LECTURES 7-8

Ceramics and Glass manufacturing

5.1 Introduction

Ceramics are a class of materials broadly defined as “inorganic, nonmetallic solids” and are commonly electrical and thermal insulators, brittle and composed of more than one element. Ceramics are compounds between metallic and nonmetallic elements for which the inter-atomic bonds are either ionic or predominantly ionic.

5.2 Types, Properties and Applications of Ceramics

Ceramics greatly differ in their basic composition. 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 and advanced ceramics

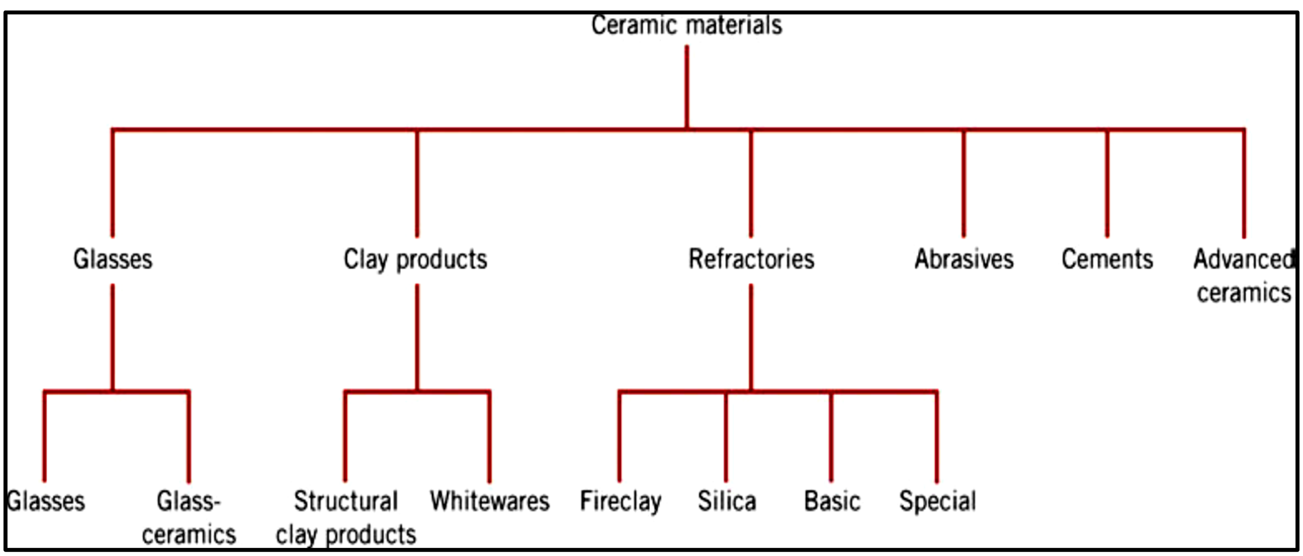


Figure1: classification of ceramic materials on the basis of application

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.

Clay products**:** clay is the one of most widely used ceramic raw material. Clay products are mainly two kinds – structural products (bricks, tiles, sewer pipes) and white-wares (porcelain, chinaware, pottery, etc.).

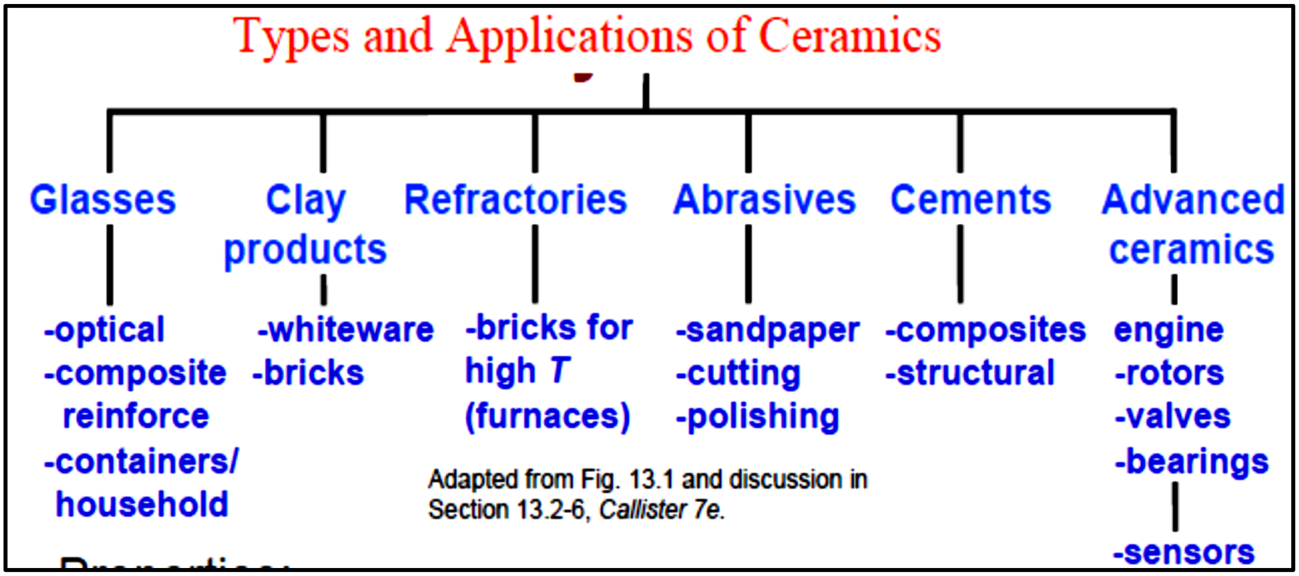
Refractories**:** these are described by their capacity to withstand high temperatures without melting or decomposing; and their inertness in severe environments. Thermal insulation is also an important functionality of refractories.

