Material Science

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Chapter 10. Applications and Processing of Ceramics

Ceramics form an important part of materials group. Ceramics are compounds between metallic and nonmetallic elements for which the inter-atomic bonds are either ionic or predominantly ionic. The term ceramics comes from the Greek word *keramikos* which means 'burnt stuff'. Characteristic properties of ceramics are, in fact, optimized through thermal treatments. They exhibit physical properties those are different from that of metallic materials. Thus metallic materials, ceramics, and even polymers tend to complement each other in service.

10.1 Types and applications of ceramics

Ceramics greatly differ in their basic composition. The properties of ceramic materials also vary greatly due to differences in bonding, and thus found a wide range of engineering applications. Classification of ceramics based on their specific applications and composition are two most important ways among many.

Based on their composition, ceramics are classified as:

Oxides,
Carbides,
Nitrides,
Sulfides,
Fluorides, etc.

The other important classification of ceramics is based on their application, such as:

Glasses,
Clay products,
Refractories,
Abrasives,
Cements,

Advanced ceramics.

In general, ceramic materials used for engineering applications can be divided into two groups: traditional ceramics, and the engineering ceramics. Typically, traditional ceramics are made from three basic components: clay, silica (flint) and feldspar. For example bricks, tiles and porcelain articles. However, engineering ceramics consist of highly pure compounds of aluminium oxide (Al_2O_3), silicon carbide (SiC) and silicon nitride (Si_3N_4).

Glasses: glasses are a familiar group of ceramics – containers, windows, mirrors, lenses, etc. They are non-crystalline silicates containing other oxides, usually CaO, Na_2O, K_2O and Al_2O_3 which influence the glass properties and its color. Typical property of glasses that is important in engineering applications is its response to heating. There is no definite temperature at which the liquid transforms to a solid as with crystalline materials. A specific temperature, known as glass transition temperature or fictive temperature is defined based on viscosity above which material is named as super cooled liquid or liquid, and below it is termed as glass.

Clay products: clay is the one of most widely used ceramic raw material. It is found in great abundance and popular because of ease with which products are made. Clay products are mainly two kinds – structural products (bricks, tiles, sewer pipes) and white-wares (porcelain, chinaware, pottery, etc.).

Refractories: these are described by their capacity to withstand high temperatures without melting or decomposing; and their inertness in severe environments. Thermal insulation is also an important functionality of refractories.

Abrasive ceramics: these are used to grind, wear, or cut away other material. Thus the prime requisite for this group of materials is hardness or wear resistance in addition to high toughness. As they may also exposed to high temperatures, they need to exhibit some refractoriness. Diamond, silicon carbide, tungsten carbide, silica sand, aluminium oxide / corundum are some typical examples of abrasive ceramic materials.

Cements: cement, plaster of paris and lime come under this group of ceramics. The characteristic property of these materials is that when they are mixed with water, they form slurry which sets subsequently and hardens finally. Thus it is possible to form virtually any shape. They are also used as bonding phase, for example between construction bricks.

Advanced ceramics: these are newly developed and manufactured in limited range for specific applications. Usually their electrical, magnetic and optical properties and combination of properties are exploited. Typical applications: heat engines, ceramic armors, electronic packaging, etc.

Some typical ceramics and respective applications are as follows:

Aluminium oxide / Alumina (Al_2O_3): it is one of most commonly used ceramic material. It is used in many applications such as to contain molten metal, where material is operated at very high temperatures under heavy loads, as insulators in spark plugs, and in some unique applications such as dental and medical use. Chromium doped alumina is used for making lasers.

Aluminium nitride (AlN): because of its typical properties such as good electrical insulation but high thermal conductivity, it is used in many electronic applications such as in electrical circuits operating at a high frequency. It is also suitable for integrated circuits. Other electronic ceramics include – barium titanate ($BaTiO_3$) and Cordierite ($2MgO$-$2Al_2O_3$-$5SiO_2$).

Diamond (C): it is the hardest material known to available in nature. It has many applications such as industrial abrasives, cutting tools, abrasion resistant coatings, etc. it is, of course, also used in jewelry.

Lead zirconium titanate (PZT): it is the most widely used piezoelectric material, and is used as gas igniters, ultrasound imaging, in underwater detectors.

