# Materials Technology

# Ceramic

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# INTRODUCTION

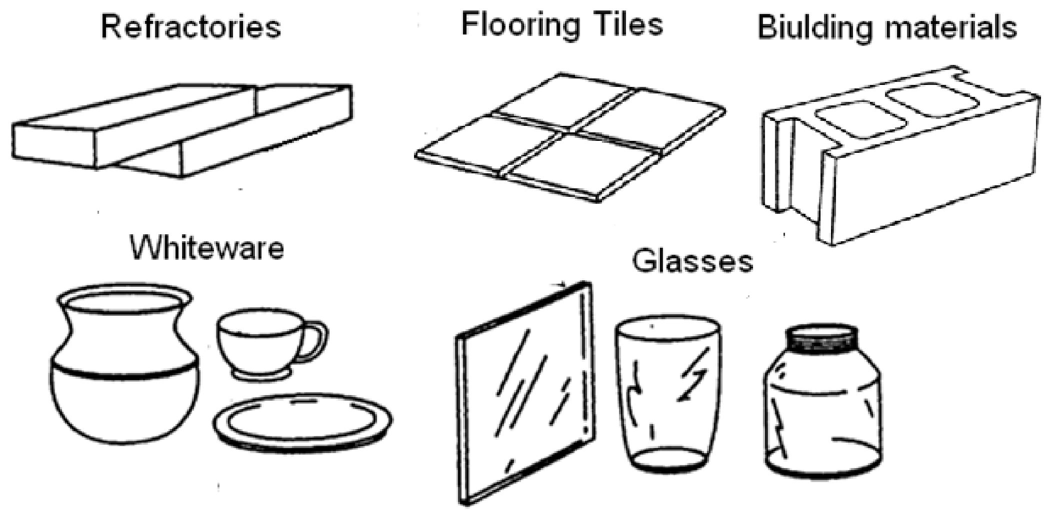
**Keramikos - burnt stuff in Greek**

**Desirable properties of ceramics are normally achieved through a high –temperature heat treatment process (firing).**

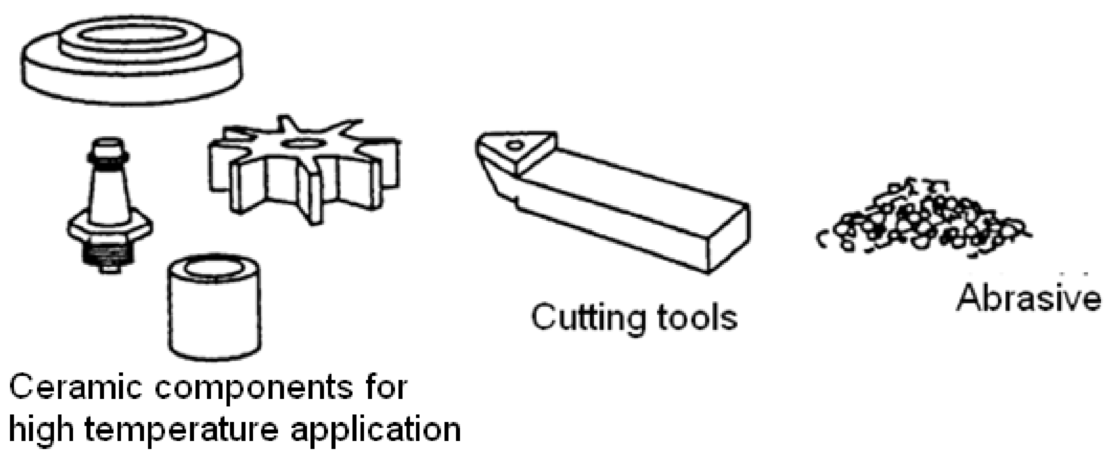
**Bonds are partially or totally ionic, or combination of ionic & covalent**

| Ceramic compound | Bonding atoms | Electronegativity difference | % ionic character | % covalent character |
|---|---|---|---|---|
| Zirconium dioxide, $ZrO_2$ | Zr–O | 2.3 | 73 | 27 |
| Magnesium oxide, MgO | Mg–O | 2.2 | 69 | 31 |
| Aluminum oxide, $Al_2O_3$ | Al–O | 2.0 | 63 | 37 |
| Silicon dioxide, $SiO_2$ | Si–O | 1.7 | 51 | 49 |
| Silicon nitride, $Si_3N_4$ | Si–N | 1.3 | 34.5 | 65.5 |
| Silicon carbide, SiC | Si–C | 0.7 | 11 | 89 |

**Generally hard and brittle**
**Generally electrical and thermal insulators**
**Can be optically opaque, semi-transparent, or transparent**
**High chemical stability and high melting temperature**




## Example of traditional ceramic products




## Example of engineering ceramic products

| Properties | Metal | Ceramic | Polymer |
|---|---|---|---|
| Density | High | Low | Very low |
| Melting Temperature | Medium to high | High | Low |
| Modulus Elasticity | Medium to high | Very high | Low |
| Ductility | Ductile | Brittle | Ductile to brittle |

## Typical Mechanical Properties

**Brittle: Kic in ~ 1 - 12 MPam$^{1/2}$ (*Al alloys have KIc - 25 - 50 MPam$^{1/2}$*).**
**High elastic moduli - greater than metals**

**High compressive strengths is typically ten times the TS**
**Very high hardness**

# Application of ceramics

**The compressive strength is typically ten times the TS. In structures, design must be done for compressive loads.**

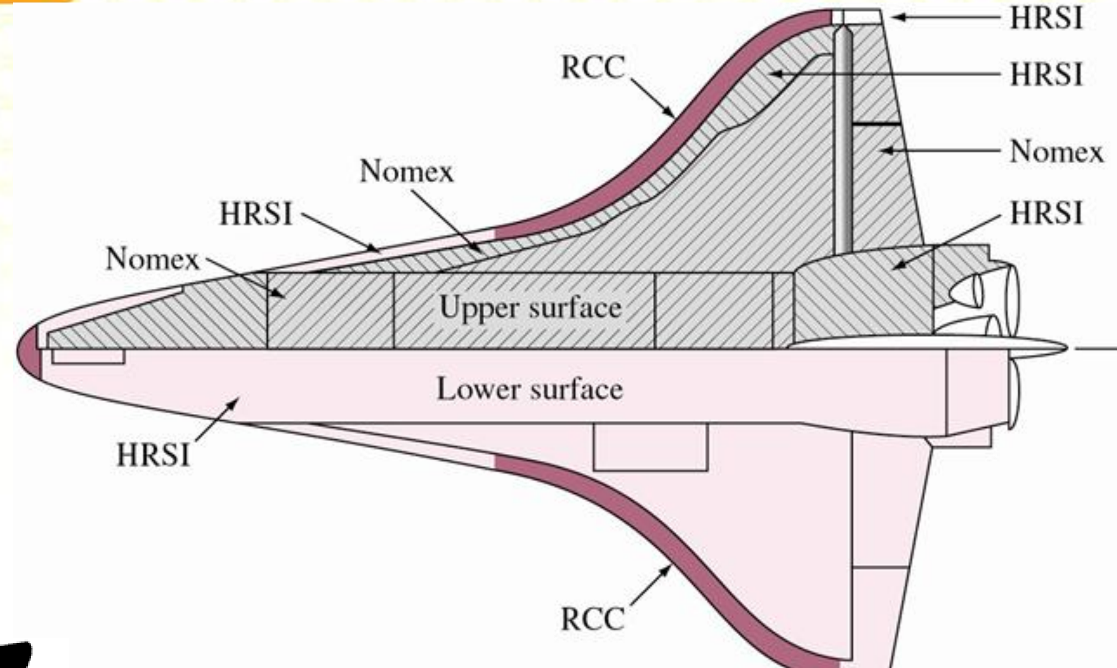
**The transparency of light of many ceramics ;**

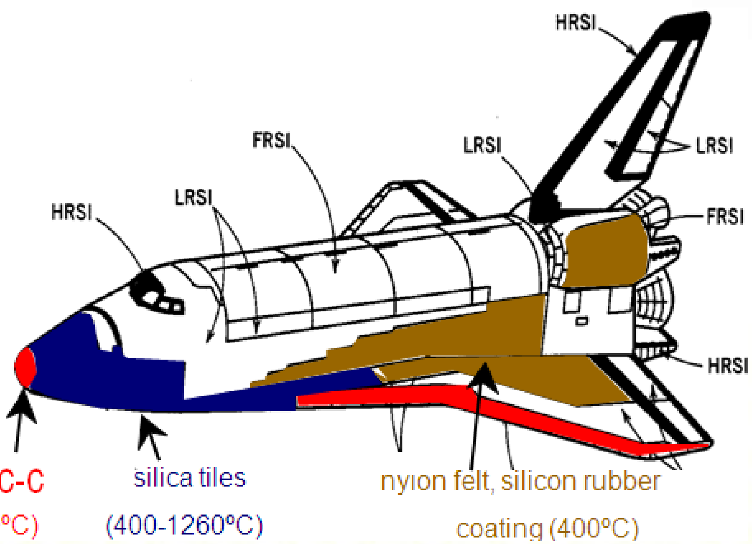
**Optical applications (windows, photographic cameras, telescopes, etc)**
**Silicate glasses (non crystalline silicates ($SiO_2$ containing other oxides) ; windows, containers, lenses, fibreglass etc..**

