# Chapter 11. Properties and Processing of Metal Powders, Ceramics, Glasses, Composites, and Superconductors

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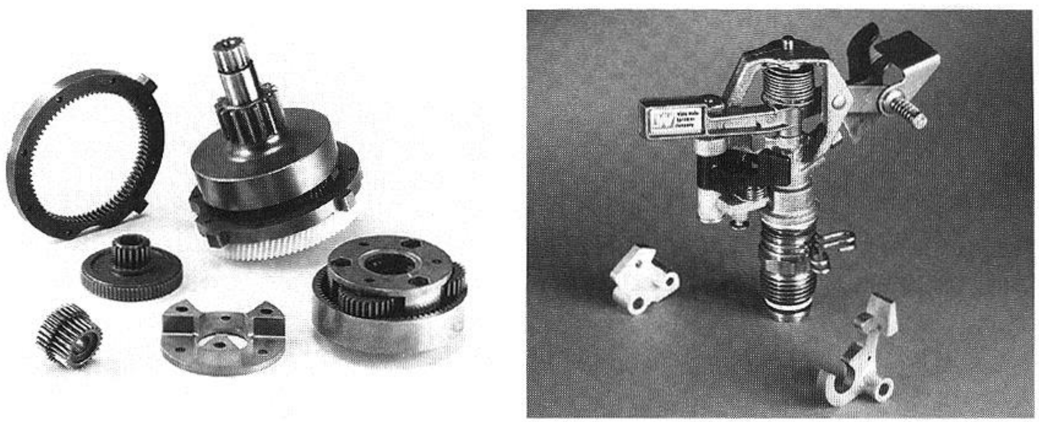
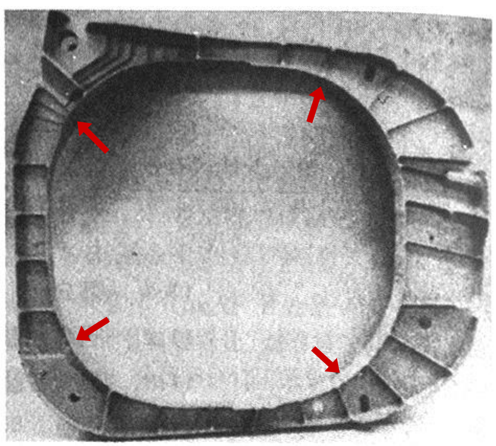
# Introduction

- **Powder Metallurgy (P/M, 분말야금)**
  - Compacting metal powders in dies and sintering them
- **Typical products**
  - Gears, cams, bushings, cutting tools, automotive components, etc.
- **Advantages**
  - Material density in P/M is a controllable variable.
    - Low density : porous filters
    - Full density : structural parts
  - Competitive with processes such as casting, forging, and machining for relatively complex parts made of high-strength and hard alloys



(a) (b)

**FIGURE 11.1**
(a) Examples of typical parts made by powder-metallurgy processes. (b) Upper trip lever for a commercial irrigation sprnkler, made by P/M. This part is made of unleaded brass alloy; it replaces a die-cast part, with a 60% cost savings. *Source*: Reproduced with permission from *Success Stories on P/M Parts*, Princeton, NJ: Metal Powder Industries Federation, 1998.



# Metal powders

- **Powder production → Blending → Compaction → Sintering → Finishing operations**

**TABLE 11.2**

**CHARACTERISTICS OF POWDER-METALLURGY PROCESSING**

ADVANTAGES

- Availability of a wide range of compositions to obtain special mechanical and physical properties, such as stiffness, damping characteristics, hardness, density, toughness, and electrical and magnetic properties. Some of the high alloyed new superalloys can be manufactured into parts only by P/M processing.
- A net- or near-net-shape technique for making parts from high-melting-point refractory metals, which would be difficult or uneconomical to make by other methods.
- High production rates on relatively complex parts, with automated equipment requiring little labor.
- Good dimensional control and, in many instances, elimination of machining and finishing operations, thus eliminating scrap and waste and saving energy.
- Capability for impregnation and infiltration for special applications.

LIMITATIONS

- Size of parts, complexity of part shapes, and press capacity.
- High cost of powder metals compared to other raw materials.
- High cost of tooling and equipment for small production runs.
- Mechanical properties, such as strength and ductility, that are generally lower than those obtained by forging. However, the properties of full-density P/M parts made by HIP or additional forging can be better than those made by other processes.

# Powder fabrication

- **Atomization (입자화)**
- **Reduction (환원) : reduction of metal oxides using gases such as hydrogen and carbon monoxide**

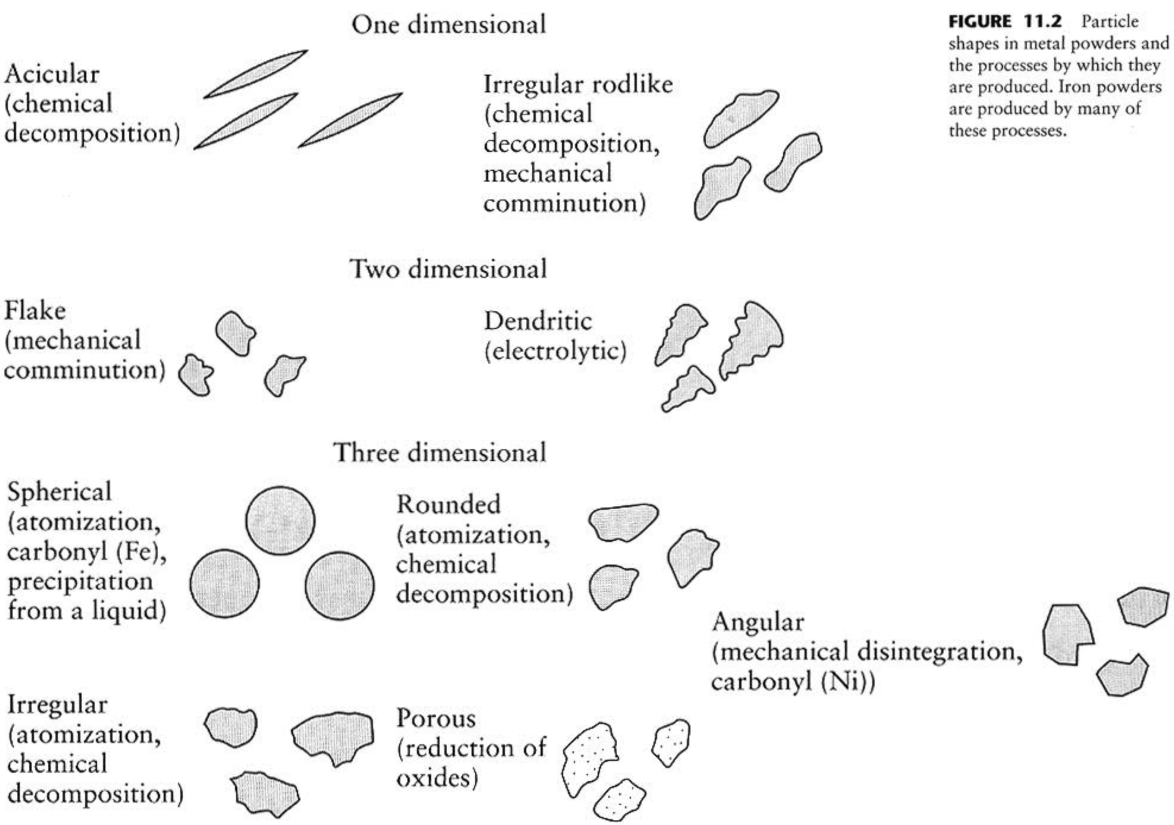
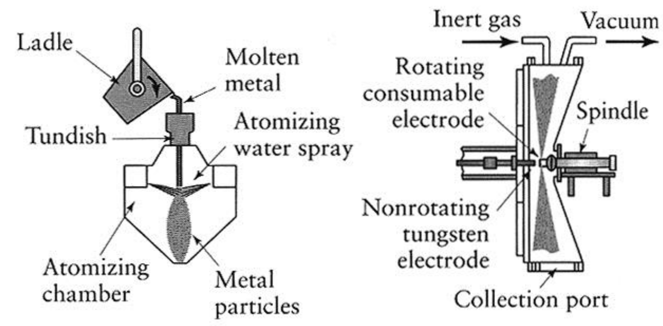



**FIGURE 11.2** Particle shapes in metal powders and the processes by which they are produced. Iron powders are produced by many of these processes.




(a) (b)

**FIGURE 11.3** Methods of metal-powder production by atomization: (a) melt atomization and (b) atomization with a rotating consumable electrode.

