative radius of curvature and a much lower vapor pressure. The smaller the particles, the greater the positive radius of curvature and the greater the driving force for vapor-phase transport. Table 7.2 shows how large an effect particle size or surface curvature can have on pressure across the curved surface and on relative vapor pressure [2].

Vapor-phase transport changes the shape of the pores and achieves bonding between adjacent particles and thus increases the material strength and decreases permeability due to open porosity. However, it does not result in shrinkage and cannot produce densification. It must be accompanied by other mechanisms that provide bulk material transport or transport of pores to external surfaces.

Table 7.1 Sintering Mechanisms

Type of sintering	Material transport mechanism	Driving energy
Vapor phase	Evaporation-condensation	Differences in vapor pressure
Solid state	Diffusion	Differences in free energy or chemical potential
Liquid phase	Viscous flow, diffusion	Capillary pressure, surface tension
Reactive liquid	Viscous flow, solution-precipitation	Capillary pressure, surface tension

Source: Adapted from Ref. 2.

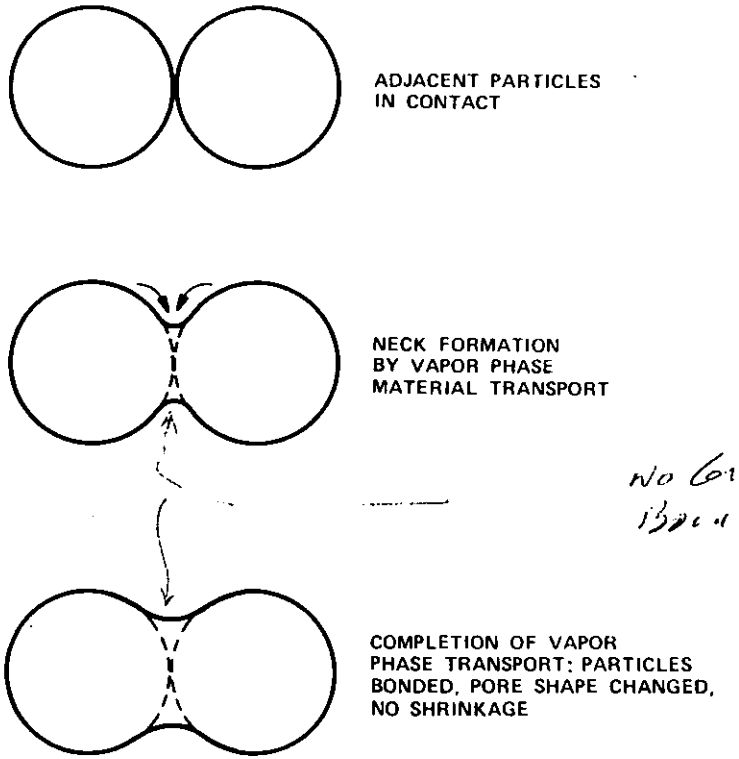


Figure 7.1 Schematic of vapor-phase material transport.

Solid-State Sintering

Solid-state sintering involves material transport by diffusion. Diffusion can consist of movement of atoms or vacancies along a surface or grain boundary or through the volume of the material. Surface diffusion, like vapor-phase transport, does not result in shrinkage. Volume diffusion, whether along grain boundaries or through lattice dislocations, does result in shrinkage, as illustrated in Fig. 7.2.

The driving force for solid-state sintering is the difference in free energy or chemical potential between the free surfaces of particles and the points of contact between adjacent particles. Mathematical models have been derived which compare favorably with experimental data and relate the rate of sintering. For instance, Kingery et al. [3] derived the following equation for the mechanism of transport of material by lattice diffusion from the line of contact between two particles to the neck region:

Table 7.2 Effect of Particle Size or Surface Curvature on the Pressure Difference and Relative Vapor Pressure across a Curved Surface

Material	Surface diameter (μm)	Pressure difference		Relative vapor pressure (P/P_0)
		MPa	psi	
Liquid water at 25°C	0.1	2.8	418	1.02
	1.0	0.28	41.8	1.002
	10.0	0.03	4.2	1.0002
Liquid cobalt at 1450°C	0.1	67.3	9750	1.02
	1.0	6.7	975	1.002
	10.0	0.67	97.5	1.0002
Silica glass at 1700°C	0.1	12.1	1750	1.02
	1.0	1.2	175	1.002
	10.0	0.12	17.5	1.0002
Solid Al_2O_3	0.1	36.2	5250	1.02
	1.0	3.6	525	1.002
	10.0	0.36	52.5	1.0002

Source: Ref. 2.

Original: Kuczynski's empirical model for volume diffusion (1947)

$$\frac{\Delta L}{L_0} = \left(\frac{20\gamma a^3 D^{*2/5}}{\sqrt{2}\,kT}\right) r^{-6/5} t^{2/5} \qquad (7.1)$$

where $\Delta L/L_0$ is the linear shrinkage (equivalent to the sintering rate), γ the surface energy, a^3 the atomic volume of the diffusing vacancy, D^* the self-diffusion coefficient, k the Boltzmann constant, T the temperature, r the particle radius (assuming equal-size spherical starting particles), and t is time.

Equations for other volume diffusion mechanisms of sintering are similar. In each case the rate of shrinkage increases with increasing temperature and with decreasing particle radius and decreases with time.

Figure 7.3a illustrates the effects of temperature and time. Figure 7.3b shows a log-log plot of the same data. The slope of the log $\Delta L/L_0$ versus log t line is approximately two-fifths for solid-state sintering. It is apparent from examination of equation (7.1) and Fig. 7.3 that control of temperature and particle size is extremely important, but that control of time is less important.

Finer-particle-size powder can be sintered more rapidly and at a lower temperature than coarser powder. Not apparent in the equation, but highly important to the final properties, are the uniformity of particle packing, the particle shape, and the particle size distribution. If particle packing is not uniform in the greenware, it will be very difficult to eliminate all the porosity during sintering. Agglomerates are a common source of nonuniformity, as discussed in Chap. 5. Nonuniformity can also result during

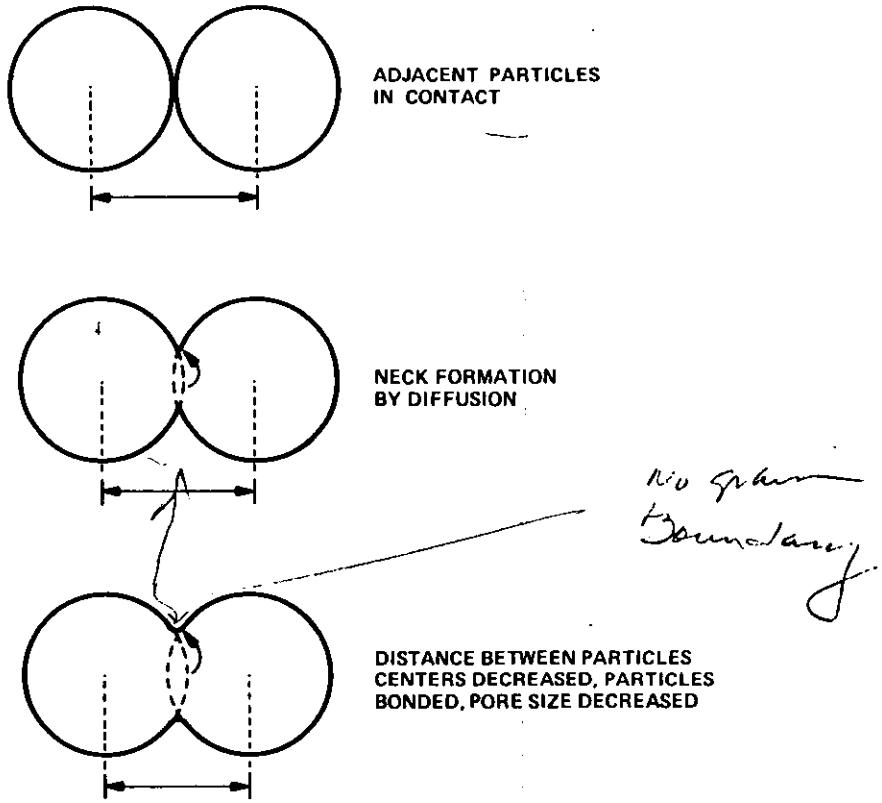


Figure 7.2 Schematic of solid-state material transport.

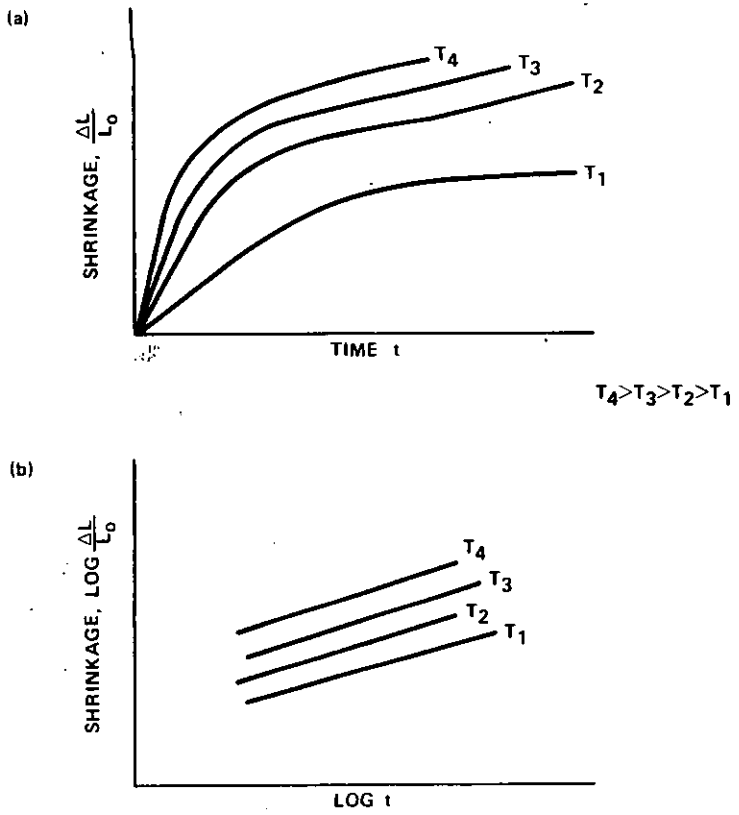


Figure 7.3 Typical sintering rate curves showing the effects of temperature and time.

shape forming due to gas entrapment, particle segregation (i.e., settling during slip casting), lamination, and fold lines (injection molding).

Particle shape can also be important. Too high a concentration of elongated or flattened particles can result in bridging during forming, producing a large or irregularly shaped pore that is difficult to remove during sintering.

Particle size distribution is also critical. Particles that are all of one size do not pack efficiently; they form compacts with large pores and a high volume percentage of porosity. Unless very uniform close packing was achieved during compacting and grain growth occurs during densification, such compacts will undergo a high percentage of shrinkage and yet will retain significant porosity. For very fine particles (500 Å) this may be acceptable and may result in very uniform properties. However, more

commonly available powder has a range of particle sizes from submicron upward. Better overall packing can be achieved during compaction, but isolated pores due to bridging and agglomerates are usually quite large and result either in porosity or large grain size after sintering.

Liquid-Phase Sintering

Liquid-phase sintering involves the presence of a viscous liquid at the sintering temperature and is the primary densification mechanism for most silicate systems. Liquid-phase sintering occurs most readily when the liquid thoroughly wets the solid particles at the sintering temperature. The liquid in the narrow channels between the particles results in substantial capillary pressure, which aids densification by several mechanisms:

Rearranges the particles to achieve better packing
Increases the contact pressure between particles, which increases the rate of material transfer by solution/precipitation, creep and plastic deformation, vapor transport, and grain growth

The magnitude of capillary pressures produced by silicate liquids can be greater than 7 MPa (1000 psi). Smaller particles result in higher capillary pressure and also have higher surface energy due to the small radius of curvature and thus have more driving energy for densification than coarser particles. Materials requiring high strength and minimum porosity are generally processed from powders having an average particle size less than 5 μm and a surface area less than 5 m^2/g.

The rate of liquid-phase sintering is also strongly affected by temperature. For most compositions a small increase in temperature results in a substantial increase in the amount of liquid present. In some cases this can be beneficial by increasing the rate of densification. In other cases it can be detrimental by causing excessive grain growth (which reduces strength) or by allowing the part to slump and deform. The amount of liquid present at a selected temperature can be predicted with the use of phase equilibrium diagrams. The following discussion reviews briefly the principles of simple phase equilibrium diagrams and illustrates how they can be used to predict liquid content versus temperature, optimum compositions and temperatures for sintering, and the resulting high-temperature properties of the densified material.

Simple Binary Eutectic Diagram Figure 7.4 shows a simple binary eutectic phase equilibrium diagram. Considerable information is available from this diagram. With no calculations at all, the following information can be read directly:

The melting temperatures of the pure components A and B are T_A and T_B, respectively.
The melting temperature decreases as B is added to A or A is added to B.
The lowest melting temperature for this system occurs for a composition of 30% A and 70% B and is referred to as the binary eutectic T_e.
Regions are defined which tell whether solid, liquid, or a mixture is present for each temperature and composition when the system is in equilibrium.

With simple calculations considerable additional information is available from the phase equilibrium diagram as illustrated by Fig. 7.5 and the following examples.

EXAMPLE 7.1 What percentage liquid and solid are present in Fig. 7.5 for composition C_1 at temperature T_1? What are the compositions of the liquid and solid? We can use the simple lever rule to calculate the percentages:

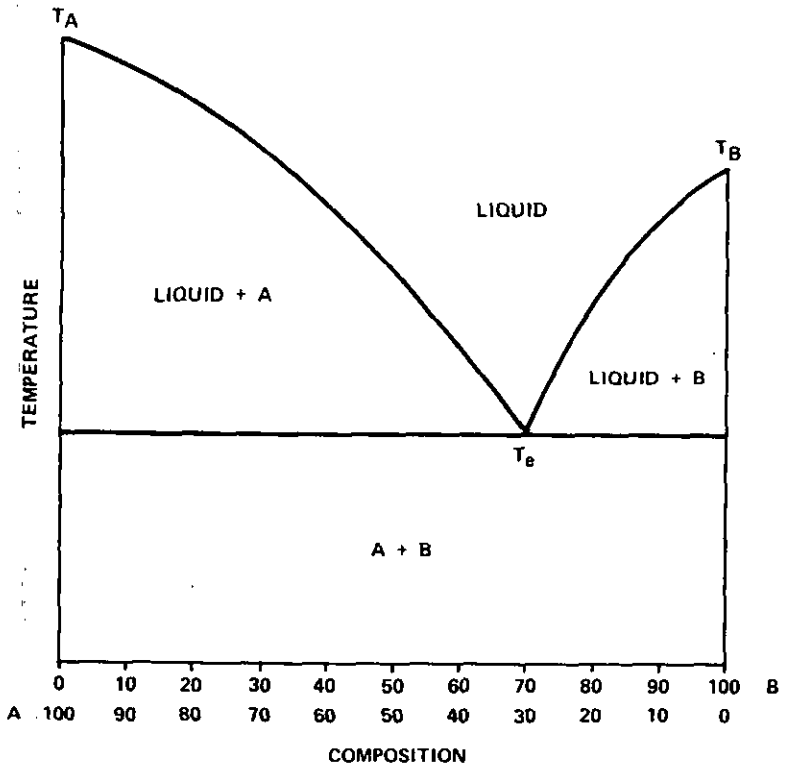


Figure 7.4 Simple binary eutectic diagram.