Silica (SiO_2): is an essential ingredient in many engineering ceramics, thus is the most widely used ceramic material. Silica-based materials are used in thermal insulation, abrasives, laboratory glassware, etc. it also found application in communications media as integral part of optical fibers. Fine particles of silica are used in tires, paints, etc.

Silicon carbide (SiC): it is known as one of best ceramic material for very high temperature applications. It is used as coatings on other material for protection from extreme temperatures. It is also used as abrasive material. It is used as reinforcement in many metallic and ceramic based composites. It is a semiconductor and often used in high temperature electronics. Silicon nitride (Si_3N_4) has properties similar to those of SiC but is somewhat lower, and found applications in such as automotive and gas turbine engines.

Titanium oxide (TiO_2): it is mostly found as pigment in paints. It also forms part of certain glass ceramics. It is used to making other ceramics like $BaTiO_3$.

Titanium boride (TiB_2): it exhibits great toughness properties and hence found applications in armor production. It is also a good conductor of both electricity and heat.

Uranium oxide (UO_2): it is mainly used as nuclear reactor fuel. It has exceptional dimensional stability because its crystal structure can accommodate the products of fission process.

Yttrium aluminium garnet (YAG, $Y_3Al_5O_{12}$): it has main application in lasers (Nd-YAG lasers).

Zirconia (ZrO_2): it is also used in producing many other ceramic materials. It is also used in making oxygen gas sensors, as additive in many electronic ceramics. Its single crystals are part of jewelry.

10.2 Fabrication and processing of ceramics

Ceramics melt at high temperatures and they exhibit a brittle behavior under tension. As a result, the conventional melting, casting and thermo-mechanical processing routes are not suitable to process the polycrystalline ceramics. Inorganic glasses, though, make use of lower melting temperatures due to formation of eutectics. Hence, most ceramic products are made from ceramic powders through powder processing starting with ceramic powders. The powder processing of ceramics is very close to that of metals, powder metallurgy. However there is an important consideration in ceramic-forming that is more prominent than in metal forming: it is dimensional tolerance. Post forming shrinkage is much higher in ceramics processing because of the large differential between the final density and the as-formed density.

Glasses, however, are produced by heating the raw materials to an elevated temperature above which melting occurs. Most commercial glasses are of the silica-soda-lime variety, where silica is supplied in form of common quartz sand, soda (Na_2O) in form of soda ash (Na_2CO_3) while the lime (CaO) is supplied in form of limestone ($CaCO_3$). Different forming methods- pressing, blowing, drawing and fiber forming- are widely in practice to fabricate glass products. Thick glass objects such as plates and dishes are produced by pressing, while the blowing is used to produce objects like jars, bottles and light bulbs. Drawing is used to form long objects like tubes, rods, fibers, whiskers etc. The pressing and blowing process is shown in figure 10.1

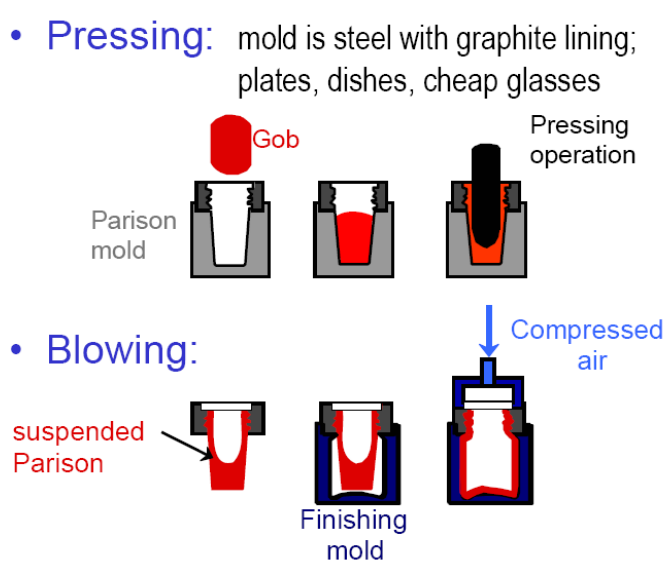

Figure 10.1: *Schematic diagram of pressing and blowing processes*

Ceramic powder processing consists of powder production by milling/grinding, followed by fabrication of green product, which is then consolidated to obtain the final product. A powder is a collection of fine particles. Synthesis of powder involves getting it ready for shaping by crushing, grinding, separating impurities, blending different powders, drying to form soft agglomerates. Different techniques such as compaction, tape casting, slip casting, injection molding and extrusion are then used to convert processed powders into a desired shape to form what is known as green ceramic. The green ceramic is then consolidated further using a high-temperature treatment known as sintering or firing.

