CERAMIC- FOURTH CLASS

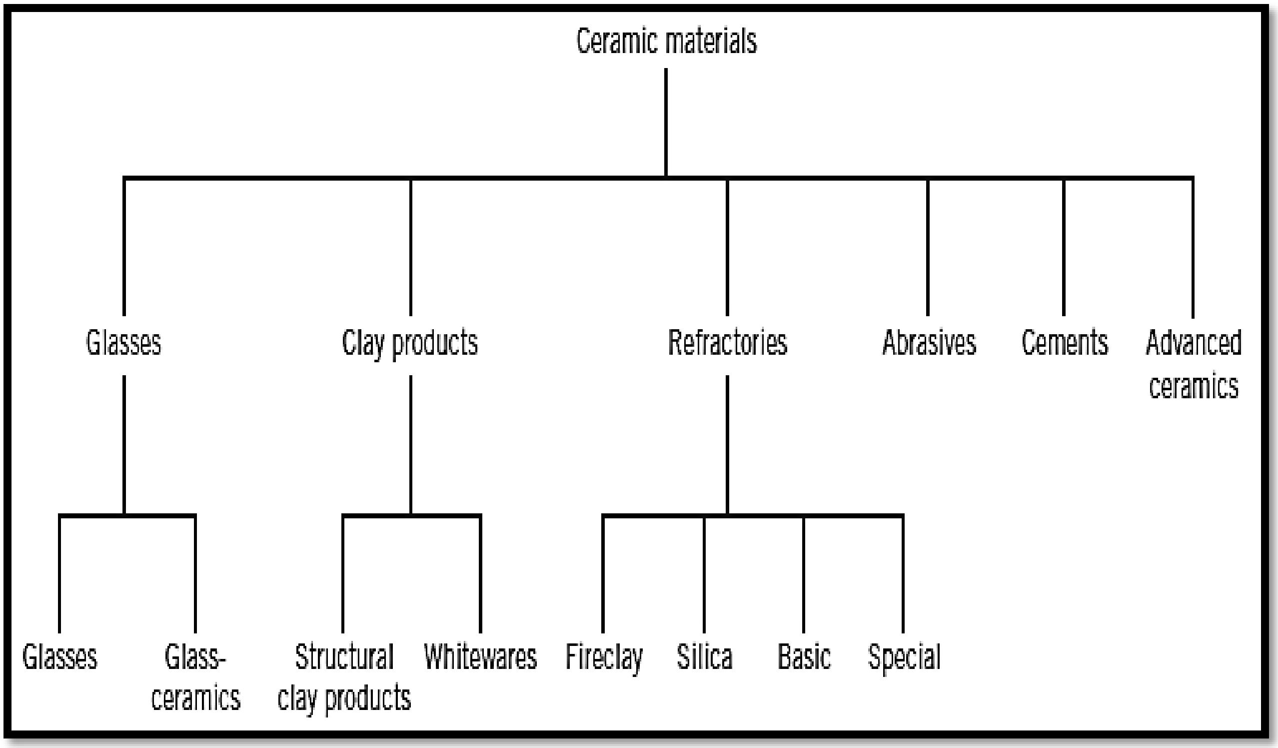
LECTURE 1

Ceramics are compounds between metallic and nonmetallic elements; they are most frequently oxides, nitrides, and carbides. For example, some of the common ceramic materials include aluminum oxide (or alumina, Al_2O_3), silicon dioxide (or silica, SiO_2), silicon carbide (SiC) and silicon nitride (Si_3N_4) in addition to traditional ceramics—those composed of clay minerals (i.e.

porcelain), as well as cement, and glass. Today ceramic may be defined as a product manufactured by the heat treatment of a material (or mixture of materials) which is inorganic and non-metallic.

Types and Applications of Ceramics

Ceramics can be classified according to their applications as follows:



- **GLASSES**

Glasses are a familiar group of ceramics; containers and lenses represent their typical applications. They are noncrystalline silicates containing other oxides, particularly CaO, Na_2O, K_2O, and Al_2O_3, which influence the glass properties. A typical soda–lime glass consists of approximately 70 wt% SiO_2, the balance being mainly Na_2O (soda) and CaO (lime). Possibly the two prime properties of these materials are their optical transparency and the relative ease of fabrication (manufacturing).

- **GLASS–CERAMICS**

Most inorganic glasses can be made to transform from a noncrystalline state to one that is crystalline by the proper high-temperature heat treatment. This process is called crystallization, and the product is a fine-grained polycrystalline material which is often called a glass–ceramic. The most common uses for these materials are tableware (dishes, plates etc.) and in high temperatures applications such as ovenware, oven windows—primarily because of their strength and excellent resistance to thermal shock.

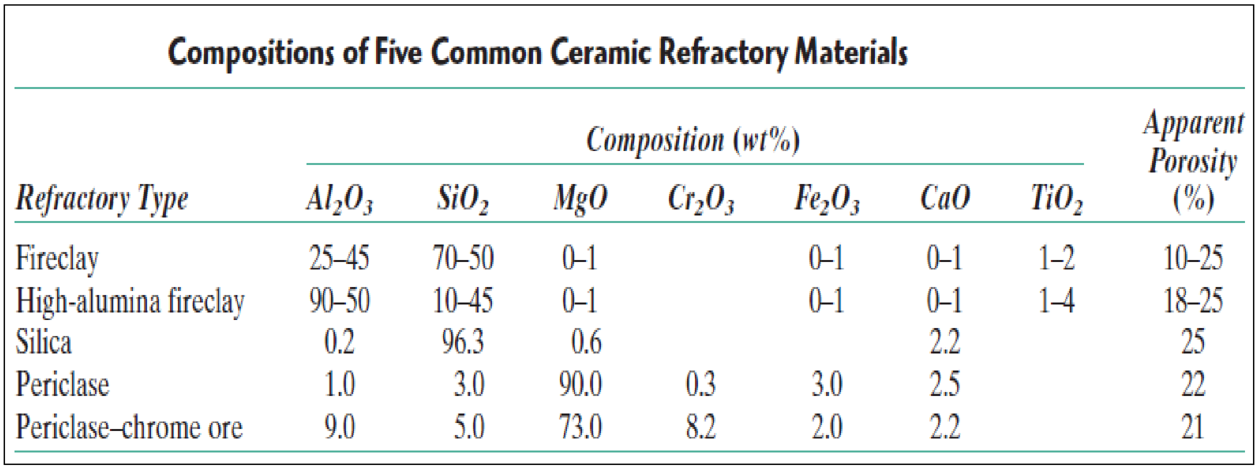
- **CLAY PRODUCTS**

One of the most widely used ceramic raw materials is clay. This inexpensive ingredient, found naturally in great abundance, often is naturally used as mined (extracted) (without any upgrading of quality). Another reason for its popularity lies in the ease of forming; when mixed in the proper proportions, clay and water form a plastic mass that is very responsive to shaping. The formed piece is dried to remove some of the moisture, after firing at an elevated temperature to improve its mechanical strength. Most of the clay-based products are classified into two groups: the structural clay products and the whitewares. Structural clay products include building bricks, tiles, and drain pipes—applications in which structural integrity is important. The whiteware ceramics become white after the high-temperature firing. Porcelain is included in this group.

LECTURE 2

- **REFRACTORIES**

Another important class of ceramics that are utilized in large weights is the refractory (inflexible) ceramics. The significant properties of these materials include the ability to withstand high temperatures without melting or decomposing, and the capacity to remain unreactive or motivated when exposed to severe environments. In addition, the ability to provide thermal insulation is often an important consideration. Refractory materials are marketed in a variety of forms, but bricks are the most common. Typical applications include furnace coatings for glass manufacturing and metallurgical heat treatment. The performance of a refractory ceramic, to a large degree, depends on its composition. There are several classifications of commercial refractories according to the table below:



Compositions of Five Common Ceramic Refractory Materials

	Composition (wt%)							*Apparent Porosity (%)*
Refractory Type	Al_2O_3	SiO_2	MgO	Cr_2O_3	Fe_2O_3	CaO	TiO_2	
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

• ABRASIVES

Abrasive ceramics are used to wear, grind, or cut away other material, which necessarily is softer. Therefore, the prime need for this group of materials is hardness or wear resistance; in addition, a high degree of toughness is essential to ensure that the abrasive particles do not easily fracture. Diamonds, both natural and synthetic (artificial), are utilized as abrasives; however, they are relatively expensive. The more common ceramic abrasives include silicon carbide, tungsten carbide (WC), aluminum oxide and silica sand.

Abrasives are used in several forms—bonded to grinding wheels, as coated abrasives. Coated abrasives are those in which an abrasive powder is coated on some type of paper or cloth material. Wood, metals, ceramics, and plastics are all frequently ground and polished using this form of abrasive.

For more information and clarification concerning Piezoelectric Ceramics visit https://youtu.be/EzoGLKh7n24 (Ceramic Abrasive Range)

- **CEMENTS**

Cements are inorganic materials produced in extremely large quantities. The characteristic feature of these materials is that when mixed with water, they form a paste that subsequently sets (settle on, does not change its shape) and hardens. Also, some of these materials act as a bonding phase that chemically binds particulate aggregates into a single cohesive structure. The bond of the cement develops at room temperature. Portland cement is the most common type of cements.

One important structure made of cement is concrete. Concrete is a mixture of cement, water, fine aggregate and coarse aggregate of sands or stones, which hardens to a stone-like mass.

• ADVANCED CERAMICS

Many of our modern technologies utilize and will continue to utilize advanced ceramics because of their unique mechanical, chemical, electrical, magnetic, and optical properties and property combinations. Piezoelectric ceramics is an example of advanced ceramics.

Piezoelectric Ceramics:

A few ceramic materials (as well as some polymers) exhibit the unusual phenomenon of piezoelectricity1—electric polarization2 (i.e., an electric field or voltage) is generated in the ceramic crystal when a mechanical strain (dimensional change) is imposed on it. The inverse piezoelectric effect is also displayed by this group of materials; that is, a mechanical strain results from the imposition of an electrical field. Piezoelectric materials may be utilized as a converter between electrical and mechanical energies. One of the early uses of piezoelectric ceramics was in sonar, wherein underwater objects (e.g., submarines) are detected and their positions determined using an ultrasonic emitting and receiving system. A piezoelectric crystal is caused to oscillate (fluctuate) by an electrical signal, which produces high-frequency mechanical vibrations that are transmitted through the water. Upon encountering an object, these signals are reflected back, and another piezoelectric material receives this reflected vibrational energy, which it then converts back into an electrical signal. Distance from the ultrasonic source and reflecting body is determined from the gone (passed) time between sending and receiving events.