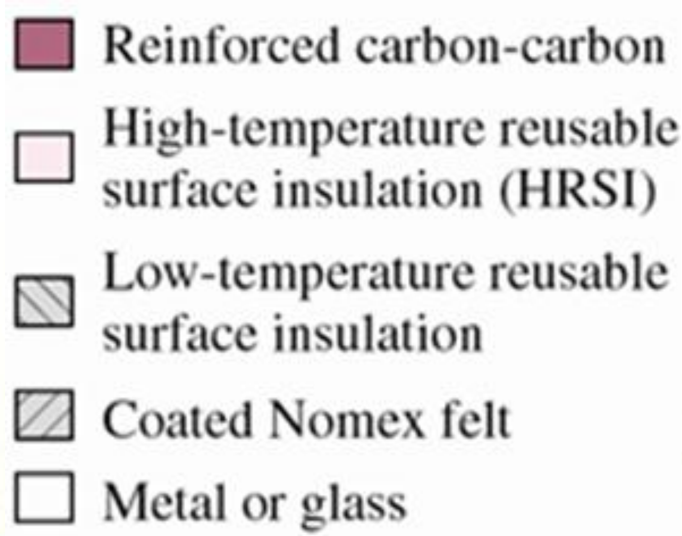
**Good thermal insulators ; used in oven, the exterior tiles of the Space Shuttle**

**Good electrical insulation ; used to support conductor in electrical and electronic application**

**Good chemical properties; applications in reactive applications**


HRSI
HRSI
RCC
Nomex
Nomex
HRSI
HRSI
Nomex
Upper surface
Lower surface
HRSI
RCC


HRSI
FRSI
LRSI
LRSI
HRSI
LRSI
FRSI
HRSI
reinf C-C
(1650°C)
silica tiles
(400-1260°C)
nylon felt, silicon rubber
coating (400°C)


Reinforced carbon-carbon
High-temperature reusable surface insulation (HRSI)
Low-temperature reusable surface insulation
Coated Nomex felt
Metal or glass

## 1. Traditional Ceramics

– based on clay (china, bricks, tiles, porcelain), glasses.

## 2. Engineering Ceramics:

- Pure compounds of metal + O, Metal + C, Metal + N

**Oxide** eg: $Al_2O_3$, ZrO
**Carbide** eg : TiC, WC, SiC
**Nitride** eg : $Si_3N_4$, , TiN, CBN

### Ceramic Materials

- **Glasses**
  - -optical
  - -composite reinforce
  - -containers/ household
- **Clay products**
  - -whiteware
  - -structural
- **Refractories**
  - -bricks for high *T* (furnaces)
- **Abrasives**
  - -sandpaper
  - -cutting
  - -polishing
- **Cements**
  - -composites
  - -structural
- **Advanced ceramics**
  - -engine rotors valves
  - -bearings
  - -sensors

# CERAMIC PROCESSING

**1. POWDER PREPARATION**

Ball mill,blending,
crushing etc
+ additives

**2. FORMING (Green Body)**

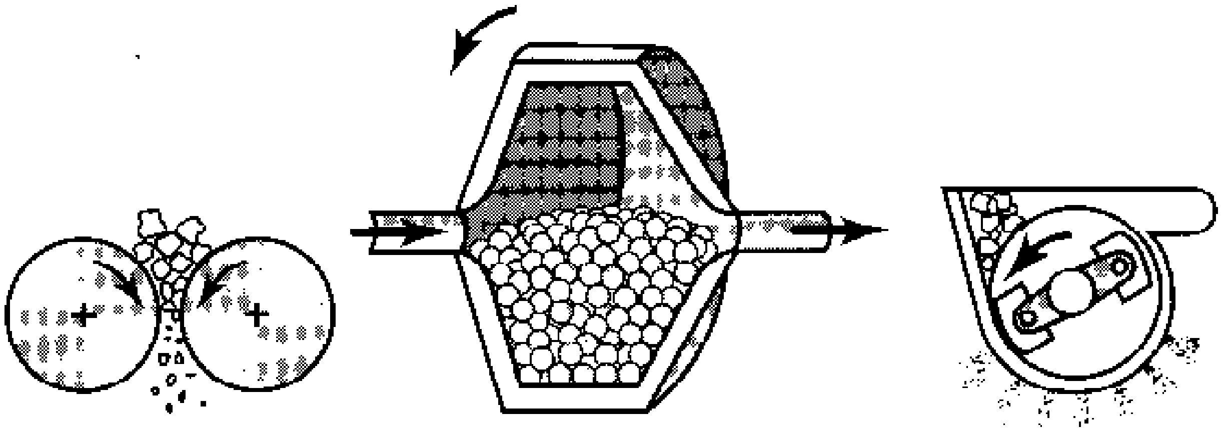
- Pressing (Compaction)
  Uniaxial, CIP, HIP
- Slip Casting
  -drain casting
  -solid casting
- Tape Casting
- Hydro plastic forming
  -Injection
  -extrusion

**3. DRYING & SINTERING**

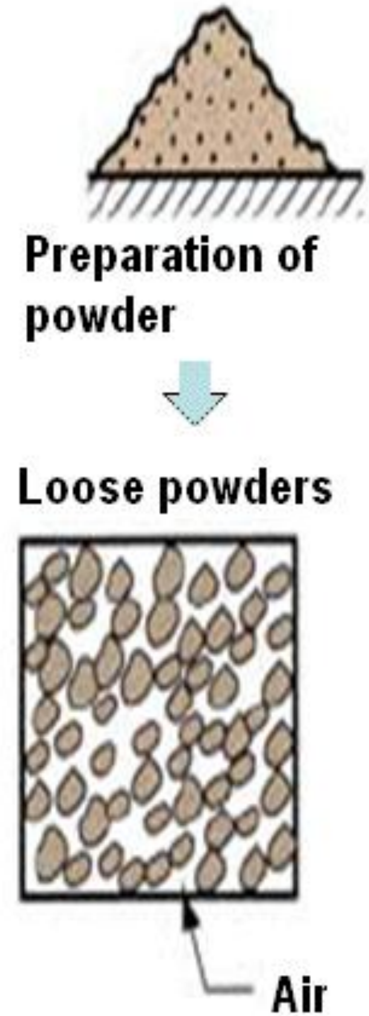
**4. FINISHING**

Cleaning, sizing, machining, glazing

# 1. POWDER PREPARATION



Roll Crushing Ball Milling Hammer Milling




**+ ADDITIVES**

**Water minimum 4% for dry processing ,up to 12% for wet processing., binder, Lubricant , Wetting agent, Plasticizer**

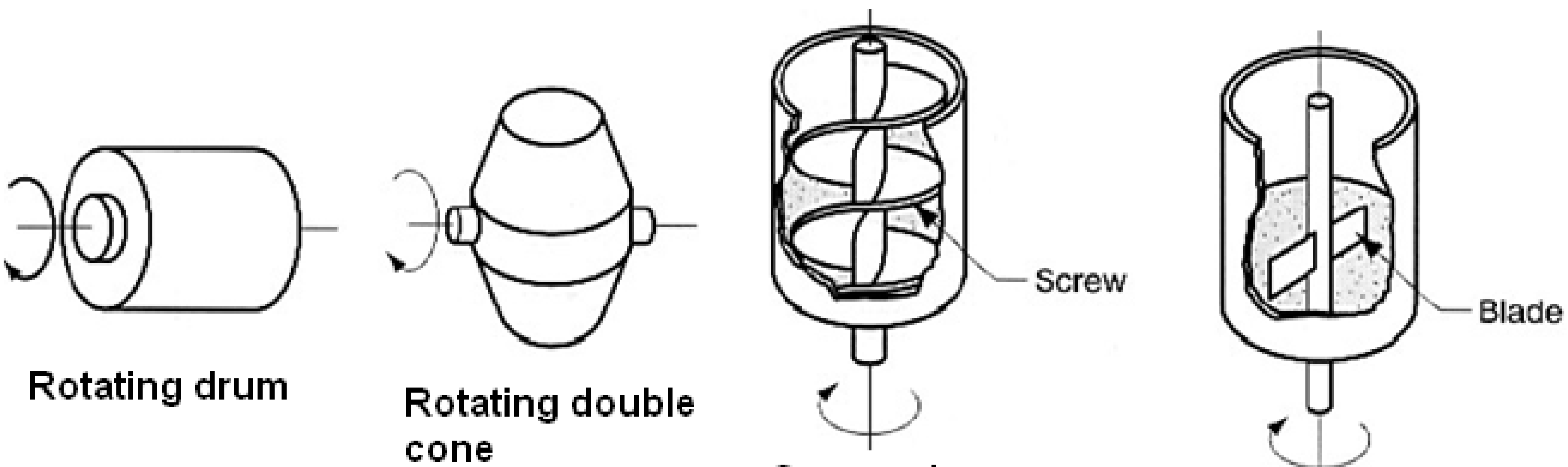
# Blending

**Blending : Mixing powder of same chemical composition but different size**
**Mixing : combining powders of different chemistries.**