# Compaction (압축) (1)

- **The step in which the blended powders are pressed into shapes in dies, using presses that are either hydraulically or mechanically actuated**

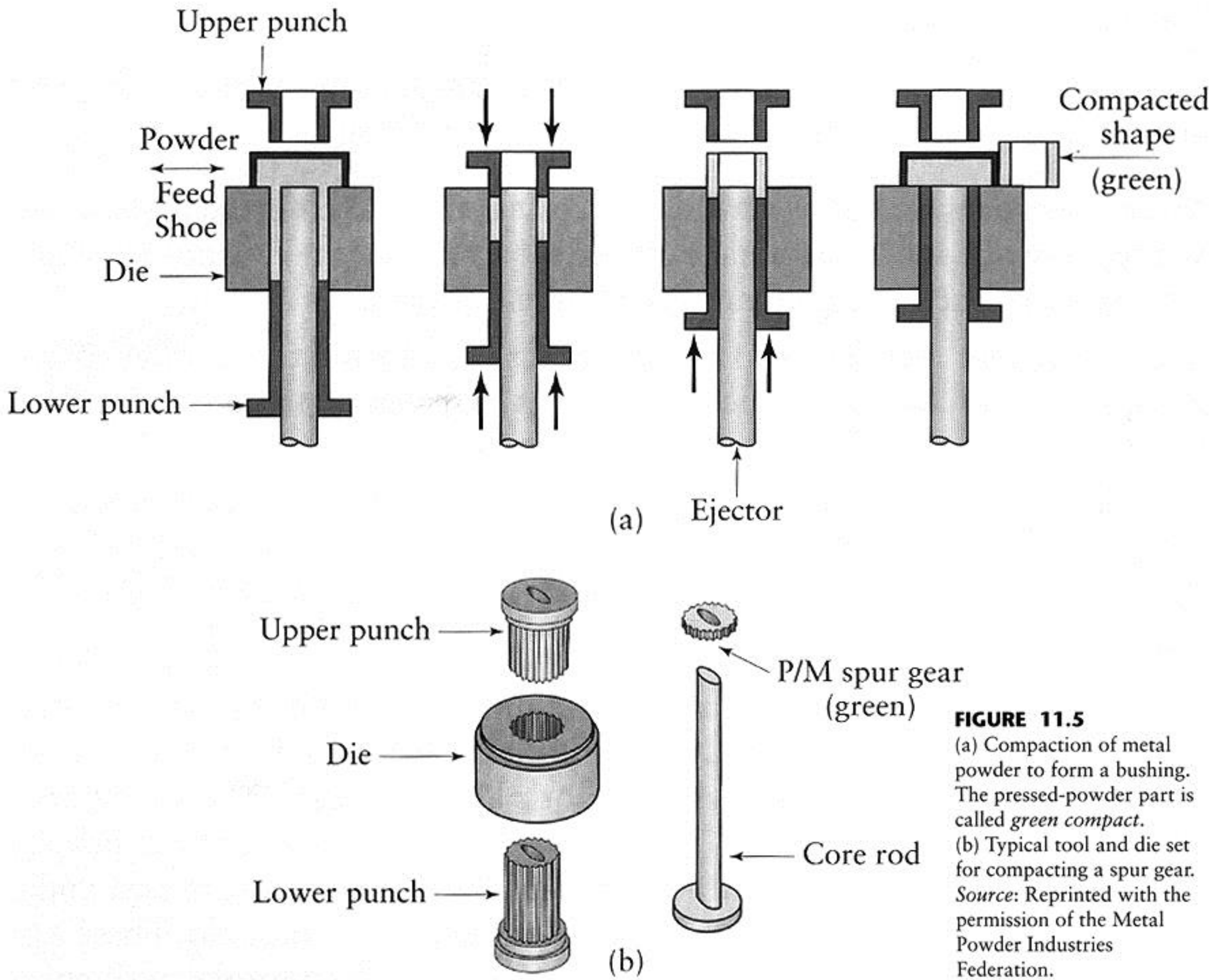



**FIGURE 11.5**
(a) Compaction of metal powder to form a bushing. The pressed-powder part is called *green compact.* (b) Typical tool and die set for compacting a spur gear. *Source:* Reprinted with the permission of the Metal Powder Industries Federation.

# Compaction (압축) (2)

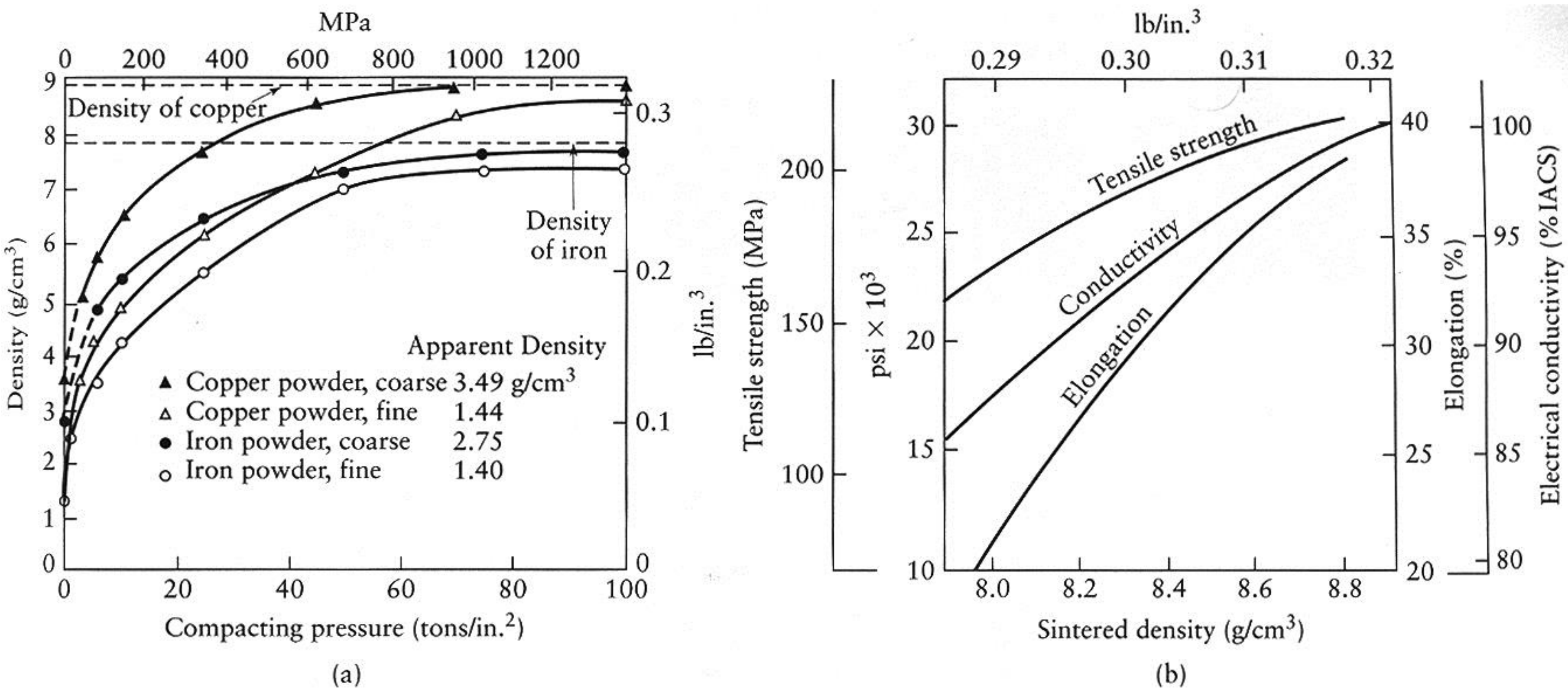



**FIGURE 11.6** (a) Density of copper- and iron-powder compacts as a function of compacting pressure. Density greatly influences the mechanical and physical properties of P/M parts. *Source*: F. V. Lenel, *Powder Metallurgy: Principles and Applications*, Princeton, NJ: Metal Powder Industries Federation, 1980. Reprinted by permission of Metal Powder Industries Federation, Princeton, NJ. (b) Effect of density on tensile strength, elongation, and electrical conductivity of copper powder. IACS means International Annealed Copper Standard for electrical conductivity.

# Isostatic pressing (균형가압)

- Cold isostatic pressing (CIP, 냉간균형가압)
- Hot isostatic pressing (HIP, 열간균형가압)

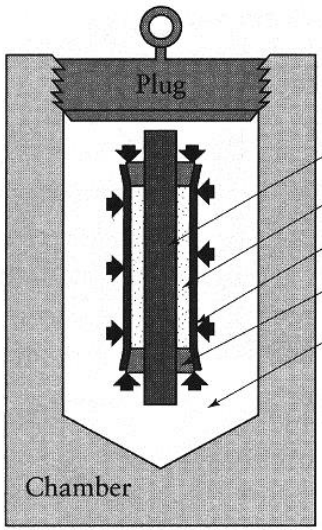



**FIGURE 11.9** Schematic illustration of cold isostatic pressing as applied to formation of a tube. The powder is enclosed in a flexible container around a solid core rod. Pressure is applied isostatically to the assembly inside a high-pressure chamber. *Source*: Reprinted with permission from Randall M. German, *Powder Metallurgy Science*, Princeton, NJ: Metal Powder Industries Federation, 1984.

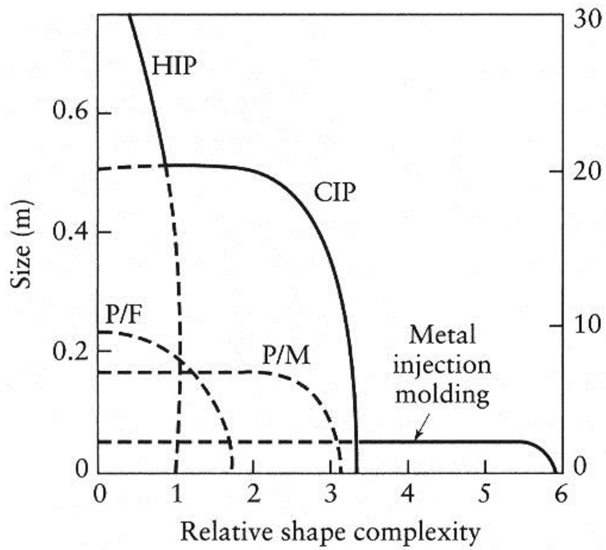



**FIGURE 11.10** Capabilities of part size and shape complexity according to various P/M operations. *P/F* means powder forging. *Source*: Metal Powder Industries Federation.

