

Third Edition

# Modern Ceramic Engineering

Properties, Processing,  
and Use in Design

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# 13 Shape-Forming Processes

The properly sized and preconsolidated powders are now ready for forming into the required shapes. Table 13.1 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.

## 13.1 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. Two categories of pressing are commonly used: (1) uniaxial and (2) isostatic. Both use powder prepared by the same procedures. Therefore, we shall discuss the procedures and the nature of the binder systems first, followed by a review of the pressing techniques. The types of problems that can be encountered in pressing and the evidence that an end-user can detect in the part will be emphasized. If the end-user can spot problems, he or she is in a better position to work with the supplier to solve the problems.

### 13.1.1 STEPS IN PRESSING

Like all the processes for forming ceramics, pressing involves a sequence of steps that all must be carefully controlled to achieve an acceptable product. Figure 13.1 shows a flowchart for two procedures of pressing. Let us review each procedure.

Procedure A is based on granulation to achieve a free-flowing powder. Raw materials are selected and weighed to the proper batch calculation. The powders are sized by dry milling. The sized powder is placed in a muller mixer with additions of the binder plus about 15 wt% water and mixed until homogeneous. The mixture is formed into granules by screening, running through a granulator, or

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**TABLE 13.1**  
**Major Compaction Techniques Used for Ceramic Fabrication**

|                                     |                            |
|-------------------------------------|----------------------------|
| <b>Pressing</b>                     | Fugitive-mold casting      |
| Uniaxial                            | Gel casting                |
| Isostatic                           | Electrophoretic deposition |
| Hot pressing <sup>a</sup>           | <b>Tape Casting</b>        |
| Hot isostatic pressing <sup>a</sup> | Doctor blade               |
| <b>Slip Casting</b>                 | Waterfall                  |
| Drain casting                       | <b>Plastic Forming</b>     |
| Solid casting                       | Extrusion                  |
| Vacuum casting                      | Roll forming               |
| Pressure casting                    | Injection molding          |
| Centrifugal casting                 | Compression molding        |

<sup>a</sup>Techniques that involve simultaneous compaction and densification and are discussed in Chapter 14.

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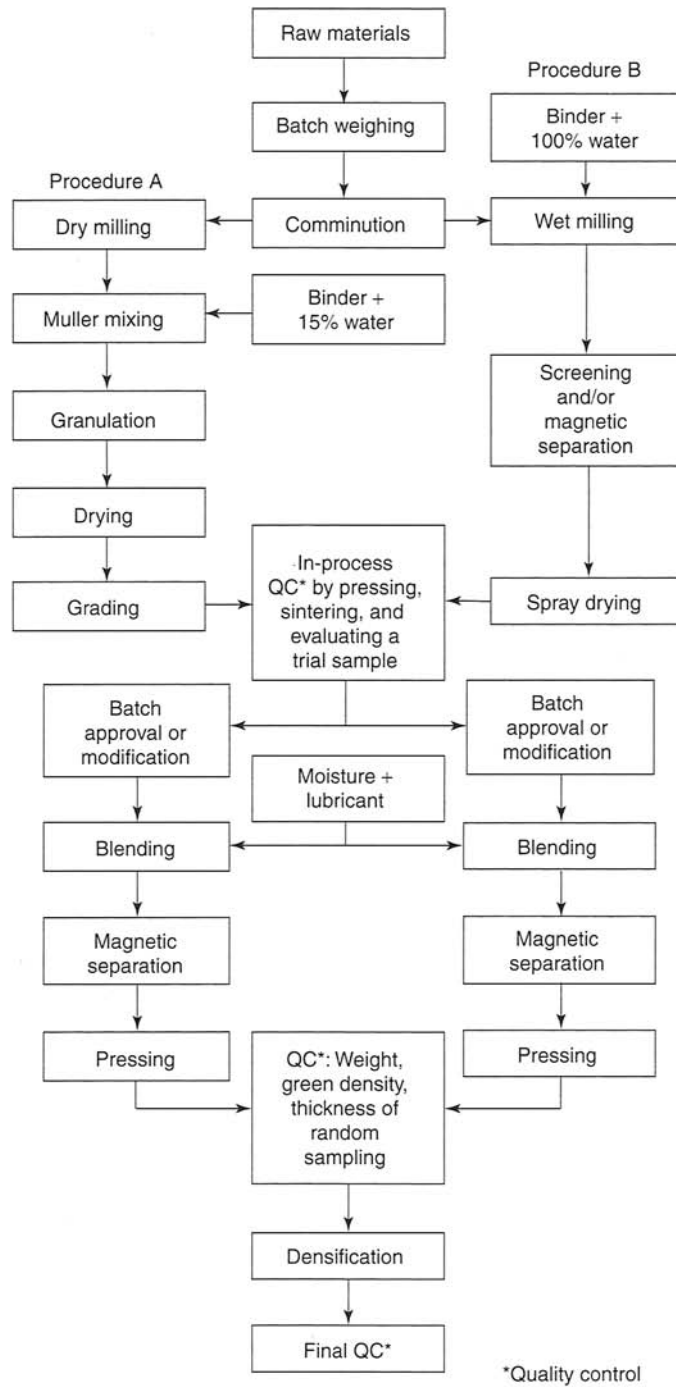


FIGURE 13.1 Typical flow sheets for fabrication by pressing. (From Ceramic Fabrication Processes, Kingery, W.D., Ed., MIT Press, Cambridge, MA, 1963. With permission.)

prepressing plus granulating. The granules are soft and damp at this stage, but become moderately hard after drying. The dried granules are graded by screening to achieve the desired size distribution. This usually involves removal of fines that are not adequately free-flowing. At this point, an in-process quality check is conducted. This typically involves pressing of a trial sample to determine

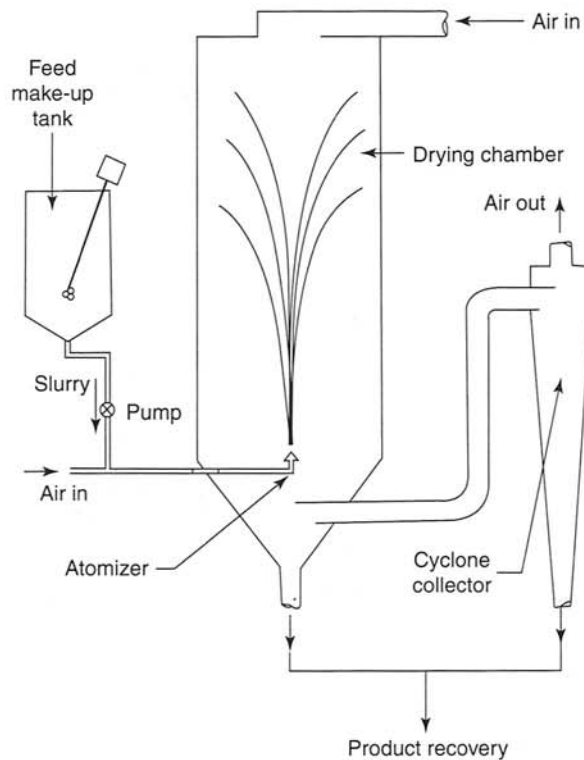


FIGURE 13.2 Schematic of one type of spray dryer. (Drawing courtesy of ASM International.)

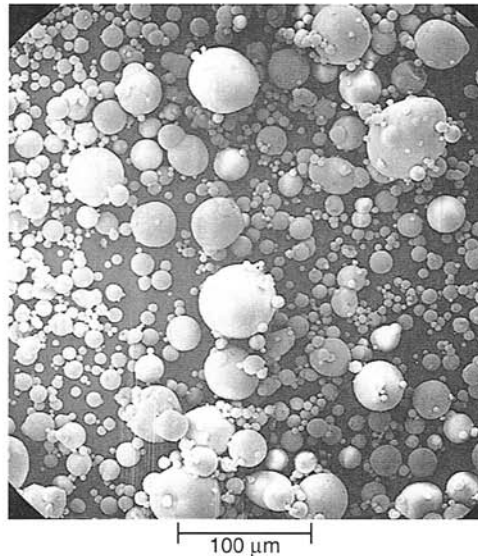
the compaction characteristics (e.g., compaction ratio\* green density, ease of release from the die) and densification characteristics (e.g., shrinkage, fired density, and key properties). Acceptable powder is then ready to be prepared for production pressing. This can involve addition of a lubricant and a little moisture and removal by magnetic separation of metal particles picked up by wear of the processing equipment. Quality is checked on random samples after pressing and again after densification.

Procedure B is based on spray drying to achieve a free-flowing powder. The weighed batch of powder plus additives is mixed with enough water to form a fluid suspension (slurry) and wet-milled to achieve homogeneous mixture and particle sizing. The slurry is passed through a screen and/or a magnetic separator to remove large particles and metallic contamination. The slurry is then spray-dried as described in Chapter 12. Figure 13.2 shows the schematic of one type of spray dryer. Figure 13.3 illustrates the morphology of typical spray-dried powder. Depending on the slurry and the spray-drying parameters, the resulting powder can consist of solid spheres, hollow spheres, or doughnut-shaped platelets. After spray drying the powder goes through the same quality control and pressing procedures as described for procedure A.

### 13.1.2 SELECTION OF ADDITIVES

The additives commonly required for pressing are a binder, a plasticizer, a lubricant, and/or a compaction aid. The binder provides some lubrication during pressing and gives the pressed part adequate strength for handling, inspection, and green machining. The plasticizer modifies the binder to make it more pliable. The lubricant reduces interparticle friction and die-wall friction. The compaction

\*Compaction ratio is the ratio between the thickness of the powder in the die to the thickness after pressing. Green density is bulk density of the compact. The term "green" is commonly used to describe the porous ceramic compact prior to densification.



**FIGURE 13.3** Photo taken with a scanning electron microscope showing the spherical morphology of spray-dried powder. (Courtesy of Ceramatec, Inc.)

aid (which is essentially a lubricant) reduces interparticle friction. The combined effects of the additives are: (1) to allow the powder particles to slide past each other to rearrange in the closest possible packing; and (2) to minimize friction and allow all regions of the compact to receive equivalent pressure. Let us discuss these in more detail and examine some examples.

#### 13.1.2.1 Binders and Plasticizers

Table 12.13 listed a variety of organic and inorganic materials that have been used as binders. Most binders and plasticizers are organic. They coat the ceramic particles and provide lubrication during pressing and a temporary bond after pressing. The amount of organic binder required for pressing is quite low, typically ranging from 0.5 to 5 wt%. Organic binders normally are decomposed during the high-temperature densification step and evolved as gases. Some binders leave a carbon residue, especially if fired under reducing conditions.

Inorganic binders also exist. The clay minerals such as kaolinite are a good example. Kaolinite has a layered structure and interacts with water to yield a flexible, plastic mixture. The clay minerals do not burn off during densification, but instead become part of the ceramic.

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 extrude between the die components, which can cause sticking or reduce the production rate.

Other binders can be classified as hard, that is, 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.

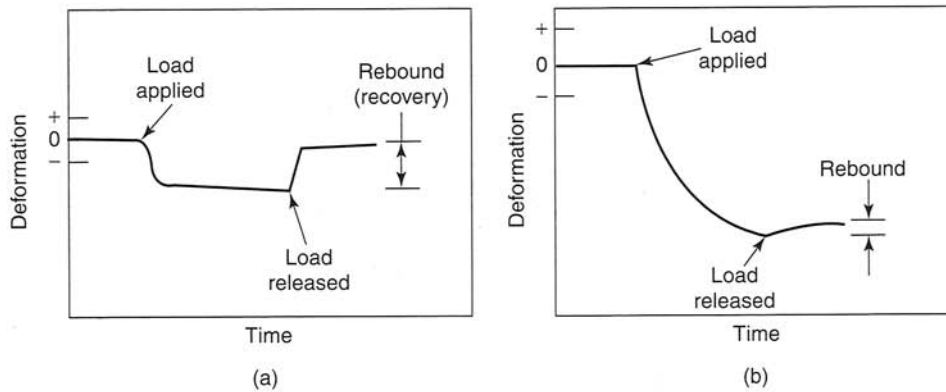


FIGURE 13.4 (a) Glassy deformation behavior below the glass transition temperature and (b) plastic behavior above the glass transition temperature. (Drawings courtesy of ASM International.)

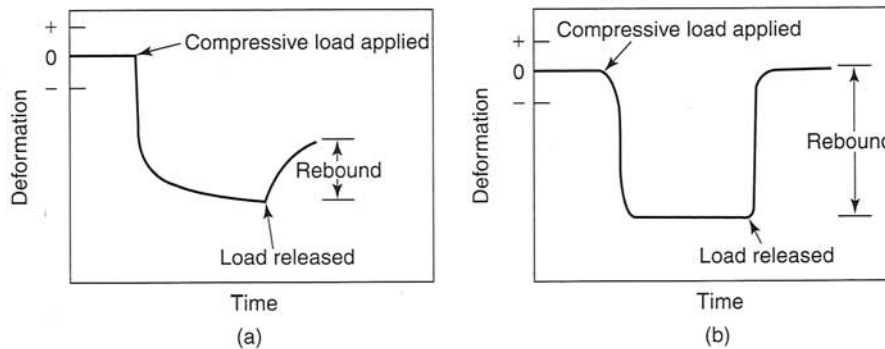
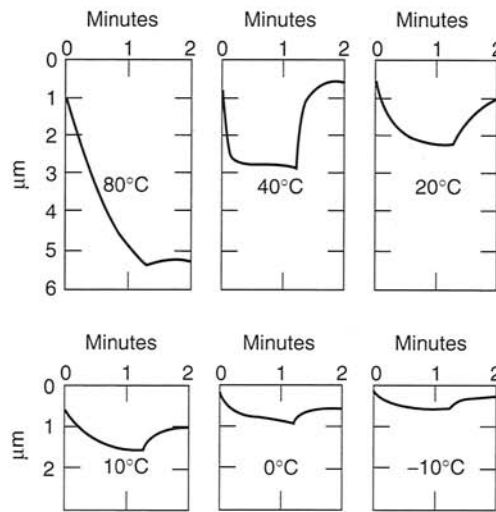


FIGURE 13.5 (a) Viscoelastic deformation behavior and (b) rubbery deformation behavior. (Drawings courtesy of ASM International.)

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

The hardness and deformation characteristics of organic binders vary with temperature, humidity, and other factors. Many of these materials go through a ductile-brittle transition and behave in a brittle fashion below the transition and in a ductile fashion above the transition. The temperature at which this ductile-brittle transition occurs is referred to as the *glass transition temperature* ( $T_g$ ). Typical load-deflection curves below and above the glass transition temperature are shown in Figure 13.4. Several aspects of these curves are important during pressing: (1) the total deformation; (2) the amount of rebound or recovery after the load is removed; (3) the load necessary to initiate deformation; and (4) the net deformation (permanent set). These are illustrated for a hypothetical load-deflection curve in Figure 13.5.

Now we can go back to Figure 13.4 and compare the behavior below and above the glass transition temperature  $T_g$ . Below  $T_g$  the deformation is primarily elastic and the behavior is categorized as “glassy.” The total deformation is low and is completely recovered after removal of the load. This behavior provides little or no binder or lubricant capability. The material has a stronger tendency to fracture than to deform. Conversely, above  $T_g$  the deformation is large and primarily plastic. Very little rebound occurs when the load is removed. This behavior provides excellent binder and lubricant capability. The curve in Figure 13.5a illustrates behavior intermediate between glassy and plastic. This behavior is referred to as *viscoelastic*. One other type of behavior is occasionally encountered.



**FIGURE 13.6** Deformation behavior of an alkyd organic binder at various temperatures showing transition from glassy to viscoelastic to rubbery to plastic. (Adapted from Rosen, S.L., *Fundamental Principles of Polymeric Materials*, Wiley, New York, 1982.)

This is shown in Figure 13.5b and is referred to as “rubbery.” It is characterized by large elastic deformation and large rebound after the load is removed. This behavior is not favorable for pressing.

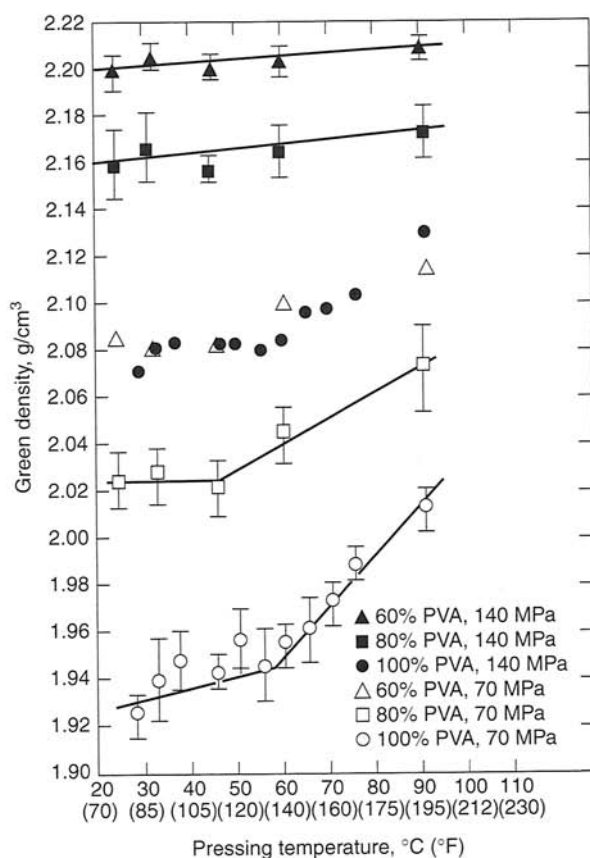
The complete range of deformation characteristics can occur for a single organic binder material over a temperature range. This is shown for an alkyd material in Figure 13.6. Between  $-10$  and  $0^{\circ}\text{C}$  ( $15$  and  $32^{\circ}\text{F}$ ) the material shows glassy behavior. Between  $10$  and  $20^{\circ}\text{C}$  ( $50$  and  $70^{\circ}\text{F}$ ) the behavior is viscoelastic. At  $40^{\circ}\text{C}$  ( $105^{\circ}\text{F}$ ) the behavior is rubbery and at  $80^{\circ}\text{C}$  ( $175^{\circ}\text{F}$ ) the behavior is plastic.

The deformation behavior can be altered by addition of plasticizers. Let us examine polyvinyl alcohol (PVA) that is commonly used as a binder in the ceramic industry. Polyethylene glycol (PEG) and water both act as plasticizers for PVA. PVA with no plasticizer has a  $T_g$  over  $60^{\circ}\text{C}$  ( $140^{\circ}\text{F}$ ) and thus has glassy deformation behavior at room temperature. Relative humidity (rh) of 50% reduces  $T_g$  to below  $50^{\circ}\text{C}$  ( $120^{\circ}\text{F}$ ). Addition of 50% PEG at 50% rh reduces  $T_g$  to  $10^{\circ}\text{C}$  ( $50^{\circ}\text{F}$ ). As would be expected from these numbers, the amount of plasticizer and the pressing temperature have a significant effect on the green density achieved during pressing. This is illustrated in Figure 13.7 for  $\text{Al}_2\text{O}_3$  powders pressed with binder-plasticizer combinations of 60% PVA–40% PEG, 80% PVA–20% PEG, and 100% PVA at different pressures and temperatures. Powder pressed at 70 MPa (10.1 ksi) at room temperature with 100% PVA binder achieved a green density of only  $1.93\text{ g/cm}^3$  ( $0.069\text{ lb/in.}^3$ ) (48.5% theoretical). Powder with 60% PVA binder–40% PEG plasticizer pressed at 140 MPa (20.3 ksi) at room temperature reached a green density of  $2.2\text{ g/cm}^3$  ( $0.079\text{ lb/in.}^3$ ) (55% theoretical).

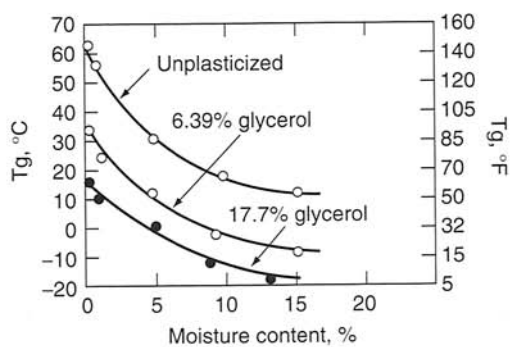
Glycerol also acts as a plasticizer for PVA. The effects of glycerol plus moisture on the  $T_g$  of PVA are shown in Figure 13.8.

### 13.1.2.2 Lubricants and Compaction Aids

Lubricants and compaction aids are essentially the same. They reduce the friction between particles, between granules, and between the powder compact and the wall of the pressing die. This results in increased uniformity of the pressed part, improved green density, extended tool life, reduced sticking (which reduces time required for tool cleaning), and decreased pressure required to eject the part from the die. The effect on ejection pressure is illustrated in Figure 13.9. One-half percent of zinc stearate reduced the ejection pressure by a factor of four. Materials with low shear strength seem to make good lubricants. Other low-shear-strength materials besides zinc stearate that have been successful as lubricants are listed in Table 13.2.



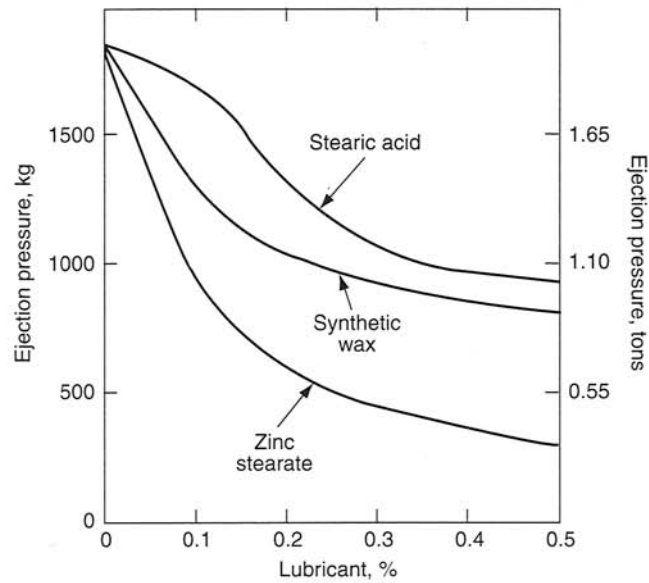
**FIGURE 13.7** Green density of  $\text{Al}_2\text{O}_3$  pressed with various ratios of polyvinyl alcohol (PVA) binder and polyethylene glycol (PEG) at different pressures and temperatures. (From Nies and Messing, *J. Am. Ceram. Soc.*, 301, 1984. With permission.)



**FIGURE 13.8** Effects of additions of glycerol and moisture on the glass transition temperature of a PVA binder. (From Nies and Messing, *J. Am. Ceram. Soc.*, 301, 1984. With permission.)

Compaction aids can result in substantial increase in green density and reduction in shrinkage during densification. This is illustrated for  $\text{Al}_2\text{O}_3$  in Table 13.3.  $\text{Al}_2\text{O}_3$  powder pressed at 34.5 MPa (5 ksi) with no compaction aid reached a green density of  $2.53 \text{ g/cm}^3$  ( $0.091 \text{ lb/in.}^3$ ) and was fired at  $1700^\circ\text{C}$  ( $3090^\circ\text{F}$ ) in 1 h to a density of  $3.85 \text{ g/cm}^3$  ( $0.138 \text{ lb/in.}^3$ ). Addition of only 2.0 wt% stearic acid increased the green density to  $3.0 \text{ g/cm}^3$  ( $0.107 \text{ lb/in.}^3$ ) and decreased the linear shrinkage during firing to only 8.3% (which is a very low value).





**FIGURE 13.9** Effects of lubricants on decreasing die-wall friction and the pressure to eject a pressed part from a die. (Drawing courtesy of ASM International.)

**TABLE 13.2**  
**Low-Shear-Strength Materials Used as Lubricants for Pressing**

|                           |                    |
|---------------------------|--------------------|
| Zinc stearate             | Paraffin           |
| Stearic acid              | Synthetic wax      |
| Oleic acid                | Lithium stearate   |
| Oils                      | Potassium stearate |
| Naphthenic acid           | Sodium stearate    |
| Boric acid                | Ammonium stearate  |
| Boron nitride (hexagonal) | Magnesium stearate |
| Graphite                  | Talc               |

**TABLE 13.3**  
**Use of Lubricants as Compaction Aids for Pressing of  $\text{Al}_2\text{O}_3$**

| Compaction Aid | Quantity, wt% | Green Density, $\text{g}/\text{cm}^3$ | Fired Density, $\text{g}/\text{cm}^3$ | Liner Shrinkage, % |
|----------------|---------------|---------------------------------------|---------------------------------------|--------------------|
| None           | 0             | 2.53                                  | 3.85                                  | 13.1               |
| Stearic acid   | 1.0           | 2.86                                  | 3.85                                  | 9.45               |
| Stearic acid   | 2.0           | 3.00                                  | 3.89                                  | 8.27               |
| Stearic acid   | 3.0           | 3.06                                  | 3.88                                  | 7.67               |
| Oleic acid     | 2.0           | 2.97                                  | 3.90                                  | 8.63               |

<sup>a</sup>All specimens pressed at 34.5 MPa (5000 psi) and fired 1 h at 1700°C (3090°F).

Source: Hart, L.D. and Hudson, L.K., *Am. Ceram. Soc. Bull.*, 43(1), 13, 1964.

### 13.1.2.3 Removal of Organic Additives

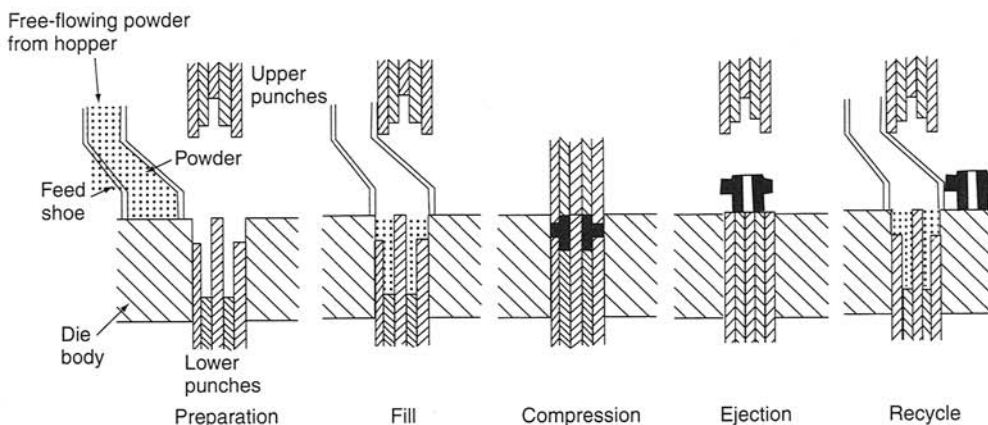
Selection of binder and other additives must be compatible with the chemistry of the ceramic and the purity requirements of the application. The binder must be removed prior to densification of the ceramic. Organic binders can be removed by thermal decomposition. If reaction between the binder and the 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 or if the atmosphere in the furnace is reducing, the binder may char rather than decompose, leaving carbon.

