Ceramics

Topics to be covered this week

Polymers – types of polymers, molecular weight, calculation of molecular weight examples, importance of molecular weight, Polymers – amorphous and crystalline polymers, Processing of polymers.
Polymers – amorphous and crystalline polymers, stress strain curves for polymers and rubbers, Creep, Stress relaxation, Glass transition temperature. Advanced polymers – UHMWPE, thermoplastic elastomers, liquid crystal polymers, Applications of polymers and their applications in various fields
Ceramics – types of ceramics and their important properties, glass transition temperature and viscosity; Heat treatment of ceramics – annealing and tempering, Processing of ceramic
Composite materials – introduction and classification of composites, properties and applications of PMCs, CMCs, and MMCs – Case study on application of composites. Processing of composite products; Nanocomposites – types of nanomaterials, properties and applications in various fields

Ceramics

- Name derived from the Greek word *"keeramikos"* meaning burnt stuff
- A ceramic is a material that is neither metallic nor organic.
- It may be crystalline, glassy or both crystalline and glassy.
- Ceramics are more than pottery and dishes: clay, bricks, tiles, glass, and cement.
- Ceramic materials are used in electronics because, depending on their composition, they may be semiconductor/superconductor/ferroelectric/insulator.
- Ceramics are also used to make objects as diverse as spark plugs, fiber optics, artificial joints, space shuttle tiles, self lubricating bearings, body armor, and skis.
- Bonding: Ionic bonding or covalent bonding

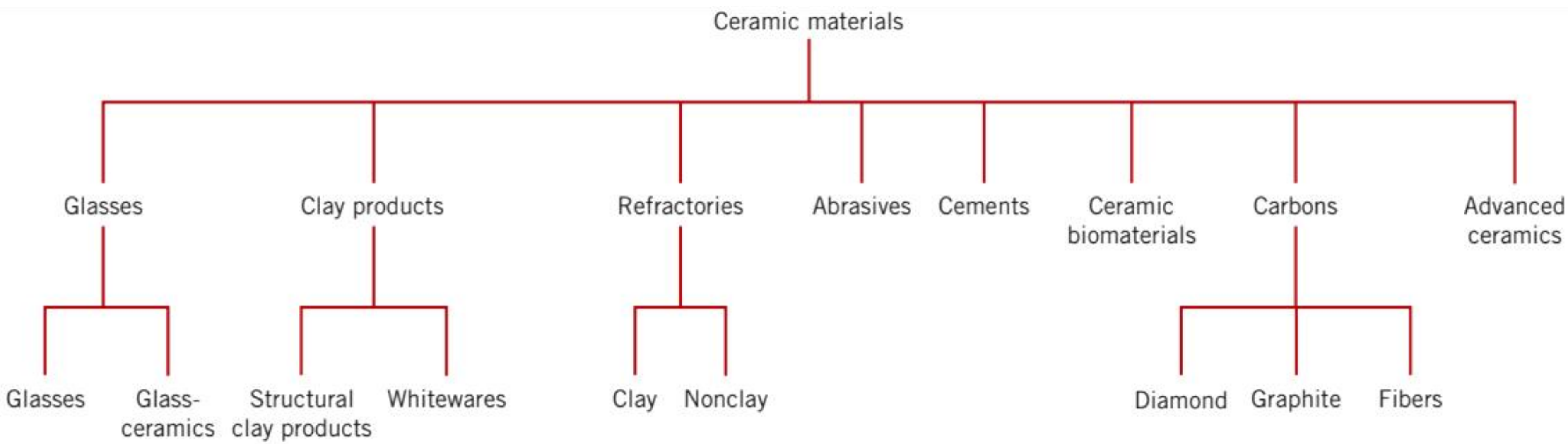
$$\%\ \text{ionic character} = \{1 - \exp[-(0.25)(X_A - X_B)^2]\} \times 100$$

X_A & X_B are electronegativities

Material	*Percent Ionic Character*
CaF_2	89
MgO	73
$NaCl$	67
Al_2O_3	63
SiO_2	51
Si_3N_4	30
ZnS	18
SiC	12

Ceramics

- Most ceramic materials fall into an application based classification scheme that includes the following groups.
- Glasses, structural clay products, whitewares, refractories, abrasives, cements, ceramic biomaterials, carbons, and the newly developed advanced ceramics.



Glasses & Glass-Ceramics

- **Glass** is a non-crystalline, often transparent amorphous solid, that has widespread optical and decorative use, It mainly contains Silica (SiO_2).

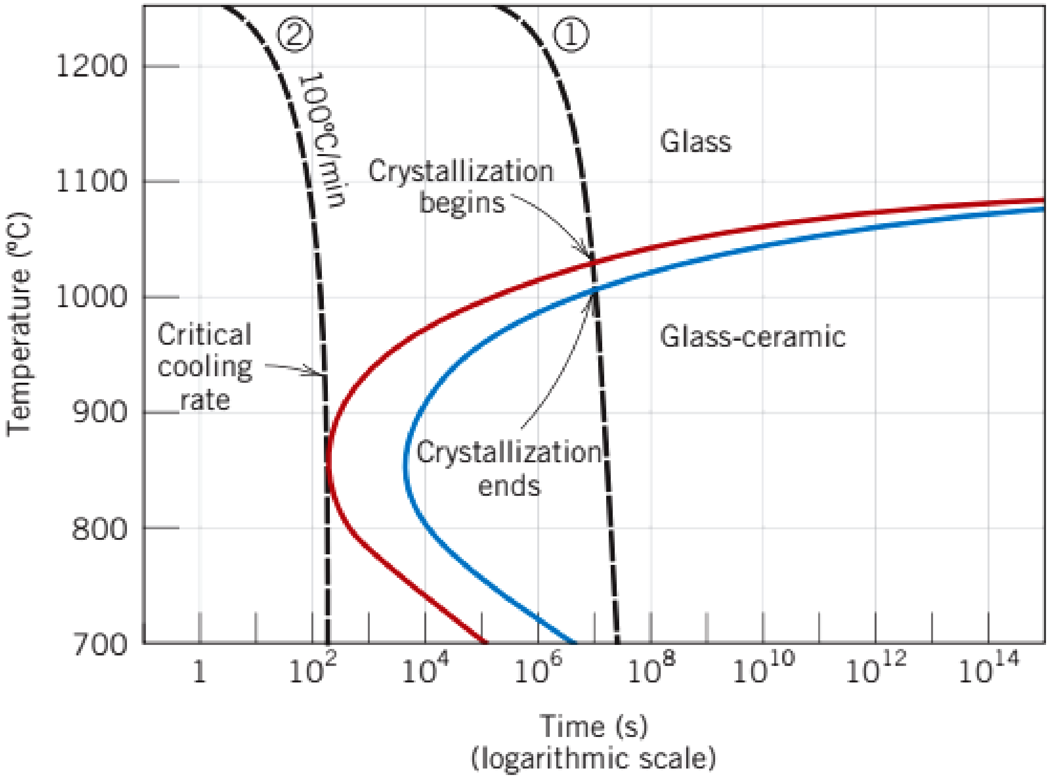
- **Crystallization:** Most inorganic glasses can be made to transform from a noncrystalline state into crystalline by proper high-temperature heat treatment. This product is a fine-grained polycrystalline material that is often called a **glass-ceramic**.

