Chemical Engineering 378

Science of Materials Engineering

Lecture 25

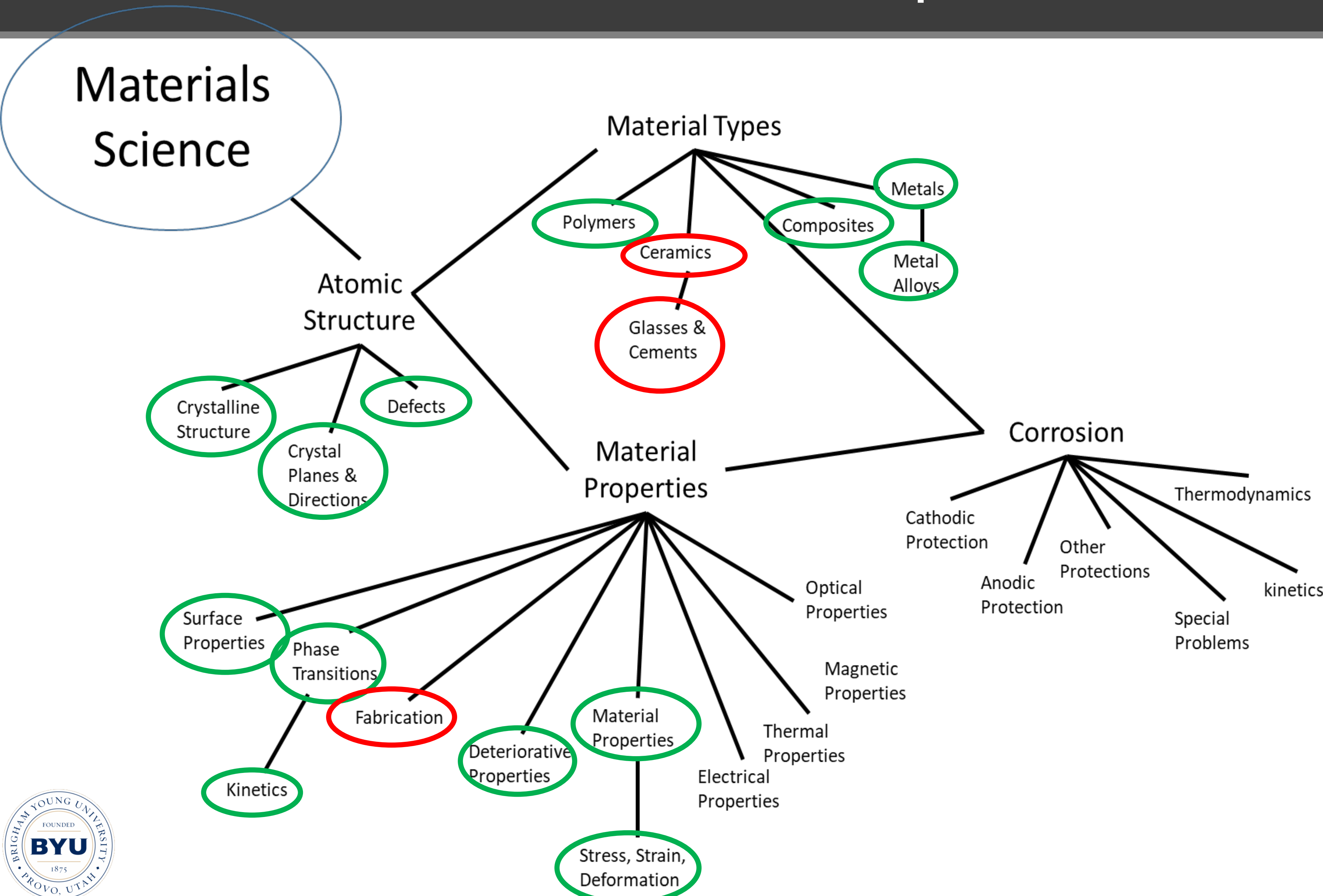
Ceramics, Processing

Spiritual Thought

"When He answers yes, it is to give us confidence. When He answers no, it is to prevent error. When He withholds an answer, it is to have us grow through faith in Him, obedience to His commandments, and a willingness to act on truth. We are expected to assume accountability by acting on a decision that is consistent with His teachings without prior confirmation. We are not to sit passively waiting or to murmur because the Lord has not spoken. We are to act."

-Elder Richard G. Scott

Materials Roadmap



Classification of Ceramics

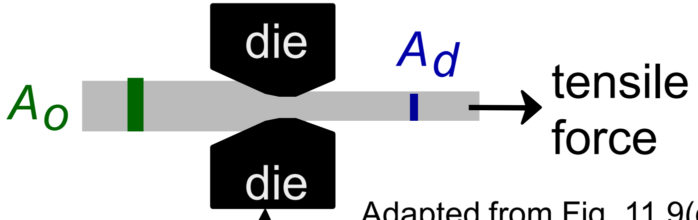
Ceramic Materials

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

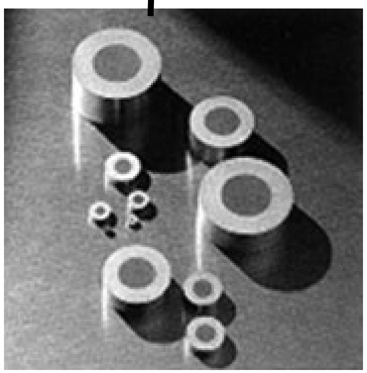
Adapted from Fig. 13.1 and discussion in Sections 13.2-10, *Callister & Rethwisch 10e.*

Ceramics Application: Die Blanks

- Die blanks:
  -- Need wear resistant properties!
- Die surface:
  -- 4 µm polycrystalline diamond particles that are sintered onto a cemented tungsten carbide substrate.
  -- polycrystalline diamond gives uniform hardness in all directions to reduce wear.



Adapted from Fig. 11.9(d), *Callister & Rethwisch 10e.*

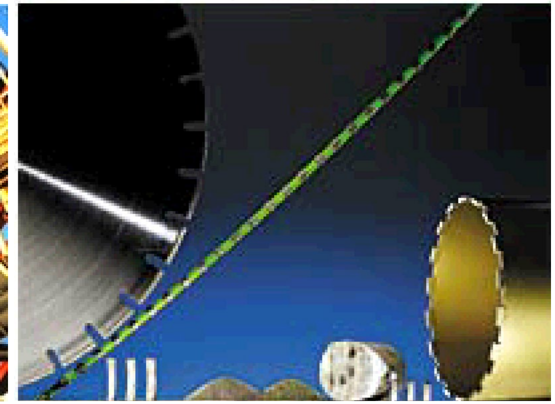


Courtesy Martin Deakins, GE Superabrasives, Worthington, OH. Used with permission.

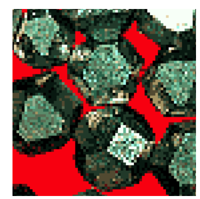
Ceramics Application: Cutting Tools

- Tools:
  - -- for grinding glass, tungsten, carbide, ceramics
  - -- for cutting Si wafers
  - -- for oil drilling
- Materials:
  - -- manufactured single crystal or polycrystalline diamonds in a metal or resin matrix.
  - -- polycrystalline diamonds resharpen by microfracturing along cleavage planes.

