23

Shaping and Forming

CHAPTER PREVIEW

This is the pottery chapter! Many of the techniques that are now being used to shape high-tech ceramics have been used by potters for millennia but have been refined for today's high-tech applications and for new ceramic materials. We try to relate shaping to the potter's craft throughout the chapter.

We can just process dry powder and sinter it, but it's much more common to add some amount of liquid, just as the potter adds water to clay; we then shape the object and fire it. Shaping transforms an unconsolidated powder mixture into a coherent, consolidated body having a chosen geometry. The selection of a shaping operation for a particular product is dependent on the size and dimensional tolerances of the product, the requisite microstructural characteristics, the levels of reproducibility required, economic considerations, and of course the required shape. We cover shaping of glass in Chapters 21 and 26, so here we consider the similarities in processing glass and crystalline ceramics. Similarly, we discuss thick films in Chapter 27; here we concentrate on three-dimensional objects ranging from fishhooks to turbine blades. However, we do cover slip casting, which we use in only a limited way for thin films.

23.1 THE WORDS

There's a special vocabulary for shaping ceramics because it's an ancient art. Once the constituent powders have been prepared in the desired purity and particle size, the next step in the processing of most ceramic products is fabricating them into useful shapes. Many shaping methods are used for ceramic products, and they can be grouped into three basic categories, which are not necessarily independent.

1. Powder compaction: e.g., dry pressing, hot pressing, cold isostatic pressing
2. Casting: using a mold with the ceramic as, or containing, a liquid or slurry
3. Plastic forming: e.g., extrusion, injection molding—using pressure to shape the green ceramic

Powder compaction is simply the pressing of a free-flowing powder. The powder may be dry pressed (i.e., without the addition of a binder) or pressed with the addition of a small amount of a suitable binder. The pressure is applied either uniaxially or isostatically. The choice of pressing method depends on the shape of the final product. We make simple shapes by applying the pressure uniaxially; more complex shapes require isostatic pressing.

Casting ceramics is carried out at room temperature and generally requires the ceramic powder particles to be suspended in a liquid to form a slurry; note that this process is quite unlike the casting of metals. The slurry is then poured into a porous mold that removes the liquid (it diffuses out through the mold) and leaves a particulate compact in the mold. This process is known as slip casting. The process has been used to form many traditional ceramic products (e.g., sanitaryware) and more recently in forming advanced ceramic products (e.g., rotor blades for gas turbines). The other main casting process for ceramics is tape casting, which, as you'd guess, is used to make thick films or sheets; it is described in Chapter 27.

Plastic forming is done by mixing the ceramic powder with a large volume fraction of a liquid to produce a mass that is deformable (plastic) under pressure. Such processes were developed and used originally for clay and have since been adapted to polymeric materials. For traditional clay-based ceramics, the liquid is mainly water. For ceramic systems that are not based on clay, an organic liquid may be used in place of, or in addition to, water. The binders are often complex and contain multiple components to achieve the required viscosity and burn-out characteristics.

Table 23.1 lists the major methods that are included in each of the above categories and the types of shape that can be produced. First, some of the words:

Binder: a component that is added to hold the powder together while we shape the body.
Slurry: a suspension of ceramic particles in a liquid.

C.B. Carter and M.G. Norton, *Ceramic Materials: Science and Engineering*,
DOI 10.1007/978-1-4614-3523-5_23, © Springer Science+Business Media New York 2013

TABLE 23.1 Various Shaping Methods for Ceramic Components

Shaping method	*Type of feed material*	*Type of shape*
Dry pressing	Free-flowing granules	Small and simple
Isostatic pressing	Fragile granules	Larger and more intricate
Extrusion	Plastic mass using a viscous polymer solution	Elongated with constant cross section
Injection molding	Organic liquid binder giving fluidity when hot	Complex
Slip casting	Free-flowing cream	Mainly hollow

Plasticizer: the component of a binder that keeps it soft or pliable. It improves the rheological properties.
Green: a ceramic before it's fired. Brown, white, or gray potter's clays are well-known green ceramics.
Slip: the liquid-like coating used to form the glaze when fired.

Some of the shaping methods we describe in this chapter produce a ceramic compact that is strong enough to be handled and machined; but it is not fully dense, and the bonds between the grains are not strong. This is called the "green" state and represents a transition state between the loose powder and the high-density sintered product. Other shaping methods—those that involve the use of high temperatures and pressures—can directly produce a very dense sintered product. Much of what we talk about here has a parallel in the field of powder metallurgy; the theme is often *processing powders*, which are not necessarily ceramic powders (e.g., they could be pharmaceuticals).

23.2 BINDERS AND PLASTICIZERS

It is often necessary to add a binder to the ceramic powder. The binder has two functions. In some shaping methods, such as extrusion, the binder provides the plasticity necessary for forming. The binder also provides the dry (green) shape with sufficient strength that it can survive the handling process between shaping and sintering. One of the most important requirements for the binder is that we must be able to eliminate it from the compact during the firing process without any disruptive effect: polymers are thus often ideal binders.

In pottery, the binder is often water, which is present in sufficient quantity to make the clay easily shaped but retains the shape during firing. The idea is that we then add a plasticizer to optimize the rheology of the material. Note that these processes are not exclusive to ceramics but are general to powder processing. The distinction between binder and plasticizer is sometimes not too clear.

Binders can also be used when metal powders are processed (e.g., PMC, or precious-metal clay).

BINDERS

Poly(vinyl alcohol) (PVA) and poly(ethylene glycol) (PEG) are the two most popular binders for dry-pressing ceramics:

PVA provides high green strength.
PEG provide a high green density.

23.3 SLIP AND SLURRY

The word slip appears to come (according to Webster's) from the Old English words meaning cream: "the suspension of curds in the liquid when making cheese." The cheese was actually sieved through a "slippe clothe."

In general, slip consists of fine (<10 μm) ceramic-powder particles that are suspended in a fluid. In the pottery industry, the liquid is usually water. The suspension can have a solid content up to ~60 vol%. Deflocculents are added to the slip to modify the electrical environment of each particle so the particles repel each other.

Deflocculants: as deflocculation is defined as the process by which floccules present in a liquid break up into fine particles producing a dispersion, a deflocculant is an additive that causes this process. In other words, deflocculation is the opposite of coagulation. (A floccule is a small piece of matter, or a floc).
Colloids: defined very generally as any substance that consists of particles substantially larger than ordinary molecules but much too small to be visible without optical magnification (~1 nm to 10 μm). They can be linked or bonded together in various ways. Colloidal systems can take several forms; the one relevant to us is the dispersions of one substance in another. Brownian motion has interested scientists for generations. Slip is a colloid. We can change the properties of the slip by adding flocculants or deflocculants.
Slurry: clay particles are suspended in a liquid (water in the case of pottery). As the amount of water is decreased, it becomes more solid. Glazes used in pottery have the same base as the clay but with more water content. Potter's clay is made by first producing a slip from naturally occurring clays. The slip is repeatedly filtered to produce a consistency that is constant over long periods of manufacture. Slabs of clay are then formed from this colloid by allowing most of the water to evaporate. The final product may be shaped by extrusion and packaged to prevent further loss of water.

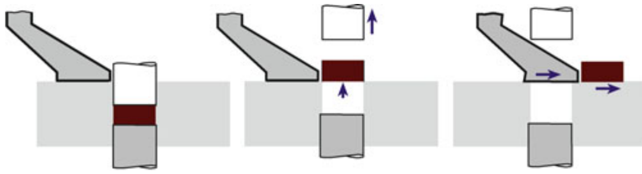

FIGURE 23.1. Stages in dry pressing.

23.4 DRY PRESSING

Dry pressing is ideally suited to the formation of simple solid shapes and consists of three basic steps: filling the die, compacting the contents, ejecting the pressed solid.