Compositions and Characteristics of Some Common Commercial Glasses

	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		4 MgO	Low melting temperature, easily worked, also durable
Fiberglass	55		16	15	10	4 MgO	Easily drawn into fibers—glass–resin composites
Optical flint	54	1				37 PbO, 8 K_2O	High density and high index of refraction—optical lenses
Glass-ceramic (Pyroceram)	43.5	14		30	5.5	6.5 TiO_2, 0.5 As_2O_3	Easily fabricated; strong; resists thermal shock—ovenware

Glass-Ceramics

- The continuous-cooling transformation diagram for the crystallization of a lunar glass is presented in Figure.



Continuous-cooling transformation diagram for the crystallization of a lunar glass

Glass Ceramic Properties

- ✓ Relatively high mechanical strengths;
- ✓ low coefficients of thermal expansion (to avoid thermal shock)
- ✓ good high-temperature capabilities;
- ✓ good dielectric properties (for electronic packaging)
- ✓ good biological compatibility.

Clay Ceramics

- One of the most widely used ceramic raw materials is **clay (Silica and Alumina).**
- This inexpensive ingredient, found naturally in great abundance, often is used as mined without any upgrading of quality.
- Most clay-based products fall within two broad classifications: the **structural clay products** and **whitewares.**
- Structural clay products include building bricks, tiles, and sewer pipes, applications in which structural integrity is important.
- **Whiteware ceramics** become white after high-temperature **firing.**
- Whirewares are porcelain, pottery, tableware, china, and plumbing fixtures (sanitary ware).

Clay and Non Clay Ceramics Refractories

Compositions of seven ceramic refractory materials

	Composition (wt%)					
Refractory Type	*Al_2O_3*	*SiO_2*	*MgO*	*Fe_2O_3*	*CaO*	*Other*
Fireclay	25–45	70–50	<1	<1	<1	1–2 TiO_2
High-alumina fireclay	50–87.5	45–10	<1	1–2	<1	2–3 TiO_2
Silica	<1	94–96.5	<1	<1.5	<2.5	
Periclase	<1	<3	>94	<1.5	<2.5	
Extra-high alumina	87.5–99+	<10	—	<1	—	<3 TiO_2
Zircon	—	34–31	—	<0.3	—	63–66 ZrO_2
Silicon carbide	12–2	10–2	—	<1	—	80–90 SiC

- The clay refractories are subclassified into two categories: fireclay and high-alumina.
- Nonclay refractories are refractories included in this group are silica, periclase, extra-high alumina, zircon, and silicon carbide materials.

Abrasives

- **Abrasive ceramics** (in particulate form) are used to wear, grind, or cut away other material, which necessarily is softer.
- The prime requisite of these materials is *hardness* or *wear resistance*; most abrasive materials have a *Mohs hardness of at least 7*.
- Naturally occurring abrasives: Diamond, corundum (aluminum oxide), emery (impure corundum), garnet, calcite (calcium carbonate), pumice, rouge (iron oxide), and sand.
- Manufactured category are as follows: diamond, corundum, borazon (cubic boron nitride or CBN), carborundum (silicon carbide), zirconia–alumina, and boron carbide.
- Fig. (middle) of a clutch lining pressure plate that is being ground by a grinding wheel.

Cements

- inorganic **cements:** lime stone or Calcium Silicate acts as binder with sand and gravel
- The characteristic feature of these materials is that when *mixed with water*, they *form a paste* that *subsequently sets and hardens*.
- It is produced by **calcination:** Grinding and intimately mixing clay and lime-bearing minerals in the proper proportions and heating the mixture to ~ 1400°C in a rotary kiln.

$$CaCO_3 \longrightarrow CaO + CO_2$$

Preparation of Portland Cement:

Grinding and mixing of clay and lime bearing minerals → **Calcination: Heating up to 1400°C** → **Clinker: The resulting powder is ground and gypsum is added to delay the setting process** → **Portland Cement**

Hydration Reaction:

$$2CaO–SiO_2 + xH_2O \rightarrow 2CaO–SiO_2–xH_2O$$

Ceramic Biomaterials

- Ceramic materials are also used in a number of *biomedical applications*.
- Properties that make them desirable for use as biomaterials include chemical inertness, hardness, wear resistance, and low coefficient of friction.
- Those ceramics typically used for implants (i.e., *bioceramics*) include crystalline oxide materials, glasses, and glass-ceramics.
- The following are typical examples of the use of bioceramic materials:
  - ✓ High-purity and dense aluminum oxide, a highly inert and unreactive ceramic, is used in *load-bearing*, *orthopedic* applications.
  - ✓ Zirconia (the tetragonal form), partially stabilized with yttria is used in *orthopedic* and *dental* applications.
  - ✓ When placed within the human body, the surfaces of some glasses and glass-ceramic materials interact with and bond to surrounding tissues (notably bone).
  - ✓ For some bone injuries, it is desirable to implant a material that is gradually infiltrated with and replaced by natural bone tissue during the healing process.

Carbons

- The crystal structures of two polymorphic forms of carbon are *diamond* & *graphite*.
- Furthermore, fibers are made of carbon materials that have other structures.
- **Diamond:** Chemically, it is very *inert and resistant* to attack by a host of corrosive media. It is the *hardest*, as a result of its extremely *strong interatomic sp^3 bonds*.
- **Graphite:** It is highly *anisotropic* and properties are depend on the crystallographic direction along which they are measured.
- The electrical resistivities parallel and perpendicular to the graphene plane are in the order of 10^{-5} and 10^{-2} Ω·m, respectively.