For more information and clarification concerning Piezoelectric Ceramics visit https://youtu.be/Bxo2TihSrNg (What Is Piezoelectricity: Part 1)

LECTURE 3

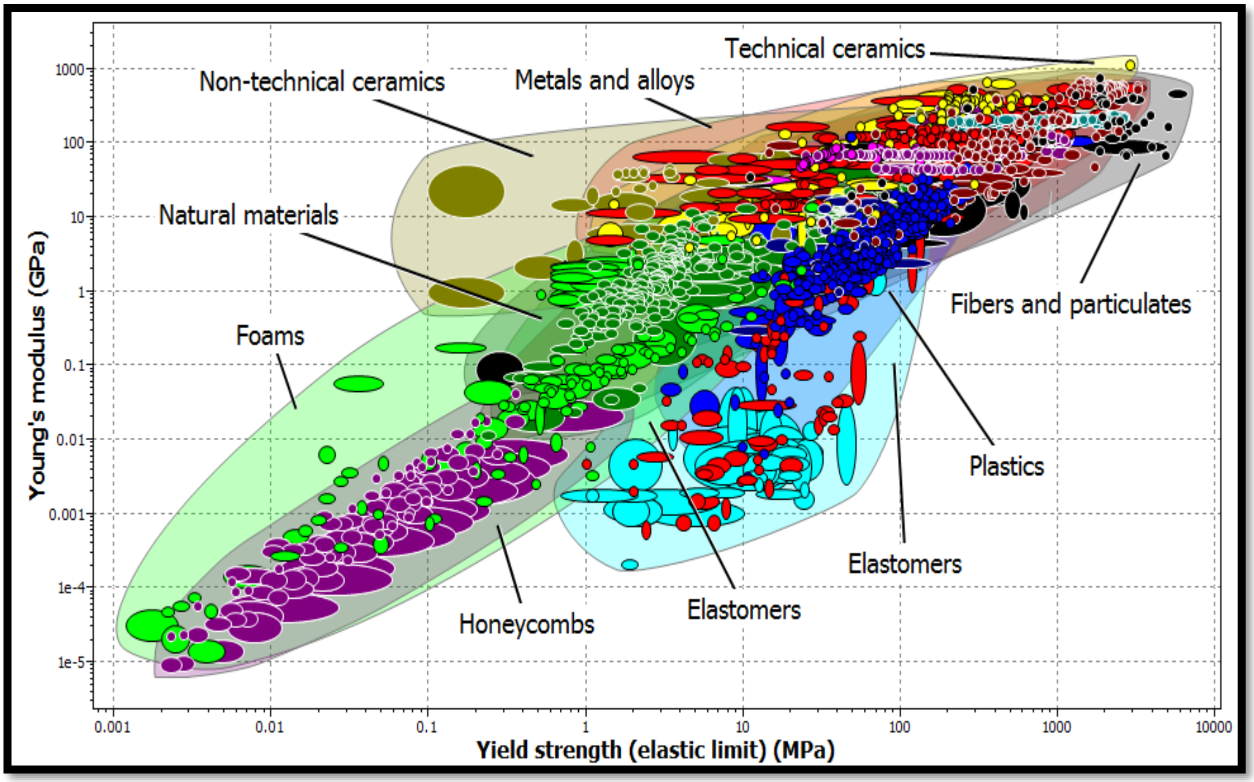
General Properties of Ceramic

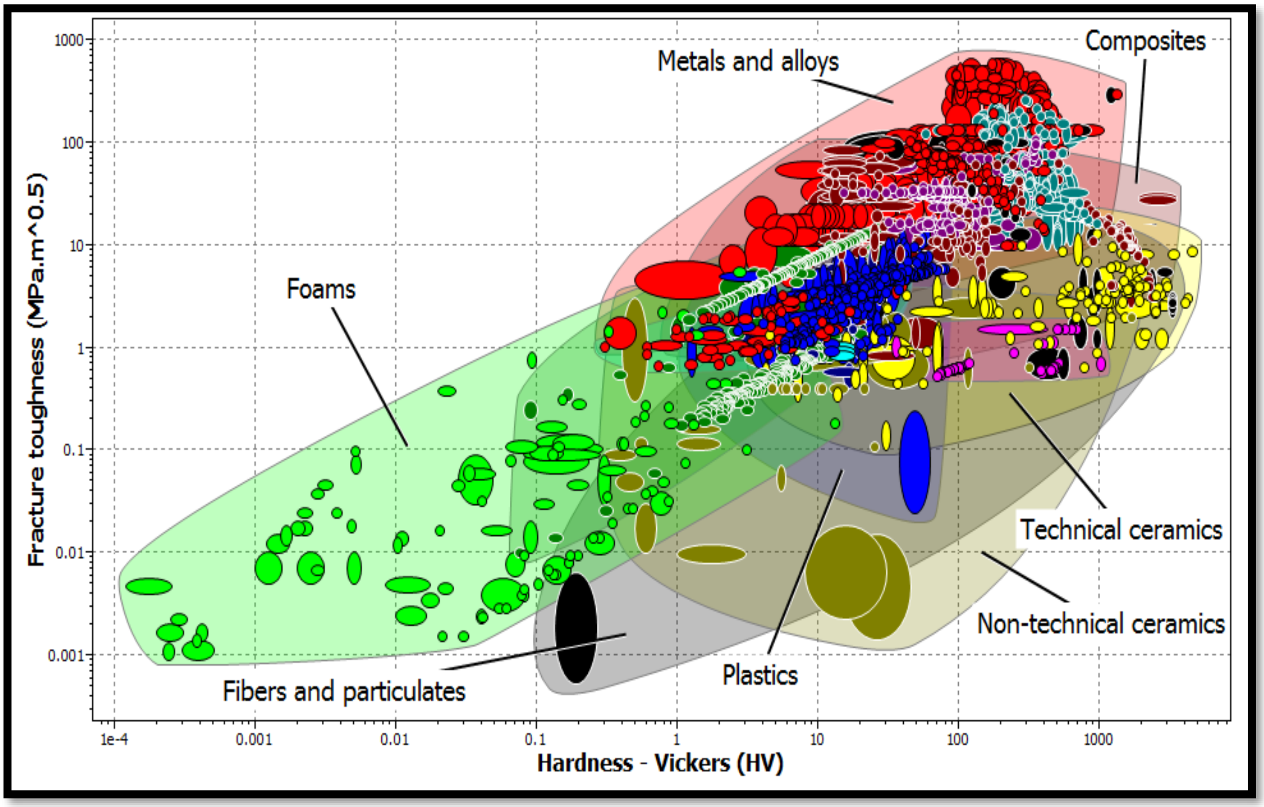
Ceramics generally have specific properties associated with them such as:

Compressive strength: Ceramics are stronger in compression than in tension, whereas metals have comparable (equivalent) tensile and compressive strengths. This difference is important when we use ceramic components for load-bearing applications. It is necessary to consider the stress distributions in the ceramic to ensure that they are compressive. An important example is in the design of concrete bridges–the concrete, a CMC (ceramic matrix ceramic), must be kept in compression. Ceramics generally have low toughness, although combining them in composites can dramatically improve this property.

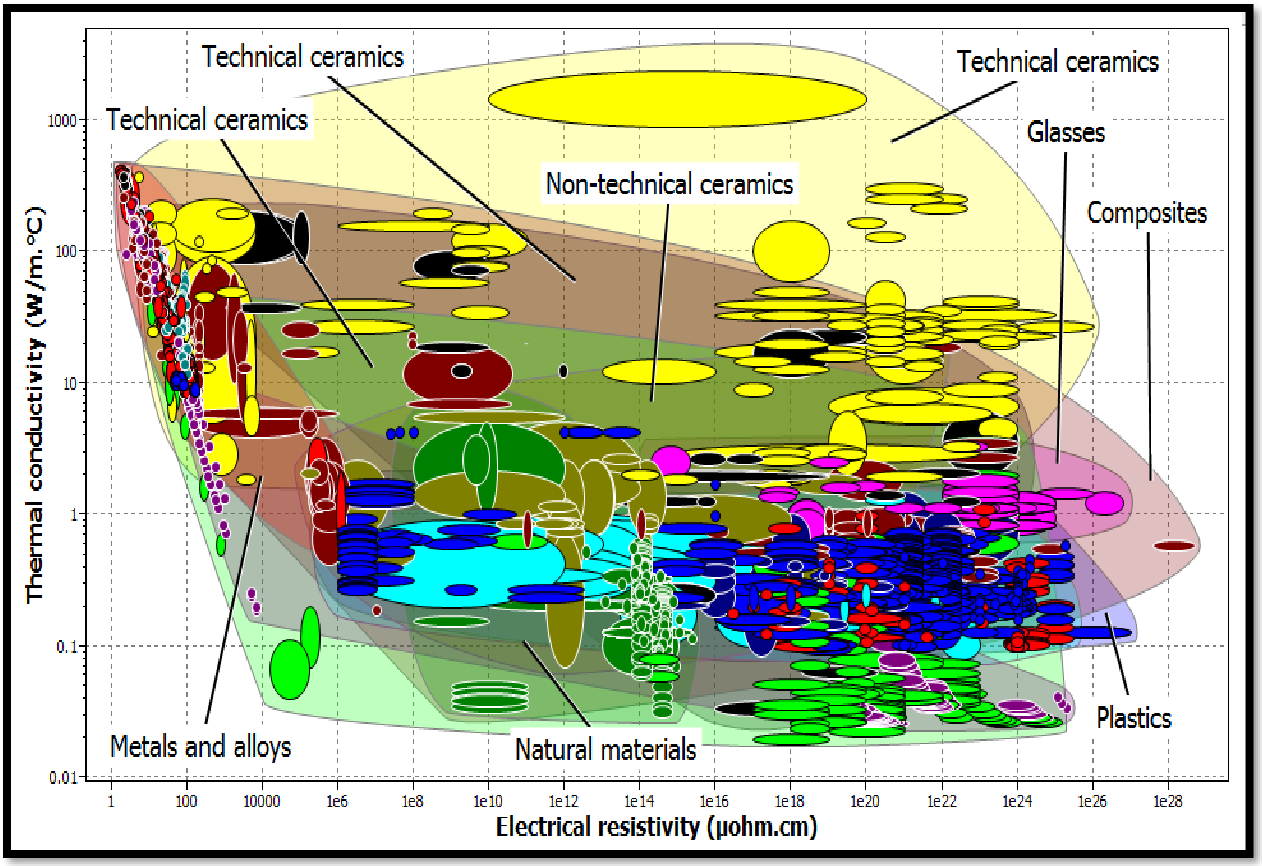
Brittleness: This probably comes from personal experiences such as dropping a glass cup or a plate. The reason that the majority of ceramics are brittle is the mixed ionic‑covalent bonding that holds the constituent atoms together. At high temperatures (above the glass transition temperature) glass no longer behaves in a brittle manner; it behaves as a viscous liquid. That is why it is easy to form glass into complicated shapes. So, what we can say is that most ceramics are brittle at room temperature but not necessarily at elevated temperatures. The brittle behaviour of ceramics gives them low fracture toughness.