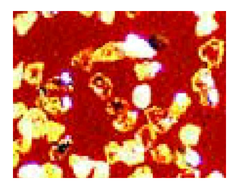
oil drill bits



blades



Single crystal diamonds



polycrystalline diamonds in a resin matrix.

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

Ceramics Application: Sensors

- Example: ZrO_2 as an oxygen sensor
- Principle: Increase diffusion rate of oxygen to produce rapid response of sensor signal to change in oxygen concentration
- Approach:

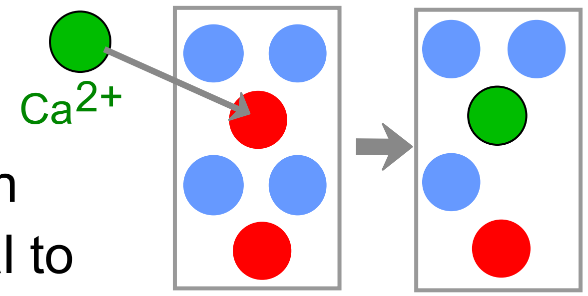
  Add Ca impurity to ZrO_2:

  -- increases O^{2-} vacancies

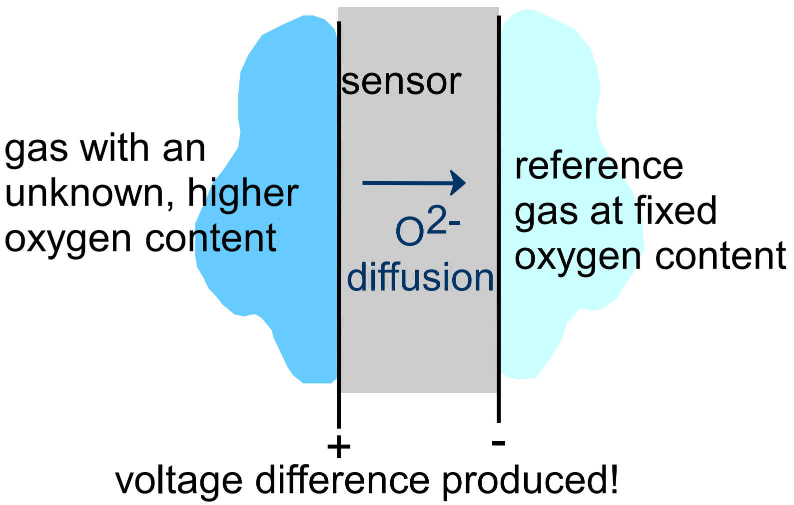
  -- increases O^{2-} diffusion rate
- Operation:

  -- voltage difference produced when O^{2-} ions diffuse from the external surface through the sensor to the reference gas surface.

  -- magnitude of voltage difference $\propto$ partial pressure of oxygen at the external surface



A substituting Ca^{2+} ion removes a Zr^{4+} ion and an O^{2-} ion.



Refractories

- Materials to be used at high temperatures (e.g., in high temperature furnaces).
- Consider the Silica (SiO_2) - Alumina (Al_2O_3) system.
- Silica refractories - silica rich - small additions of alumina depress melting temperature (phase diagram):

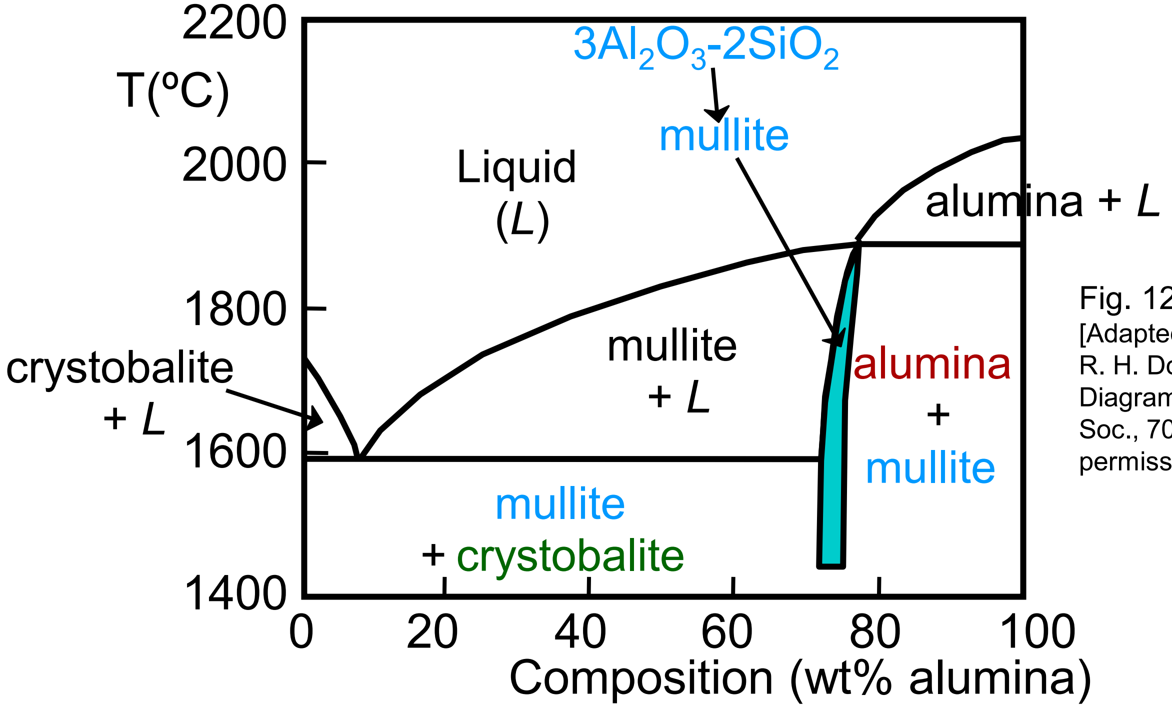


Fig. 12.25, *Callister & Rethwisch 10e.* [Adapted from F. J. Klug, S. Prochazka, and R. H. Doremus, "Alumina–Silica Phase Diagram in the Mullite Region," J. Am. Ceram. Soc., 70[10], 1987, p.758. Reprinted by permission of the American Ceramic Society.]

Advanced Ceramics: Materials for Automobile Engines

- Advantages:
  - Operate at high temperatures – high efficiencies
  - Low frictional losses
  - Operate without a cooling system
  - Lower weights than current engines
- Disadvantages:
  - Ceramic materials are brittle
  - Difficult to remove internal voids (that weaken structures)
  - Ceramic parts are difficult to form and machine

- Potential candidate materials: Si_3N_4, SiC, & ZrO_2
- Possible engine parts: engine block & piston coatings

Advanced Ceramics: Materials for Ceramic Armor

Components:

-- Outer facing plates
-- Backing sheet

Properties/Materials:

-- Facing plates -- hard and brittle
  — fracture high-velocity projectile
  — Al_2O_3, B_4C, SiC, TiB_2

-- Backing sheets -- soft and ductile
  — deform and absorb remaining energy
  — aluminum, synthetic fiber laminates

Nanocarbons

- Fullerenes – spherical cluster of 60 carbon atoms, C_{60}
  - Like a soccer ball
- Carbon nanotubes – sheet of graphite rolled into a tube
  - Ends capped with fullerene hemispheres