### 13.1.3 UNIAXIAL PRESSING — PRESSES AND TOOLING

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.<sup>1,2</sup> Most uniaxial presses are either mechanical or hydraulic. Mechanical presses typically have a higher production rate and are easy to automate. Figure 13.10 shows schematically the automated pressing sequence of a typical uniaxial 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 compaction. The feed shoe then moves into position and fills the cavity with free-flowing 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 910 to 18,200 kg (1 to 20 tons), but some operate up to 91,000 kg (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 910 to 91,000 kg (1 to 100 tons).

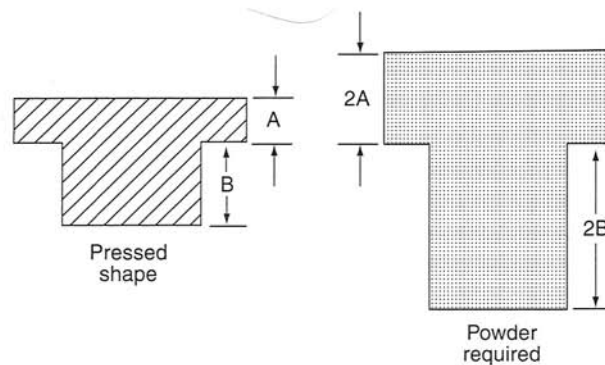
Yet another type of mechanical press is the toggle press. It is commonly used for pressing refractory brick and is capable of exerting pressure up to about 727,000 kg (800 tons). The toggle press closes to a set volume so that the final density is controlled largely by the characteristics of the feed.



**FIGURE 13.10** Schematic illustrating automated uniaxial pressing. (Adapted from Thurnauer, H., Controls required and problems encountered in production dry pressing, in *Ceramic Fabrication Processes*, Kingery, W.D., Ed., MIT Press, Cambridge, MA, 1963, pp. 62–70.)

**TABLE 13.4**  
**Uniaxial Pressing Part and Tool Classifications**

| Class | Definition  | Type of Tooling                | Typical Part Cross Sections |
|-------|---|--------------------------------|-----------------------------|
| I     | Thin, one-level parts that can be pressed from one direction      | Single action                  |                             |
| II    | Thick, one-level parts that require pressing force from both ends | Double action                  |                             |
| III   | Two-level parts that require pressing force from both ends        | Double action, multiple motion |                             |
| IV    | Multiple-level parts that require pressing force from both ends   | Double action, multiple motion |                             |



**FIGURE 13.11** Schematic illustrating the different distances a punch must move to accomplish uniform compaction of the powder. Based on a powder with a compaction ratio of 2:1. (Drawing courtesy of ASM International.)

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, but have a much lower cycle rate than mechanical presses.

The type of press and tooling selected is based largely on the size and shape of the part to be pressed. The parts can be divided into classes, as is done in powder metallurgy. The classes are defined in Table 13.4. Parts with a constant thickness and thin cross section can be successfully pressed with single-action, that is, with the die and bottom punch stationary and only the top punch moving. Thicker parts do not achieve uniform compaction if only pressed from one end. These require tooling where the top and bottom punches move, that is, double-action tooling. Parts with variations in cross-sectional thickness require an independent punch for each level of thickness. This again is necessary to achieve uniform compaction throughout the part. This is illustrated in Figure 13.11 for a powder with a compaction ratio of 2:1. The punch only has to travel a distance  $A$  to achieve compaction of the thin section, but must travel a distance  $A + B$  to compact the thick section. Both cannot be achieved with a single rigid punch. Two punches are required. Figure 13.12 shows the schematic of tooling needed to uniformly press a three-level part.

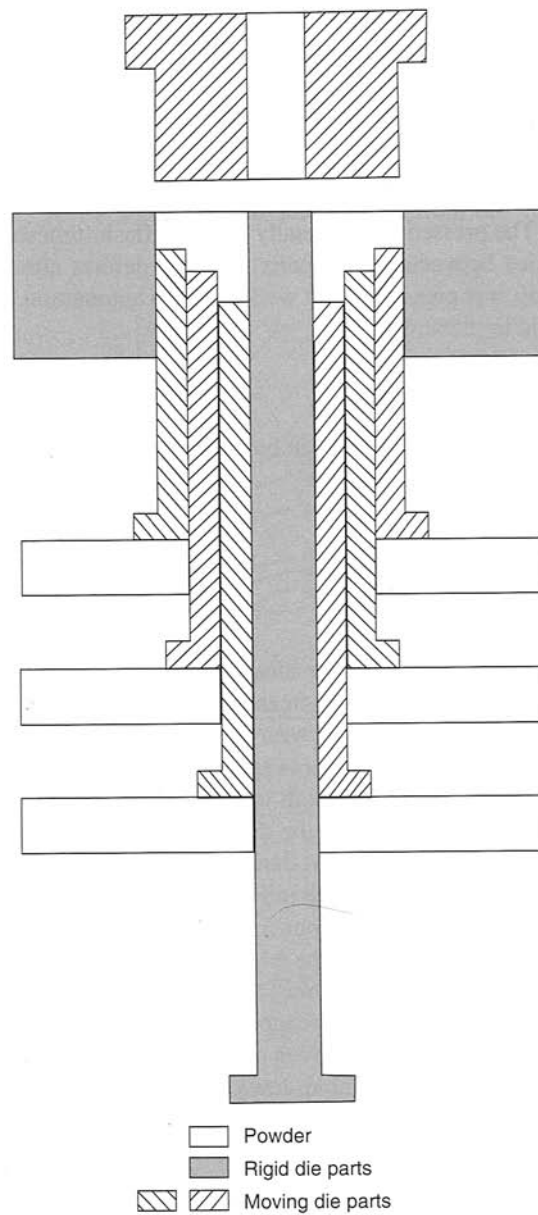


FIGURE 13.12 Schematic of tooling to uniaxially press a three-level part. (Drawing courtesy of ASM International.)

### 13.1.3.1 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  $\pm 1\%$  are normally achieved in routine applications, and closer tolerances have been achieved in special cases.

### 13.1.3.2 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  $\pm 2\%$ .

### 13.1.3.3 Uniaxial Pressing Problems

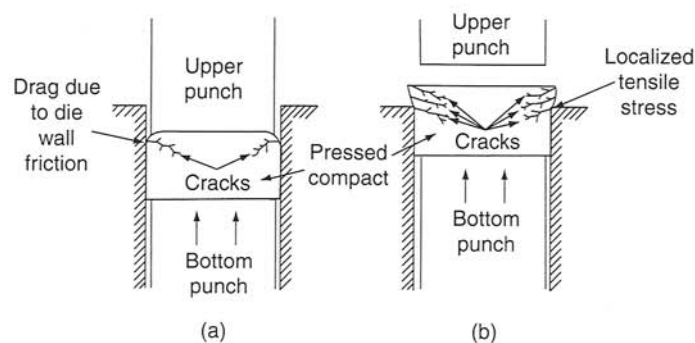
The following are some of the problems that can be encountered with uniaxial pressing.

- 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.

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-wall friction, die wear, or other causes. Often a crack initiates at the top edge of the part during pressure release or ejection of the part. Two mechanisms of this type cracking are illustrated in Figure 13.13. The first, shown in Figure 13.13a, occurs as pressure is released from the upper punch. The material rebounds near the top center of the compact, but is restricted momentarily at the edges due to frictional drag between the compact and the wall of the die. This results in a tensile stress concentrated at the upper edge of the compact. Cracks due to this mechanism (called endcapping) can be avoided by (1) use of a lubricant to minimize die-wall friction; (2) increasing the green strength of the part through binder selection; (3) minimizing rebound; and (4) maintaining a hold-down pressure on the upper punch during ejection.

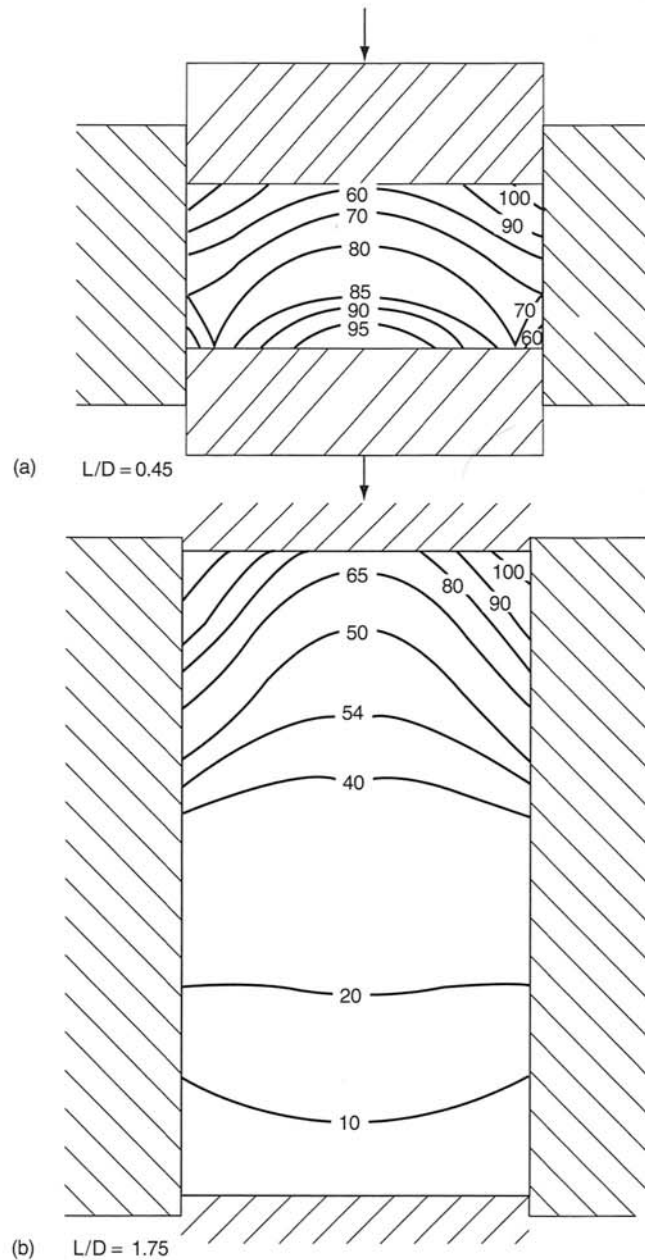
The second mechanism is illustrated in Figure 13.13b. This also involves rebound. As the part clears the top of the die during ejection, the material rebounds to a larger cross section. This places



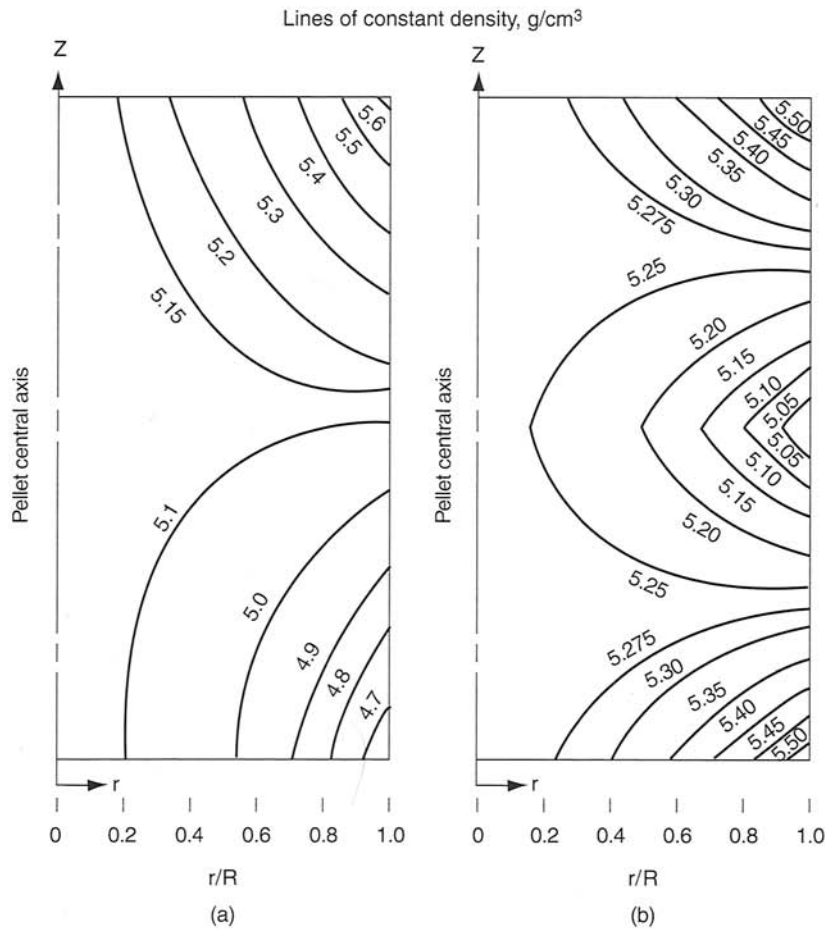
**FIGURE 13.13** Mechanism of formation of laminar cracks in uniaxially pressed parts. (a) Pressure being released from upper punch and (b) material rebound at top of die. (Drawing courtesy of ASM International.)

a tensile stress in the material just above the top of the die and can result in a series of laminar cracks. This mechanism can be minimized by selecting a binder system that provides good green strength with minimum rebound.

Another important problem to be overcome in uniaxial pressing is nonuniform density.<sup>3-5</sup> 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. As shown in Figure 13.14, a uniaxial pressure applied from one end of a die full of powder



**FIGURE 13.14** 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*, Kingery, W.D., Ed., MIT Press, Cambridge, MA, 1963.)



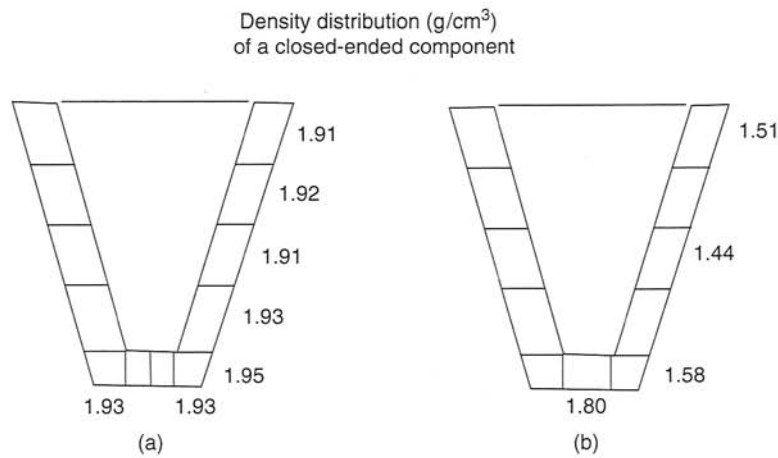
**FIGURE 13.15** Decrease in pressure curves and increase in uniformity of green density by pressing compact from opposing directions with a double-acting press. (a) Single-acting press and (b) double-acting press. (From Thompson, R.A., *Am. Ceram. Soc. Bull.*, 60(2), 237–243, 1981. With permission.)

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. This is illustrated in Figure 13.15.

A second source of nonuniform density is nonuniform fill of the die. Powder that is heaped or otherwise nonuniformly stacked in the die will not reposition during pressing. The region with the largest amount of powder will compact to a higher green density. This region of decreased porosity will shrink less during densification, resulting in distortion of the part.

A third source of nonuniform green density is the presence of hard agglomerates (clusters of particles) in the powder or a range of hardness of the granules in a free-flowing granulated powder. The hard granules will shield surrounding softer powder or granules from exposure to the maximum pressing pressure, resulting in pore clusters that reduce strength. Sometimes the surrounding powder



**FIGURE 13.16** Improvement in green density uniformity of a thin-wall crucible achieved by isostatic pressing. (a) After isostatic pressing and (b) after die pressing. (From Gill, R.M. and Bryne, J., in *Science of Ceramics*, Vol. 4, Stewart, G.H., Ed., British Ceramic Research Association, London, 1968. With permission.)

will compact uniformly, but the hard agglomerate will trap porosity. The hard agglomerate may then shrink more than the surrounding material during densification and leave a large pore.

Note that the cause of nonuniform density is more associated with the condition of the powder loaded into the pressing die than with the pressing operation itself. Further, note that the problem may not show up until after the densification step of fabrication. This is another reminder that all of the processing steps are interlinked and that all must be coordinated and controlled to achieve the desired characteristics of the final product.

### 13.1.4 ISOSTATIC PRESSING

Uniaxial pressing has limitations as described in the prior section. Some of the limitations can be overcome by applying pressure from all directions instead of only one or two directions. This is referred to as *isostatic pressing* or *cold isostatic pressing* (CIP). It has also been referred to as hydrostatic pressing.<sup>6</sup>

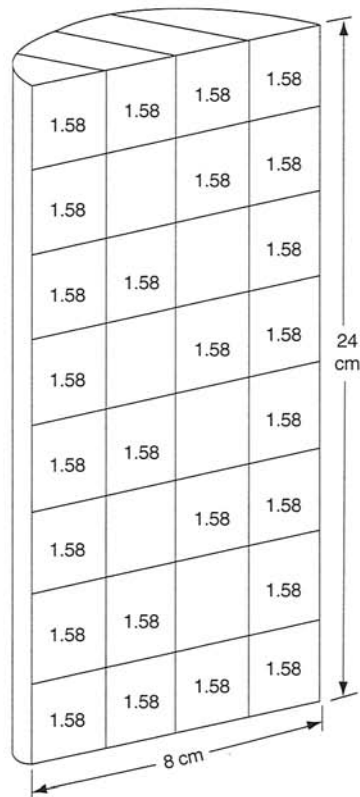
Application of pressure from multiple directions achieves greater uniformity of compaction and increased shape capability. Figure 13.16 compares the green density uniformity achieved in a thin-wall crucible fabricated by isostatic vs. uniaxial pressing. The green density of the isostatically pressed part is higher and much more uniform. Green density for the isopressed part ranges from 1.91 to 1.95  $\text{g}/\text{cm}^3$  (0.068 to 0.070  $\text{lb}/\text{in}^3$ ) compared to 1.44 to 1.80  $\text{g}/\text{cm}^3$  (0.054 to 0.065  $\text{lb}/\text{in}^3$ ) for the uniaxially pressed part. Figure 13.17 shows the density uniformity achieved by isostatic pressing of a larger solid cylinder. Compare this with the density contours shown previously in Figure 13.15 for a uniaxially pressed solid cylinder.

Two types of isostatic pressing are commonly used: (1) wet-bag and (2) dry-bag. These are described in the following paragraphs.

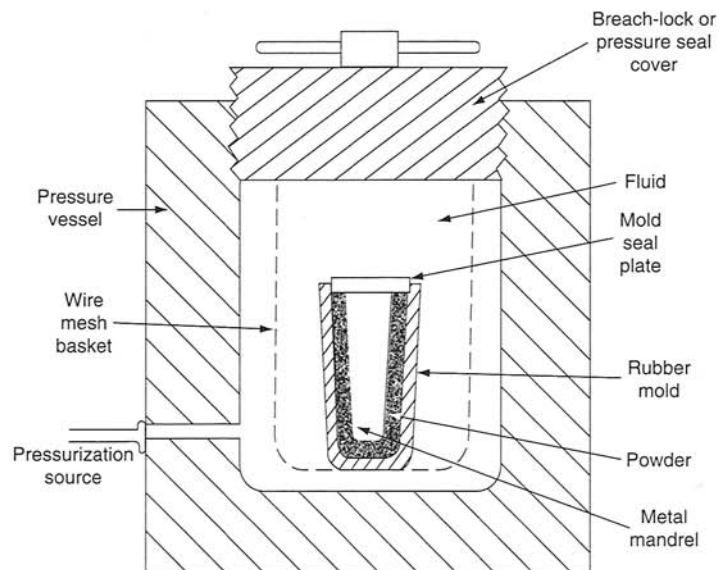
#### 13.1.4.1 Wet-Bag Isostatic Pressing

Wet-bag isostatic pressing is illustrated in Figure 13.18. The powder is sealed in a water-tight die. The walls of the die are flexible. The sealed die is immersed in a liquid contained in a high-pressure chamber. The chamber is sealed using a threaded or breach lock cover. The pressure of the liquid is increased by hydraulic pumping. The walls of the die deform and transmit the pressure uniformly to





**FIGURE 13.17** Density uniformity achieved in a large, solid cylinder by isostatic pressing. (From Gill, R.M. and Bryne, J., in *Science of Ceramics*, Stewart, G.H., Ed., British Ceramic Research Association, London, 1968. With permission.)



**FIGURE 13.18** Schematic of a wet-bag isostatic pressing system. (© Drawing courtesy of ASM International.)

the powder, resulting in compaction. The walls of the die spring back after the pressure is removed, allowing the compact to easily be removed from the die after the cap of the die is removed.

Any noncompressible fluid can be used for isopressing. Water is commonly used, although fluids such as hydraulic oil and glycerine also work. The flexible walls of the die or mold are made of an elastomer such as rubber or polyurethane. The flexibility and wall thickness are carefully selected to allow optimum dimensional control and release characteristics. Natural rubber, neoprene, butyl rubber, nitrile, silicones, polysulphides, polyurethanes, and plasticized polyvinyl chloride have all been used.

Laboratory isostatic presses have been built with pressure capabilities among from 35 to 1380 MPa (5 to 200 ksi). However, production units usually operate at 400 MPa (58 ksi) 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.

As with other processes, wet-bag isopressing has advantages and disadvantages. The advantages are density uniformity, versatility, and low cost of tooling. Coupled with green machining, a wide variety and size of parts can be fabricated with minimum equipment investment. The disadvantages are long cycle time, high labor requirement, and difficulty to automate. Cycles are in minutes and tens of minutes, so production rates are low compared to uniaxial pressing.

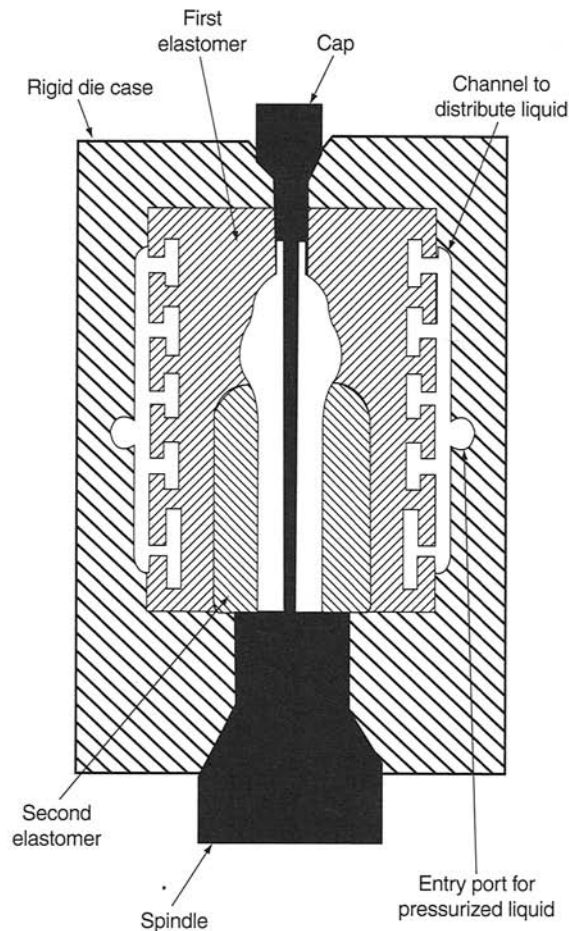
#### 13.1.4.2 Dry-Bag Isostatic Pressing

Dry-bag isopressing was developed to achieve increased production rate and close dimensional tolerances. Rather than immerse the tooling in a fluid, the tooling is built with internal channels into which the high-pressure fluid is pumped. This minimizes the amount of pressurized fluid required and allows the use of stationary tooling. The major challenge is constructing the tooling so that pressure is uniformly transmitted to the powder to achieve the desired shape. This is accomplished through careful positioning and shaping of the fluid channels, often by use of several different elastomer materials in a single die and by optimization of the external constraints of the die. Once a tool has been properly designed and automated, parts can be pressed at a rate of 1000 to 1500 cycles per hour.

Dry-bag isostatic pressing has been used for many years to press spark plug insulators. A schematic cross section of a pressing die is shown in Figure 13.19. Multiple dies are built into a single tool. Pressing and green machining are automated as shown in Figure 13.20 for fabrication of the zirconia electrolyte for an oxygen sensor. The rubber mold or die forms the outer circumference to the sensor. The spindle moves into the die from the bottom and forms the inner cavity of the sensor. The die is filled from the top and capped. Pressure is applied uniformly around the circumference of the die to compact the powder. After pressure release, the spindle and green compact are withdrawn from the bottom of the die. The compact is transferred automatically to a grind spindle that brings the compact in contact with a contoured grinding wheel for final shaping. The finished shape is then conveyed to a furnace for binder removal and densification.

#### 13.1.5 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.



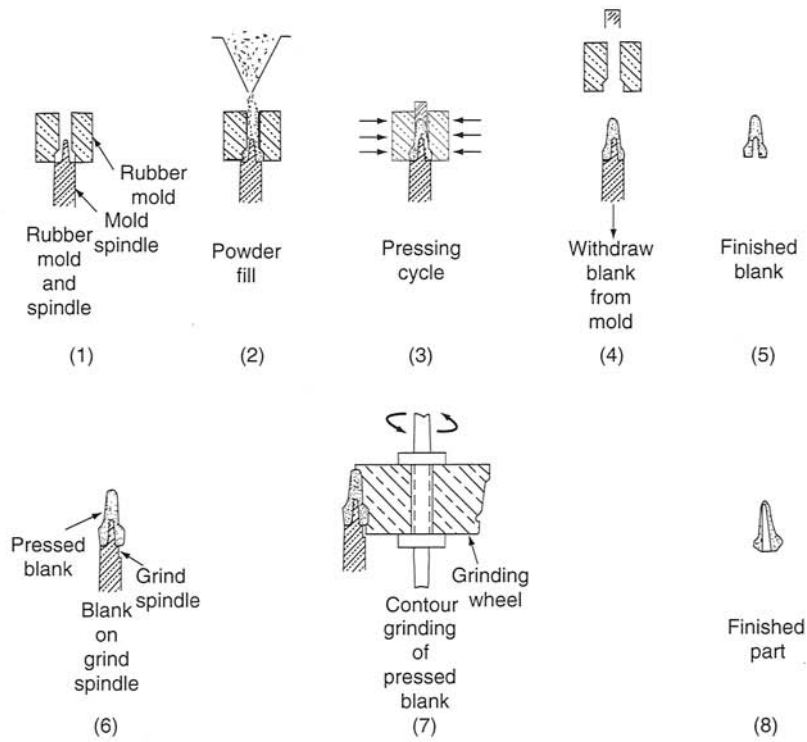
**FIGURE 13.19** Schematic of a die for dry-bag isostatic pressing of a spark plug insulator. (Drawing courtesy of ASM International.)