Ceramic materials are relatively stiff and strong—stiffness and strength are comparable (similar) to those of the metals. In addition, ceramics are typically very hard. On the other hand, they are extremely brittle (lack ductility) and are highly vulnerable to fracture.

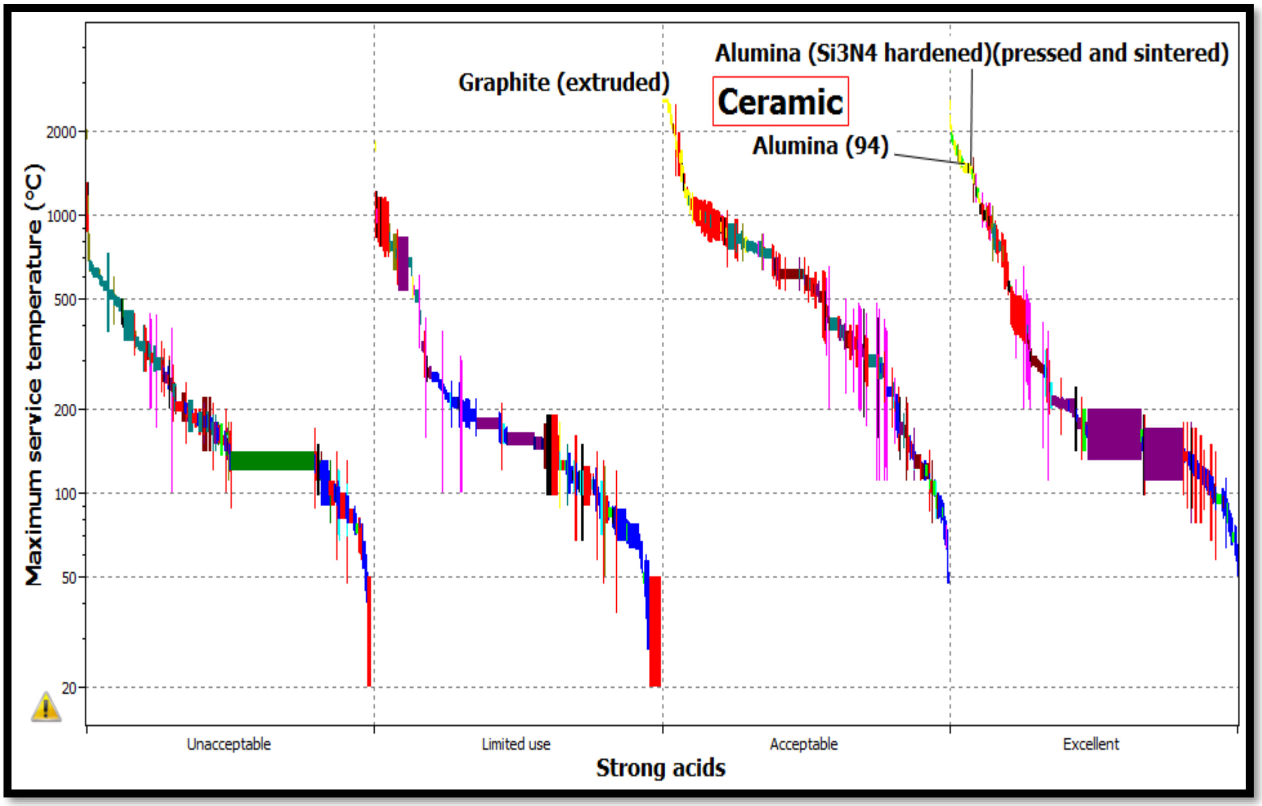

Technical ceramics
Non-technical ceramics
Metals and alloys
Natural materials
Fibers and particulates
Foams
Plastics
Elastomers
Honeycombs
Elastomers
Young's modulus (GPa)
1000
100
10
1
0.1
0.01
0.001
1e-4
1e-5
0.001
0.01
0.1
1
10
100
1000
10000
Yield strength (elastic limit) (MPa)


Composites
Metals and alloys
Foams
Technical ceramics
Non-technical ceramics
Plastics
Fibers and particulates
Fracture toughness (MPa.m^0.5)
1000
100
10
1
0.1
0.01
0.001
1e-4
0.001
0.01
0.1
1
10
100
1000
Hardness - Vickers (HV)

Poor electrical and thermal conduction except for Diamond and the oxide ceramic, ReO3. The valence electrons are tied up in bonds and are not free as they are in metals. In metals, it is the free electrons that determine many of their electrical and thermal properties.



Chemical insensitivity: A large number of ceramics are stable in both harsh chemical and thermal environments. Pyrex glass is used widely in chemistry laboratories specifically because it is resistant to many corrosive chemicals, stable at high temperatures (it does not soften until 1100 K), and is resistant to thermal shock because of its low coefficient of thermal expansion (33 × 10–7 K^{-1}). It is also widely used in bakeware.



So, they are more resistant to high temperatures and harsh environments than metals and polymers.

Transparency: Many ceramics such as precious stones and optical fibres are transparent. Metals are transparent to visible light only when they are very thin, typically less than 0.1 μm. Although it is always possible to find at least one ceramic that shows a typical behaviour, the properties we have mentioned here are in many cases different from those shown by metals and polymers.

LECTURE 4

Fabrication and Processing of Ceramics

One chief concern in the application of ceramic materials is the method of fabrication.

Many of the metal-forming operations rely on casting and/or techniques that involve some form of plastic deformation. Since ceramic materials have relatively high melting temperatures, casting them is normally impractical. Furthermore, in most instances the brittleness of these materials prevents (prohibits) deformation. Some ceramic pieces are formed from powders (or particulate collections) that must ultimately be dried and fired. Glass shapes are formed at elevated temperatures from a fluid mass that becomes very viscous upon cooling. A scheme for the several types of ceramic-forming techniques is presented in Figure 1:

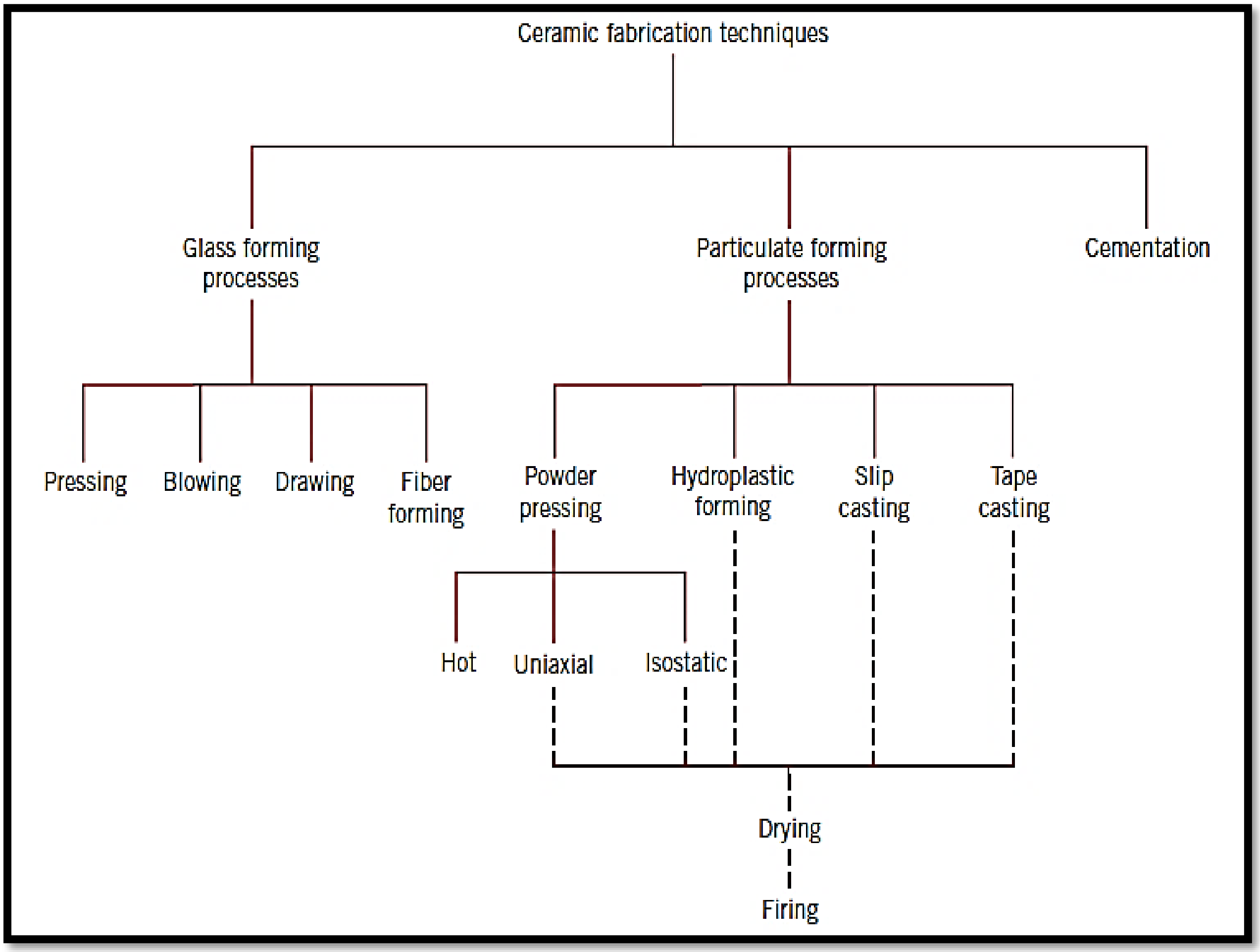


Figure 1: A classification scheme for ceramic forming techniques.

FABRICATION AND PROCESSING OF GLASSES AND GLASS–CERAMICS

Glass Properties

Before we discuss specific glass-forming techniques, some of the temperature sensitive properties of glass materials must be presented. Glassy, or noncrystalline, materials do not solidify in the same sense as do those that are crystalline. Upon cooling, a glass becomes more and more viscous in a continuous manner with decreasing temperature; there is no definite temperature at which the liquid transforms to a solid as with crystalline materials. In fact, one of the distinctions between crystalline and noncrystalline materials lies in the dependence of **specific volume** (or volume per unit mass) on temperature, as illustrated in Figure 2.