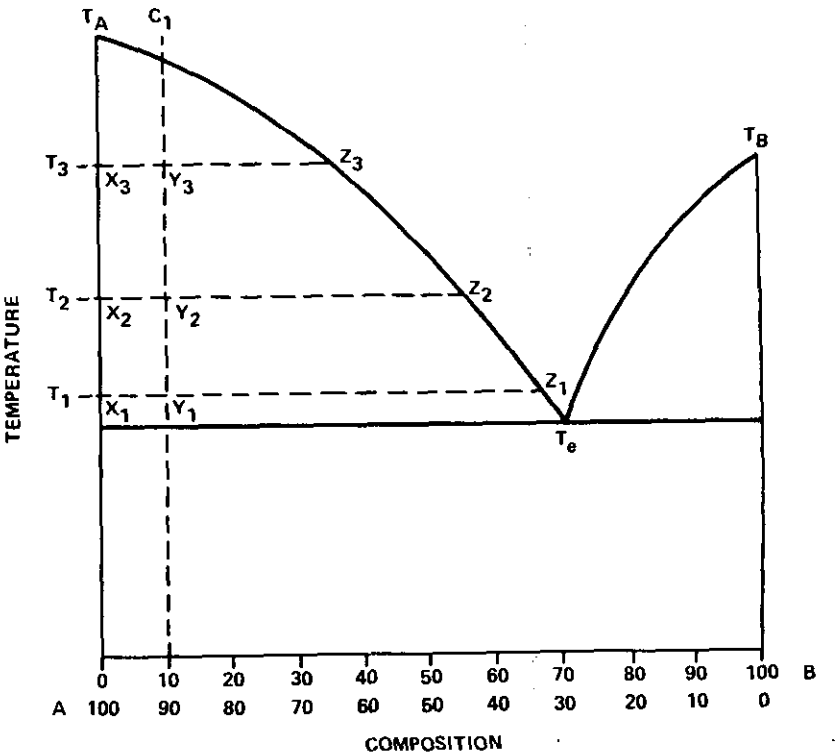


Figure 7.5 Binary eutectic diagram used with Examples 7.1 and 7.2 to describe methods of calculating percentages of solid and liquid for composition C_1 at various temperatures.

$$\% \text{ Solid} = \frac{X_1Z_1 - X_1Y_1}{X_1Z_1} = \frac{67 - 10}{67} = 85^*$$

$$\% \text{ Liquid} = \frac{X_1Z_1 - Y_1Z_1}{X_1Z_1} = \frac{67 - 57}{67} = 15$$

The composition of the liquid is defined by the intersection of the T_1 line and the liquidus (the curve that extends between T_e and T_A and thus separates

*Which is all A because the composition C_1 is in the liquid + A region of the diagram.

the region of all liquid from liquid + A) and is thus Z_1: Composition of liquid = Z_1 = 67% B and 33% A. We can now check to see if our calculations are correct by adding up all the A and B in the liquid and the solid to see if they equal our starting composition C_1:

	Percent in solid	Percent in liquid	Total
A	85	33 × 0.15 = 5	90
B	0	67 × 0.15 = 10	10

Composition C_1 is 90% A and 10% B, so our calculations are correct.

EXAMPLE 7.2 What percentages of liquid and solid are present for composition C_1, at temperatures T_2 and T_3? What are the corresponding liquid compositions?

$$\% \text{ Solid at } T_2 = \frac{X_2Z_2 - X_2Y_2}{X_2Z_2} = \frac{55 - 10}{55} = 82\%$$

$$\% \text{ Liquid at } T_2 = \frac{X_2Z_2 - Y_2Z_2}{X_2Z_2} = \frac{55 - 45}{55} = 18\%$$

Composition liquid at $T_2 = Z_2$ = 55% B and 45% A

$$\% \text{ Solid at } T_3 = \frac{X_3Z_3 - X_3Y_3}{X_3Z_3} = \frac{35 - 10}{35} = 71\%$$

$$\% \text{ Liquid at } T_3 = \frac{X_3Z_3 - Y_3Z_3}{X_3Z_3} = \frac{35 - 25}{35} = 29\%$$

Composition liquid at $T_3 = Z_3$ = 35% B and 65% A

Besides showing how useful calculations can be made with simple binary eutectic diagrams, the examples above illustrate some important considerations in liquid-phase sintering. First, small additions of a second component (B in this case) can result in a substantial quantity of liquid at a temperature well below the melting temperature of the pure component A. This aids in sintering, but if too much liquid is present can result in distorting, bloating, reaction with setter plates in the furnace, and insufficient

high-temperature properties for the intended application. Therefore, the composition must be carefully selected and controlled to achieve a suitable amount of liquid at the selected sintering temperature.

Second, by comparing Examples 7.1 and 7.2, one can see that temperature has a strong effect on the amount of liquid present, and therefore must also be carefully selected and controlled. Another related consideration is that the liquid present at high temperature normally solidifies to a glass during cooling. Softening of this glass during subsequent usage of the part can result in creep and slow crack growth which will limit the operating temperature and life of the part. However, since one can estimate from the phase equilibrium diagrams the composition and percentage of this glass, one can design the starting composition and sintering process to satisfy the objectives of the application. Another option is to select a glass composition that can be crystallized by an appropriate heat treatment before the part is put in service. Even though the crystalline phase may have the same composition as the glass, it will not be subject to intermediate temperature softening typical of the glass.

One can also use Fig. 7.5 to understand better what happens during solidification or crystallization of a ceramic composition. Let us look again at composition C_1. At temperatures above the liquidus, only a liquid is present having a composition of 90% A and 10% B. As soon as the temperature cools down to the liquidus, crystals of component A begin to form in the liquid. The liquid correspondingly becomes increasingly richer in component B as the temperature is decreased and more A crystallizes. By the time the eutectic temperature T_e is reached, only about 14% liquid remains and is a mixture of 70% B and 30% A. This crystallizes at T_3 as a mixture of A and B crystals. Below T_e only a solid mixture of A and B is present.

The binary eutectic represents one of the simplest interactions of two components. The two components affect each other by reducing melting temperatures, but otherwise do not interact either chemically or structurally. Other systems are more complex and have solid solution between components or chemical interactions that result in intermediate compositions. These features are also included in the phase equilibrium diagram and can provide the engineer with very useful information on the nature of the materials he or she is dealing with.

Other Binary Phase Equilibrium Diagrams Figure 7.6a shows a binary system with an intermediate congruently melting compound (AB). It is basically just two binary eutectic diagrams attached, each having its own eutectic (e_1 and e_2). The term congruent melting means that the compound is solid until it reaches its melting temperature. A, B, and AB all melt congruently. Figure 7.6b shows a binary system with an intermediate incongruently melting compound. In this case, the intermediate compound AB does not melt directly, but decomposes to a liquid plus B. In this case the eutectic is replaced by what is referred to as a peritectic (p_1 in Fig.

7.6b). Both congruently melting and incongruently melting system are common for ceramics.

Some compounds are stable only over a limited temperature range. This information is also available in the phase equilibrium diagram, as shown in Fig. 7.7. Such dissociating compounds are not common, but may be encountered and can affect sintering.

Much more important and widespread and critical to sintering is the effect of solid solution. Solid solution involves the ability of one atom or group of atoms to substitute into the crystal structure of another atom or group of atoms without resulting in a change in structure. Solid solution must be distinguished from mixtures. In a mixture two or more components are present, but they retain their own identity and crystal structure. In a solid solution one component is "dissolved" in the other component such that only one continuous crystallographic structure is detectable. This concept was discussed in Chap. 1 under bonding and crystal structure. Crystallographic substitutions take place most easily if two atoms are

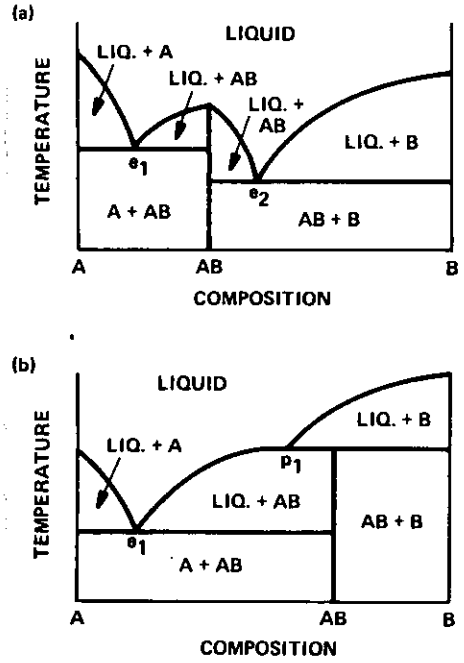


Figure 7.6 (a) Binary system with intermediate congruently melting compound. (b) Binary system with intermediate incongruently melting compound.

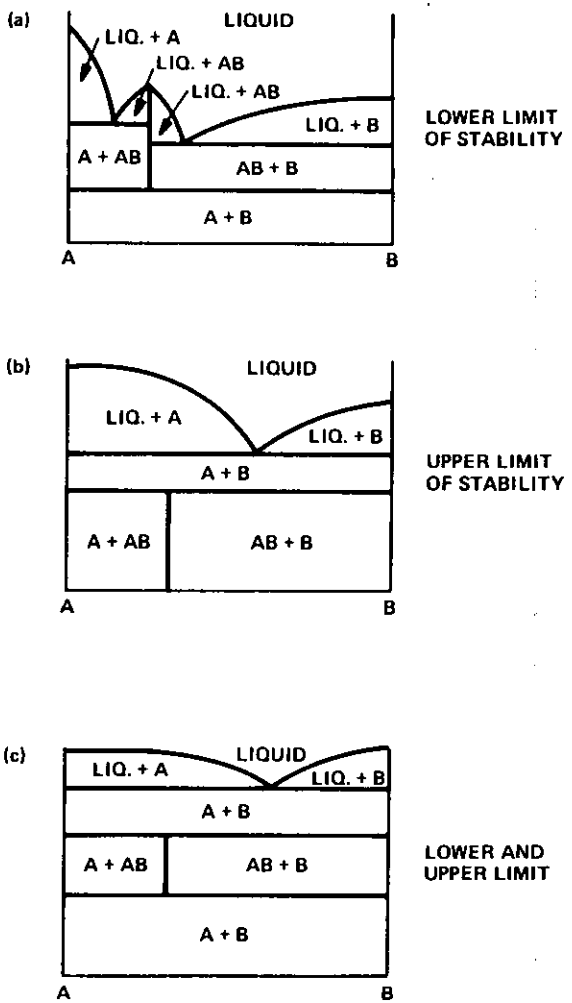


Figure 7.7 Representation of dissociating compounds on a phase equilibrium diagram.

similar in size and valence. For instance, Mg^{2+}, Co^{2+}, and Ni^{2+} are all similar in size and can readily replace each other in the cubic rock salt structure. In fact, each can replace the other up to 100% in the oxide, resulting in continuous solid solution. Figure 7.8a is the phase equilibrium diagram for the system MgO-NiO, showing complete solid solution between the MgO and NiO [4]. This is the most common type of continuous solid solution. Figure 7.8b and c show less common types in which either a

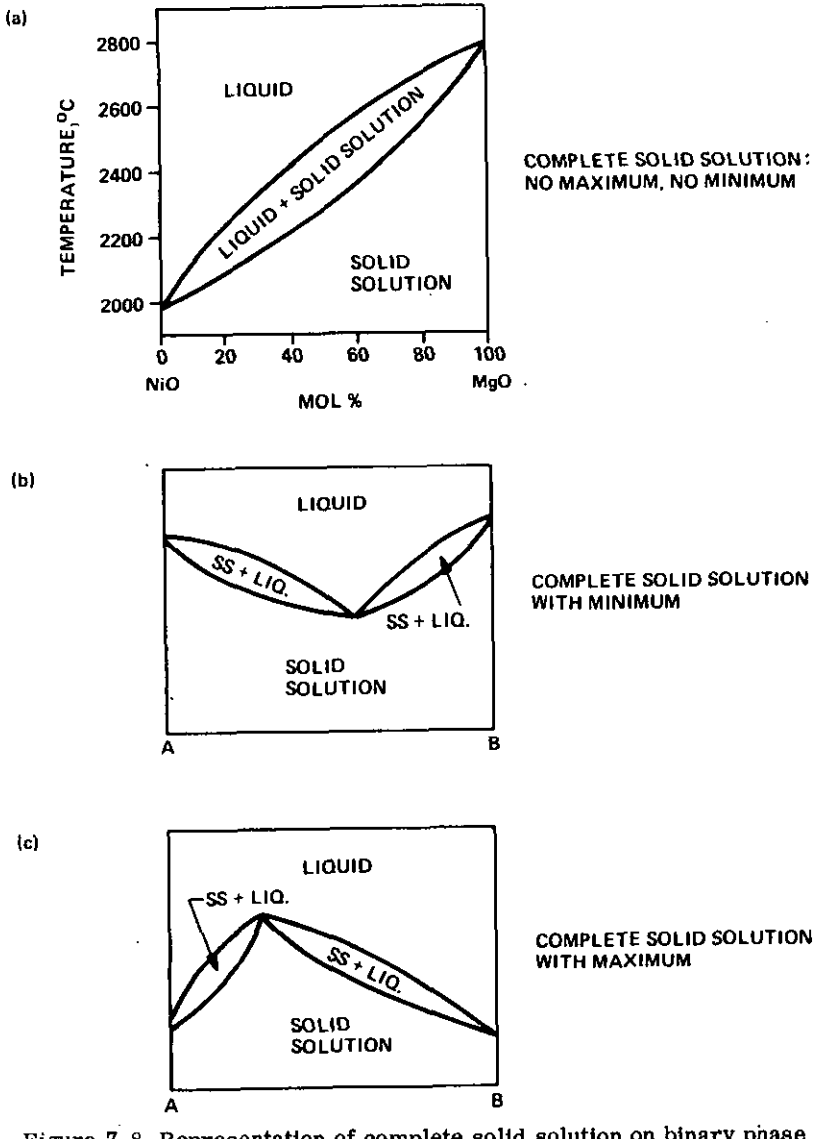


Figure 7.8 Representation of complete solid solution on binary phase equilibrium diagrams. (From Ref. 4.)

