Chemical Engineering 378

Science of Materials Engineering

Lecture 25
Ceramics, Processing
Spiritual Thought
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
  - composites
  - abrasives

- Carbon
  - composites
  - abrasives
  - engine rotors
  - valves
  - bearings
  - sensors

- Advanced ceramics

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.

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 ∝ partial pressure of oxygen at the external surface

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

Reference gas at fixed oxygen content

Gas with an unknown, higher oxygen content

Voltage difference produced!
• Materials to be used at high temperatures (e.g., in high temperature furnaces).
• Consider the Silica (SiO$_2$) - Alumina (Al$_2$O$_3$) system.
• Silica refractories - silica rich - small additions of alumina depress melting temperature (phase diagram):

![Phase Diagram](image)

Refractories

<table>
<thead>
<tr>
<th>Composition (wt% alumina)</th>
<th>T(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1400</td>
</tr>
<tr>
<td></td>
<td>1600</td>
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<tr>
<td></td>
<td>2000</td>
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<tr>
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</table>

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$_3$N$_4$, 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
  — $\text{Al}_2\text{O}_3$, $\text{B}_4\text{C}$, 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
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)

- **Blowing of Glass Bottles:**
  - Gob
  - Parison mold
  - Pressing operation
  - Compressed air
  - Finishing mold
  - Suspended parison

- **Pressing:** plates, cheap glasses
  - Glass formed by application of pressure
  - Mold is steel with graphite lining

- **Fiber drawing:**
  - Wind up

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

\[
\begin{align*}
\text{SiO}_4 \quad &\text{tetrahedron} \\
\text{Si}^{4+} &\quad \text{O}^{2-}
\end{align*}
\]

Glass is noncrystalline (amorphous)
• Fused silica is SiO₂ to which no impurities have been added
• Other common glasses contain impurity ions such as Na⁺, Ca²⁺, Al³⁺, and B³⁺

• Quartz is crystalline

\[
\text{SiO}_2:
\]

Adapted from Fig. 12.11, Callister & Rethwisch 10e.
Glass Properties

• **Specific volume** \((1/\rho)\) 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 grain boundaries to scatter light

Adapted from Fig. 13.13, *Callister & Rethwisch 10e.*
Glass Properties: Viscosity

- **Viscosity, $\eta$:**
  - relates shear stress ($\tau$) and velocity gradient ($dv/dy$):

\[
\eta = \frac{\tau}{dv/dy}
\]

$\eta$ has units of (Pa-s)
Log Glass Viscosity vs. Temperature

- Viscosity decreases with $T$

- soda-lime glass: 70% SiO$_2$
  balance Na$_2$O (soda) & CaO (lime)

- borosilicate (Pyrex):
  13% B$_2$O$_3$, 3.5% Na$_2$O, 2.5% Al$_2$O$_3$

- Vycor: 96% SiO$_2$, 4% B$_2$O$_3$

- 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:

  - before cooling: hot
  - initial cooling: cooler
  - at room temp.: compression
  - tension
  - compression

-- 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)

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

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.
Drying and Firing

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

![Drying Diagram](image)

Fig. 13.20, *Callister & Rethwisch 10e.*

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 SiO₂ particles. (Flux lowers melting temperature).

![Firing Diagram](image)

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

- SiO₂ particle (quartz)
- glass formed around the particle
- 70 μm
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
Sintering occurs during firing of a piece that has been powder pressed
-- powder particles coalesce and reduction of pore size

Aluminum oxide powder:
-- sintered at 1700° C for 6 minutes.

Fig. 13.23, Callister & Rethwisch 10e.

Fig. 13.24, Callister & Rethwisch 10e.
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.*
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