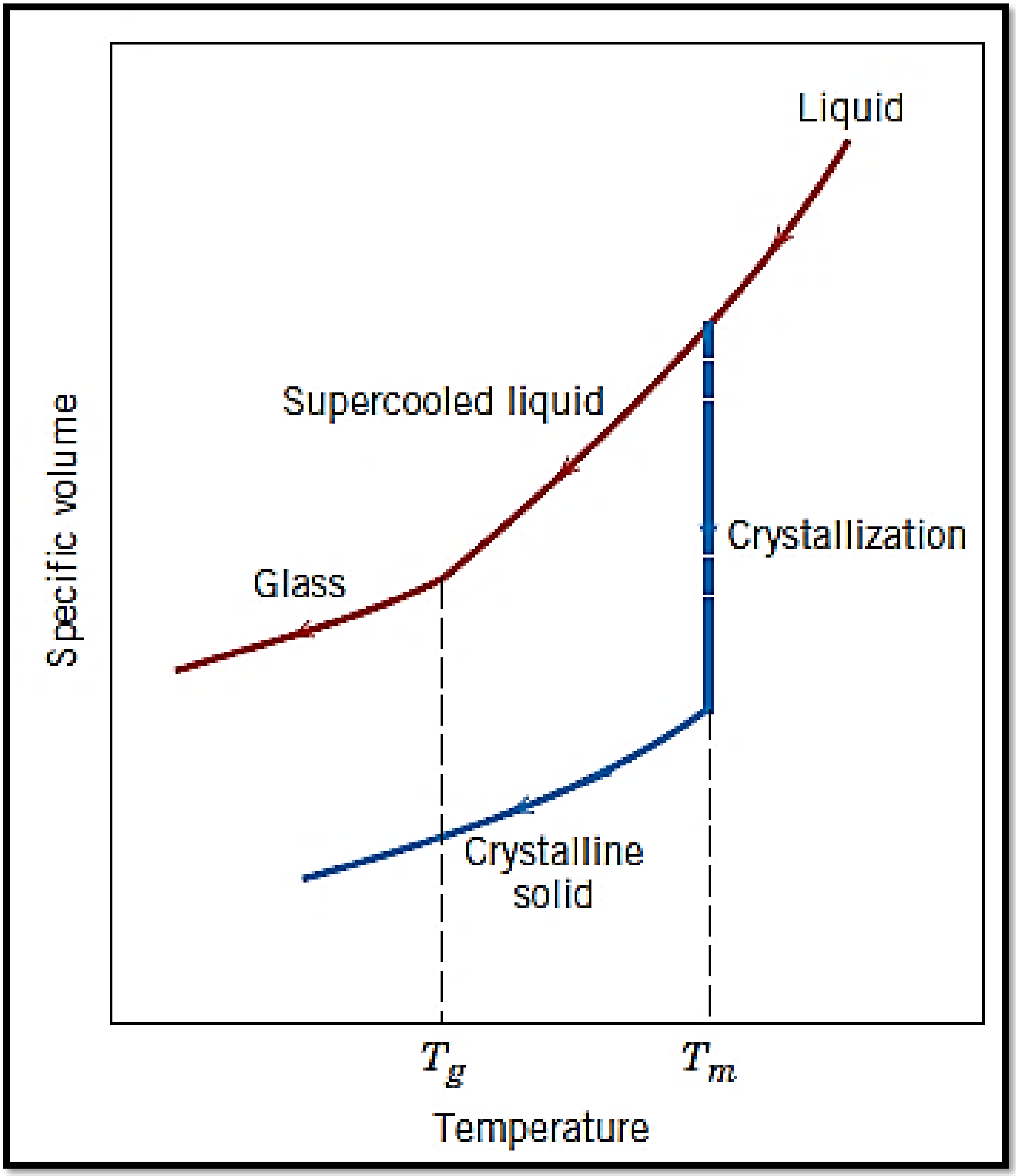


Figure 2: Contrast of specific volume versus- temperature behavior of crystalline and noncrystalline materials. Crystalline materials solidify

at the melting temperature Tm Characteristic of the noncrystalline state is the glass transition temperature Tg.

For crystalline materials, there is a discontinuous decrease in volume at the melting temperature Tm. However, for glassy materials, volume decreases continuously with temperature reduction; a slight decrease in slope of the curve occurs at what is called the glass transition temperature, below this temperature, the material is considered to be a glass; above, it is first a super cooled liquid, and finally a liquid.

Also important in glass-forming operations are the viscosity–temperature characteristics of the glass. Figure 3 plots the logarithm of viscosity versus the temperature for fused silica, high silica, borosilicate, and soda–lime glasses.

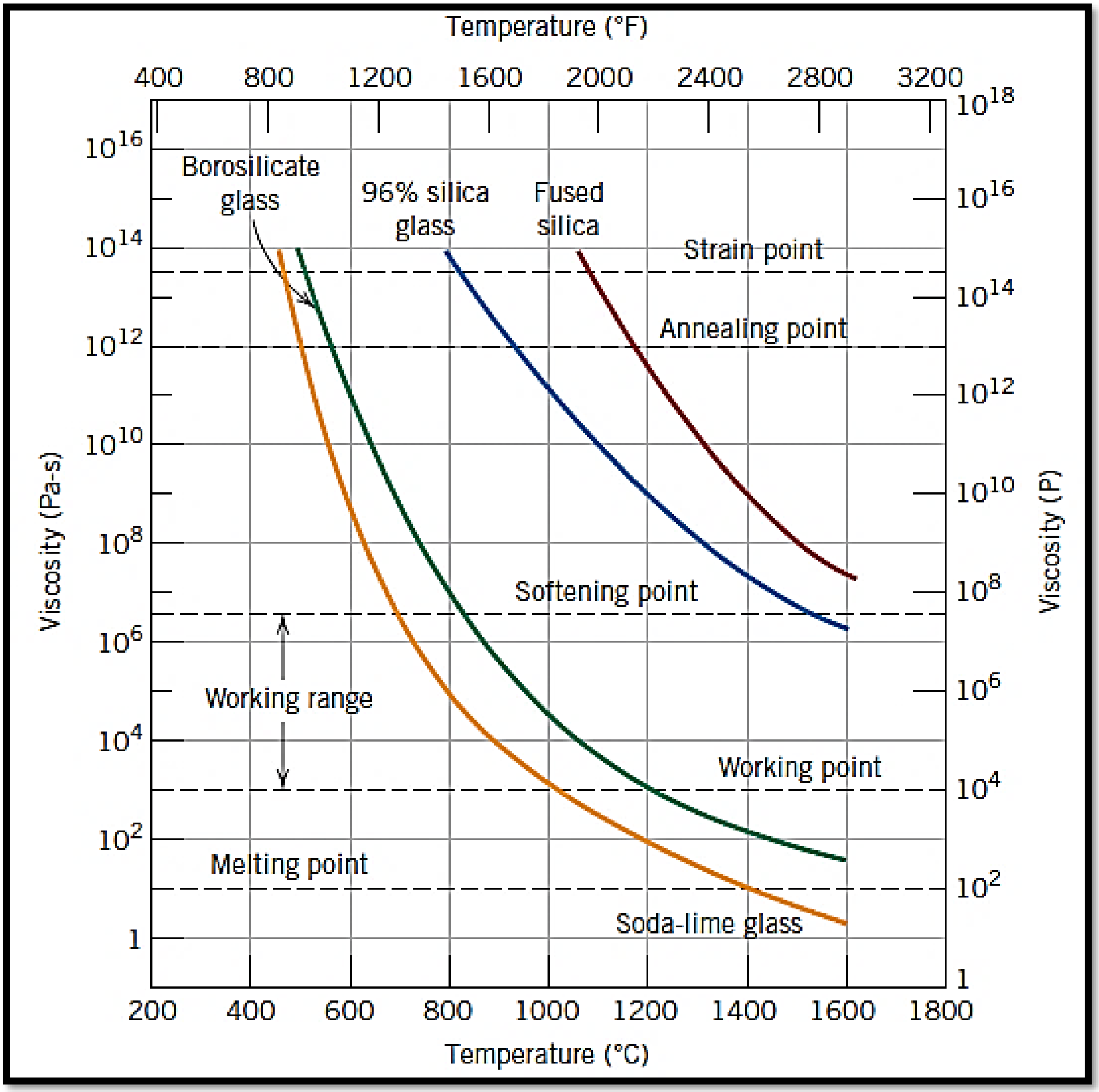


Figure 3: Logarithm of viscosity versus temperature for fused silica and three silica glasses.

On the viscosity scale several specific points that are important in the fabrication and processing of glasses are labeled:

1. The **melting point** corresponds to the temperature at which the viscosity is 10 Pa-s (100 P); the glass is fluid enough to be considered a liquid.

2. The **working point** represents the temperature at which the viscosity is 10^3

Pa-s (10^4 P); the glass is easily deformed at this viscosity.

3. The **softening point,** the temperature at which the viscosity is 4x 10^6 Pa-s (4x 10^7 P), is the maximum temperature at which a glass piece may be handled without causing significant dimensional alterations.

4. The **annealing point** is the temperature at which the viscosity is 10^{12} Pa-s (10^{13} P); at this temperature, atomic diffusion is sufficiently rapid that any residual stresses may be removed within about 15 min.

5. The **strain point** corresponds to the temperature at which the viscosity becomes 3×10^{13} Pa-s (3×10^{14} P); for temperatures below the strain point (less than 450 ^{0}C for soda lime glass for example), fracture will occur before the beginning of plastic deformation. The glass transition temperature will be above the strain point.

Most glass-forming operations are carried out within the working range—between the working and softening temperatures. Of course, the temperature at which each of these points occurs depends on glass composition. For example, the softening points for soda–lime and 96% silica glasses from Figure 3 are about 700 and 1550 ^{o}C, respectively.

That is, forming operations may be carried out at significantly lower temperatures for the soda–lime glass.

LECTURE 5

Glass Forming

Glass is produced by heating the raw materials to a high temperature above which melting occurs. Silica is usually supplied as common quartz sand, whereas Na_2O and CaO are added as soda ash (Na_2CO_3) and limestone ($CaCO_3$). For most applications, especially when optical transparency is important, it is essential that the glass product be homogeneous and pores free. Homogeneity is achieved by complete melting and mixing of the raw ingredients. Four different forming methods are used to fabricate glass products: pressing, blowing, drawing, and fiber forming.