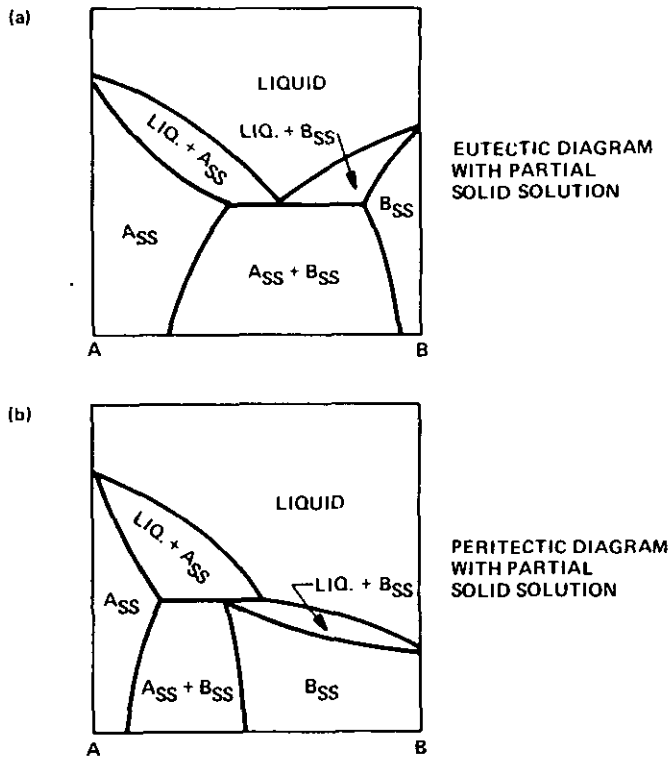


Figure 7.9 Binary phase equilibrium diagrams showing partial solid solution.

maximum or minimum is present. These maxima and minima are neither compounds nor eutectics, just limits in melting temperature for the solid solution.

Solid solution does not have to be complete between two different components and generally is not. Usually, one chemical component will have limited solid solubility in the other. The limits are determined by the similarity in the crystal structures and the size of ions or atoms. Figure 7.9 illustrates partial solid solution for a binary eutectic system and a binary peritectic system. For the eutectic system in Fig. 7.9a, component A can contain up to about 40% B in solid solution (at the eutectic temperature) and B can contain up to about 17% A. For the peritectic system shown, A can contain up to 20% B and B up to 60% A.

The presence of solid solution can have a dramatic effect on the sintering behavior of a ceramic system by significantly changing the percent liquid

available at a given temperature. This is illustrated by comparing Fig. 7.5 with Fig. 7.10 and Examples 7.1 and 7.2 with Examples 7.3 and 7.4.

EXAMPLE 7.3 Figure 7.10 represents a binary eutectic system identical to the one shown in Fig. 7.5 (same melting temperatures of A and B and same eutectic temperature and composition), except that the system in Fig. 7.10 has partial solid solubility of both A in B and B in A. What are the percentages of liquid and solid for composition C_1, at the same temperatures evaluated in Examples 7.1 and 7.2 (T_1, T_2, and T_3)?

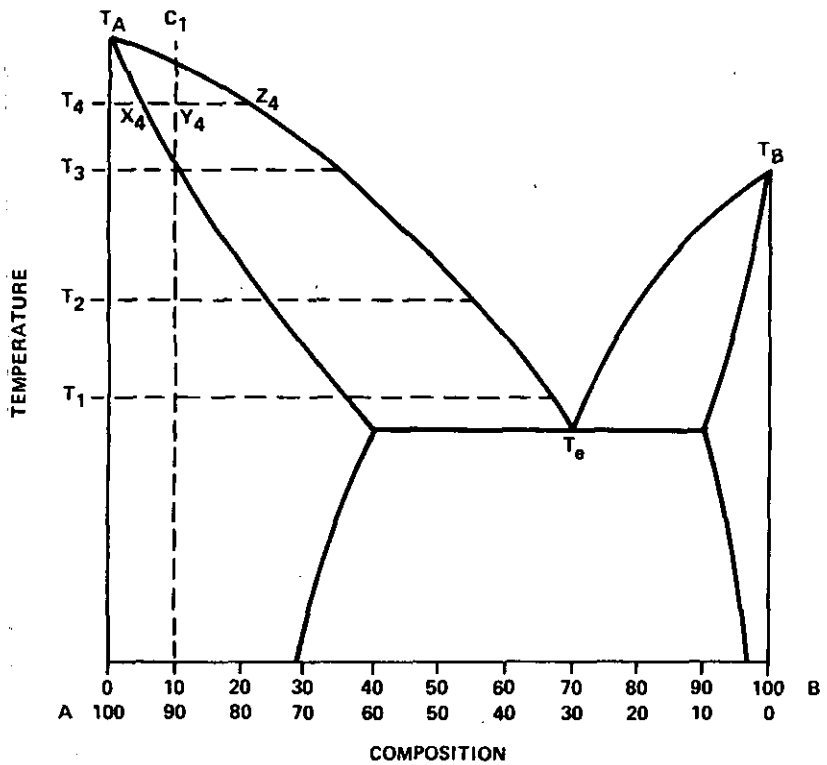


Figure 7.10 Binary eutectic diagram with partial solid solution, used with Examples 7.3 and 7.4 to describe methods of calculating percentages of solid and liquid versus composition and temperature and for comparison with similar calculations with the binary eutectic diagram without solid solution shown in Fig. 7.5.

T_1 = 100% solid, 0% liquid

T_2 = 100% solid, 0% liquid

T_3 = 100% solid, 0% liquid

It is obvious from this example that different sintering conditions would be required for the system with solid solution than for the system with no solid solution. The system without solid solution had 15% liquid at composition C_1 and temperature T_1 and could have probably been easily sintered by liquid-phase sintering at any temperature above the eutectic temperature. The system with solid solution would not have any liquid present under equilibrium conditions until slightly above temperature T_3 and thus would require a very high temperature for liquid-phase sintering. However, once sintered, the solid solution system would have much better high-temperature properties.

EXAMPLE 7.4 What are the percentages of solid and liquid for composition C_1 at temperature T_4 in Fig. 7.10? What are the compositions of the liquid and solid?

$$\% \text{ Solid} = \frac{X_4Z_4 - X_4Y_4}{X_4Z_4} = \frac{(21 - 6) - (10 - 6)}{(21 - 6)} = 73\%$$

$$\% \text{ Liquid} = \frac{X_4Z_4 - Y_4Z_4}{X_4Z_4} = \frac{15 - 11}{15} = 27\%$$

Composition of solid = X_4 = 94% A and 6% B

Composition of liquid = Z_4 = 79% A and 21% B

To check our calculations:

	Percent in solid	Percent in liquid	Total
A	0.73 × 94 = 69	0.27 × 79 = 21	90
B	0.73 × 6 = 4	0.27 × 21 = 6	10

The total adds up to 90% A and 10% B, which is the correct composition for C_1.

Another important material property which can affect sintering is polymorphic transformation. This information also shows up on phase equilibrium diagrams, as illustrated in Fig. 7.11 for a simple eutectic binary and a eutectic binary with solid solution of component B in each of the component A polymorphs.

Ternary Systems In many applications the ceramic is composed of or fabricated from three chemical components which can be represented by a

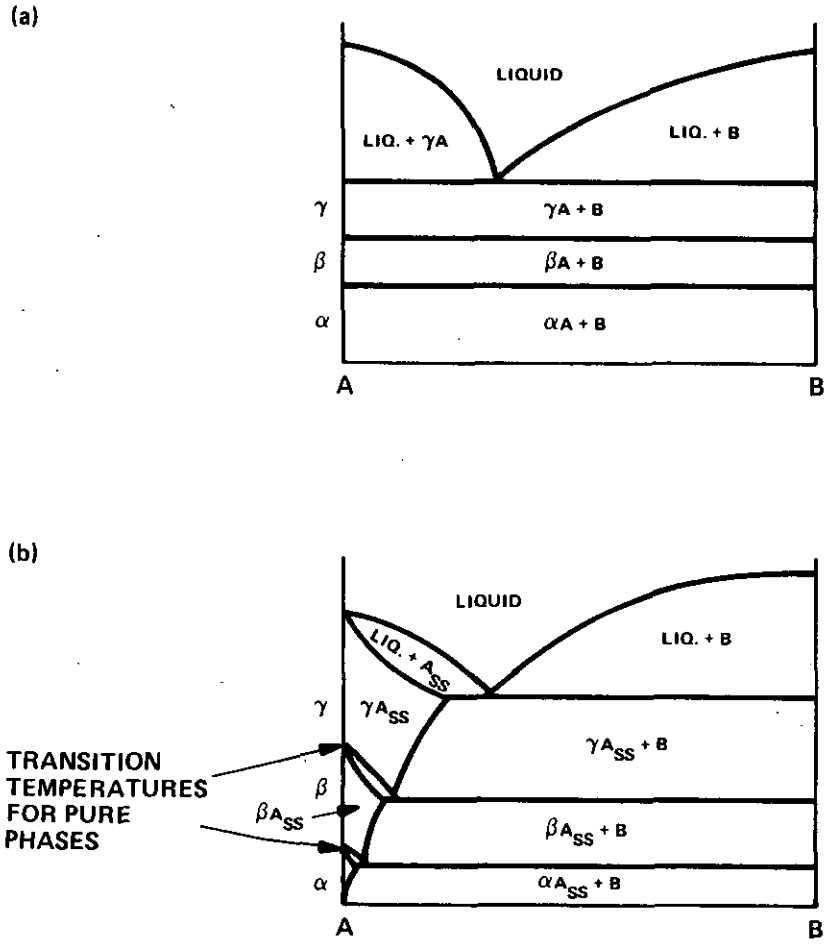


Figure 7.11 (a) Simple binary eutectic showing polymorphic transformations. (b) Binary eutectic with solid solution and polymorphic transformation.

ternary phase equilibrium systems. For instance, lithium aluminum silicate can be represented by the ternary system $LiO-Al_2O_3-SiO_2$ and cordierite by the system $MgO-Al_2O_3-SiO_2$.

The phase equilibrium diagrams for ternary systems can be useful in predicting or understanding sintering behavior in the same fashion that the binary system diagrams are. The same information regarding melting temperatures, compositions, percent liquid or solid, solid solution, and polymorphism are present.

A simple eutectic ternary diagram is illustrated in Fig. 7.12a. It is the top view of the liquidus surface formed by placing the three binary diagrams from the system end to end as shown in Fig. 7.12b. The corners of the triangular diagram represent the melting temperatures of the three pure components. The dashed lines show contours of constant melting temperature and thus allow one to estimate the melting temperature for any composition in the ternary system. The eutectics of each binary system show up along the lines connecting the corners of the triangle and are labeled e_1, e_2, and e_3 in Fig. 7.12. Melting temperatures typically decrease with further progression toward the interior of the ternary diagram, reaching the minimum value at the ternary eutectic labeled E. If intermediate compounds are present in any of the binary systems, more than one ternary eutectic will occur in the ternary system.

It is beyond the scope of this text to go into further detail on ternary systems. For further study, the reader is referred to Refs. 5 through 7. However, the key points being made in this brief discussion are that much information relevant to sintering behavior is available in ternary diagrams, and particularly that a third chemical component further reduces the temperature capability of the system. This latter point is especially important in selection of starting powders and their processing. Impurities can act as modifying chemical components which substantially reduce melting temperatures and result in more liquid phase at the sintering temperature than the manufacturer predicted and not as good high-temperature properties as the user requires.

Reactive Liquid Sintering

Reactive liquid sintering is also referred to as transient liquid sintering. A liquid is present during sintering to provide the same types of densification driving forces as discussed for liquid-phase sintering, but the liquid either changes composition or disappears as the sintering process progresses or after it is completed. Since the liquid phase is consumed in the reaction, the resulting material can have extremely good high-temperature properties and in some cases can even be used at temperatures above the sintering temperature.

One means of achieving reactive liquid sintering is to select starting powders or additives that go through a series of chemical combinations or

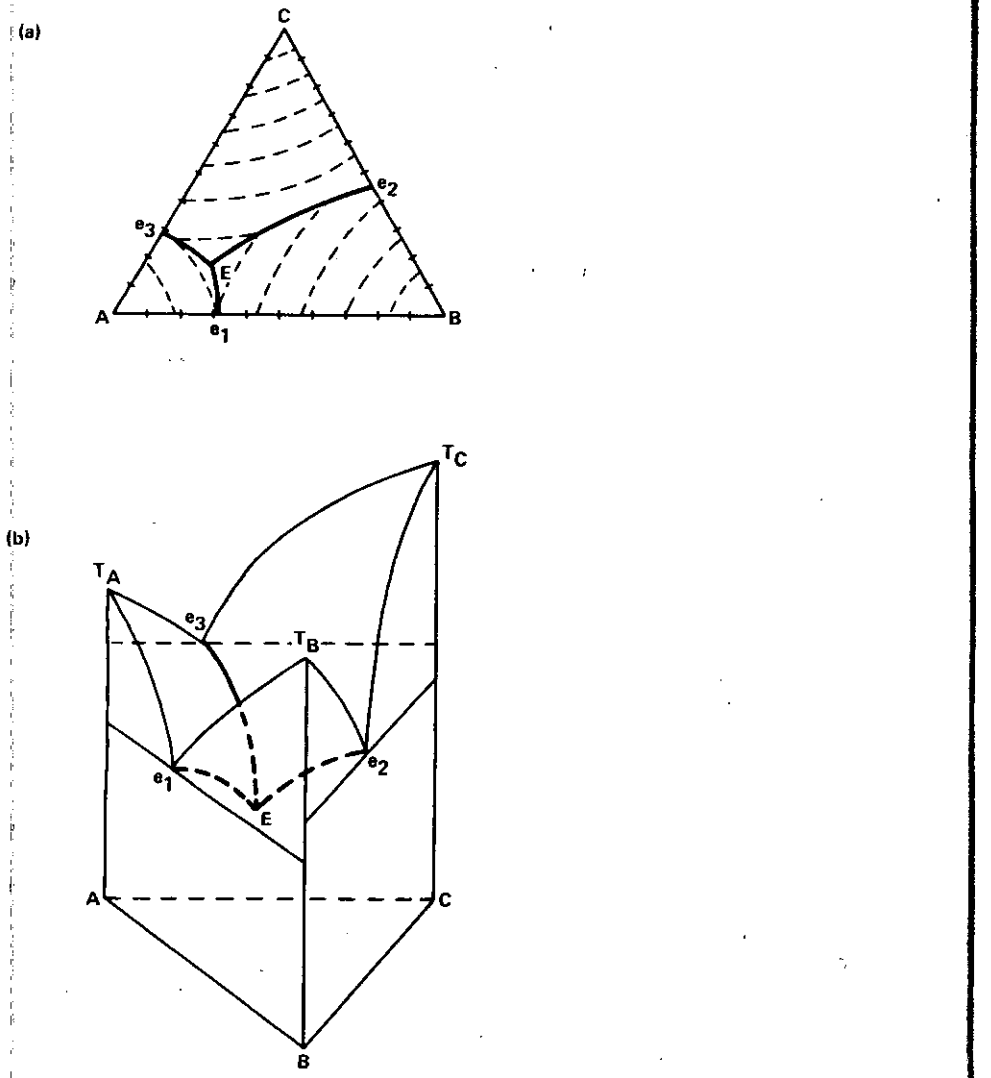


Figure 7.12 (a) Simple ternary triangular composition diagram showing the three components, the binary eutectics, the ternary eutectic, and constant melting-temperature contours. (b) Three-dimensional view showing how the ternary is related to its three constituent binaries.

reactions before the final stable compound is formed, with one or more of the intermediate compounds being liquid and the final compound being solid. Another is to use starting powders that will form a solid solution at equilibrium but will pass through a liquid stage before equilibrium is reached. A third approach (which is not really reactive liquid sintering, but gives the same results) is to liquid-phase sinter, cool to yield a glass at the grain boundaries, and then heat treat to crystallize the glass.