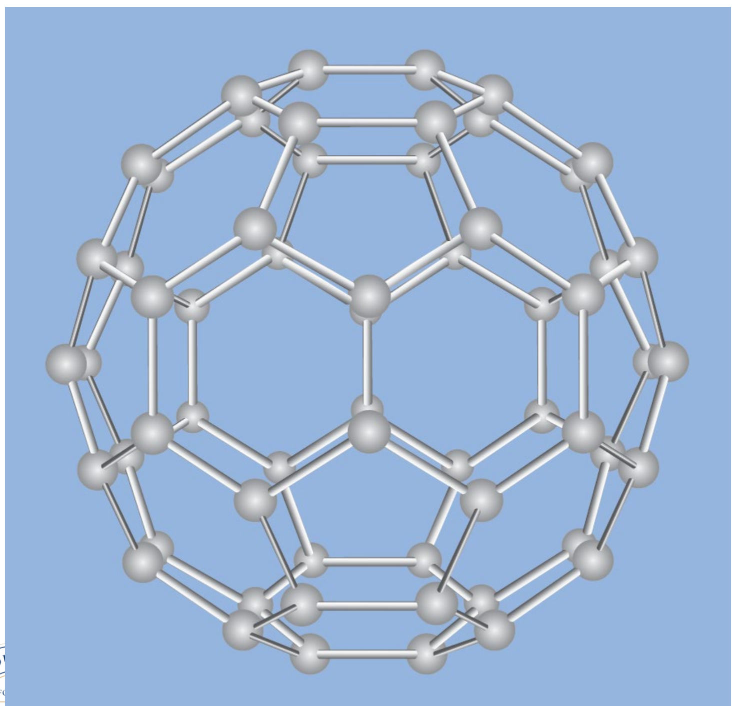


Fig. 13.9, *Callister & Rethwisch 10e.*

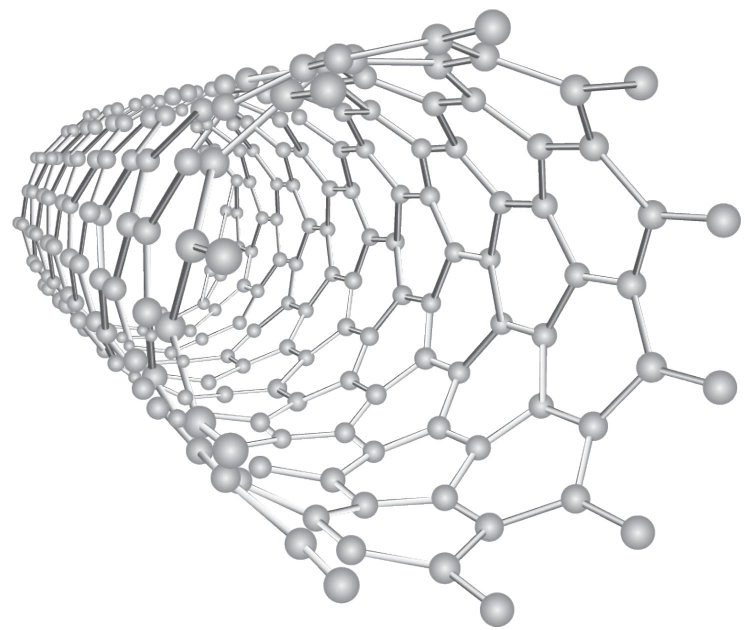


Fig. 13.10, *Callister & Rethwisch 10e.*

Nanocarbons (cont.)

- Graphene – single-atomic-layer of graphite
  - composed of hexagonally *sp*^{2} bonded carbon atoms

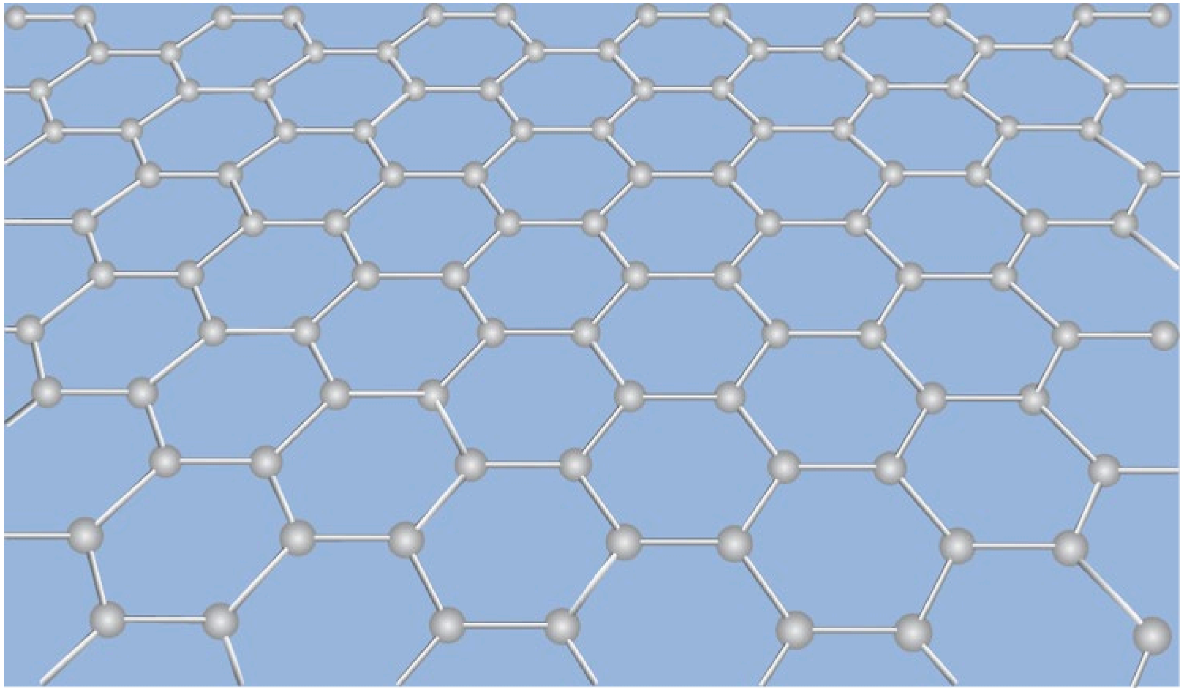


Fig. 13.11, *Callister & Rethwisch 10e.*

Ceramic Fabrication Methods (i)

GLASS FORMING | PARTICULATE FORMING | CEMENTATION

- Blowing of Glass Bottles:

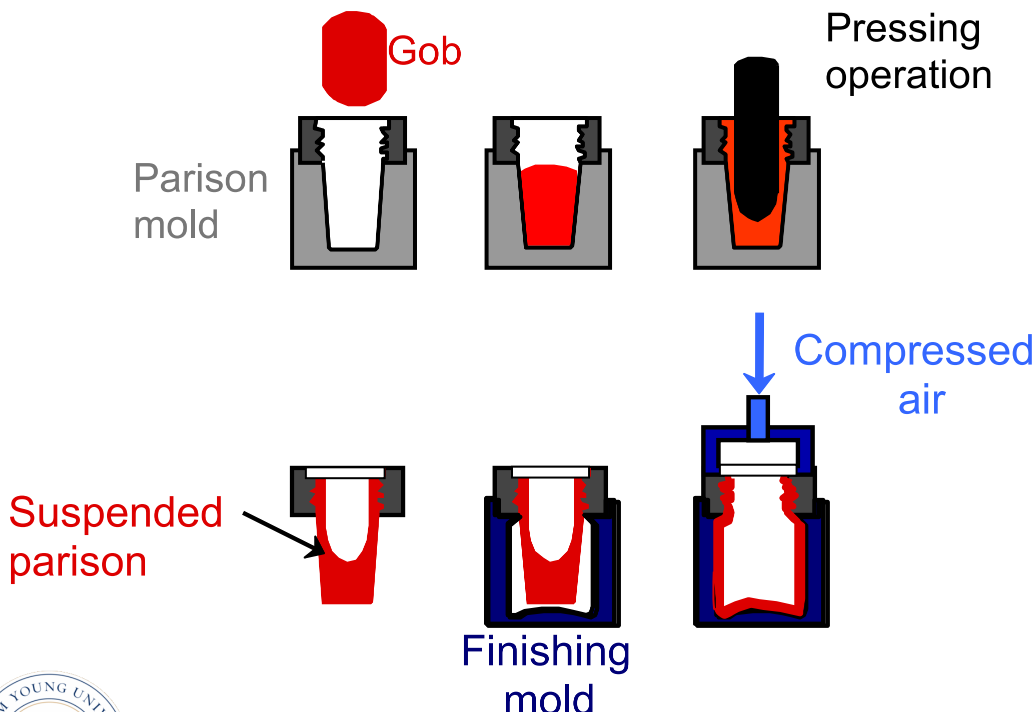
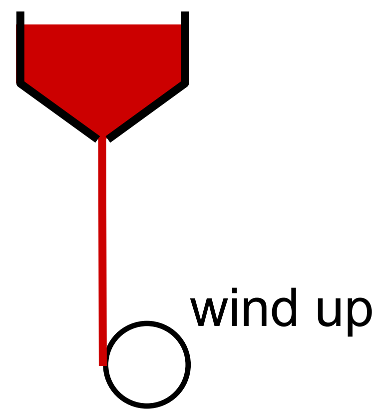


Fig. 13.15, *Callister & Rethwisch 10e*. (Adapted from C.J. Phillips, *Glass: The Miracle Maker*. Reproduced by permission of Pittman Publishing Ltd., London.)

- **Pressing:** plates, cheap glasses
  - -- glass formed by application of pressure
  - -- mold is steel with graphite lining
- **Fiber drawing:**



Sheet Glass Forming

- Sheet forming – continuous casting
  - sheets are formed by floating the molten glass on a pool of molten tin

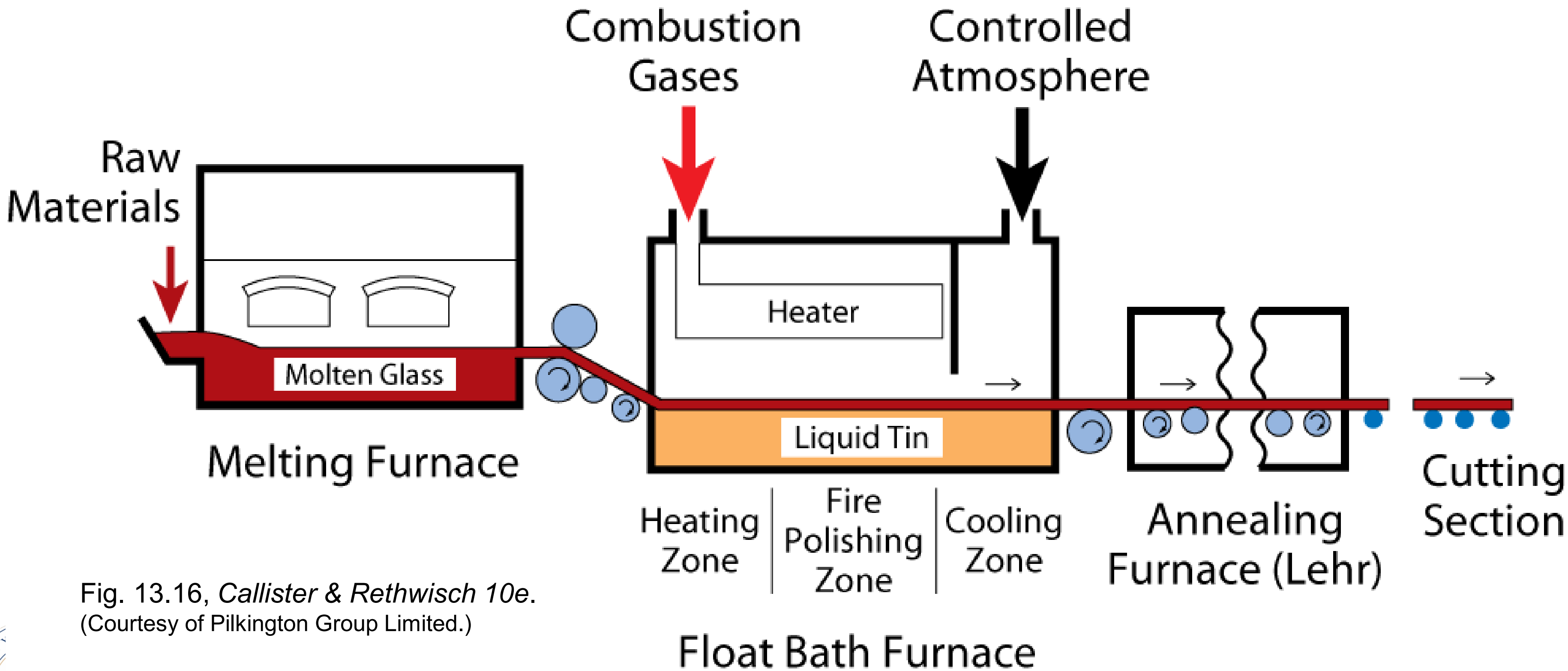
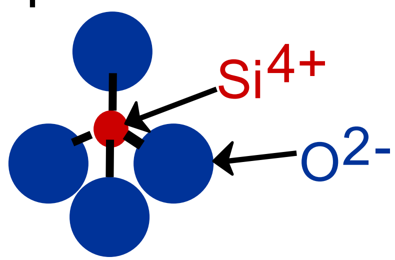


Fig. 13.16, *Callister & Rethwisch 10e*.
(Courtesy of Pilkington Group Limited.)