**Blending and mixing  are accomplished y mechanical means**

**Lubricants :  to reduce the particle-die friction**

**Binders :  to achieve enough strength before sintering**




Rotating drum

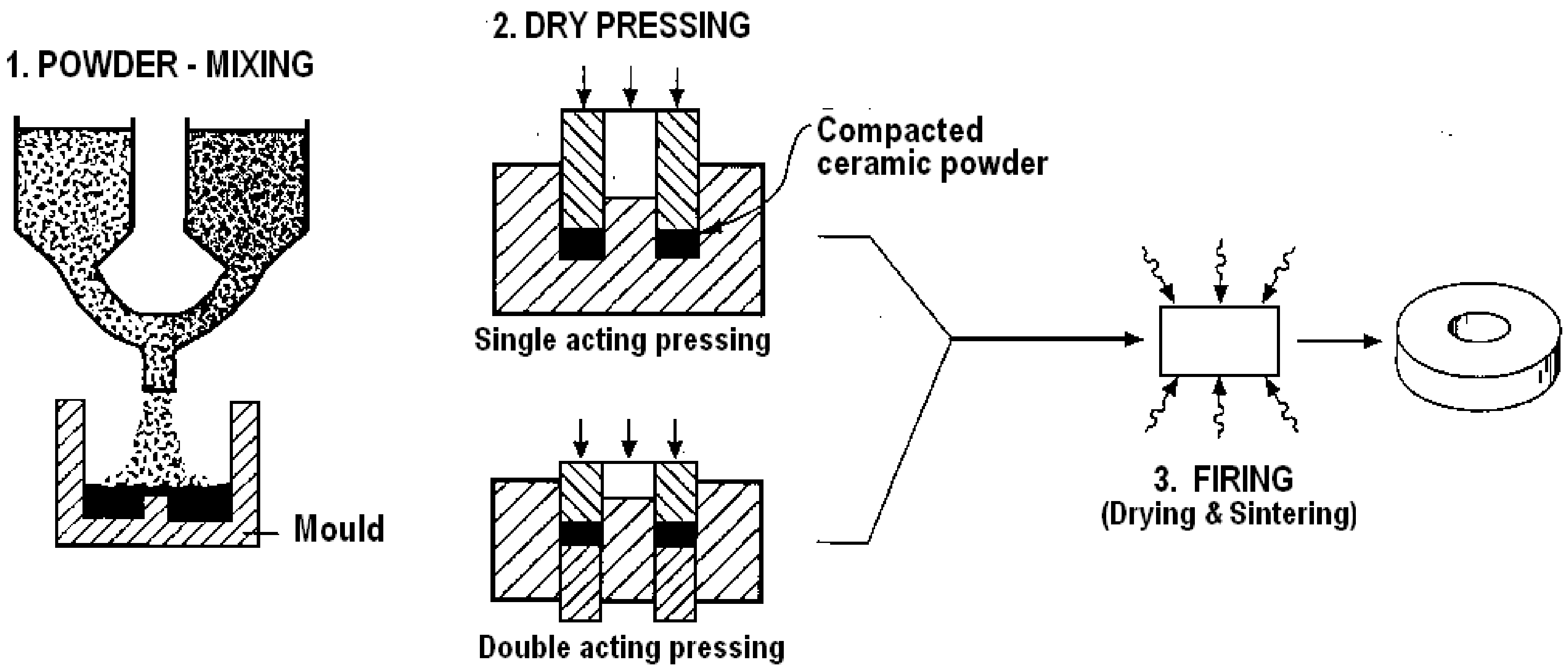
Rotating double cone

Screw mixer

Blade mixer

# 2. FORMING (Green Body)

## i. Dry Pressing



- **Dry Pressing:**

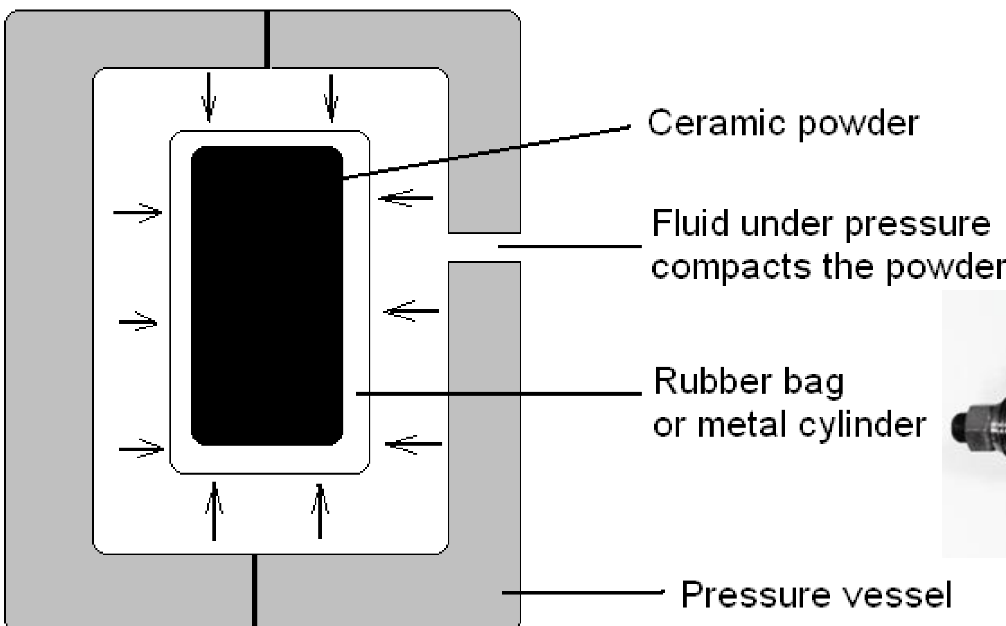
  **Simultaneous uniaxial compaction and shaping of power along with binder.**

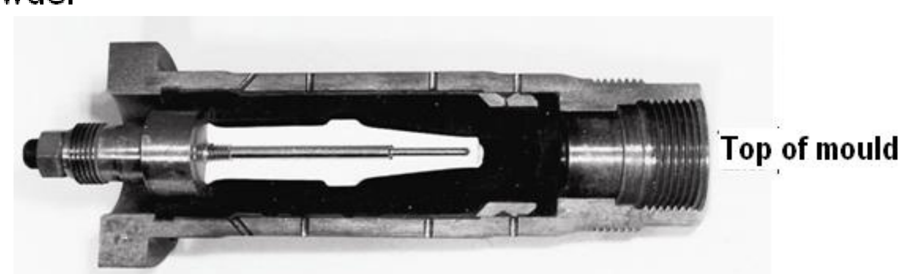
  **Wide variety of shapes can be formed rapidly and accurately.**

- **Isolatic pressing (CIP, HIP):**

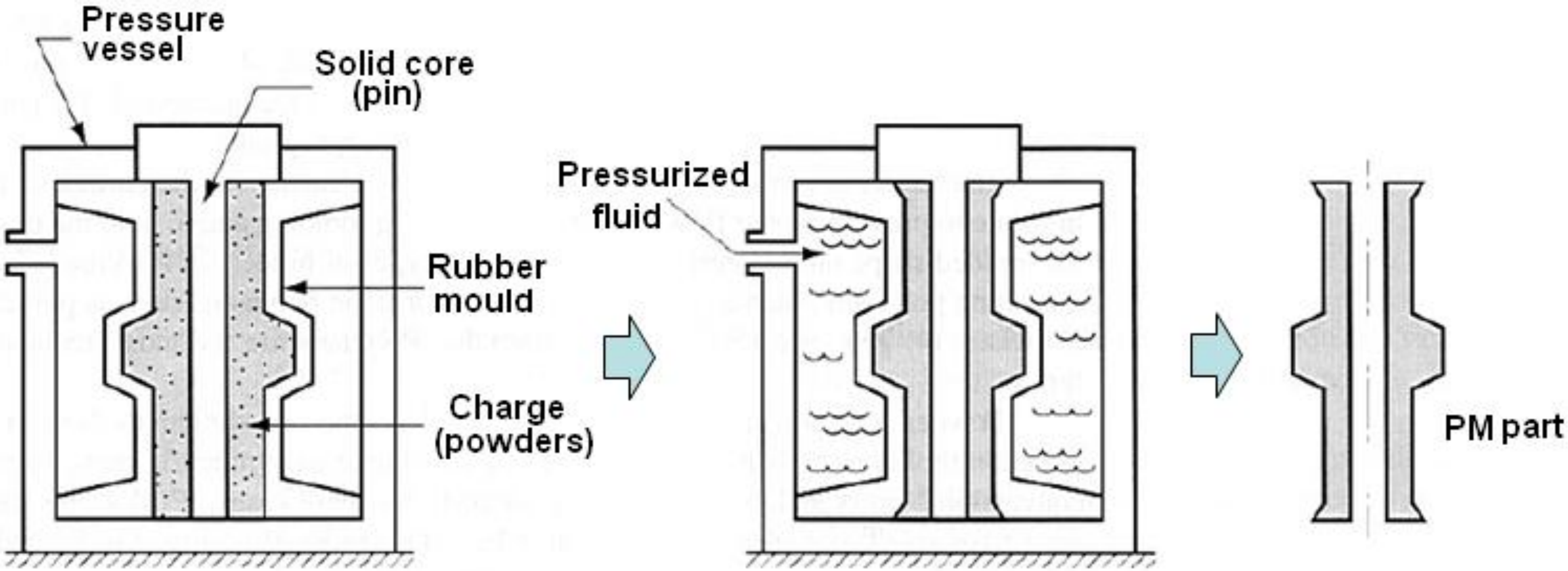
  **Ceramic powder is loaded into a flexible chamber and pressure is applied outside the chamber with hydraulic fluid.**