Sintering Problems

A variety of conditions can result in improper sintering and have a deleterious effect on the material properties. Normally, the manufacturer will detect these problems either during processing or during quality control inspection. However, sometimes defective or inferior material is not detected by the manufacturer and is shipped to the user, where the defect does not show up until the component fails prematurely in service. Under these circumstances the source of the problem and a feasible solution must be found quickly. The responsible engineer will have a distinct advantage if he or she knows generally how the ceramic was processed and knows what possible problems to look for. The following paragraphs describe some of the problems that can occur during sintering and some of the artifacts in the ceramic component that will help the engineer to identify the cause.

Warpage Warpage is a common problem and usually is detected before the part is put into service. It increases reject rate and hence the cost per part. It also can cause delays if it arises intermittently. Warpage usually results from inadequate support during sintering or from density variations in the greenware. The former can be corrected by shifting the orientation of the part in the furnace or by supporting the part with saggers (refractory, nonreactive ceramic pieces which restrict the component from deforming during sintering). The latter can be corrected only by solving the problem in an earlier processing step that caused the inhomogeneity. The two sources of warpage can usually be distinguished from each other by dimensional inspection or by examination of a polished section of the microstructure. Warpage due to sagging will not show variations in thickness or microstructure across the cross section, but warpage due to density variation will.

Overfiring Overfiring is another of the more common sintering problems with ceramics. It can cause warpage, reaction with surrounding furnace structures, bloating, or excessive grain growth. The first three are usually easy to detect visually. Excessive grain growth is more difficult to detect during routine inspection and may require preparation of a polished surface, etching to accentuate the grain structure, and examination by reflected light microscopy.

However, the presence of large grains is readily visible on a fracture surface at low magnification and can provide the engineer with valuable insight into the cause of a component failure. As discussed in Chap. 3, an increase in grain size usually results in a decrease in strength. This is true even if only a portion of the grains have increased size. Sometimes overfiring results in exaggerated grain growth, where a few grains preferentially grow very large compared to other grains in the microstructure and compared to the optimum grain size required for the intended application.

Burn-Off of Binders As discussed in Chap. 5, binders are often added to the ceramic powder prior to compaction. These are usually organic and can leave a carbon residue in the ceramic during sintering if the time/temperature/atmosphere parameters are not properly controlled. If large percentages of binders are present, such as in injection molded ceramics, the binder may have to be removed very slowly as a gas or liquid by thermal decomposition or capillary extraction. Too-rapid removal results in formation of cracks in the component.

The author once conducted experiments on sintering compacts of glass powders. A variety of binders were evaluated in glass compositions having a wide range in melting temperature. If the glass started to soften before the binder was completely burned off, discoloration would result. In one case the binder subsequently decomposed to produce a gas after the glass had partially sintered and expanded the glass into a porous foam having many times the volume of the original compact.

Proper binder removal is normally accomplished by slowly raising the temperature to a level at which the binder can volatilize, and holding at this temperature until the binder is gone. The temperature can then be safetly increased to the sintering temperature. However, if the temperature is increased before the binder has completely volatilized, the portion remaining will char and leave a residue of carbon.

In some materials, the carbon will be relatively inert, but in others it can cause severe chemical reactions during sintering. In one case the carbon resulted in localized reducing conditions in the core of a part causing bloating and severe dark discoloration. The surface of the same part was white and sintered properly.

Decomposition Reactions Ceramics are frequently prepared using a different starting composition than the final composition. For instance, carbonates, sulfates, nitrates, or other salts are often used rather than the oxides, even though the final product is an oxide. There are a variety of reasons for doing this. The salts are often purer or more reactive or can be mixed more uniformly. However, during sintering the salt must decompose to the oxide and react with other constituents to form the desired final composition. If the salt does not decompose early enough, the component can be damaged by gas evolution. If the salt does not decompose completely,

an off-composition or inhomogeneous condition can result. The degree of sensitivity of a component to this is dependent on the sintering temperature, the time-temperature schedule, and the decomposition temperature and kinetics of the salt. Problems are usually not encountered with hydrates and nitrates because they have low decomposition temperatures. Carbonates tend to have higher decomposition temperatures, but usually do not pose a problem if the sintering temperature is above 1000°C (1832°F). Some sulfates do not completely decompose until 1200 to 1300°C (2200 to 2372°F).

Polymorphic Transformations Polymorphic transformations do not usually cause problems during sintering, but can cause problems during cooldown after sintering if a sudden volume change is involved. A good example is ZrO_2. ZrO_2 is monoclinic from room temperature up to about 1000°C (1832°F), at which point it transforms abruptly to a tetragonal form. No problem occurs during heat-up because the individual ZrO_2 particles are not constrained. However, after sintering the original particles are now grains that are solidly bonded to adjacent grains and are thus restrained. They are also randomly oriented. Now, when the component goes through the transformation temperature, the grains are not free to move. Very high internal stresses result at the grain boundaries and many cracks are initiated, significantly weakening the material.

The problem with ZrO_2 has been resolved by controlled additions of CaO, MgO, or Y_2O_3 which produce a cubic form of ZrO_2 that does not undergo a transformation.

Many ceramic materials undergo polymorphic transformations which can decrease the strength of sintered material either during cooldown or by further thermal cycling. Quartz and cristobalite forms of SiO_2 both have displacive transformations accompanied by substantial volume change.

An engineer has several ways of determining if a material is susceptible to damage by polymorphic transformation. First, he or she can determine what crystallized compositions are present in the material by x-ray diffraction analysis. Then the engineer can look up phase equilibrium diagrams for the material and its constituents. These diagrams will show if polymorphic phases are present. Figure 7.11 showed simplified examples having three different polymorphs. Unfortunately, the equilibrium diagram provides no information about the volume change during transformation. This can be obtained by thermal expansion measurement.

7.2 MODIFIED DENSIFICATION PROCESSES

So far only conventional sintering where a powder compact is densified under the influence of temperature has been discussed. Other processes are also available which achieve densification, deposition of a solid phase,

or strong bonding. In this section attention is given to hot pressing, reaction sintering, chemical vapor deposition, liquid particle deposition, and cementicious bonding.

Hot Pressing

Hot pressing is analogous to sintering except that pressure and temperature are applied simultaneously [8]. Hot pressing is often referred to as pressure sintering. The application of pressure at the sintering temperature accelerates the kinetics of densification by increasing the contact stress between particles and by rearranging particle positions to improve packing. It has been established that the energy available for densification is increased by greater than a factor of 20 by the application of pressure during sintering, providing several processing and property advantages:

1. Reduces densification time
2. Can reduce densification temperature, often resulting in less grain growth than would occur with pressureless sintering
3. Minimizes residual porosity
4. Results in higher strength than can be achieved through pressureless sintering, due to the minimization of porosity and grain growth

The following sections describe how hot pressing is conducted, some of the unique properties, and some of the interesting applications.

Hot-Pressing Equipment Figure 7.13 shows a simple schematic of a uniaxial hot-pressing setup. It consists of a furnace surrounding a high-temperature die with a press in line to apply a controlled load through the die piston. The type of furnace is dependent on the maximum temperature and uniformity of the hot zone required. Induction heating, with water-cooled copper coils and a graphite susceptor, is most commonly used and has a temperature capability greater than 2000°C (3632°F). The furnace must either be evacuated or back-filled with N_2, He, or Ar during operating to minimize oxidation of the graphite. Furnaces with graphite or other resistance heating elements can also be used for hot pressing. The author is not aware of gas-fired furnaces in use for hot pressing.

The source of pressure is usually a hydraulic press with a water-cooled platen attached to the ram. However, this does not provide adequate cooling to extend the ram into the furnace, so blocks of graphite or other refractory material are used. Obviously, the size of the press is dependent on the size of the part being hot pressed and the pressure required. Most hot pressing is done in the range 6.9 to 34.5 MPa (1000 to 5000 psi).

The die material is perhaps the most important element of the hot press. It must withstand the temperature, transient thermal stresses, high hot-pressing loads, and be chemically inert to the material being hot pressed.

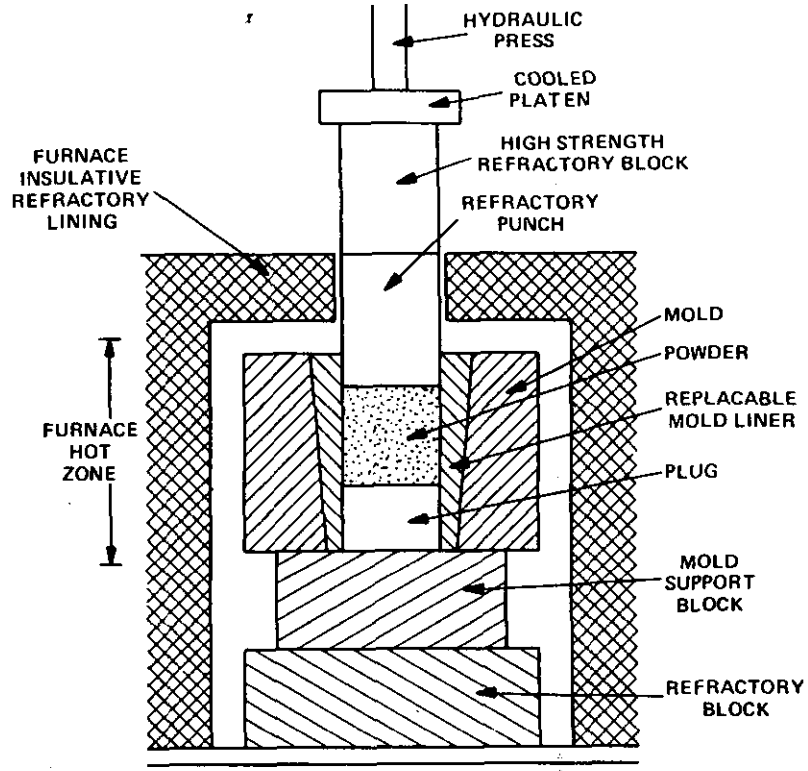


Figure 7.13 Schematic showing the essential elements of a hot press.

Graphite is the most widely used die and piston material. It has high-temperature capability, its strength increases with temperature, and it has low friction. It does not react with most materials and can be coated with a boundary layer such as boron nitride (BN) to prevent direct contact with material it might interact with. As with the graphite susceptor, though, graphite does oxidize and must be used under a protective environment.

Refractory metal dies such as molybdenum, tantalum, and the molybdenum alloy TZM have been used in limited cases. However, they are expensive, have high reactivity, and deform easily at high temperatures. Leipold [9] recommends TZM coated with $MoSi_2$ or a composite die consisting of a molybdenum jacket surrounding an Al_2O_3 liner. This latter approach takes advantage of the strength of the molybdenum and the abrasion resistance, creep resistance, and lower thermal expansion coefficient of the Al_2O_3.

Superalloys have also been used for hot-pressing dies for ceramics, but only at temperatures below 900°C (1652°F) and loads below 104 MPa (15,000 psi). A major problem with these materials is high thermal expansion. If the expansion of the die is higher than that of the material being hot pressed, the die will essentially shrink fit around the material during cooling and make ejection extremely difficult.

Ceramic dies, especially Al_2O_3 and SiC, are used frequently for hot pressing. They have reasonably low thermal expansion, are nonreactive, and have excellent resistance to galling and abrasion. Al_2O_3 can be used to approximately 1200°C (2192°F), dense SiC to about 1400°C (2552°F).

Reactivity is a special concern of die assemblies. Many of the carbides, ferrites, and other materials are very susceptible to property alteration through variations in stoichiometry and must be hot pressed under very controlled conditions. Graphite dies are often lined with a "wash" or spray coating of BN or Al_2O_3. Dies used for ferrites and some other electronic ceramics are often lined with ZrO_2 or Al_2O_3 powder.

The nature of the powder to be hot pressed is equally important to correct selection of the die material. The same type of fine-grained powders suitable for pressureless sintering are usually acceptable for hot pressing. In most cases a densification aid or a grain-growth inhibitor is added to achieve maximum density and minimum grain size. Table 7.3 summarizes sintering aids and grain-growth modifiers for a variety of oxides, carbides, nitrides, and borides. Specific references on the hot pressing of each of these ceramic materials are listed in Refs. 9 and 10.

Hot pressing is typically conducted at approximately half the absolute melting temperature of the material [9], which is usually a lower temperature than the material can be densified by pressureless sintering. Time at temperature is also reduced. The reduced temperature and time at temperature combine to minimize grain growth, thus providing better potential for improved strength.

Powder to be hot pressed can be loaded directly into the die or can be precompacted separately into a powder preform or compact that is then loaded into the die. Loading powder directly into the die is the most common procedure. However, the problems with this method are the difficulty in achieving uniformity and the pickup of contamination. Another disadvantage involves the low packing density of the loose powder and the resulting increase in the stack height to achieve a given part thickness. This reduces the number of parts that can be produced in a hot-pressing run and also increases the die wall friction. Increased die wall friction increases the variation of pressure within the compact and increases the chances for nonuniformity in the final part. The author encountered another problem with loose powder die loading while scaling up the hot pressing of Si_3N_4 from 7.6-cm (3-in.)-diameter development samples to 15.2-cm (6-in.)-diameter pilot production billets. The 7.6-cm (3-in.) samples had a strength of 897 MPa (130,000 psi) and were uniform across the diameter. The early

Table 7.3 Densification Aids and Grain-growth Modifiers

Material	Densification aids	Grain-growth inhibitors	Modifiers, enhancers
Al_2O_3	LiF	Mg, Zn, Ni, W, BN, ZrB_2	H_2, Ti, Mn
MgO	LiF, NaF	MgFe, Fe, Cr, Mo, Ni, BN	Mn, B
BeO	Li_2O	Graphite	--
Si_3N_4	MgO, Y_2O_3, $BeSiN_2$	--	--
SiC	B, Al_2O_3, Al	--	--
TaC, TiC, WC	Fe, Ni, Co, Mn	--	--
ZrB_2, TiB_2	Ni, Cr	--	--
ThO_2	F	Ca	--
ZrO_2	--	H_2, Cr, Ti, Ni, Mn	--
$BaTiO_3$	--	Ti, Ta, Al/Si/Ti	--
Y_2O_3	--	Th	--
$Pb(ZrTi)O_3$	--	Al, Fe, Ta, La	--

Source: Refs. 9 and 10.

15.2-cm (6-in.) billets were near theoretical density around the edges, but of decreased density in the interior. The overall density was within specification. The strength also appeared within specification since it was being measured on material sliced from the edge of the part. From all appearances the billets were of equivalent quality to the smaller development samples and were acceptable for delivery to a customer. However, when further testing was conducted, which included an evaluation of the billet interior, it was found that this region had density below specification and a strength of less than 690 MPa (100,000 psi). The source of the problem turned out to be a combination of loose powder loading and nonuniform temperature distribution. The loose powder had a very low thermal conductivity such that the edges in close proximity to the graphite die heated up faster than the interior and began to sinter. This physically shifted material from the center toward the edge and ultimately resulted in the density and strength gradient. The lesson is that flaws may result in a part that are not readily detectable, but if the engineer is aware of the mechanisms of processing and of some of the things that can go wrong, he or she will have a better chance of solving a problem that occurs or producing a quality control specification that will minimize such occurrences. The problem was resolved by precompacting the powder better and by modifying the time-temperature profile during hot pressing. Recurrence was prevented by initiating a more rigid density specification and strength certification procedure.