Figure 23.1 shows the double-action dry-pressing process. In a double-action press, both the top and bottom punches are movable. When the bottom punch is in the low position, a cavity is formed in the die; and this cavity is filled with free-flowing powder. In dry pressing, the powder mixture contains 0–5 wt% of a binder (so dry does not imply that there is no binder). Once the cavity has been filled, the powder is struck off level with the top of the die. The top punch descends and compresses the powder either to a predetermined volume or to a set pressure. During pressing, the powder particles must flow between the closing punches so that the space between them is uniformly filled. A particle size distribution of 20–200 μm is often preferred for dry pressing: a high volume fraction of small particles causes problems with particle flow and also results in sticking of the punches. The pressures used in dry pressing may be as high as 300 MPa, depending on the material and press type, to maximize the density of the compact. After pressing, both punches move upward until the bottom punch is level with the top of the die and the top punch is clear of the powder-feeding mechanism. The compact is then ejected, the bottom punch lowered, and the cycle repeated.

Because the dry-pressing process is so simple and involves low-cost capital equipment, it is the most widely used high-volume forming process for ceramics. Production rates depend on the size and shape of the part and on the type of press used. For large components (e.g., refractories) or complex parts (e.g., grinding wheels), the production rates are 1–15 parts per minute. During a tour of the Wedgwood factory, you can see dinner plates being dry-pressed in a continuous process. Simpler or smaller shapes (e.g., seal rings and nozzles) can be produced at rates up to several hundred per minute. Small flat parts (e.g., insulators, chip carriers, cutting tools) can be produced at rates up to several thousand per minute.

23.5 HOT PRESSING

Pressing can also be performed at high temperatures; this process is known as hot pressing. The die assembly used for hot pressing is very similar to that described in Section 23.4 for dry pressing. The main difference is that in hot pressing the die assembly is contained within a high-temperature furnace, as shown in Figure 23.2. During hot pressing the ceramic powders may sinter together to form a high-density component.

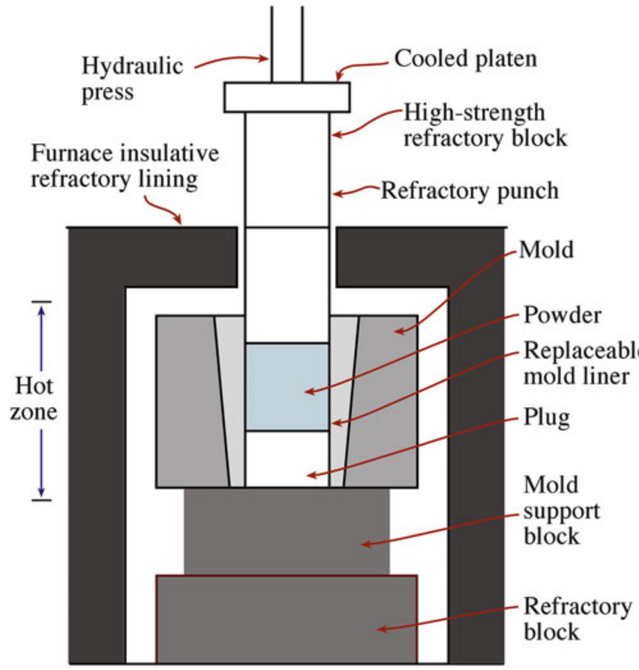

FIGURE 23.2. Essential elements of a hot press.

We can summarize the advantages of this process.

- The powder does not have to be of the highest quality.
- Large pores that are caused by nonuniform mixing are easily removed.
- We can densify at lower temperatures (typically half the melting temperature of the material) than are needed for conventional pressureless sintering.
- Extensive grain growth or secondary recrystallization does not occur when we keep the temperature low during densification.
- We can densify covalently bonded materials such as B_4C, SiC, and Si_3N_4 without additives. The principal disadvantage is also important.
- Dies for use at high temperatures are expensive and generally don't last long.

Most metals are of little use as die materials >1,000°C because they become ductile, and the die bulges. Special alloys, mostly based on Mo, can be used up to 1,000°C at pressures of about 80 MPa. Ceramics such as Al_2O_3, SiC, and Si_3N_4 can be used up to about 1,400°C at similar pressures. Graphite is the most widely used die material and can be used at temperatures up to 2,200°C and pressures of 10–30 MPa. The difficulty is that a graphite die tends to produce a very reducing environment. (You can make an Al_2O_3 sample vanish using a graphite die!)

However, graphite does have many properties that make it suitable for a die.

- Easy to machine (but the dust is toxic if inhaled—like coal dust)
- Inexpensive
- Strength increases with increasing temperature
- Good creep resistance
- Excellent thermal conductivity
- Relatively low coefficient of thermal expansion

Hot pressing, like dry pressing, is limited to simple solid shapes, such as flat plates, blocks, and cylinders. More complex or large shapes are difficult and often impossible to produce by hot pressing. Hot pressing is widely used in the research laboratory for processing very dense, high-purity ceramic components. Although it is extensively used in university and government laboratories, the technique is limited as a production tool because of its high cost and low productivity. For any mass-produced ceramic product, there would be considerable commercial pressure for a company to find a less expensive alternative. However, some commercial hot-pressed ceramic products are available. These products are those that require a small grain size, high density (low porosity), or low impurity levels. Examples of such products are given in Table 23.2.

Isostatic pressing involves the application of hydrostatic pressure to a powder in a flexible container. The advantages of applying pressure in all directions are that there is more uniform compaction of the powder and more complex shapes can be produced than with uniaxial pressing. Isostatic pressing can be performed either with or without applied heat.

TABLE 23.2 Hot Pressed Products

Product	*Types of material*
Optical windows	IR: MgF_2, ZnS, ZnSe. Visible: Y_2O_3, $MgAl_2O_4$
Ceramic armor	B_4C, TiB_2, SiC, Al_2O_3
Cutting tools	Al_2O_3 particle-reinforced TiC, Si_3N_4, Si_3N_4-AlN-Al_2O_3
Tooling (molds and dies)	Al_2O_3-SiC_w composites, SiC, Al_2O_3
Sputtering targets	Cr-SiO, TiN, Si_3N_4, B_4C, Al_2O_3
Heat engine components	Si_3N_4, SiC
Ceramic bearings	Si_3N_4
Microwave absorbers	MgO–SiC particulate composites, BeO–SiC, Al_2O_3–SiC
Varistors	ZnO
Electro-optic materials	PLZT
Titanates	$BaTiO_3$, $CaTiO_3$
Microelectronic packages	Co-fired W-metallized AlN
Resistors	Si_3N_4 matrix with particulates of TiB_2, TiC, TiN, or SiC as the dispersed conducting phase

23.6 COLD ISOSTATIC PRESSING

There are many variations on using the cold isostatic press (CIP); here we just emphasize some basic themes. Figure 23.3 illustrates the so-called wet-bag CIP process. Powder is weighed into a rubber bag, and a metal mandrel is inserted that makes a seal with the mouth of the rubber bag. The sealed bag is placed inside a high-pressure chamber that is filled with a fluid (normally, a soluble oil–water mixture) and hydrostatically pressed. The pressures used can vary from ~20 MPa up to 1 GPa depending on the press and the application. For production units, the pressure is usually ≤400 MPa. Once pressing is complete, the pressure is released slowly, the mold is removed from the pressure chamber, and the pressed component is removed from the mold.

The advantages of the wet-bag process are:

- Wide range of shapes and sizes that can be produced
- Uniform density of pressed product
- Low tooling costs

The disadvantages are:

- Poor shape and dimensional control (particularly for complex shapes)
- Products often require green machining (described in Section 23.14) after pressing
- Long cycle times (typically 5–60 min) that give low production rates

A small wet-bag isostatic press, for producing laboratory samples and low-volume production parts, might have an internal diameter of 150 mm and a depth of 460 mm. Large wet-bag presses may have cavity diameters >1.8 m and lengths up to 3.7 m. The wet-bag CIP process can be automated.

