Mechanical Properties

We know that ceramics are more brittle than metals. Why?

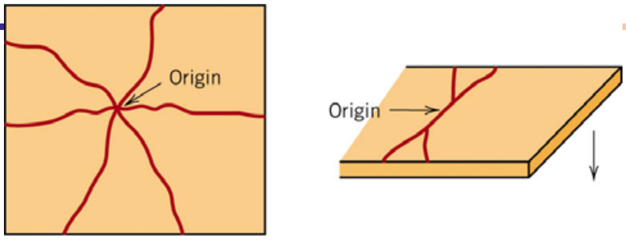
- Consider method of deformation

  slippage along slip planes

    in ionic solids this slippage is very difficult

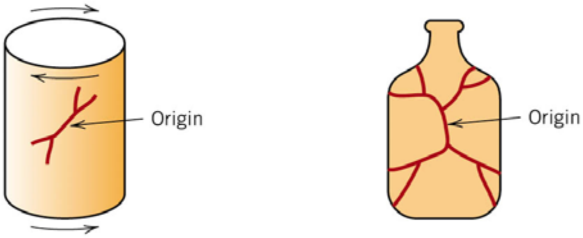
    too much energy needed to move one anion past another anion

Ceramic Fracture



Impact or point loading (a)

Bending (b)



Torsion (c)

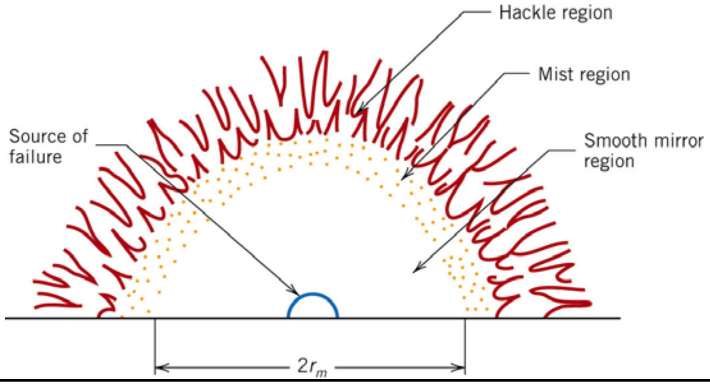
Internal pressure (d)

Ceramic Fracture

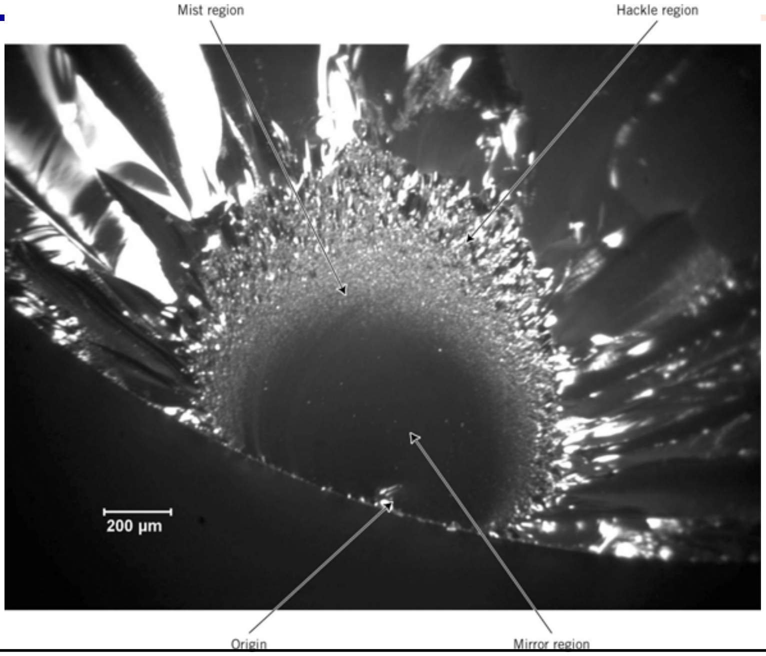
Mirror region the first region of a brittle fracture surface, which is very smooth. Associated with slow but accelerating crack growth.

Mist region the second region of a brittle fracture surface; cloudy look caused by the crack propagating at up to the maximum velocity, but insufficient energy is being released to cause branching.

Hackle region the third region of a brittle fracture surface, rough and ridged. The crack branches while growing at maximum velocity, often resulting in a piece of material being ejected.