Unique Hot-Pressed Properties Hot pressing permits achieving near-theoretical density and very fine grain structure, which result in optimization of strength. It also permits reduction of the amount of sintering aid required to obtain full density. This can result in orders-of-magnitude improvement in high-temperature properties such as creep and stress rupture life.

Table 7.4 compares the properties of several sintered and hot-pressed Si_3N_4 compositions developed during the past 10 years or currently under development. Similar differences exist between sintered and hot-pressed varieties of other materials such as Al_2O_3, SiC, spinel, and mullite.

Hot pressing can cause preferred orientation of the grain structure of some materials and result in different properties in different directions. This occurs predominantly when powders with a large aspect ratio such as rods or needles are used. It can also occur due to flattening of agglomerates or laminar distribution of porosity perpendicular to the direction of hot pressing. Figure 7.14 illustrates the strength variations measured for specimens cut from various orientations from a hot-pressed Si_3N_4 billet. The strength was greatest in the plane perpendicular to the direction of hot pressing. This was thought to be due to a combination of preferred orientation of Si_3N_4 grains and laminar density contours.

Table 7.4 Comparison of Densities and Strengths Achieved by Hot Pressing Versus Sintering

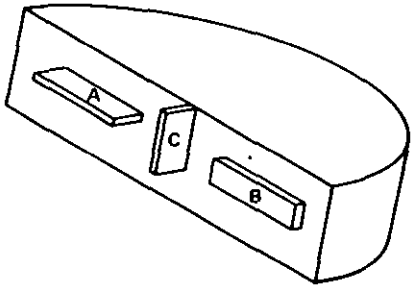
Material	Sintering aid	Density (% theoretical)	RT MOR[a]		1350°C MOR	
			MPa	kpsi	MPa	kpsi
Hot-pressed Si_3N_4[b]	5% MgO	>98	587	85	173	25
Sintered Si_3N_4[b]	5% MgO	~90	483	70	138	20
Hot-pressed Si_3N_4[c]	1% MgO	>99	952	138	414	60
Sintered Si_3N_4[d]	$BeSiN_2$ + SiO_2	>99	560	81	--	--
Sintered Si_3N_4[e]	6% Y_2O_3	~98	587	85	414	60
Hot-pressed Si_3N_4[e]	13% Y_2O_3	>99	897	130	669	97

[a] Room-temperature modulus of rupture.
[b] G. R. Terwilliger, J. Am. Ceram. Soc. 57(1), 48-49 (1974).
[c] D. W. Richerson, Am. Ceram. Soc. Bull. 52, 560-562, 569 (1973).
[d] C. D. Greskovich and J. A. Palm, U.S. DOE Conf.-791082, 1979, pp. 254-262.
[e] Data from C. L. Quackenbush, GTE Laboratories, Waltham, Mass.

Strength test specimens are normally cut from the plane perpendicular to the hot-pressing direction. This is usually the strongest direction (if anisotropy is present) and may give the engineer false confidence in the material. The engineer should be aware that the strength and other properties in the other directions may be inferior and adjust the material qualification testing accordingly.

Hot-Pressing Limitations The major limitation of hot pressing is shape capability. Flat plates, blocks, or cylinders are relatively easy to hot press. Long cylinders, nonuniform cross sections, and intricate or contoured shapes are difficult and often impossible by conventional uniaxial techniques. Figure 7.15 and the following paragraphs describe the nature of the problem.

The starting powder goes into the die as a relatively uniform stack of powder or as a uniform preform. During densification the powder or preform will compact in the axial direction of pressure application until the porosity has been eliminated and near-theoretical density achieved. The amount of compaction required to go from the loose powder or preform to the pore-free part is referred to as the compaction ratio. The compaction ratio for a well-compacted preform usually ranges from 2:1 to 3:1 and can be even higher for loose powder having a very fine particle size. For instance, one batch of Si_3N_4 powder had a compaction ratio of 8:1.



	A	B	C
AVERAGE 4-PT. BEND STRENGTH	876 MPa (127 Kpsi)	762 MPa (110 Kpsi)	713 MPa (103 Kpsi)
STANDARD DEVIATION	105 MPa (15.3 Kpsi)	142 MPa (20.6 Kpsi)	92 MPa (13.3 Kpsi)

Figure 7.14 Variations in the strength of hot-pressed Si_3N_4 as a function of direction.

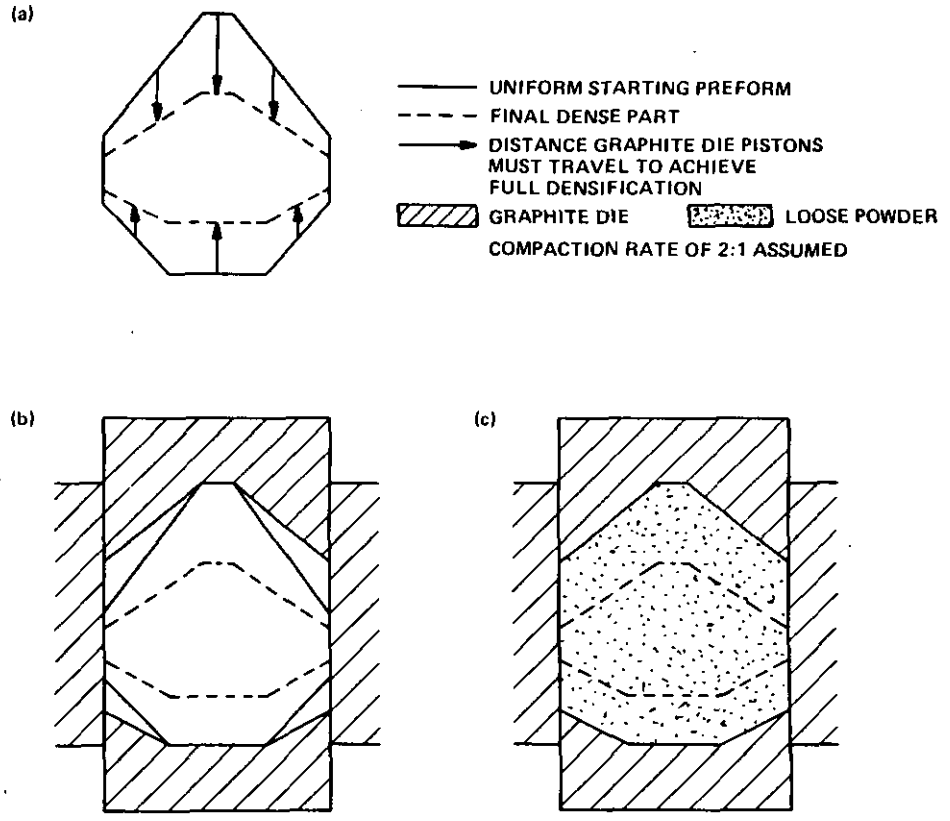


Figure 7.15 Problems associated with complex shape hot pressing. (a) Assuming a uniform starting preform or powder stack, the preform will have to shrink different amounts to achieve uniform final density and the required shape. (b) A preform with the correct powder distribution has a different shape than the die. (c) Loose powder fill requires a powder redistribution during hot pressing.

Figure 7.15a illustrates the shape of a preform having a compaction ratio of 2:1 that would be required to make a fully dense part of an arbitrary nonuniform cross section. The shape of the preform is different than the final shape and the required movement of the graphite die punches is greater for thick sections than for thin sections. For instance, in the example in Fig. 7.15, the total shrinkage in the thick section of the part is four times greater than the shrinkage in the thin section, even though the percentage is the same in each case. And this is only for a minimal compaction ratio of 2:1. The shrinkage difference is greater for higher compaction ratios.

How can one design rigid graphite tooling to accommodate the differences in distance and still achieve the required shape? Usually, it cannot be done. One either has to make the preform a different shape than the graphite tooling (as shown in Fig. 7.15b) and hope the preform does not break up prematurely and alter the powder distribution, or one has to load loose powder to fill the die cavity (as shown in Fig. 7.15c) and hope that the powder will redistribute to the required distribution during hot pressing.

The latter approach has been used with success for some materials and shapes and is worth trying because the tooling is usually not prohibitively expensive. The former approach requires two sets of tooling and has not yet been developed, but may also be worth considering.

Another approach to uniaxial hot pressing of shapes having nonuniform cross section is the use of nonrigid tooling. Two concepts are illustrated in Fig. 7.16. The first is referred to as pseudoisostatic hot pressing. A preform is prepared by cold pressing, slip casting, or other approach. The dimensions are selected (with knowledge of the compaction ratio for the specific material) such that the required shape will result after densification. The preform is embedded in loose powder in the hot-press die cavity. The loose powder is selected so that it will not densify and will not chemically react with the preform being hot pressed. Hexagonal boron nitride and graphite powders have both been used successfully and work especially well because of their self-lubricating character and excellent chemical stability. During hot pressing the loose powder transmits pressure from the die punches to the preform. A true isostatic pressure distribution is not achieved, but enough pressure is apparently transmitted to the preform to allow densification. Most shapes hot pressed by this approach have achieved near-theoretical density but have undergone some distortion during pressing. However, once the distortions are accounted for in the preform, near net shape can probably be reproducibly achieved.

Figure 7.16b illustrates the second nonrigid tooling approach. In this case three preforms having the same compaction ratio are required. The center preform will densify to become the required shaped part. The other two preforms are simply conforming layers between the flat die punch surfaces and the contoured part surface. A nonreactive boundary layer such as boron nitride is placed between the preforms so that they can be separated after hot pressing. This approach simulates hot pressing of a flat plate of uniform cross section and results in uniform density and properties in the finished part.

Hot Isostatic Pressing Recently, substantial progress has been made in hot isostatic pressing (HIP) of ceramics. Apparatus for HIP consists of a high-temperature furnace enclosed in a water-cooled autoclave capable of withstanding internal gas pressures up to about 32,000 kg/mm^2 (45,000 psi) and providing a uniform hot-zone temperature up to about 2000°C (3632°F) [11]. Pressurization gas is either argon or helium. Heating is usually by molybdenum or graphite resistance-heated elements.

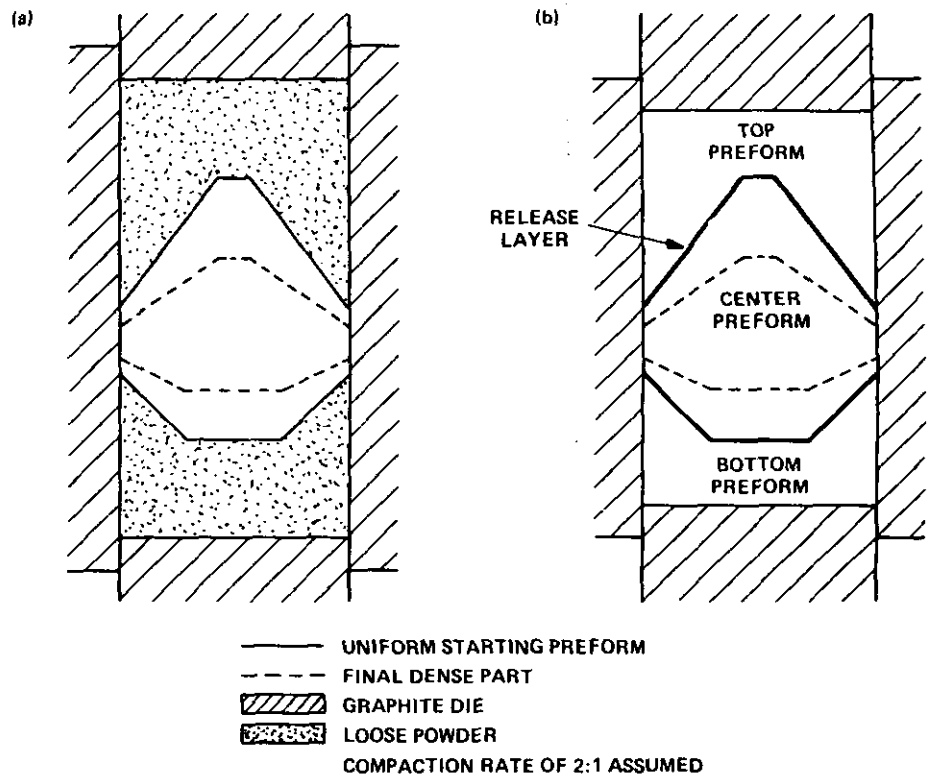


Figure 7.16 Nonrigid tooling approaches for hot pressing. (a) Pseudoisostatic approach. (b) Multiple preforms simulating a flat plate approach.

To achieve densification of a ceramic preform, the preform must first be evacuated and then sealed in a gas-impermeable envelope. If any high-pressure gas leaks into the preform, pressure is equalized and the preform cannot hot press. The earliest HIP studies encapsulated the ceramic in tantalum or other refractory metal, depending on the temperature required for densification. However, this severely limited the shape capability. Current studies are directed toward the use of glass encapsulation. The glass can be applied as a preformed envelope, which is sealed around the part under vacuum and then collapsed at high temperature to conform to the ceramic preform shape. This has worked for relatively simple shapes. ASEA in Sweden and Battelle in the United States have developed techniques to apply the glass as a particulate coating. The preform with this coating is then placed in the HIP autoclave and evacuated. The temperature is raised until the glass softens and forms a continuous layer on the surface. The pressure and temperature are then increased to the levels required to

accomplish densification of the ceramic preform. Battelle has demonstrated that individual gas turbine rotor blades of Si_3N_4 can be fabricated by this approach. ASEA has fabricated small [~12.7 cm (5 in.)] integral axial rotors of Si_3N_4 by this approach.

HIP has the potential of resolving some of the major limitations of uniaxial hot pressing. It makes possible net shape forming because the pressure is equally applied from all directions. This also results in greater material uniformity by eliminating die wall friction effects and preferred orientation, resulting in higher strength and Weibull modulus. Also, much higher pressures and temperatures can be used, making possible more complete densification and greater flexibility in selection of composition. For instance, the higher pressure and temperature may permit densification of compositions containing less sintering aid and having dramatically improved stress rupture life and oxidation resistance.

HIP has been used to improve the strength and wear resistance of some MgZn and NiZn ferrites, yttrium iron garnet, and $BaTiO_3$, especially for applications such as magnetic recording heads. The ceramic is first sintered to closed porosity and is then further densified by HIP without a requirement for encapsulation [12].

Reaction Sintering

Unique processes have been developed in England for achieving moderately strong Si_3N_4 and SiC shapes without undergoing the large shrinkage of conventional sintering [13,14]. These processes are referred to as reaction sintering or reaction bonding.

Reaction-Sintered Silicon Nitride Reaction-sintered Si_3N_4 is fabricated from silicon powder. The silicon powder is processed to the desired particle size distribution and formed into the required shape by pressing, slip casting, injection molding, or other suitable process. The compacted Si shape is then placed in a furnace under a nitrogen or mixed nitrogen/hydrogen or nitrogen/helium atmosphere and heated initially to about 1200 to 1250°C (2200 to 2282°F). The nitrogen permeates the porous Si compact and begins to react with the Si to form Si_3N_4. Initially, α-Si_3N_4 fibers grow from the Si particles into the pores. As the reaction progresses, the temperature is slowly raised to approximately 1400°C (2552°F), near the melting temperature of Si. As the temperature increases, the reaction rate increases and primarily β-Si_3N_4 is formed. Great care is necessary in controlling the rate of temperature increase and nitrogen flow. The reaction of N_2 and Si is exothermic and, if allowed to proceed too fast, will cause the silicon to melt and exude out of the surface of the part. A typical nitriding cycle in which the exotherm is controlled and no exuding occurs is on the order of 7 to 12 days, depending on the volume of material in the furnace and the green density of the starting Si compacts.