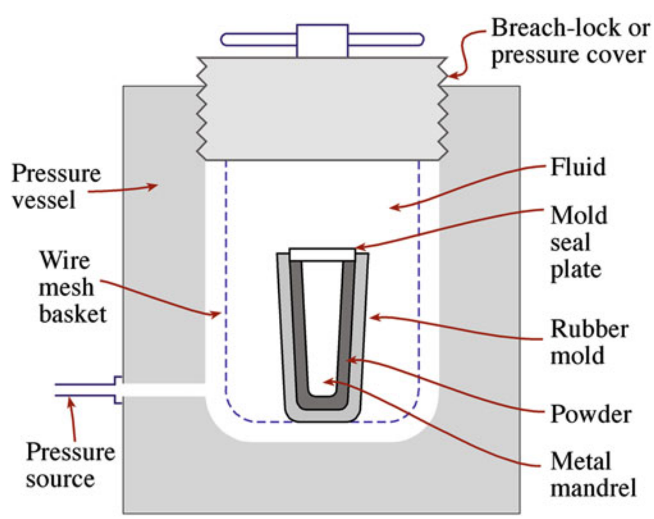

FIGURE 23.3. Wet-bag isostatic pressing system.

A mold for the dry-bag CIP is shown in Figure 23.4. The main distinction of the dry-bag process is that the rubber mold is now an integral part of the press. The high-pressure fluid is applied through channels in the mold. After pressing, the pressed part is removed without disturbing the mold at all. Hence, the dry-bag press can be readily automated. Fully automated units are widely available and have been operating in the high-volume production of ceramic parts for over two decades. Production rates of up to one part per second are being achieved industrially.

The dry-bag CIP has been used for many years to press spark-plug insulators. The steps in this process are shown in Figure 23.5. Notice the insertion of the inner pin in the mold. The world's largest producers of spark plugs produced by this method are Champion and AC Spark Plug.

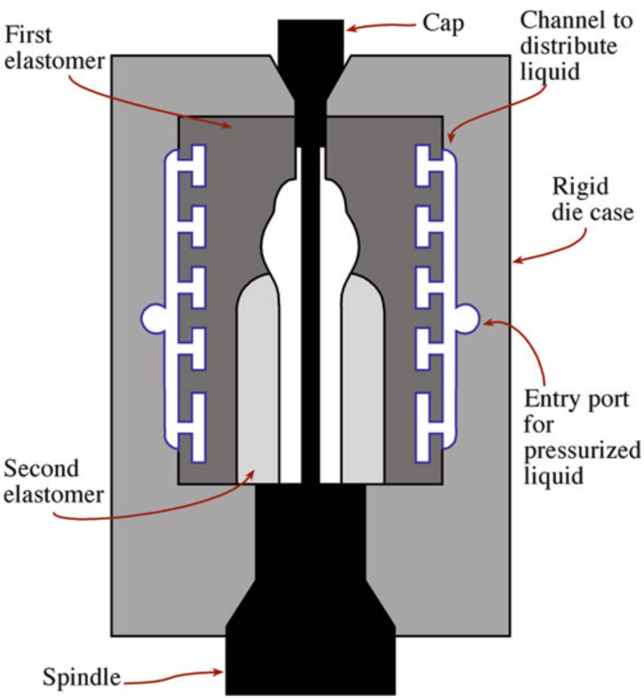

FIGURE 23.4. A die for dry-bag isostatic pressing of a spark plug insulator.

23.7 HOT ISOSTATIC PRESSING

The hot isostatic press (HIP) uses the simultaneous application of heat and pressure. We refer to this process as HIPing and the product as being HIPed (but you see variations on these abbreviations). A furnace is constructed within a high-pressure vessel, and the objects to be pressed are placed inside. Figure 23.6 shows a typical HIP arrangement. Temperatures can be up to 2,000°C, and pressures are typically in the range 30–100 MPa. A gas is used as the pressure medium—unlike in the CIP where a liquid is often used. Argon is the most common gas used for

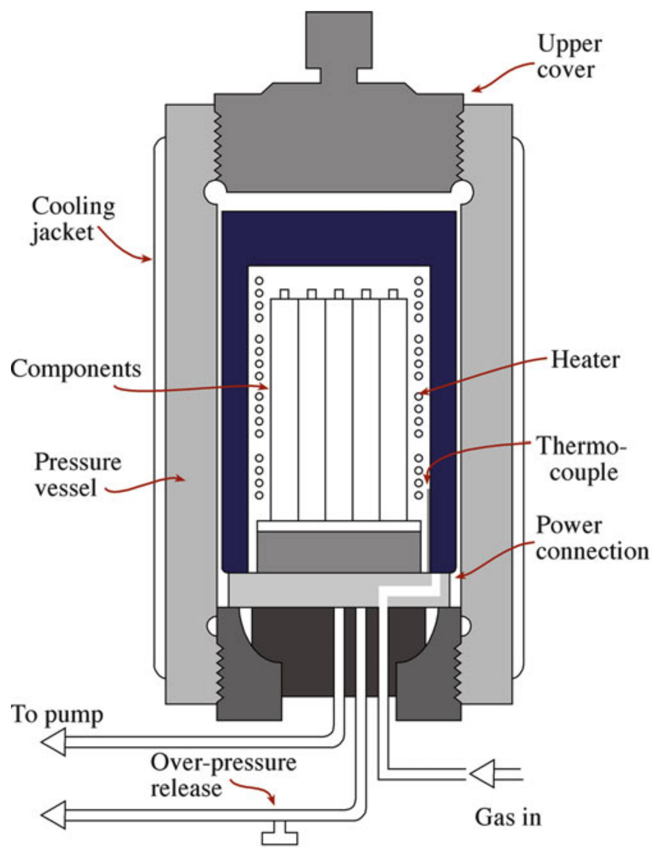

FIGURE 23.6. Hot isostatic pressing apparatus.

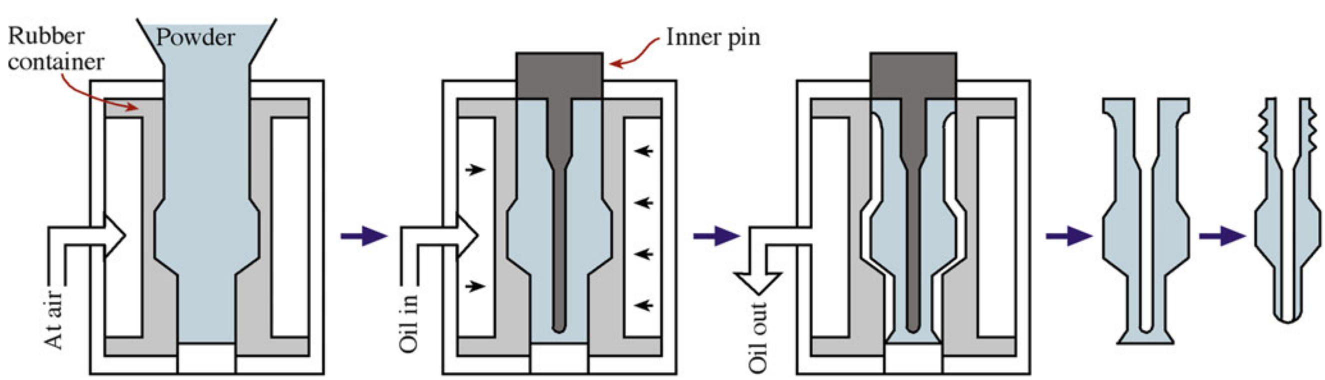

FIGURE 23.5. Making spark plugs. Hydrostatic pressure is applied by pumping oil around the rubber container, which is part of the press and thus easily removed.