Pressing is used in the fabrication of relatively thick-walled pieces such as plates and dishes. The glass piece is formed by pressure application in a graphite-coated cast iron mold having the desired shape; the mold is normally heated to ensure an even (flat/smooth) surface.

Although some glass **blowing** is done by hand, especially for art objects, the process has been completely automated for the production of glass jars (containers), bottles, and light bulbs. The several steps involved in one such technique are illustrated in Figure 1.

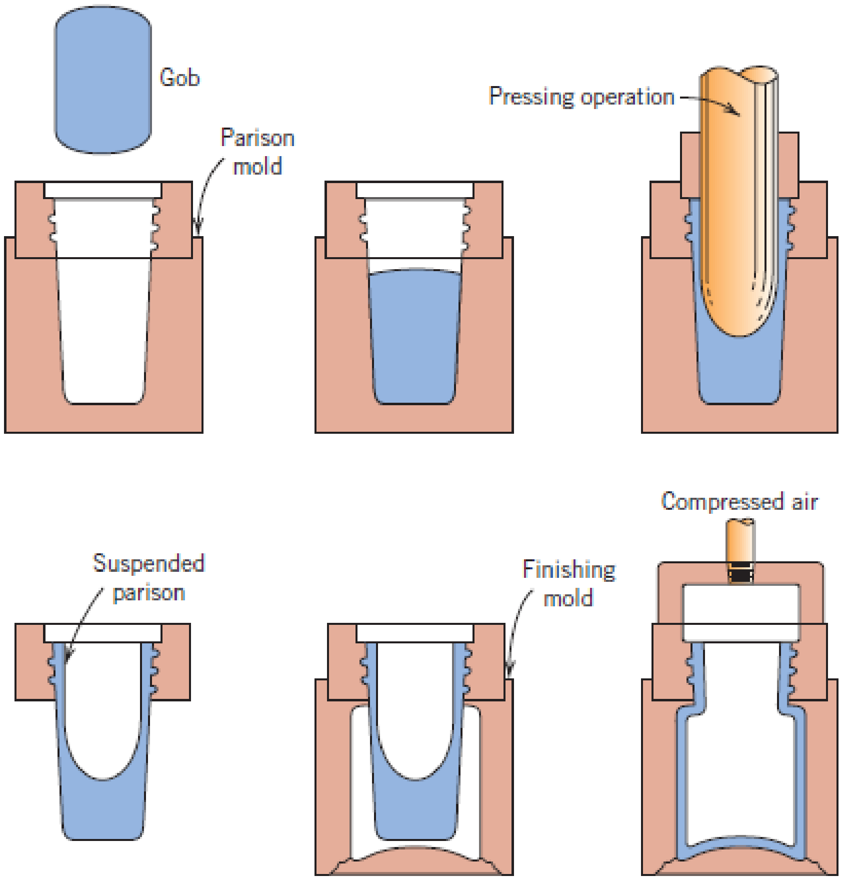


Figure 1 The press-and-blow technique for producing a glass bottle. (Adapted from C. J. Phillips, *Glass: The Miracle Maker*. Reproduced by permission of Pitman Publishing Ltd., London.)

A temporary shape is formed by mechanical pressing in a mold. This piece is inserted into a finishing or blow mold and forced to fit in the mold contours (outlines/shape) by the pressure created from a blast of air.

Drawing is used to form long glass pieces such as sheet, rod, tubing, and fibers, which have a constant cross section. Continuous glass fibers are formed in a rather sophisticated drawing operation. The molten glass is placed in a platinum heating chamber (small room). Fibers are formed by drawing the molten glass through many small holes (outlets) at the chamber base. The glass viscosity, which is critical, is controlled by chamber and outlets temperatures.

It may also be fabricated by hot **rolling**. Flatness and the surface finish may be improved significantly by floating or moving the sheet on a bath of molten tin at an elevated temperature; the piece is slowly cooled and subsequently heat treated by annealing.

For more info visit glass forming.mp4

LECTURE 6

Heat Treating of Glasses and glasses ceramic

Annealing

When a ceramic material is cooled from an elevated temperature, internal stresses, called thermal stresses, may be introduced as a result of the difference in cooling rate and thermal contraction between the surface and interior regions. These thermal stresses are important in brittle ceramics, especially glasses, since they may weaken the material or, in extreme cases, lead to fracture, which is termed thermal shock. Normally, attempts are made to avoid thermal stresses, which may be accomplished by cooling the piece at a sufficiently slow rate. Once such stresses have been introduced, however, elimination, or at least a reduction in their magnitude, is possible by an annealing heat treatment in which the glass is heated to the annealing point, then slowly cooled to room temperature.

Glass Tempering

The strength of a glass piece may be enhanced by intentionally inducing (generating) compressive residual surface stresses. This can be accomplished by a heat treatment procedure called thermal tempering. With this technique, the glassware is heated to a temperature below the softening point. It is then cooled to room temperature in a stream of air or, in some cases, an oil bath. The residual stresses arise from differences in cooling rates for surface and interior regions. Initially, the surface cools more rapidly and, once having dropped to a temperature below the strain point, becomes rigid. At this time, the internal parts of the glassware, having cooled less rapidly, is at a higher temperature (above the strain point) and, therefore, is still plastic. With continued cooling, the interior attempts to contract to a greater degree than the now rigid exterior will allow. Thus, the inside tends to draw in the outside, or to impose inward radial stresses. As a consequence, after the glass piece has cooled to room temperature, it stands compressive stresses on the surface, with tensile stresses at interior regions. The room-temperature stress distribution over a cross section of a glass plate is represented schematically in Figure 2. The failure of ceramic materials almost always results from a crack that is initiated at the surface by an applied tensile stress. To cause fracture of a tempered glass piece, the magnitude of an externally applied tensile stress must be great enough to first overcome the residual compressive surface stress and, in addition, to stress the surface in tension sufficiently to initiate a crack, which may then propagate. For an untempered glass, a crack will be introduced at a lower external stress level, and, consequently, the fracture strength will be smaller. Tempered glass is used for applications in which high strength is important; these include large doors and eyeglass lenses.

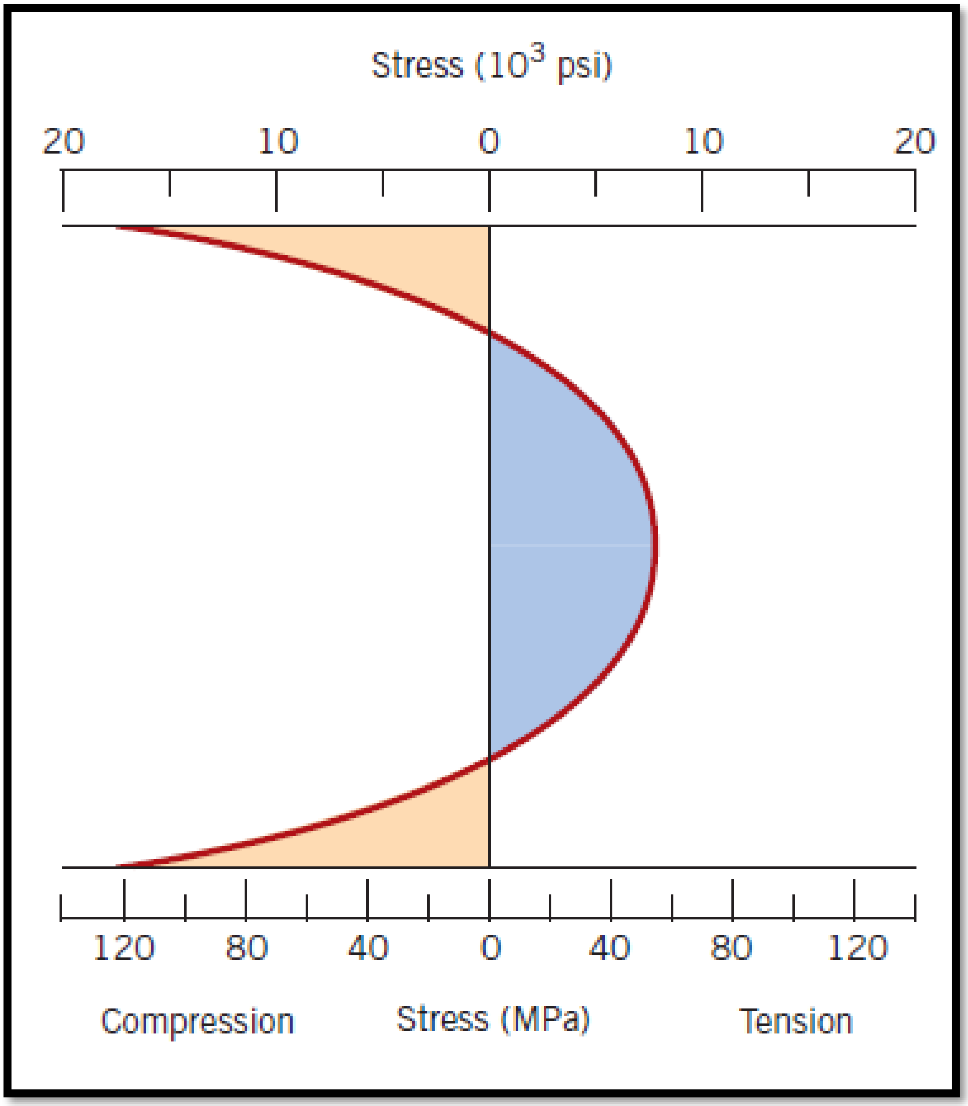


Figure 2: Room-temperature residual stress distribution over the cross section of a tempered glass plate.

LECTURE 7

FABRICATION AND PROCESSING OF CLAY PRODUCTS

This class of materials includes the structural clay products and the whitewares. In addition to clay (being composed of alumina (Al_2O_3) and silica (SiO_2)), many of these products also contain other ingredients. After having been formed, pieces most often must be subjected to drying and firing operations; each of the ingredients influences the changes that take place during these processes and the features of the finished piece.

The as-mined raw materials usually have to go through a milling or grinding operation in which particle size is reduced; this is followed by screening or sizing to produce a powdered product having a desired range of particle sizes. For multicomponent systems, powders must be thoroughly (totally) mixed with water and perhaps other ingredients to give flow characteristics that are compatible with the particular forming technique. The formed piece must have sufficient mechanical strength to remain intact during transporting, drying, and firing operations. Two common shaping techniques are utilized for forming clay-based compositions: **hydroplastic forming** and **slip casting.**

Hydroplastic Forming

As mentioned above, clay minerals, when mixed with water, become highly plastic and flexible and may be molded without cracking; however, they have extremely low yield strengths. The consistency (water–clay constant ratio) of the hydroplastic mass must give a yield strength sufficient to permit a formed ware to maintain its shape during handling and drying.