Isostatic pressing, typically in conjunction with green machining, 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. Bulky components for the paper industry have also been produced. Small components with a large length-to-width ratio are also fabricated by isostatic pressing and machining.

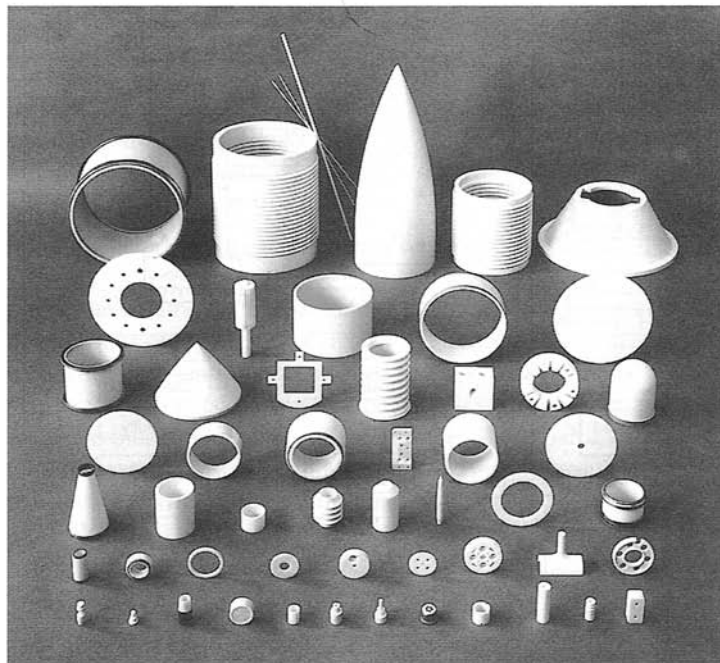
Figure 13.21 shows a variety of ceramic parts that have been fabricated by uniaxial and isostatic pressing.

## 13.2 CASTING

When most people hear the term “casting,” they automatically think of metal casting in which 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  $\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  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. The technique of casting molten ceramic refractories is called *fusion casting*.



**FIGURE 13.20** Automated dry-bag isostatic pressing and formed-wheel green machining of a zirconia electrolyte for an automotive oxygen sensor. (Drawings courtesy of ASM International.)



**FIGURE 13.21** Ceramic parts formed by uniaxial and isostatic pressing, some with green machining. (Courtesy of Western Gold and Platinum Company, Subsidiary of GTE Sylvania, Inc.)

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 that 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 principles 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 other techniques.

### 13.2.1 SLIP CASTING

Most commercial slip casting involves ceramic particles suspended in water and cast into porous plaster molds. Figure 13.22 identifies the critical process steps in slip casting and some of the process parameters that must be carefully controlled to optimize strength or other critical properties.

#### 13.2.1.1 Raw Materials

Selection of the starting powder is dependent on the requirements of the applications. Most applications require a fine powder, typically – 325 mesh (44  $\mu\text{m}$ ). Applications requiring high strength require even finer powders, averaging under 5  $\mu\text{m}$  (0.0002 in.), with a substantial portion under 1  $\mu\text{m}$  (0.00004 in.).

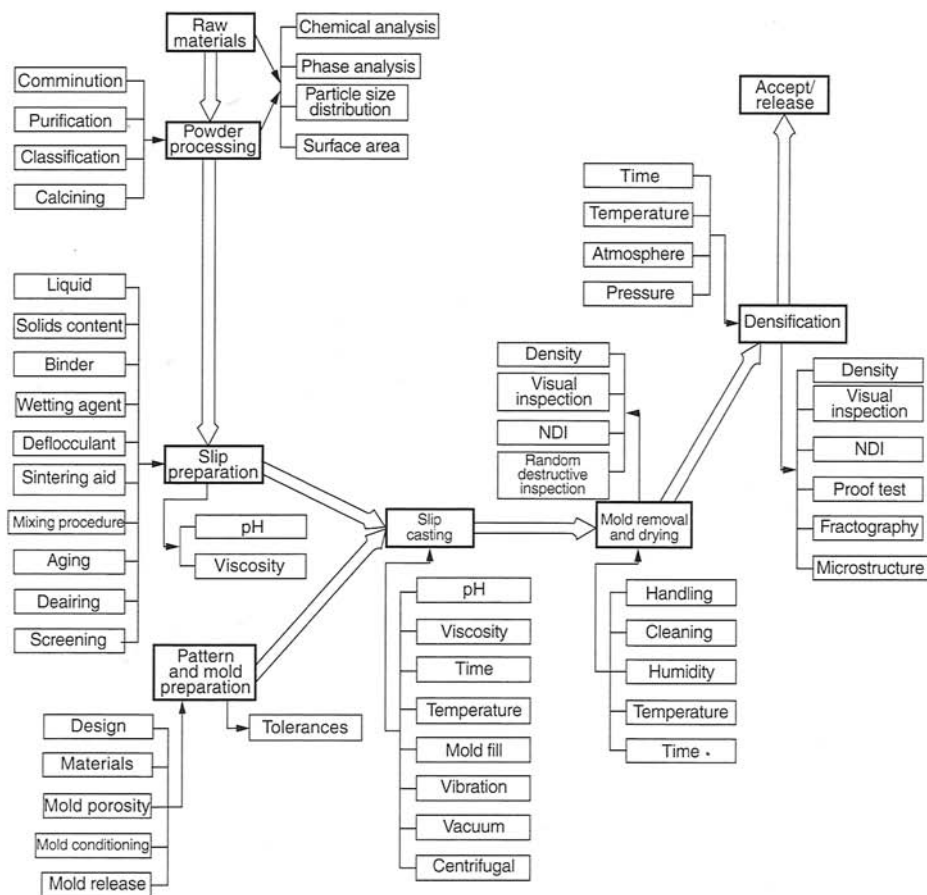


FIGURE 13.22 Critical process steps in slip casting and some of the process parameters that must be carefully controlled.

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 powder and additives. Impurities and second phases can have pronounced effects on high-temperature properties.

### 13.2.1.2 Powder Processing

As discussed in Chapter 12, 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 binder, wetting 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 processes that provide 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.

### 13.2.1.3 Slip Preparation and Rheology

To understand slip preparation considerations, one needs to understand a little about rheology. Rheology is the study of the flow characteristics of matter, for example, suspensions of solid particles in a liquid, and is described quantitatively in terms of viscosity  $\eta$ . For low concentrations of spherical particles where no interaction occurs between the particles, the Einstein relationship applies:

$$\frac{v}{v_0} = 1 + 2.5V \quad (13.1)$$

where

$v$  = viscosity of the suspension

$v_0$  = viscosity of the suspending fluid

$V$  = volume fraction of solid particles

This idealized relationship implies that the resulting viscosity is 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 shape, particle surface charges, and degree of agglomeration vs. dispersion. All of these are interrelated. The viscosity is essentially determined by how close particles approach each other and by the degree of attraction or repulsion between the particles. As we have discussed previously, particles of a material have incomplete bonds at the surface. These particles tend to adsorb  $H_2O$  and other molecules. It has been suggested that these adsorbed species result in a "sphere of influence" of about  $20 \text{ \AA}$  around each particle. When adjacent particles approach within  $\sim 20 \text{ \AA}$  of each other, they tend to interact. When all of the particles in the suspension approach  $20 \text{ \AA}$ , the force to move particles past each other will increase and the viscosity will significantly increase.

### 13.2.1.4 Particle Size and Shape Effects

The size and shape of particles determine the volume fraction at which particles approach the  $20 \text{ \AA}$  sphere of influence. This is illustrated by calculations from Reference 7. To estimate the sensitivity

of particle size, how close spherical particles of specific sizes would approach each other in a suspension containing 40 vol% of the particles was calculated:

| Diameter of Spherical Particles ( $\mu\text{m}$ ) | Mean Separation Distance for 40 vol% Solids Suspension ( $\text{\AA}$ ) |
|---|---|
| 10  | 9200  |
| 1   | 920   |
| 0.1   | 92  |
| 0.05  | 20  |
| 0.01  | 9.2   |

The particles would all have to be about  $0.05\ \mu\text{m}$  to approach  $20\ \text{\AA}$  at 40 vol% concentration. Increasing the volume fraction of particles causes the critical size to be larger.

The effect of particle shape was then estimated by a calculation assuming plate-shaped particles with an edge length ten times the thickness. This ratio was selected because it is representative of kaolinite clay particles that are a major constituent of slip-cast traditional ceramics. In this case, the volume fraction of ceramic plates at which the mean particle separation would be  $20\ \text{\AA}$  was calculated:

| Edge Length of Plate ( $\mu\text{m}$ ) | Thickness of Plate ( $\mu\text{m}$ ) | Volume Fraction of Solid at Which Mean Distance between Particle Surfaces Is $20\ \text{\AA}$ |
|--|--------------------------------------|---|
| 10                                     | 1                                    | 30  |
| 1                                      | 0.1                                  | 30  |
| 0.1                                    | 0.01                                 | 28  |
| 0.01                                   | 0.001                                | 17  |

It is apparent that shape has a large effect. The larger the deviation from spherical, the smaller the volume fraction of solids for  $20\ \text{\AA}$  separation.

Particle size distribution is also important. One objective with casting is to achieve a high green density and to minimize shrinkage during densification. As was shown for pressing, this objective of close packing can be achieved best by a distribution of particle sizes. A distribution of particle sizes also helps to achieve increased solids loading in the slip. This is illustrated schematically in Figure 13.23 and by the example in Figure 13.24. The example shows the viscosity characteristics (plotted as flow rate vs. shear stress) for three particle size distributions of  $\text{SiO}_2$  powder. The size distributions are plotted as "percent finer" vs. "equivalent spherical diameter," which is the common way of graphically displaying particle size distribution data. Compare the size range for each powder between 90% finer and 10% finer. Powder A consists in this range of particles between about 2 and  $18\ \mu\text{m}$ . Powder B consists in this 90 to 10% range of particles between 0.35 and  $7\ \mu\text{m}$ . A 50-50 mixture of A + B has a broader particle size range containing some of the finer particles from B and coarser particles from A. All three powders were successfully prepared into slips containing approximately 50 vol% solids. Note from Figure 13.24 that the finer powder B had the highest viscosity (lowest flow rate), the coarser powder had intermediate viscosity, and the mixture had the lowest viscosity. For the slips in this example, the viscosity appears to be influenced by a combination of particle size and particle packing.

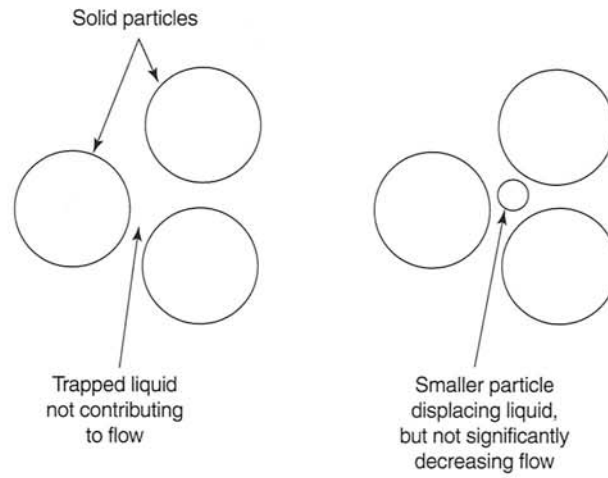


FIGURE 13.23 Comparison of fluid requirements for slip containing one size of particles in suspension vs. a range of sizes. (Drawing courtesy of ASM International.)

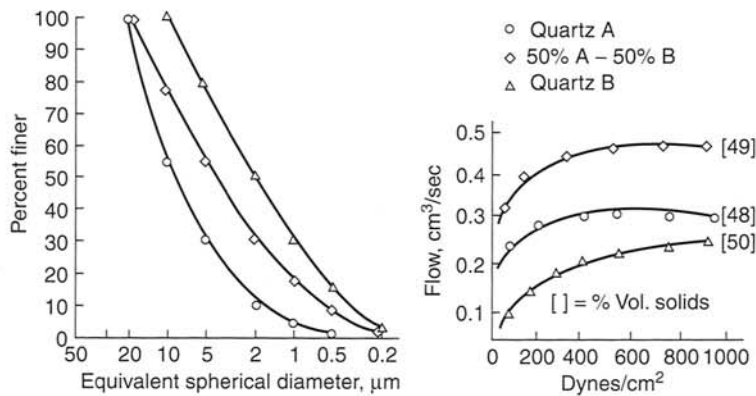


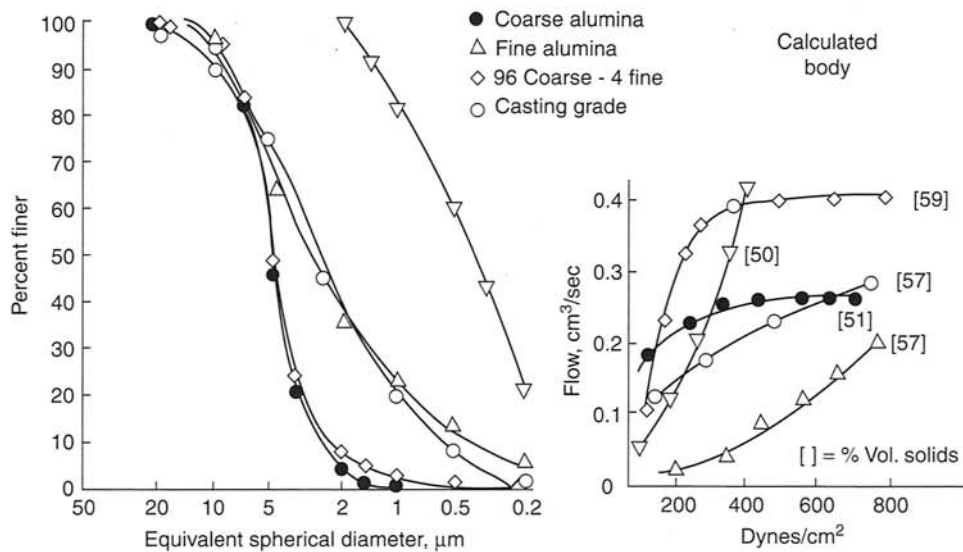
FIGURE 13.24 Effect of particle size distribution of air-elutriated SiO<sub>2</sub> in water using sodium silicate as a defloculant. (From Phelps and McLaren, in *Ceramic Processing Before Firing*, Onoda, G. and Hench, L., Eds., Wiley, New York, 1978, Chapter 17. With permission.)

An example for Al<sub>2</sub>O<sub>3</sub> is illustrated in Figure 13.25. The curves on the left identify the particle size distributions. The curves on the right show the rheology behavior. The broad particle size distribution had the best rheology for casting. The 96 coarse-4 fine powder in a 59 vol% suspension showed shear-thinning behavior, that is, low viscosity at high shear rate and higher viscosity as the shear rate decreased. In other words, the slip became thinner when stirred. This behavior is also sometimes referred to as *pseudoplasticity*. Extreme cases are used for paint. The low viscosity at high shear allows the paint to flow smoothly during spraying or brushing. The high viscosity at low shear keeps the particles in suspension during storage and minimizes running once the paint has been applied. Figure 13.26 shows an example of how this behavior is controlled with the addition of different molecular weights of a polymer.

### 13.2.1.5 Particle Surface Effects

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





**FIGURE 13.25** Rheology behavior of slips prepared with various particle size distributions of  $\text{Al}_2\text{O}_3$ . (From Phelps and McLaren, in *Ceramic Processing Before Firing*, Onoda, G. and Hench, L., Eds., Wiley, New York, 1978, Chapter 17. With permission.)

result in a decrease in viscosity. In other cases, especially for very high solids content, the agglomerates can interact with each other and increase the viscosity. The degree of agglomeration can be controlled with additives.

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.<sup>8-10</sup> 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.

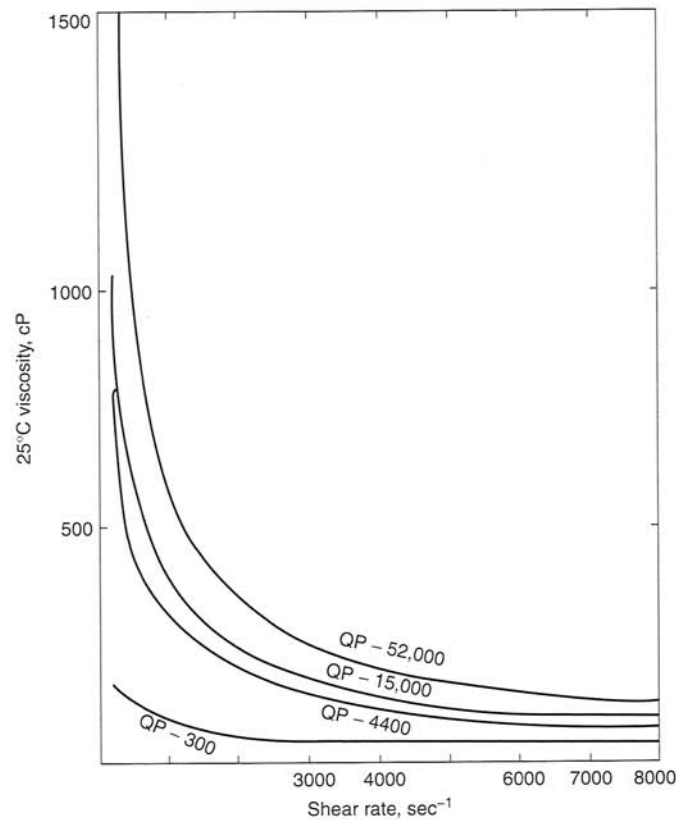
Two approaches are commonly used to control and manipulate the surface characteristics of ceramic particles in a suspension: (1) electrostatic repulsion and (2) steric stabilization.

*Electrostatic repulsion* involves the buildup of charges of the same polarity on all the particles. Like charges repel, so the particles are held apart in the suspension by electrostatic forces. The higher the electrical charge at the surface of the particles, the better the degree of dispersion and the less agglomeration. The electrostatic forces dominate for particle separations between about 20 and 200 Å.

The charge at the surface of particles is controlled by pH of the liquid and by addition of chemicals that supply monovalent cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Li}^+$ ) for absorption at the surface of the particles. 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.  $\text{Al}_2\text{O}_3$  powder can be dispersed in water by either adding an acid to achieve a low pH or a base to achieve a high pH. For instance, an  $\text{Al}_2\text{O}_3$  slip with a specific gravity of  $2.8 \text{ g/cm}^3$  had a viscosity of 65 cP\* at a pH of 4.5, but 3000 cP at a pH of 6.5. 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  $2.6 \text{ g/cm}^3$  resulted in only a factor of two decrease in viscosity. For comparison, decreasing the specific gravity of the pH 6.5 slip to  $2.6 \text{ g/cm}^3$  resulted in a tenfold decrease in viscosity.

Clay material also can be dispersed by electrostatic repulsion. Kaolinite 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

\*cP = centi-Poise, the English unit for viscosity.



**FIGURE 13.26** Addition of different molecular weights of polymers to control the degree of pseudoplasticity. (From Onoda, G., in *Ceramic Processing Before Firing*, Wiley, New York, 1978, Chapter 19. With permission.)

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.<sup>8</sup>

Proper dispersion of the slip is perhaps the most important parameter in slip casting. Obtaining the optimum dispersion can be aided by the use of several pieces of equipment: a pH meter, a zeta meter, and a viscometer.

The zeta meter requires description. It consists of a thin glass tube, electrodes that attach to the ends of the tube, a DC electrical source, and a microscope mounted on a calibrated track. The tube is filled with the selected liquid (with the pH adjusted to the desired level and the desired dispersant added) containing a small number of particles of the ceramic. A particle is centered in the view of the microscope and the coordinates on the track scale recorded. A known electric field is then

applied to the electrodes at the ends of the tube. A particle with a positive charge at the surface will begin moving toward the negative electrode, and vice versa for a particle with a negative charge. The motion of the particle is followed with the microscope and the coordinates on the scale recorded as a function of time. The apparent surface charge on the particle can be calculated from this information and is referred to as the *zeta potential*. This can be repeated for different values of pH and concentrations of additives and plotted on a graph to show the behavior of the material over a broad range. Optimum conditions can then be estimated for slip preparation.

An example of zeta potential vs. pH curve is shown in Figure 13.27 for silicon particles in water. The particles have a positive zeta potential below pH 4, a zero zeta potential at pH 4, and a negative zeta potential at pH above 4. The higher the absolute value of zeta potential, the greater the electrostatic repulsion between particles and the greater the degree of powder dispersion in the slip.

The curve in Figure 13.27 is similar to a typical curve for oxide ceramics. Silicon is known to have a molecular layer of  $\text{SiO}_2$  at the surface, which apparently is dominating the rheological behavior of the particles in suspension.

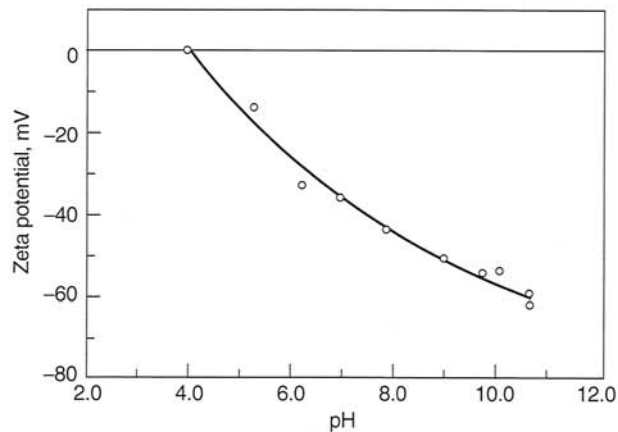


FIGURE 13.27 Zeta potential vs. pH for silicon particles in water. (Drawing courtesy of ASM International.)

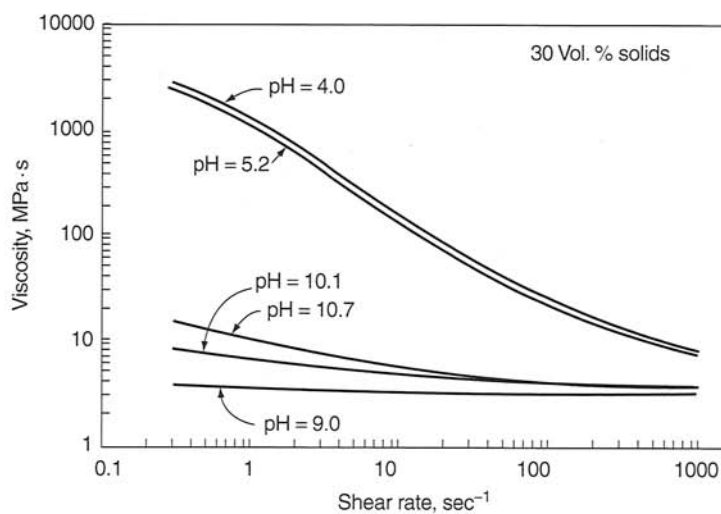


FIGURE 13.28 Viscosity vs. pH of slips containing 30 vol% silicon in water. (Drawing courtesy of ASM International.)

The silicon powder used for the zeta meter measurements was prepared in slips of varying pH using a powder concentration of 30 vol%. The viscosity of each slip was measured with a viscometer and is plotted vs. pH in Figure 13.28. High pH resulted in excellent dispersion and low viscosity. A pH of about 9 was judged to be optimum. Slips with higher solids content were then prepared and the viscosity measured at various shear rates. The results are illustrated in Figure 13.29. All of the slips were successfully cast. A viscosity of approximately 100 MPa · s (100 cP) or lower is suitable for casting.

The microstructures of the cast silicon compacts were evaluated using mercury porosimetry to estimate the total porosity and radius of interconnected pore channels. The results are summarized in Table 13.5. Sonication refers to use of an ultrasonic probe to try and break up agglomerates in the slips. Slips with low pH and near-zero zeta potential contained large agglomerates, had high viscosity, and resulted in compacts with high porosity and large pores. Slips with pH of about 7 to 9 and high negative zeta potential contained minimum agglomerates, had low viscosity, and resulted

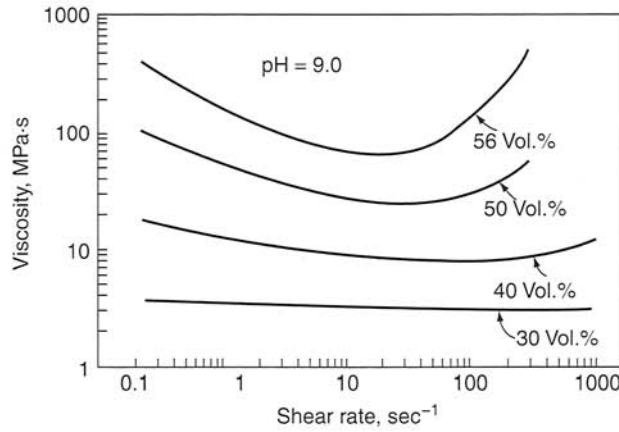


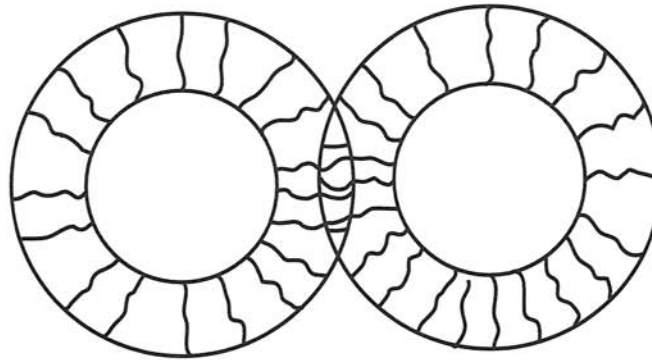
FIGURE 13.29 Viscosity of various volume fractions of silicon powder in water. (Drawing courtesy of ASM International.)