HIPing, but oxidizing and reactive gases can also be used. Note that the high-pressure vessel is not inside the furnace.

There are two variants of HIPing.

- Encapsulated: using a deformable container
- Not encapsulated: shape and sinter first, then HIPed

In the original HIPing method, the ceramic powder was filled into a deformable metal can and then subjected to heat and pressure. This method was subsequently modified for small particle size powders. The powder compact was preformed to the desired shape by a process such as dry pressing or injection molding. The green compact was then encapsulated in a glass envelope that could be removed from the product after HIPing, as shown in Figure 23.7.

The second variant does not involve encapsulation at all. The ceramic powder is first compacted using another shaping method, such as dry pressing or injection molding, and then sintered at relatively high temperatures in a furnace to close all the surface pores, thereby preventing the entry of the gas during subsequent HIPing. The steps in this process, which is sometimes referred to as sinter-plus-HIP, are shown in Figure 23.8.

HIP & HIPING

Used initially for fabricating the cladding for nuclear fuel elements and was called "gas-pressure bonding." We use the acronym HIP to identify the press and HIPing to identify the action. You will also see HIP used to mean HIPing and you will see HIPing spelt HIPping! We then say a sample has been HIPed rather than HIPped. Only nano is HYPed

Now HIPing is used for a wide variety of ceramic (and metallic) components, such as alumina-based tool bits and the silicon nitride nozzles used in flue-gas desulfurization plants by the utility industry. The advantages of the HIPing process are becoming more important as interest in structural ceramics (e.g., Si_3N_4) grows.

Nonoxide ceramics can be HIPed to full density while keeping the grain size small and not using additives. Very high densities combined with small grain sizes (because of the relatively low temperatures) leads to products with special mechanical properties. HIPing has also been applied to the formation of piezoelectric ceramics—

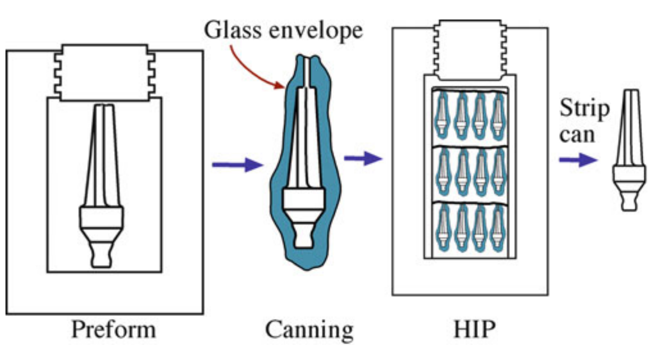

FIGURE 23.7. Individual steps of milling, cold preforming, canning, HIPing, and stripping in the standard HIPing process.

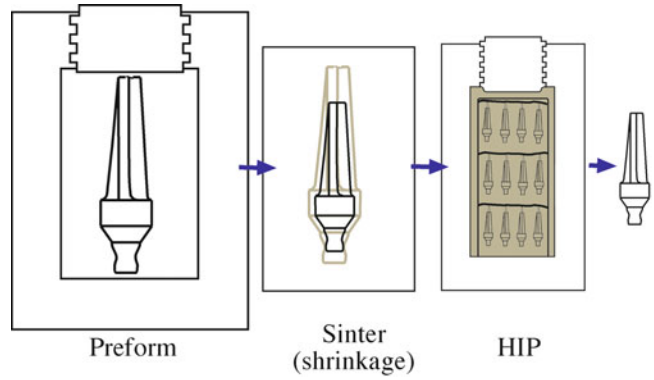

FIGURE 23.8. Individual steps of milling, cold forming, sintering, and HIPing in the sinter plus HIPing process.

e.g., $BaTiO_3$, $SrTiO_3$, lead zirconate titanate (PZT)—for use in acoustic wave filters and oscillators.

Uses: produces dense materials without growing the grains

Disadvantage: cost

23.8 SLIP CASTING

For slip casting, the slip is poured into a mold (usually plaster of Paris: $2CaSO_4 \cdot H_2O$) that has been made by casting around a model of the required shape, which was itself suitably enlarged to allow for shrinkage of the cast ceramic on drying and sintering. The fineness of the powder (in the slip) and the consequent high surface area ensure that electrostatic forces dominate gravity so that settling does not occur. The electrochemistry of the slip is quite complex: Na silicate (or soda ash) is added to the slip to deflocculate the particles. The water passes, via capillary action, into the porous plaster, leaving a layer of the solid on the wall of the mold. (We consider this model in Section 25.7.) Once a sufficient thickness has been cast, the surplus slip is poured out, and the mold and cast are allowed to dry. These steps are shown in Figure 23.9. This variant of slip casting, which is the most widely used, is also called *drain casting*. A very effective technique used by some potters is to produce a multilayer slip, parts of which are removed before firing.

Slip casting is a low-cost way to produce complex shapes. In the traditional pottery industry, it is the accepted method for the production of teapots, jugs, and figurines, although handmade items are likely to be hand-thrown. Large articles, such as wash-hand basins and other whitewares, are also mass-produced by slip casting. (Whitewares are not necessarily white.) One of the telltale signs of a ceramic product made by slip casting is that it is hollow. A variant of the slip casting process is solid casting.

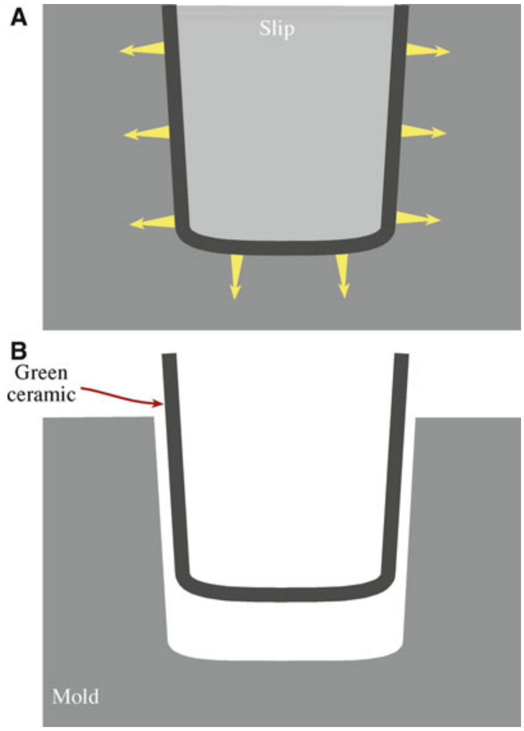

FIGURE 23.9. Drain-casting process. (A) Fill mold with slip. Mold extracts liquid, forming compact along the mold's walls. (B) After excess slip is drained, the dried green ceramic is removed.

In solid casting, slip is continually added until a solid cast is made. These items will not be hollow—relatively, they will be heavier.

Slip casting is also used in the fabrication of some technical and structural ceramics. It is the standard method used to make alumina crucibles and has been successfully used to make complex structural ceramic components such as gas-turbine rotors. The technique of doctor-blading, which we discuss in Chapter 27, is just another method of shaping the slip—ensuring that the slip is spread as a uniform layer.

23.9 EXTRUSION

Extrusion involves forcing a deformable mass through a die orifice (e.g., toothpaste from a tube). The process is widely used to produce ceramic components having a uniform cross section and a large length-to-diameter ratio, such as ceramic tubes and rods, as illustrated in Figure 23.10. Clay with a suitable rheology for the extrusion process (essentially a paste) can be made by controlling the amount of water. Clay-free starting materials (e.g., Al_2O_3) are mixed with a viscous liquid such as polyvinyl alcohol or methylcellulose and water to produce a plastically deformable mass. Table 23.3 lists examples of compositions of extrusion bodies. Extrusion of polymers has been used since the 1860s; early on, it was used to process natural rubber. An extrusion press such as that shown in Figure 23.11 is standard equipment in the potter's barn.