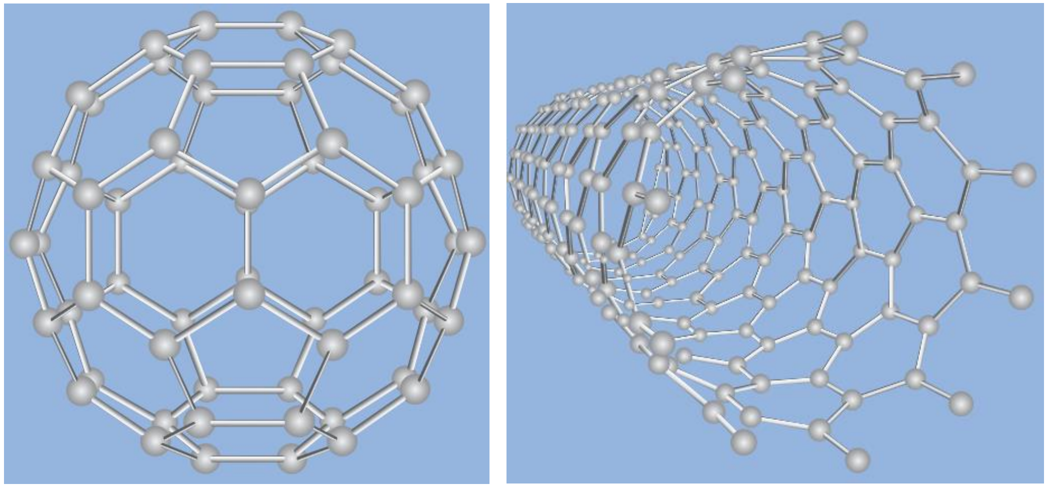
Properties of Diamond, Graphite, and Carbon (for Fibers)

	Material			
		Graphite		
Property	*Diamond*	*In-Plane*	*Out-of-Plane*	*Carbon (Fibers)*
Density (g/cm^3)	3.51	2.26		1.78–2.15
Modulus of elasticity (GPa)	700–1200	350	36.5	230–725[a]
Strength (MPa)	1050	2500	—	1500–4500[a]
Thermal Conductivity (W/m·K)	2000–2500	1960	6.0	11–70[a]
Coefficient, Thermal Expansion (10^{-6} K^{-1})	0.11–1.2	−1	+29	−0.5–−0.6[a] 7–10[b]
Electrical Resistivity (Ω·m)	10^{11}–10^{14}	1.4×10^{-5}	1×10^{-2}	9.5×10^{-6}–17×10^{-6}

Advanced Ceramics

- **Micro-Electro Mechanical Systems (MEMS):** Various processing techniques such as *photolithography*, *ion implantation*, *etching* & *deposition techniques* are used.
- Micromachining techniques are also available to manufacture such miniaturized components. Silicon is the material currently under use.
- Silicon carbonitrides are being considered to be used instead of Silicon alone.
- **Nanocarbons:** A class of recently discovered carbon materials, the **nanocarbons,** have novel and exceptional properties.
- They are currently being used in some cutting-edge technologies and will certainly play an important role in future high-tech applications.

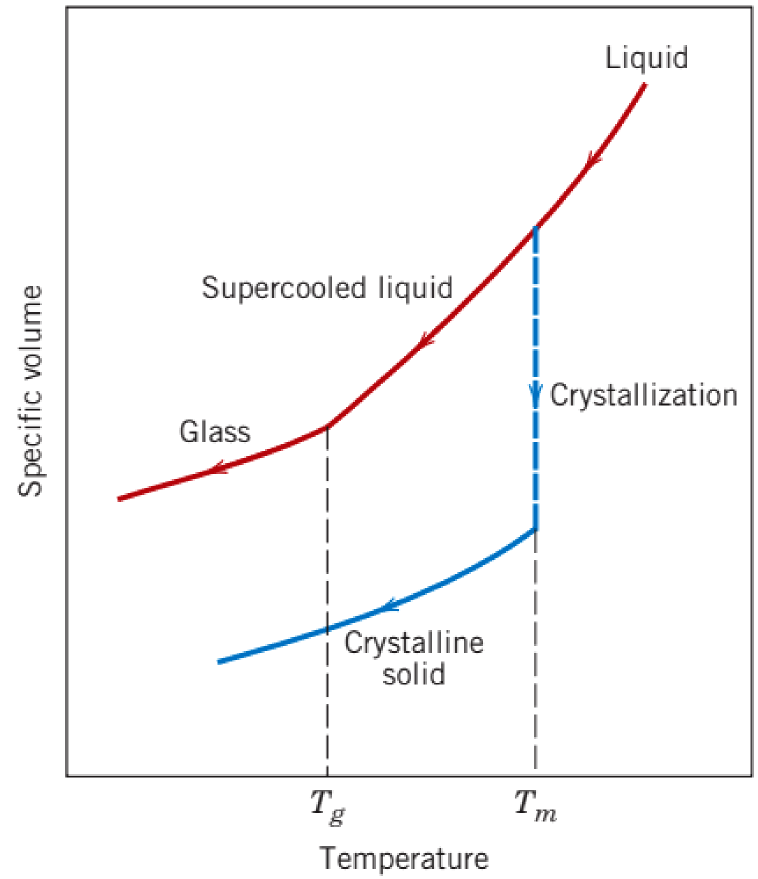
Rack & Pinion Arrangement–miniaturization



The structures of **a C60 fullerene** molecule and **single-walled carbon nanotube**

Glass transition temperature

- One of the distinctions between crystalline and noncrystalline materials lies in the dependence of specific volume (reciprocal of density) on temperature.
- For crystalline materials, there is a discontinuous decrease in volume at the melting temperature T_m as shown in figure.
- 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,** or *fictive* temperature, T_g.



Contrast of specific volume-versus-temperature behavior of crystalline and noncrystalline materials

- Crystalline materials solidify at the melting temperature T_m.
- Characteristic of the noncrystalline state is the glass transition temperature T_g.

Viscosity-Temperature characteristics

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

- The **melting point** corresponds to the temp at which the viscosity is 10 Pa•s.

(glass is fluid enough to be considered a liquid)

- The **working point** represents the temp at which the viscosity is 10^3 Pa•s.

(glass is easily deformed at this viscosity)

- At the **softening point** the temperature by which the viscosity is 4×10^6 Pa•s.