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, optical fiber, Microelectromechanical systems (MEMS), ceramic ball bearings: Si3N4, ceramic armors, electronic packaging, etc

5.2.1 Applications of Ceramics



5.2.2 Advantages of Advanced Ceramics

- Run at higher temperature
- Excellent wear & corrosion resistance
- Low frictional losses
- Ability to operate without a cooling system
- Low density

5.2.3 Disadvantages:

- Brittle
- Too easy to have voids weaken the engine
- Difficult to machine (Possible parts – engine block, piston coatings, jet engines Ex: Si3N4, SiC, & ZrO_2)

5.3 Fabrication Techniques and Processing of Ceramics

5.3.1 Particular Forming (Compaction) Processes

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. In some cases, compaction involves application of pressure using oil/fluid at room temperatures, called cold iso-static pressing (**CIP**).

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.

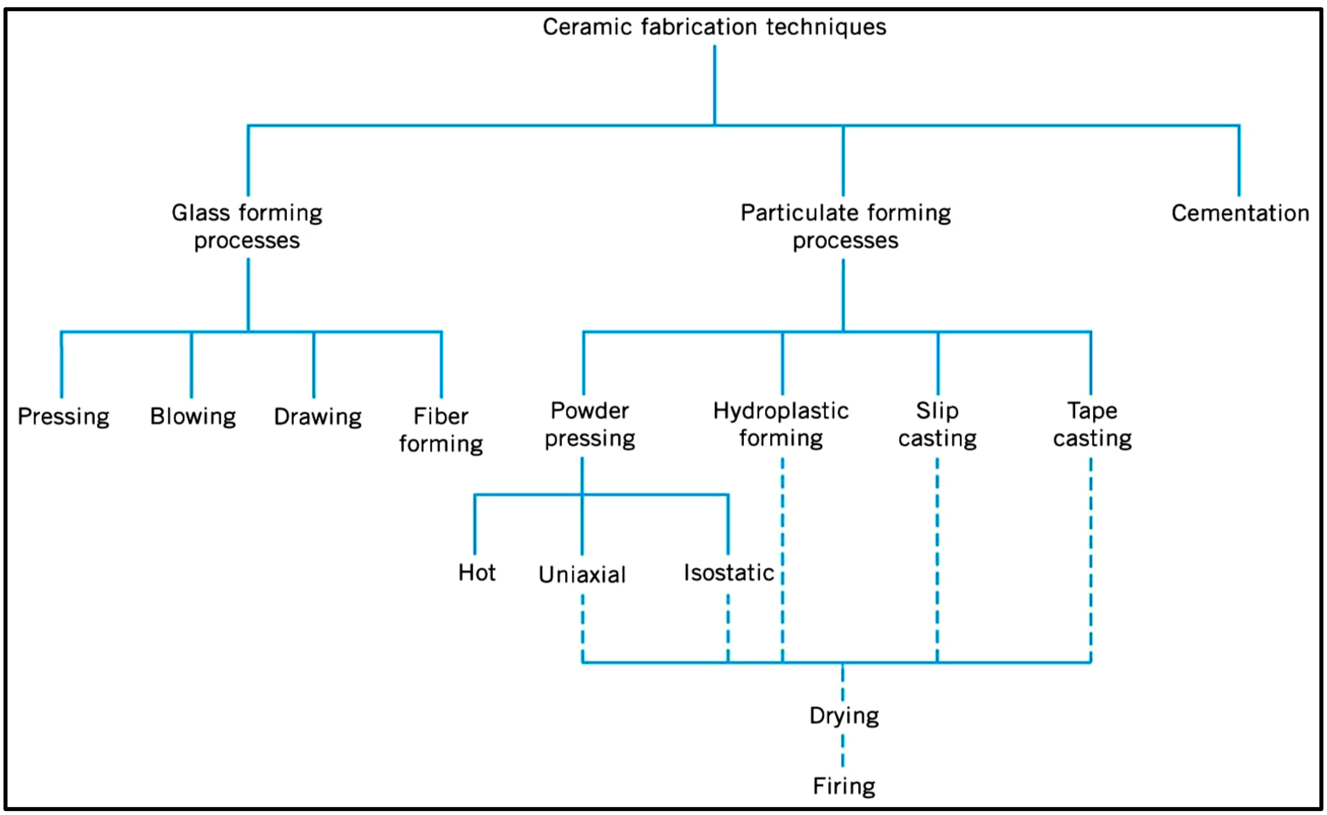


Figure 2: Fabrication and Processing of Glasses and Glass-Ceramics

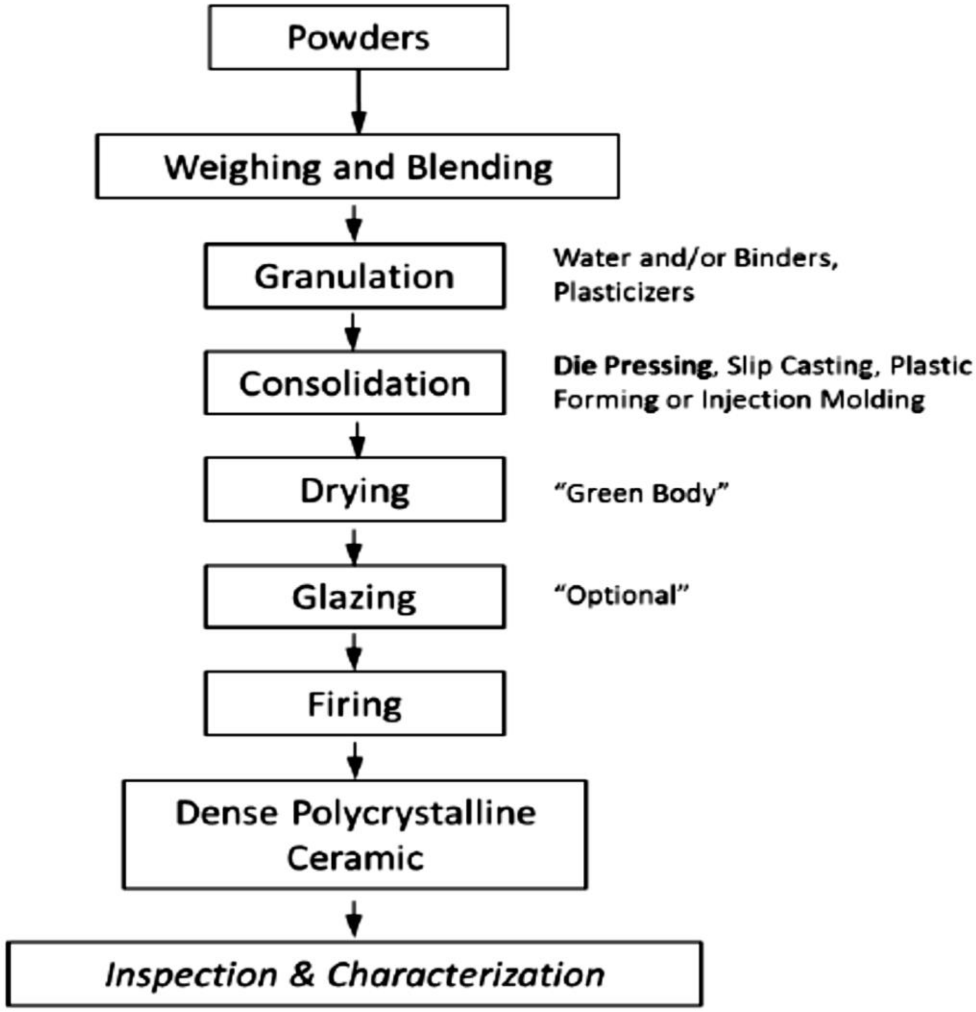


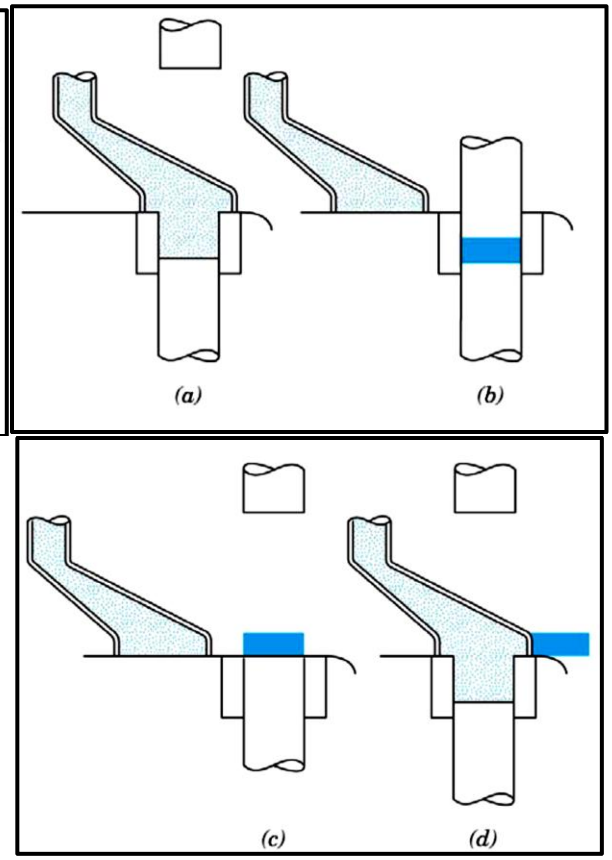
Figure 3. Basic flow-chart for the production of polycrystalline ceramics by firing of consolidated powders.

5.3.2 Powder Die Pressing

Pressing is the most popular method for the shaping of ceramics having simple geometrical shapes; common examples are wall and floor tiles, flat porcelain ware, refractories, structural clay products, cutting tools, electronic ceramics, and magnetic ceramics. Prior to the pressing operation the ceramic powders are granulated with a small amount of water, and/or a suitable binder, so that they attain good flow and diefilling capabilities. The size of the granules may range anywhere from 100 to 200 microns.

5.3.2.1 Uniaxial compression - compacted in single direction