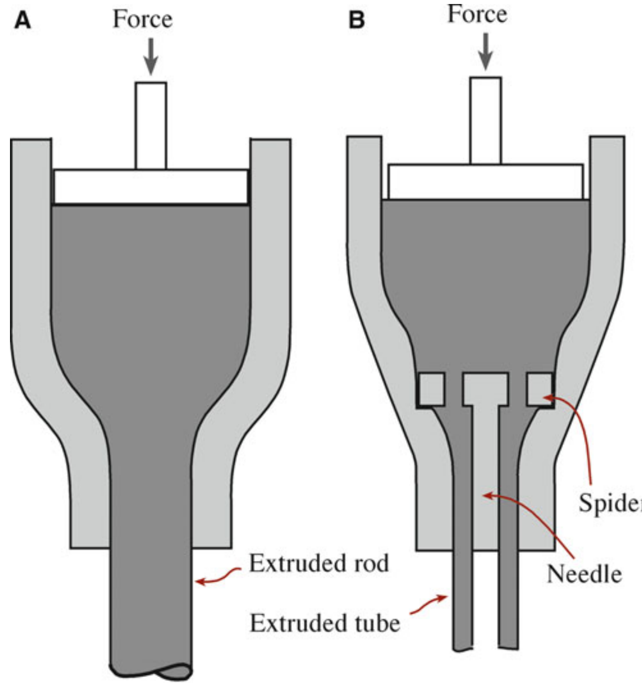

FIGURE 23.10. Extrusion of (A) a rod and (B) a tube.

Extrusion is also used to produce the alumina shells for sodium vapor lamps and the honeycomb-shaped catalyst supports for automotive emission-control devices (see Chapter 38). The catalyst supports are designed to give a high surface area; they can consist of hundreds of open cells per square centimeter and a wall thicknesses of <100 μm. To produce these shapes, the cordierite ceramic powder is mixed with a hydraulic-setting polyurethane resin.

TABLE 23.3 Examples of Compositions of Extruded Bodies

Refractory alumina	*vol%*	*High alumina*	*vol%*	*Electrical Porcelain*	*vol%*
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
$AlCl_3$	<1	Water	48	Ball clay	16
(pH >8.5)		$MgCl_2$	<1	Water	36
				$CaCl_2$	<1

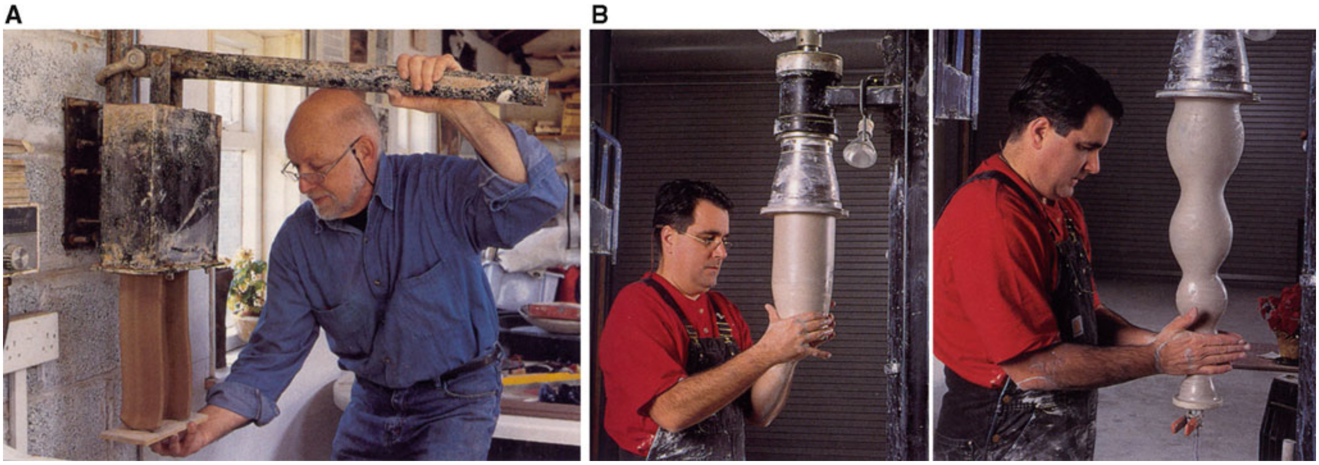

FIGURE 23.11. Extruding clay. Manual and electric extruders.

The mix is extruded into a water bath at a rate that matches the rate of cure of the polyurethane (~2 mm/s). It is then fired to produce the final ceramic.

23.10 INJECTION MOLDING

Injection molding is another technique that is widely used in shaping thermoplastic polymers. A thermoplastic polymer is one that softens when heated and hardens when cooled. Such processes are totally reversible and may be repeated. Injection molding can be applied to shaping and forming ceramic components if the ceramic powder is added to a thermoplastic polymer. When forming ceramics by injection molding, the polymer is usually referred to as the binder (but we could instead have called the material a ceramic-loaded polymer). The ceramic powder is added to the binder and usually mixed with several other organic materials to provide a mass that has the desired rheological properties. Table 23.4 shows the additives that have been used to form SiC shapes by injection molding. The organic part of the mix accounts for about 40 vol%.

The plastic mass is first heated, at which point the thermoplastic polymer becomes soft; and then it is forced into a mold cavity, as shown in Figure 23.12. The heated mixture is very fluid and is not self-supporting (this is different from the situation encountered in extrusion). The mixture is allowed to cool in the mold, during which time the thermoplastic polymer hardens. Because of the large volume fraction of organic material used in the mixture, there is a high degree of shrinkage of injection-molded components during sintering. Shrinkage of 15–20% is typical, so precise control of component dimensions is difficult. However, complex shapes are retained with very little distortion during sintering because the densities, though low, are uniform.

Injection molding is used to fabricate ceramic components with complex shapes; and because cycle times can be rapid, injection molding can be a high-volume process. The major limitation is that the initial tooling costs of the mold can be quite high. The mold to fabricate an individual turbine blade can be >$10,000 and a

TABLE 23.4 Additives for Injection Molding of SiC

Function	*Example*	*Quantity (wt%)*	*Volatilization temperature (°C)*
Thermoplastic resin	Ethyl cellulose Polyethylene Polyethylene glycol	9–17	200–400
Wax or high-temperature volatilizing oil	Paraffin Mineral oils Vegetable oils	2.0–3.5	150–190
Low-temperature volatilizing hydrocarbon or oil	Animal oils Vegetable oils Mineral oils	4.5–8.5	50–150
Lubricant or mold release	Fatty acids Fatty alcohols Fatty esters	1–3	
Thermosetting resin	Epoxy Polyphenylene Phenol formaldehyde		Gives carbon 450–1,000

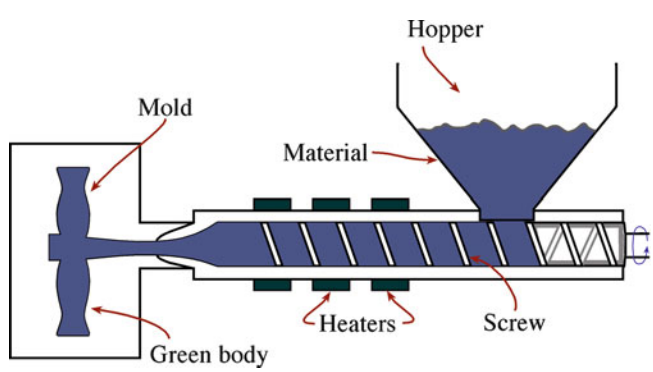

FIGURE 23.12. Cross-sectional side view of a screw-type machine.

mold for a turbine rotor >$100,000, but such molds are reusable because they are never subjected to high temperatures.