TABLE 13.5  
Correlation between Zeta Potential, Viscosity, and Packing Density of Slip-Cast Silicon Powder

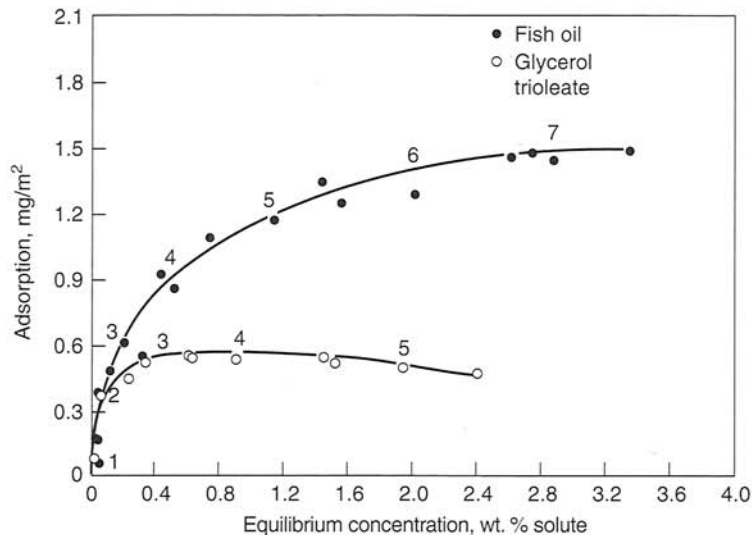
| Solids Loading, vol% | pH   | Zeta Potential, mV | Viscosity, MPa · s at 1.05 <sup>-1</sup> | Sonication Time, min | Total Porosity, vol% | Median Pore Radius, nm |
|----------------------|------|--------------------|--|----------------------|----------------------|------------------------|
| 40                   | 4.1  | 0                  | >1000                                    | 0                    | 46.46                | 310,320                |
| 40                   | 4.1  | 0                  | >1000                                    | 15                   | 44                   | 290                    |
| 40                   | 6.3  | -33                |  | 0                    | 44                   | 250                    |
| 40                   | 9.0  | -50                | >20                                      | 0                    | 31                   | 190                    |
| 40                   | 9.8  | -56                |  | 0                    | 34                   | 200                    |
| 40                   | 10.7 | -60                |  | 0                    | 39,39                | 240,240                |
| 50                   | 6.3  | -33                |  | 0                    | 42                   | 260                    |
| 50                   | 7.8  | -44                |  | 0                    | 29                   | 130                    |
| 50                   | 7.8  | -44                |  | 10                   | 25                   | 110                    |
| 50                   | 9.0  | -50                | 60                                       | 0                    | 29                   | 130                    |
| 56                   | 7.8  | -44                |  | 0                    | 28                   | 105                    |
| 56                   | 7.8  | -44                |  | 15                   | 23,24                | 82,87                  |
| 56                   | 7.8  | -44                |  | 30                   | 22,22                | 73,72                  |
| 56                   | 9.0  | -50                | 200                                      | 30                   | 19                   | 66                     |

in compacts with low porosity and relatively small pores. Sonication effectively improved dispersion and resulted in smaller pores and lower porosity. A pH greater than 9.0 resulted in a slight increase in viscosity and porosity. This was due to too high an electrolyte strength (too many charged ions in the water) shielding the charge effect of the particles.

The above examples of  $\text{Al}_2\text{O}_3$ , kaolinite, and silicon illustrate the control of dispersion (deflocculation) and agglomeration (flocculation) that can be achieved with electrostatic repulsion. A second important approach is called *steric stabilization* or *steric hindrance*. It involves the addition of chainlike organic molecules that are adsorbed onto the ceramic particles, as shown in Figure 13.30, and provide a buffer zone around each particle. One end of the chain attaches or anchors to the ceramic and has limited solubility in the solvent. The other end extends away from the particle and is soluble in the solvent. These molecules provide a mechanical barrier to agglomeration and allow particles to approach closer than would be possible without the adsorbed molecules.



**FIGURE 13.30** Adsorption of chain polymers onto the surface of ceramic particles to provide dispersion by steric hindrance. (Drawing courtesy of ASM International.)

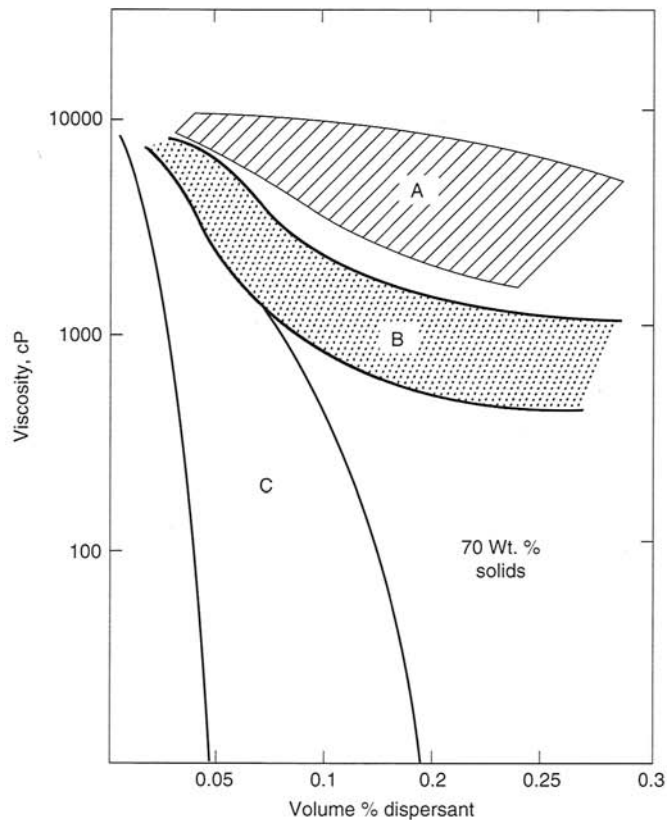


**FIGURE 13.31** Adsorption vs. concentration for fatty acid polymers on  $\text{Al}_2\text{O}_3$  particles in toluene. (From Tormey, E.S., et al., in *Advances in Ceramics, Forming of Ceramics*, Vol. 9, Mangels, J. and Messing, G., Eds., American Ceramic Society, Ohio, 1984, p. 143. With permission.)

Several factors influence steric hindrance:

1. the affinity of one end of a chain molecule to be adsorbed at the surface of the ceramic particle
2. the resistance of the tail end of the molecule to attach to the ends of adjacent molecule tails
3. the characteristics of the fluid, the length of the organic molecule

Different polymers have different affinity for different ceramics in different liquids. Figure 13.31 shows adsorption vs. concentration for two fatty acid polymers on  $Al_2O_3$  in toluene. Note the small



| Region A          |                | Region B         |               |
|-------------------|----------------|------------------|---------------|
| Monazoline-T      | AMP-95         | Witcamine PA-78B | Drewfax-007   |
| Monazoline-C      | Alkazine-TO    | Monawet MM-80    | Aerosol-OT    |
| Sedisperse-D      | Alkazine-O     | Aerosol AY-100   | Duponol-G     |
| Zonyl FSN         | Emerest 2423   | Aerosol C-61     | PVB           |
| Monazoline-O      | Dispersinol-HP | Monawet MB-45    | Aerosol TR-70 |
| Witconol H31-A    | Sedisperse-F   | Monawet MO-70    | Amerlate LFA  |
| Flourad FC-170-C  |                | Dispersinol-C    |               |
| Region C          |                |                  |               |
| Menhaden fish oil |                |                  |               |
| Emphos PS-21A     |                |                  |               |
| Zonyl-A           |                |                  |               |

**FIGURE 13.32** Summary of the effect of the dispersants listed in Table 13.6 on the viscosity of slips consisting of  $BaTiO_3$  in a MEK-ethanol solvent. (Adapted from Mikeska, K. and Cannon, W.R., Dispersants for tape casting pure barium titanate, in *Advances in Ceramics, Forming of Ceramics*, Vol. 9, Mangels, J. and Messing, G., Eds., American Ceramic Society, Ohio, 1984, pp. 164-183.)

amounts required to saturate the surface of the particles. For the glycerol trioleate, no further adsorption occurs above about 0.4 wt%.

Other polymers that provide steric hindrance for specific powders in specific solvents include some other fatty acids (e.g., oleic acid), amines, esters, organotitanates, branched carboxylic acids, organosilanes, polystyrene, and silanized polystyrene and are reported in Reference 11.

The adsorption characteristics and effect on viscosity for a variety of commercially available dispersants with BaTiO<sub>3</sub> powders in a methyl ethyl ketone (MEK)-ethanol solvent have been explored in Reference 12. The results are summarized in Figure 13.32. The materials in group A had little effect, those in group B had moderate effect, and those in group C had strong effect. The dispersants and their sources are listed in Table 13.6.

**TABLE 13.6**  
**Commercial Dispersants Tested for Dispersion of BaTiO<sub>3</sub> Tape-Casting Slip**

| Trade Name         | Manufacturer                       | Identify  |
|--------------------|------------------------------------|---|
| Monazoline-T       | Mona Industries                    | Substituted imidazoline (1-hydroxyethyl-2-alkyl-imidazolines) from tall oil acids |
| Monazoline-C       | Mona Industries                    | Substituted imidazoline (1-hydroxyethyl-2-alkyl-imidazolines) from coconut acids  |
| Sedisperse-D       | Micromeritics                      | Saturated aliphatic hydrocarbons  |
| Zonyl-FSN          | E. I. du Pont de Nemours & Co.     | Fluorinated surfactant  |
| Monazoline-O       | Mona Industries                    | Substituted imidazoline (1-hydroxyethyl-2-alkyl-imidazolines) from oleic acids    |
| AMP-95             | International Minerals & Chemicals | 2-amino-2-methyl-1-propanol   |
| Sedisperse-F       | Micromeritics                      | Saturated aliphatic hydrocarbons  |
| Witconol H31-A     | Witco Chemical Co.                 | Polyethylene glycol 400 monostearate  |
| Alkazine-TO        | Alkaril Chemicals                  | Tall oil hydroxyethylimidazoline  |
| Fluorad FC-170-C   | 3M Co.                             | Fluorinated surfactant  |
| Alkazine-O         | Alkaril Chemicals                  | Oleic hydroxyethylimidazoline   |
| Emerest 2423       | Emery Industries                   | Glycerol trioleate  |
| Dispersinol-HP     | Arkansas Co.                       | Proprietary   |
| Duponol-G          | E. I. du Pont de Nemours & Co.     | Proprietary   |
| Ameriate LFA       | Amerchol Corp.                     | Lanolin fatty acids   |
| Poly(vinylbutyral) | Rohm and Haas                      | Poly(vinylbutyral)  |
| Aerosol TR-70      | American Cyanamid                  | Sodium bis(tridecyl)sulfosuccinate  |
| Witcamine PA-78B   | Witco Chemical Co.                 | Salt of fatty imidazoline   |
| Monawet MB-45      | Mona Industries                    | Diisobutyl sodium sulfosuccinate  |
| Dispersinol-C      | Arkansas Co.                       | Proprietary   |
| Aerosol-OT-75      | American Cyanamid                  | Sodium dioctylsulfosuccinate  |
| Monawet MO-70      | Mona Industries                    | Sodium dioctylsulfosuccinate  |
| Drewfax-007        | Drew Chemical                      | Sodium dioctylsulfosuccinate  |
| Aerosol C-61       | American Cyanamid                  | Ethoxylated alkylguanidine amine  |
| Monawet MM-80      | Mona Industries                    | Sodium dihexylsulfosuccinate  |
| Aerosol AY-100     | American Cyanamid                  | Sodium diisobutylsulfosuccinate   |
| Zonyl-A            | E. I. du Pont de Nemours & Co.     | Ethoxylate  |
| Fish oil           | Spencer Kellogg                    | Fatty acid  |
| Emphos PS-21A      | Witco Chemical Co.                 | Phosphate ester   |

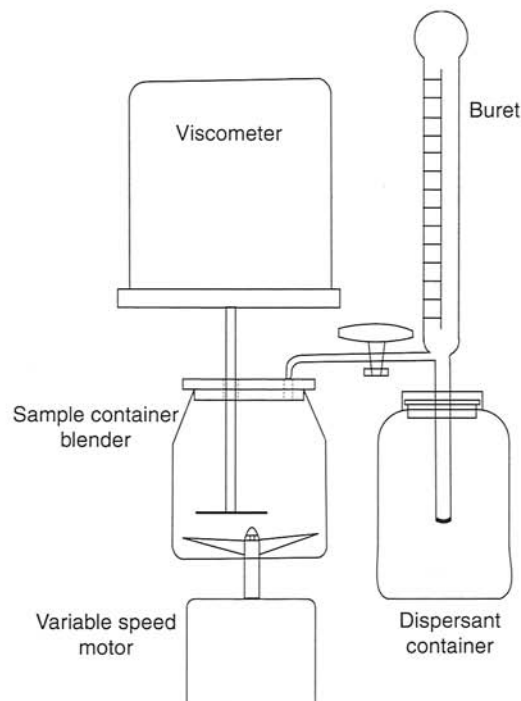
Source: From Mikeska, K. and Cannon, W.R., Dispersants for tape casting pure barium titanate, in *Advances in Ceramics, Forming of Ceramics*, Vol. 9, Mangels, J. and Messing, G., Eds., American Ceramic Society, Ohio, 1984, pp. 164–183, p. 169.

A simple apparatus was used for studying slip viscosity vs. volume of dispersant. The apparatus is illustrated schematically in Figure 13.33. The powder and liquid were premixed to form a dispersion containing 70 wt% solids. This was placed in a variable-speed blender and blended until homogeneous. The blender was stopped and the viscosity was measured with a rotating-disk viscometer. A known amount of dilute dispersant was added through a graduated buret, the slip was reblended, and the viscosity was measured. This procedure was repeated to provide the data for plotting viscosity vs. dispersant concentration for each dispersant. The above examples identify toluene and MEK-ethanol as fluids for slip preparation. These are referred to as *nonaqueous* (non-water-based). Another non-aqueous system uses trichloroethylene plus ethanol. Nonaqueous systems work well with steric hindrance because they are adequate solvents for the chain polymers. Some of the polymers also provide steric hindrance in an *aqueous* (water-based) system, for example, phosphate esters.

Aqueous slips using electrostatic repulsion are commonly used for slip casting. Techniques of slip preparation and slip casting are discussed in the following sections. Nonaqueous slips utilizing steric hindrance are commonly used for tape casting. Tape casting is discussed later in this chapter.

#### 13.2.1.6 Slip Preparation

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



**FIGURE 13.33** Schematic of simple apparatus for the study of slip viscosity vs. vol% dispersant. (From Mikeska, K. and Cannon, W.R., Dispersants for tape casting pure barium titanate, in *Advances in Ceramics, Forming of Ceramics*, Vol. 9, Mangels, J. and Messing, G., Eds., American Ceramic Society, Ohio, 1984, pp. 164–183, p. 170. With permission.)

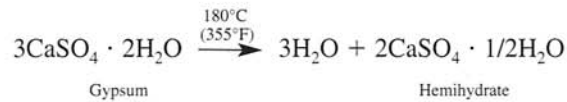


reduction. The slip is then allowed to age until its characteristics are relatively constant. It is then ready for final viscosity checking (and adjustment, if necessary), deairing, and casting.

### 13.2.1.7 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 traditional mold material has been plaster.<sup>13</sup> Some newer molds, especially for pressure casting, are made of a porous plastic material.

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:



The reaction is reversible; addition of water to the hemihydrate results in precipitation of very fine needle-shaped crystals of gypsum that 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.

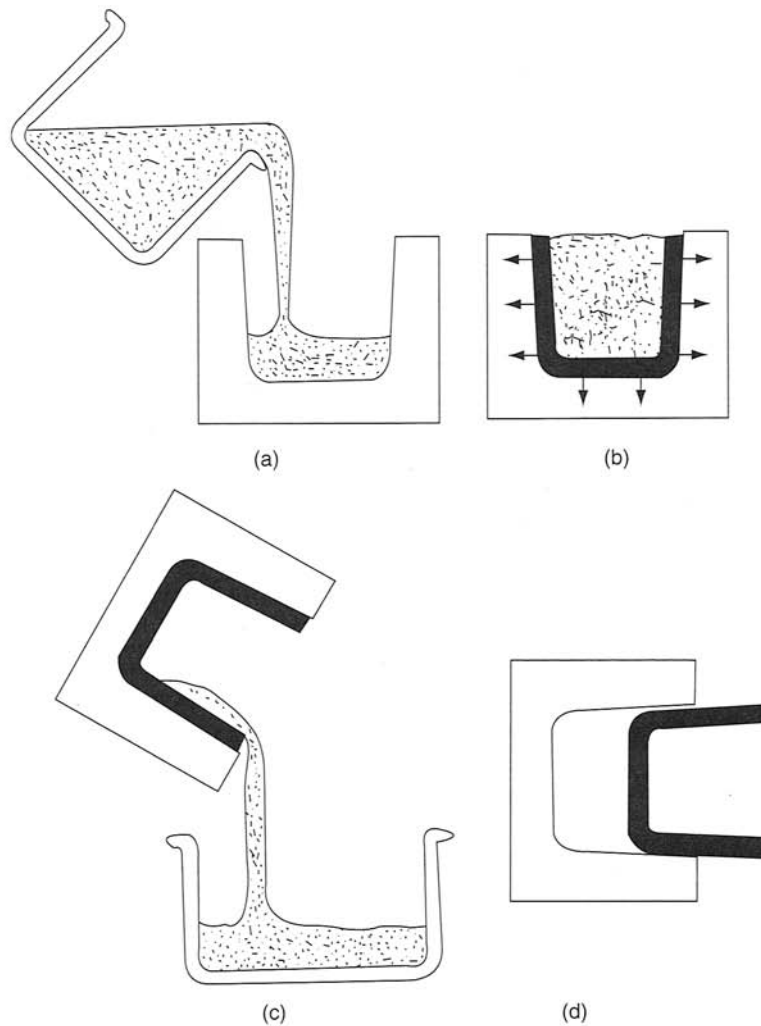
The setting rate of plaster can be widely varied by impurities.

### 13.2.1.8 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
- pressure casting
- soluble-mold casting
- gel casting
- casting with nonabsorbing pins or mandrels inserted into the mold

Figure 13.34 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. 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.



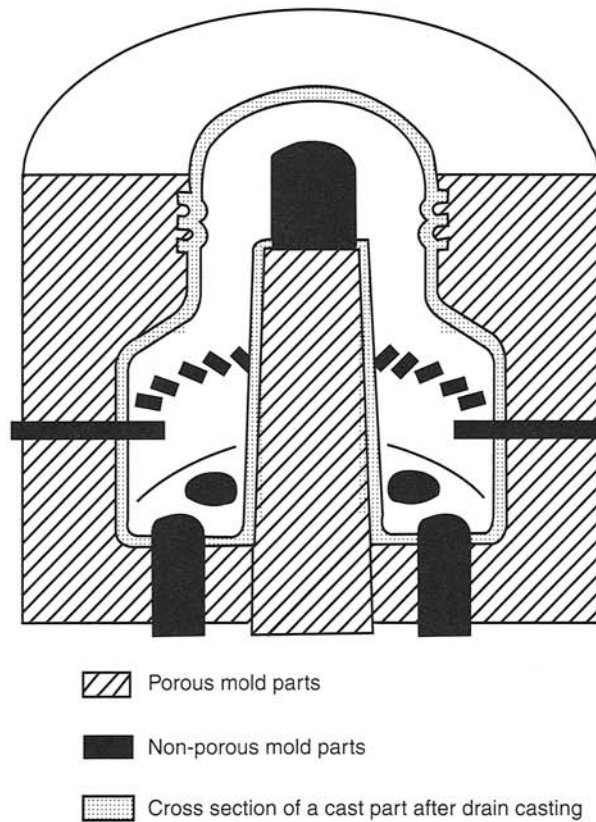
**FIGURE 13.34** Schematic illustrating the drain-casting process. (a) Fill mold with slip, (b) mold extracts liquid, forms compact along mold walls, (c) excess slip drained, and (d) casting removed after partial drying.

*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. The mold can consist of a rigid permeable form or of a thin permeable membrane (like filter paper) lining a porous rigid form. Vacuum casting is commonly used in the production of porous refractory fiberboard for lining high-temperature furnaces.

*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.

One limitation with most slip-casting processes is the long time required to cast articles in the mold. This results in a large inventory of molds, high labor, and large floor space, all of which add to cost. Application of pressure to the slip increases the casting rate. This is referred to as *pressure casting*.<sup>14-16</sup> It is similar to filter pressing. In filter pressing water or other liquid is removed from a powder by pressing the powder or liquid mixture against a permeable membrane. In pressure casting the slip is pressed into a shaped permeable mold. Original pressure casting was conducted with



**FIGURE 13.35** Cross section of the mold arrangement to drain cast a cylinder within a cylinder with large holes through the bottom and small holes through the outer circumference. (Drawing courtesy of ASM International.)

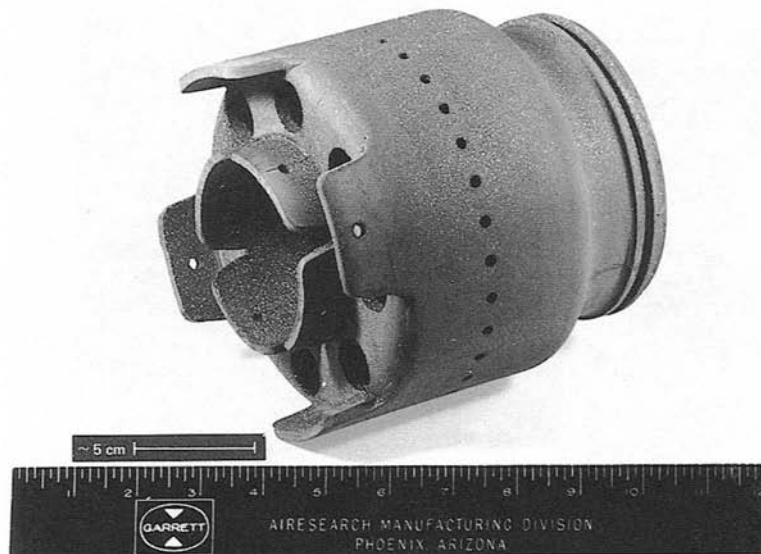
plaster molds. However, because of the low strength of the plaster, the amount of pressure that could be applied was limited. Development of porous plastic molds allowed the pressure to be increased by ten times the values of 3 to 4 MPa (30 to 40 bar or 435 to 580 psi).

Reference 14 reports some results with pressure casting. For a porcelain composition, casting time for a 6-mm thick compact was reduced from about 45 to 15 min by increasing the pressure from 0.025 to 0.4 MPa (0.25 to 4.0 bar or 3.6 to 58 psi). Increasing the pressure to 4 MPa resulted in a casting time of about 65 sec for a 6-mm thick compact of a modified porcelain slip. A 6-mm thick compact of  $\text{Al}_2\text{O}_3$  was cast in 100 sec and of an earthenware composition in 240 sec at a pressure of 4 MPa (40 bar or 580 psi).

Nonporous, nonabsorbing mold parts such as pins and mandrels can be used to achieve increased complexity of parts cast by the above techniques. Figure 13.35 shows schematically how a mandrel and pins were used to drain cast a complex-shaped combustor for a gas-turbine engine. The finished part is shown in Figure 13.36.

Further complexity of shape can be achieved using the *soluble-mold casting* technique.<sup>17,18</sup> This is a relatively new approach based on the much older technology of investment casting. It is also referred to as *fugitive wax slip casting* 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 nonwater-soluble wax to form a thin layer over the pattern.

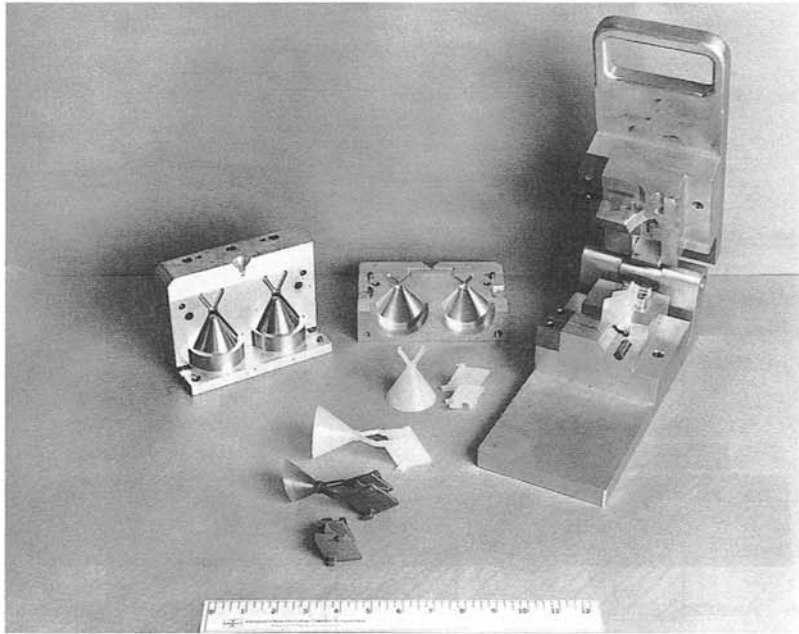


**FIGURE 13.36** Annular combustor for gas-turbine engine fabricated by drain casting using nonabsorbing pins and mandrels inserted into the mold. Courtesy of Garrett Turbine Engine Company (currently Honeywell Engines, Systems & Services), fabricated by Norton Company (currently Saint-Gobain/Norton Advanced Ceramics).

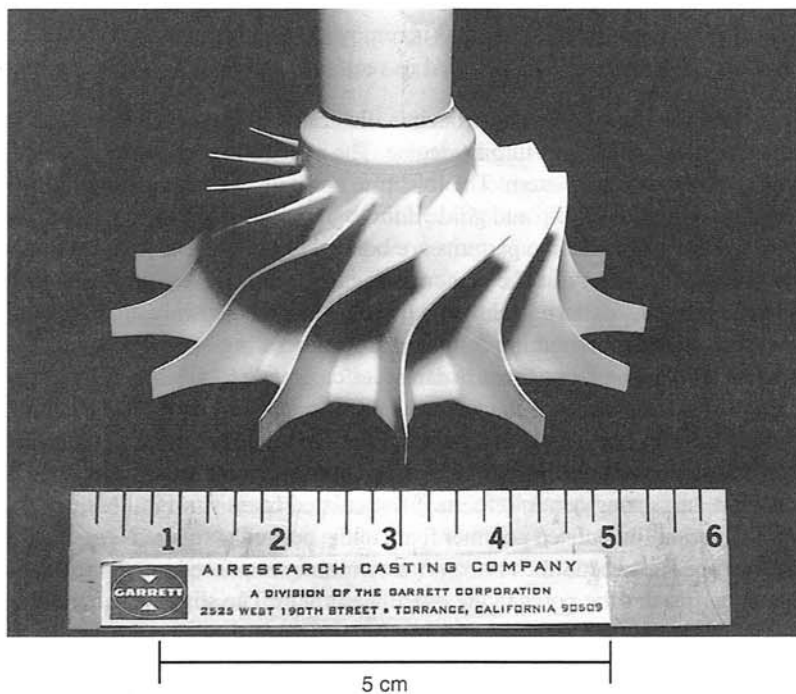
3. The pattern wax is dissolved in water, leaving the nonwater-soluble wax as an accurate mold of the shape.
4. The wax mold is trimmed, attached to a plaster block, and filled with the appropriate casting slip.
5. After the casting is complete, the mold is removed by dissolving in a solvent.
6. The cast shape is dried, green-machined as required, and densified at high temperature.