  **Examples: Spark plug insulators, carbide tools.**



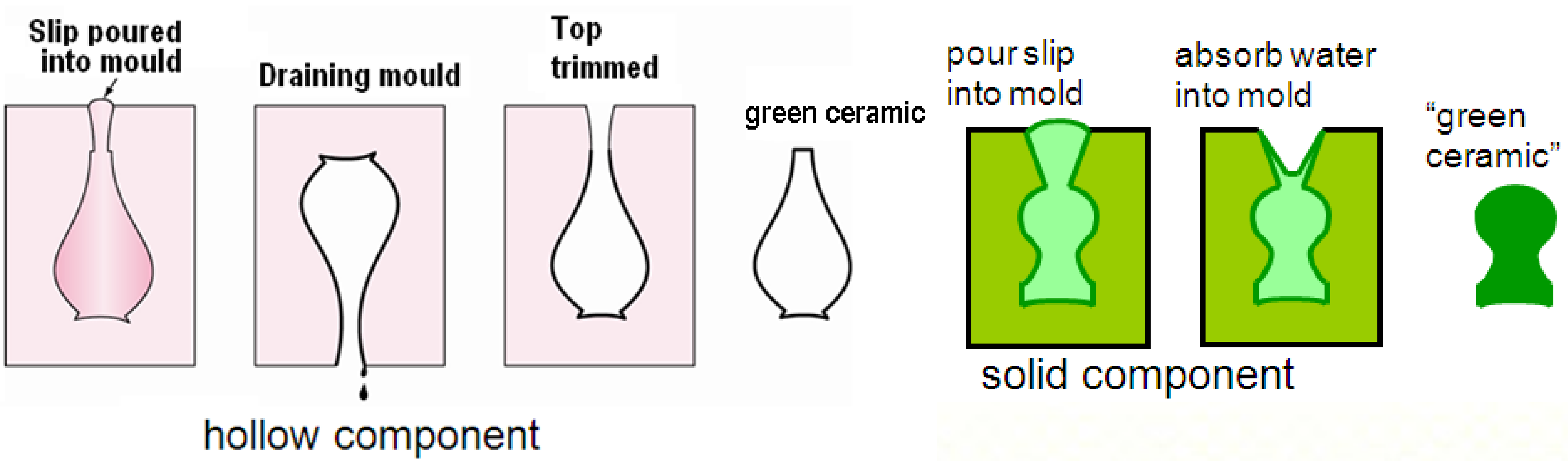

After J.S. Reed and R.B. Runk, "Ceramic Fabrication Process," vol 9: "1976, p.74.




# Cold Isostatic Pressing (CIP)

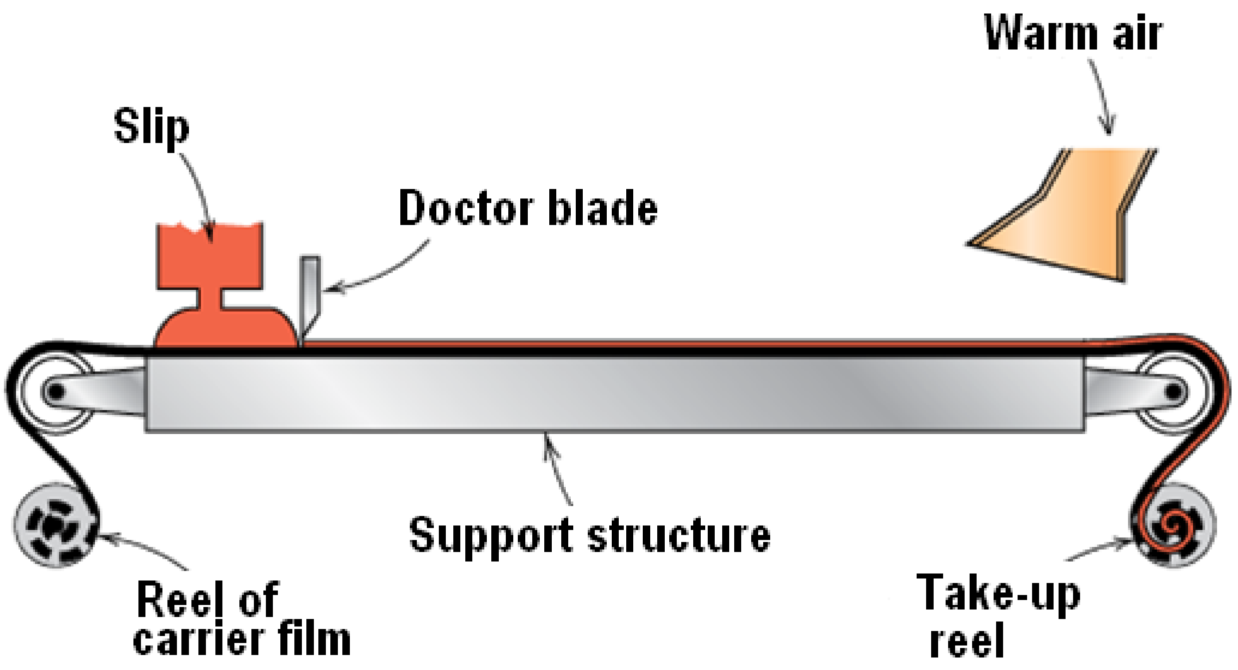
# Slip Casting

- Powdered ceramic material and a liquid mixed to prepare a stable suspension (slip).
- Slip is poured into porous mold and liquid portion is partially absorbed by mold.
- Layer of semi-hard material is formed against mold surface.
- Excess slip is poured out of cavity or cast as solid.
- The material in mold is allowed to dry and then fired.



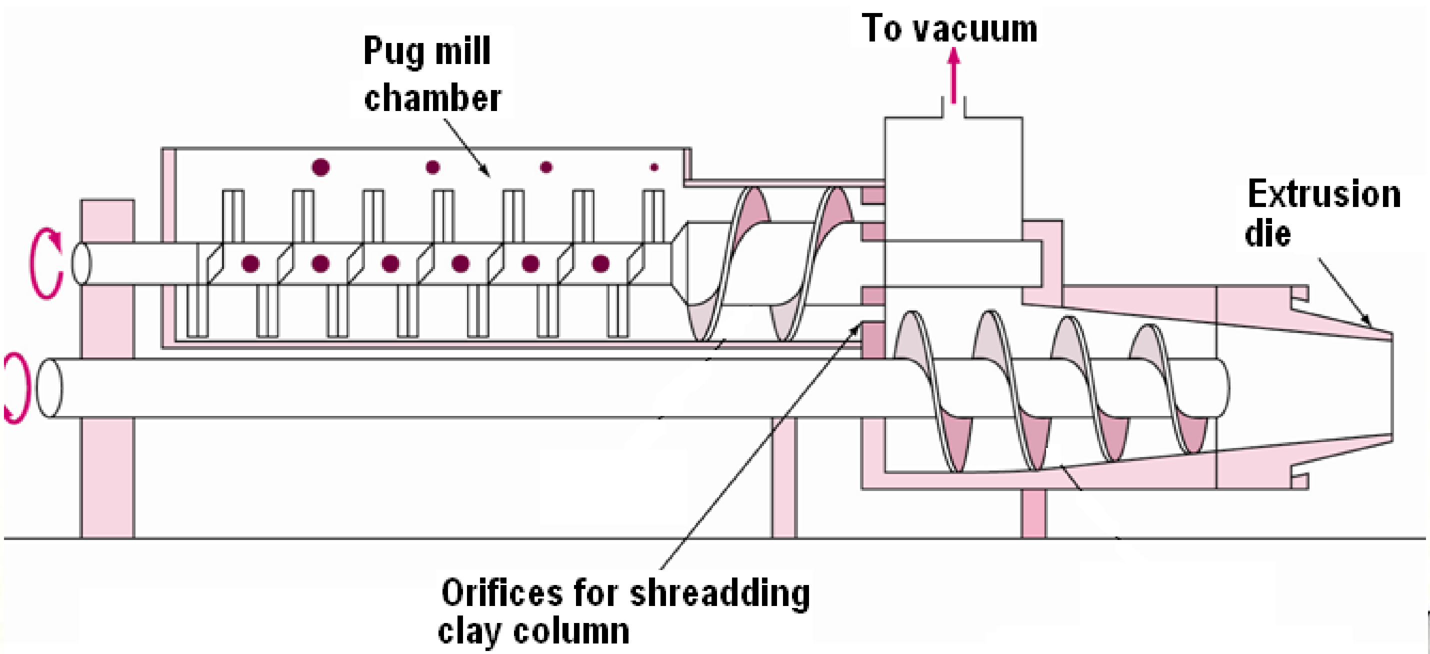
## Tape Casting

- Thin sheets of green ceramic cast as flexible tape (0.2 to 2 mm)
- Used for integrated circuits and capacitors
- Slip = suspended ceramic particles + organic liquid
  (contains binders, plasticizers)