Approximately 60% weight gain occurs during nitriding, but less than 0.1% dimensional change. This makes possible excellent dimensional control. Bulk densities up to 2.8 g/cm^3 (0.101 lb/in.^{3}) have been achieved (compared to a theoretical density for Si_3N_4 of about 3.2 g/cm^3).

The earliest reaction bonded Si_3N_4 had a density of about 2.2 g/cm^3 and a strength under 138 MPa (20,000 psi). Current 2.8-g/cm^3 material has 4-point flexure strength in the range 345 MPa (50,000 psi).

Another advantage of the reaction-sintered Si_3N_4 is its creep resistance. No sintering aids are added to achieve densification, so no glassy grain boundary phases are present. Strength is retained to temperatures greater than 1400°C (2552°F) and the creep rate is very low. The strength versus temperature and creep rate were compared with other materials in Figs. 3.11 and 4.6.

The primary disadvantage of reaction-bonded Si_3N_4 is its porosity. The porosity is interconnected and can result in internal oxidation and accelerated surface oxidation at high temperature. The internal oxidation appears to affect the thermal stability of a component. For instance, Ford Motor Company observed that experimental turbine engine parts fractured when the weight gain due to oxidation reached about 2%. The mechanism was not determined, but could have been associated with internal stresses induced by the thermal expansion mismatch between the Si_3N_4 and the cristobalite formed during oxidation.

Reaction-sintered Si_3N_4 has a relatively low elastic modulus and coefficient of thermal expansion and a relatively high thermal conductivity (considering its porosity). These properties, combined with a moderately high strength give reaction-sintered Si_3N_4 good thermal shock resistance and make it a feasible candidate for such applications as welding nozzle tips, gas turbine static structure components, and aluminum metal processing.

Reaction-Sintered Silicon Carbide Reaction-sintered SiC is processed from an intimate mixture of SiC powder and carbon. This mixture is formed into the desired shape and exposed at high temperature to molten or vapor-phase Si. The silicon reacts with the carbon to form in situ SiC, which bonds the original SiC particles together. The remaining pores are filled with metallic Si. The resulting material is basically a nonporous Si-SiC composite and can have a broad range of strength and elastic modulus, depending on the particle size distribution and the percent Si. Table 7.5 summarizes data for several reaction-sintered SiC materials [15,16].

Reaction-sintered SiC materials have a relatively flat strength versus temperature curve nearly up to the melting temperature of silicon, at which point the strength drops off rapidly. A typical strength versus temperature curve is shown in Fig. 7.17 compared to reaction-bonded Si_3N_4, hot-pressed Si_3N_4, and sintered SiC [15].

Reaction-sintered SiC has similar advantages to reaction-bonded Si_3N_4 for complex shape fabrication; it undergoes dimensional change of less than

1% during densification. The initial shape can be formed by casting, plastic molding, pressing, extrusion, and any of the other processes applicable to ceramics. It is especially suitable for the plastic processes such as extrusion and compression molding. The plasticizer can be a thermosetting resin such as a phenolic. Instead of having to remove the plasticizer after molding, as is required with other ceramics, the plasticizer is simply charred to provide the carbon source for reaction with the silicon.

Another interesting method of fabricating reaction-sintered SiC is to start with woven carbon fibers or felt, as reported by Hillig et al. [16]. Laminae of carbon fiber weave are laid up much the same as fiberglass to form the desired shape. This can then be reacted with molten silicon to form a composite of SiC-Si or C-SiC-Si. By controlling the type of fibers and the weave, a complete range of composites with varying SiC-to-Si ratios can be engineered. Ones with high Si have low elastic modulus ($\sim 30 \times 10^6$) and relatively low strength (<30,000 psi); ones with high SiC have high elastic modulus ($>50 \times 10^6$ psi) and high strength (~70,000 psi). The range of composites can be further expanded by pitch impregnation or deposition of pyrolytic carbon or glassy carbon prior to siliconizing.

Vapor Deposition

Vapor deposition is a generic term that can refer to a variety of techniques that deposit essentially nonporous ceramic coatings on a substrate. Chemical vapor deposition (CVD) and sputtering are perhaps the most widely used and will be discussed briefly.

CVD is typically accomplished by heating the part to be coated in a vacuum chamber and passing a controlled gas or gas mixture over the part. The gas mixture is selected such that it will react or decompose when it comes in contact with the part preheated to a specific temperature. Deposition rates are usually less than 250 μm (0.010 in.) per hour and careful control is required to obtain a uniform coating. However, the coatings are very fine grained and impervious and are usually of higher purity and hardness than can be achieved by other ceramic fabrication processes.

Table 7.5 Properties of Reaction Sintered SiC Materials Illustrating Variations Achievable by Varying Microstructure and Silicon Content

Material	Volume % silicon	Young's modulus, E (psi)	Flexure strength, σ (psi)
NC-435[a]	~20	50.7×10^6	57,200
Refel[b]	--	57.5×10^6	44,900
Type TH[c]	15-20	57×10^6	70,000
Type THL[c]	55-60	44×10^6	48,000
Type F[c]	75-80	29×10^6	30,000

[a] Norton Company, Worcester, Mass.
[b] British Nuclear Fuels, Ltd., U.K.
[c] General Electric Company, Schenectady, N.Y.
Source: Refs. 15 and 16.

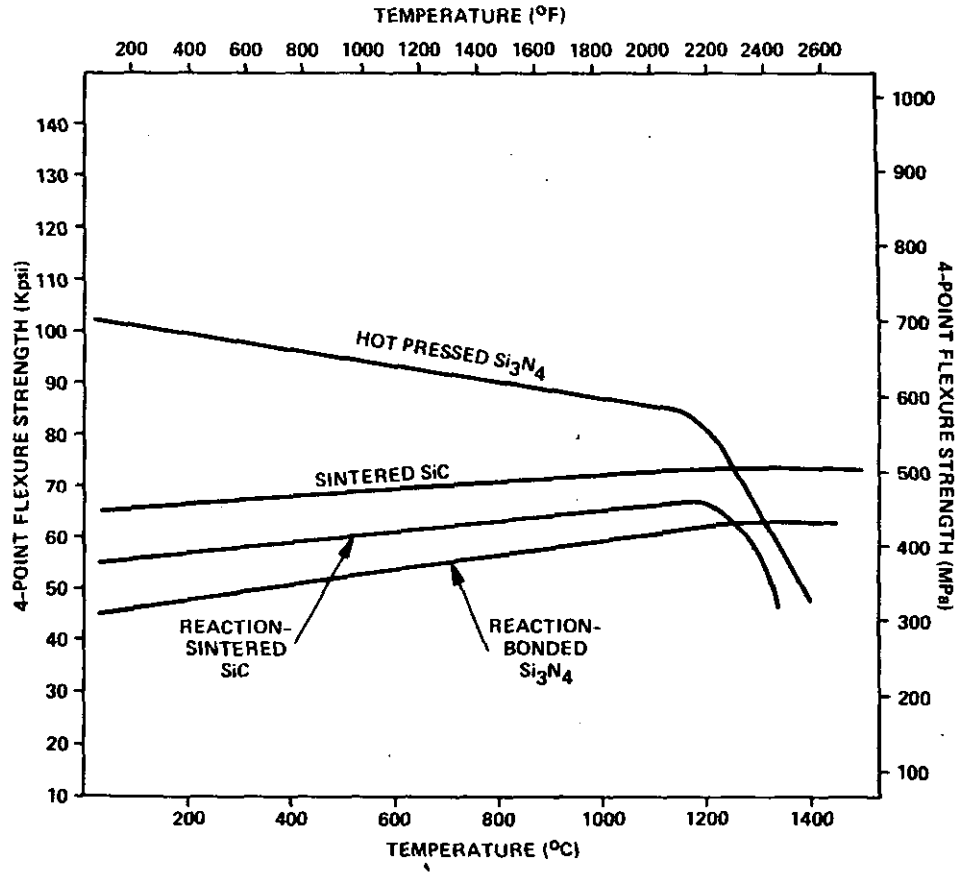


Figure 7.17 Strength of reaction-sintered SiC compared to other Si_3N_4 and SiC ceramics. (From Ref. 15.)

Figure 7.18b shows a CVD Si_3N_4 coating on reaction-bonded Si_3N_4. Note the difference in porosity between the reaction-bonded Si_3N_4 and the CVD coating. Also note the columnar structure of the coating, with the grains oriented perpendicular to the surface. This is typical of CVD coatings and is usually not desirable. Figure 7.17a shows a CNTD SiC coating on hot-pressed SiC. Note the extremely fine grain size and the lack of columnar growth. CNTD stands for Controlled Nucleation Thermochemical Deposition and was developed by Chemetal, Inc., specifically to eliminate the deficiencies of columnar growth. Tungsten carbide with strength approaching 3450 MPa (500,000 psi) has been deposited by the CNTD approach.

A second important technique for depositing ceramic coatings is sputtering. The part to be coated is placed in an evacuated chamber in close proximity to a flat plate of the coating material. This flat plate is called the target and is bombarded by a beam of electrons. The electrons essentially knock atoms off the target onto the surface of the part facing the target. Only the portion of the part directly exposed to the target gets coated. Coating rates are very slow and only thin coatings can be produced effectively. The major advantages are that the purity of the coating can be controlled and that the part is not heated during coating. An application where this might be important is in a miniaturized electrical device where a ceramic coating would provide protection and electrical insulation.

Molten Particle Deposition [17]

Molten particle deposition is most commonly referred to as flame spray or plasma spray. It consists of impacting small molten particles of ceramic against the surface to be coated. Almost any oxide, carbide, boride, nitride, or silicide that does not sublime or decompose can be applied by molten particle techniques. Coatings are most often applied, but free-standing parts can also be made by using a removable mandrel or form.

The first widely used molten particle approach was the oxyacetylene powder gun, more frequently referred to as the flame-spray gun. Ceramic powder is aspirated into the oxyacetylene flame and melts. The molten particles exit the gun through a nozzle and strike the substrate to be coated at a velocity of about 45 m/sec (150 ft/sec). By moving either the substrate or the gun, a uniform coating can be built up having approximately 10 to 15 vol % porosity and a surface finish of 150 to 300 μin. rms.

A similar approach is the oxyacetylene rod gun. Instead of using ceramic powder, a sintered rod of the coating material is fed into the oxyacetylene flame. Molten ceramic at the tip of the rod is carried to the substrate by bursts of air traveling at about 180 m/sec (600 ft/sec). Surface finishes are similar to those produced by the powder gun, but porosity is usually lower (6 to 10%) because the particles are completely molten and the impact velocity is higher.

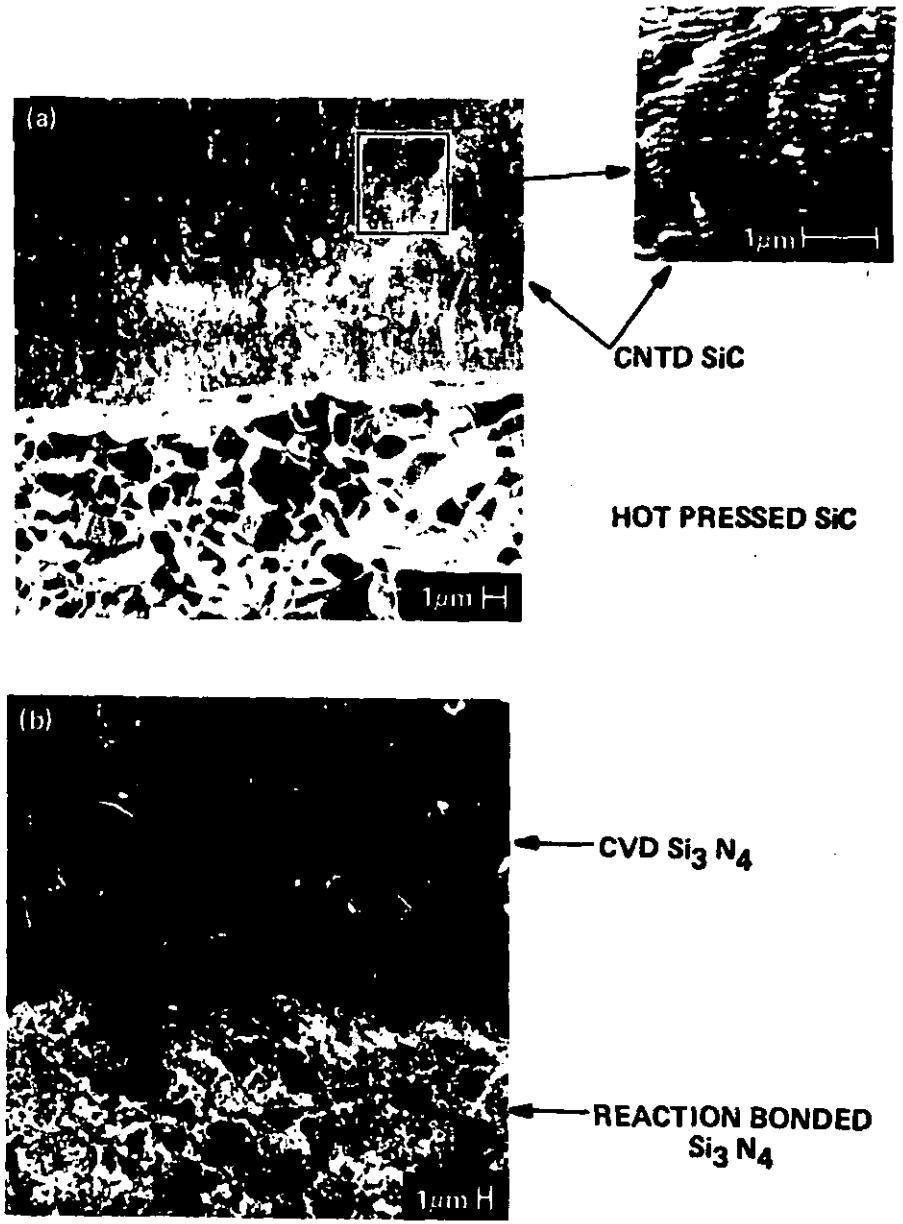


Figure 7.18 (a) CNTD SiC coating on hot-pressed SiC. (b) CVD Si_3N_4 coating on reaction-bonded Si_3N_4. (Courtesy of the Garrett Turbine Engine Company, Division of Garrett Corporation, Phoenix, Ariz.)

The oxyacetylene guns are widely used. Another widely used approach is the arc-plasma gun. A high-intensity direct-current arc is maintained in a chamber. Helium or argon is passed through the chamber, heated by the arc, and expelled through a water-cooled copper nozzle as a high-temperature high-velocity plasma. Ceramic particles are injected into the plasma, where they are melted and directed against the substrate. Velocities as high as 450 m/sec (1500 ft/sec) have been obtained, yielding coatings with porosity as low as 3% and surfaces with a finish in the range 75 to 125 μin. rms. The major difficulty of the arc-plasma gun is the temperature of the plasma. Ceramic substrates may have to be preheated to avoid thermal shock damage and metal substrates may have to be cooled to avoid melting.