The most common hydroplastic forming technique is extrusion, in which a stiff plastic ceramic mass is forced through a die cavity having the desired cross-sectional geometry; it is similar to the extrusion of metals. Brick, pipe, ceramic blocks, and tiles are all commonly fabricated using hydroplastic forming.

Slip Casting (solid and drain)

Another forming process used for clay-based compositions is slip casting. A slip is a suspension of clay and/or other nonplastic materials in water. When poured into a porous mold, water from the slip is absorbed into the mold, leaving behind a solid layer on the mold wall the thickness of which depends on the time. This process may be continued until the entire mold cavity becomes solid (solid casting). Or it may be finished when the solid shell wall reaches the desired thickness, by inverting the mold and pouring out the excess slip; this is termed drain casting. As the cast piece dries and shrinks, it will release from the mold wall; at this time the mold may be disassembled (take to pieces) and the cast piece removed. The nature of the slip is extremely important; it must have a high specific gravity and yet be very fluid and pourable. These characteristics depend on the solid to water ratio and other agents that are added. An acceptable casting rate is an essential requirement. In addition, the cast piece must be free of bubbles, and it must have a low drying shrinkage and a relatively high strength.

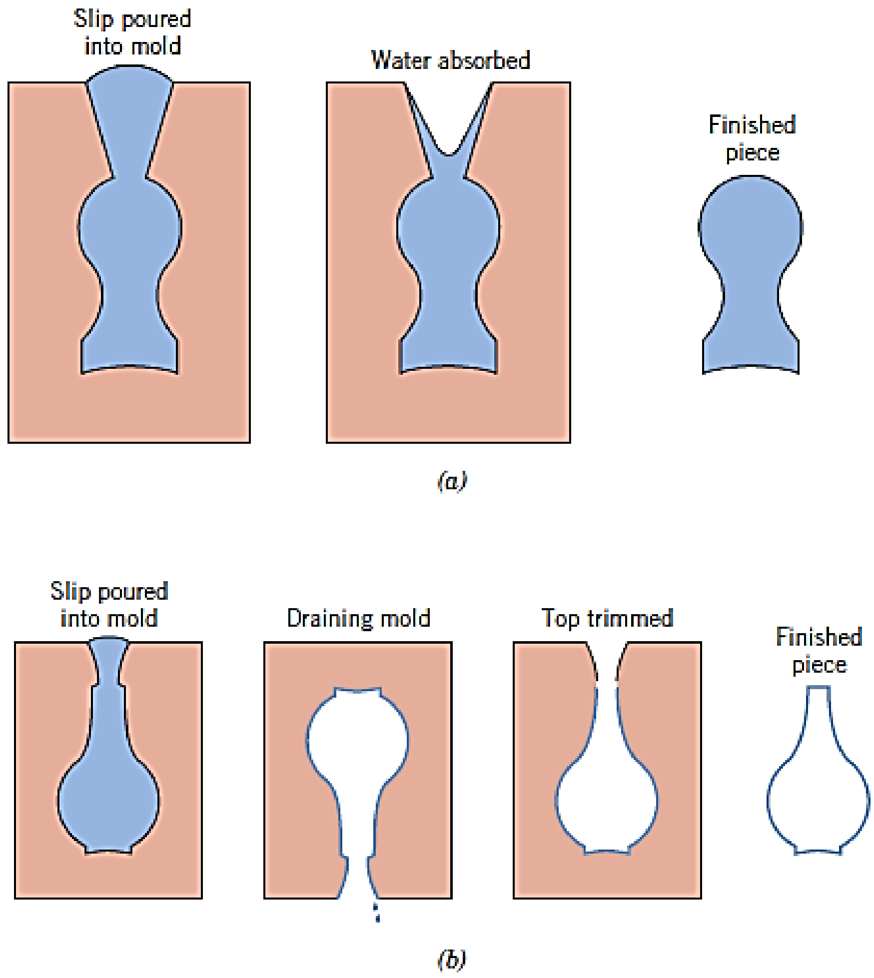


Figure The steps in (*a*) solid and (*b*) drain slip casting using a plaster of paris mold. (From W. D. Kingery, *Introduction to Ceramics.* Copyright © 1960 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

The properties of the mold itself influence the quality of the casting. Normally, plaster of Paris, which is economical, relatively easy to fabricate into complicated shapes is used as the mold material. Most molds are multipiece items that must be assembled before casting. Also, the mold porosity may be diverse to control the casting rate. The relatively complex ceramic shapes that may be produced by means of slip casting include art objects, and specialized scientific laboratory ware such as ceramic tubes.

LECTURE 8

Drying and Firing

A ceramic piece that has been formed hydroplastically or by slip casting retains significant porosity and insufficient strength for most practical applications. In addition, it may still contain some liquid (e.g., water), which was added to assist in the forming operation. This liquid is removed in a drying process; density and strength are enhanced as a result of a high-temperature heat treatment or firing procedure. A body that has been formed and dried but not fired is termed green. Drying and firing techniques are critical since defects (e.g., distortion, and cracks) may be introduced during the operation. These defects normally result from stresses that are set up from nonuniform shrinkage.

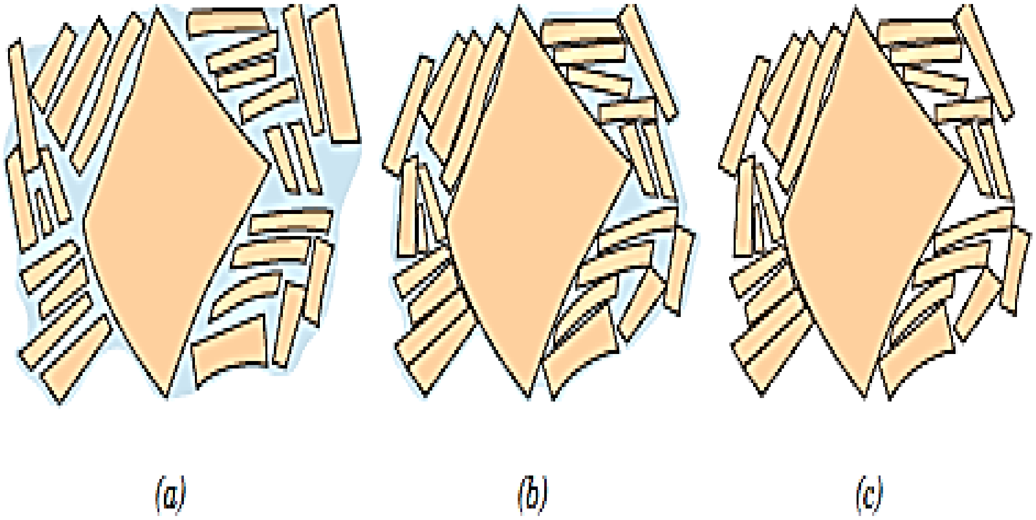
Drying

As a clay-based ceramic body dries, it also experiences some shrinkage. In the early stages of drying the clay particles are virtually surrounded by and separated from one another by a thin film of water. As drying progresses and water is removed, the interparticle separation decreases, which is revealed as shrinkage.

During drying it is critical to control the rate of water removal. Drying at interior regions of a body is accomplished by the diffusion (dispersion) of water molecules to the surface where evaporation occurs. If the rate of evaporation is greater than the rate of diffusion, the surface will dry (and as a consequence shrink) more rapidly than the interior, with a high probability of the formation of the above-mentioned defects. The rate of surface evaporation should be diminished to, at most, the rate of water diffusion; evaporation rate may be controlled by temperature, humidity (moisture), and the rate of airflow.

Other factors also influence shrinkage. One of these is body thickness; nonuniform shrinkage and defect formation are more obvious (apparent/clearer) in thick pieces than in thin ones. Water content of the formed body is also critical: the greater the water content, the more extensive the shrinkage.

Consequently, the water content is ordinarily kept as low as possible. Clay particle size also has an influence; shrinkage is enhanced as the particle size is decreased. To minimize shrinkage, the size of the particles may be increased, or nonplastic materials having relatively large particles may be added to the clay. Microwave energy may also be used to dry ceramic wares. One advantage of this technique is that the high temperatures used in conventional methods are avoided; drying temperatures may be kept to below 50 ^{0}C. This is important because the drying of some temperature-sensitive materials should be kept as low as possible.



(a) (b) (c)

Figure Several stages in the removal of water from between clay particles during the drying process. (*a*) Wet body. (*b*) Partially dry body. (*c*) Completely dry body. (From W. D. Kingery, *Introduction to Ceramics*. Copyright © 1960 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

LECTURE 9

Firing

After drying, a body is usually fired at a temperature between 900 and 1400 ^{O}C; the firing temperature depends on the composition and desired properties of the finished piece. During the firing operation, the density is further increased (with an attendant (related) decrease in porosity) and the mechanical strength is enhanced.

When clay-based materials are heated to elevated temperatures, some rather complex and involved reactions occur. One of these is vitrification, the gradual formation of a liquid glass that flows into and fills some of the pore volume. The degree of vitrification depends on firing temperature and time, as well as the composition of the body. The temperature at which the liquid phase forms is lowered by the addition of fluxing agents such as feldspar. This fused phase flows around the remaining unmelted particles and fills in the pores as a result of surface tension forces (or capillary action); shrinkage also accompanies this process. Upon cooling, this fused phase forms a glassy matrix that results in a dense, strong body. Thus, the final microstructure consists of the vitrified phase, any unreacted quartz particles, and some porosity. Figure 13.14 is a scanning electron micrograph of a fired porcelain in which may be seen these microstructural elements.

The degree of vitrification, of course, controls the room-temperature properties of the ceramic ware; strength, durability, and density are all enhanced as it increases.

The firing temperature determines the extent to which vitrification occurs; that is, vitrification increases as the firing temperature is raised. Building bricks are ordinarily fired around and are relatively porous. On the other hand, firing of highly vitrified porcelain, which borders on being optically translucent, takes place at much higher temperatures. Complete vitrification is avoided during firing, since a body becomes too soft and will collapse.