FIGURE 13.13 Schematic representation of the steps in uniaxial powder pressing. (*a*) The die cavity is filled with powder. (*b*) The powder is compacted by means of pressure applied to the top die. (*c*) The compacted piece is ejected by rising action of the bottom punch. (*d*) The fill shoe pushes away the compacted piece, and the fill step is repeated. (From W. D. Kingery, Editor,

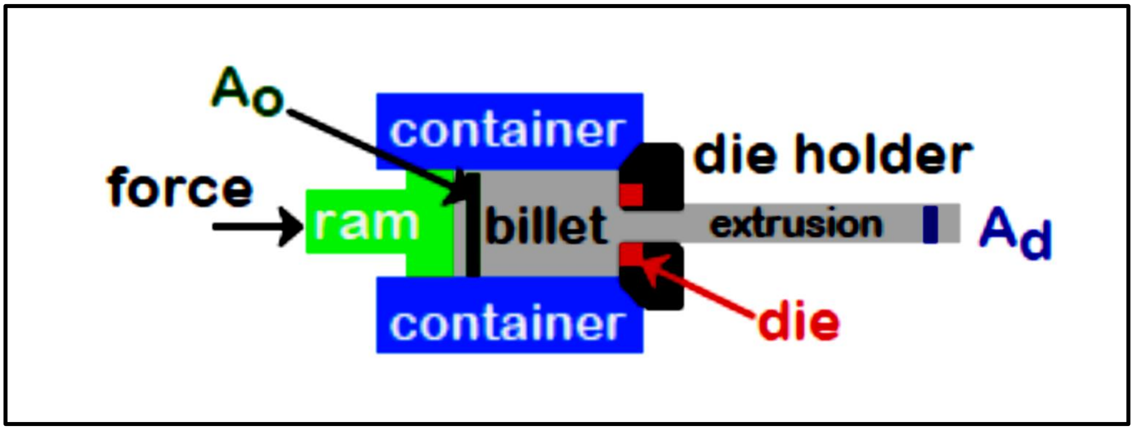


5.3.2.2 Hydrostatic Forming

Isostatic (hydrostatic) compression - pressure applied by fluid - powder in rubber envelope

- Adopted for clay-based
  - compositions Ceramic is mixed with water to form a stiff plastic ceramic mass
  - The mass is forced through a die orifice having the required cross-sectional geometry (extruded)
  - Air is removed in a vacuum chamber to enhance the density

- Bricks, pipes, ceramic blocks and tiles are all commonly fabricated by this technique.