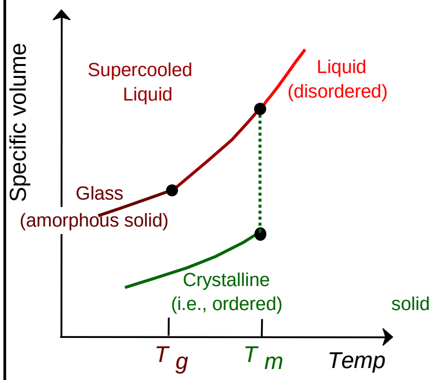


Ceramic Fracture



Glass Properties

- Specific volume (1/ρ) vs Temperature (*T*):

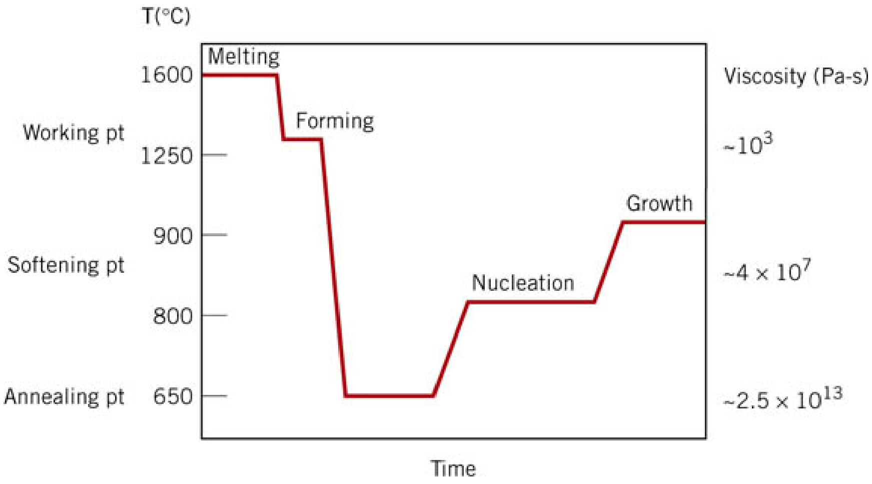


- Crystalline materials:
  crystallize at melting temp, T_m
  have abrupt change in spec. vol. at T_m

- Glasses:
  do not crystallize
  change in slope in spec. vol. curve at
  glass transition temperature, T_g
  transparent
  no crystals to scatter light

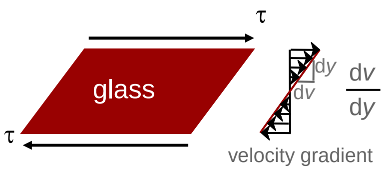
Adapted from Fig. 13.6, *Callister, 7e*.

Glass Crystallization



Glass Properties: Viscosity

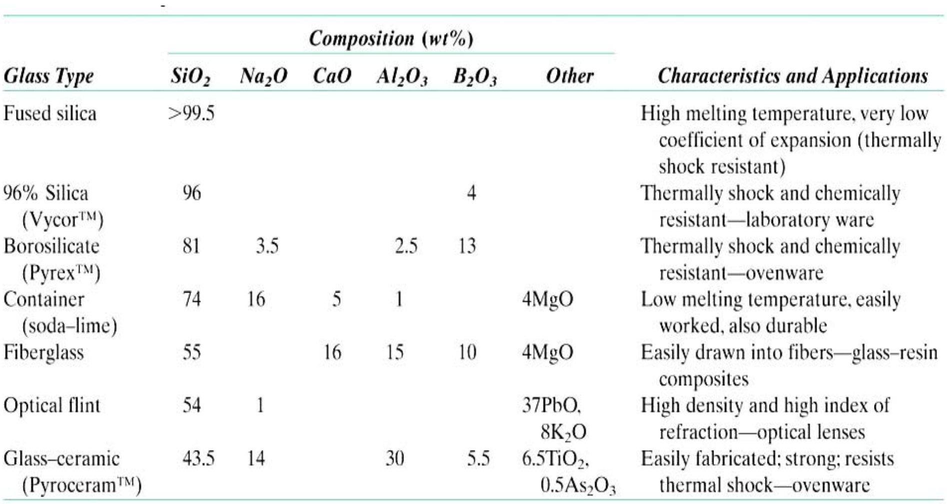
- Viscosity, η:
  relates shear stress and velocity gradient:



$$\tau = \eta \frac{dv}{dy}$$

η has units of (Pas)