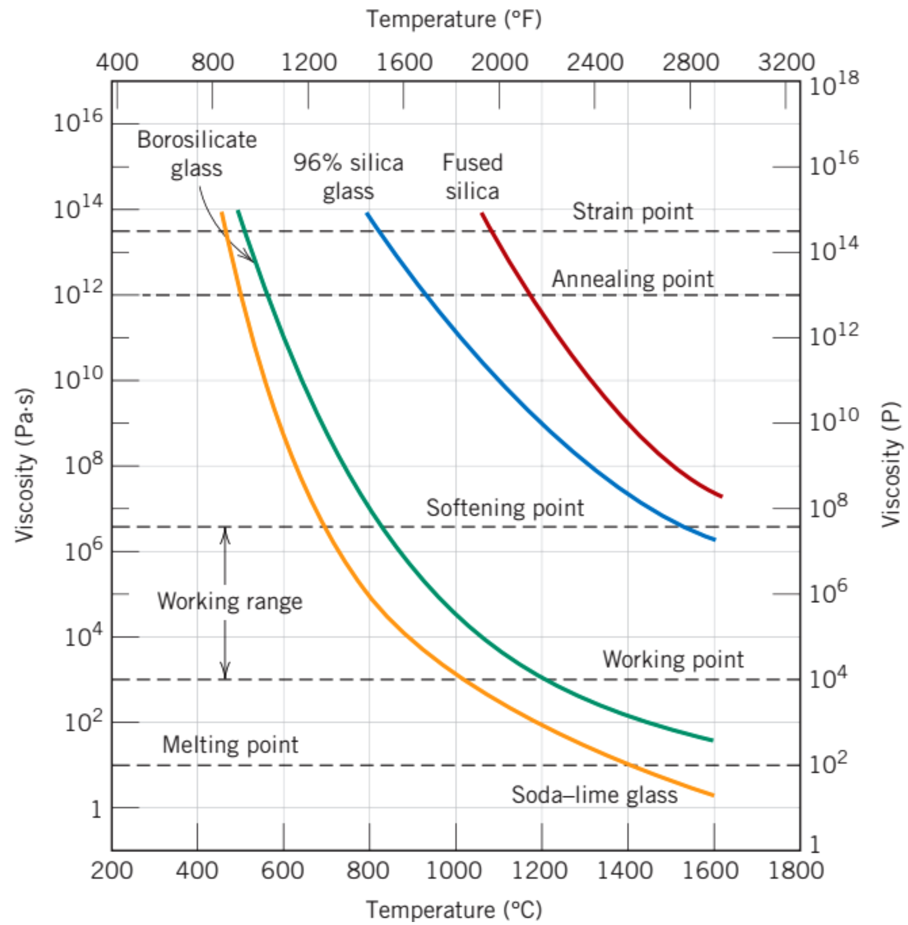
(glass piece get without dimensional change)

- The **annealing point** is the temp at which the viscosity is 10^{12} Pa•s.

(atomic diffusion sufficiently rapid within 15 min)

- The **strain point** corresponds to the temp at which the viscosity becomes 3×10^{13} Pa•s.

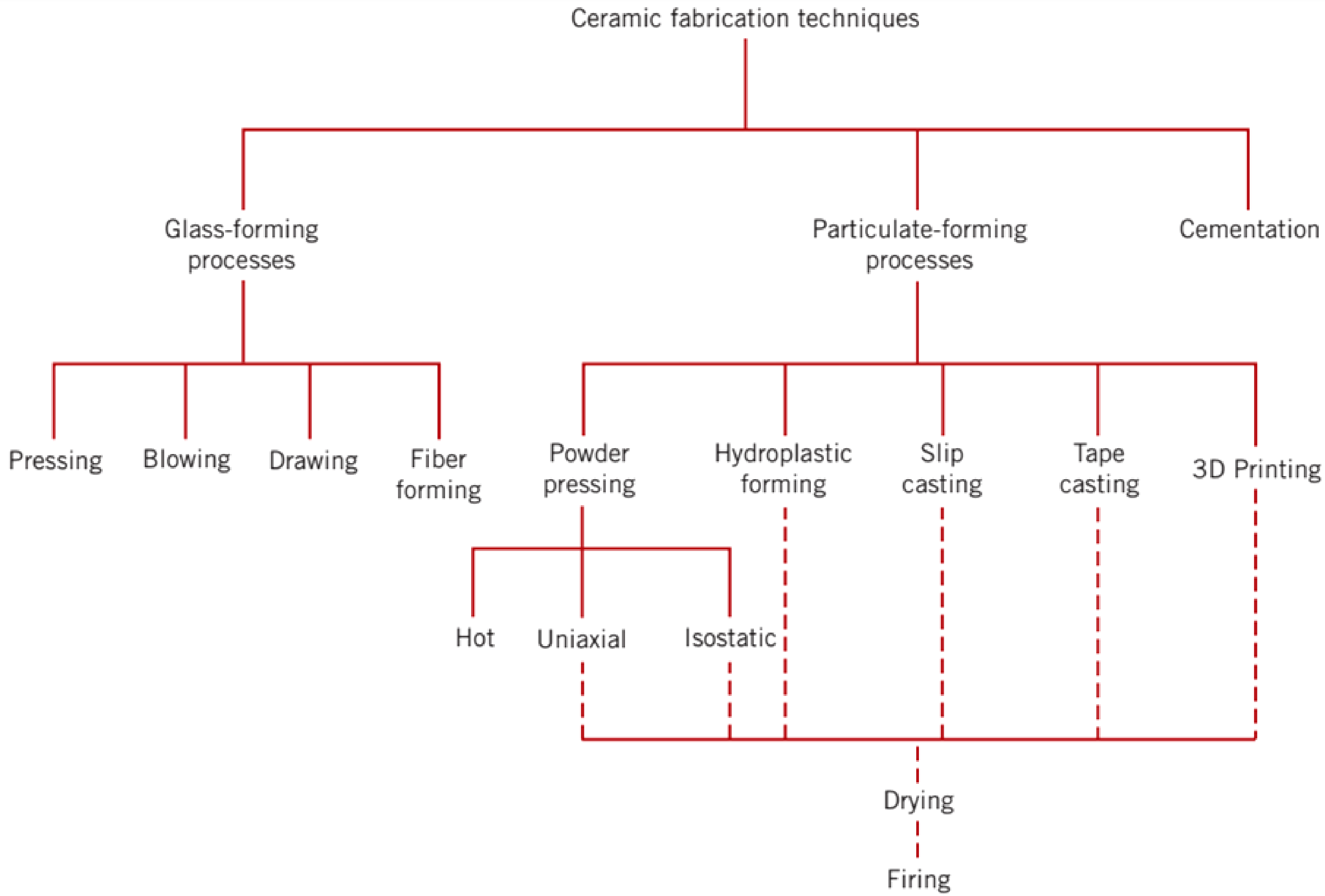
(below the strain point, fracture will occur)