5.3.2.3 Tape casting,

Also known as *doctor blade process*, is used for the production of thin ceramic tapes. 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.

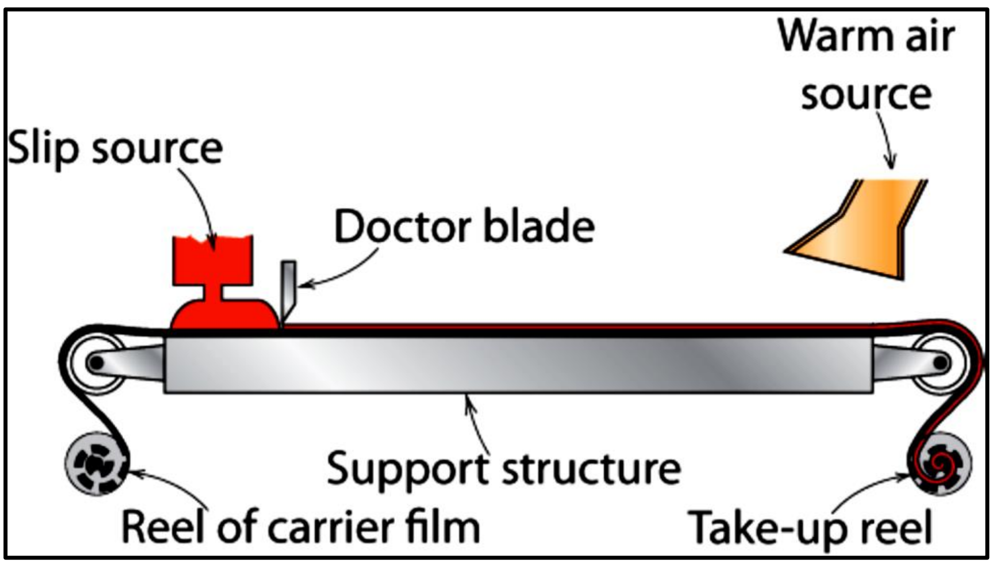


Figure 4: *Schematic diagram of tape casting process*

5.3.2.4 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).

- A slip is a suspension of clay or other non-plastic materials in water. The slip must have proper solid to water ratio.
    - The slip is formed and poured into a porous mold commonly made of Plaster of Paris.
    - Water from the slip will be absorbed into the mold, leaving behind a solid layer on the mold wall, the thickness of which depends on time.
    - The process is continued until the entire mold cavity becomes solid or stopped at the required thickness.
- Eg.: Clay products, Sanitary wares, art objects, radomes

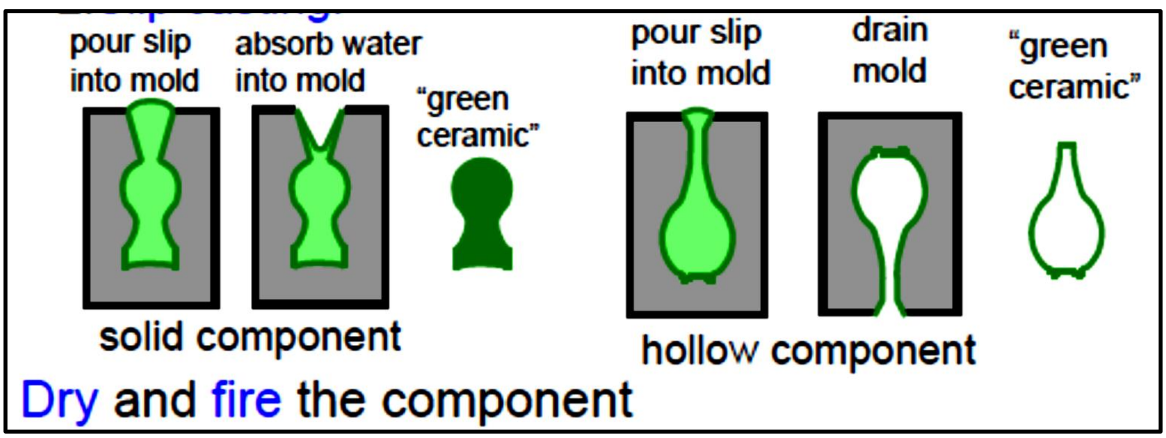


Figure 56: *Schematic diagram of slip casting process*

5.3.2.5 Injection Molding

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. Ceramic injection molding is suitable for producing complex shapes. Figure 6 shows schematically the injection molding process