## Extrusion

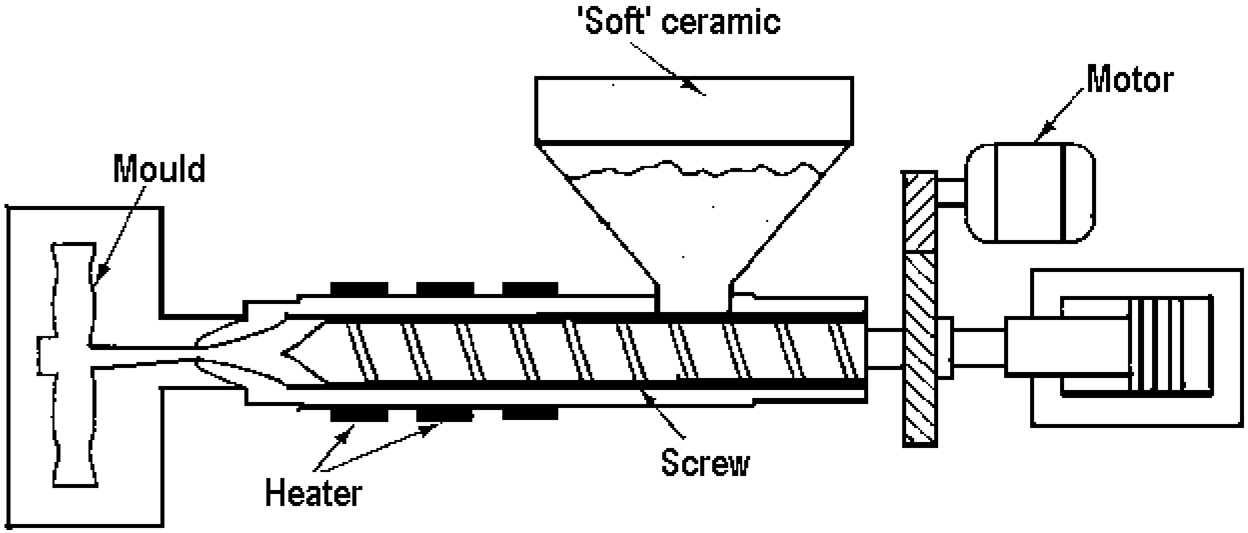
- Single cross sections and hollow shapes of ceramics can be produced by extrusion.
- Plastic ceramic material is forced through a hard steel or alloy die by a motor driven augur.
- Examples: Refractory brick, sewer pipe, hollow tubes.



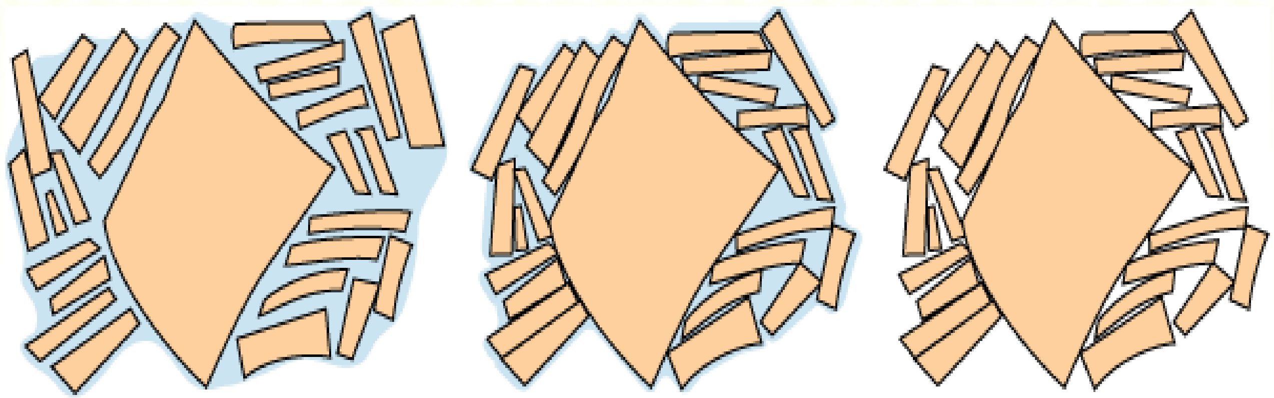
## Injection Moulding

**Ceramic powder + binder**

**Binder :** TP plastic spt PP, LDPE, ethylene vinyl acetate



# 3. FIRING ( Drying and Sintering)



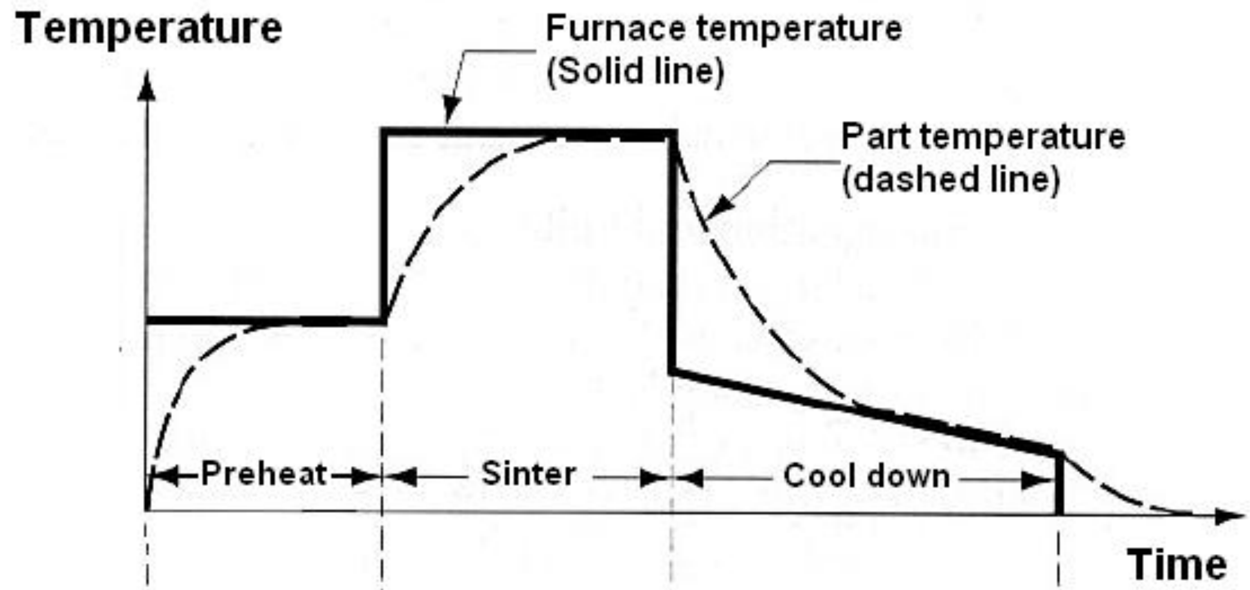
**wet body** **partially dry** **completely dry**

- **Drying**:
  - as water is removed – interparticle spacings decrease – shrinkage .

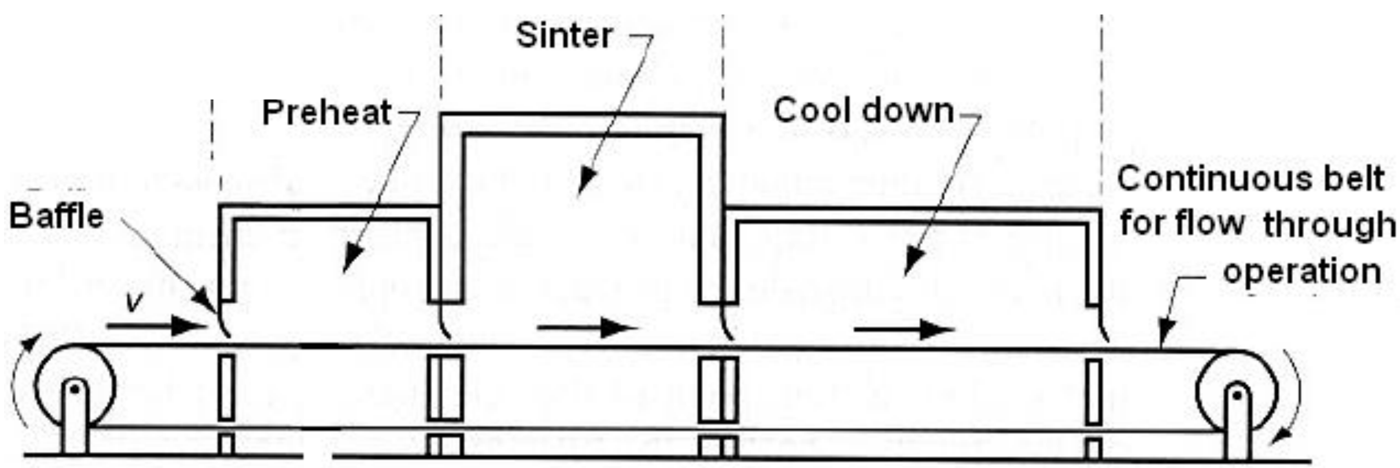
  Drying too fast causes sample to warp or crack due to non-uniform shrinkage

- **Firing**:
  - -- heat treatment between 900-1400ºC
  - -- **vitrification**: liquid glass forms from clay and flux – flows between $SiO_2$ particles. (Flux lowers melting temperature).