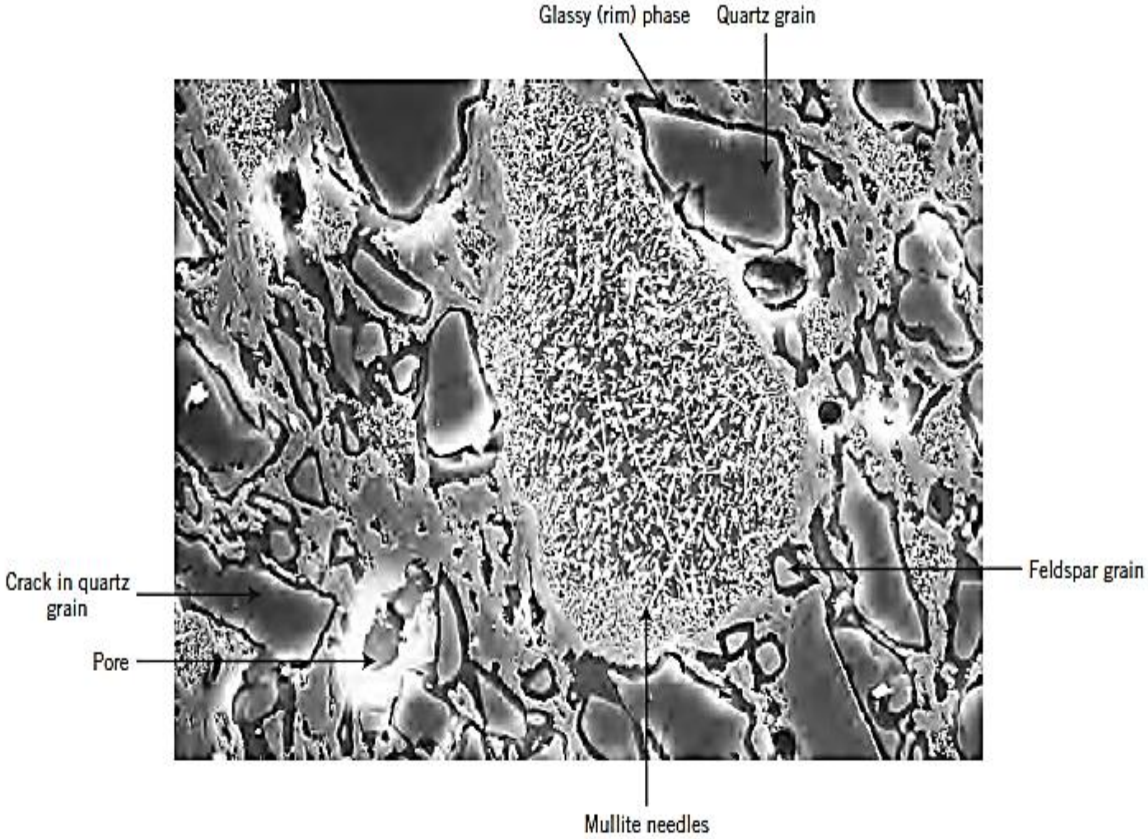


Figure 13.14 Scanning electron micrograph of a fired porcelain specimen (etched 15 s, 5°C, 10% HF) in which may be seen the following features: quartz grains (large dark particles), which are surrounded by dark glassy solution rims; partially dissolved feldspar regions (small unfeatured areas); mullite needles; and pores (dark holes with white border regions). Also, cracks within the quartz particles may be noted, which were formed during cooling as a result of the difference in shrinkage between the glassy matrix and the quartz. 1500×. (Courtesy of H. G. Brinkies, Swinburne University of Technology, Hawthorn Campus,

POWDER PRESSING

Several ceramic-forming techniques have already been discussed relative to the fabrication of glass and clay products. Another important and commonly used method that warrants a brief treatment is powder pressing. Powder pressing, the ceramic analogue to powder metallurgy, is used to fabricate both clay and nonclay compositions, including electronic and magnetic ceramics as well as some refractory brick products.

In essence, a powdered mass, usually containing a small amount of water or other binder, is compacted into the desired shape by pressure. The degree of compaction is maximized and fraction of void space is minimized by using coarse and fine particles mixed in appropriate proportions. There is no plastic deformation of the particles during compaction, as there may be with metal powders. One function of the binder is to lubricate the powder particles as they move past one another in the compaction process. There are three basic powder-pressing procedures: uniaxial, isostatic (or hydrostatic), and hot pressing. For uniaxial pressing, the powder is compacted in a metal die by pressure that is applied in a single direction. The formed piece takes on the configuration of die and platens through which the pressure is applied. This method is confined to shapes that are relatively simple; however, production rates are high and the process is inexpensive. The steps involved in one technique are illustrated in the Figure below:

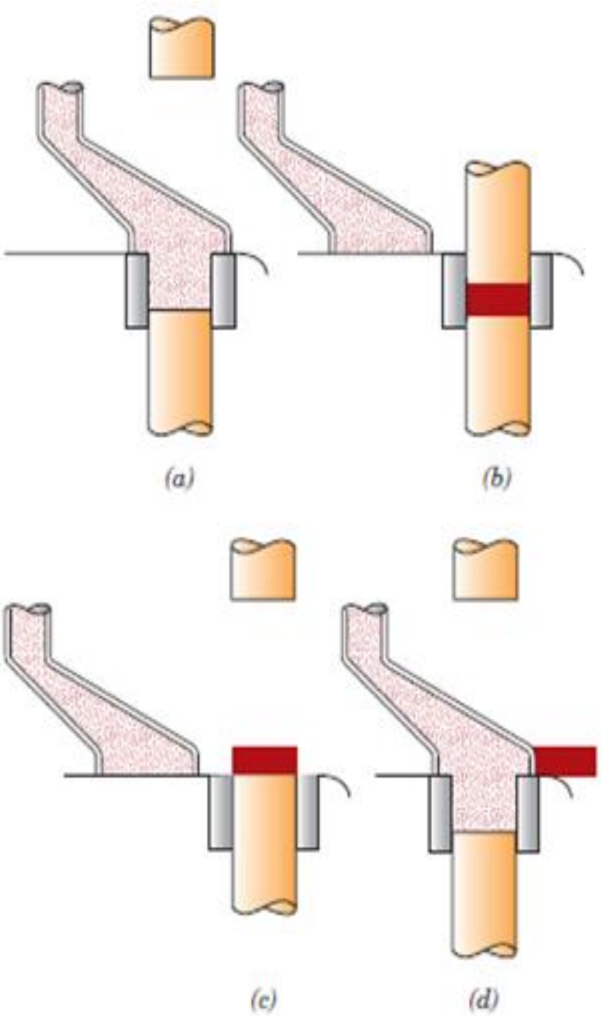


Figure 2 Schematic representation of the steps in uniaxial powder pressing. (*a*) The die cavity is filled with powder. (*b*) The powder is compacted by means of pressure applied to the top die. (*c*) The compacted piece is ejected by rising action of the bottom punch. (*d*) The fill shoe pushes away the compacted piece, and the fill step is repeated. (From W. D. Kingery, Editor, *Ceramic Fabrication Processes,* MIT Press. Copyright © 1958 by the Massachusetts Institute of Technology.)

For isostatic pressing, the powdered material is contained in a rubber envelope and the pressure is applied by a fluid, isostatically (i.e., it has the same magnitude in all directions). More complicated shapes are possible than with uniaxial pressing; however, the isostatic technique is more time consuming and expensive. For both uniaxial and isostatic procedures, a firing operation is required after the pressing operation.

During firing the formed piece shrinks, and experiences a reduction of porosity and an improvement in mechanical integrity. These changes occur by the coalescence of the powder particles into denser mass in a process termed sintering. The mechanism of sintering is schematically illustrated in Figure 3. After pressing, many of the powder particles touch one another (Figure 3.a). During the initial sintering stage, necks form along the contact regions between adjacent particles; in addition, a grain boundary forms within each neck, and every interstice between particles becomes a pore (Figure 3.b). As sintering progresses, the pores become smaller and more spherical in shape (Figure 3.c). A scanning electron micrograph of a sintered alumina material is shown in Figure 3. The driving force for sintering is the reduction in total particle surface area; surface energies are larger in magnitude than grain boundary energies.

Sintering is carried out below the melting temperature so that a liquid phase is normally not present. Mass transport necessary to effect the changes shown in Figure 3 is accomplished by atomic diffusion from the bulk particles to the neck regions.

With hot pressing, the powder pressing and heat treatment are performed simultaneously— the powder aggregate is compacted at an elevated temperature. The procedure is used for materials that do not form a liquid phase except at very high and impractical temperatures; in addition, it is utilized when high densities without

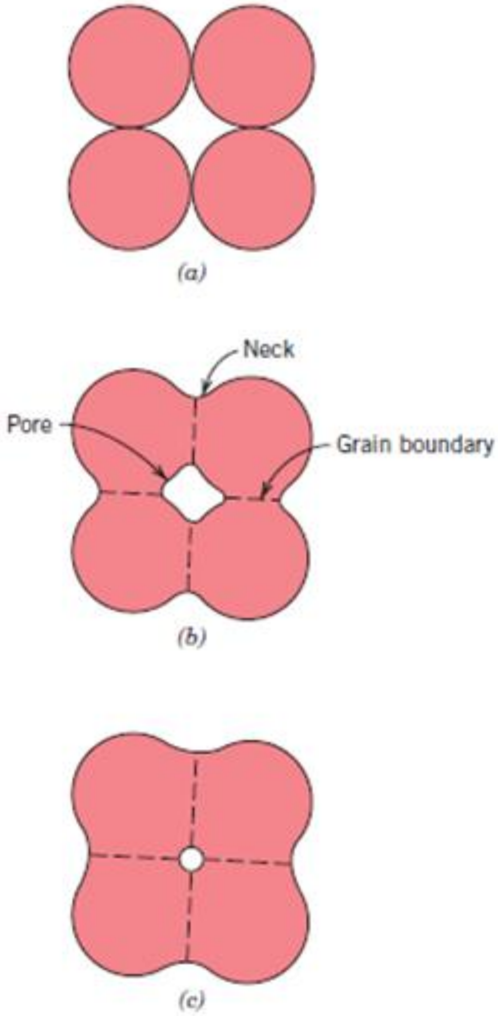


Figure 3 For a powder compact, microstructural changes that occur during firing. (*a*) Powder particles after pressing. (*b*) Particle coalescence and pore formation as sintering begins. (*c*) As sintering proceeds, the pores change size and shape.

appreciable grain growth are desired. This is an expensive fabrication technique that has some limitations. It is costly in terms of time, since both mold and die must be heated and cooled during each cycle. In addition, the mold is usually expensive to fabricate and ordinarily has a short lifetime.