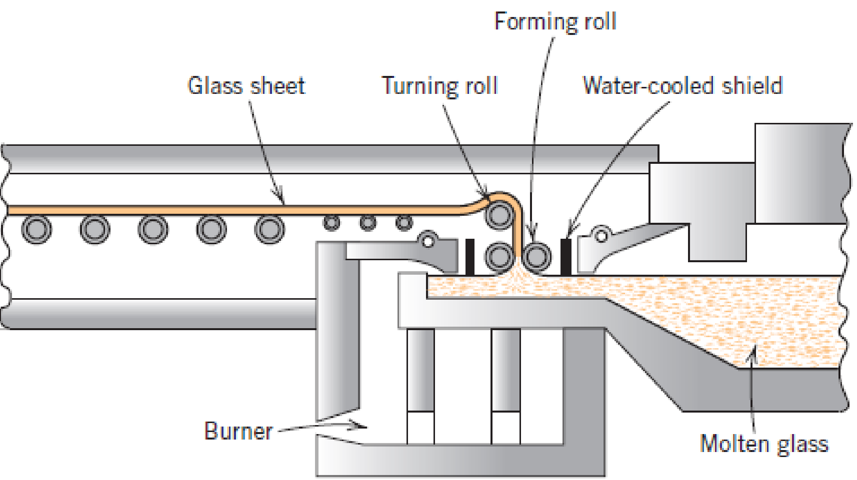
Logarithm of viscosity versus temperature for fused silica and three silica glasses

Fabrication and Processing of Ceramics

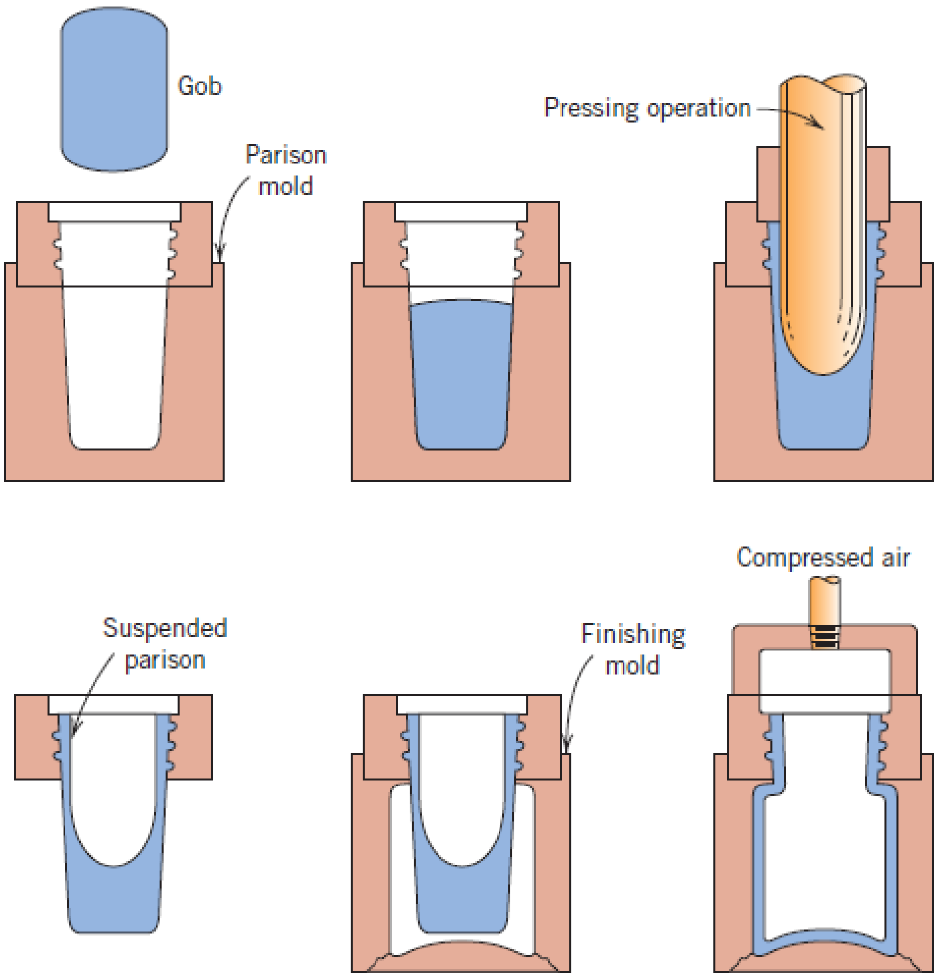
- The ceramic materials have relatively *high melting temperatures*, casting them is normally impractical.
- Furthermore, in most instances the brittleness of these materials prevents the deformation.
- Cements are shaped by placing into forms a fluid paste that hardens and assumes a permanent set by virtue of chemical reactions.



Glass Forming
– Pressing, blowing, drawing and fiber forming

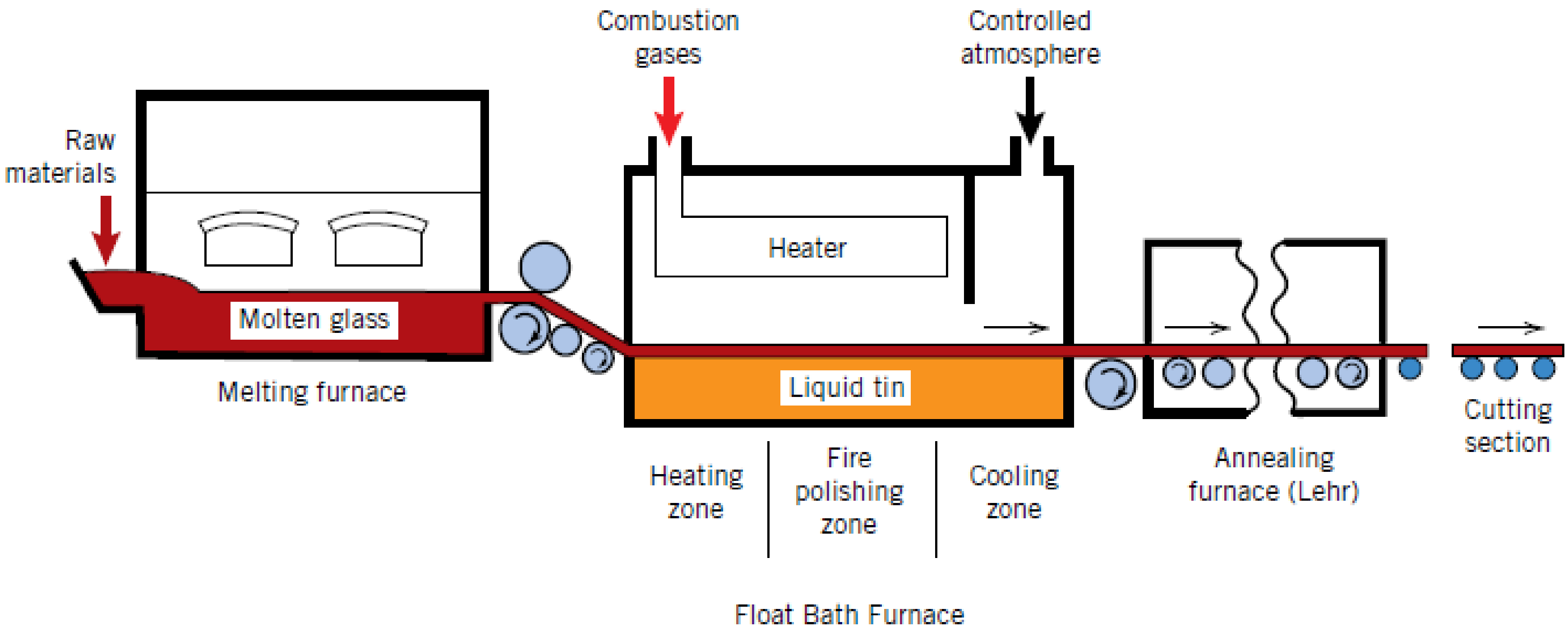


Glass Drawing



Glass Pressing & Blowing

Making of a sheet glass



A more economical float process was patented in 1959 in England.

this continuous glass ribbon “floats” on the surface of the molten tin, gravitational and surface tension forces cause the faces to become perfectly flat and parallel and the resulting sheet to be of uniform thickness.