Glass Structure

- Basic Unit:

$Si0_4^{4-}$ tetrahedron

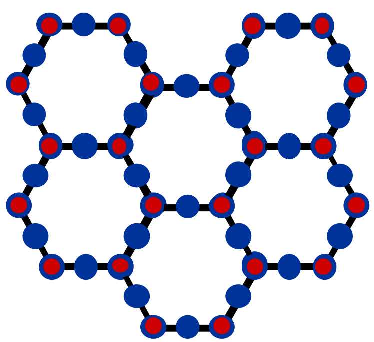


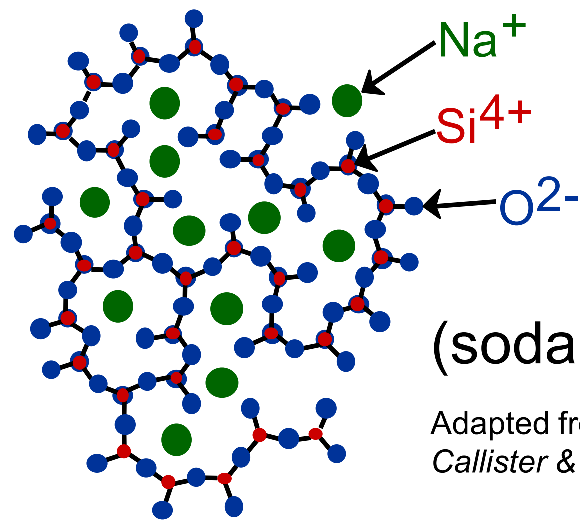
Glass is noncrystalline (amorphous)

- Fused silica is SiO_2 to which no impurities have been added
- Other common glasses contain impurity ions such as Na^+, Ca^{2+}, Al^{3+}, and B^{3+}

- Quartz is crystalline

SiO**2**:



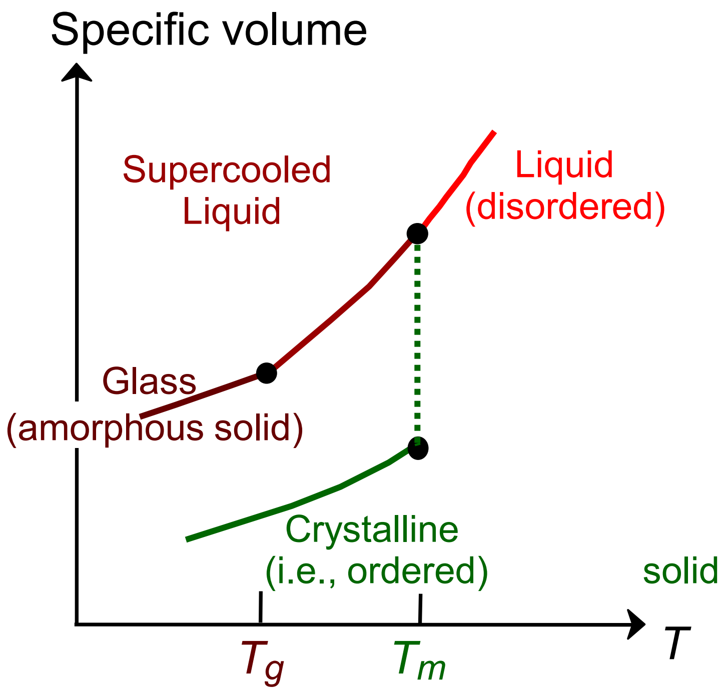


(soda glass)

Adapted from Fig. 12.11, *Callister & Rethwisch 10e*.

Glass Properties

- Specific volume ($1/\rho$) vs Temperature (T):



Adapted from Fig. 13.13, *Callister & Rethwisch 10e*.

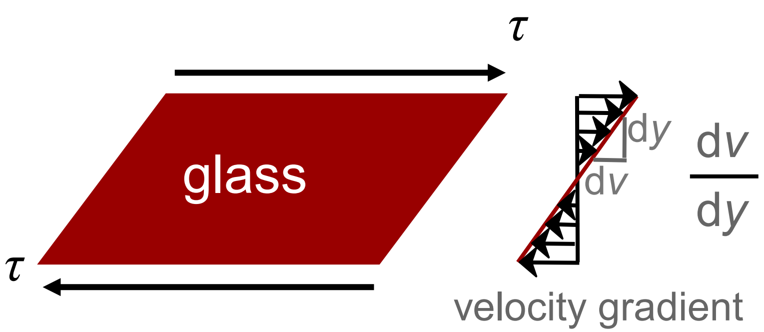
- Crystalline materials:
  -- crystallize at melting temp, T_m
  -- have abrupt change in spec. vol. at T_m

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

Glass Properties: Viscosity

- Viscosity, η:

  -- relates shear stress (τ) and velocity gradient *(dv/dy):*



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

η has units of (Pa-s)

Log Glass Viscosity vs. Temperature

- Viscosity decreases with *T*

- soda-lime 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

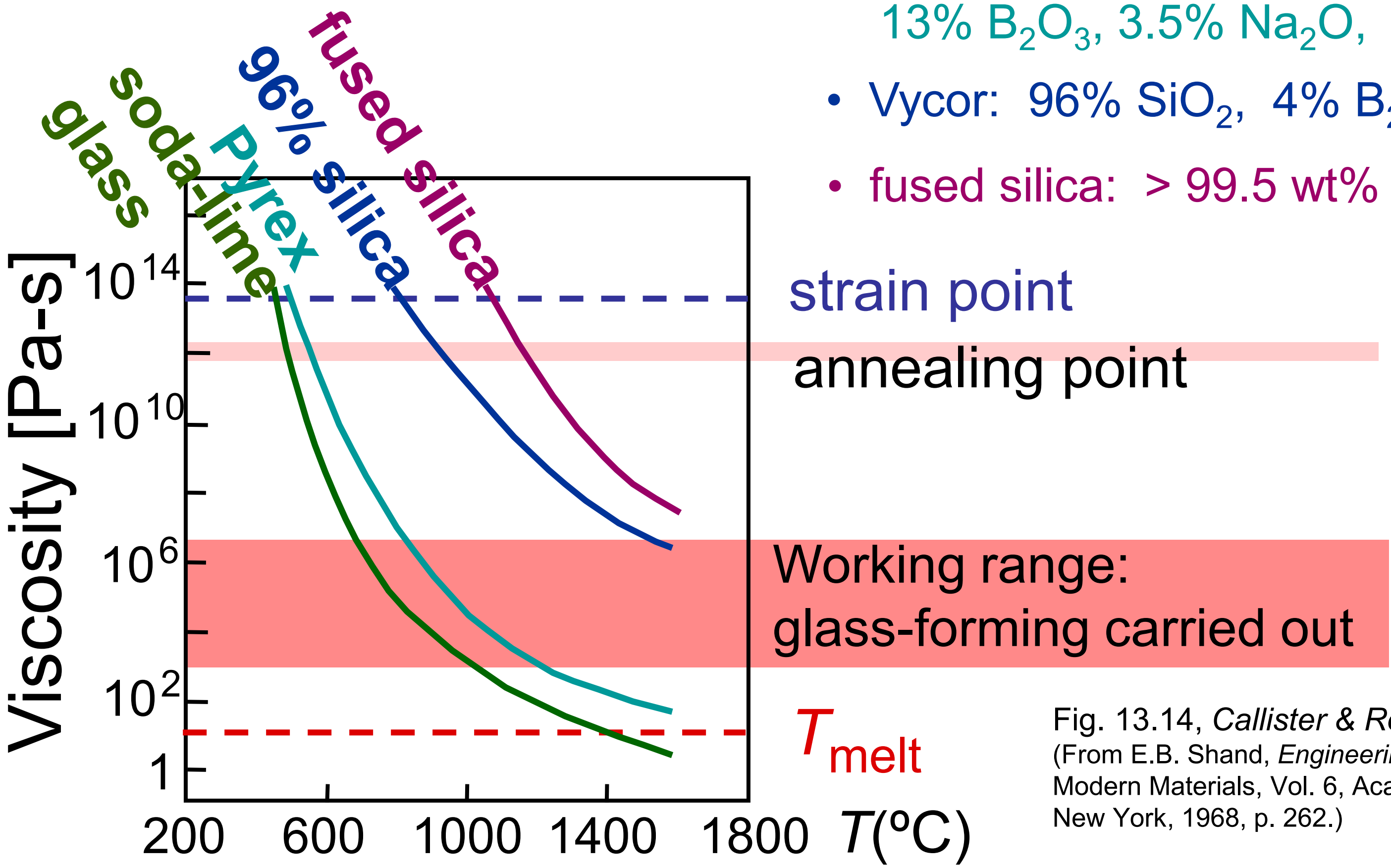
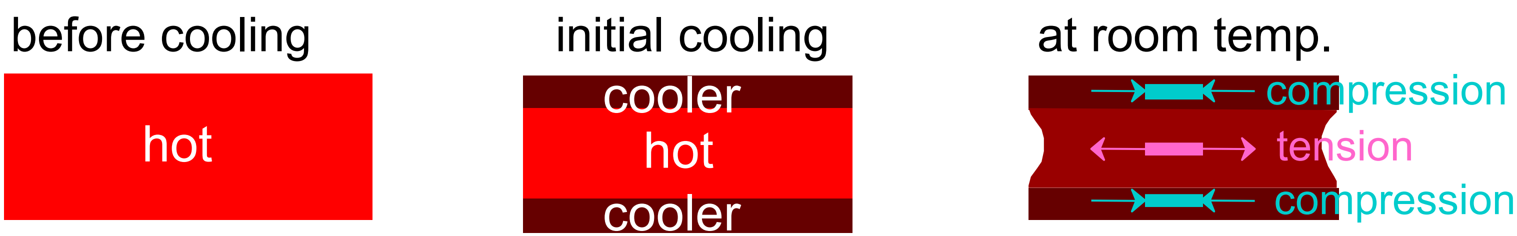