Glass Compositions

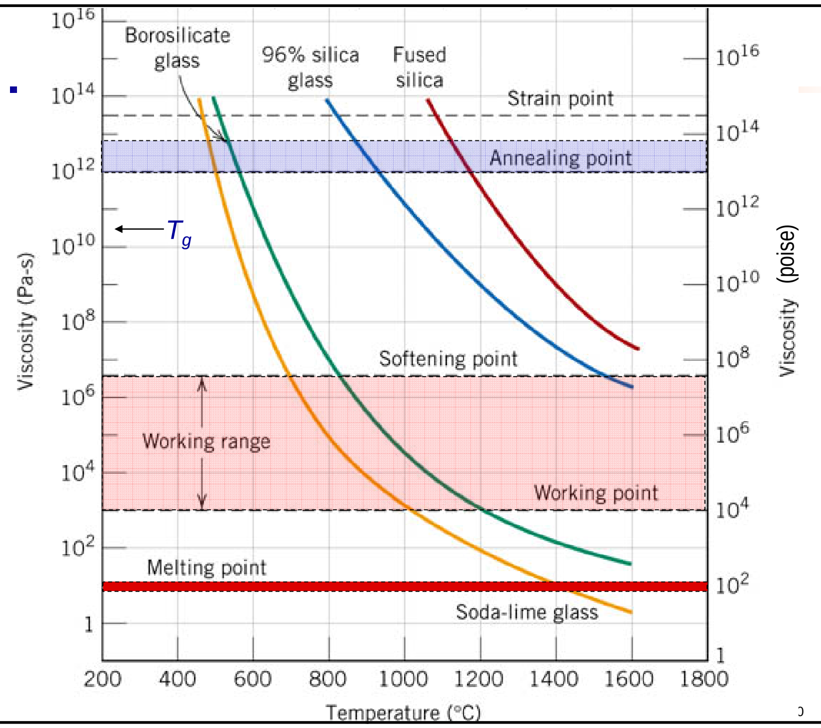


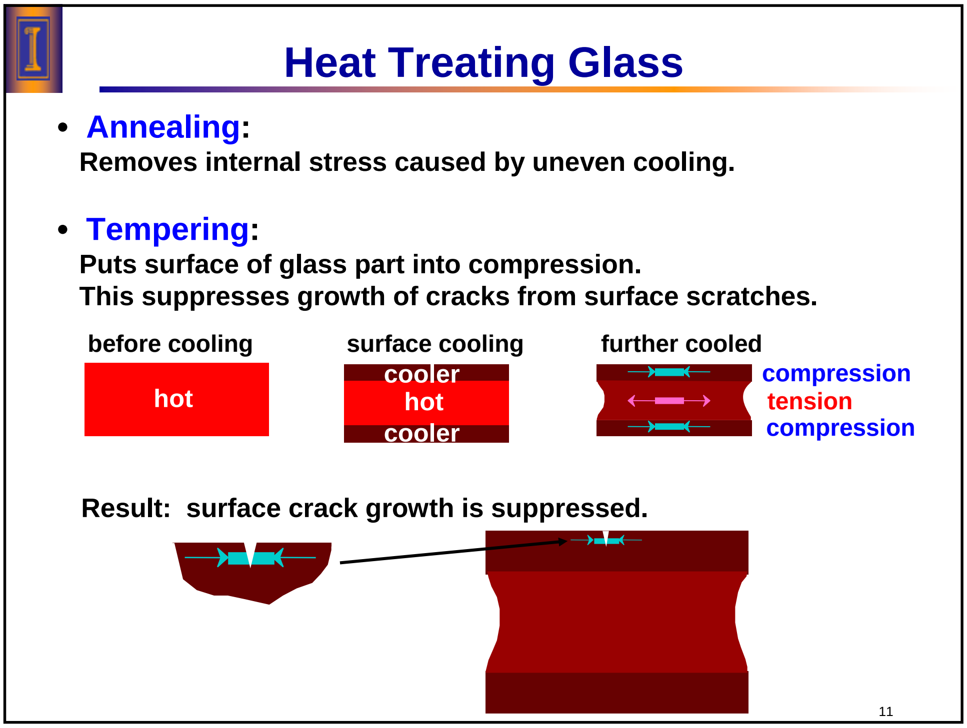
Glass Type	Composition (wt%) SiO_2	Na_2O	CaO	Al_2O_3	B_2O_3	Other	Characteristics and Applications
Fused silica	>99.5						High melting temperature, very low coefficient of expansion (thermally shock resistant)
96% Silica (Vycor™)	96				4		Thermally shock and chemically resistant—laboratory ware
Borosilicate (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

Glass Viscosity vs. T and Impurities

- **sodalime glass: 70% SiO_2 balance Na_2O (soda) & CaO (lime)**
- **borosilicate (Pyrex): 13% B_2O_3, 3.5% Na_2O, 2.5% Al_2O_3**
- **Vycor: 96% SiO_2, 4% B_2O_3**
- **fused silica: > 99.5 wt% SiO_2**

- Viscosity decreases with *T*
- Strain Point: fracture before deformation
- Annealing Point: atomic diffusion fast enough to release strain in ~ 15 min.
- Softening Point: Impurities lower T_{deform}
- Working Point: limit of easy deformati