23.11 RAPID PROTOTYPING

Rapid prototyping (RP), or solid free-form fabrication (SFF), is a relatively recent approach to forming ceramic components. There are various forms of RP techniques, but they are based on a common principle: a computer directly controls the shaping process by accessing computer-aided design (CAD) files. We can thus use RP to form a three-dimensional component without the use of a die or a mold. RP techniques are used commercially for fabrication of parts from polymers for design verification and form-and-fit applications; these techniques have more recently been applied to forming parts out of ceramics.

In this section we look at just two of the several RP methods.

Stereolithography (SLA)
Fused deposition modeling (FDM)

Both these methods have been successfully used to form ceramic components. The SLA process is illustrated in Figure 23.13. In SLA, the component is formed from an epoxy resin. As the z-stage elevator is lowered, an ultraviolet laser beam whose position is controlled by a computer cures successive layers of the uncured resin. In this way, a three-dimensional component is made, one layer at a time. It can take many hours to build a large complex object, but this is still rapid compared to the time taken to form a component by, for example, injection molding, where fabrication of the tools can take a considerable amount of time. To form ceramic components by SLA, it is necessary that the polymer is loaded with ceramic powders. Si_3N_4, SiO_2, and Al_2O_3 powders have all been used for SLA.

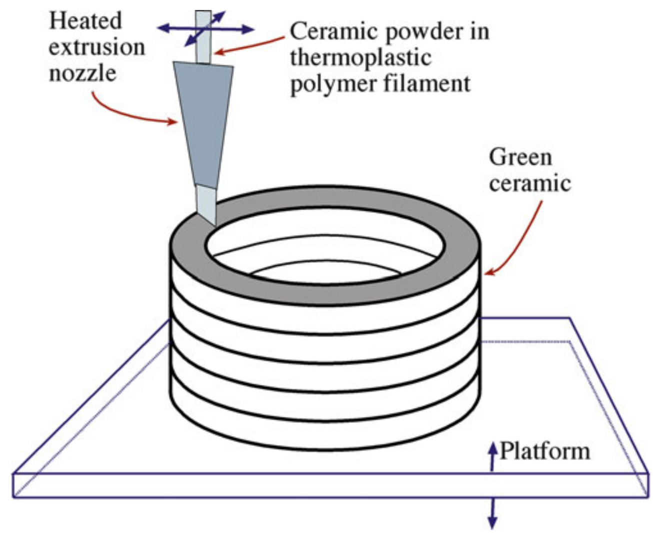

FIGURE 23.14. Fused deposition (FD) SFF process.

In FDM, the source material is a thermoplastic polymer filament that is heated and extruded to form the product, as shown in Figure 23.14. The product is formed in a layer-by-layer manner, similar to building up layers of icing on a cake. The computer controls the *x-y* position of the filament and the deposition rate. The filament can be loaded with up to 60 vol% ceramic powders; once the part is completed, the binder is removed and the part is sintered. Most of the work in the RP of ceramic parts by FDM has involved Si_3N_4. The feasibility of making components out of Al_2O_3, SiO_2, and PZT has also been demonstrated. The abbreviation FDC (fused deposition of ceramics) is used to identify this special application of FDM.

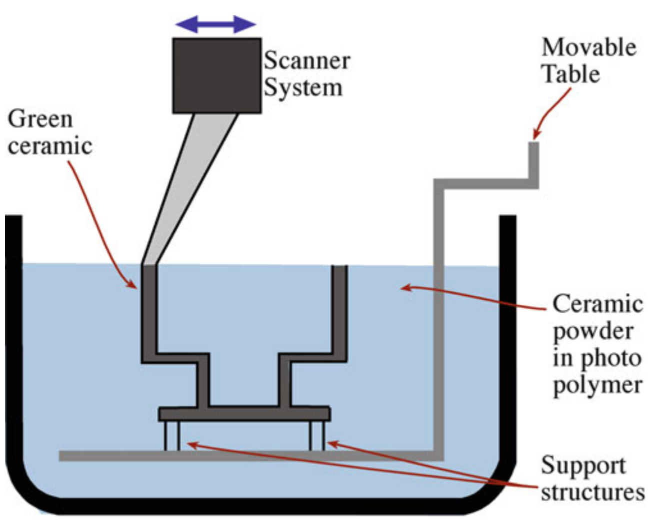

FIGURE 23.13. Stereolithography (SLA) solid free-form fabrication (SFF) process.

23.12 GREEN MACHINING

To obtain the desired shape of a ceramic product, it is often necessary to machine it. Machining can be performed either before or after the product has been sintered. If the machining is done before sintering, while the component is still in the green state, the process is called green machining. The advantages of green machining compared to machining the sintered product are that there is a considerable reduction (10×) in machining time and a 20× reduction in cost because of less tool wear and the possibility of using cheaper tools. Table 23.5 compares the use of different tool materials in the green machining of a Si compact before nitriding it to form Si_3N_4.

In the processing of spark plug insulators, the final step prior to firing involves green machining, as shown earlier in Figure 23.5.

TABLE 23.5 Comparison of Cutting Speed Versus Tool Life for Selected Abrasives, Showing Cost-Effectiveness of Green Machining of a Presintered Silicon Compact in the Fabrication of Reaction-Bonded Si_3N_4

Tool material	*Cutting speed (m/min)*	*Workpiece material removed (cm^3)*	*Relative cost factor*
Cubic BN	30	8.2	×
Ti-coated carbide	30	13.1	×
Co-coated WC	30	19.7	×
Diamond	90	8,500	10×

23.13 BINDER BURNOUT

In pottery, the binder burnout is the removal of water from the shaped clay. The rest of the firing process causes structure changes and transformations in the silicate itself. Forming methods for engineering ceramics (e.g., injection molding) produce green bodies that can contain 30–50 vol% of organic binder. We generally want to remove this binder without cracking or distorting the ceramic compact. Binder burnout is one of the most likely stages to form defects in the processing of a ceramic: macroscopic defects, such as cracks and blisters, can be introduced at this stage; and they affect the mechanical strength and other properties. An additional complication is that the binder system used in fabricating many commercial ceramic parts often consists of several components. These components have different boiling points and decomposition temperatures.

The components with low boiling points (e.g., waxes) may be removed by evaporation at fairly low temperatures.

Oxidation or decomposition at higher temperatures removes components with high molecular weight.

For oxide ceramics, the binder can be oxidized to form H_2O, CO, and CO_2 when the green compact is heated in air. Binder burnout in air generally presents no problem. However, there are some situations where binder burnout in air can be a problem. An example is the use of poly(vinyl butyral) with Al_2O_3, where carbon residues can be as high as thousands of parts per million even after burnout in air at 700°C for 24 h. Nonoxide ceramics generally cannot be heated in oxidizing environments, and binder burnout in inert or reducing atmospheres is more difficult. Pyrolysis of many binders in these environments is not well understood, and most binders leave some carbonaceous residue that could be detrimental to the subsequent sintering stage.

The process of binder removal is kept slow to reduce the possibility of macrodefects being produced. Figure 23.15 shows a plot of a binder removal cycle. In this plot, a pressurized gas, called a *sweep gas*, has been passed over the part to help sweep away the vapor. The cycle time depends on the size of the part. Thin sections take much shorter times than thick sections. The *debinding* time is proportional to the square of the section thickness of the compact—the familiar parabolic kinetics seen in our discussion of reactions.