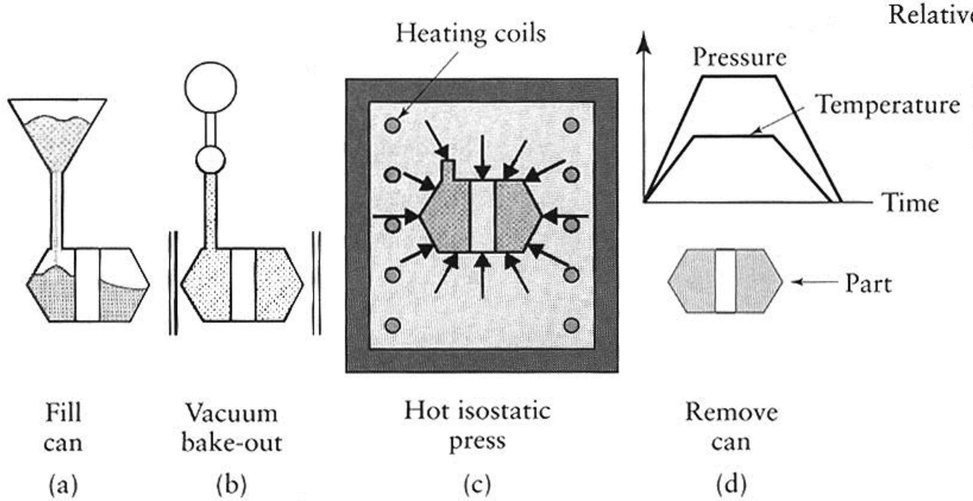



**FIGURE 11.11** Schematic illustration of hot isostatic pressing. The pressure and temperature variation versus time are shown in the diagram. *Source*: Reprinted with permission from Randall M. German, *Powder Metallurgy Science*, Princeton, NJ: Metal Powder Industries Federation, 1984.

# Sintering (소결) (1)

- **The process whereby compressed metal powder is heated in a controlled-atmosphere (hydrogen, ammonia, nitrogen) furnace to a temperature below its melting point, but sufficiently high to allow bonding of the individual particles**
- **Sintering temp. : 70% ~ 90% of the melting point of the metal or alloy**
- **Continuous-sintering furnace : for most production today**

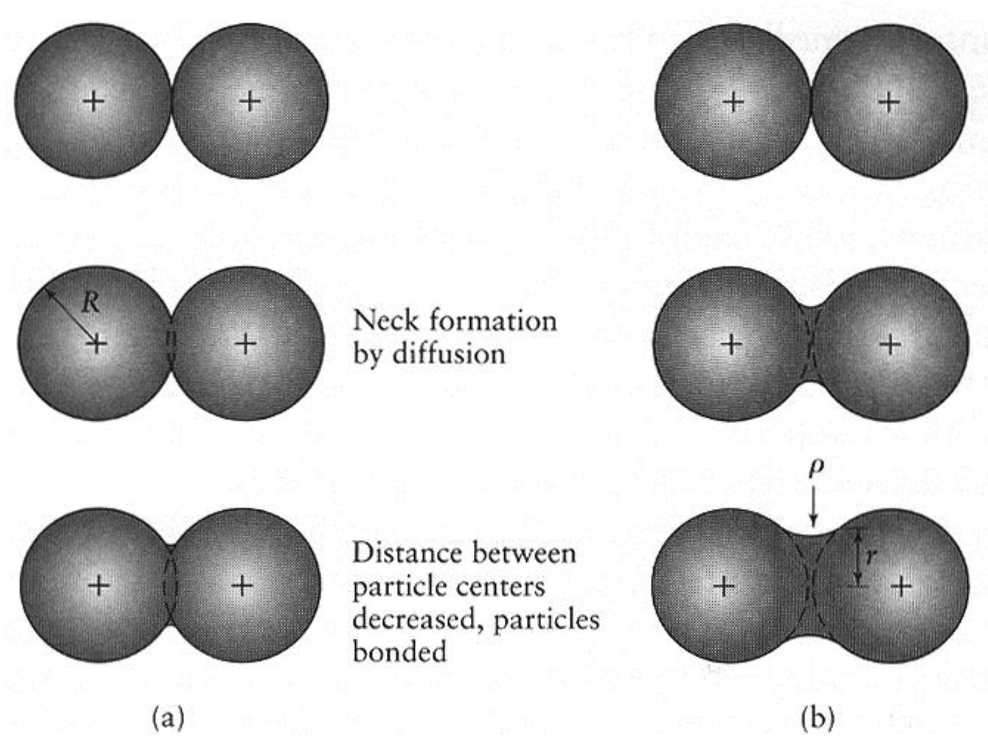



**FIGURE 11.13** Schematic illustration of two mechanisms for sintering metal powders: (a) solid-state material transport; and (b) liquid-phase material transport. $R$ = particle radius, $r$ = neck radius, and $\rho$ = neck profile radius.

# Sintering (소결) (2)

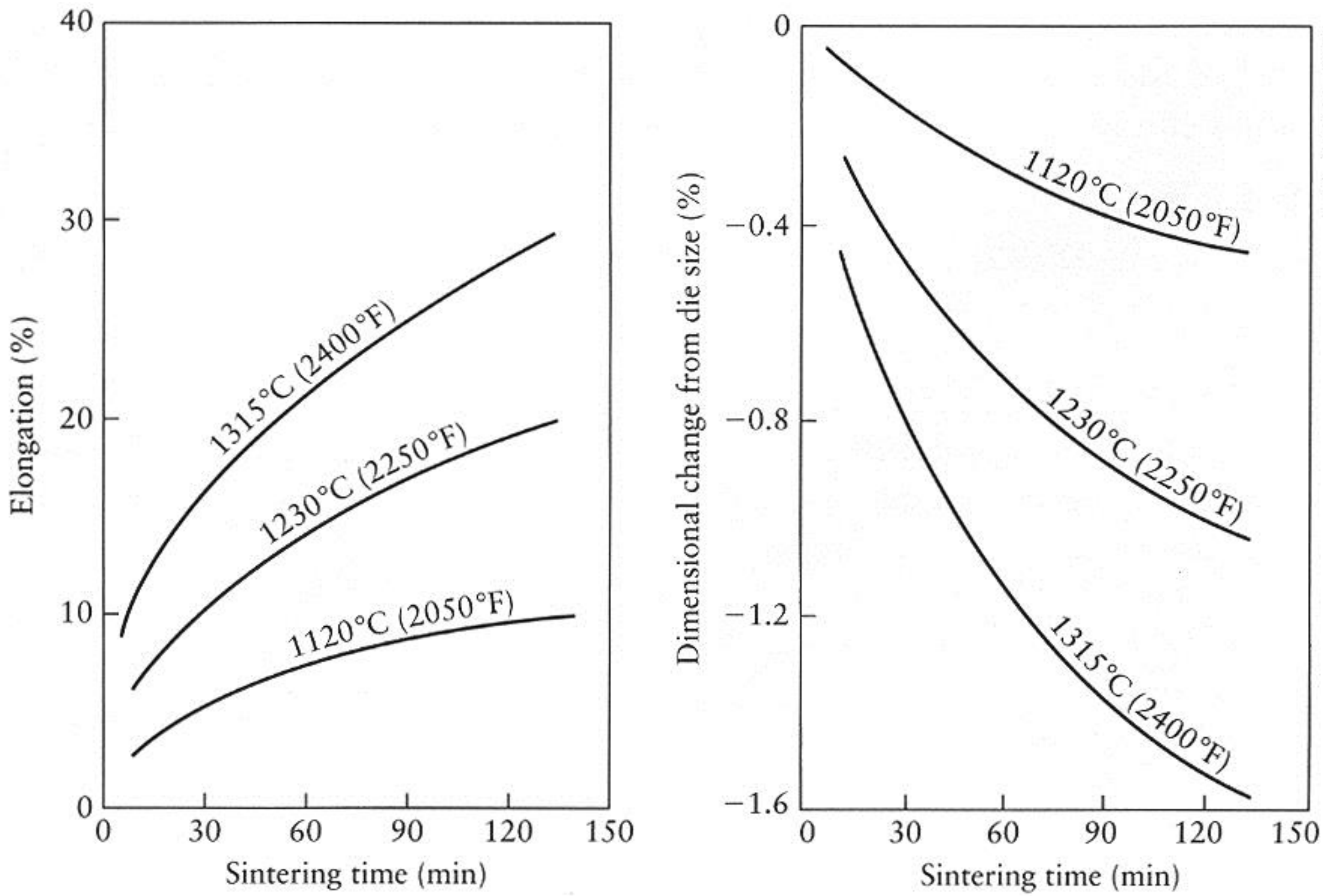



**FIGURE 11.14** Effect of sintering temperature and time on elongation and dimensional change during sintering of type 316L stainless steel. *Source*: ASM International.