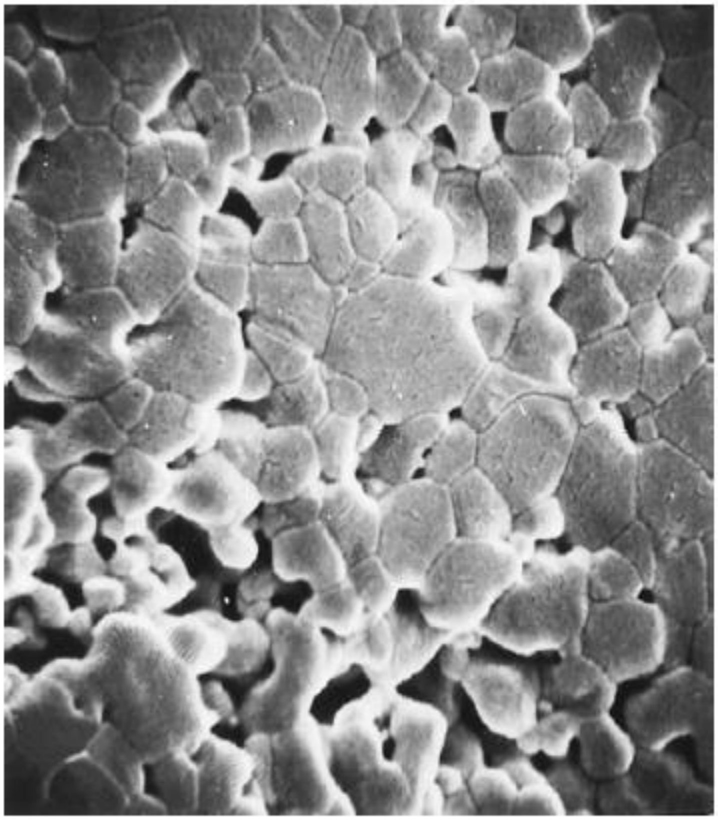


Figure 13.17 Scanning electron micrograph of an aluminum oxide powder compact that was sintered at 1700°C for 6 min. 5000×. (From W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics,* 2nd edition, p. 483. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

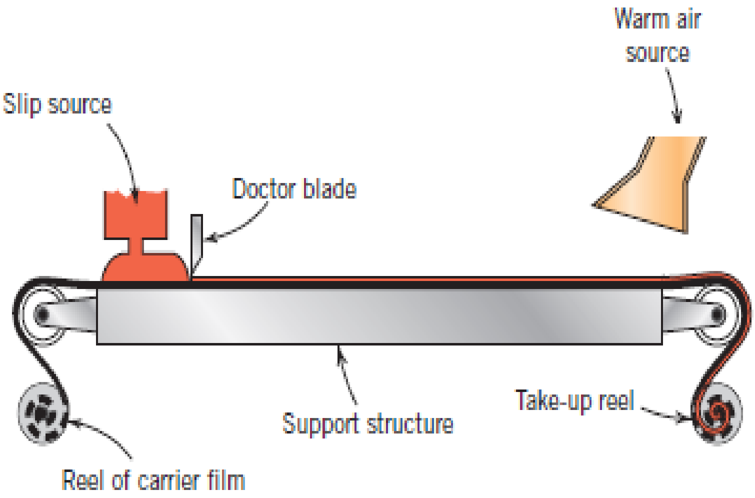


Figure 13.18 Schematic diagram showing the tape-casting process using a doctor blade. (From D. W. Richerson, *Modern Ceramic Engineering,* 2nd edition, Marcel Dekker, Inc., NY, 1992. Reprinted from *Modern Ceramic Engineering,* 2nd edition, p. 472 by courtesy of Marcel Dekker, Inc.)

TAPE CASTING

An important ceramic fabrication technique, tape casting, will now be briefly discussed.

As the name implies, thin sheets of a flexible tape are produced by means of a casting process. These sheets are prepared from slips, in many respects similar to those that are employed for slip casting. This type of slip consists of a suspension of ceramic particles in an organic liquid that also contains binders and plasticizers that are incorporated to impart strength and flexibility to the cast tape. De-airing in a vacuum may also be necessary to remove any entrapped air or solvent vapor bubbles, which may act as crack-initiation sites in the finished piece.

The actual tape is formed by pouring the slip onto a flat surface (of stainless steel, glass, a polymeric film, or paper); a doctor blade spreads the slip into a thin tape of uniform thickness, as shown schematically in Figure 13.18. In the drying process, volatile slip components are removed by evaporation; this green product is a flexible tape that may be cut or into which holes may be punched prior to a firing operation.

Tape thicknesses normally range between 0.1 and 2 mm (0.004 to 0.08 in.).

Tape casting is widely used in the production of ceramic substrates that are used for integrated circuits and for multilayered capacitors.

Cementation is also considered to be a ceramic fabrication process.

The cement material, when mixed with water, forms a paste that, after being fashioned into a desired shape, subsequently hardens as a result of complex chemical reactions.

LECTURE 10

SUMMARY

Glasses

Glass–Ceramics

These lectures began by discussing the various types of ceramic materials. The familiar glass materials are noncrystalline silicates that contain other oxides; the most desirable trait of these materials is their optical transparency.

Glass–ceramics are initially fabricated as a glass, then crystallized.

Clay Products

Clay is the principal component of the whitewares and structural clay products. Other ingredients may be added, such as feldspar and quartz, which influence the changes that occur during firing.

Refractories

The materials that are employed at elevated temperatures and often in reactive environments are the refractory ceramics; on occasion, their ability to thermally insulate is also utilized. On the basis of composition and application, the four main subdivisions are fireclay, silica, basic, and special.

Abrasives

The abrasive ceramics, being hard and tough, are utilized to cut, grind, and polish other softer materials. Diamond, silicon carbide, tungsten carbide, corundum, and silica sand are the most common examples. The abrasives may be employed in the form of loose grains, bonded to an abrasive wheel, or coated on paper or a fabric.

Cements

When mixed with water, inorganic cements form a paste that is capable of assuming just about any desired shape. Subsequent setting or hardening is a result of chemical reactions involving the cement particles and occurs at the ambient temperature.

For hydraulic cements, of which Portland cement is the most common, the chemical reaction is one of hydration.

Advanced Ceramics

Many of our modern technologies utilize and will continue to utilize advanced ceramics because of their unique mechanical, chemical, electrical, magnetic, and optical properties and property combinations. The following advanced ceramic materials were discussed briefly: piezoelectric ceramics, microelectromechanical systems (MEMS), and ceramic ball bearings.

Fabrication and Processing of Glasses and Glass–Ceramics.

The next major section of these lectures discussed the principal techniques used for the fabrication of ceramic materials. Since glasses are formed at elevated temperatures, the temperature–viscosity behavior is an important consideration. Melting, working, softening, annealing, and strain points represent temperatures that correspond to specific viscosity values. Knowledge of these points is important in the fabrication and processing of a glass of given composition. Four of the more common glass-forming techniques—pressing, blowing, drawing, and fiber forming—were discussed briefly. After fabrication, glasses may be annealed and/or tempered to improve mechanical characteristics.

Fabrication and Processing of Clay Products

For clay products, two fabrication techniques that are frequently utilized are hydroplastic forming and slip casting. After forming, a body must be first dried and then fired at an elevated temperature to reduce porosity and enhance strength.

Shrinkage that is excessive or too rapid may result in cracking and/or warping, and a worthless piece. Densification during firing is accomplished by vitrification, the formation of a glassy bonding phase.

Powder Pressing

Tape Casting

Some ceramic pieces are formed by powder compaction; uniaxial and isostatic techniques are possible. Densification of pressed pieces takes place by a sintering mechanism during a high-temperature firing procedure. Hot pressing is also possible in which pressing and sintering operations are carried out simultaneously.

Thin ceramic substrate layers are often fabricated by tape casting.

LECTURE 11

QUESTIONS AND PROBLEMS

Glasses

Glass–Ceramics

13.1 Cite the two desirable characteristics of glasses.

13.2 (a) What is crystallization?

(b) Cite two properties that may be improved by crystallization.

Refractories

13.3 For refractory ceramic materials, cite three characteristics that improve with and two characteristics that are adversely affected by increasing porosity.

Cements

13.8 Compare the manner in which the aggregate particles become bonded together in clay-based mixtures during firing and in cements during setting.

Fabrication and Processing of Glasses and Glass–Ceramics

13.9 Soda and lime are added to a glass batch in the form of soda ash ($Na2CO3$) and limestone ($CaCO3$). During heating, these two ingredients decompose to give off carbon dioxide ($CO2$), the resulting products being soda and lime. Compute the weight of soda ash and limestone that must be added to 125 lbm of quartz (SiO_2) to yield a glass of composition 78 wt% SiO_2, 17 wt% Na_2O, and 5 wt% CaO.

13.10 What is the distinction between glass transition temperature and melting temperature?

13.11 Compare the temperatures at which soda– lime, borosilicate, 96% silica, and fused silica may be annealed.

13.12 Compare the softening points for 96% silica, borosilicate, and soda–lime glasses.

13.15 (a) Explain why residual thermal stresses are introduced into a glass piece when it is cooled.

(b) Are thermal stresses introduced upon heating? Why or why not?

13.16 Borosilicate glasses and fused silica are resistant to thermal shock. Why is this so?

13.17 In your own words, briefly describe what happens as a glass piece is thermally tempered.

13.18 Glass pieces may also be strengthened by chemical tempering. With this procedure, the glass surface is put in a state of compression by exchanging some of the cations near the surface with other cations having a larger diameter. Suggest one type of cation that, by replacing Na+, will induce chemical tempering in a soda–lime glass.

Fabrication and Processing of Clay Products

13.19 Cite the two desirable characteristics of clay minerals relative to fabrication processes.

13.20 From a molecular perspective, briefly explain the mechanism by which clay minerals become hydroplastic when water is added.

13.21 (a) What are the three main components of a whiteware ceramic such as porcelain?

(b) What role does each component play in the forming and firing procedures?

13.22 (a) Why is it so important to control the rate of drying of a ceramic body that has been hydroplastically formed or slip cast?

(b) Cite three factors that influence the rate of drying, and explain how each affects the rate.

13.23 Cite one reason why drying shrinkage is greater for slip cast or hydroplastic products that have smaller clay particles.

13.24 (a) Name three factors that influence the degree to which vitrification occurs in claybased ceramic wares.

(b) Explain how density, firing distortion, strength, corrosion resistance, and thermal conductivity are affected by the extent of vitrification.

Powder Pressing

13.25 Some ceramic materials are fabricated by hot isostatic pressing. Cite some of the limitations and difficulties associated with this technique.

DESIGN PROBLEM

13.D1 Some of our modern kitchen cookware is made of ceramic materials.

(a) List at least three important characteristics required of a material to be used for this application.

(b) Make a comparison of three ceramic materials as to their relative properties and, in addition, to cost.

(c) On the basis of this comparison, select the material most suitable for the cookware.