Deposition rates for molten particle spray are much higher than for chemical vapor deposition, in the kilograms per hour range rather than in grams or milligrams per hour. However, for some applications this is not enough. One technique has been developed which has demonstrated 2 to 4 kg/min and is projected to scale up to 200 kg/min. The ceramic powder is mixed with fuel oil to form a slurry and is burned in oxygen in a water-cooled gun. Al_2O_3, mullite, and SiO_2 have been successfully sprayed by this method to form refractory linings for high-temperature furnaces such as the oxygen converters in steel mills.

Molten particle spray techniques have been used extensively to deposit wear-resistant and chemically-resistant coatings on a wide variety of metal and ceramic products. One interesting example is the spraying of chromium oxide (Cr_2O_3) on the propeller shafts of large seagoing ships. The chromium oxide greatly reduces erosive wear, provides a good surface to seal against (after surface grinding to achieve a suitable surface finish), and inhibits seawater corrosion.

Coatings are also applied to provide thermal protection. Stabilized ZrO_2 has a very low thermal conductivity and emissivity and is applied to stainless steel and superalloy parts as a thermal barrier coating. Although other oxide ceramics have similar thermal properties, ZrO_2 was selected because it has a coefficient of expansion similar to the metals. This is one case for a ceramic where a high coefficient of thermal expansion is beneficial.

An important advantage of molten particle spray techniques is that a wide range of size and shape of substrates can be coated. On-site repairs are even feasible. Flame spray has great versatility and an engineer should be aware of the various techniques, sources, and capabilities.

Cementicious Bonding

All of the densification processes discussed so far involve high-temperature operations to achieve a strong, useful part. Another important approach is cementicious bonding, in which an inorganic ceramic adhesive bonds together an aggregate of ceramic particles. The adhesion results primarily

from hydrogen bonding. The resulting materials are not of high strength, but are adequate for many wear-resistance, building, and refractory applications. Major advantages are that the cement can be poured, troweled, or gunned into place, has little dimensional change during setting, and can be repaired on-site.

Many different cements have been developed, ranging from common concrete to very high temperature furnace linings. The cements can be classified according to the mechanism of bind formation: hydraulic bonds, reaction bonds, and precipitation bonds [18].

Hydraulic Cements Hydraulic cements set by interaction with water. The most common hydraulic cement is portland cement, which is primarily an anhydrous calcium silicate. It is slightly soluble in water and sets by a combination of solution-precipitation and reaction with water to form a hydrated composition. The reaction is exothermic and care must be taken to ensure that adequate water is initially present and that the heat of reaction does not dry out the cement prematurely. This explains why a competent cement contractor keeps the surface of freshly laid concrete damp.

The ratio of water to cement in the initial mix has a primary effect on the final strength of the cement. As long as adequate water is added for hydration and for workability, the lower the water-to-cement ratio, the higher the resulting strength.

Calcium aluminate cements are also hydraulic setting, but have much higher temperature capability than portland cement and are thus used for refractory applications such as furnace linings. Other hydraulic cements include natural lime-silica cements, barium silicate and barium aluminate cements, slag cements, and some ferrites.

Similar to hydraulic cements are gypsum cements such as plaster of paris and Keene's cement. They set by a hydration reaction but are much more soluble than the hydraulic cements and recrystallize to a highly crystalline structure that has little adhesion. Rather than being used for bonding aggregates, plaster of paris is used alone to make wallboard, plaster molds for slip casting and metal casting, and decorative knick-knacks and statuettes.

Reaction Cements Reaction cements are formed by a chemical reaction between two constituents other than water. One of the most common is monoaluminum phosphate, formed by the reaction of aluminum oxide powder with phosphoric acid. This cement sets in air at room temperature, but is usable over a very broad temperature range. Above 310°C (500°F) the cement is dehydrated to form the metaphosphate, which is then stable up to very high temperature. In fact, the strength increases as the temperature is increased.

Most metal oxides form phosphate cements when reacted with phosphoric acid. In addition to Al_2O_3, the following metal oxides have been shown by

Kingery [19] to form phosphate cements: BeO, CdO, Fe_2O_3, Y_2O_3, ZnO, ZrO_2, CrO_3, CuO, CO, ThO_2, V_2O_5, and SnO. Compositions based on ZnO have been widely used for dental cements.

Most of the ceramic cements are porous and brittle and require an aggregate to provide durability. An interesting reaction cement that has some resiliency is magnesium oxychloride cement. It has been used for floors, building facings, signs, and a variety of other applications.

Precipitation Cements Precipitation cements are primarily gels formed by precipitating colloidal suspensions by adjusting the pH or ion concentration. Sodium silicate is perhaps the best known and most widely used precipitation cement. It is inexpensive and its composition can be controlled to achieve setting by drying, heating, or chemical means. Chemical setting is achieved by addition of acid salts, especially sodium silicofluoride. The setting rate can be controlled by the amount and grain size of the silicofluoride and the amount of water in the cement. Organic materials such as esters (ethyl acetate) and alcohols also precipitate alkali silicate cements.

Another important precipitation cement is prepared from ethyl orthosilicate. It is precipitated by dehydration. Reaction can be accelerated by addition of magnesia or by heating.

Precipitation cements are used extensively in applications where acid resistance is critical. They are also used for some abrasion resistance applications, for bonding low-temperature refractories, and for forming of foundry molds for metal casting.

Development of ceramic cements is very competitive and most compositions and specific processing approaches are proprietary. A variety of cements are available commercially and can be purchased ready to mix or ready to use. Sources can be obtained by referring to the Ceramic Products Issue included each year in the Bulletin of the American Ceramic Society. More detailed technical information can be found in Ref. 18.

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8

Final Machining

Some ceramic parts can be fabricated to net shape by the methods described in Chap. 7. However, more frequently, machining of some of the surfaces is required to meet dimensional tolerances, achieve improved surface finish, or remove surface flaws. This machining can represent a significant portion of the cost of fabrication and thus should be minimized and conducted as efficiently as possible.

8.1 MECHANISMS OF MATERIAL REMOVAL

Ceramic materials are difficult and expensive to machine due to their high hardness and brittle nature. Machining must be done carefully to avoid brittle fracture of the component. Most ceramics cannot be successfully machined with the type of cutting tools used for metal because these tools are either not hard enough to cut the ceramic or because they apply too great a local tensile load and cause fracture. The tool must have a higher hardness than the ceramic being machined and must be of a configuration that removes surface stock without overstressing the component.

Ceramic material can be removed by mechanical, thermal, or chemical action. Mechanical approaches are used most commonly and are discussed first. They can be divided into three categories: mounted abrasive, free abrasive, and impact.

Mounted Abrasive Machining

Mounted abrasive tools consist of small, hard, abrasive particles bonded to or immersed in a softer matrix. The abrasive particles can be SiC, Al_2O_3, Al_2O_3-ZrO_2, or other hard ceramic material, and the matrix can be rubber, organic resin, glass, or a crystalline ceramic composition softer than the abrasive particles. Good examples are the wide variety of grinding wheels used extensively in home workshops and industry. For

machining very hard ceramics such as Al_2O_3, Si_3N_4, and SiC, diamond is usually the most efficient abrasive, mounted in a matrix of soft metal or organic resin.

Mounted abrasive tools can be made in a wide variety of configurations and compositions. Coarse abrasives are used for rough machining, where rapid stock removal is desired. Finer abrasives are used for final machining, where close tolerances and smooth surface finishes are required.

Stock removal is achieved by moving the tool in relation to the ceramic workpiece while simultaneously applying pressure. The abrasive particles are small and irregular in shape such that a sharp corner of the particle is usually in contact with the ceramic. This small contact area produces high localized stress concentration and the particle plows a microscopic groove across the surface of the ceramic. The larger the abrasive, the larger the groove and the greater the depth of damage in the ceramic. This will be discussed in more detail later in a section on effects of machining on material strength, including suggested procedures to minimize strength reduction.

Free Abrasive Machining

Free abrasive machining consists of the use of loose abrasive and is usually used for achieving the final surface finish with very fine particle size abrasive. Lapping is the most commonly used free abrasive approach. The fine abrasive is placed on a soft material such as cloth or wood, which is then moved in relation to the ceramic being lapped. Because of the fine abrasive size, material removal rate is very slow. However, very smooth surfaces with flatness measured in wavelengths of light can be achieved. These surfaces result in very low friction and have been used in bearing and seal applications.

Free abrasive is also used in trepanning. This is a technique used for drilling circular holes in a ceramic. The tool consists of a thin-walled hollow cylinder of a soft metal such as brass. The loose abrasive is placed between the tool and the workpiece together with a coolant such as water or oil, and pressure is applied simultaneously with rotation to achieve grinding action.

Impact Abrasive Machining

The two previous machining methods remove stock essentially by sliding motion. Material can also be removed by impact. Sandblasting is the primary impact approach. Abrasive particles are carried by compressed air through a nozzle which directs them at high velocity against the workpiece. Rate of material removal for a ceramic increases with particle size, hardness of the abrasive and velocity, and for angles of impingement approaching 90°. Al_2O_3 and SiO_2 are the most commonly used abrasives.

Sandblasting has been used in sculpture and for fabrication of tombstones, but is not used often for fabrication of ceramic components for engineering applications. The primary drawbacks are difficulty in achieving close tolerances or a uniform surface.

Sandblasting is used for cleaning the surface of ceramics and also as a test method for evaluating the wear resistance of materials.

A second type of impact machining makes use of ultrasonics. However, the nature of the impact is significantly different than that which occurs during sandblasting. In ultrasonic machining the abrasive is suspended in a water slurry which flows over the surface of the tool. The tool is vibrated at high frequency, which accelerates each abrasive particle over a very short distance to strike the workpiece. Impact occurs only where the tool is in close proximity to the workpiece, so that close tolerances can be achieved by control of the tool and abrasive dimensions. No pressure is applied between the tool and abrasive so that very little strength-limiting damage to the ceramic results. Boron carbide is frequently used as the abrasive because it is harder than most other ceramics (except diamond), is less expensive than diamond, and is available in narrow size ranges.

Chemical Machining

Chemical machining is used primarily to achieve improved surface finish and thus increased strength or decreased friction. It is achieved by immersing the surface to be machined into a liquid in which the ceramic is soluble. Most silicate glass compositions can be etched or chemically machined with hydrofluoric acid (HF). Al_2O_3 can be etched with molten $Na_2B_4O_7$. These treatments are often referred to as chemical polishing because they produce such a smooth surface.

Photoetching

Some glass compositions can be chemically machined into very complex geometries using photoetching [1]. One such glass contains Ce_2O_3 and Cu_2O. A mask or photo negative is placed on the glass and irradiated with ultraviolet light. In the unmasked areas the Cu_2O is reduced by the Ce_2O_3 by the reaction $Ce^{3+} + Cu^{+} \longrightarrow Ce^{4+} + Cu$. The glass is then exposed to a controlled heat treatment in which the Cu particles act as nucleation sites for localized crystallization. The crystallized material can be etched in hydrofluoric acid at a rate 15 times the rate of the original glass.

Some very intricate configurations have been produced by this photoetching technique. An example is a 600-mesh sieve.

Electrical Discharge Machining

Electrical discharge machining (EDM) can be performed only with electrically conductive materials. A shaped tool is held in close proximity to the part being machined, retaining a constant predetermined gap with the use of a servomechanism that responds to change in the gap voltage. A dielectric liquid is flowed continuously between the tool and workpiece. Sparks produced by electrical discharge across this dielectric erode the ceramic by a combination of vaporization, cavitation, and thermal shock produced by the intense local heating [2].

EDM has been used successfully with conductive carbides, silicides, borides, and nitrides. The advantages are that no mechanical load is applied during EDM and that holes, recesses, and outer dimensions can be produced in the same types of shapes that could be formed in metal by stamping or in dough by a cookie cutter. The disadvantages are the slow rate of cut, the limitation to conductive materials, and the relatively poor surface finish achieved. The surface is typically pitted and microcracked and results in substantial strength reduction.

Laser Machining

Only a few studies have been reported on laser machining of ceramics. Lumley [3] reports the use of laser machining to score Al_2O_3 electronic substrates to allow them to be fractured to the desired size. The mechanism of material removal appeared to be localized thermal shock spalling.

Copley et al. [4] have reported machining of SiC, Si_3N_4, and SiAlON using a CO_2 laser. In this case material removal was apparently by evaporation, since all three of these materials decompose rather than melt. A hot-pressed Si_3N_4 cylinder containing 1/4 in. × 20 threads was laser machined from rectangular stock. A SiAlON cylinder was also machined. Surface finish measurement determined that the maximum nonsmoothness from peak to valley was 7.5 μm. This suggests that laser machining of ceramics may be a feasible approach and should be evaluated further. In particular, the effects on material strength should be assessed.

8.2 EFFECTS ON STRENGTH

To understand the effects of machining on the strength of a ceramic material, we must examine the interactions that occur at the tool-workpiece interface and define the flaws that are initiated in the ceramic. First, let us consider a single mounted abrasive particle plowing a furrow in a ceramic workpiece. Material directly in the path of the abrasive particle sees very high stress and temperatures and is broken and deformed. Material adjacent

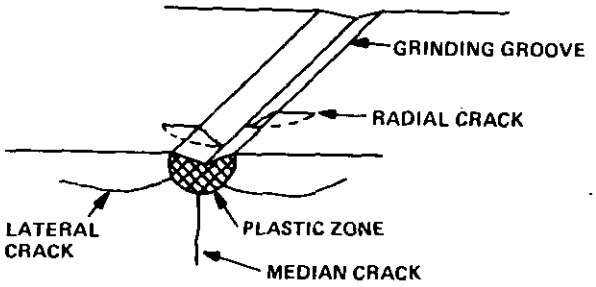

Figure 8.1 Schematic showing the cracks and material deformation that occurs during grinding with a single abrasive particle.

to the abrasive particle is placed in compression and may also deform plastically. After the abrasive particle passes, this material rebounds and either cracks or spalls off, due to the resulting tensile stresses [5,6]. Thus the size of the machining groove for most ceramics is larger than the size of the abrasive particle.

Figure 8.1 shows schematically the types of cracks that can form adjacent to the grinding groove [7-10]. The median crack is parallel to the direction of grinding and perpendicular to the surface, and results from the high stresses at the bottom of the grinding groove. Because it is parallel to the direction of grinding, it has also been called a longitudinal crack. It is usually the deepest crack and produces the greatest strength reduction.

Lateral cracks are parallel to the surface and extend away from the plastic zone. They result from the high tensile stress that exists at the edge of the plastic zone and extend as the material relaxes immediately after the abrasive particle passes. Lateral cracks tend to curve toward the surface and often result in a chip spalling off. Because lateral cracks are parallel to the surface, they do not result in stress concentration during subsequent mechanical loading and thus do not significantly reduce the strength of the material. However, they do account for a substantial portion of stock removal during grinding.