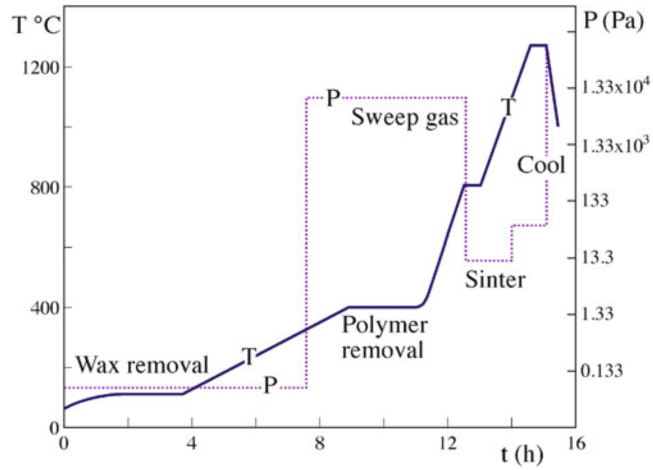

FIGURE 23.15. Pressure-induced binder removal cycle.

Binder burnout continues to be an active area of ceramics research, with one of the main thrusts being in developing models of binder decomposition and diffusion.

23.14 FINAL MACHINING

Ideally, the shaping and forming processes that are employed would produce the ceramic component in the desired shape with the specified dimensional tolerances and with an acceptable surface finish. However, in many cases, this is not the situation and some final machining (after firing/sintering) of the ceramic is necessary. Generally, final machining is required to:

- Meet dimensional tolerances
- Improve the surface finish
- Remove surface flaws

Machining fired ceramics can be expensive and can represent a significant fraction of the total fabrication costs. Ceramic materials are difficult to machine because they are hard and brittle. The tooling costs are high because diamond tools are likely to be required; or if conventional tools are used, the tool life is very short. Also, the time required to machine ceramics is long because high tensile loads cannot be applied to the ceramic part; otherwise, it may fracture.

Mechanical approaches to machining ceramics include:

- *Grinding* using tools where abrasive particles are embedded in a softer matrix such as glass, rubber, or polymer resin, or even a metal (as for WC in Co).
- *Lapping* using loose abrasive particles placed on a soft cloth.

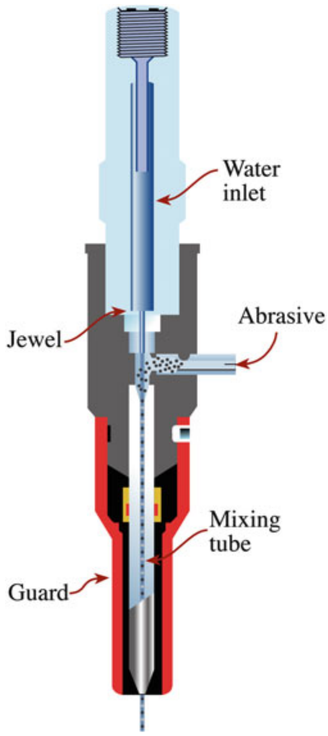

FIGURE 23.16. Abrasive waterjet cutting process.

- *Sandblasting* using abrasive particles accelerated by compressed air and directed through a nozzle at high velocity.
- *Water-jet machining* using a high-pressure (~400 MPa pumping pressure) water jet to transport the abrasive particles to the ceramic surface.

The water-jet method is gaining popularity as a high-speed method for machining hard ceramics. Figure 23.16 shows the basic components of an abrasive water jet cutter. Cutting rates depend on the material being cut and can vary from 130 mm/min for glass to 5 mm/min for a dense hard ceramic such as TiB_2. In a waterjet, the water is pressurized to ~380 MPa and forced through a sapphire orifice at a velocity of up to ~750 m/s. In the abrasive jet, the speeds may be a little lower, but garnet powder is pulled into the water stream and acts as the abrasive to cut through, for example, 25 mm of Ti or steel. It can also cut through ceramics and glass. Dentists use the same technique when working on our teeth. The Grand Canyon was formed on a larger scale by essentially the same process. Masons use sandblasting to clean the surfaces of old stone buildings.

23.15 MAKING POROUS CERAMICS

In many traditional applications for ceramics, particularly in structural and electrical applications, the sintered ceramic component is required to have minimum porosity. However, in a growing number of applications (e.g., in ceramic humidity and gas sensors), porosity is not just desirable, it is required. Several different methods can be used to produce porous structures.

- Use large particles with a very small size distribution to avoid dense packing.
- Underfire a green compact to leave a large amount of fine pores.
- Add organic particles (diameter >20 μm) to the powder mixture. When they burn out, they leave behind porosity. We use a controlled version of this technique elsewhere to produce mesoporous photonic materials.
- Use a binder system that contains a foaming agent and produces a large amount of gas bubbles in the mixture.
- Impregnate a foam that has continuous porosity, and then burn it out.
- Use a glass composition that phase-separates and then leaches out (e.g., using an acid) one of the phases to produce a porous glass.

Mesoporous materials, which have quite a uniform distribution and a very high density of pores, were discussed in Chapter 15.

23.16 SHAPING POTTERY

We stated at the beginning that this is the pottery chapter. We now summarize where many of the techniques described above have been used in pottery—in some cases for millennia. Then we can do the same for glass. Classical porcelain can be as thin as a sheet of paper (<0.2 mm). Bone china, so called because even today it is made by adding ~50% bone ash to a conventional hard-porcelain clay mixture, can be so thin that it is translucent. This ingredient is so critical that the United Kingdom imports bone ash from Argentina.

Paper clay is a relative new material for the potter, being a mixture of clay and paper in approximately equal amounts by volume. The paper (cellulose fiber) gives added strength to the green body, so it can even be made into a sheet that can then be cut and shaped before firing. The firing burns out the organics and leaves a ceramic body that is lighter than usual. Figure 23.17 shows a sheet of paper clay being lifted off the plaster "substrate" (see also Section 25.7). As you might guess, there are many variations on this process, which of course is related to the ancient use of straw in making house bricks.

Throwing a pot, as shown in Figure 23.18, is the process of producing hollow clay objects on a revolving pottery wheel. The potter may use her or his hands, as shown here, or other tools—the step to industry is then a small one.

Coiling, *pinching*, and *slabbing* are used to form large pottery objects. Their common feature is that the total

FIGURE 23.17. Removing paper clay from the substrate.

FIGURE 23.18. Throwing a pot.

thickness of the ceramic piece is kept constant so that the drying and firing process is even. *Wedging* is not a shaping process, although the end result is a slab of clay. Rather, the process is used to remove porosity from clay before it is used to make a pot. This is now carried out mechanically in a pug mill. If you pinch the clay or carve it, you can combine different colored clays and then shape and fire them to produce the neriage (marbled) style—the potters' version of millefiori.

23.17 SHAPING GLASS

Glass can be shaped using many different processes.

Casting or *molding*: examples are the 20-in. thick Palomar telescope mirror and sub-millimeter thick molded-glass aspheric lenses that are used in everything from laser printers to optical disk storage devices and optical communications systems.

Pressing needs a mold that is gray cast iron (to 1,000°C), stainless steel (can use for borosilicates at 1,185°C and glass ceramics at 1,480°C), or even bronze. Usually, though, the mold is cooled. The process uses a viscosity of ~4 kP and has been applied to objects weighing 5 g to 15 kg. The finished object can be fire-polished. This process, shown in Figure 23.19, is quite similar to the HIPing technique shown in Figure 23.2 and predates it, of course.

Sagging or *slumping* is a simple method whereby the glass is heated, so that it "slumps" into the mold. The technique can also be used for clay; effectively, it is pressing, with gravity providing half the press.

Glass *blowing* was clearly in use in the first century BCE. The temperature is critical as it determines the working range. There are other factors as well, such as the air pressure, the role of gravity and the centrifugal force produced by the blower. The craftsman produces free-blown objects or can blow the glass inside a mold. When a ribbon or hub machine is used, the glass is invariably blown into a mold.