Furthermore, sheet faces acquire a bright, “fire-polished” finish in one region of the furnace. T

Heat Treatment of Ceramics

Annealing:

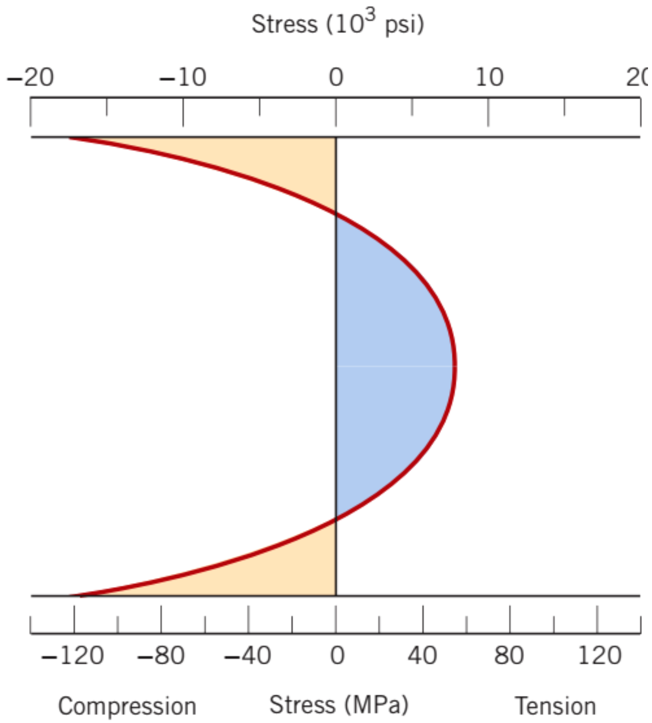
- When a *ceramic material is cooled from an elevated temperature*, internal stresses (thermal stresses) may be introduced between the surface and interior regions.
- These *thermal stresses* are important in brittle ceramics (glasses), because they may weaken the material and *lead to fracture*, which 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.

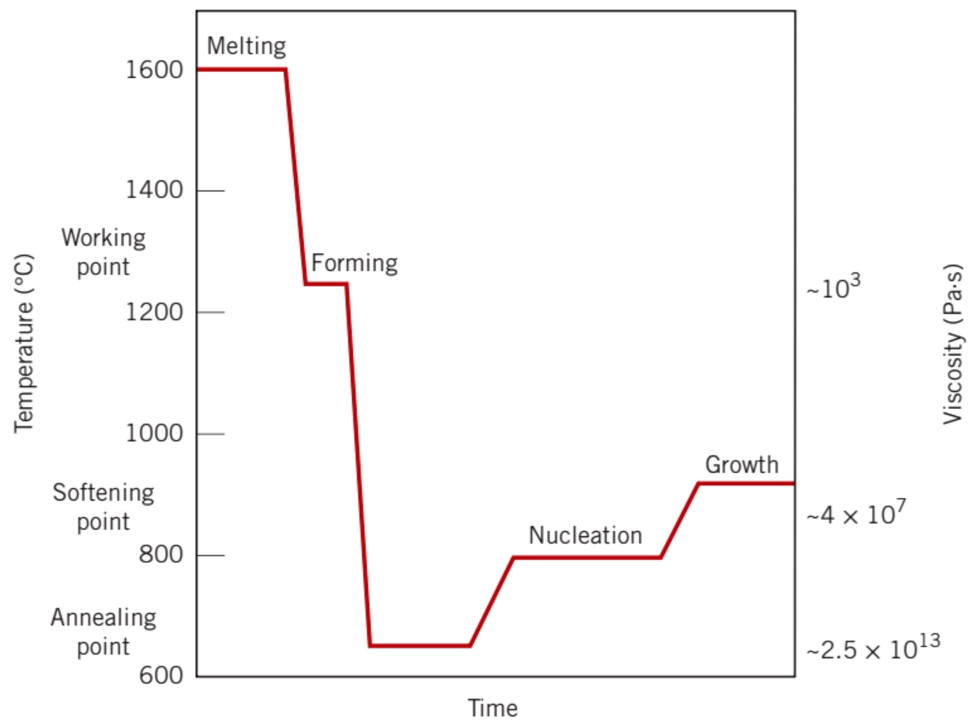
Glass Tempering:

- The *strength of a glass piece* is enhanced by *intentionally inducing compressive residual surface stresses*.
- This can be accomplished by a heat treatment process called **thermal tempering**.
- Initially, the surface cools more rapidly to a temperature below the strain point, it becomes rigid.
- At this time, the interior cooled less rapidly and is having still plastic behaviour.
- With continued cooling, the interior attempts to contract to a greater degree.
- Thus, the inside tends to draw in the outside, or to impose inward radial stresses.

Heat Treatment of Ceramics

- The *room-temperature stress distribution* over a cross-section of a glass plate is represented schematically in Left side Figure.
- The *failure of ceramic materials* always *results from a crack* that is initiated at the surface by an applied tensile stress.
- Tempered glass is used for applications in which high strength is important, include large doors and eyeglass lenses.
- Conversion of the *glass* into a *glass-ceramic* is obtained by appropriate heat treatments.
- One such set of heat treatments for a Li_2O-Al_2O_3-SiO_2 glass-ceramic is detailed in the time Vs. temperature plot of Right side Fig.