Radial cracks normally result from single particle impact or indentation and extend radially from the point of impact. They are perpendicular to the surface, but are usually shallow and do not degrade the strength as much as a median crack. The cracks shown in Fig. 8.1 which are perpendicular to the grinding groove are analogous to radial cracks. There can be many of these along the length of the grinding groove. They have been referred to in the literature as transverse, chatter, or crescent cracks, but their mechanism of formation has generally not been discussed. It is most likely that they are initiated by the high tensile stress that arises at the trailing edge of the contract of the abrasive particle and the workpiece. This biaxial stress mechanism for high-friction situations was discussed in Chap. 3.

Effect of Grinding Direction

Most ceramics are machined with tools containing many abrasive particles rather than just one single point. However, it is likely that the resulting surface flaws are similar for both types of tools and that the median and radial cracks control the strength. Which flaw controls the strength depends on the orientation of the grinding grooves to the direction of stress application. This is shown schematically in Fig. 8.2 for specimens loaded in bending.

As the load is applied and the specimens begin to bend, stress concentration will occur at the tips of cracks perpendicular to the stress axis but not at cracks parallel to the stress axis. Thus for specimens ground in the longitudinal direction, stress concentration will occur at the radial (transverse) cracks, and for specimens ground in the transverse direction, stress concentration will occur at the median (longitudinal) cracks. Since the median cracks are usually the most severe, one would expect the strength to be lowest for transverse grinding, where the grooves and median cracks are perpendicular to the tensile stress axis. This can be seen in Table 8.1.

From Table 8.1 it is obvious that substantial differences in load-bearing capability for a ceramic component can result, depending on the orientation of grinding with respect to the stress distribution in the component. This anisotropy of strength is an important consideration for an engineer designing a component that must withstand high stress.

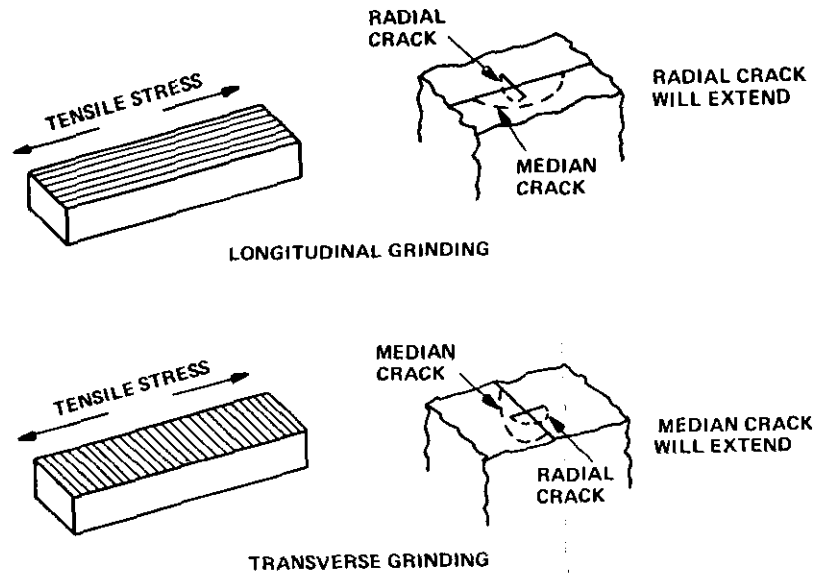

Figure 8.2 Grinding direction and crack distribution versus tensile stress axis.

Table 8.1 Strength Versus Grinding Direction Orientation with Respect to Tensile Stress Axis

Material	Longitudinal grinding		Transverse grinding	
	MPa	psi	MPa	psi
Hot-pressed Si_3N_4	669	97,000	428	62,000
Soda-lime glass	97	14,100	68	9,900
Mullite	319	46,300	259	37,600
MgF_2	87	12,600	53	7,700
B_4C	374	54,200	154	22,300

Source: Refs. 11 (Si_3N_4 data) and 12 (data for other materials).

Effects of Microstructure

The microstructure of the ceramic material has a pronounced effect on the rate of machining and on the residual strength after machining. Rice [5] reports that fine-grained ceramics require higher grinding force and longer time to slice or machine. This is shown for several ceramic materials in Fig. 8.3. Uniformly distributed porosity increases the rate of machining, but also decreases the smoothness of surface finish that can be achieved.

The degree of strength reduction resulting from machining is dependent on a comparison of the size of flaws initially present in the ceramic to those produced by machining. Machining has very little effect on the strength of ceramics containing high porosity or large grain size because the flaws introduced during machining are no larger than the microstructure flaws initially present. On the other hand, the strength of fine-grained ceramics such as most Si_3N_4 and Al_2O_3 can be reduced significantly.

Effects of Grinding Parameters

The parameters selected for machining a ceramic have a large effect on the rate of machining and tool wear and on the resulting properties of the ceramic. Table 8.2 summarizes general trends associated with variations in individual machining parameters. It should be emphasized that these are just trends and that they may not hold true for all ceramic materials and all levels of variation. Also, most of these parameters are interactive and may have a different effect when combined than when considered individually.

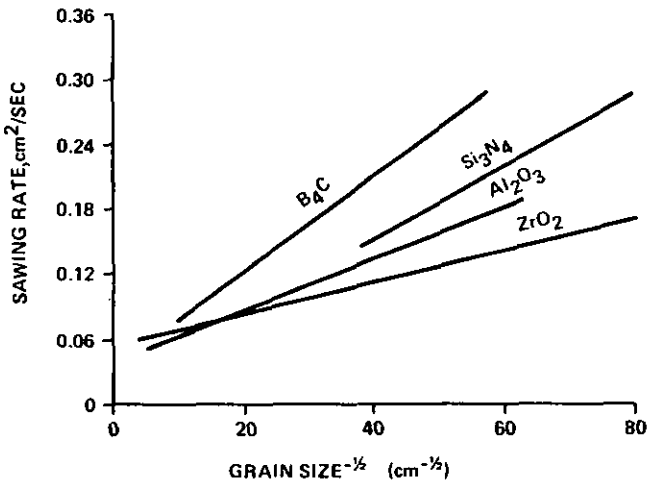

Figure 8.3 Effect of machining rate on grain size. (From Ref. 5.)

Large abrasive particles result in a greater depth of grinding damage and are used for roughing operations. Finer abrasives are used to remove the subsurface damage produced by the large abrasive during roughing and to achieve the final tolerances and surface finish.

To achieve maximum strength, grinding is usually done in several steps, decreasing the abrasive size in each step and removing enough surface stock to remove subsurface damage resulting from the prior step. Sometimes, intermediate machining steps are skipped to save time and decrease cost. The desired tolerances and surface finish can be achieved, but the strength requirements may not, and the component may fail in service.

Harder ceramic materials are more difficult to cut and grind than softer materials and require higher force. This results in increased wheel wear, higher interface temperatures, and greater danger of damage to the ceramic. Increased wheel speed decreases the required force and usually results in lower tool wear, lower temperatures, and less surface damage. The use of water or other suitable lubricant or coolant provides similar benefits.

Minimizing Machining Effect on Properties

The deleterious effects of machining on ceramic properties can be decreased by experimental optimization of the machining parameters. This includes selecting the appropriate abrasive and wheel bond, wheel speed, downfeed, coolant, and abrasive size sequence. Postmachining procedures

Table 8.2 Effects of Machining Parameters

Parameter variation	Effect on machining rate[a]	Effect on tool wear[a]	Effect on material strength[a]
Increasing abrasive size	Increases rate	Depends more on other factors	Decreases strength
Increasing downfeed or table speed	Increases rate	Increases wear	Decreases strength
Increasing wheel speed	Increases rate	Usually decreases wear	Increases strength
Use of lubricants and coolants	May increase rate	Usually decreases wear	Usually increases strength
Increasing abrasive hardness	Increases rate	Decreases wear	Depends more on other factors
Changing abrasive concentration and wheel bond	Different optimum for different materials and configurations	Can be optimized	Can be optimized

[a]Relative to an arbitrary baseline.

have been developed to obtain further improvement in the properties. These include the following:

Lapping
Annealing
Oxidation
Chemical etching
Surface compression
Flame polishing

Each of these approaches either removes surface and subsurface flaws resulting from machining or reduces the stress concentration due to the flaw.

Lapping Lapping involves the use of very fine free abrasive particles suspended in a slurry and applied to the workpiece surface with a soft tool surface such as cloth or wood. It is equivalent to mechanical polishing used in preparation of metallographic samples for microstructure examination. The size of the abrasive determines the final surface finish that can be achieved. However, as mentioned before, the strength does not necessarily increase as the surface smoothness increases. To achieve strength increase, machining and lapping must be done in a diminishing abrasive size sequence such that each step successfully removes the worst surface damage produced by the prior step. A suitable sequence might be to rough machine with 200-grit diamond, finish machine with 320- and 600-grit diamond, rough lap with 30- and 9-μm Al_2O_3 or CeO_2, and finish lap with 3-, 0.3-, and 0.06-μm Al_2O_3 or CeO_2. Final lapping can also be done with diamond.

The degree of lapping or surface finishing is obviously dependent on the cost restraints and the criticality of the application. Because of the fine grain structure and hardness of advanced ceramic materials, excellent surface finish and tolerances can be achieved. For example, the following capabilities have been reported for dense Al_2O_3 by Western Gold and Platinum Co. (WESGO) in their Technical Circular No. L-779:

"Flat lapping to half a light band (0.000006 in. or 0.000152 mm flatness)
Parallelism to 0.000010 in. (0.00025 mm)
Dimensional tolerances of 0.000010 in. (0.00025 mm)
Cylindrical outside diameters between 0.060 in. (1.524 mm) and 3 in. (76.2 mm) lapped to 0.000005 in. (0.000127 mm) dimensional tolerance and roundness to 0.000005 in. (0.000127 mm)
Stepped diameters lapped to 0.000050 in. (0.00127 mm) concentricity
Outside-inside mating diameters lapped to 0.000050 in. (0.00127 mm) tolerance of mating clearance
Cylindrical inside diameters between 0.060 in. (1.524 mm) and 2 in. (50.8 mm) lapped to 0.000005 in. (0.000127 mm) dimensional tolerance and roundness to 0.000005 in. (0.000127 mm)

Blind holes and intersecting holes lapped to 0.000005 in. (0.000127 mm) dimensional tolerance and roundness to 0.000005 in. (0.000127 mm)
Radial and spherical concave and convex surfaces lapped to within 0.000010 in. (0.00025 mm) of true radius and 0.000010 in. (0.00025 mm) roundness."

Most applications do not require such precise lapping. Some of the more critical applications in terms of surface finish or tolerances include optical glass, laser ceramics, bearings, seals, some papermaking components and thread guides.

Annealing Since ceramic materials are normally processed at very high temperature, internal stresses often result during cooldown. Sometimes these residual stresses can improve strength, but often they reduce strength. Annealing at high temperature followed by slow cooldown can often relieve these stresses. Annealing can also relieve surface stresses resulting from machining and actually heal subsurface flaws such as median cracks. Annealing can also crystallize glass phases and achieve improved strength or stability.

Oxidation Oxidation has been demonstrated to increase the strength of machined hot pressed Si_3N_4 [11] and other nitrides and carbides. In the case of Si_3N_4, the reaction $Si_3N_4 \longrightarrow 3SiO_2 + 2N_2$ can increase the strength by completely removing the depth of surface containing the residual machining cracks or by rounding the crack tip and reducing stress concentration. This approach was used effectively for improving the load-bearing capability of hot-pressed Si_3N_4 rotor blades [11]. The blade machining process resulted in transverse grinding perpendicular to the tensile stress axis such that the median crack was strength controlling. The as-machined strength was about 428 MPa (62,000 psi). Oxidation at 960°C (1800°F) for 50 hr increased the strength to 635 MPa (92,000 psi).

Chemical Etching Chemical etching has been used for many years for removing machining or other surface damage, especially the use of hydrofluoric acid with glass. Strength increases greater than tenfold have been achieved both for glass compositions and for oxide ceramics.

Surface Compression Placing the surface in compression obviates the effects of surface flaws by preventing concentration of tensile stresses at the crack tip. The surface compressive stress must first be exceeded by an applied tensile stress before the stress concentration will begin to build up and lead to crack propagation.

Perhaps the most common example of surface compression is in safety glass. Surface compression is achieved in glass most commonly by either ion exchange or quenching. In the former case, glass is exposed at elevated temperature to positive ions that are larger than those initially in the glass. Since the glass structure is expanded at the elevated temperature, these larger ions are able to trade places with smaller ions near the surface. When the glass is cooled, these ions no longer fit, but are trapped in the structure and result in surface compression. An example is that of exchanging calcium ions for sodium ions.

Ion exchange can also be applied to crystalline materials. The exchange ion can cause compression by size difference or by producing a surface composition with a lower coefficient of thermal expansion [13].

Quenching has also been known for a long time as a method of improving strength. Kirchner [13] discusses in detail the use of quenching to strengthen Al_2O_3, TiO_2, spinel, steatite ($MgSiO_3$), forsterite (Mg_2SiO_4), SiC, and Si_3N_4. Quenching Al_2O_3 rods from 1600°C into a silicone oil resulted in an increase in the average strength from 331 MPa (47,900 psi) to 694 MPa (100,600 psi).

For quenching to be effective, the material must be heated to a temperature such that some plasticity is present. A temperature of 1500 to 1600°C is appropriate for Al_2O_3, but 1900 to 2000°C is required for SiC. During quenching the surface cools very rapidly and is placed in compression as the interior cools more slowly.

Surface compression can also be achieved with glazes (glass surface coatings). The glaze composition is selected to have a lower coefficient of expansion than the matrix material. For instance, Kirchner used a glaze with a thermal expansion of 5.3×10^{-6} per °C for coating Al_2O_3 with a thermal expansion of 6.5×10^{-6} per °C. Glazes can be used in conjunction with quenching or ion exchange to achieve additional benefits. Kirchner achieved a strength of 767 MPa (111,200 psi) for Al_2O_3 that was glazed and quenched, compared to 331 MPa (47,900 psi) for as-received material.

Flame Polishing Flame polishing is used primarily for reducing the size and quantity of surface flaws in small-diameter rods or filaments, especially of sapphire or ruby (single-crystal Al_2O_3). Flame polishing is conducted by rotating the rod or filament and passing it through a H_2-O_2 flame such that the thin surface layer melts. Noone and Heuer [14] report bend strengths for flame-polished ruby and sapphire in the range 4000 to 5000 MPa (580,000 to 724,000 psi) compared to approximately 300 MPa (43,500 psi) for as-ground specimens. Stokes [15] compares the tensile strength of flame polished single-crystal Al_2O_3 with other surface preparations. His results are summarized in Table 8.3.

Stokes [15] also discussed the effects of machining on properties other than strength. The shape of the hysteresis loop in magnetic ferrites is significantly changed by near-surface stresses resulting from machining. Polishing, annealing, and etching procedures are routinely used to attain reproducibly the desired loop shape. Electrical and optical properties are also affected strongly by machining and surface condition.

Table 8.3 Surface Preparation Versus Tensile Strength for Single-Crystal Al_2O_3

Surface preparation	Tensile strength	
	MPa	psi
As-machined	440	60,000
Polished by centerless grinding	590	90,000
Annealed in oxygen after polishing by centerless grinding	1,040	150,000
Chemical polished with molten borax	6,860	1,000,000
Flame polished	7,350	1,100,000
Pristine whiskers	15,900	2,300,000

Source: Ref. 15.

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