As-mined raw materials are put through a milling or grinding operation in which particle size is reduced to and physically 'liberate' the minerals of interest from the rest of the 'gangue' material. Wet milling is much more common with ceramic materials than with metals. The combination of dry powders with a dispersant such as water is called slurry. Ball- and vibratory- milling is employed to further reduce the size of minerals and to blend different powders.

Ceramic powders prepared are shaped using number of techniques, such as casting, compaction, extrusion/hydro-plastic forming, injection molding. **Tape casting**, also known as *doctor blade process*, is used for the production of thin ceramic tapes. The schematic diagram of tape casting process is shown in figure 10.2. In this technique slurry containing ceramic particles, solvent, plasticizers, and binders is then made to flow under a blade and onto a plastic substrate. The shear thinning slurry spreads under the blade. The tape is then dried using clean hot air. Later-on the tape is subjected to binder burnout and sintering operations. Tape thickness normally range between 0.1 and 2 mm. Commercially important electronic packages based on alumina substrates and barium titanate capacitors are made using this technique. A schematic diagram of doctor blade process is shown in the figure.

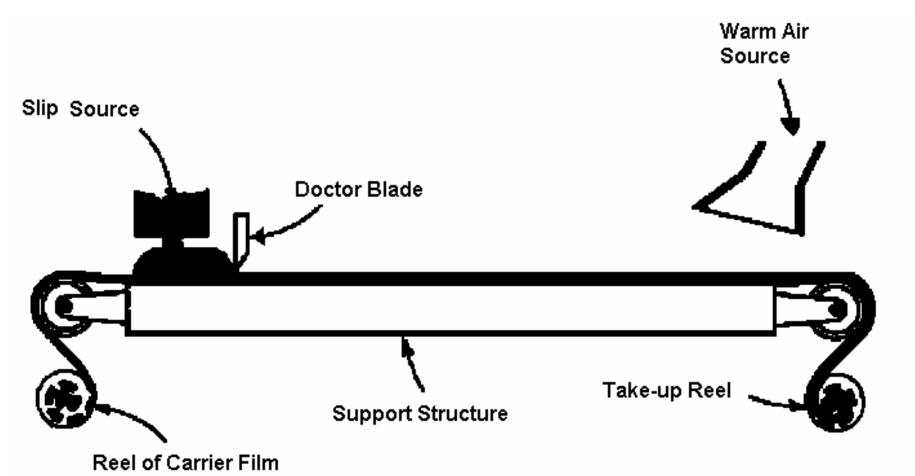

Figure 10.2: *Schematic diagram of tape casting process*

Slip casting is another casting technique widely used. This technique uses aqueous slurry, also known as slip, of ceramic powder. The slip is poured into a plaster of Paris ($CaSO_4$:$2H_2O$) mold. As the water from slurry begins to move out by capillary action, a thick mass builds along the mold wall. When sufficient product thickness is built, the rest of the slurry is poured out (drain casting). It is also possible to continue to pour more slurry in to form a solid piece (solid casting). The schematic diagram of slip casting process is shown in figure 10.3