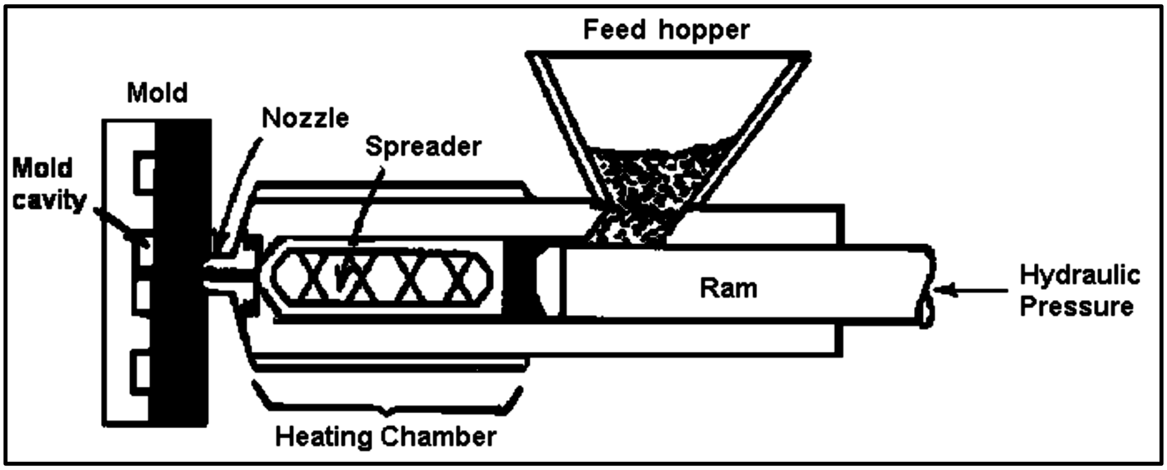


Figure 6: *Schematic diagram of Injection molding* After drying, the green

5.4 FEATURES OF CLAY

Al2O3, SiO2

- Clay is inexpensive
- Adding water to clay (hydroplasticity)
  - --allows material to shear easily along weak van der Waals bonds
  - --enables extrusion
  - --enables slip casting
- Structure of Kaolinite Clay: $Al_2(Si_2O_5)\ (OH)_4$

5.5 Composition of Clay product

A mixture of components used:a typical porcelain(50%)

1. Clay (25%)
2. Filler – e.g. quartz (finely ground) (25%)
3. Fluxing agent (Feldspar): binds it together K+, Na+, Ca+ aluminosilicates

5.6 Drying and Firing

5.6.1 Drying

- Drying is a process in which the water content in the ceramic is removed. As the ceramic dries it also experiences shrinkage. The drying rate is controlled by temperature and humidity.
- Drying too fast causes sample to warp or crack due to non-uniform shrinkage

wet slip partially dry "green" ceramic

5.6.2 Firing

- After drying the ceramic piece is fired at high temperatures between 900 and 1400oC. The firing temperature depends on the composition and the desired property of the finished piece. During firing the density of the ceramic piece increases.

5.6.3 Sintering

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.

5.7 Cementation

- Produced in extremely large quantities.
- Portland cement:
  - mix clay and lime bearing materials
  - calcinate (heat to 1400°C)
  - primary constituents:

tri-calcium silicate

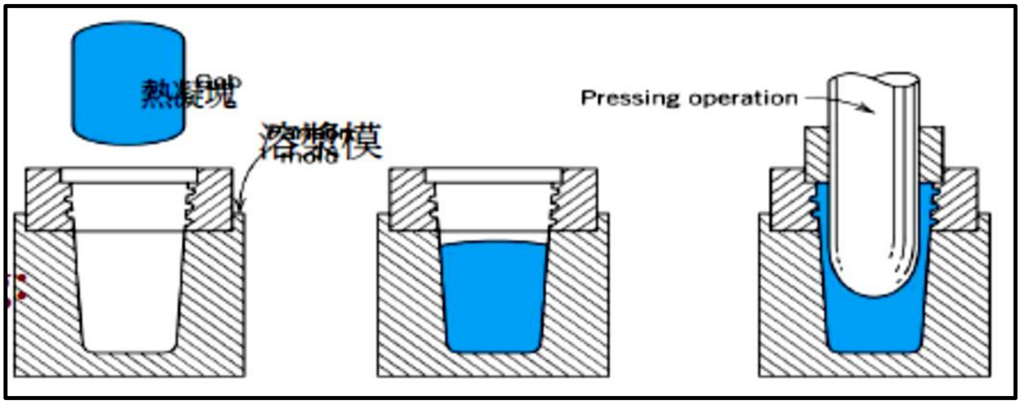
di-calcium silicate

- Adding water
    - produces a paste which hardens
    - hardening occurs due to hydration (chemical reactions with the water).
- Forming: done usually minutes after hydration begins.

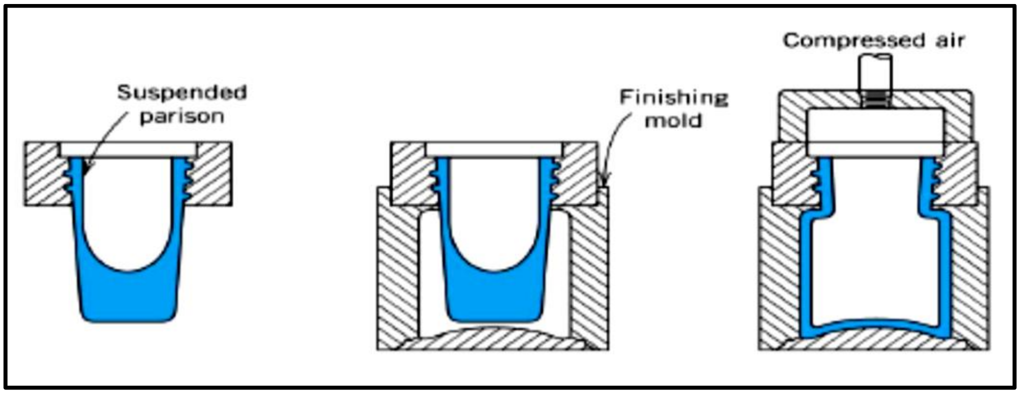
5.8 Fabrication and processing of glasses

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.