The application of the fugitive-wax approach is illustrated in Figure 13.37 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 that 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 Figure 13.37. 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. The stator vane discussed above required less than 1-h casting time. Some solid castings require much longer time, such as the prototype gas-turbine rotor shown in Figure 13.38. It required over 12 h. The slip must be very stable for such long casting time to avoid settling of large particles or adverse changes in viscosity.

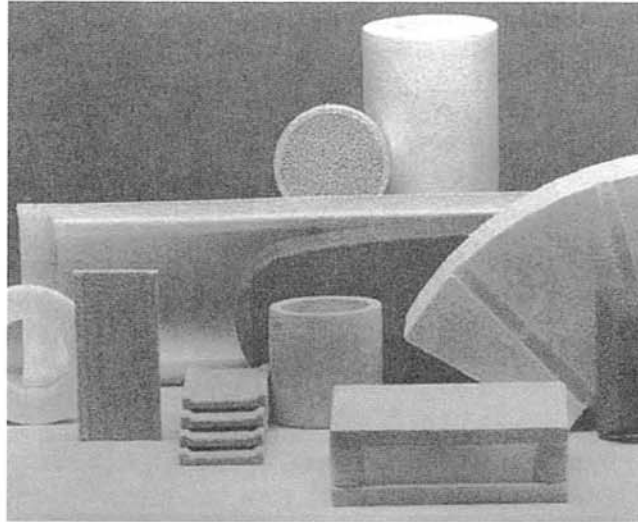
Other fugitive mold techniques have been developed to fabricate special shapes. One technique produces low weight, but strong ceramic foam.<sup>19</sup> Reticulated foam similar to a dishwashing sponge is used as the mold interior. Reticulated polymer foam of the desired pore size is cut to the desired shape and placed in a container in a vacuum chamber. A ceramic slip is poured into the container and under vacuum completely infiltrates the pores in the reticulated foam. The slip is dried and fired to burn off the polymer foam and densify the ceramic. The resulting part consists of an internal cast of the spongelike foam. Its major characteristic is continuous interconnected links of ceramic and continuous pore channels. Such a cellular structure can be very lightweight and surprisingly strong. Examples are shown in Figure 13.39. Note from the photograph that a variety of pore sizes have been achieved from several different ceramic materials. The materials are successfully used for molten metal filtration and kiln furniture and are being evaluated for removing particles from the exhaust of diesel engines.



**FIGURE 13.37** The fugitive-wax technique for preparing a complex-shape mold for slip casting; example of fabrication of a stator vane for a gas-turbine engine. (Courtesy of AiResearch Casting Company, Division of The Garrett Corporation, presently Honeywell Ceramic Components, Torrance, CA.)



**FIGURE 13.38** Prototype gas-turbine rotor fabricated by slip casting using a fugitive-wax-type process. (Courtesy of AiResearch Casting Company, Division of the Garrett Corporation, presently Honeywell Ceramic Components, Torrance, CA.)



**FIGURE 13.39** Ceramic components of controlled porosity fabricated by infiltration of a ceramic casting slip into a polymer sponge structure. (Photo courtesy of Hi-Tech Ceramics, Alfred, NY.)

Some components are too complex to be fabricated in one piece by casting. An example is the turbine scroll shown in Figure 13.40a. The turbine scroll is an important component in many gas-turbine designs. It changes the direction of the hot gases coming out of the combustor to allow them to pass through the rotor. The scroll in Figure 13.40a is SiC. It was fabricated by assembling the parts shown in Figure 13.40b.<sup>20</sup> The shroud, sleeve, and ring were formed by isostatic pressing and green machining. The body and duct were fabricated by slip casting. The parts were successfully bonded together with a CrVTi braze developed at Oak Ridge National Laboratories (ORNL).

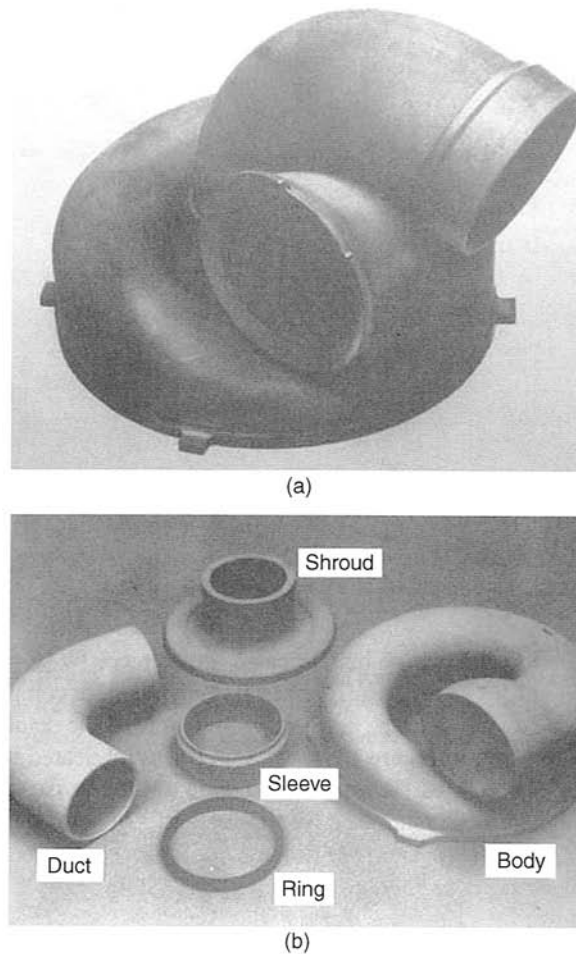
A final casting technique is *electrophoretic deposition* (EPD). It uses an electrostatic charge to consolidate ceramic particles from a suspension. An electrical polarity is applied to the mold that is opposite to the polarity at the surface of the ceramic particles. The ceramic particles are electrically attracted to the mold surface and deposit as a uniform compact. When the desired thickness of deposit is achieved, either the mold is removed from the container of slip or the slip is poured from the mold. Electrophoretic deposition is generally used to deposit a thin coating or to produce a thinwalled body such as a tube. It is also used to achieve very uniform deposition of spray paint onto a conductive surface.

All of the casting techniques discussed above result in a relatively weak ceramic powder compact. A technique developed at ORNL results in a much stronger compact. This technique is referred to as *gel casting*. The ceramic powder is mixed with a liquid and a polymerizable additive to form a fluid slurry similar to a casting slip. The slip is poured into a container of the desired shape. Polymerization is caused to occur before the powder in the slip has time to settle. The resulting powder compact is quite uniform and strong. However, removal of the liquid is more difficult than for conventional slip casting. Furthermore, monomers are generally toxic and require careful handling. For example, the initial material used by ORNL was acrylamid, which is a neurotoxin and has largely been discontinued because of handling concerns.

### 13.2.1.9 Casting Process Control

As was illustrated in Figure 13.22, careful process control is necessary in the slip-casting process. Some of the critical factors include:

- constancy of properties
- viscosity



**FIGURE 13.40** (a) Assembled SiC gas-turbine scroll. (b) Individual parts that were bonded together to form the scroll. (Photos courtesy of Carborundum Company for parts fabricated for Allison Gas Turbine Division of General Motors under sponsorship of the U.S. Department of Energy and administration of NASA-Lewis Research Center.)

settling rate  
 freedom from air bubbles  
 casting rate  
 drain properties  
 shrinkage  
 release properties  
 strength

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. Sometimes, 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.

### 13.2.1.10 Drying

Compacts fabricated by casting are saturated with the casting fluid. The fluid is trapped in all the pores, as well as forming a film on some of the particles. The fluid must be completely removed by a drying operation before the compact can be taken to high temperature for densification.<sup>21,22</sup> The ease of removal of the fluid is dependent on several factors: (1) the amount of porosity; (2) the size of interconnected pore channels; (3) the vapor pressure of the fluid; and (4) the thickness of the compact.

The porosity distribution is particularly important. Large pores and pore channels allow easy removal of the fluid. However, these result in low green density, shrinkage during drying, and difficulty in firing to a dense, fine-grained microstructure. Conversely, cast compacts with close-packed particles, small pores, and narrow pore channels are easy to densify to a fine-grained microstructure, but are difficult to dry. The fine channels result in large capillary pressures and stresses that can easily crack the compact if the fluid is not removed uniformly. For example, the gas-turbine rotor shown in Figure 13.38 required a dense, fine-particle-size cast compact that was very difficult to dry. The thin blades tended to dry quickly while the thick hub was still saturated. This resulted in cracking near the base of the blades during drying. Drying time greater than a week with careful control of humidity and temperature was necessary to achieve a crack-free part.

## 13.2.2 TAPE CASTING

Some applications such as substrates and packages for electronics and dielectrics for capacitors require thin sheets of ceramics. Tape casting has been developed to fabricate these thin sheets in large quantity and at low cost. It is similar to slip casting, except that the slip contains about 50 vol% organic binder and is spread onto a flat surface rather than being poured into a shaped mold.

### 13.2.2.1 Doctor Blade Process

The most common approach for tape casting is the doctor blade process.<sup>23</sup> A schematic of a doctor blade apparatus is illustrated in Figure 13.41. The technique consists of casting a slurry onto a moving carrier surface (usually a thin film of cellulose acetate, Teflon™, Mylar™, or cellophane) and spreading the slurry to a controlled thickness with the edge of a long, smooth blade. The slurry contains a binder system dissolved in a solvent. Enough binder is present so that a flexible tape will result when the solvent is removed. Solvent removal is achieved by evaporation. As with slip casting, the fluid must be removed slowly to avoid cracking, bubbles, or distortion. This is the purpose of the long portion of the tape-casting apparatus between the doctor blade and the take-up reel. The evaporation is achieved either by controlled heating or airflow. The dry flexible tape is rolled onto a reel to be stored for use. The uses of the tape are described later in this chapter.



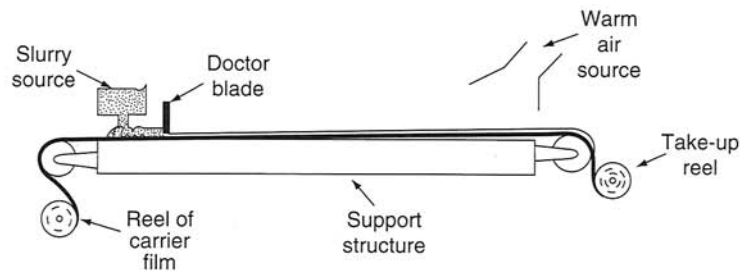


FIGURE 13.41 Schematic illustrating the doctor blade tape-casting process.

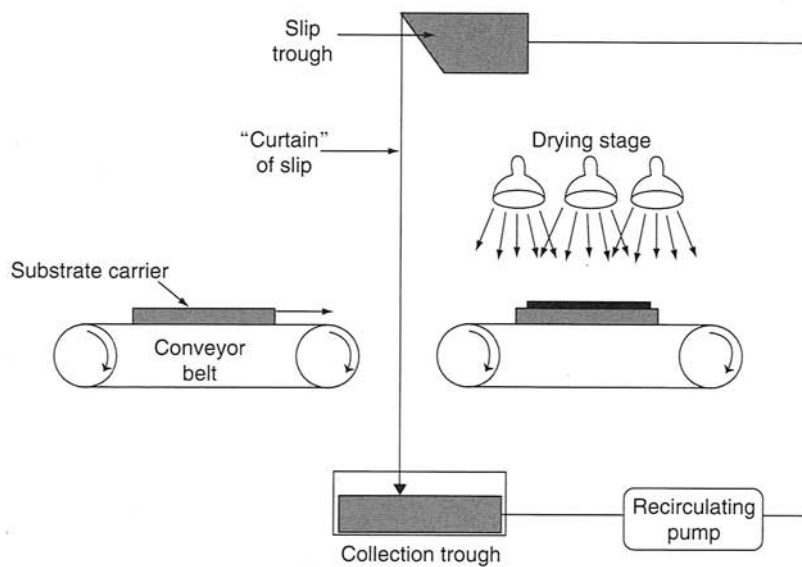


FIGURE 13.42 Schematic illustrating the "waterfall" tape-casting process. (From J. Adair, The Pennsylvania State University. With permission.)

### 13.2.2.2 Other Tape-Casting Processes

A second tape-casting process is the "waterfall" technique. It is illustrated in Figure 13.42. The slurry is pumped in a recirculating system to form a continuous curtain. A conveyor belt carries a flat surface through the slurry. The uniform, thin layer of slurry on the carrier is then transferred by conveyor to the drying stage. This technique has been used to form thin tape for capacitor dielectrics and thicker tape for porous electrodes for fuel cells. It is also commonly used for applying the chocolate coating to candy bars.

A third tape-casting process is the *paper-casting process*. It is illustrated in Figure 13.43. Low-ash paper is passed through a slurry. The slurry wets the paper and adheres to it. The thickness of adherence depends on the viscosity of the slurry and the nature of the paper. The coated paper passes through a drier, and the resulting tape is rolled onto a take-up reel. The paper is later removed during a firing process. This technique has been used in fabrication of honeycomb structures for heat exchangers, as shown in Figure 13.44.

### 13.2.2.3 Preparation of Tape-Casting Slurries

Tape-casting slurries are rheologically similar to slip-casting slurries, but contain a larger quantity of binder. In addition, the binder and plasticizer system is generally selected to be thermoplastic,

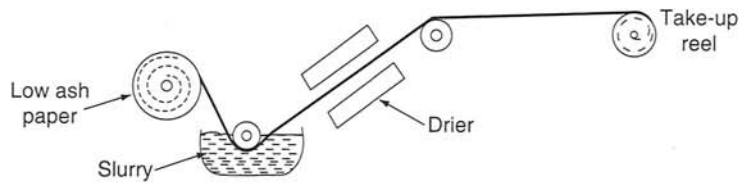


FIGURE 13.43 Schematic illustrating the paper-casting tape-forming process.

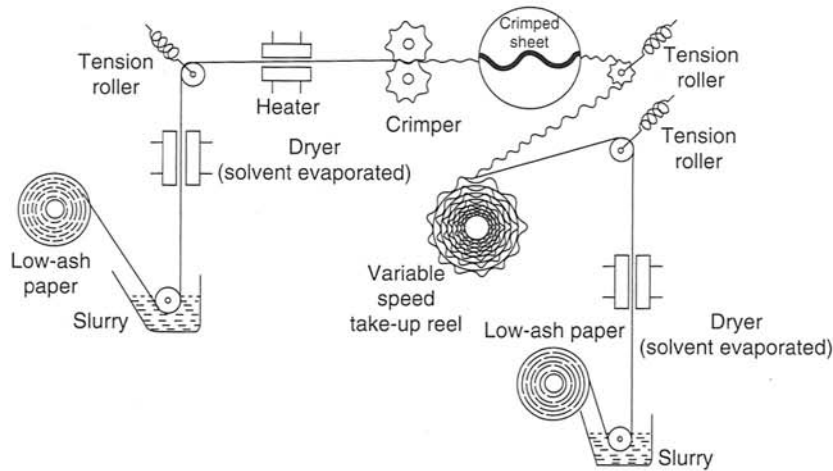


FIGURE 13.44 Use of the paper-casting process to fabricate a honeycomb structure for a heat exchanger.

that is, it can be softened by heating to moderate temperatures. This allows layers to be bonded together by lamination.

Table 13.7 describes the characteristics of the organic components commonly added to achieve an acceptable tape-casting slurry. These include a binder, a plasticizer, a dispersant, a wetting agent, and an antifoam agent. Each combination must be selected and optimized for a specific fluid (solvent). Examples of solvents are methyl ethyl ketone (MEK), alcohols, toluene, hexane, trichloroethylene, and water. Examples of binders are polyvinyl butyral, polyvinyl acetate, polyvinyl chloride, polyvinyl alcohol, polyacrylic emulsion, polystyrene, polymethacrylates, and cellulose nitrates. The criteria for the binder include: (1) forms tough, flexible film when dry; (2) volatilizes to a gas when heated and leaves no residual carbon or ash; (3) remains stable during storage, especially with no change in molecular weight; and (4) is soluble in an inexpensive, volatile, nonflammable solvent.

Tables 13.8 and 13.9 identify binder and solvent and plasticizer systems that have been reported for tape casting of  $\text{Al}_2\text{O}_3$  for fabrication of electrically insulative substrates for integrated circuit electronic devices.<sup>24</sup> Figure 13.45 shows a flowchart that identifies the sequence of steps in fabrication of such a substrate by tape casting. Table 13.10 identifies a tape-casting system for  $\text{BaTiO}_3$ .

#### 13.2.2.4 Applications of Tape Casting

The major applications of tape casting are for fabrication of dielectrics for multilayer capacitors and of  $\text{Al}_2\text{O}_3$  for substrates and multilayer packages for integrated circuits. Figure 13.46 illustrates the use of tape casting for multilayer capacitors. Figure 13.47 shows schematically the cross section of a multilayer package for a silicon chip device. The white layers of the package are  $\text{Al}_2\text{O}_3$ . The black lines and grids are electrically conductive metal (tungsten or molybdenum). The  $\text{Al}_2\text{O}_3$  isolates the metal circuit lines and allows miniaturization of complex circuits. Each  $\text{Al}_2\text{O}_3$  layer is

**TABLE 13.7**  
**Functions of Organic Components of Tape-Casting Binder Systems**

**Binders**

10,000 to 30,000 molecular weight polymers mixed with powder suspension: after drying provide flexibility and integrity to green tape

**Plasticizers**

Small- to medium-sized molecule that decreases cross-linking among binder molecules; this makes the tapes more pliable, e.g., polyethylene glycol

**Dispersants**

Typically 1000 to 10,000 molecular weight polymer molecules that aid in dispersion of ceramic particles, e.g., isooctylphenylpolyethoxyethanol

**Defoaming Agents**

Various organic substances used to minimize frothing usually due to addition of dispersant (one of the defoaming agent's actions may be to increase surface tension of slip), e.g., tributyl phosphate

**Wetting Agents**

Small- to medium-sized molecules that impart wettability to the ceramic powder by the solvent system, e.g., isooctylphenylpolyethoxyethanol

Source: Courtesy J. Adair, The Pennsylvania State University.

**TABLE 13.8**  
**Additives to  $Al_2O_3$  for the Western Electric Company ERC-105 Doctor-Blade Process**

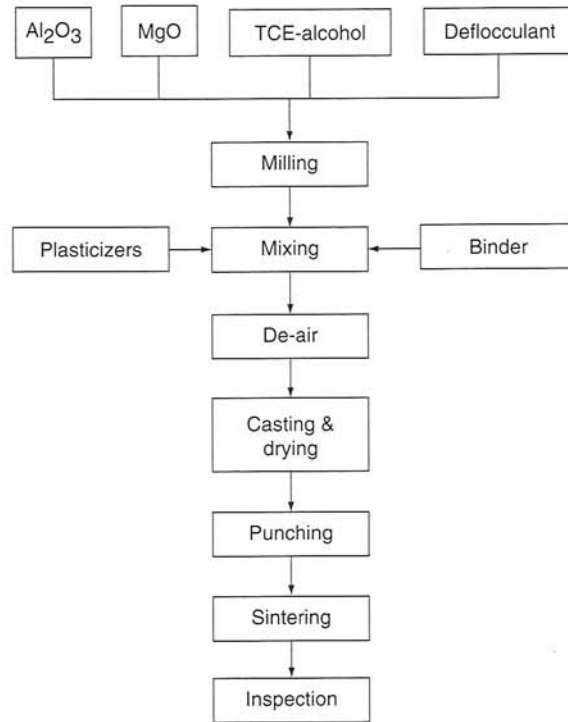
| Material            | Function               |
|---------------------|------------------------|
| MgO                 | Grain-growth inhibitor |
| Menhaden fish oil   | Deflocculant           |
| Trichloroethylene   | Solvent                |
| Ethyl alcohol       | Solvent                |
| Polyvinyl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

Source: Shanefield, D.J. and Mistler, R.E., Fine grained alumina substrates: I, the manufacturing process. *Am. Ceram. Soc. Bull., Part I* 53, 416–420, 1974.

**TABLE 13.9**  
**Examples of Binder-Solvent-Plasticizer Systems for Tape Casting of  $Al_2O_3$**

| Thickness of Tape | Binder                      | Solvent      | Plasticizer                |
|-------------------|-----------------------------|--------------|----------------------------|
| >0.25 mm          | 3.0 Polyvinyl butyral       | 35.0 Toluene | 5.6 Polyethylene glycol    |
| <0.25 mm          | 15.0 Vinyl chloride-acetate | 85.0 MEK     | 1.0 Butyl benzyl phthalate |

Source: Mistler, R.E., Shanefield, D.J., and Runk, R.B., in *Ceramic Processing Before Firing*, Onoda, G. and Hench, L., Eds., Wiley, New York, 1978, p. 414.



**FIGURE 13.45** Flowchart for fabrication of Al<sub>2</sub>O<sub>3</sub> substrates by tape casting. (From Mistler, R., et al., in *Ceramic Processing Before Firing*, Onoda, G. and Hench, L., Eds., Wiley, New York, 1978, With permission.)

**TABLE 13.10**  
Example of a Tape-Casting System for BaTiO<sub>3</sub>

| Ingredient                                      | Function     | Parts by Weight |
|---|--------------|-----------------|
| BaTiO <sub>3</sub>                              | Ceramic      | 100             |
| MEK and ethanol (50 wt% mixture)                | Solvent      | 20              |
| Menhaden fish oil <sup>a</sup>                  | Deflocculant | 1               |
| Santicizer 160 (Butyl benzyl phthalate)         | Plasticizer  | 4               |
| Carbowax 400 <sup>c</sup> (Polyethylene glycol) | Plasticizer  | 4               |
| Cyclohexanone                                   | Homogenizer  | 0.7             |
| Acryloid B-7 MEK <sup>d</sup> (30% solution)    | Binder       | 13.32           |

<sup>a</sup>Defloc Z-3, Spencer Kellogg Inc., Buffalo, N.Y.

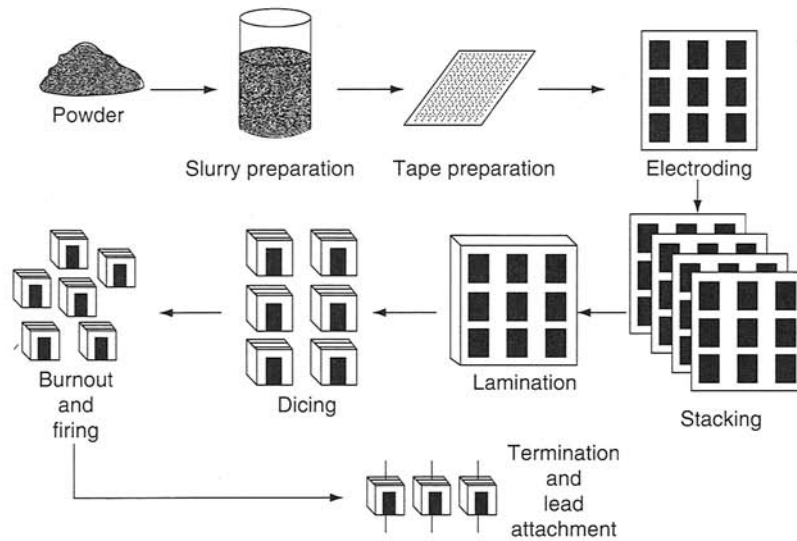
<sup>b</sup>Monsanto Inc., St. Louis, Mo.

<sup>c</sup>Rohm and Haas Co., Philadelphia, Pa.

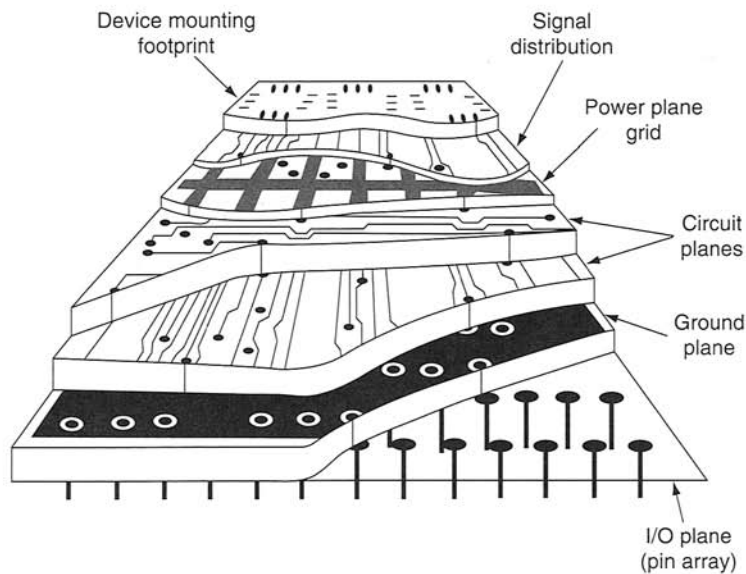
<sup>d</sup>Carbide and Carbon Chemical Co., N.Y.

Source: Mackinnon, R.J. and Blum, J.B., in *Advances in Ceramics, Forming of Ceramics*, Vol. 9, Mangels, J. and Messing, G., Eds., American Ceramic Society, Ohio, 1984, pp. 150–157.

prepared from a tape-cast section. The metal patterns are screen-printed onto the tape. The layers of tape with the appropriate metal patterns are stacked and bonded together. The binders are then carefully removed at moderate temperature and the Al<sub>2</sub>O<sub>3</sub> powder compact densified at high temperature. The metal circuits are trapped in the Al<sub>2</sub>O<sub>3</sub> and protected from the external environment.



**FIGURE 13.46** Process steps for fabrication of multilayer capacitors by tape casting. (Courtesy of J. Adair, The Pennsylvania State University.)