# Sintering (소결) (3)

TABLE 11.3

**Typical Mechanical Properties of Selected P/M Materials**

| Designation | MPIF type | Condition | Ultimate Tensile Strength (MPa) | Yield Stress (MPa) | Hardness | Elongation in 25 mm (%) | Elastic Modulus (GPa) |
|---|---|---|---|---|---|---|---|
| FERROUS | | | | | | | |
| FC-0208 | N | AS | 225 | 205 | 45 HRB | <0.5 | 70 |
| | | HT | 295 | — | 95 HRB | <0.5 | 70 |
| | R | AS | 415 | 330 | 70 HRB | 1 | 110 |
| | | HT | 550 | — | 35 HRC | <0.5 | 110 |
| | S | AS | 550 | 395 | 80 HRB | 1.5 | 130 |
| | | HT | 690 | 655 | 40 HRC | <0.5 | 130 |
| FN-0405 | S | AS | 425 | 240 | 72 HRB | 4.5 | 145 |
| | | HT | 1060 | 880 | 39 HRC | 1 | 145 |
| | T | AS | 510 | 295 | 80 HRB | 6 | 160 |
| | | HT | 1240 | 1060 | 44 HRC | 1.5 | 160 |
| ALUMINUM | | | | | | | |
| 601 AB, | | AS | 110 | 48 | 60 HRH | 6 | — |
| pressed bar | | HT | 252 | 241 | 75 HRH | 2 | — |
| BRASS | | | | | | | |
| CZP-0220 | T | — | 165 | 76 | 55 HRH | 13 | — |
| | U | — | 193 | 89 | 68 HRH | 19 | — |
| | W | — | 221 | 103 | 75 HRH | 23 | — |
| TITANIUM | | | | | | | |
| Ti-6Al-4V | | HIP | 917 | 827 | — | 13 | — |
| SUPERALLOYS | | | | | | | |
| Stellite 19 | | — | 1035 | — | 49 HRC | <1 | — |

*Note*: MPIF = Metal Powder Industries Federation; AS = as sintered; HT = heat treated; HIP = hot isostatically pressed.

# Sintering (소결) (4)

TABLE 11.4

**Mechanical Property Comparisons for Ti-6Al-4V Titanium Alloy**

| Process | Density (%) | Yield Stress (MPa) | Ultimate Tensile Strength (MPa) | Elongation (%) | Reduction of Area (%) |
|---|---|---|---|---|---|
| Cast | 100 | 840 | 930 | 7 | 15 |
| Cast and forged | 100 | 875 | 965 | 14 | 40 |
| Powder metallurgy | | | | | |
| Blended elemental (P + S)* | 98 | 786 | 875 | 8 | 14 |
| Blended elemental (HIP)* | >99 | 805 | 875 | 9 | 17 |
| Realloyed (HIP)* | 100 | 880 | 975 | 14 | 26 |

(*) P + S = pressed and sintered; HIP = hot isostatically pressed.
*Source*: R. M. German.

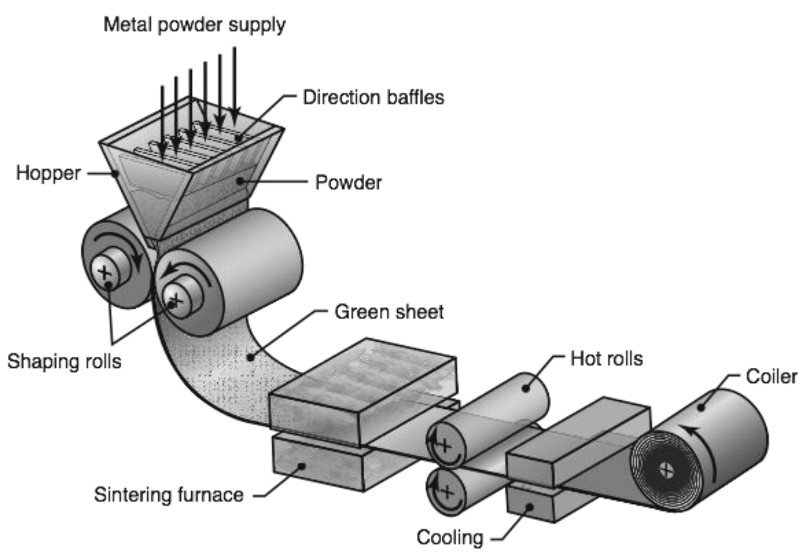



**FIGURE 11.12** An example of powder rolling. The purpose of direction baffles in the hopper is to ensure uniform distribution of powder across the width of the strip.

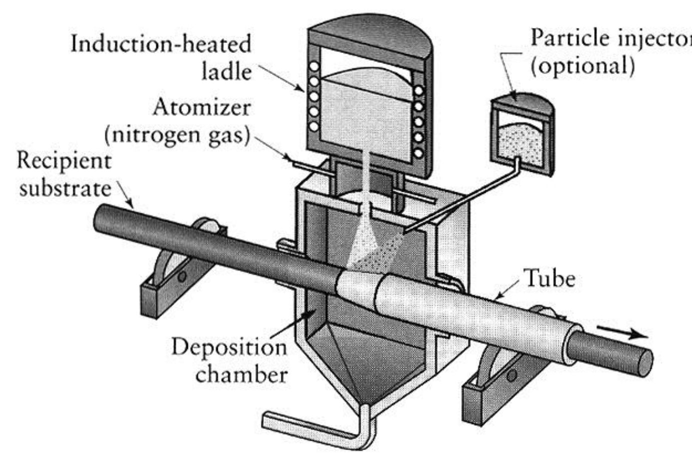



**FIGURE 11.12** Spray casting (Osprey process) in which molten metal is sprayed over a rotating mandrel to produce seamless tubing and pipe. *Source*: After J. Szekeley, "Can Advanced Technology Save the U.S. Steel Industry," *Scientific American*, July 1987, © George V. Kelvin/Scientific American.

# Design considerations

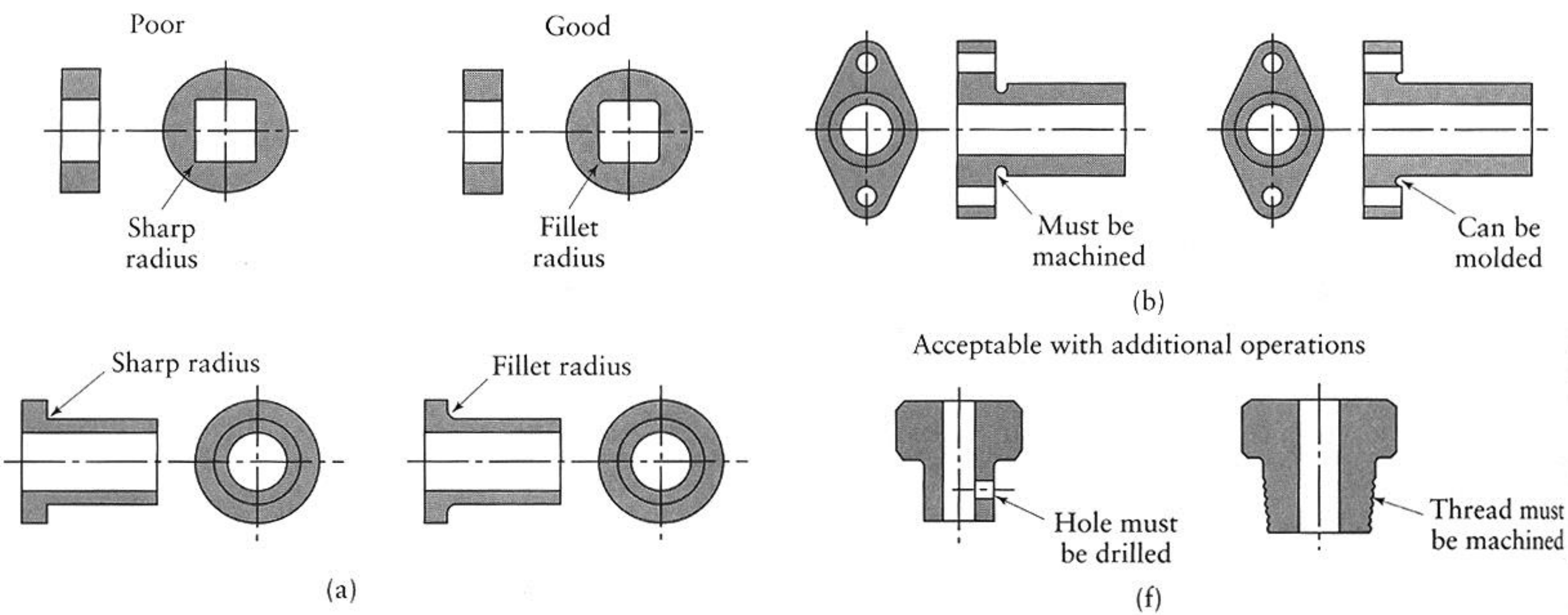



**FIGURE 11.17** Examples of P/M parts, showing poor and good designs. Note that sharp radii and reentry corners should be avoided, and that threads and transverse holes have to be produced separately by additional machining operations. *Source*: Metal Powder Industries Federation.