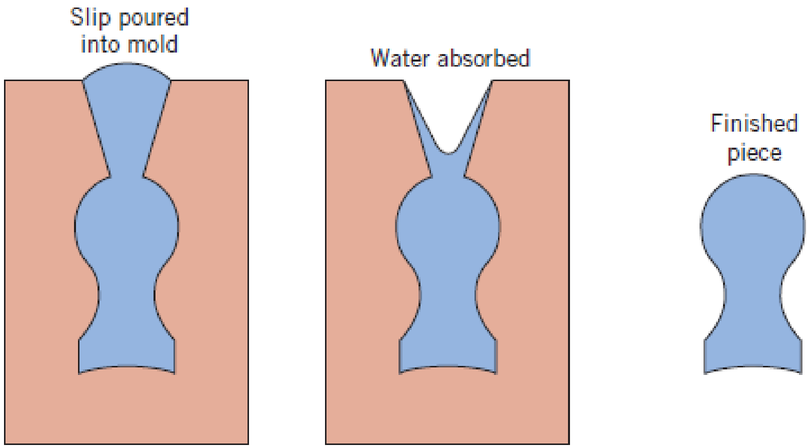




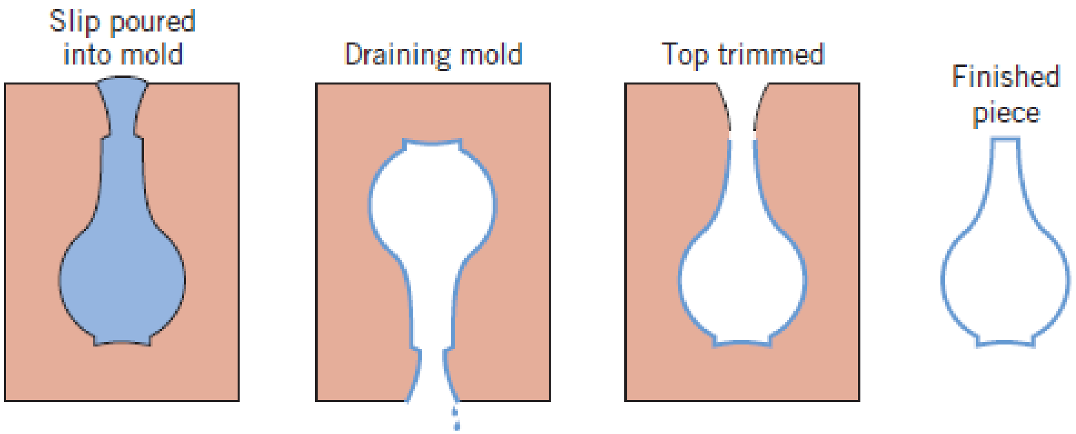
Clay Products

Slip Casting 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 (commonly made of plaster of Paris), water from the water is absorbed into the mold, leaving behind a solid layer on the mold wall, the thickness of which depends on the time.