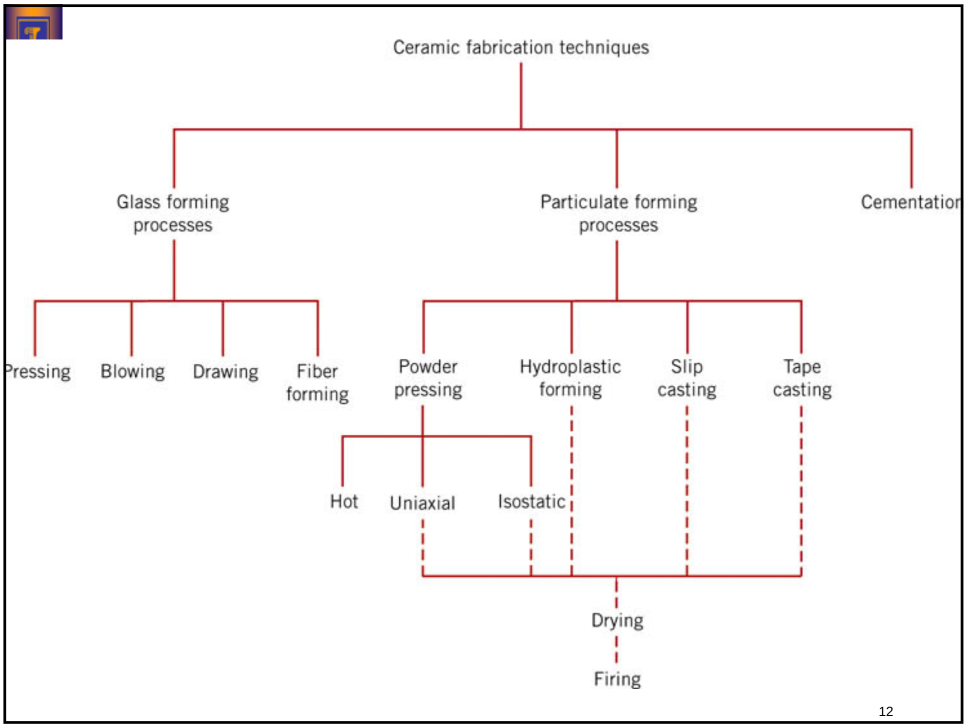




Heat Treating Glass

- **Annealing**:
  Removes internal stress caused by uneven cooling.
- **Tempering**:
  Puts surface of glass part into compression.
  This suppresses growth of cracks from surface scratches.

Result: surface crack growth is suppressed.



Ceramic fabrication techniques

- Glass forming processes
  - Pressing
  - Blowing
  - Drawing
  - Fiber forming
- Particulate forming processes
  - Powder pressing
    - Hot
    - Uniaxial
    - Isostatic
  - Hydroplastic forming
  - Slip casting
  - Tape casting
- Cementatio

Drying

Firing

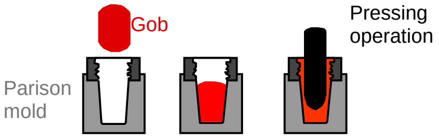
Ceramic Fabrication Methods I

GLASS FORMING

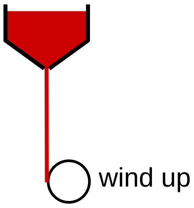
PARTICULATE FORMING

CEMENTATION

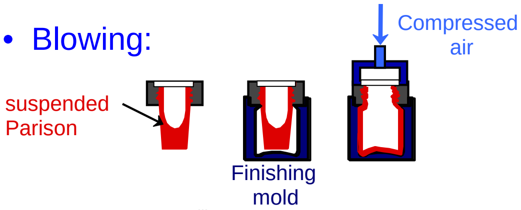
- **Pressing:** mold is steel with graphite lining; plates, dishes, cheap glasses



- **Fiber drawing:**



- **Blowing:**

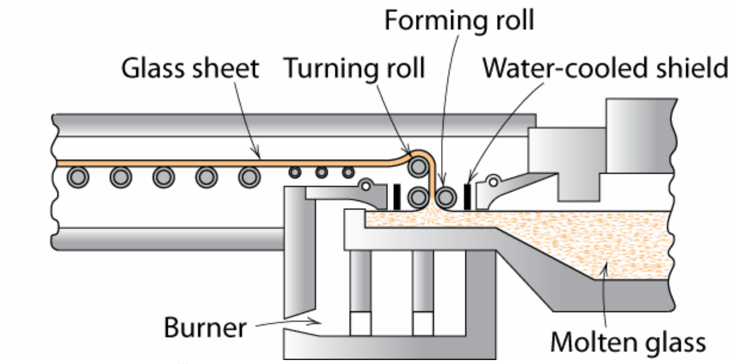


Adapted from Fig. 13.8, *Callister, 7e*. (Fig. 13.8 is adapted from C.J. Phillips, *Glass: The Miracle Maker*, Pittman Publishing Ltd., London.)