**Typical heat treatment cycle in sintering**



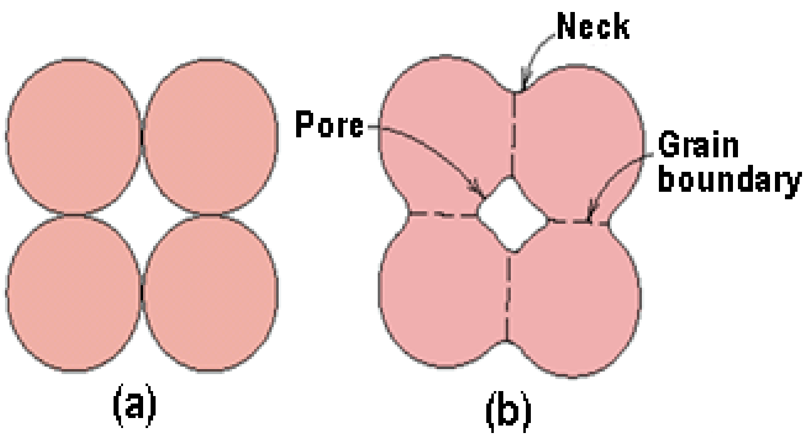

**Schematic cross section of a continuous sintering furnace**

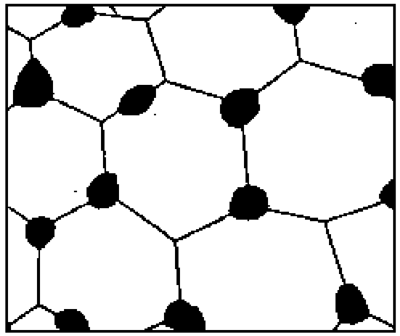


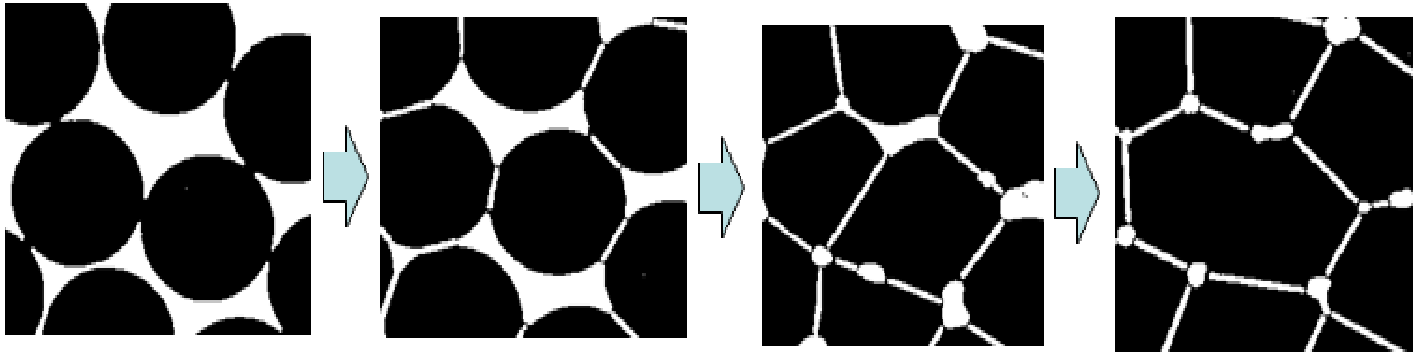
# Sintering

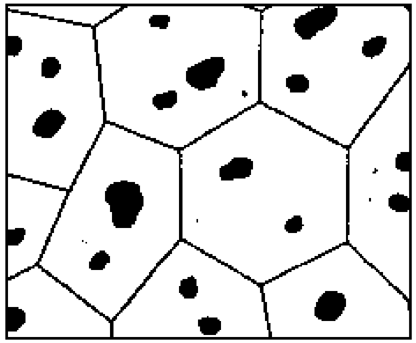
**Sintering occurs during firing of a piece that has been powder pressed**

**-- powder particles coalesce and reduction of pore size**





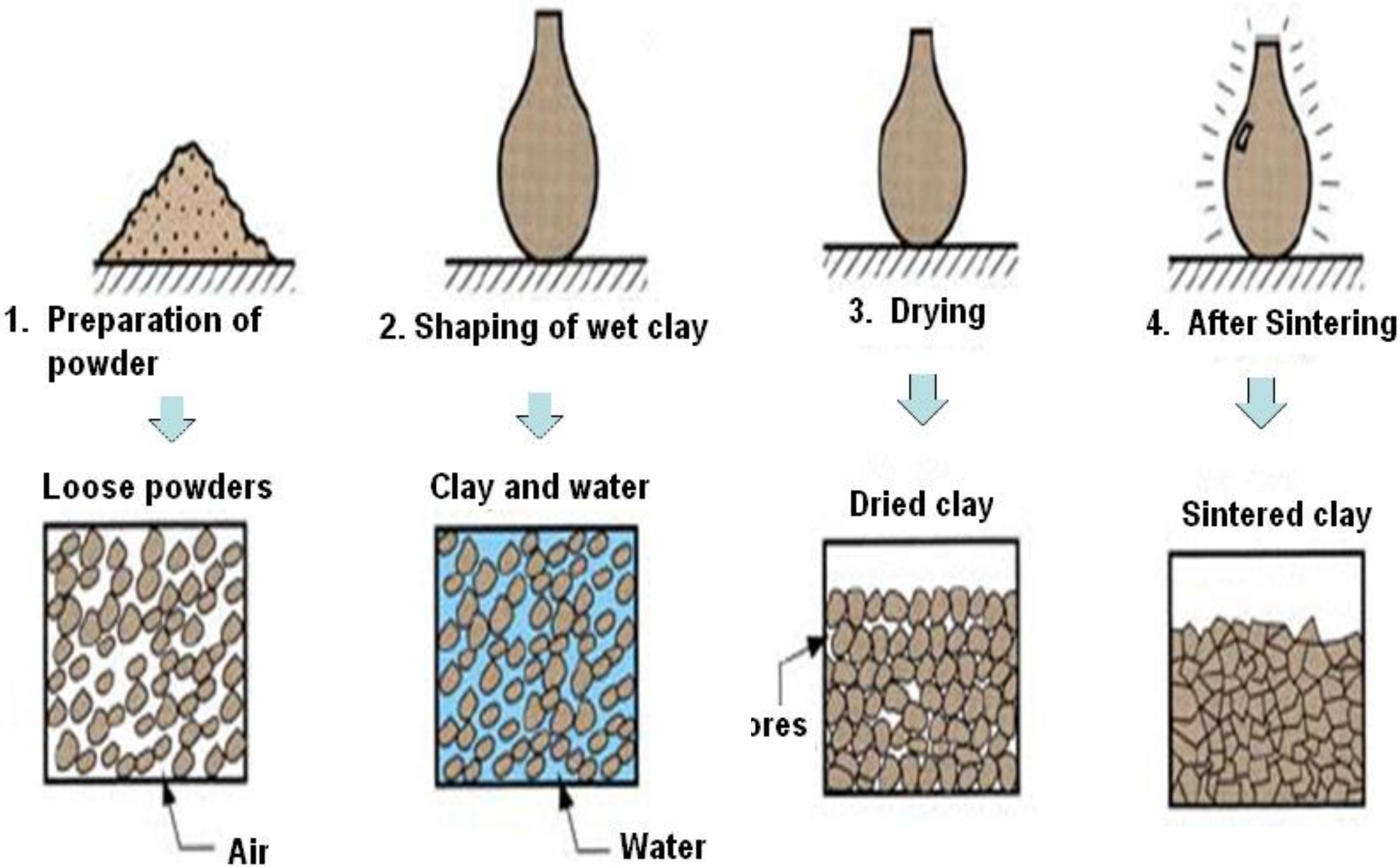


# Traditional Ceramics

- **Made up of clay, silica and fledspar.**
- **Clay: Provide workability and hardness.**
- **Silica: Provide better temperature resistance and MP.**
- **Potash Fledspar: Makes glass when ceramic is fired.**