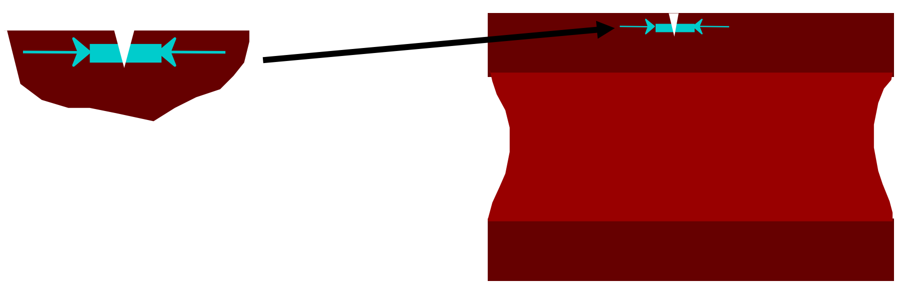
Fig. 13.14, *Callister & Rethwisch 10e*.
(From E.B. Shand, *Engineering Glass*, Modern Materials, Vol. 6, Academic Press, New York, 1968, p. 262.)

Heat Treating Glass

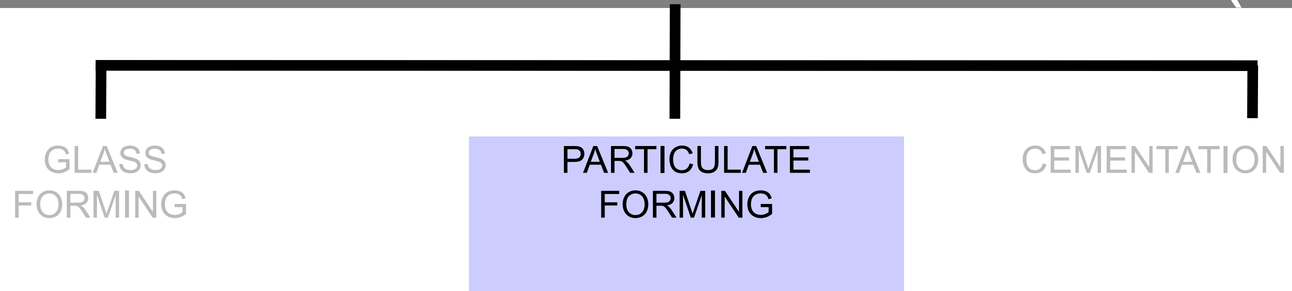
- Annealing:
  -- removes internal stresses caused by uneven cooling.
- Tempering:
  -- puts surface of glass part into compression
  -- suppresses growth of cracks from surface scratches.
  -- sequence:



-- Result: surface crack growth is suppressed.



Ceramic Fabrication Methods (iia)



Hydroplastic forming:

- Mill (grind) and screen constituents: desired particle size
- Extrude this mass (e.g., into a brick)

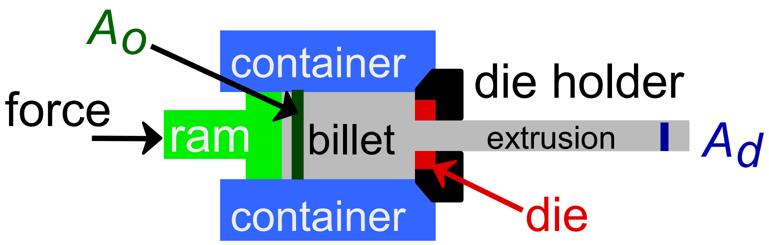


Fig. 11.9 (c), *Callister & Rethwisch 10e*.

- Dry and fire the formed piece

Ceramic Fabrication Methods (IIa)

GLASS FORMING | **PARTICULATE FORMING** | CEMENTATION

Slip casting:

- Mill (grind) and screen constituents: desired particle size
- Mix with water and other constituents to form slip
- Slip casting operation

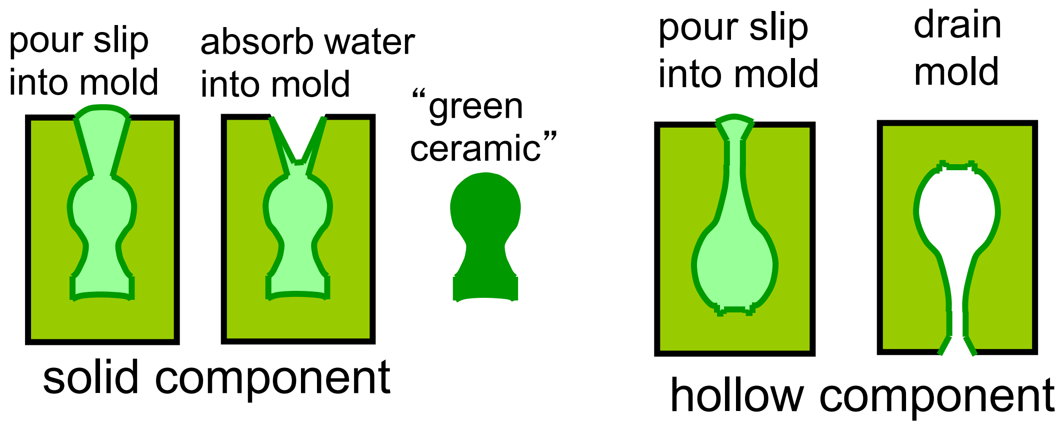


Fig. 13.19, *Callister & Rethwisch 10e*. (From W.D. Kingery, *Introduction to Ceramics*, Copyright © 1960 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