**FIGURE 13.47** Schematic cross section showing the complexity of the metallized circuit patterns in a ceramic multilayer integrated circuit package. (From Ryshkewitch, E. and Richerson, D., *Oxide Ceramics*, 2nd ed., General Ceramics, Inc., N.J., 1985, p. 466. With permission.)

### 13.3 PLASTIC FORMING

Plastic forming involves producing shapes from a mixture of powder and additives that are deformable under pressure. Such a mixture can be obtained in systems containing clay minerals by addition of water and small amounts of a flocculant, 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 or other fluid to provide the plasticity. About 25 to 50 vol% organic additive is required to achieve adequate plasticity for forming.

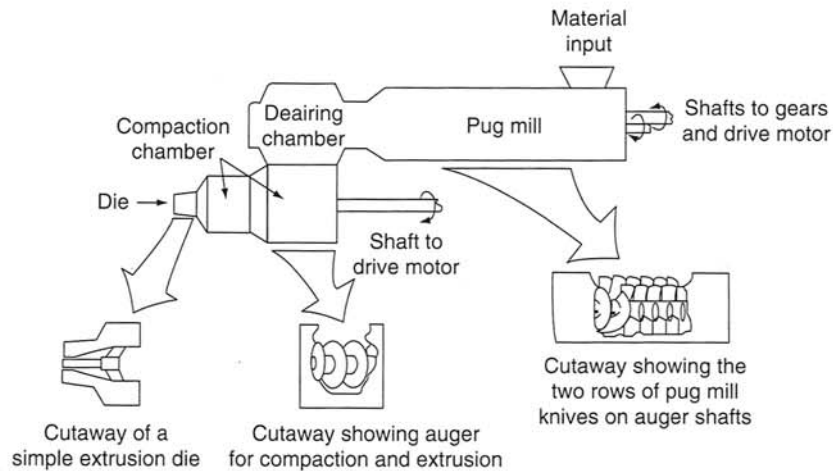


FIGURE 13.48 Schematic of an auger-type extruder.

A major difficulty in plastic-forming processes is removing the organic material prior to firing. In the case of a water-clay system, substantial shrinkage occurs during drying, increasing the risk of shrinkage cracks. In the case of organic additives, the major problems are forming a flaw-free green part 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. Modern ceramics generally do not contain clay and require organic additions to achieve plasticity.

The following sections of this chapter describe the key plastic-forming techniques that are being used or developed for shape fabrication of modern ceramics. Extrusion and injection molding are described in detail. Other techniques such as compression molding and roll forming are briefly discussed.

### 13.3.1 EXTRUSION

Extrusion is a plastic-forming method that has been used extensively for many years for fabrication of ceramics for furnace tubes, bricks, insulators, pipe, tile, tubular capacitors, catalyst supports, magnets, heat-exchanger tubes, and other parts with a constant cross section. The extrusion process consists of forcing a highly viscous, doughlike plastic mixture of ceramic powder plus additives through a shaped die.<sup>22,25,26</sup> It is analogous to squeezing frosting out of a cake decorator, although the pressures are higher and the mixture is much stiffer than frosting. The consistency is similar to that of molding or potter's clay.

#### 13.3.1.1 Extrusion Equipment

The schematics of the two types of extruders commonly used are shown in Figures 13.48 and 13.49. One is an auger-type extruder in which the plasticized mix is forced through a shaped die by the rotation of an auger. The second type of extruder uses a piston in place of an auger. The piston-type extruder generally results in less contamination by wear.

An auger extruder consists of several sections and is capable of continuous operation. The first section is a *pug mill*. The pug mill contains two rows of blades mounted on auger shafts. The shafts rotate in opposite directions, providing a high-shear mixing action of material squeezed between the blades. The doughlike premix (ceramic powder plus liquid plus additives such as binders, plasticizers,

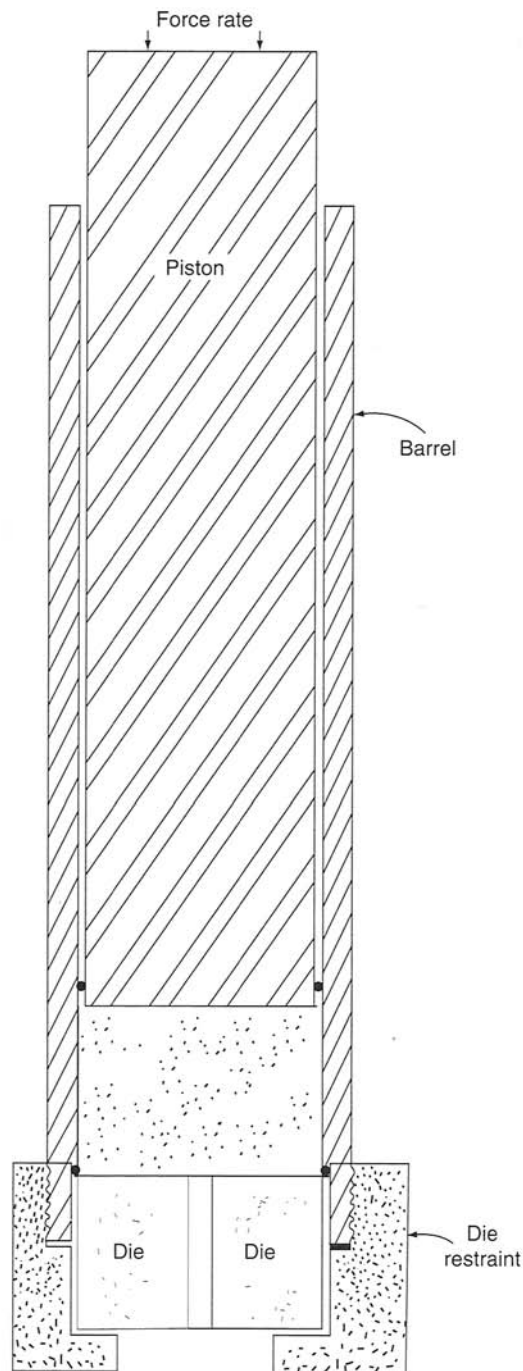


FIGURE 13.49 Schematic of a piston-type extruder. (Drawing courtesy of ASM International.)

dispersants, flocculants, lubricants and surfactants) is fed into the pug mill. The pug mill kneads the premix to provide homogeneity, to maximize plasticity, and to squeeze out excess air. The mixture then enters a *deairing chamber* that uses auger motion plus an applied vacuum (in some equipment) to remove as much air as possible. The mixture finally moves to the *compaction chamber* where auger motion or pressure from a piston precompacts the mixture to remove as much void space as

possible prior to extrusion through a *shaped die*. The plasticized mixture is then forced under high pressure through the shaped die. The resulting long strands of constant-cross-section compacted ceramic are supported in trays and cut to the desired length prior to drying and firing.

### 13.3.1.2 Binders and Additives for Extrusion

Additives to a ceramic powder are required to achieve a mixture that has characteristics suitable for extrusion. The nature of the additives depends on whether the extrusion is conducted at room temperature with a combination of a binder and fluid or at elevated temperature with a thermosetting polymer. The following are some of the key characteristics that must be considered:

1. The mixture must be plastic enough to flow under pressure into the desired cross-section, yet rigid enough (high enough wet strength) to resist deformation due to slumping or handling.
2. The mixture must not stick to the die or other tooling and must yield smooth surfaces after extrusion.
3. The fluid and ceramic must not separate under an applied pressure.
4. The mixture must have reproducible porosity such that shrinkage during drying and firing are predictable.
5. Organics must be low-ash content to leave minimal residue during firing.

The flow characteristic (rheological behavior) is the dominant factor. As was the case for slip casting, additives and volume fraction solids are used to control the flow characteristics. Extrusion is most commonly conducted at room temperature, so we will concentrate our discussion on additives that provide flow at room temperature. The nature of the additives selected depend on the ceramic powder and the liquid. Compositions containing no clay require a substantial percentage of organic additives and either water or a solvent. Compositions containing a clay mineral such as kaolinite can be plasticized with water additions and do not require organics. Clay has a structure that absorbs water between the sheet layers, resulting in natural plasticity.

Modern ceramic compositions such as  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ , and  $\text{BaTiO}_3$  do not contain clay and thus must have organic additives. The major additive is the *binder*. It provides a coating over each ceramic particle to allow flow during extrusion and green strength after extrusion. Binders are available in a wide range of viscosity. Examples of water-soluble binders and their range of viscosity are identified in Table 13.11. The viscosity is based primarily on the molecular weight and the strength of molecular bonds of the organic. Examples of several systems that have been successfully extruded are listed in Tables 13.12 and 13.13.

Other additives include lubricants, surfactants (wetting agents), dispersants, flocculants, plasticizers, algicides, and antifoam agents. The *plasticizer* modifies the rheology of the binder to achieve plastic behavior at the temperature of extrusion. The *lubricant* reduces particle-particle and die-wall friction, prevents sticking and aids in achieving an acceptable surface finish. *Surfactants* enhance the wetting ability of the binder onto the ceramic particles. *Dispersants* and *flocculants* control the degree of dispersion or agglomeration of the particles. For some particle size distributions, dispersion is preferred. For others, a high degree of flocculation works better so coagulants are added. Examples are included in Table 13.14. The extrusion characteristics can be broadly varied by changing the degree of dispersion. As with slips, the dispersion characteristics can be altered by control of pH and by additives that provide electrostatic surface charges or steric hindrance.

### 13.3.1.3 Extrusion Steps

The steps of extrusion are similar to the steps of other processes for forming ceramic particulate compacts. They include powder sizing, batch formulation, mixing, extrusion, drying, densification, and quality control.



**TABLE 13.11**  
**Viscosity Ranges for Some Water-Soluble Binders**

| Binder                        | Viscosity Grade |     |        |      |           |   |   |
|-------------------------------|-----------------|-----|--------|------|-----------|---|---|
|                               | Very Low        | Low | Medium | High | Very High |   |   |
| Gum arabic                    |                 | •   |        |      |           |   |   |
| Lignosulfonates               |                 | •   |        |      |           |   |   |
| Lignin liquor                 |                 | •   |        |      |           |   |   |
| Molasses                      |                 | •   |        |      |           |   |   |
| Dextrins                      | •               | —   |        |      |           |   |   |
| Poly(vinylpyrrolidone)        | •               | —   |        |      |           |   |   |
| Poly(vinyl alcohol)           | •               | —   | •      |      |           |   |   |
| Polyethylene oxide            |                 | •   | —      | •    |           |   |   |
| Starch                        |                 | •   | —      | •    |           |   |   |
| Acrylics                      |                 | •   | —      |      |           |   |   |
| Polyethylenimine PEI          |                 | •   | —      |      |           |   |   |
| Methylcellulose               |                 |     | •      | —    | •         |   |   |
| Sodium carboxymethylcellulose |                 |     | •      | —    | •         |   |   |
| Hydroxypropylmethylcellulose  |                 |     | •      | —    | •         |   |   |
| Hydroxyethylcellulose         |                 |     | •      | —    | •         |   |   |
| Sodium alginate               |                 |     |        | •    | —         | • |   |
| Ammonium alginate             |                 |     |        |      | •         | — | • |
| Polyacrylamide                |                 |     |        |      | •         | — | • |
| Scleroglucan                  |                 |     |        |      |           |   | • |
| Irish moss                    |                 |     |        |      |           |   | • |
| Xanthan gum                   |                 |     |        |      |           |   | • |
| Cationic galactomanan         |                 |     |        |      |           |   | • |
| Gum tragacanth                |                 |     |        |      |           |   | • |
| Locust bean gum               |                 |     |        |      |           |   | • |
| Gum karaya                    |                 |     |        |      |           |   | • |
| Guar gum                      |                 |     |        |      |           |   | • |

Source: Adapted from Onoda, G., in *Ceramic Processing Before Firing*, Onoda, G. and Hench, L., Eds., Wiley, New York, 1978, p. 242.

As with other forming processes, particle size and shape and degree of agglomeration are extremely important. Fine particles (under  $1\ \mu\text{m}$  or  $0.00004\ \text{in.}$ ) are generally easiest to extrude.

Mixing is a critical step in extrusion. All particles must be uniformly coated with the binder-liquid solution. Obtaining uniformity is difficult because the final extrudable mix is so stiff. Imagine stirring flour into honey. Without high-intensity mixing, pockets of binder and powder can remain that can cause nonuniform extrusion and also end up as strength-limiting defects in the final part. Several different mixing techniques have been used successfully. One is the "brute force" technique in which the ingredients are weighed out to their final formulations and mixed directly to the final, stiff consistency in a high-shear mixer such as a pug mill or muller. A second technique is to add excess liquid to provide improved wetting and then partially dry to the required consistency after thorough mixing. Another technique is to mix the water and powder first to form a low-viscosity mixture and then to add the binder incrementally to bring the mix uniformly up to the extrudable viscosity.

Viscosity is not the only key parameter for successful extrusion. The mix must have the proper flow characteristics when a load is applied. The options of flow behavior are illustrated in Figure 13.50 for apparent viscosity vs. shear rate. The preferred flow behaviors are *shear-thinning* or *Bingham*.

Other important factors for successful extrusion are die design and alignment. The purpose of the die is to achieve the final compaction of the ceramic mix and to form the desired cross section.

**TABLE 13.12**  
**Examples of Extrusion of Nonclay Compositions**

| Composition   | Additives  | Conditions              | Shape                                       |
|---|--|-------------------------|---|
| Graphite  | 50–60 parts phenol formaldehyde emulsion                               | –                       | 1.6- and 2.54-cm (5/8- and 1-in.) rods      |
| Petroleum coke  | Coal-tar pitch plus heavy oil  | 90–110°C<br>(195–230°F) | –   |
| Al <sub>2</sub> O <sub>3</sub> –5% Cr <sub>2</sub> O <sub>3</sub><br>30% Si–70% SiC | Gum ghatti plus mogul starch<br>4% guar gum, 20% water,<br>3% silicone | –                       | Round, square, and triangular tubes<br>–    |
| BeO   | 10–18% mogul starch, 15–18%<br>water-glyceryl mixture                  | –                       | Rods, tubes, thin-walled multicell<br>tubes |
| MgO   | 30–40% flour paste   | –                       | Vacuum-tube parts                           |

Source: From Hyde, C., Vertical extrusion of nonclay composition, in *Ceramic Fabrication Processes*, Kingery, W.D., Ed., MIT Press, Cambridge, MA, 1963, pp. 107–111.

**TABLE 13.13**  
**Examples of Compositions of Extrusion Bodies**

| Composition (vol%)     |    |                   |    |                      |    |
|------------------------|----|-------------------|----|----------------------|----|
| Refractory Alumina     |    | High Alumina      |    | Electrical Porcelain |    |
| Alumina (<20 μm)       | 50 | Alumina (<20 μm)  | 46 | Quartz (<44 μm)      | 16 |
| Hydroxyethyl cellulose | 6  | Ball clay         | 4  | Feldspar (44 μm)     | 16 |
| Water                  | 44 | Methylcellulose   | 2  | Kaolin               | 16 |
| AlCl <sub>3</sub>      | <1 | Water             | 48 | Ball clay            | 16 |
| (pH 8.5)               |    | MgCl <sub>2</sub> | <1 | Water                | 36 |
|                        |    |                   |    | CaCl <sub>2</sub>    | 1  |

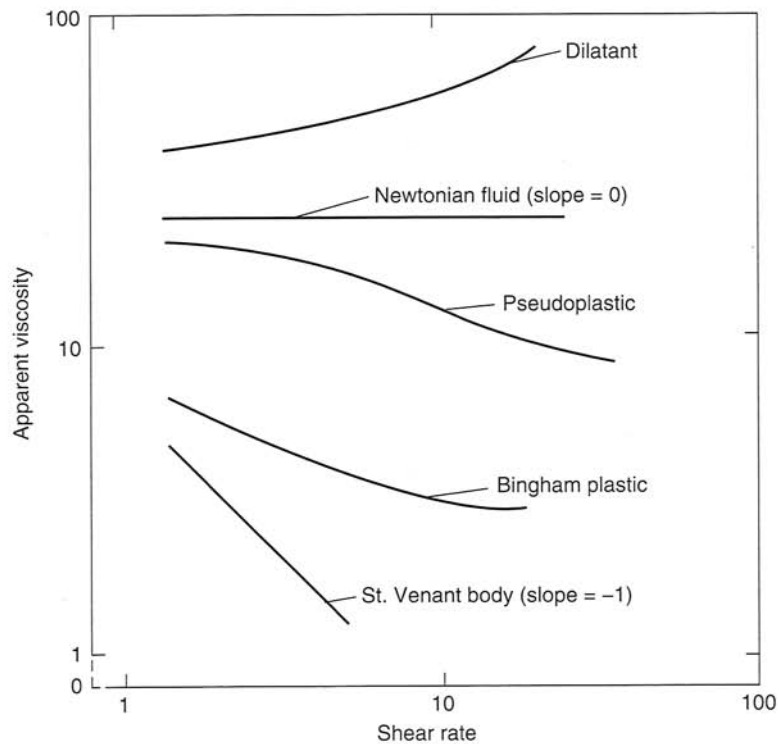
Source: From Reed, J.S., *Principles of Ceramic Processing*, Wiley, New York, 1988, p. 359.

**TABLE 13.14**  
**Additives Used in Nonclay Aqueous Extrusion Bodies**

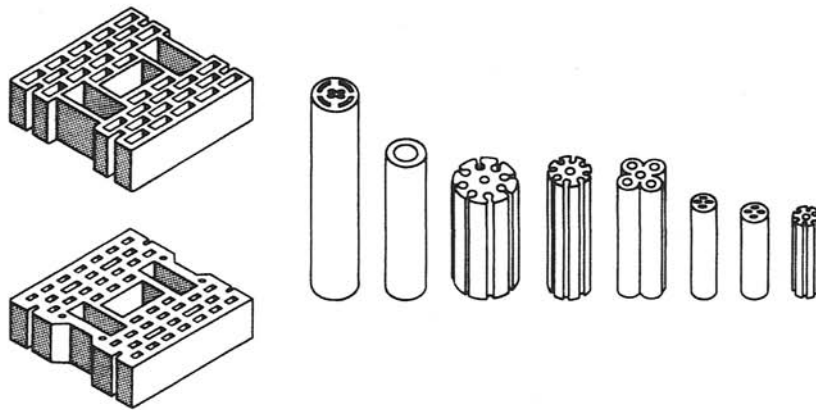
| Flocculant and Binder  | Coagulant         | Lubricant          |
|------------------------|-------------------|--------------------|
| Methylcellulose        | CaCl <sub>2</sub> | Various stearates  |
| Hydroxyethyl cellulose | MgCl <sub>2</sub> | Silicones          |
| Polyvinyl alcohol      | MgSO <sub>4</sub> | Petroleum oil      |
| Polyacrylimides        | AlCl <sub>3</sub> | Colloidal talc     |
| Polysaccharides        | CaCO <sub>3</sub> | Colloidal graphite |

Source: From Reed, J.S., *Principles of Ceramic Processing*, Wiley, New York, 1988, p. 360.

The cross section can be very simple such as a solid rod or hollow cylinder or can be very complex such as a thin-wall honeycomb. Some examples of extruded cross sections are illustrated in Figures 13.51 and 13.52. For these sections to be complete and the extruded lengths straight, the ceramic mix must flow uniformly through the die. If it hangs up in one place or flows at a nonuniform rate,



**FIGURE 13.50** Options for plastic-flow behavior. (From Mutsuddy, B., *Ind. Res. & Dev.*, 78, 1983. With permission.)



**FIGURE 13.51** Examples of the types of shapes that are commonly extruded. (Drawing courtesy of ASM International.)

the extruded compact will deform as it exits the die. Major effort is required to design a die that allows uniform flow and to align the die to tight tolerances.

Extruded material contains a substantial percentage of liquid. This is removed by evaporation using the same type of careful control discussed earlier for slip-cast ceramics. In addition to liquid, the extruded compact contains a much higher binder content than a cast compact. This binder must be removed before the compact can be densified. Most binders used for extrusion can be burned off in an oxidizing atmosphere in the temperature range of 300 to 1000°C (570 to 1830°F). This burn



**FIGURE 13.52** A variety of ceramic parts that have been fabricated by extrusion. (Photo courtesy of Superior Technical Ceramics Corporation, St. Albans, VT.)

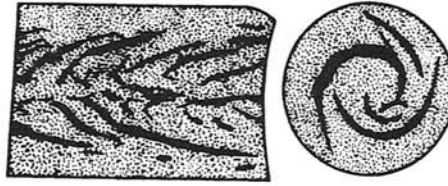
off must be done slowly and carefully to allow the carbonaceous gases generated by the decomposition of the organics to escape through the pores of the compact. Too rapid a rate of burn off can crack or fracture the compact. Each binder has its unique temperature range for burn off. The allowable rate of burn off is largely determined by the particle size distribution, the degree of particle packing, and the thickness of the compact. Most organic binders will not burn off properly in a nonoxidizing atmosphere. Instead, they will decompose and leave a carbon residue. The acrylic binders are an exception. They burn out cleanly in inert and reducing atmospheres as well as oxidizing atmospheres.

#### 13.3.1.4 Common Extrusion Defects

Extrusion is often more of an art than a science. Quality is controlled by careful inspection of extruded compacts for defects. Defects that can occur for extrusion include warpage or distortion, lamination, tearing, cracking, segregation, porosity, and inclusions.<sup>27</sup>

*Warpage* or *distortion* can occur during drying or firing due to density variations or during extrusion due to improper die alignment or die design. If the alignment or balance of the die is not correct, greater pressure on one side of the die will occur. This will cause more material to extrude from this side and result in bending of the extruded column as it exits the die.

*Laminations* are cracks that generally form a pattern or orientation. Examples are shown in Figure 13.53. A common cause is incomplete re-knitting as the plastic mix is cut by the auger or flows past the spider portion of the die. The spider is the portion of the die that supports any shaped channels in the die. For example, to extrude a circular tube, a solid rod of the inner diameter of the tube must be supported at the center of the die. It is generally supported by three prongs at  $120^\circ$  to each other that run parallel to the length of the die and are attached to the inside of the die. The material being extruded must squeeze around these prongs and reunite into a continuous hollow cylinder before leaving the die. Laminations occur if the material does not completely re-knit.



**FIGURE 13.53** Drawings of the cross sections of extruded parts illustrating the appearance of severe laminations that can occur as extrusion defects. (From Robinson, G.C., *Extrusion defects*, in *Ceramic Processing Before Firing*, Onoda, G.Y. and Hench, L.L., Eds., Wiley-Interscience, New York, 1978. With permission.)



**FIGURE 13.54** Drawings of the cross section of an extruded part illustrating the appearance of tearing. (From Robinson, G.C., *Extrusion defects*, in *Ceramic Processing Before Firing*, Onoda, G.Y. and Hench, L.L., Eds., Wiley-Interscience, New York, 1978. With permission.)

*Tearing* consists of surface cracks that form as the material exits the extruder. This is illustrated in Figure 13.54. The cracks extending from the surface inward result from the contact stresses and friction that are discussed earlier in this chapter. Too dry a mix with inadequate cohesiveness will tear. A mix with high rebound may also tend to tear. Die design involving a slight divergent taper at the die exit can help prevent tearing.

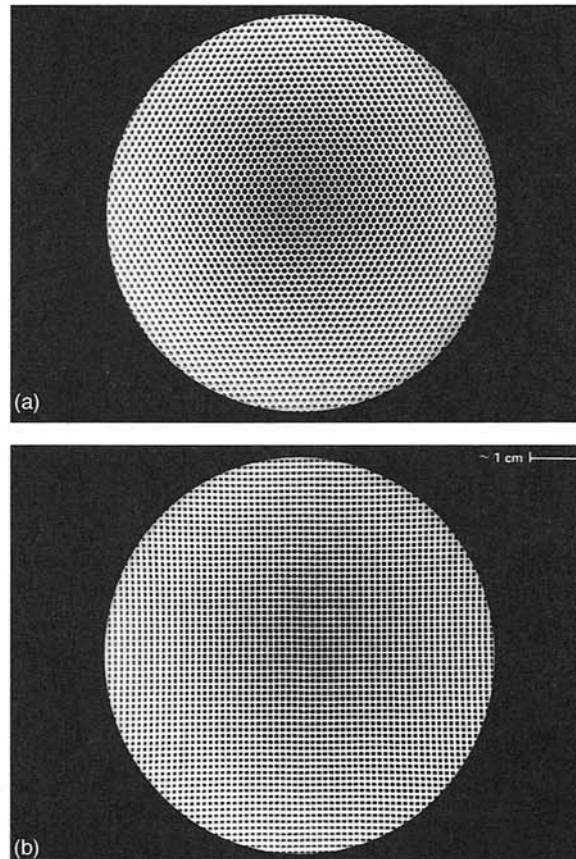
Lamination and tearing are two sources of cracking. Other cracks can occur due to poor mixing, shrinkage variation, and partially dried debris from a prior extrusion run.

*Segregation* involves a separation of the liquid and solid portions of the mix during extrusion. This can result in cracking or distortion during extrusion or during subsequent drying or firing.

The defects discussed so far are macrodefects that should be observable by visual inspection or radiography (discussed in Chapter 16). Microdefects such as pores and inclusions can also occur. Pores result from trapped air, powder agglomerates, and pockets of binder or other organic matter that burn off during firing and leave a hole in the material. Inclusions result from foreign material in the starting powder, in the binder, or picked up as contamination during mixing or extrusion. Binder solutions frequently contain contamination or undissolved binder and should be filtered if possible prior to use. Linings and surfaces of blades and augers in mixers and extruders introduce metal particles due to wear.

### 13.3.1.5 Applications of Extrusion

Extrusion is a low-cost method of forming large quantities of product. It has been used for many years to produce brick, furnace tubes, kiln furniture, thermocouple protection tubes, electronics substrates, tile, sewer pipe, magnets, refractories, and whiteware. More recently extrusion has been used to fabricate heat-exchanger tubes and honeycomb-shaped catalyst supports. The catalyst supports are particularly complex in shape, as illustrated in Figure 13.55. They consist of hundreds of open cells per square centimeter with wall thickness under  $100\ \mu\text{m}$  (0.004 in.). A unique procedure was invented for extrusion of such a complex cross section. The ceramic powder was mixed with a hydraulic-setting polyurethane resin. The mix was then extruded into a water bath at a rate that matched the rate of cure of the polyurethane. This rate was about 2 mm/sec.



**FIGURE 13.55** Cross sections of extruded honeycomb structures of cordierite for use as catalyst supports for automotive emission-control devices. (Courtesy of NGK Insulators.)