Life history of a triaxial body

| Temperature (°C) | Reactions |
|---|---|
| Up to 100 | Loss of moisture |
| 100–200 | Removal of absorbed water |
| 450 | Dehydroxylation |
| 500 | Oxidation of organic matter |
| 573 | Quartz inversion to high form. Little overall volume damage |
| 980 | Spinel forms from clay. Start of shrinkage |
| 1000 | Primary mullite forms |
| 1050–1100 | Glass forms from feldspar, mullite grows, shrinkage continues |
| 1200 | More glass, mullite grows, pores closing, some quartz solution |
| 1250 | 60% glass, 21% mullite, 19% quartz, pores at minimum |


1. Preparation of powder
2. Shaping of wet clay
3. Drying
4. After Sintering
Loose powders
Clay and water
Dried clay
Sintered clay
Air
Water
ores

# 5. FINISHING OPERATIONS

To further improve the properties of sintered product :

i. Re- pressing : also called coining and sizing

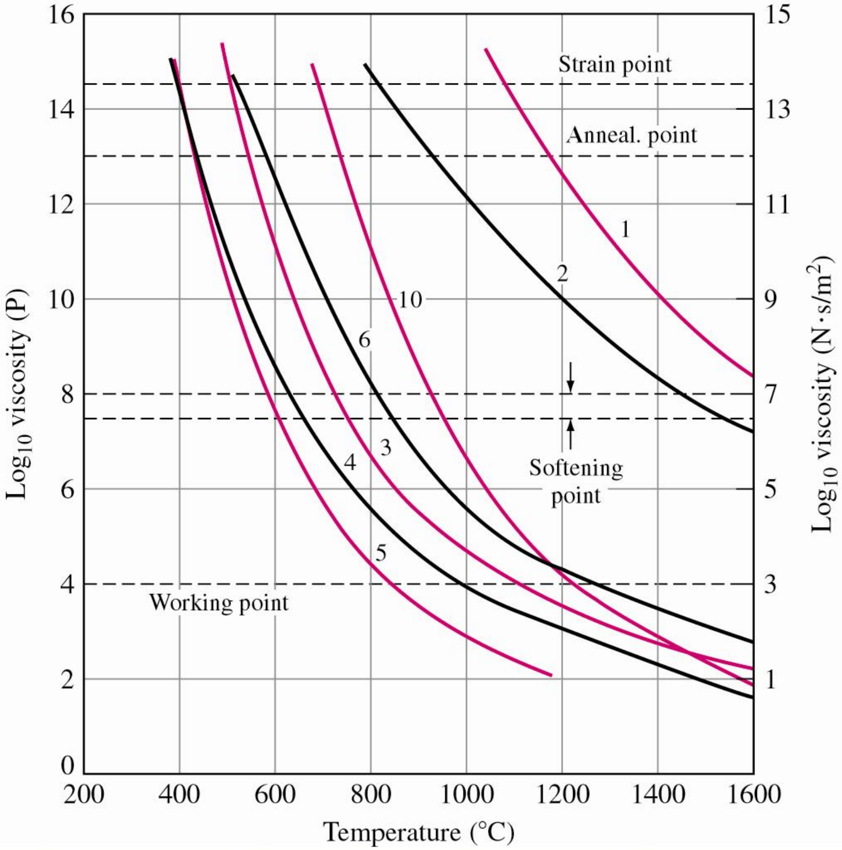
ii. Forging, grinding

iii. Heat treatment : quenching and tempering

iv. Machining : milling, grinding, ultra sonic, laser, electrical-discharge machining (EDM)

v. Glazing, plating, painting

# Glass : Effect of temperature



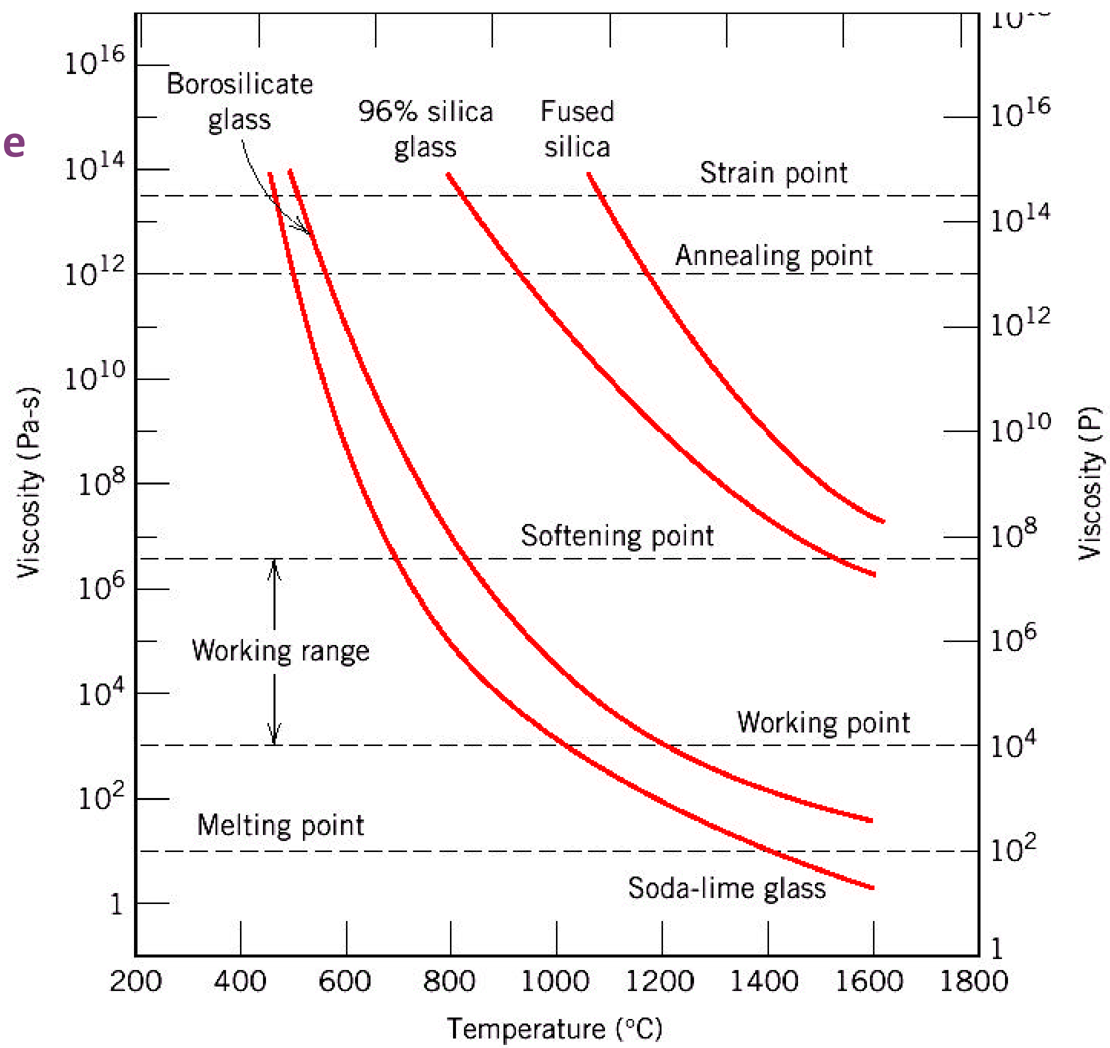

**Viscous Deformation of glasses.**

1. **Working point: $10^3$ PaS**
   **– glass fabrication can be carried out**
2. **Softening point: $10^7$ PaS**
   **– glass flows under its own weight.**
3. **Annealing point: $10^{12}$ PaS**
   **– Internal stresses can be relieved.**
4. **Strain point: $10^{13.5}$ PaS**
   **– glass is rigid below this point.**

**Units are Pa-s, or Poises (P)**
**1 P = 0.1 Pa-s**
**Viscosity of water at room temp is ~ $10^{-3}$ P**
**Viscosity of typical glass at room temp >> $10^{16}$ P**

# Question :

A piece of silica glass having the viscosity of $10^{13}$ P at 940°C (annealed point) and the viscosity of $10^{8}$ P at 1470°C (softening point). Calculate the activation energy for viscous flow in this temperature range for this glass




# Solution :

**Annealing point of glass,**

$T_{ap} = 1213K, \ \eta_{ap} = 10^{13}P$

**Softening point of glass,**

$T_{sp} = 1743K, \ \eta_{sp} = 10^{8}$ P,

R = 8.314 J/(mol.K)