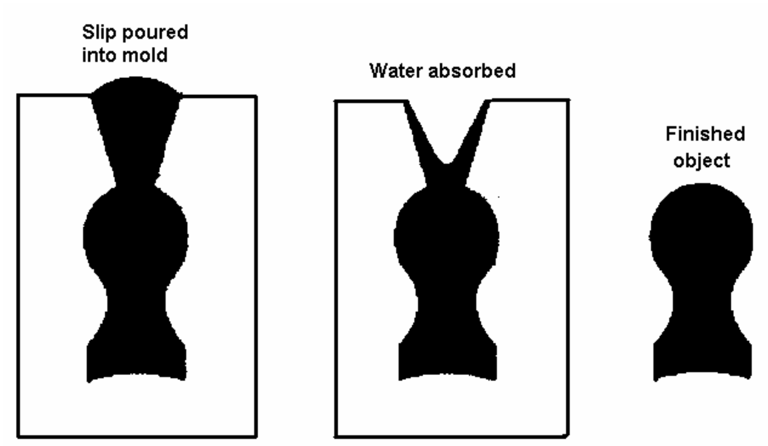

Figure 10.3: *Schematic diagram of slip casting process*

Extrusion and injection molding techniques are used to make products like tubes, bricks, tiles etc. The basis for **extrusion** process is a viscous mixture of ceramic particles, binder and other additives, which is fed through an extruder where a continuous shape of green ceramic is produced. The product is cut to required lengths and then dried and sintered. **Injection molding** of ceramics is similar to that of polymers. Ceramic powder is mixed with a plasticizer, a thermoplastic polymer, and additives. Then the mixture is injected into a die with use of an extruder. The polymer is then burnt off and the rest of the ceramic shape is sintered at suitable high temperatures. Ceramic injection molding is suitable for producing complex shapes. Figure 10.4 shows schematically the injection molding process

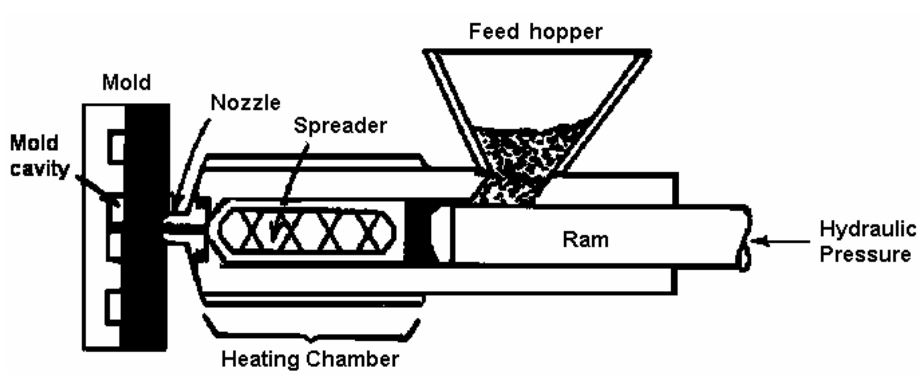

Figure 10.4: Schematic diagram of Injection molding

Most popular technique to produce relatively simple shapes of ceramic products in large numbers is combination of compaction and sintering. For example: electronic ceramics, magnetic ceramics, cutting tools, etc. **Compaction** process is used to make green ceramics that have respectable strength and can be handled and machined. Time for compaction process varies from within a minute to hours depending on the complexity and size of the product. Basically compaction process involves applying equal pressure in all directions to a mixture ceramic powder to increase its density. In some cases, compaction involves application of pressure using oil/fluid at room temperatures, called cold iso-static pressing (**CIP**). Then the green ceramic is sintered with or without pressure. CIP is used to achieve higher ceramic density or where the compaction of more complex shapes is required. In some instances, parts may be produced under conditions in which compaction and sintering are conducted under pressure at elevated temperatures. This technique is known as hot iso-static pressing (**HIP**), and is used for refractory and covalently bonded ceramics that do not show good bonding characteristics under CIP. HIP is also used when close to none porosity is the requirement. Another characteristic feature of HIP is high densities can be achieved without appreciable grain growth.

Sintering is the firing process applied to green ceramics to increase its strength. Sintering is carried out below the melting temperature thus no liquid phase presents during sintering. However, for sintering to take place, the temperature must generally be maintained above one-half the absolute melting point of the material. During sintering, the green ceramic product shrinks and experiences a reduction in porosity. This leads to an improvement in its mechanical integrity. These changes involve different mass transport mechanisms that cause coalescence of powder particles into a more dense mass. With sintering, the grain boundary and bulk atomic diffusion contribute to densification, surface diffusion and evaporation condensation can cause grain growth, but do not cause densification. After pressing, ceramic particles touch one another. During initial stages of sintering, necks form along the contact regions between adjacent particles thus every interstice between particles becomes a pore. The pore channels in the compact grow in size, resulting in a significant increase in strength. With increase in sintering time, pores become smaller in size. The driving force for sintering process is the reduction in total particle surface area, and thus the reduction in total surface energy. During sintering, composition, impurity control and oxidation protection are provided by the use of vacuum conditions or inert gas atmospheres.

References

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