# Ceramics

TABLE 11.6

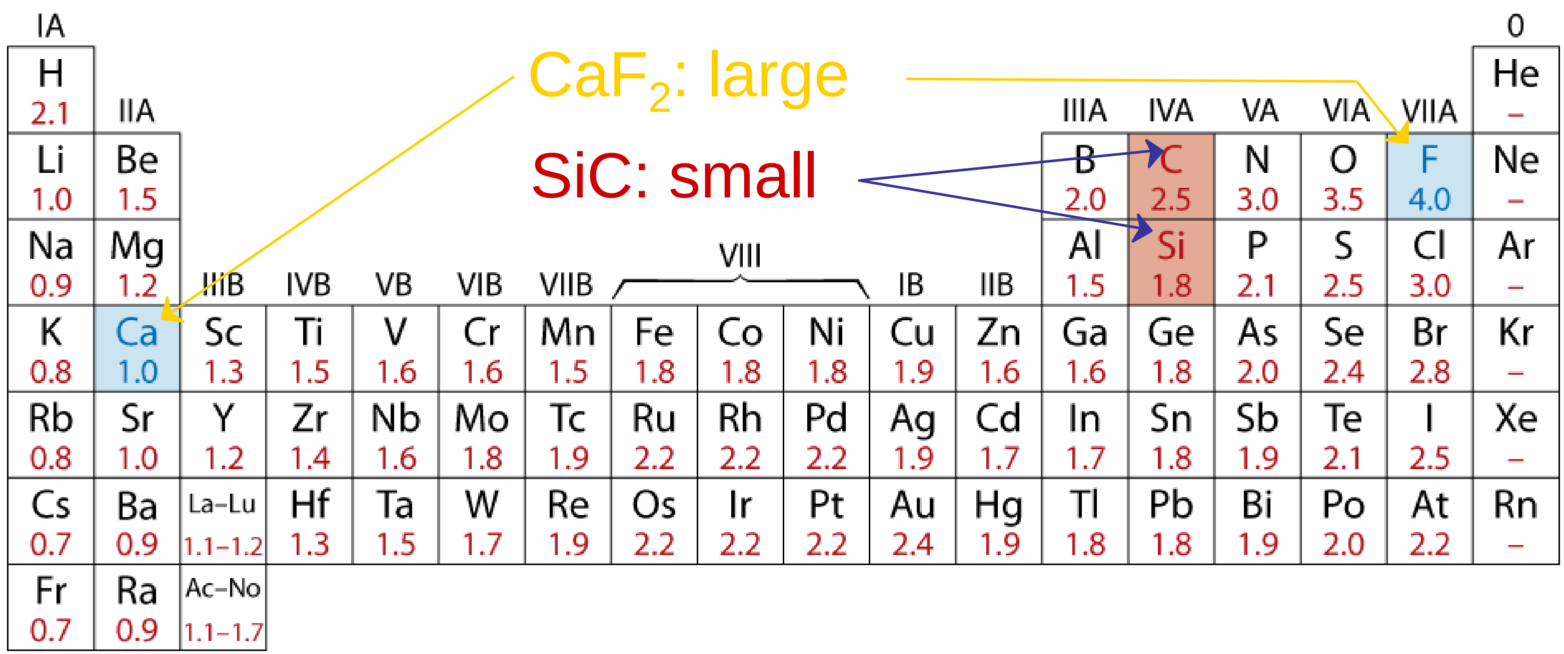
**Types and General Characteristics of Ceramics and Glasses**

| Type | General Characteristics |
| --- | --- |
| Oxide Ceramics | |
| Alumina | High hot hardness and abrasion resistance, moderate strength and toughness; most widely used ceramic; used for cutting tools, abrasives, and electrical and thermal insulation. |
| Zirconia | High strength and toughness; resistance to thermal shock, wear, and corrosion; partially-stabilized zirconia and transformation-toughened zirconia have better properties; suitable for heat-engine components. |
| Carbides | |
| Tungsten carbide | High hardness, strength, toughness, and wear resistance, depending on cobalt binder content; commonly used for dies and cutting tools. |
| Titanium carbide | Not as tough as tungsten carbide, but has a higher wear resistance; has nickel and molybdenum as the binder; used as cutting tools. |
| Silicon carbide | High-temperature strength and wear resistance, used for heat engines and as abrasives. |
| Nitrides | |
| Cubic boron nitride | Second hardest substance known, after diamond; high resistance to oxidation; used as abrasives and cutting tools. |
| Titanium nitride | Used as coatings on tools, because of its low frictional characteristics. |
| Silicon nitride | High resistance to creep and thermal shock; high toughness and hot hardness; used in heat engines. |
| Sialon | Consists of silicon nitrides and other oxides and carbides; used as cutting tools. |
| Cermets | Consist of oxides, carbides, and nitrides; high chemical resistance but is somewhat brittle and costly; used in high-temperature applications. |
| Nanophase ceramics | Stronger and easier to fabricate and machine than conventional ceramics; used in automotive and jet-engine applications. |
| Silica | High temperature resistance; quartz exhibits piezoelectric effects; silicates containing various oxides are used in high-temperature, nonstructural applications. |
| Glasses | Contain at least 50% silica; amorphous structure; several types available, with a wide range of mechanical, physical, and optical properties. |
| Glass ceramics | High crystalline component to their structure; stronger than glass; good thermal-shock resistance; used for cookware, heat exchangers, and electronics. |
| Graphite | Crystalline form of carbon; high electrical and thermal conductivity; good thermal-shock resistance; also available as fibers, foam, and buckyballs for solid lubrication; used for molds and high-temperature components. |
| Diamond | Hardest substance known; available as single-crystal or polycrystalline form; used as cutting tools and abrasives and as die insert for fine wire drawing; also used as coatings. |

# Ceramic Bonding

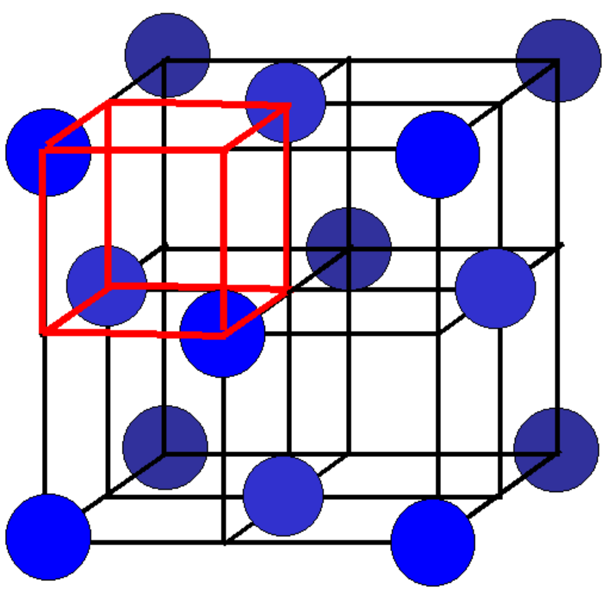
- **Bonding :**
  - **Mostly ionic, some covalent**
  - **% ionic character increases with difference in electronegativity.**

- **Large vs. small ionic bond character :**

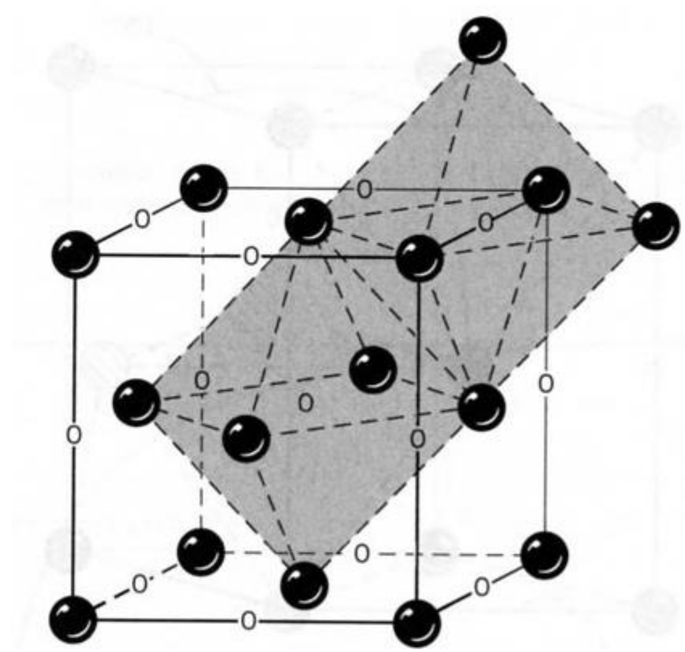


# Ceramic Crystal Structures

- **Oxide structures**
  - **Oxygen anions are much larger than metal cations.**
  - **Close packed oxygen in a lattice (usually FCC)**
  - **Cations in the holes of the oxygen lattice**



Tetrahedral site



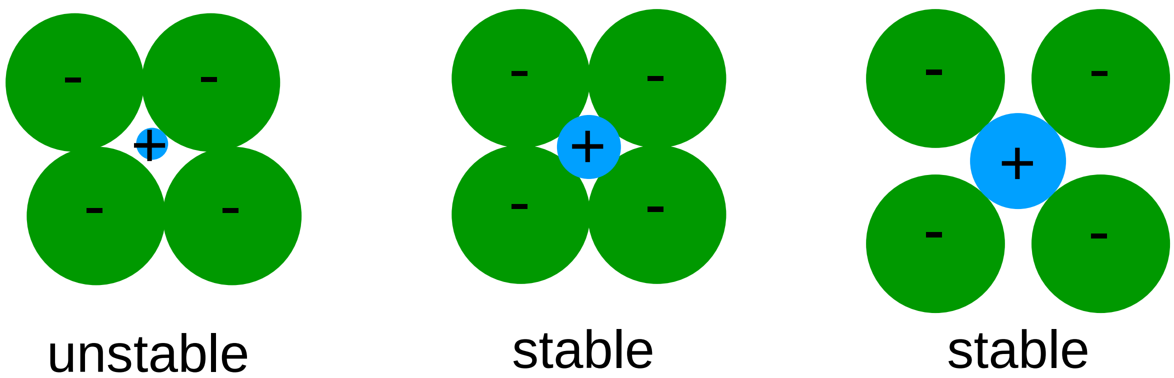
Octahedral site

# What determines crystal structure?

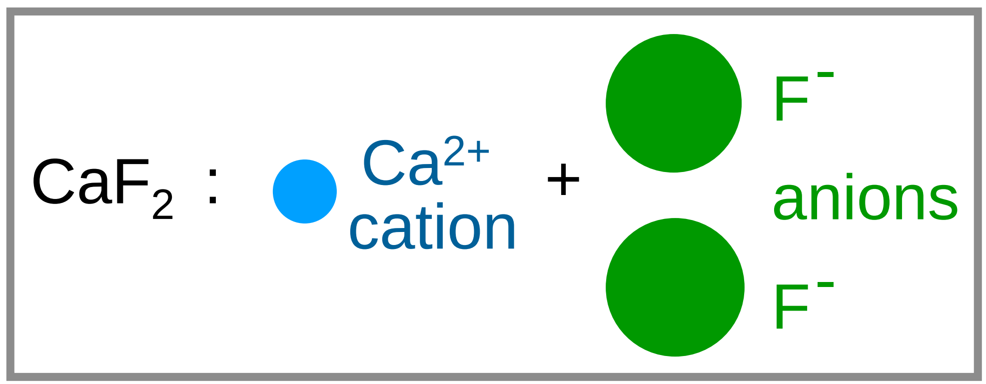
1. Magnitude of electrical charge on each of component ions
   - Crystals must be electrically neutral.
2. Relative sizes of cations and anions
   - Does the cation fit in the site.