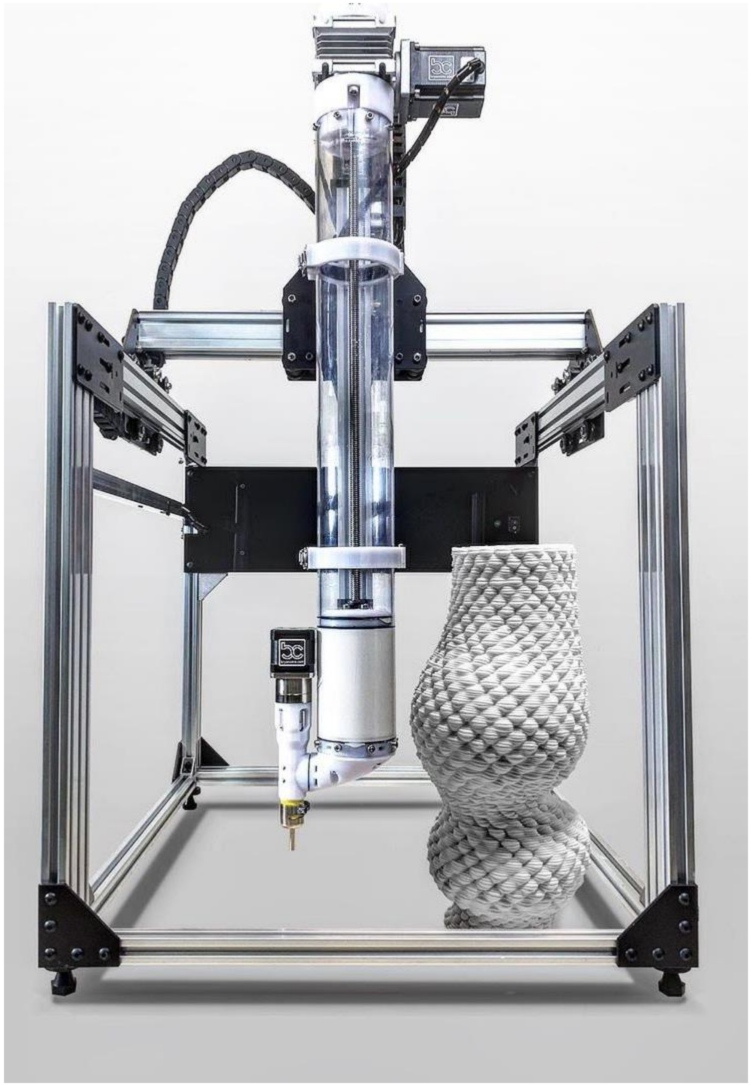
Solid slip



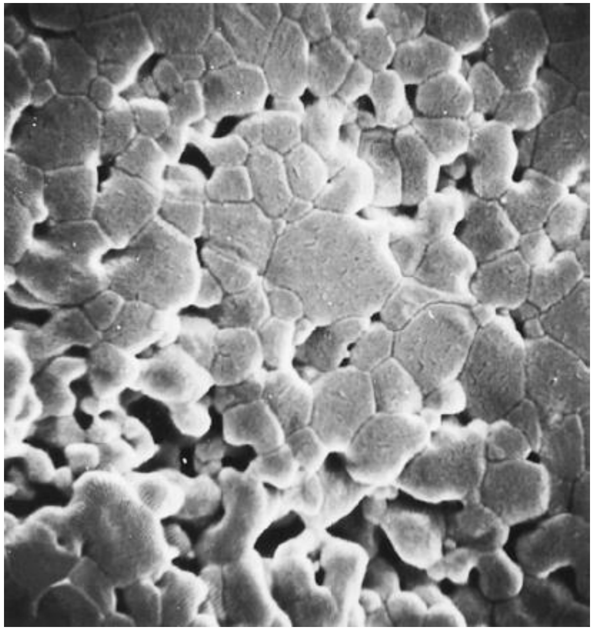
Drain slip casting

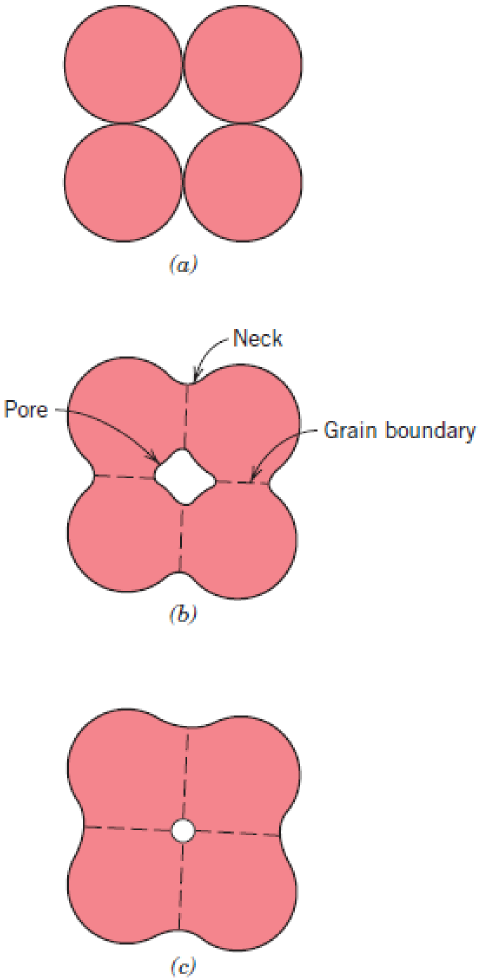
Hydroplastic 3D Clay Extrusion

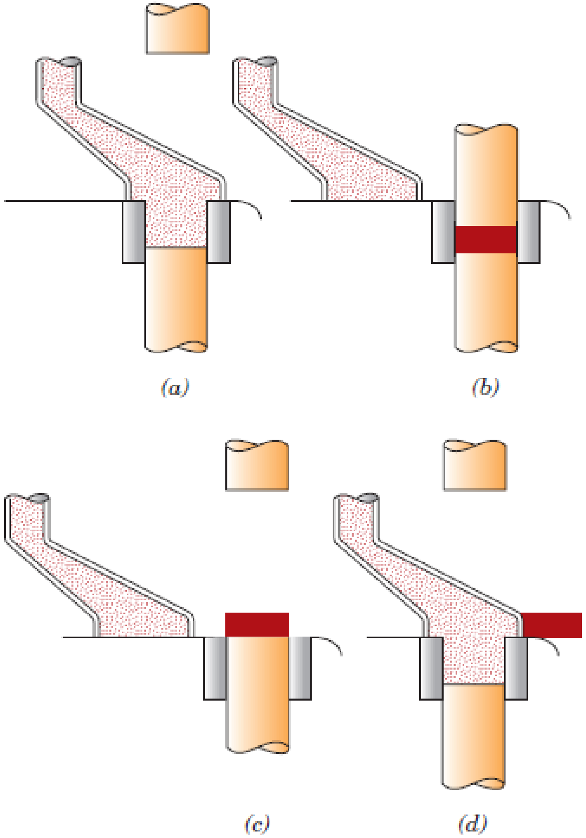
used in several different areas including pottery (plates, cups, saucers, mugs) and ornamental/ artisanal (statues, figurines, jewelry, planters).



Powder Pressing





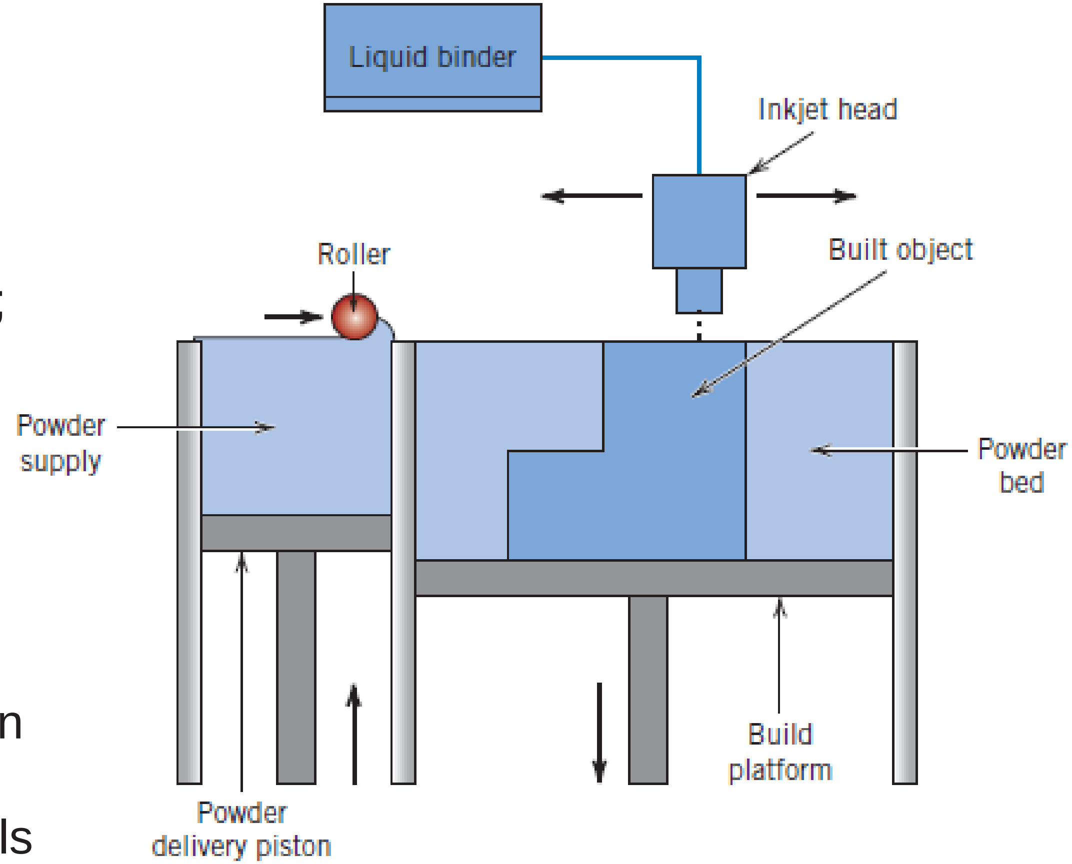


3D PRINTING OF CERAMIC MATERIALS

Ceramic Jet Printing

- A roller mechanism first spreads a thin layer of ceramic powder onto the build platform; an ink jet then selectively "prints" a binder onto only those regions of powder that are to be part of this layer for the desired solid part

- The binder used will depend on the ceramic material being printed. Typical binder materials include polymers and colloidal silica.
- Porcelain



Ceramic Jet Printer

Stereolithographic (SLA) 3D Printing

- The stereolithographic technique for 3D printing of ceramic powder-photocurable polymer suspensions.
- Alumina, zirconia, tricalcium phosphate and hydroxyapatite