Sheet Glass Forming

- Sheet forming – continuous draw

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



Adapted from Fig. 13.9, *Callister 7e.*

Ceramic Fabrication Methods II

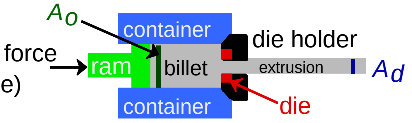
GLASS FORMING | PARTICULATE FORMING | CEMENTATION

- Milling and screening: desired particle size
- Mixing particles & water: produces a "slip"
- Form a "green" component
- Dry and fire the component

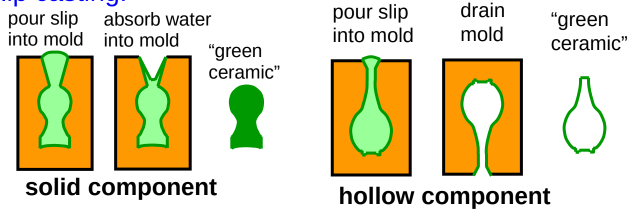
Ceramic Fabrication Methods II

GLASS FORMING | PARTICULATE FORMING | CEMENTATION

Hydroplastic forming:
extrude the slip (e.g., into a pipe)



Slip casting:



Clay Composition

A mixture of components used

(50%) 1. Clay

(25%) 2. Filler – e.g. quartz (finely ground)

(25%) 3. Fluxing agent (Feldspar)

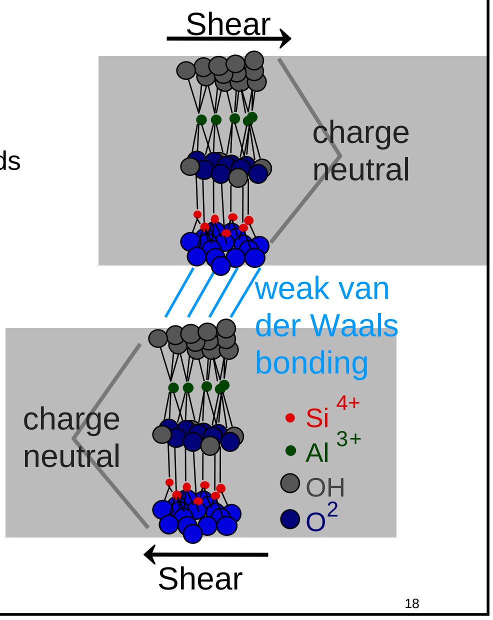
binds it together

aluminosilicates + K^+, Na^+, Ca^+

Features of a Slip

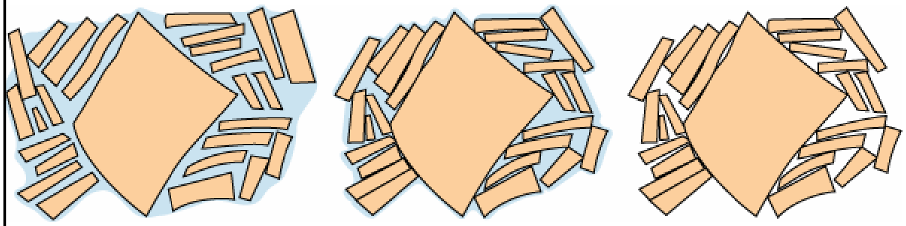
- **Clay** is inexpensive
- Adding water to clay
  - allows material to shear easily along weak van der Waals bonds
  - enables extrusion
  - enables slip casting

Structure of Kaolinite Clay:



Drying

- Drying: layer size and spacing decrease.



wet slip

partially dry

“green” ceramic

Drying too fast causes sample to warp or crack due to nonuniform shrinkage.
Surface tension forces tight packing. Aerogel vs. Xerogel.

Firing

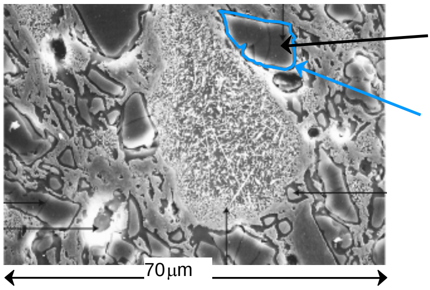
- Firing:

  T raised to (900 to 1400°C).

  vitrification: liquid glass forms from clay and flows between SiO_2 particles.

  Flux melts at lower *T*.

micrograph of
porcelain



$Si0_2$ particle
(quartz)

glass formed
around
the particle

Ceramic Fabrication Methods II

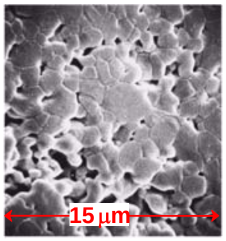
GLASS FORMING

PARTICULATE FORMING

CEMENTATION

Sintering: useful for both clay and nonclay compositions.

- Procedure:
  - produce ceramic and/or glass particles by grinding
  - place particles in mold
  - press at elevated *T* to reduce pore size.
- Aluminum oxide powder:
  - sintered at 1700°C for 6 minutes.



Adapted from Fig. 13.17, *Callister 7e*. (Fig. 13.17 is from W.D. Kingery, H.K. Bowen, and D.R. Uhlmann, *Introduction to Ceramics*, 2nd ed., John Wiley and Sons, Inc., 1976, p. 483.)