### 13.3.2 INJECTION MOLDING

Injection molding uses equipment<sup>28</sup> that has a cross section similar to an extruder, as shown in Figure 13.56. However, the process is very different from extrusion. The feed material for injection molding generally consists of a mixture of the ceramic powder with a thermoplastic polymer plus a plasticizer, wetting agent, and antifoam agent. The mixture 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 that 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 into the tool cavity. The mixture is much more fluid at this point than an extrusion mix and could not form a self-supporting shape. The strand piles on itself until the cavity is full and the material has “knit” or fused together under the pressure and temperature to produce a homogeneous part. The shaped tool is cooler than the injection-molding mix such that the mix becomes rigid in the tool cavity. The part can be removed from the tool as soon as it is rigid enough to handle without deformation. Cycle times can be rapid, providing the potential for injection molding to be a high-volume, low-cost process for fabrication of ceramics into complex shapes.

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.<sup>29</sup>

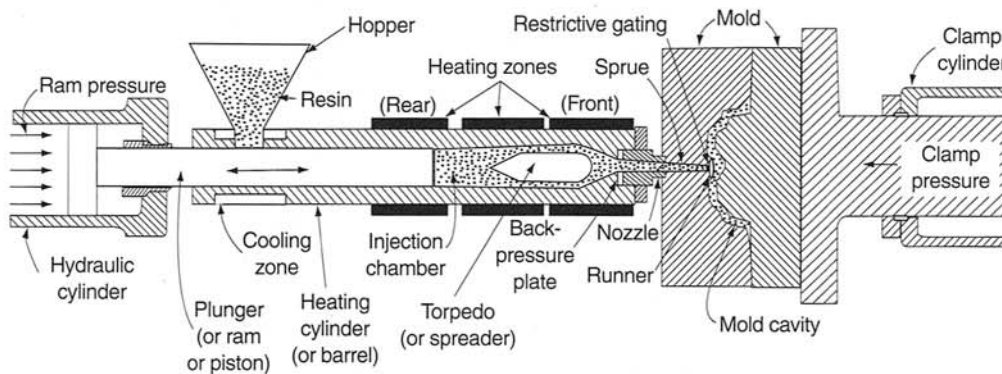


FIGURE 13.56 Cross section of a plunger- (piston-)type injection-molding machine. (From Quackenbush, C.L., et al., *Ceram. Eng. and Sic. Proc.*, 3(1-2), 31, 1982. With permission.)

Ceramic parts are made with the same injection-molding equipment, but with dies made of harder, more wear-resistant metal alloy. The ceramic powder is essentially added to the plastic as a filler. After injection molding, the plastic is then removed by careful thermal treatments.

### 13.3.2.1 Injection-Molding Parameters

Figure 13.57 lists the general steps in injection molding and some of the controls and inspection procedures that must be considered. The sequence of process steps is similar to that for the other forming processes we have discussed: raw material selection, powder processing, preconsolidation, consolidation, extraction of organics, and densification. The following paragraphs describe some of the process steps and parameters for injection molding.

**Particle Sizing.** Particle size distribution is important in injection molding, as we have determined for other forming processes, to achieve the densest packing and to minimize the amount of organic material. Both particle packing and sizing affect viscosity. It has been reported<sup>30</sup> 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, complex shapes of silicon powder having 76.5 vol% solids were successfully injection-molded. Those tests<sup>31</sup> were conducted on a plunger-type injection machine at a cylinder pressure of 13.8 MPa (2 ksi) and a temperature 10°C (50°F) above the melting temperature of the organic binder.

**Preconsolidation for Injection Molding.** Preconsolidation consists primarily of mixing the ceramic powder homogeneously with the organic additives. The mixing is conducted in a high-shear mixer at a temperature above the softening point of the binder and plasticizer mixture. The objective is to coat each particle with a thin layer of the polymers.<sup>32</sup> Once mixing is complete, the mixture is granulated or pelletized and cooled. The cooled material is hard like plastic or wax.

**Consolidation.** The objective of the consolidation step is to inject the ceramic powder and binder mixture such that it completely fills the die or mold without leaving porosity, cracks, or other defects. Many factors affect this and must be considered. Major factors include die design, material rheology, and injection parameters, all of which are interactive.

To understand the importance of die design, try to picture what happens during injection. The hot polymer and ceramic powder mixture is squirted into a cool die. Wherever the mixture touches the die, the polymer begins to cool and increase in viscosity. Injection is essentially a race to fill the die uniformly before the polymer becomes too rigid to flow. Variations in die design and sprue design can make a big difference in the uniformity and completeness of die fill. This is discussed later in the section on injection-molding defects.

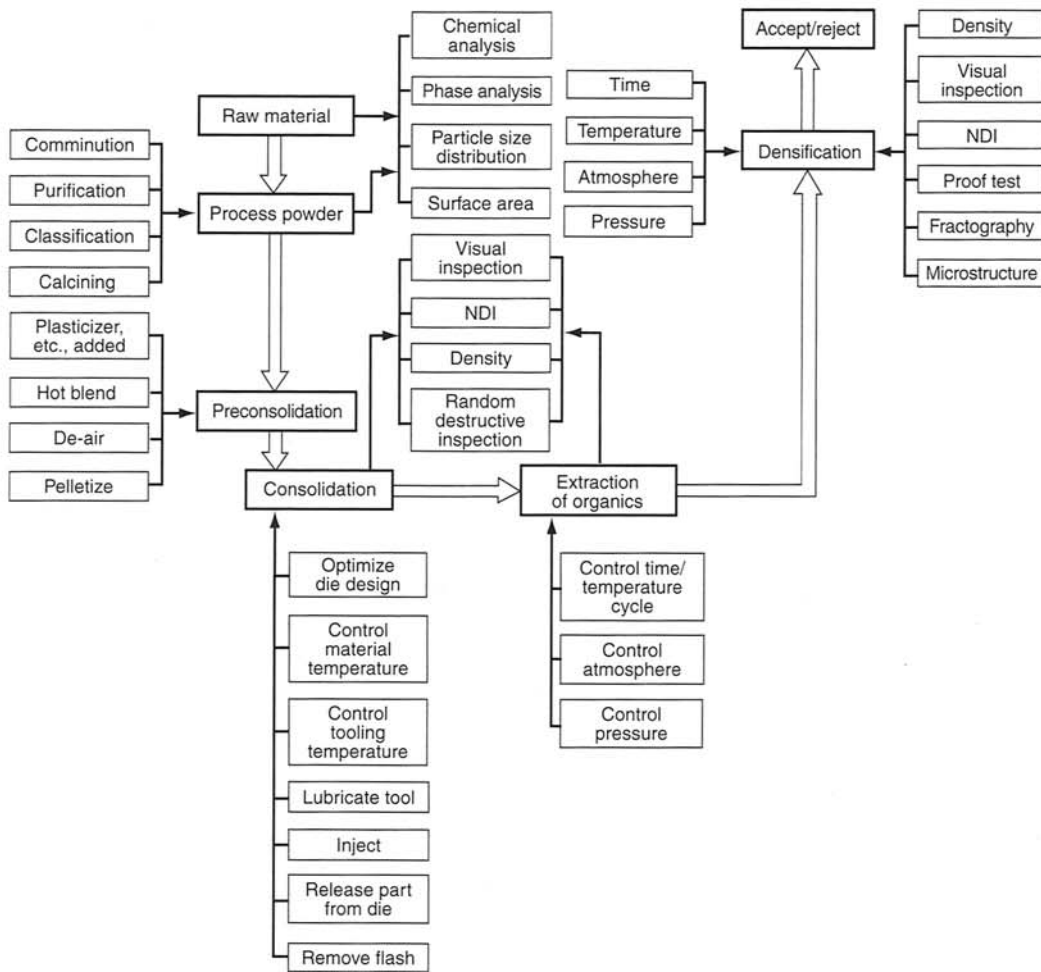


FIGURE 13.57 Flowchart for injection molding.

A second die-design factor is removal of the part after injection. For very complex shapes, the die may have to be very complex and contain removable pins and shaped inserts.

The rheology of an injection-molding mixture is determined by the vol% solids and by the nature of the binders, plasticizer, and other additives. More than one binder is often used.<sup>33,34</sup> The major binder is added in large quantity and provides to the mixture the general range of binder properties and injection parameters. Some of the characteristics of the major binder include: (1) to provide adequate fluidity to the powder to permit defect-free filling of the mold cavity; (2) to wet the powder; (3) to remain stable under mixing and molding conditions; (4) to provide strength to the powder compact during the initial stage of binder removal; (5) to leave a low residue during burnoff; and (6) to be commercially available at an acceptable cost.

A minor binder is often added to aid in the binder-removal cycle. The minor binder melts or decomposes at a lower temperature than the major binders. During binder removal, it volatilizes first and leaves channels or paths through which the major binder can be more easily removed at a higher temperature. Table 13.15 identifies an injection-molding system for SiC that includes more than one binder plus other additives.<sup>35</sup>

A plasticizer is added to increase the fluidity of the ceramic and binder mixture. Specific plasticizers work with specific binders.



**TABLE 13.15**  
**Additives for Injection Molding of SiC**

| Function  | Options  | Quantity, wt% | Characteristics  |
|---|--|---------------|--|
| Thermoplastic resin                             | Acrylic<br>Ethyl cellulose<br>Hydroxypropyl cellulose<br>Polyethylene<br>Oxidized polyethylene<br>Cellulose acetate<br>Nylon<br>Polystyrenes<br>Polybutylene<br>Polysulfone<br>Polyethylene glycol | 9–17          | Volatilization temperature between 200–400°C (390–750°F) |
| Wax or high-temperature volatilizing oil        | Paraffin<br>Mineral oils<br>Vegetable oils<br>Waxes  | 2–3.5         | Volatilization temperature between 150–190°C (300–375°F) |
| Low-temperature volatilizing hydrocarbon or oil | Animal<br>Vegetable oils<br>Mineral oils   | 4.5–8.5       | Volatilization temperature between 50–150°C (120–300°F)  |
| Lubricant or mold release                       | Fatty acids<br>Fatty alcohols<br>Fatty esters<br>Hydrocarbon waxes   | 1–3           |  |
| Thermosetting resin                             | Epoxy<br>Polyphenylene<br>Phenol formaldehyde  |               | Source of carbon; char. in range 450–1000°C (840–1830°F) |

Source: From Ohnsorg, R., U.S. Patent 4,233,256, Nov. 11, 1980.

Other additives are used mainly as surfactants to improve the wetting characteristics between the binder and ceramic during mixing. Functions of other selected additives include deagglomeration, reduction in melt viscosity, lubrication, and die release.

The optimum binder content is generally 102 to 115% of the void volume.<sup>34</sup> The optimum flow characteristics are Bingham or pseudoplastic flow at an intermediate yield stress. A viscosity of less than 10<sup>4</sup> cP at a shear range of 100 to 1000 sec<sup>-1</sup> is generally acceptable.

Table 13.16 lists a variety of binders, plasticizers, and lubricants that have been used for injection molding of ceramics. Most of the binders commonly used are thermoplastic, that is, they reversibly soften when cooled. Examples include the waxes, polypropylene, polyethylene, and polystyrene.<sup>36</sup> Wax-based compositions can be injected at relatively low temperature and pressure. For example, a paraffin or beeswax system can be injected at 60 to 100°C (110 to 212°F) and at pressures as low as 305 kPa (3 atm or 44.1 psi). This allows use of a very simple, inexpensive apparatus that uses compressed gases for injection and cooled aluminum for tooling. Cycle time per injection can be less than 60 sec.

Polyethylene and polypropylene systems are injection-molded at higher temperatures and pressures than wax-based compositions. In Reference 33 for example, a polypropylene-based system was molded at 225°C (435°F) and 150 MPa (~1500 atm 21.8 ksi). A screw-type injection-molding machine with steel tooling was used. Pressure was held for 120 sec with a total cycle time of 150 sec. The mold temperature was 30°C (85°F).

Limited injection molding of ceramics has been conducted with thermosetting binders such as phenolfurfural or epoxy resins. Thermosetting resins solidify by *cross-linking*, which is not a reversible

**TABLE 13.16**  
**Examples of Binders, Plasticizers, and Lubricants That**  
**Have Been Used for Injection Molding of Ceramics**

**Binders (Thermoplastic)**

Polypropylene  
 Polyacetal polymers  
 Ethylene vinyl acetate (low molecular weight)  
 Atactic polypropylene (molecular weight 5000–12000)  
 Styrene-butadiene copolymer  
 Poly (*n*-butyl methacrylate)  
 Polyethylene  
 Polybutene  
 Polystyrene  
 Waxes

**Binders (Thermosetting)**

Epoxy resin  
 Phenol furfural  
 Phenol formaldehyde  
 Nylon

**Binders (Water-Soluble)**

Methyl cellulose  
 Hydroxypropylmethyl cellulose  
 Hydroxyethyl cellulose  
 Polacrylamides

**Plasticizers**

Polyethylene glycol  
 Other phthalates  
 Beeswax  
 Diethyl phthalate  
 Butyl stearate  
 Light oils

**Lubricants**

Stearic acid  
 Hydrogenated peanut oil  
 Glycerol monostearate  
 Paraffin wax  
 Tritolyl phosphate  
 Ester wax  
 Oleic acid

*Source:* From Richerson, D.W., *Introduction to Modern Ceramics*, ASM Mat. Eng. Inst. Course 56, Lesson 11, p. 11. ASM Int., 1990.

process. The cross-linking is induced thermally or by chemical additions. For injection molding of a thermosetting resin, the mold generally is held at a higher temperature than the injection temperature. Cycle time is high to allow cross-linking to occur.

A third category of binders includes water-soluble compositions. These can be injected at or near room temperature. The challenge is achieving rigidization in the die. This is generally achieved by thermal gelation. The die is held at a temperature around 60°C (140°F) at which the cellulose-based binder gels into a structure that is rigid enough for the part to be carefully removed from the die.

Injection-molding compositions and parameters for production forming of ceramics are generally considered proprietary by the company developing the technology. Table 13.17 identifies some injection-molding compositions that have been reported in the literature.

**TABLE 13.17**  
**Examples of Injection-Molding Batch Formulations**

| Ceramic powder  | Additives   | Reference |
|---|---|-----------|
| 83 wt% Al <sub>2</sub> O <sub>3</sub> or ZrO <sub>2</sub> | 16.1 wt% paraffin, 0.9 wt% oleic acid                       | 1         |
| 91.5 wt% BaTiO <sub>3</sub>                               | 8.0 wt% paraffin, 0.5 wt% beeswax                           | 1         |
| 87.6 wt%  | 4.8 wt% (15.2 vol%) Carnauba wax,                           | 2         |
| (68.7 vol%) Al <sub>2</sub> O <sub>3</sub> plus           | 3.1 wt% (8.8 vol%) epoxy resin,                             |           |
|   | 0.8 wt% (2.4 vol%) silicone oil                             |           |
| 3.7 wt%   |   |           |
| (5.0 vol%) SiO <sub>2</sub>                               |   |           |
| 100 parts Si or Al <sub>2</sub> O <sub>3</sub>            | 20 parts atactic polypropylene, 5 parts paraffin            | 3         |
| 82.44 wt% Si  | 11.71 wt% polypropylene, 3.9 wt% wax, 1.95 wt% stearic acid | 4         |
| 63.0 vol% steatite  | 24.3 vol% wax, 7.3 vol% epoxy resin,                        | 5         |
|   | 3.2 vol% coumarone-indene resin,                            |           |
|   | 2.2 vol% phenol formaldehyde resin                          |           |
| 47 vol% SiC,  | 47 vol% phenol furfural-phenol formaldehyde                 | 6         |
| 5 vol% graphite   | copolymer, 1 vol% zinc stearate                             |           |

References

1. Operation and Maintenance Manual for Hot Molding of Ceramic Parts Under Low Pressure, Peltsman Corporation.
2. Newfield, S.E. and Gac, F.D., Injection Moldable Ceramics, Los Alamos Nat. Lab Rept. LA-6960, March 1978.
3. U.S. Patent 4,248,813.
4. Edirisinghe, M.J. and Evans, J.R.G., *J. Mater. Sci.*, 22, 2267–2273, 1987.
5. Strivens, *Am. Ceram. Soc. Bull.*, 42, 13–19, 1963.
6. Whalen and Johnson, *Am. Ceram. Soc. Bull.*, 60, 216–220, 1981.

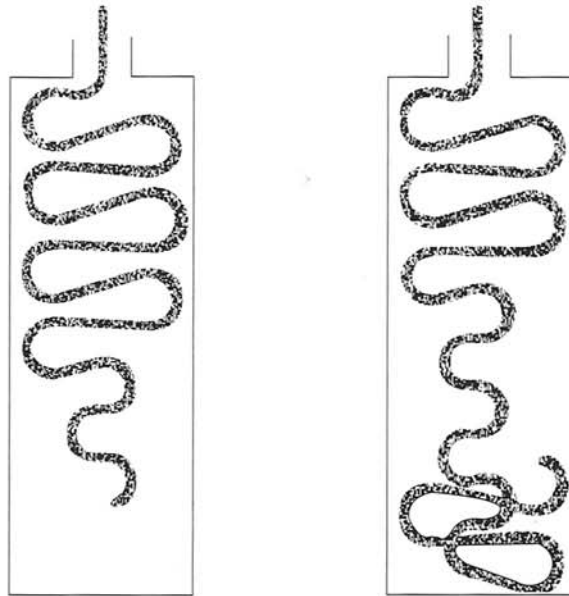
**Binder Removal.** Binder removal is a major step in the injection-molding process. The large volume fraction of organic materials must be removed without cracking or distortion of the ceramic powder compact. The following techniques are used: evaporation (or distillation), solvent extraction, capillary action, decomposition, and oxidation. Often these are mixed by utilizing more than one binder. One, such as a low-temperature wax, may be removed by evaporation or solvent extraction. Another, such as a thermosetting resin, will then be removed at higher temperature by oxidizing or dissociation.

*Evaporation* involves slow volatilization of the organic material at elevated temperature. The temperature depends on the vaporization characteristics of the specific binder composition. The temperature is increased slowly to avoid too-rapid evolution of the vapor that would cause fracture or distortion of the weak ceramic compact. The cycle time of binder removal also depends on the binder composition, but also on the particle packing (and resulting permeability) and on the cross-section thickness of the part. An 8-hr cycle may be adequate for a thin cross section (a few mm), whereas a 20-hr or even one-week cycle may be required for a thicker section (1 cm or 0.39 in.). Evaporation can be conducted under vacuum, at atmospheric pressure or at an overpressure.

*Solvent extraction* is accomplished by dissolving one of the binders with liquid-phase or vapor-phase solvent. This can only be done if a nonsoluble binder is also present to hold the ceramic particles together while the soluble binder is being extracted. Solvent extraction can be conducted at lower temperature than evaporation and potentially minimizes capillary and vapor stresses.

*Capillary extraction* involves packing the injection-molded parts in a fine powder such as activated carbon. The temperature is then increased until the binder is fluid enough to move from the part into the surrounding powder by capillary action.

*Decomposition and oxidation reactions* are used to remove the secondary binder plus any residue remaining from the major binder. These reactions occur at higher temperatures than evaporation, that is, typically above 500°C (930°F) and result in gas phases such as H<sub>2</sub>O, CO, or CO<sub>2</sub>. The



**FIGURE 13.58** Schematic showing how a thin strand can inject into the mold and pile up without fully bonding to result in knit lines. (Drawing courtesy of ASM International.)

temperature must be raised slowly to allow the gases to form and diffuse out of the porous compact without building up enough pressure to cause fracture.

### 13.3.2.2 Injection-Molding Defects

A variety of defects can occur during the injection-molding operation. These can be divided into two categories: micro and macro. Microdefects include inclusions and microporosity due to agglomerates and improper particle size distribution. These are similar to the microdefects that can occur with any other particulate forming process.

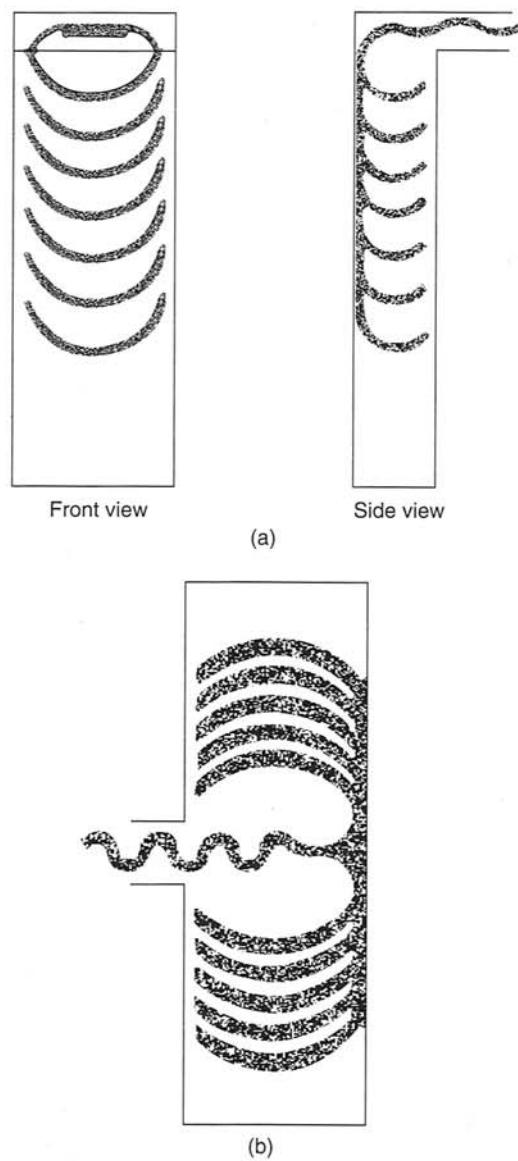
The second category, macrodefects, can be divided into two subgroups: (1) mold-filling defects and (2) solidification defects. *Mold-filling* defects include incomplete fill, porosity, and knit lines. *Solidification* defects include void nucleation and microcracking due to residual stresses. These types of defects are defined and described in the following paragraphs.

Incomplete mold fill is easy to detect visually on an injected part. Essentially, a portion of the part is missing. This can occur for several reasons. First, the die design may not be optimum and may result in solidification before the die is completely full. This can result sometimes due to *gate freeze-off*. The gate is the opening through which material enters the mold. Since the mold is at a lower temperature, sometimes the material in the gate solidifies and blocks further injection. This can be prevented by better control of temperature and by modification of the mold design.

Porosity can occur during injection due to air entrapment. The air can either be in the ceramic and binder mix or can be trapped during mold fill. Molds are usually vented to allow a route for air to escape. Overflows are also often included in mold design to allow the initial material entering the mold to pass through the mold and accumulate in a waste cavity. Excess mold-release agent plus foreign debris in the mold will be swept into the overflow cavity where it can be discarded.

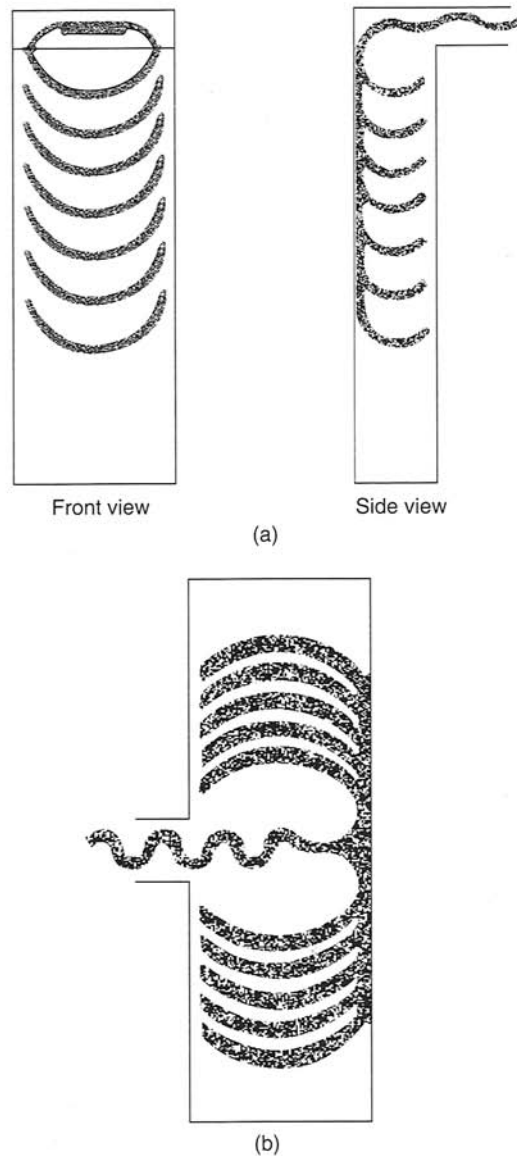
The final mold-filling defect we shall discuss is *knit lines*. Knit lines are areas where the injected material does not properly fuse together. They represent a discontinuity or a weak region in the part. They usually have a laminar or folded appearance. Some can be severe and are easily visible if they intersect the outer surface of the part. Others are very subtle and difficult to detect, even with nondestructive inspection techniques such as radiography and ultrasonics. Figure 13.58 illustrates

schematically how flow lines form. The thin stream of ceramic and binder mix “jets” through the sprue into the mold cavity and begins to pile up like a strand of spaghetti. The first part that touches the mold wall begins to cool and solidify. If it solidifies too much, it will not fuse together into a single continuous compact, but instead will leave open spaces. The tendency to form knit lines can be reduced by proper mold design, especially by orientation of the gate and sprue. Figure 13.58 shows injection into a rectangular mold cavity where the gate was located on the end directed parallel to the length of the cavity. Knit lines were difficult to avoid with this geometry. Figure 13.59 shows the flow pattern with alternate sprue and gate designs. In Figure 13.59a, the gate is at the end, but is directed perpendicular to the length of the cavity. In Figure 13.59b, the gate is directed perpendicular, but placed at the center of the mold cavity. Plug flow resulted in both cases and

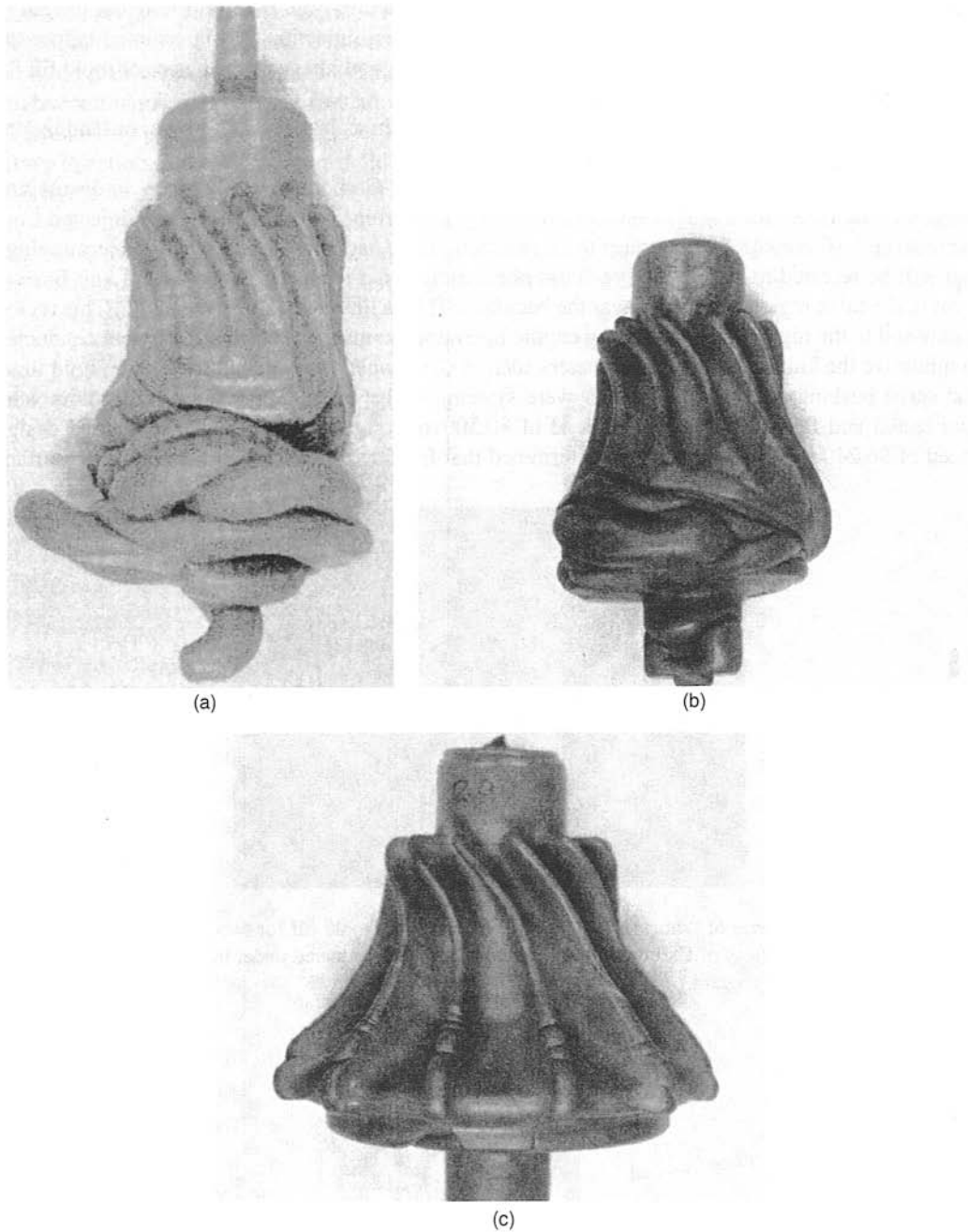


**FIGURE 13.59** Alternate mold sprue and gate designs that result in plug flow rather than “jetting” and minimize formation of knit lines. (Drawing courtesy of ASM International.)