Dry and fire the cast piece

Typical Porcelain Composition

(50%) 1. Clay

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

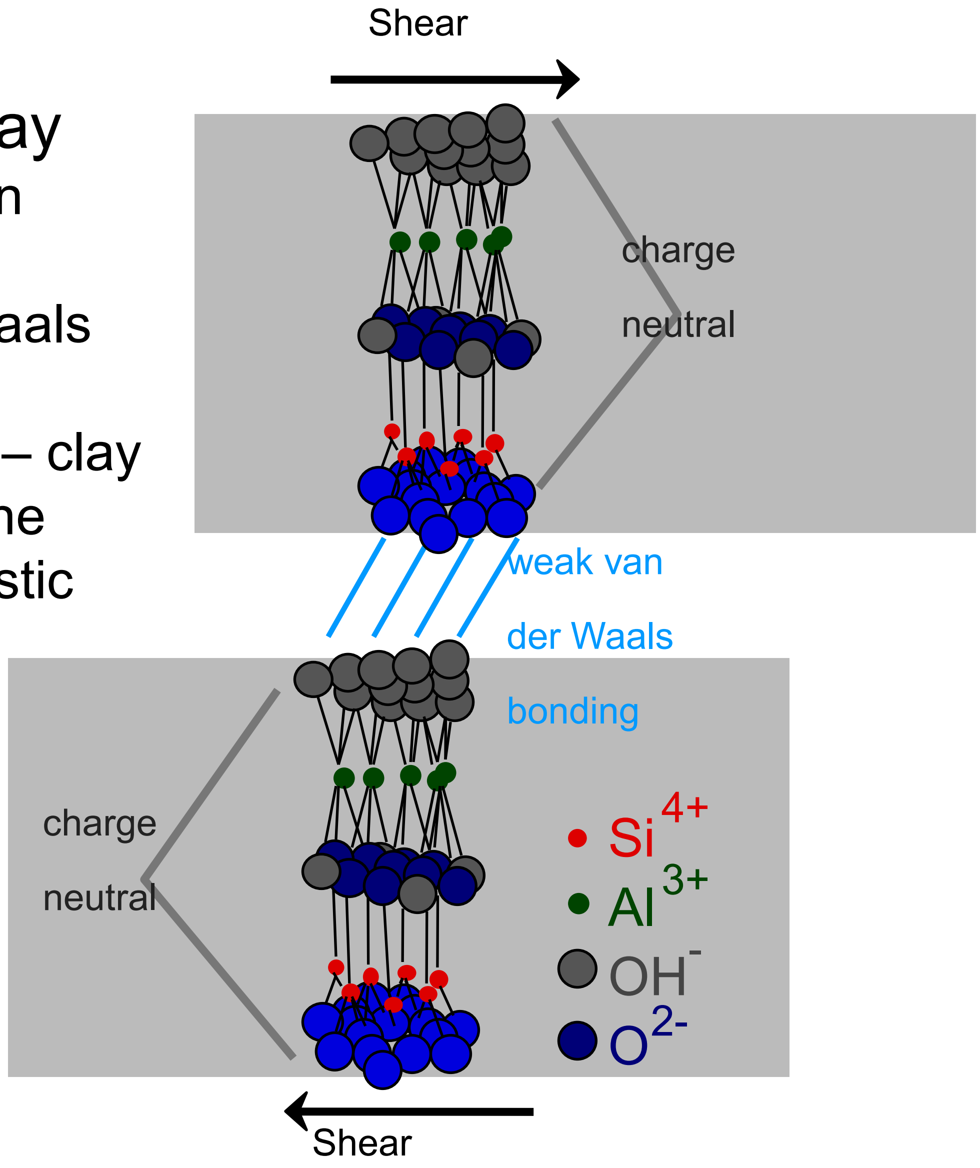
(25%) 3. Fluxing agent (Feldspar)

-- aluminosilicates plus K^+, Na^+, Ca^+

-- upon firing - forms low-melting-temp. glass

Hydroplasticity of Clay

- Clay is inexpensive
- When water is added to clay
  - -- water molecules fit in between layered sheets
  - -- reduces degree of van der Waals bonding
  - -- when external forces applied – clay particles free to move past one another – becomes hydroplastic



- Structure of Kaolinite Clay:

Fig. 12.14, *Callister & Rethwisch 10e*.
[Adapted from W.E. Hauth, "Crystal Chemistry of Ceramics", *American Ceramic Society Bulletin*, Vol. 30 (4), 1951, p. 140.]

Drying and Firing

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

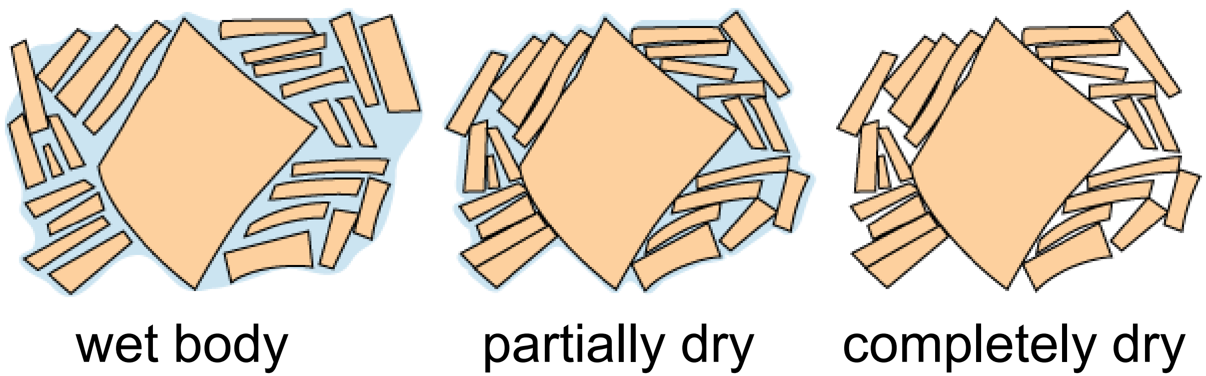


Fig. 13.20, *Callister & Rethwisch 10e*. (From W.D. Kingery, *Introduction to Ceramics*, Copyright © 1960 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

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

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

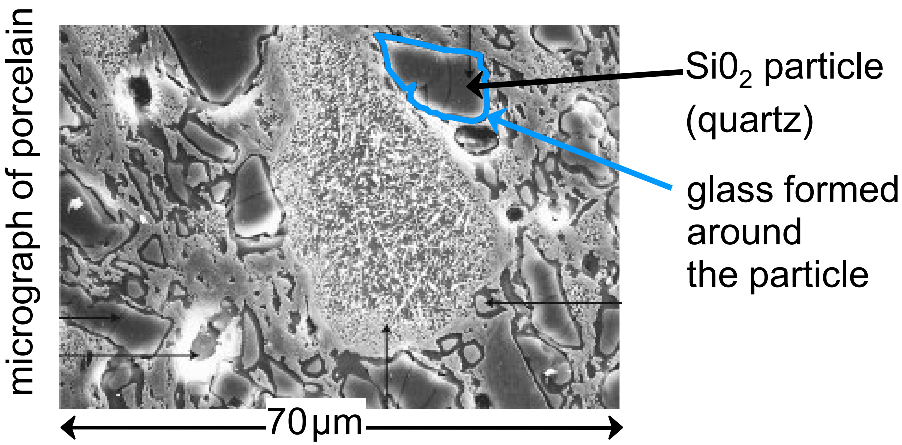


Fig. 13.21, *Callister & Rethwisch 10e*. (Courtesy H.G. Brinkies, Swinburne University of Technology, Hawthorn Campus, Hawthorn, Victoria, Australia.)