# Ionic Bonding & Structure

- **Size - stable structures :**
  - **- Maximize the number of nearest oppositely charged neighbors.**




- **Charge neutrality :**
  - **- Net charge in the structure should be zero.**




**- General form :** $A_m X_p$

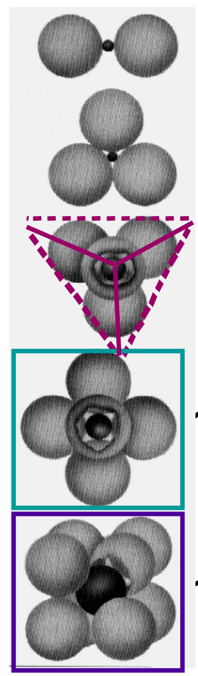
**m, p determined by charge neutrality**

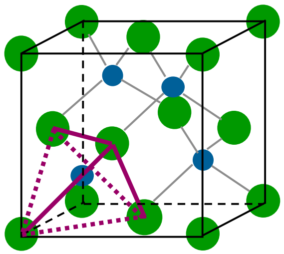
# Coordination number and Ionic Radii

- Coordination number increases with $\frac{r_{cation}}{r_{anion}}$

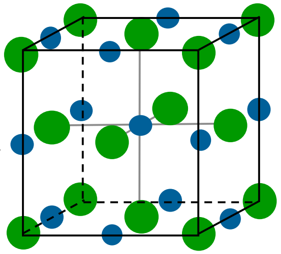
Issue: How many anions can you arrange around a cation?

| $\frac{r_{cation}}{r_{anion}}$ | Coord. # | |
|---|---|---|
| < 0.155 | 2 | linear |
| 0.155 - 0.225 | 3 | triangular |
| 0.225 - 0.414 | 4 | $T_D$ |
| 0.414 - 0.732 | 6 | $O_H$ |
| 0.732 - 1.0 | 8 | cubic |

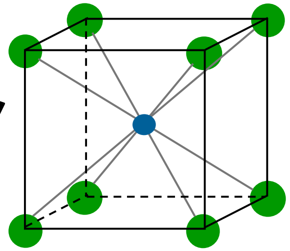




ZnS (zincblende)

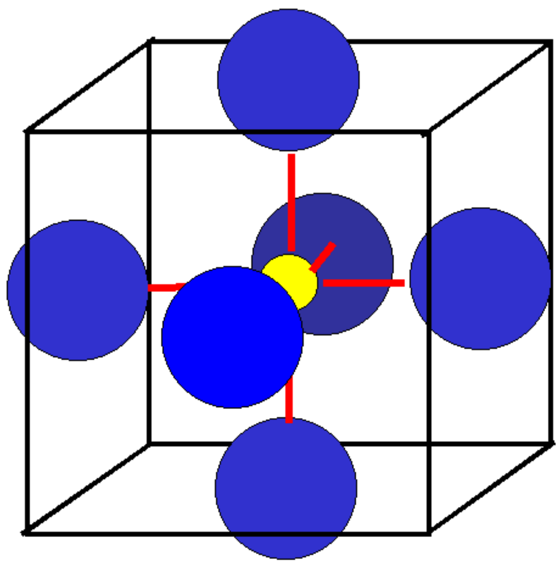


NaCl (sodium chloride)

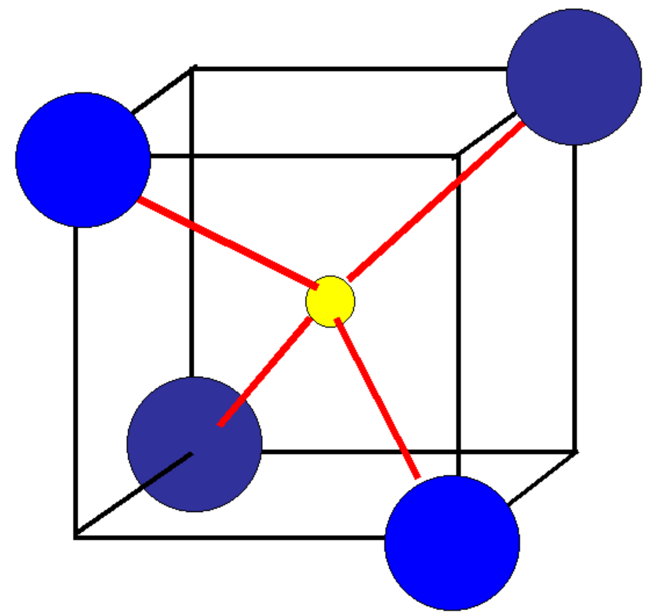


CsCl (cesium chloride)

# Interstitial Sites



Octahedral sites

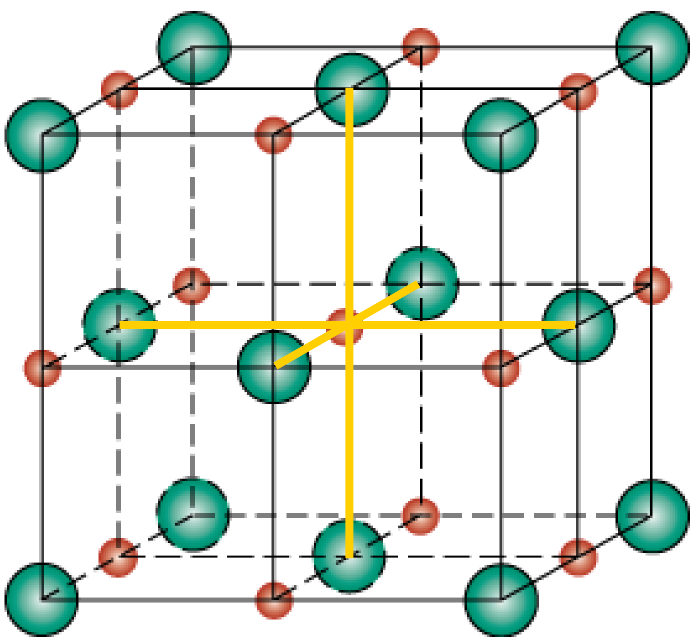


Tetrahedral sites

# Rock Salt Structure

- **Same concepts can be applied to ionic solids in general.**

**Example : NaCl (rock salt) structure**



$Na^{+}$ $r_{Na}$ = 0.102 nm

$Cl^{-}$ $r_{Cl}$ = 0.181 nm

$r_{Na}/r_{Cl}$ = 0.564

∴ cations prefer $O_H$ sites

# Effect of Porosity

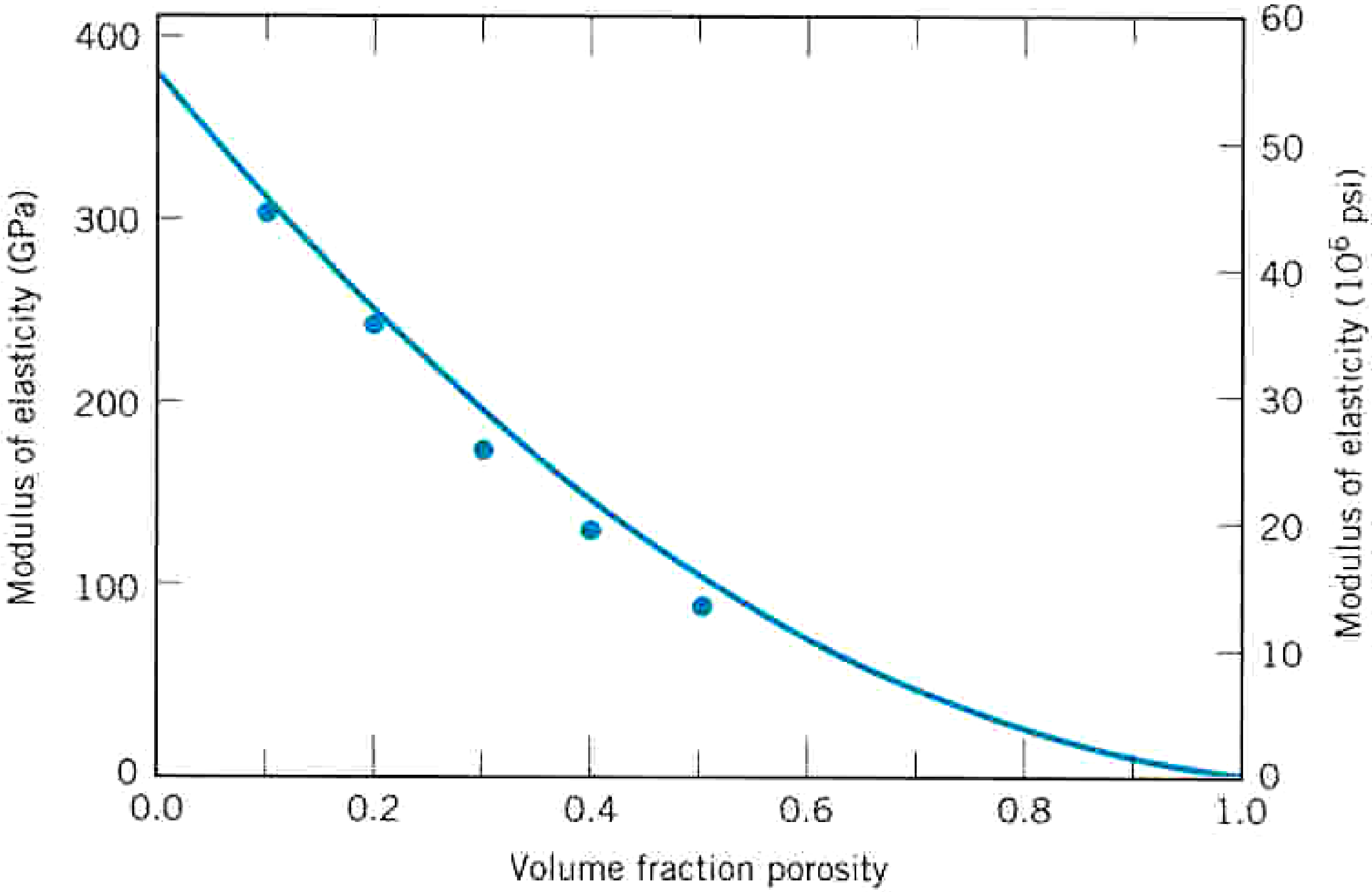
- Residual Porosity :
  Elastic Modulus and Strength ⇒ Lower
  Elastic Modulus, *E*