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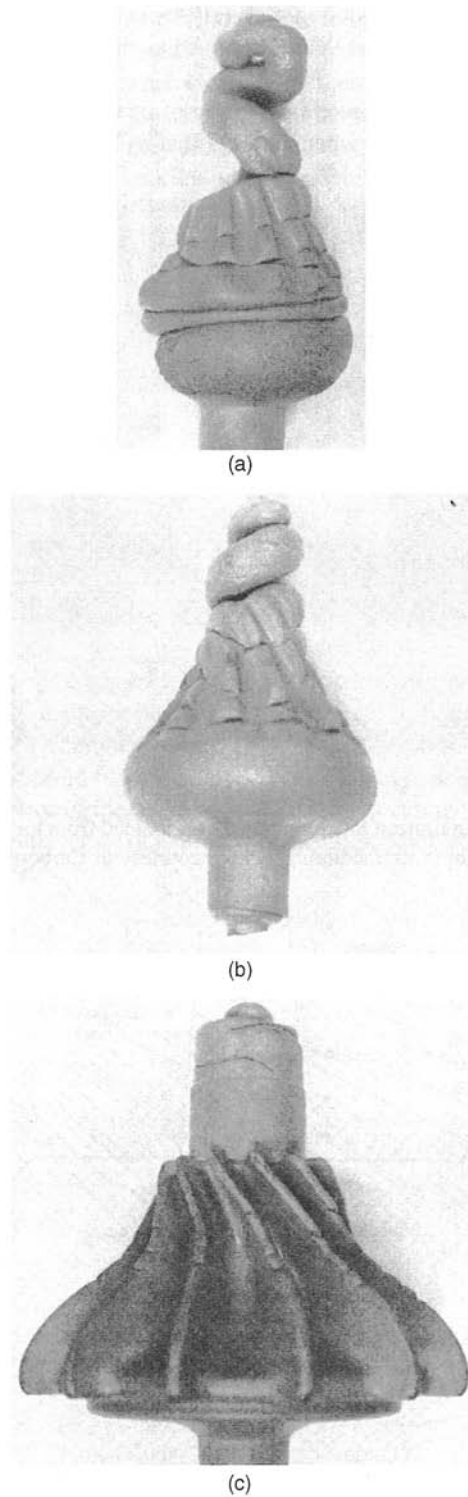
**FIGURE 13.59** Alternate mold sprue and gate designs that result in plug flow rather than “jetting” and minimize formation of knit lines. (Drawing courtesy of ASM International.)



**FIGURE 13.62** Sequence of short shots for injection molding of a SiC rotor from the nose end. Note the knit lines in the hub and backface regions. (Photos courtesy of Carborundum Company for parts fabricated for Allison Gas Turbine Division of General Motors under sponsorship of the U.S. Department of Energy and administration of NASA-Lewis Research Center.)

flaws in the highly stressed region of the backface. Approximately 1.25 mm was machined off the backface of 30 rotors. These failed at an average of 95,100 rpm.

Whereas the backface of the rotor is exposed to high stresses, the stresses in the nose end are relatively low. An alternate approach to machining the backface was pursued. This involved injection molding from the shaft end. A sequence of short shots for this approach is shown in Figure 13.63.

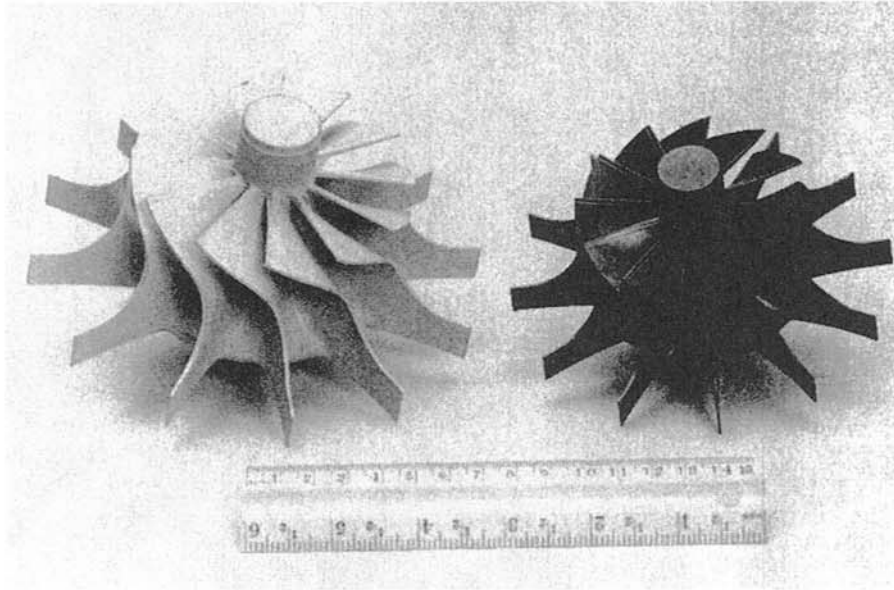


**FIGURE 13.63** Sequence of short shots for injection molding of a SiC rotor from the shaft end. Note the absence of knit lines in the hub and backface region. (Photos courtesy of Carborundum Company for parts fabricated for Allison Gas Turbine Division of General Motors under sponsorship of the U.S. Department of Energy and administration of NASA-Lewis Research Center.)

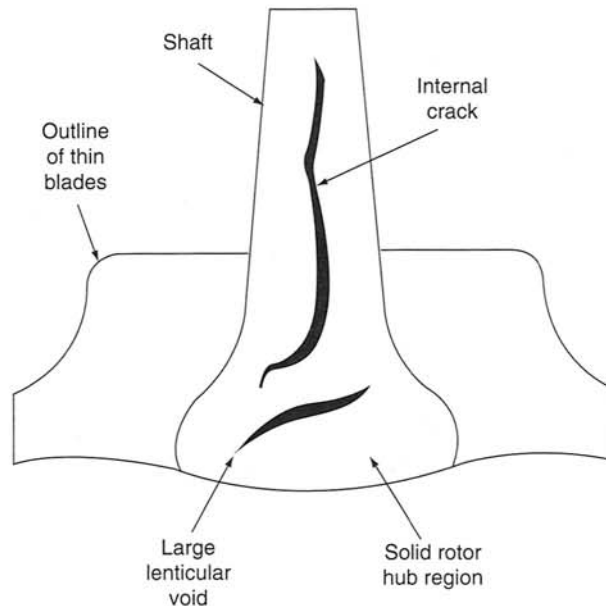


Note the absence of knit lines in the hub region. Forty-two rotors fabricated by shaft-end injection were spin-tested with average failure at 96,200 rpm. An as-molded and a sintered (densified) rotor are illustrated in Figure 13.64.

Now we are ready to discuss the second subgroup of injection-molding macrodefects: solidification defects. Imagine what happens when material that is 225°C (435°F) is injected rapidly into



**FIGURE 13.64** Examples of optimized SiC rotors injection-molded from the shaft end. The rotor on the left is as-molded, the one on the right is after sintering. (Photo courtesy of Carborundum Company.)



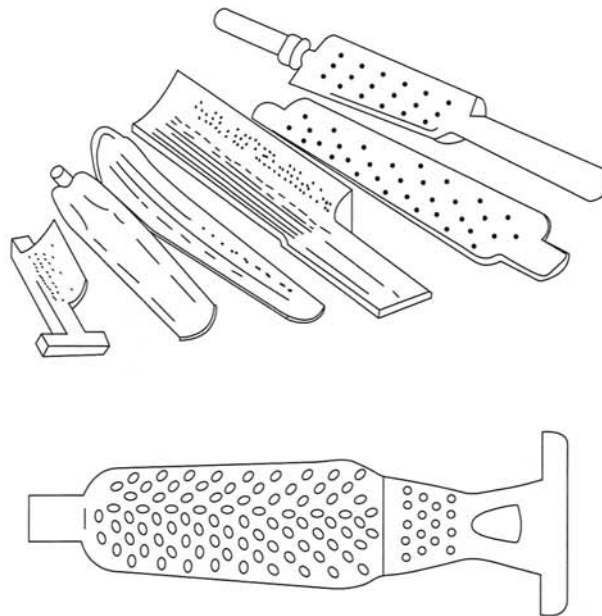
**FIGURE 13.65** Sketch of the cross section of an injection-molded Si<sub>3</sub>N<sub>4</sub> turbocharger rotor showing the internal void that resulted during cooling in the mold due to a combination of surface quenching and shrinkage of the interior toward the surface. (Drawing courtesy of ASM International.)

a mold that is only 30°C (85°F). The material at the surface of the part cools more quickly than the material in the interior. If the gradient is too high or the part too thick, residual stresses and even nucleation of voids can occur. This is aggravated by the high thermal-expansion coefficient of the binder polymers and the additional shrinkage that occurs when the binder goes from liquid to solid or non-crystalline to crystalline. For example, the volume change for one polypropylene system due to thermal contraction was about 2.75 vol% and due to crystallization was about 1.75 vol% for a total of about 4.5 vol%. If the outer shell is rigid and cannot shrink, while the inner material is more fluid and can reposition during further cooling, 4.5% shrinkage is adequate to form a void or crack through the center of the part. Such a void or crack is typically not visible by examining the surface of the injection-molded part and may not even be visible after densification. Figure 13.65 illustrates a large lenticular (lens-shaped) void in a  $\text{Si}_3\text{N}_4$  turbocharger rotor that resulted primarily from this mechanism.

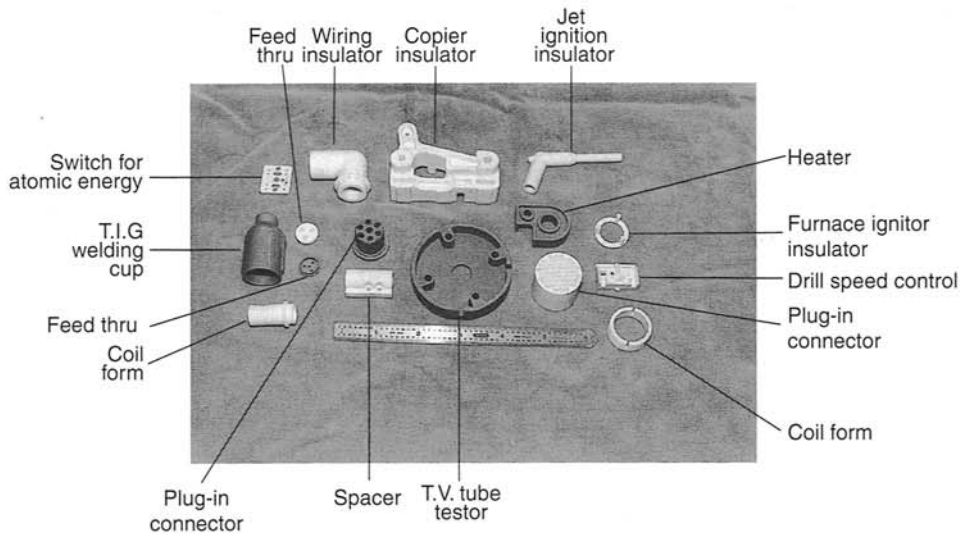
### 13.3.2.3 Applications of Injection Molding

Injection molding is usually selected for ceramics only after other processes have been rejected. It can produce a high degree of complexity, but the initial cost of tooling is very high. For example, a mold to fabricate an individual turbine blade can cost over \$10,000 and a mold for a turbine rotor over \$100,000. Molds for simple shapes and molds made of aluminum for low-pressure injection molding are much less expensive. As a result, the use of injection molding of ceramics is increasing.

Injection molding is presently used to manufacture a variety of parts including cores for investment (lost-wax) casting of metals, weld caps, thread guides, threaded fasteners (nut and bolt pairs), radomes, and prototype gas-turbine engine components. Drawings of complex investment casting cores for cooled metal gas-turbine blades or stator vanes are shown in Figure 13.66. During investment casting, the core is mounted in a ceramic mold. Molten superalloy is poured into the mold around the core. The ceramic mold is removed from the outside of the metal part. The injection-molded ceramic core is leached from the interior of the blade or vane to leave a complex cooling path. This substantially reduces the cost of manufacturing of internally cooled superalloy stator vanes and rotor blades for advanced gas-turbine engines.



**FIGURE 13.66** Drawings of injection-molded ceramic cores for investment casting of cooled rotor blades or stator vanes for gas-turbine engines. (Drawing courtesy of ASM International.)



**FIGURE 13.67** Examples of  $\text{Al}_2\text{O}_3$  parts fabricated by injection molding. (Courtesy of Diamonite Division of W.R. Grace.)

Examples of other injection-molded ceramic parts are illustrated in Figures 13.67 through 13.69.

#### 13.3.2.4 Nonthermoplastic Injection Molding

Injection molding of ceramics has traditionally been conducted with thermoplastic binders or a combination of thermoplastic and thermoset binders. Some success has also been achieved with cellulose derivatives that gel with a suitable change in temperature. Two additional approaches to injection molding have been reported in recent years. One uses polysaccharides (in particular, agar and agarose) as a gel-forming binder and water as the fluid.<sup>38</sup> A relatively small percentage (3 wt%) of agarose is required (compared to thermoplastic systems), so drying and binder removal are reported to be simplified.

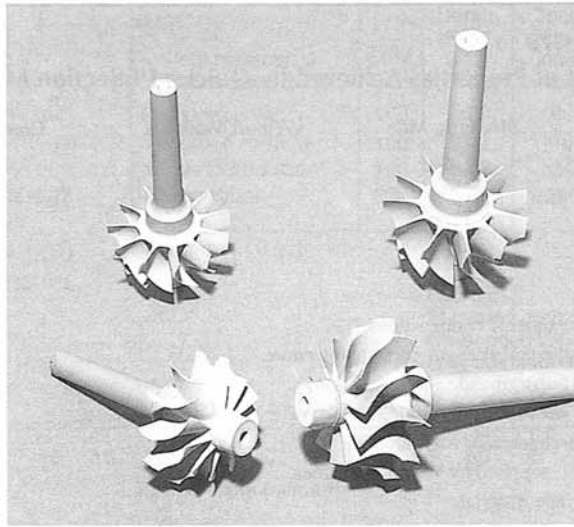
The second new approach is identified as Quickset\* injection molding.<sup>39</sup> It is sort of a cross between casting, injection molding, and freeze drying and appears to provide some of the benefits of each, while avoiding some of the problems. It uses a slurry (typically with a viscosity under 1000 centipoise) that is injected at typically less than 50 psi pressure into a closed cavity, nonporous mold. The pore fluid is solidified by freezing and subsequently removed by sublimation. Volume change during freezing is negligible and stresses during sublimation are substantially lower than for removal of water or thermoplastic polymers.

Quickset injection molding has been successfully accomplished with both aqueous and non-aqueous suspensions and with a variety of ceramic powders. Table 13.18 lists the properties achieved for different materials formed by the Quickset process. In addition to the excellent properties, tight dimensional tolerances are readily achieved. For example, dimensional tolerances for a SiAlON component only varied in as-fired parts by 0.09%.

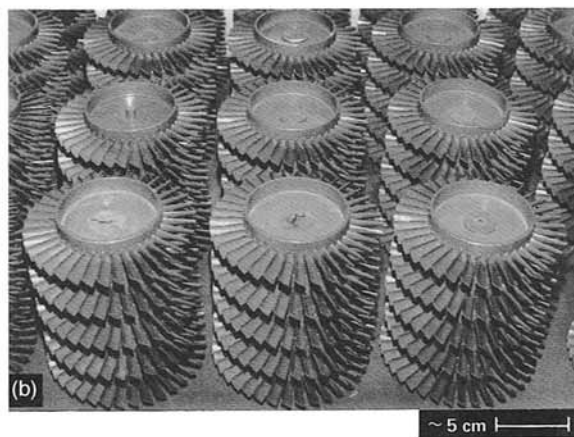
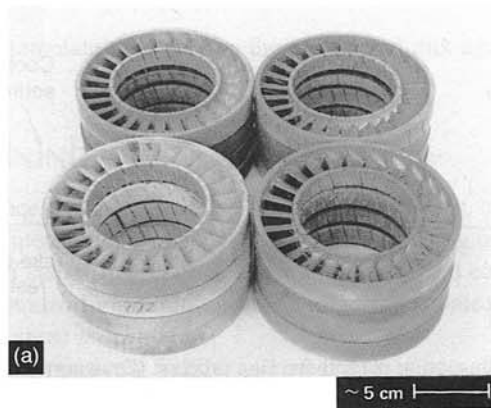
### 13.3.3 COMPRESSION MOLDING

Compression molding is analogous to forging. A block of plastic mix is placed between the platens of a shaped die, and uniaxial pressure is applied until the block deforms to the shape of the die cavity.

\* Trademark of Ceramics Process Systems, Milford, MA.



**FIGURE 13.68** Prototype sintered silicon nitride turbocharger rotors fabricated by injection molding. (Courtesy of Garrett Ceramic Components Division of Allied-signal Aerospace.) Fabricated by AiResearch Casting Company (Currently Honeywell Ceramic Components, Torrance, CA.)



**FIGURE 13.69** Complex shapes made by injection molding. (a) Integral stators. (b) Rotor blade rings. (Courtesy of Ford Motor Company, Dearborn, MI.)

**TABLE 13.18**  
**Examples of Properties Achieved by Quickset Injection Molding**

| Material <sup>a</sup> | Strength, MPa <sup>b</sup> | Weibull Modulus | Comments                                    |
|-----------------------|----------------------------|-----------------|---|
| Alumina <sup>c</sup>  | 489                        | 10              |   |
| Zirconia <sup>d</sup> | 850                        | 20              | $K_{Ic} = 8 \text{ MPa}\cdot\text{m}^{1/2}$ |
| ZTA <sup>e</sup>      | 1100                       | 22              |   |
| SiAlON <sup>f</sup>   | 968                        | 11              | UTS <sup>h</sup> = 650 MPa                  |
| AlN <sup>g</sup>      | 380                        | —               | 230–259 W/mK                                |

<sup>a</sup>Pressureless sintered compositions.

<sup>b</sup>Four-point flexural strength, room temperature.

<sup>c</sup>Alcoa A16 Superground.

<sup>d</sup>Tetragonal zirconia polycrystal, 3 mol% yttria.

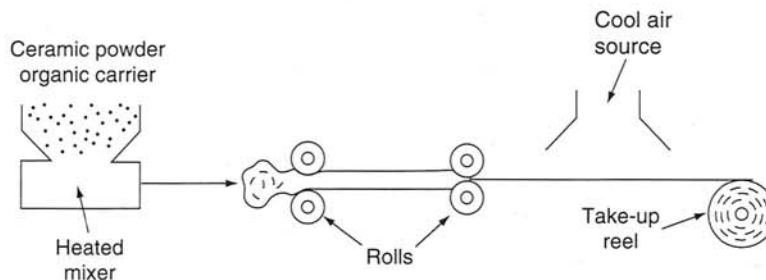
<sup>e</sup>30 vol% 3Y-zirconia/70 vol% alumina.

<sup>f</sup>SiAlON 101, supplied by Vesuvius Zyalons.

<sup>g</sup>CPS-200 grade material.

<sup>h</sup>UTS = Ultimate tensile strength.

Source: From Novich, B.E., Lee, R.R., Franks, G.V., and Ouellette, D., Quickset™ injection molding of high temperature gas turbine engine components, in *Proceedings of the 27th Automotive Technology Development Contractors' Coordination Meeting*, SAE publication P-230, 1990.



**FIGURE 13.70** Schematic illustrating the roll-forming process. (Drawing courtesy of ASM International.)

Compression molding can be conducted hot or cold, depending on the nature of the binder system. It works especially well for systems containing thermosetting resins.

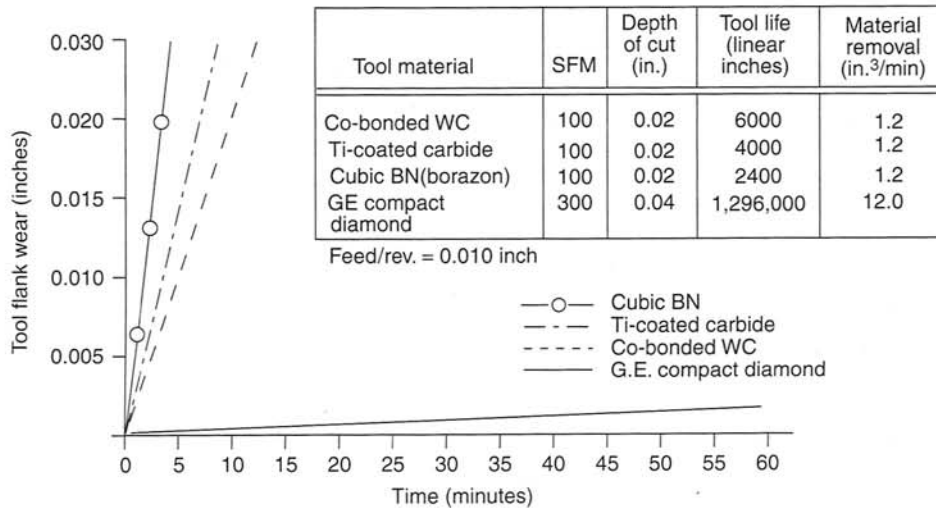
### 13.3.4 ROLL FORMING

A plastic mix is passed between two cylinders that are rotating in opposite directions as shown in Figure 13.70. The plastic mix passing between the rolls is compacted, as well as being pressed to a thickness equivalent to the spacing of the rolls. Multiple passes at diminishing roll separation can yield a constant-thickness sheet of high uniformity.

Roll forming can be conducted at room temperature using a mix equivalent to an extrusion mix or at elevated temperature using a thermoplastic polymer system. Warm roll forming has been used for many years to fabricate resin-bonded and rubber-bonded grinding wheels. It has also been used to form much thinner layers suitable for heat-exchanger fabrication.

### 13.3.5 JIGGERING

Jiggering is commonly used to fabricate cooking ware, electrical porcelain, and refractories. A segment of de-aired extruded mix (or other plasticized feedstock) is placed on a shaped rotating



**FIGURE 13.71** Tool wear for different tool insert materials for green machining of a presintered silicon compact in the fabrication of reaction-bonded Si<sub>3</sub>N<sub>4</sub>. (From Richerson, D.W. and Robare, M.W., Turbine component machining development, in *The Science of Ceramic Machining and Surface Finishing*, Vol. II, Hockey, B.J. and Rice, R.W., Eds., NBS Special Publication 562, U.S. Government Printing Office, Washington, DC, 1979, pp. 209–220.)

wheel. A shaped roller or template then presses the plasticized mix against the wheel to forge the shape.

### 13.4 GREEN MACHINING

The final shape and tolerances cannot always be achieved by pressing, casting, and plastic forming. In many cases, the final dimensions are achieved by surface grinding or other finishing operations following the densification step. This requires diamond tooling and can be very expensive. Final machining can often be avoided by machining the ceramic particulate compact prior to densification. This is referred to as *green machining*.

Unfired green 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 either by simple mechanical gripping or by bonding or potting with a combination of beeswax and precision metal fixtures. The part must be held rigidly, but with no distortion or stress concentration.

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, depending on the binder present and whether or not the part has been bisque-fired.\* In either case, the compact is abrasive and results in tool wear. A wear land on the cutting edge as little as 0.1-mm (0.0039-in.) wide can cause a buildup of cutting pressure and result in 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 13.71 summarizes a green machining study comparing several cutting-tool materials. A 5° positive rake and 10° clearance

\* Fired at a high enough temperature to form bonds at particle-particle contact points, but not at a high enough temperature to produce densification.

angle were used in the study. The 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 61 surface meters/min (200 sfm) with 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 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 a 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, as was discussed earlier in this chapter for green machining of spark plug insulators and oxygen-sensor electrolytes.

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