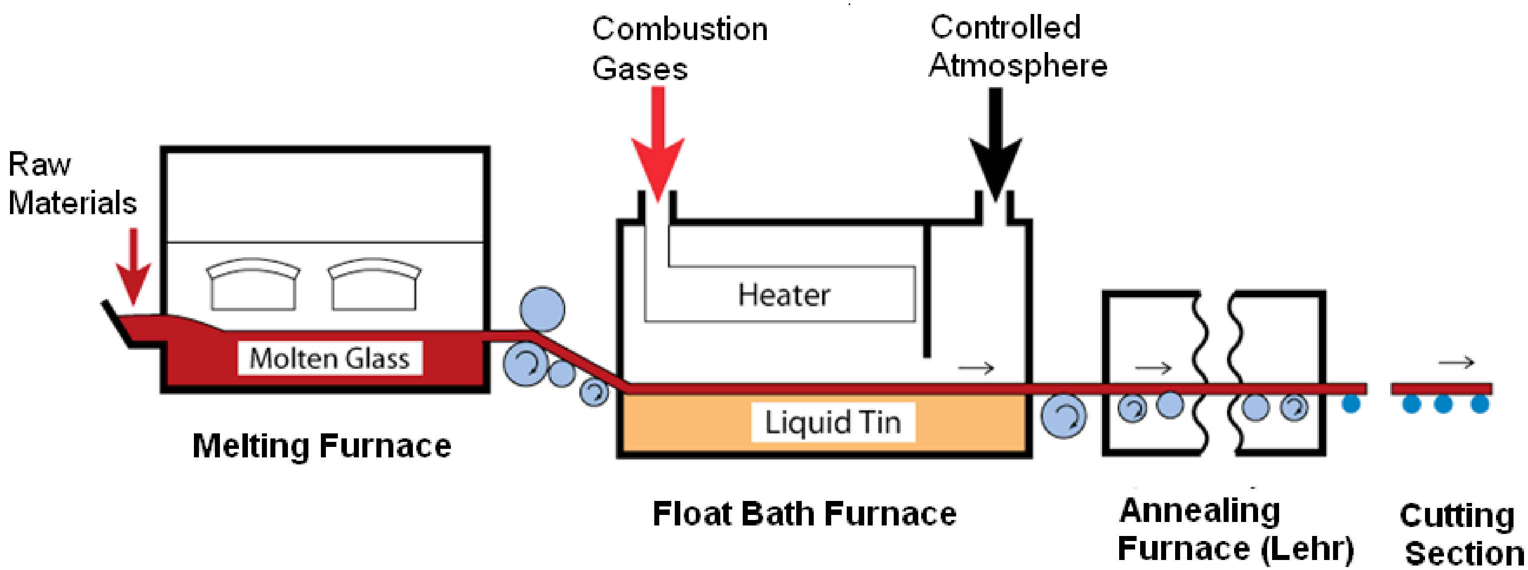
Use Equation: $\eta = \eta_o e^{+Q/RT}$

Q = 8.32 x $10^{5}$ j/mol

# GLASS PROCESSING

## 1. Sheet Glass Forming

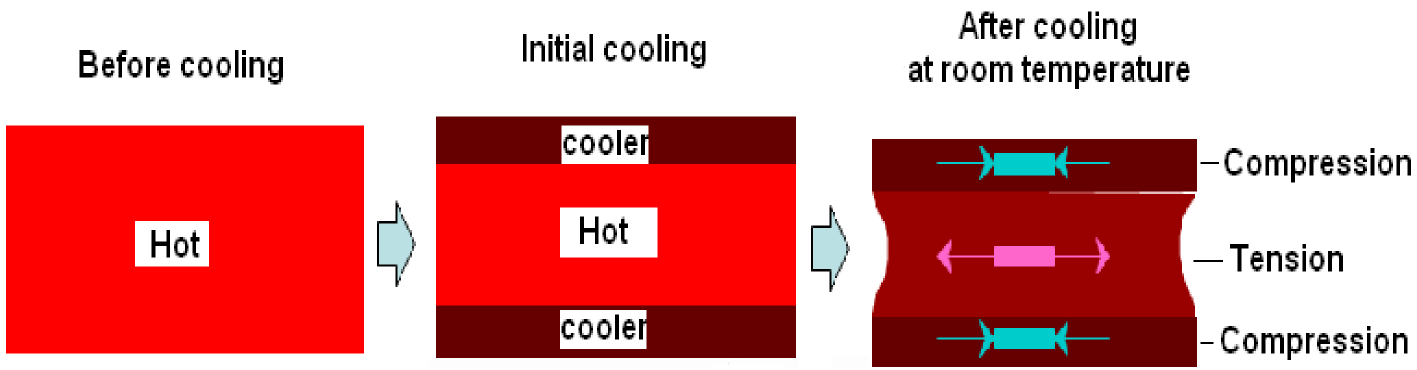
- Sheet forming – continuous casting
  Sheets are formed by floating the molten glass on a pool of molten tin
- Forming sheet and plate glass:
  Ribbon of glass moves out of furnace and floats on a bath of molten tin.
- Glass is cooled by molten tin.
- After it is hard, it is removed and passed through a long annealing furnace.



# HEAT TREATMENT OF GLASS

## 1. Thermal Tempering

- Glass is heated into near softening point and rapidly cooled.
- Surface cools first and contracts.
- Interior cools next and contracts causing tensile stresses in the interior and compressive stress on the surface.
- suppresses growth of cracks from surface scratches
- Tempering strengthens the glass.
- Examples: Auto side windows and safety glasses.



## 2. Chemically Strengthened Glass

**Special treatment increases chemical resistance of glasses.**

**Example:- Sodium alumino silicate glasses are immersed in a bath of potassium nitrate at $50^0$C for 6 to 10 hours**

- **Large potassium ions are induced into surface causing compressive stress**
- **Compressive layer is much thinner than that in thermal tempering.**
- **Used for supersonic aircraft glazing and lenses.**

## 3. Laminated glass

**Laminate Strengthening method ; two pieces of flat glass are assembled with a thin sheet of tough plastic (eg . Polyninyl butyral, PVB) between them.**

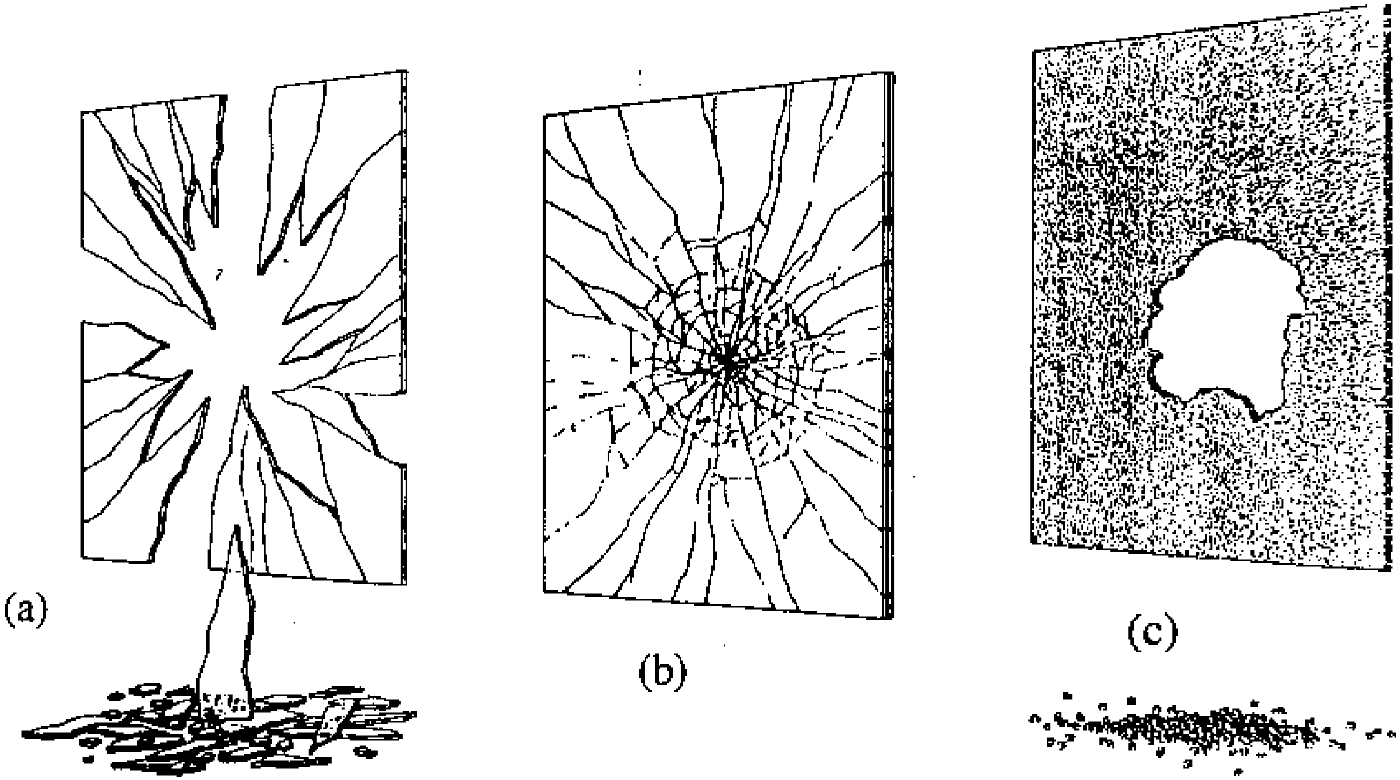
**When the glass is broken, its pieces are held together by the plastic sheet.**

## 4. Annealing

**When ceramic materials is cooled from an elevated temp. internal stresses (thermal stresses,) is introduced as a result of the difference in cooling rate and thermal contraction between the surface and interior region.**

**Method :**

**The glassware is heated to the annealing point, then slowly cooled to room temperature**



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