$$E = E_0 (1 - 1.9P + 0.9P^2)$$

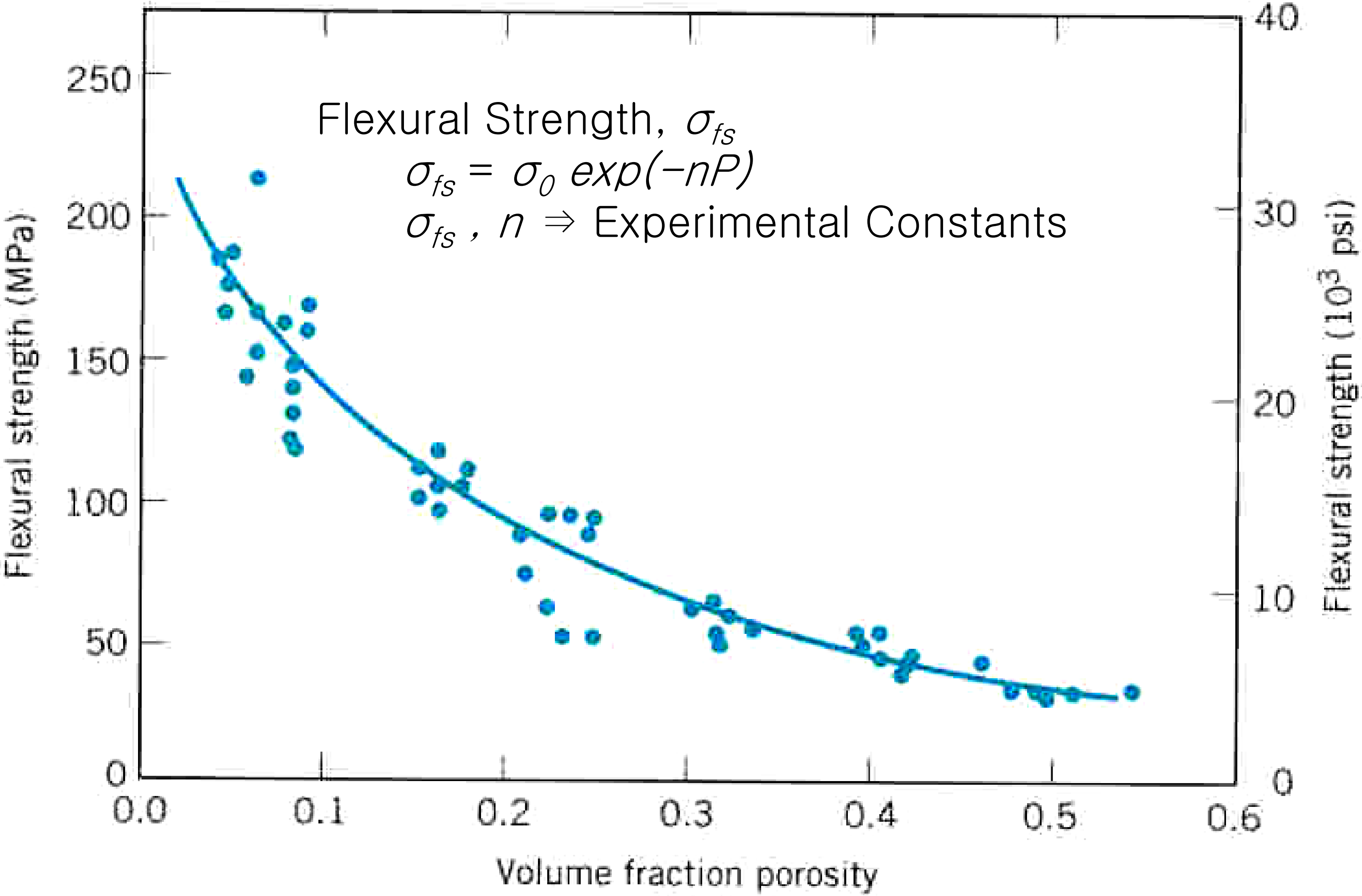
$P$ : Volume Fraction of Porosity
$E_0$ : Elastic Modulus of Material

Reasons : strength lowered by porosity
(1) Cross-Sectional Area ⇒ Reduce
(2) Stress Concentrators

# $Al_2O_3$ Elastic Modulus vs. Porosity



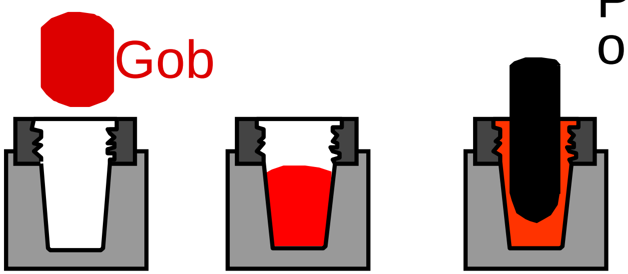
# $Al_2O_3$ Flexural Strength vs. Porosity



# Ceramic Fabrication Methods (1)

GLASS FORMING | PARTICULATE FORMING | CEMENTATION

- Pressing:

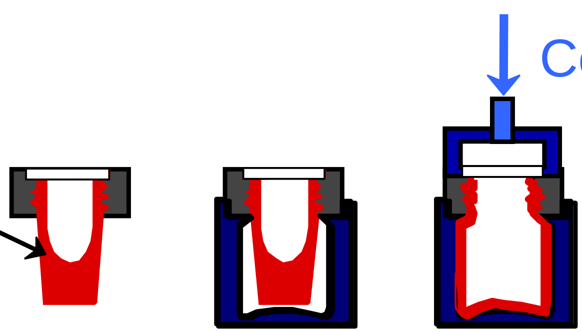


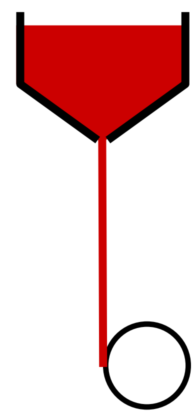

- Fiber drawing:

plates, dishes, cheap glasses

- Mold is steel with graphite lining

- Blowing:

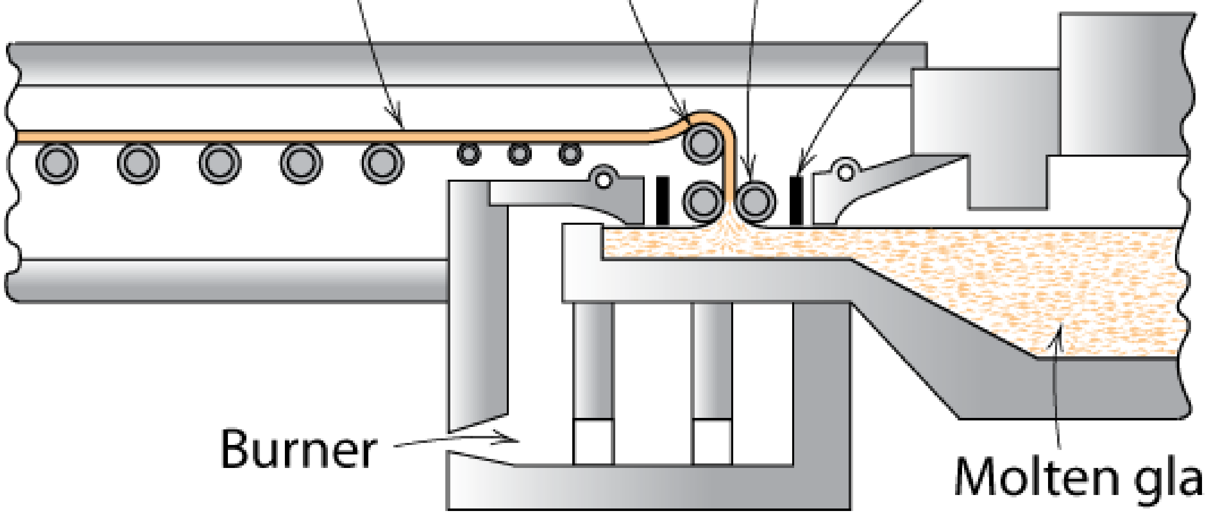


# Sheet Glass Forming

- **Sheet forming – continuous draw**

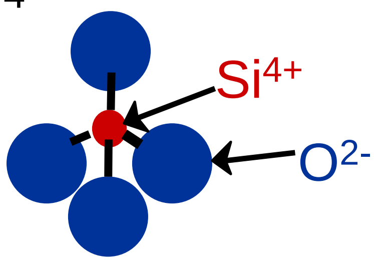
  Originally sheet glass was made by “floating” glass on a pool of tin.