Powder Pressing

Sintering powder touches forms neck & gradually neck thickens

add processing aids to help form neck

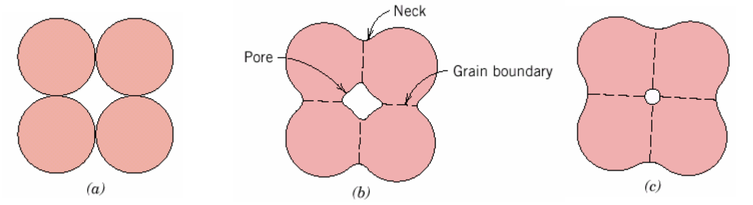
little or no plastic deformation

Uniaxial compression compacted in single direction

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

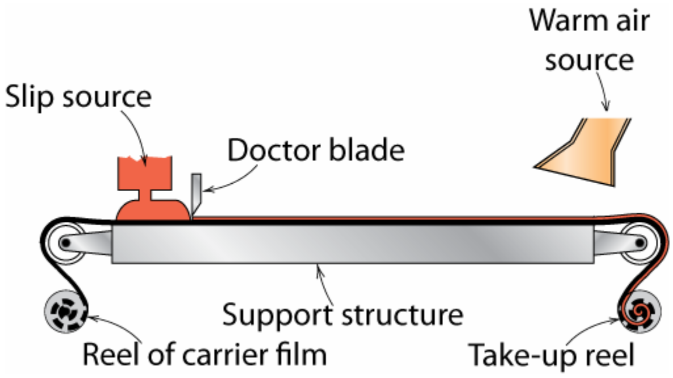
Hot pressing pressure + heat

Adapted from Fig. 13.16, *Callister 7e*.



Tape Casting

- **thin sheets of green ceramic cast as flexible tape (<2 mm)**
- **used for integrated circuits and capacitors**
- **cast from liquid slip (ceramic + organic solvent)**



Adapted from Fig. 13.18, *Callister 7e*.

Ceramic Fabrication Methods III

GLASS FORMING | PARTICULATE FORMING | CEMENTATION

Clinker: Partially dehydrated mineral that forms cement or plaster with water

Concrete: Aggregate of cement, sand, rock, air, water

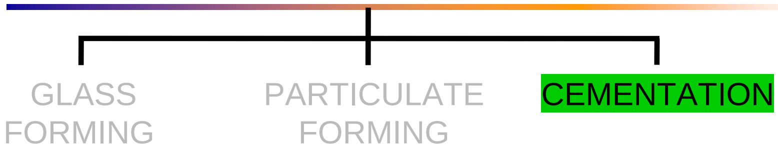
Good Compressive Strength.

Mediocre tensile Strength (against stretching)

Reinforced Concrete: Metal Rods internal to add to Tensile strength

1906, Unitarian Church, Oak Park, IL
Frank Lloyd Wright

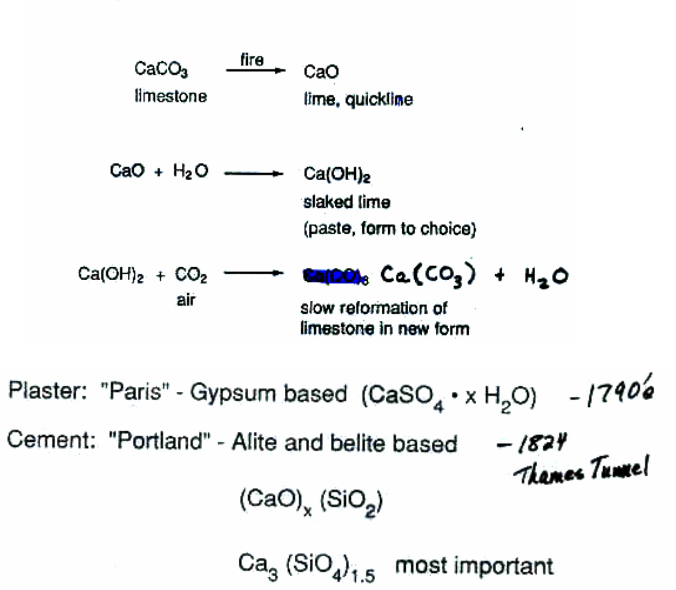
Ceramic Fabrication Methods III



- Produced in extremely large quantities.
- Portland cement:
  - mix clay and lime bearing materials
  - calcinate (heat to 1400°C)
  - primary constituents:
    - tricalcium silicate
    - dicalcium silicate
- Adding water
  - produces a paste which hardens
  - hardening occurs due to hydration
- Forming: done usually minutes after hydration begins.