Drawing is used for glass tubes and sheets. For tubes, the variations are Danner (e.g., tubes for fluorescent lights), Vello (large-diameter tubes), downdrawn tubes (used for vacuum tubes or uses a vacuum), and updrawn tubes (for glass thermometers). Sheets are drawn in the same way: using a slot orifice, with an overflow pipe, using updraw or floating.

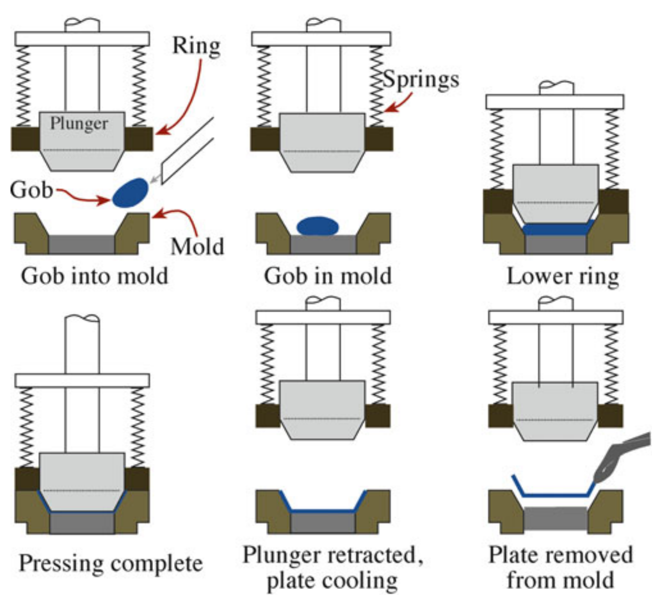

FIGURE 23.19. Automated pressing glass.

Spinning is used for fibers and is very reminiscent of the beginnings of industry (the spinning jenny).

Rolling is an old technique that is still in use. It is similar to slabbing in pottery.

The *lost wax process* of forming glass shapes has been used since the fifth century CE to make glass shapes. Originally, the molten glass was poured into an outer mold made of beeswax, which could easily be removed.

Inlays in glass, such as sandwiched-gold glass—gold leaf is pressed between two layers of glass—was made perhaps as early as ~250 BCE.

Final *machining* is done using Vycor (the "cor" is from Corning), Macor, or similar specially treated glasses. (Vycor contains "built-in" pores; Macor contains small grains of mica).

Core forming was one of the earliest methods used to shape glass (see Figure 21.2) A shape was fashioned in clay, and the glass was then trailed around the core until it completely covered it. It could be heated further so that the coils fused together. When cool, the clay core would be removed, leaving a stand-alone glass vessel.

CHAPTER SUMMARY

In this chapter, we described the methods used to shape and form ceramic components. There are a number of possible choices, and the best one depends on the shape being produced, the cost of the component, and the number of units being made. For predominantly covalently bonded ceramics, it is necessary to use shaping techniques that involve the application of pressure and heat if the objective is to obtain a high-purity material. Because ceramics can't be softened in the same way as polymers and metals, it is often necessary to form a plastic mixture of the ceramic prior to shaping. These methods may leave a large amount of organic residue that must be removed during sintering. Binder removal is tricky because it can lead to the formation of voids and cracks in the ceramic component. Machining of ceramics is often performed when they are in the green state—before sintering. This is because the presintered component is much softer, and tooling costs are significantly reduced. A relatively recent approach to forming ceramic components is rapid prototyping. The advantage of this technique is that three-dimensional parts can be made without using a die or a mold. The technique has been well established for producing parts made of polymeric materials and is now being extensively investigated for forming ceramic components.

PEOPLE AND HISTORY

Brown, Robert was the Scottish botanist (1773–1858) who, among other activities, studied the movement of particles (pollen and inorganic) in water and thus recognized Brownian motion.

Champion, Albert founded two companies: Champion and AC Spark Plug. In the 1990s, between them they produced over one-half of the world's spark plugs. McDougal (1949) gave a review of these two companies.

Hamada, Shoji (1892–1978) was born in Tokyo. His home and pottery are in Mashiko, which is a ceramics town just a short drive north of Tsukuba.

Kawai, Kanjiro (1890–1966) lived in Kyoto in a house that is now another wonderful museum.

Leach, Bernard Howell (1887–1979) is probably the best-known British potter. He was born in Hong Kong and worked in Japan (with Shoji Hamada) and at St. Ives in England.

Spode, Josiah (1733–1797) founded his pottery in 1770 at Stoke. He developed the formula for bone china that is still used.

Tomimoto, Kenkichi (1795–1835) was born and raised in Japan and helped make style part of everyday Japanese pottery.

Wedgwood, Josiah (1730–1792) was born in Burslem, Staffordshire. He joined the firm of Thomas Wheildon at Fenton, who gave him the freedom to experiment. He then founded a factory in Etruria with his business partner Thomas Bentley. Elected a Fellow of the Royal Society for inventing the pyrometer, he used the fact that porcelain shrinks in the furnace to measure the temperature of the furnace. His daughter, Susannah, had a son, Charles Darwin.

Yanagi, Soetsu (1889–1961) created the mingei (folk art) movement in Japan in the 1920s; this movement has influenced much of Japan's stunning pottery.

EXERCISES

23.1 Explain briefly why melting and solidification can be used for shaping glasses (as well as many metals and polymers) but, in general, not for forming crystalline ceramics.

23.2 Briefly describe the differences between hot pressing and cold pressing.

23.3 Explain why hot pressing is often used when ceramics with a small grain size are required. For what applications must grain growth be minimized?

23.4 Why are graphite dies widely used for hot pressing? Under what conditions would the use of graphite not be appropriate?

23.5 Which method would you choose to form each of the following shapes: (a) a cylinder; (b) a tube; (c) a cube; (d) a teapot; (e) a rotor blade; (f) a spark plug insulator; (g) an insulator for a power cable? Briefly justify your choice.

23.6 Why is it necessary to use an organic binder when forming a ceramic component by extrusion? What are the main requirements for the binder?

23.7 Why is it difficult to use injection molding for near net shape manufacturing?

23.8 Briefly explain why it is better to machine in a ceramic component when it is in its green state rather than when it has been fired.

23.9 Keramica is a new company that wants to manufacture alumina furnace tubes, and they hire you as a consultant. You are asked to propose a process for the fabrication of such tubes. Give a general description of the process you would propose. Explain the roles of the different steps involved.

23.10 Porcelain figurines are manufactured worldwide in large quantities. In most cases, many figures are made with an identical shape. As you know, such figures are often hollow. Explain the process used to form such figures economically.

23.11 We say that shaping ceramics is an ancient art. How ancient is it for clay, porcelain, alumina, Si_3N_4, and mullite? Do we use slips and slurries for any of these materials?

23.12 What is PMC?

23.13 A pharmaceutical company consults you about improving their manufacture of tablets. What concepts from this chapter would carry over and which would not?

23.14 Clays can be extruded. List as many other examples of extrusion as you can and summarize the mechanical properties of each material during extrusion. Can you use extrusion for crystalline ceramics?

23.15 Use the Internet or other sources to find the largest and smallest applications of extrusion for ceramics. Explain why this method is chosen for this application.

23.16 Critique the methods for making and shaping porous ceramics. What is the most porous natural and synthetic ceramic, and how do these porosities compare quantitatively?

23.17 What technical ceramics are made by a technique similar to that shown in Figure 23.17?

23.18 Glass blowing has been used for centuries. Estimate the pressure needed to blow a 12-in. spherical vase, explaining all your assumptions.

23.19 Drawing has been used for making glass tubes. We list some variations. Give a more complete list and describe the industrial facility needed for the thermometer tubing.

23.20 Ceramic capacitors and MCMs (multilayer chip modules) can use the same ceramics processing. List as many different ceramics as you can find that are processed in this way and explain what the processes have in common.

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