5.8.1 Pressing



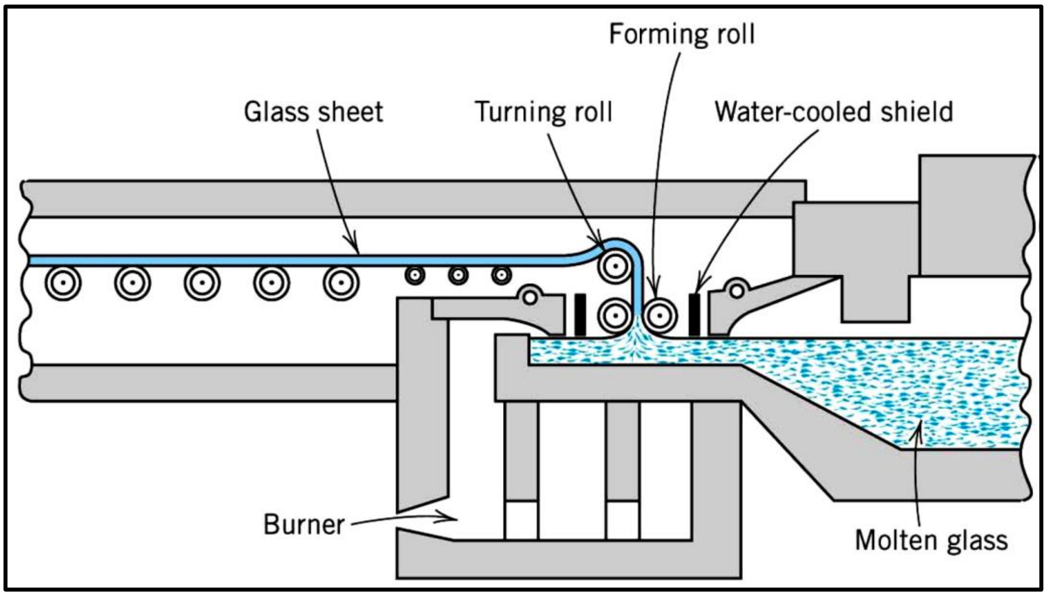
5.8.2 Blowing



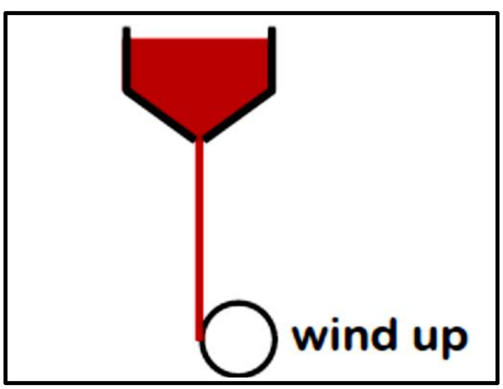
5.3.3. Drawing

Sheet forming – continuous draw

– originally sheet glass was made by “floating” glass on a pool of mercury



5.8.4 Fiber Drawing



5.9 HEAT TREATING GLASSES

Used to

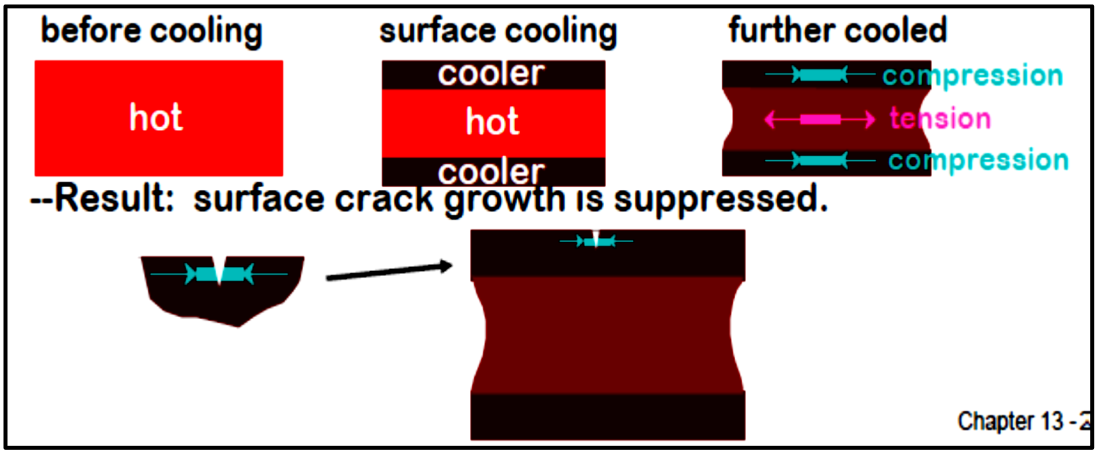
- alleviate residual stress from cooling,
- produce fracture resistant components by putting surface into compression.

1. Annealing:

- removes internal stress caused by uneven cooling rate between the surface and interior regions.

2. Tempering:

- puts surface of glass part into compression
- suppresses growth of cracks from surface scratches.
- sequence: the glassware is heated to a temperature above the Tg rg yet below the softening point. It is then cooled to room temperature jet of air or, in some cases, an oil bath.



	Composition (wt%)						
Glass Type	SiO_2	Na_2O	CaO	Al_2O_3	B_2O_3	Other	**Characteristics and Applications**
Fused silica	>99.5						High melting temperature, very low coefficient of expansion (thermally shock resistant)
96% Silica (Vycor™)	96				4		Thermally shock and chemically resistant—laboratory ware
Borosilicate (Pyrex™)	81	3.5		2.5	13		Thermally shock and chemically resistant—ovenware
Container (soda–lime)	74	16	5	1		4MgO	Low melting temperature, easily worked, also durable
Fiberglass	55		16	15	10	4MgO	Easily drawn into fibers—glass–resin composites
Optical flint	54	1				37PbO, $8K_2O$	High density and high index of refraction—optical lenses
Glass–ceramic (Pyroceram™)	43.5	14		30	5.5	$6.5TiO_2$, $0.5As_2O_3$	Easily fabricated; strong; resists thermal shock—ovenware

Table 2: compositions of five common ceramic refractory materials

	Composition (wt%)							
Refractory Type	Al_2O_3	SiO_2	MgO	Cr_2O_3	Fe_2O_3	CaO	TiO_2	**Apparent Porosity (%)**
Fireclay	25–45	70–50	0–1		0–1	0–1	1–2	10–25
High-alumina fireclay	90–50	10–45	0–1		0–1	0–1	1–4	18–25
Silica	0.2	96.3	0.6			2.2		25
Periclase	1.0	3.0	90.0	0.3	3.0	2.5		22
Periclase–chrome ore	9.0	5.0	73.0	8.2	2.0	2.2		21