Early Cement

Etruscans



$CaCO_3 \xrightarrow{\text{fire}} CaO$

limestone — lime, quicklime

$CaO + H_2O \longrightarrow Ca(OH)_2$

slaked lime
(paste, form to choice)

$Ca(OH)_2 + CO_2 \longrightarrow$ ~~$Ca(CO)_3$~~ $Ca(CO_3) + H_2O$

air

slow reformation of
limestone in new form

Plaster: "Paris" - Gypsum based ($CaSO_4 \cdot x\, H_2O$) – 1790's

Cement: "Portland" - Alite and belite based – 1824
Thames Tunnel

$(CaO)_x\,(SiO_2)$

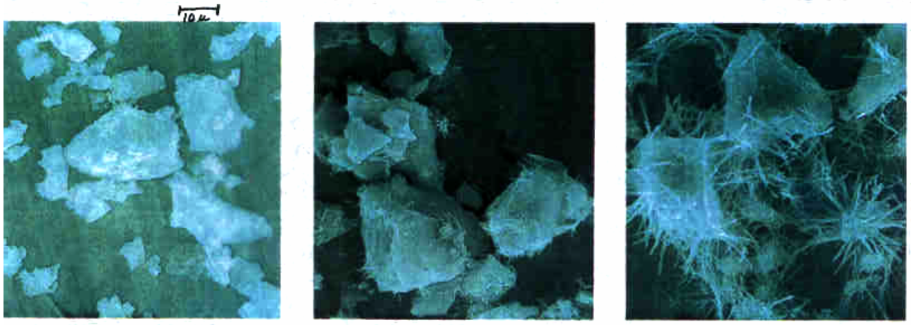
$Ca_3\,(SiO_4)_{1.5}$ most important

Early Cement

Clinker

Partial Hydration

Final Microstructure



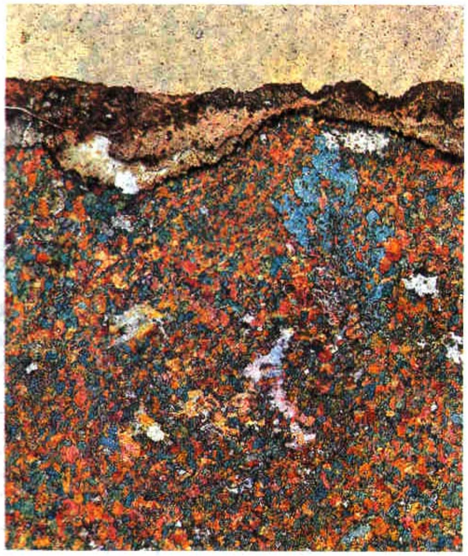
$3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$
↑

Needles:
$3CaO \cdot Al_2O_3 \cdot 3CaSO_4$
$\cdot 32\ H_2O$
↑

Early Cement

Several of the components present in modern cement powder are also found in the natural clinker larnite, which is *beta*-dicalcium silicate. As can be seen in this optical photomicrograph of a thin section, weathering effects at the surface of the mineral produce a primitive form of concrete.

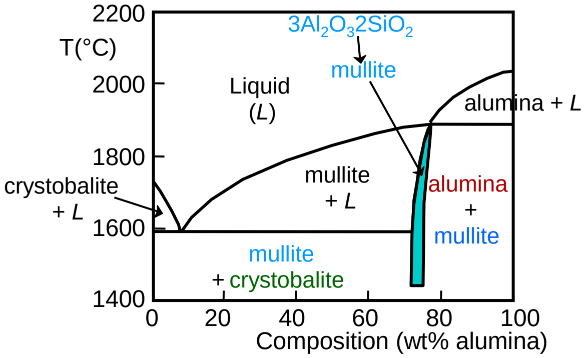
$Ca_2\ SiO_4$



Application: Refractories

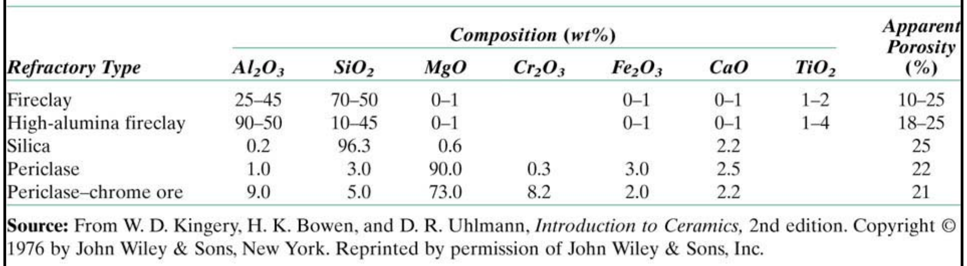
- **Need a material to use in high temperature furnaces.**
- **Consider the Silica (SiO_2) - Alumina (Al_2O_3) system.**
- **Phase diagram shows:**

  mullite, alumina, and crystobalite as candidate refractories.



Adapted from Fig. 12.27, *Callister 7e.* (Fig. 12.27 is adapted from F.J. Klug and R.H. Doremus, "Alumina Silica Phase Diagram in the Mullite Region", *J. American Ceramic Society* **70**(10), p. 758, 1987.)