Ceramic Fabrication Methods (IIb)

GLASS FORMING | **PARTICULATE FORMING** | CEMENTATION

Powder Pressing: used for both clay and non-clay compositions.

- Powder (plus binder) compacted by pressure in a mold
  -- Uniaxial compression - compacted in single direction
  -- Isostatic (hydrostatic) compression - pressure applied by fluid - powder in rubber envelope
  -- Hot pressing - pressure + heat

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Sintering

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

-- powder particles coalesce and reduction of pore size

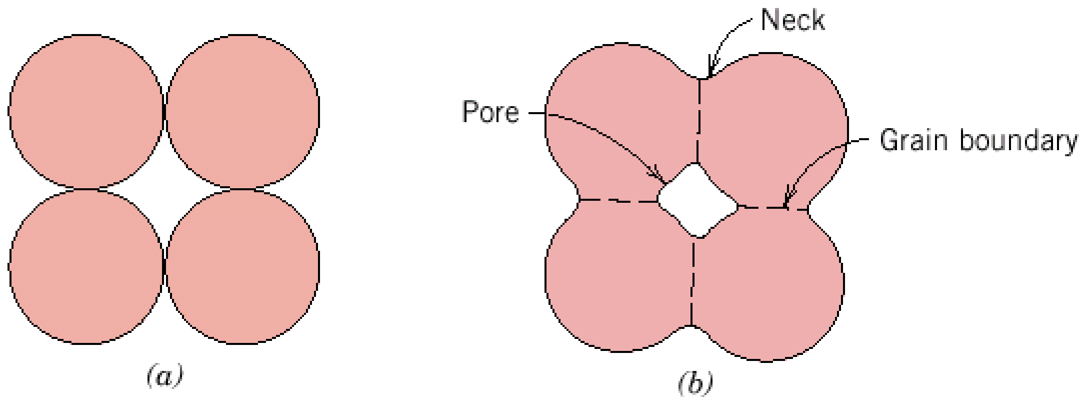

Fig. 13.23, *Callister & Rethwisch 10e*.

Aluminum oxide powder:

-- sintered at 1700° C for 6 minutes.

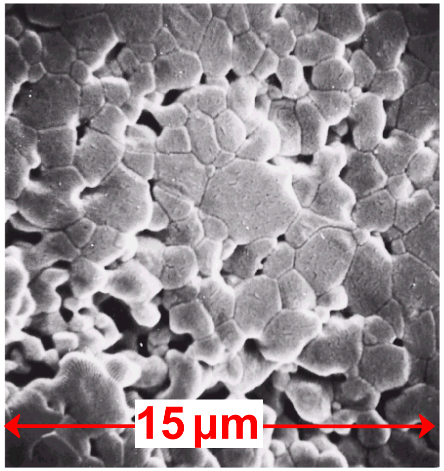

Fig. 13.24, *Callister & Rethwisch 10e*. (From W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, Introduction to Ceramics, 2nd edition, p. 483. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

Tape Casting

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

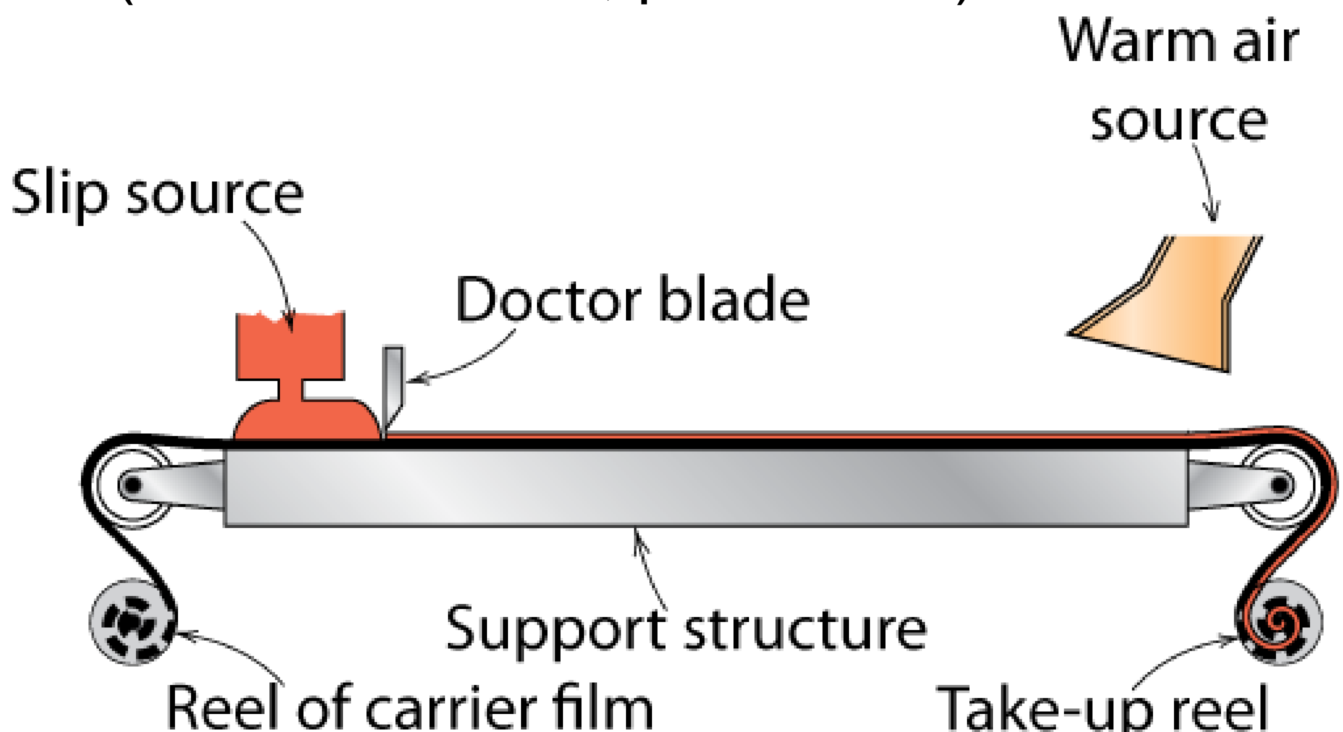

Fig. 13.25, *Callister & Rethwisch 10e*.

Ceramic Fabrication Methods (iii)

GLASS FORMING | PARTICULATE FORMING | **CEMENTATION**

- Hardening of a paste – paste formed by mixing cement material with water
- Formation of rigid structures having varied and complex shapes
- Hardening process – hydration (complex chemical reactions involving water and cement particles)
- Portland cement – production of:
  -- mix clay and lime-bearing minerals
  -- calcine (heat to 1400°C)
  -- grind into fine powder