Application: Refractories



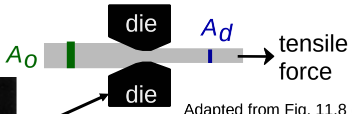
Refractory Type	*Composition (wt%)*							*Apparent Porosity (%)*
	Al_2O_3	*SiO_2*	*MgO*	*Cr_2O_3*	*Fe_2O_3*	*CaO*	*TiO_2*	
Fireclay	25–45	70–50	0–1		0–1	0–1	1–2	10–25
High-alumina fireclay	90–50	10–45	0–1		0–1	0–1	1–4	18–25
Silica	0.2	96.3	0.6			2.2		25
Periclase	1.0	3.0	90.0	0.3	3.0	2.5		22
Periclase–chrome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

Source: From W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics,* 2nd edition. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

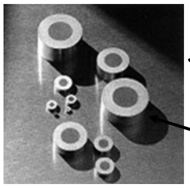
Application: Die Blanks

- **Die blanks:**

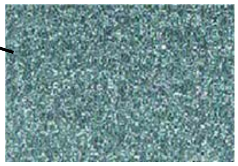
  Need wear resistant properties!



Adapted from Fig. 11.8 (d), *Callister 7e*.



Courtesy Martin Deakins, GE Superabrasives, Worthington, OH. Used with permission.



Courtesy Martin Deakins, GE Superabrasives, Worthington, OH. Used with permission.

- **Die surface:**

  4 μm polycrystalline diamond particles that are sintered onto a cemented tungsten carbide substrate.

  polycrystalline diamond helps control fracture and gives uniform hardness in all directions.

Application: Cutting Tools

- **Tools:**

  for grinding glass, tungsten, carbide, ceramics

  for cutting Si wafers

  for oil drilling

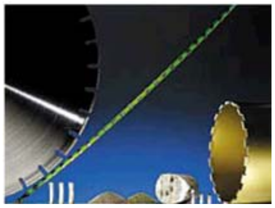
- **Solutions:**

  manufactured single crystal or polycrystalline diamonds in a metal or resin matrix.

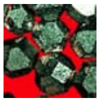
  optional coatings (e.g., Ti to help diamonds bond to a Co matrix via alloying)

  polycrystalline diamonds resharpen by microfracturing along crystalline planes.

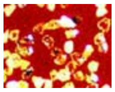
oil drill bits



blades



coated single crystal diamonds

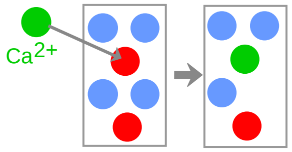


polycrystalline diamonds in a resin matrix.

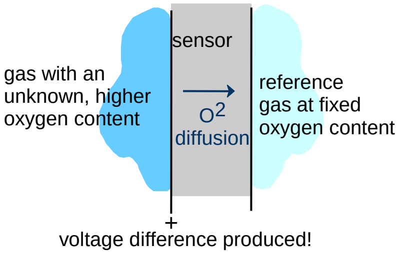
Photos courtesy Martin Deakins, GE Superabrasives, Worthington, OH. Used with permission.

Application: Sensors

- Example: Oxygen sensor ZrO2
- Principle: Make diffusion of ions fast for rapid response.
- Approach:
  Add Ca impurity to ZrO2:
  increases O^2 vacancies
  increases O^2 diffusion rate
- Operation:
  voltage difference produced when O^2 ions diffuse from the external surface of the sensor to the reference gas.



A Ca^{2+} impurity removes a Zr^{4+} and a O^2 ion.



voltage difference produced!

Applications: Advanced Ceramics

Heat Engines

- **Advantages:**
  - **Run at higher temperature**
  - **Excellent wear & corrosion resistance**
  - **Low frictional losses**
  - **Ability to operate without a cooling system**
  - **Low density**
- **Disadvantages:**
  - **Brittle**
  - **Too easy to have voids weaken the engine**
  - **Difficult to machine**

- **Possible parts – engine block, piston coatings, jet engines**

Ex: Si_3N_4, SiC, & ZrO_2

Applications: Advanced Ceramics

- Ceramic Armor

  Al_2O_3, B_4C, SiC & TiB_2

  Extremely hard materials

  shatter the incoming projectile

  energy absorbent material underneath

Applications: Advanced Ceramics

Electronic Packaging

- Chosen to securely hold microelectronics & provide heat transfer
- Must match the thermal expansion coefficient of the microelectronic chip & the electronic packaging material. Additional requirements include:
  - good heat transfer coefficient
  - poor electrical conductivity
- Materials currently used include:
  - Boron nitride (BN)
  - Silicon Carbide (SiC)
  - Aluminum nitride (AlN)
    - thermal conductivity 10x that for Alumina
    - good expansion match with Si

Summary

- Room T mechanical response is elastic,
  but fracture is brittle, with negligible deformation.

- Elevated T creep properties are generally superior
  to those of metals (and polymers).

- **Fabrication Techniques:**
  glass forming (impurities affect forming temp).
  particulate forming (needed if ductility is limited)
  cementation (large volume, room *T* process)

- **Heat treating: Used to**
  alleviate residual stress from cooling,
  produce fracture resistant components by putting
  surface into compression.