# Glass Structure

- Basic Unit:

  $SiO_4^{4-}$ tetrahedron




- Glass is amorphous.
- Amorphous structure

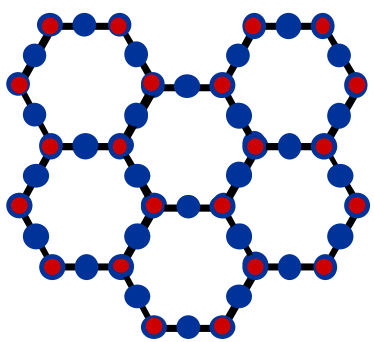
  occurs by adding impurities.

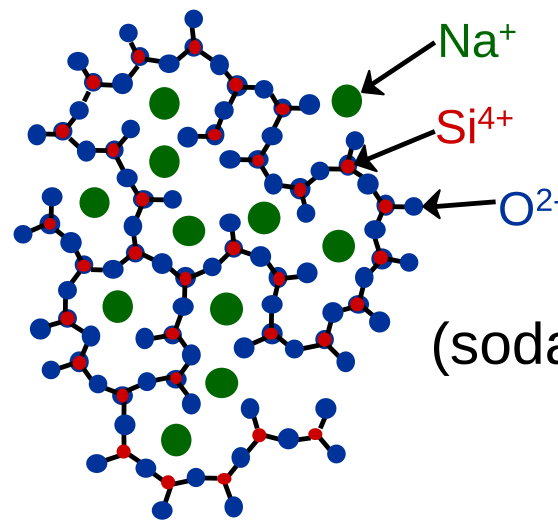
  ($Na^{+}$, $Mg^{2+}$, $Ca^{2+}$, $Al^{3+}$)
- Impurities:

  interfere with formation of crystalline structure

- Quartz is crystalline.

  $SiO_2$:

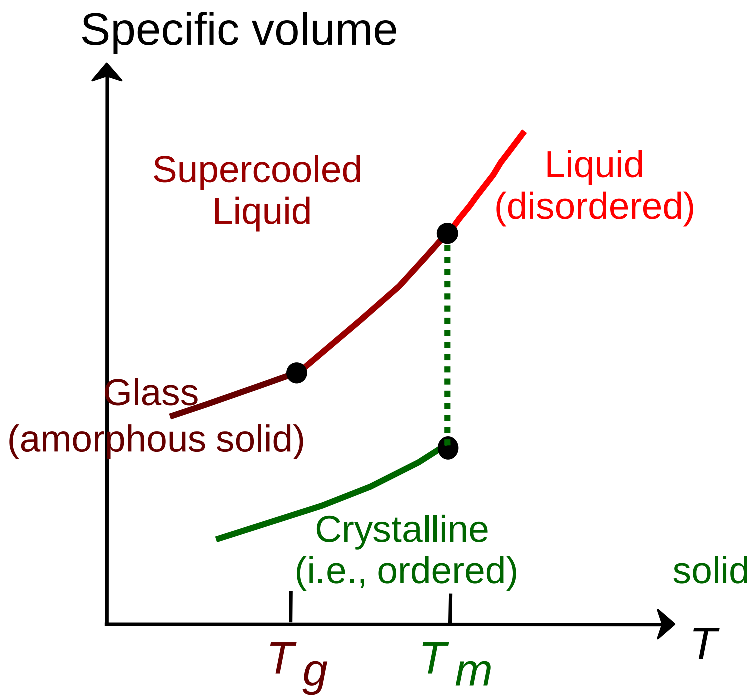





(soda glass)

# Glass Properties

- Specific volume (1/r) vs. Temperature (T):




- Crystalline materials:
  - crystallize at melting temp, $T_{m}$.
  - have abrupt change in spec. vol. at $T_{m}$.

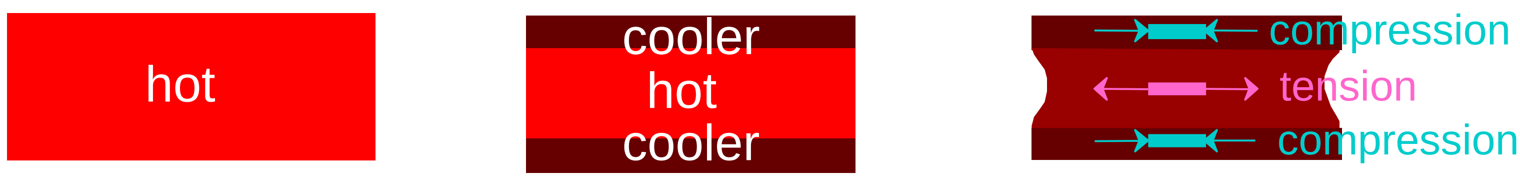
- Glasses:
  - do not crystallize.
  - change in slope in spec. vol. curve at glass transition temperature, $T_{g}$.
  - transparent
    no crystals to scatter light.

# Heat Treating Glass

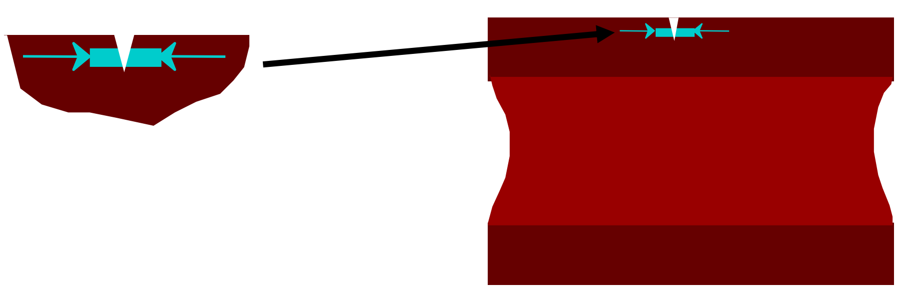
- Annealing:
  - removes internal stress caused by uneven cooling.
- Tempering:
  - puts surface of glass part into compression.
  - suppresses growth of cracks from surface scratches.

- Sequence :

before cooling | surface cooling | further cooled



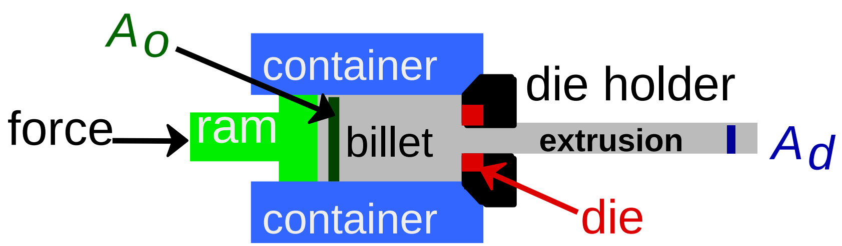

- Result : surface crack growth is suppressed.



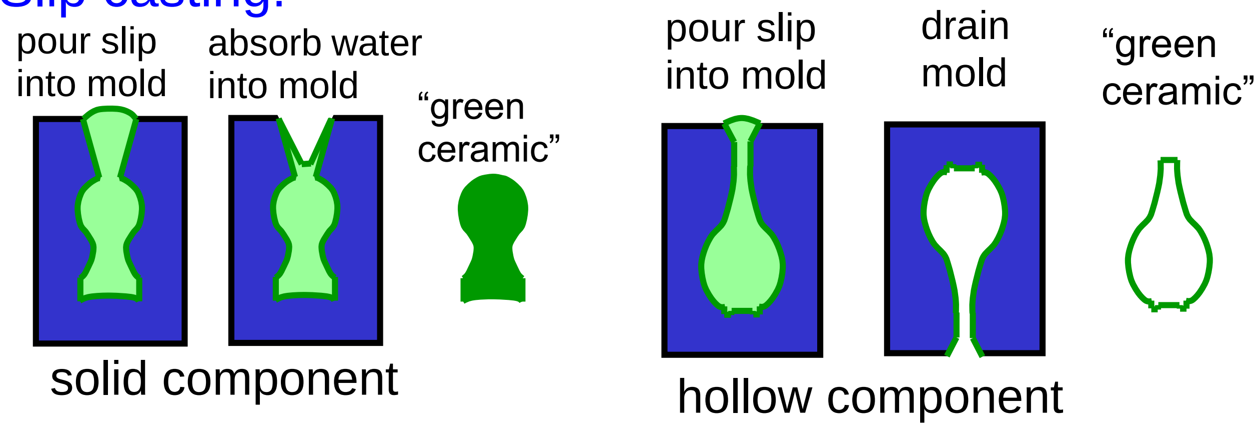
# Ceramic Fabrication Methods (2)

GLASS FORMING | **PARTICULATE FORMING** | CEMENTATION

- Milling and screening : desired particle size
- Mixing particles & water : produces a "slip"
- Form a "green" component
  - Hydroplastic forming:
    extrude the slip (e.g., into a pipe)




  - Slip casting:

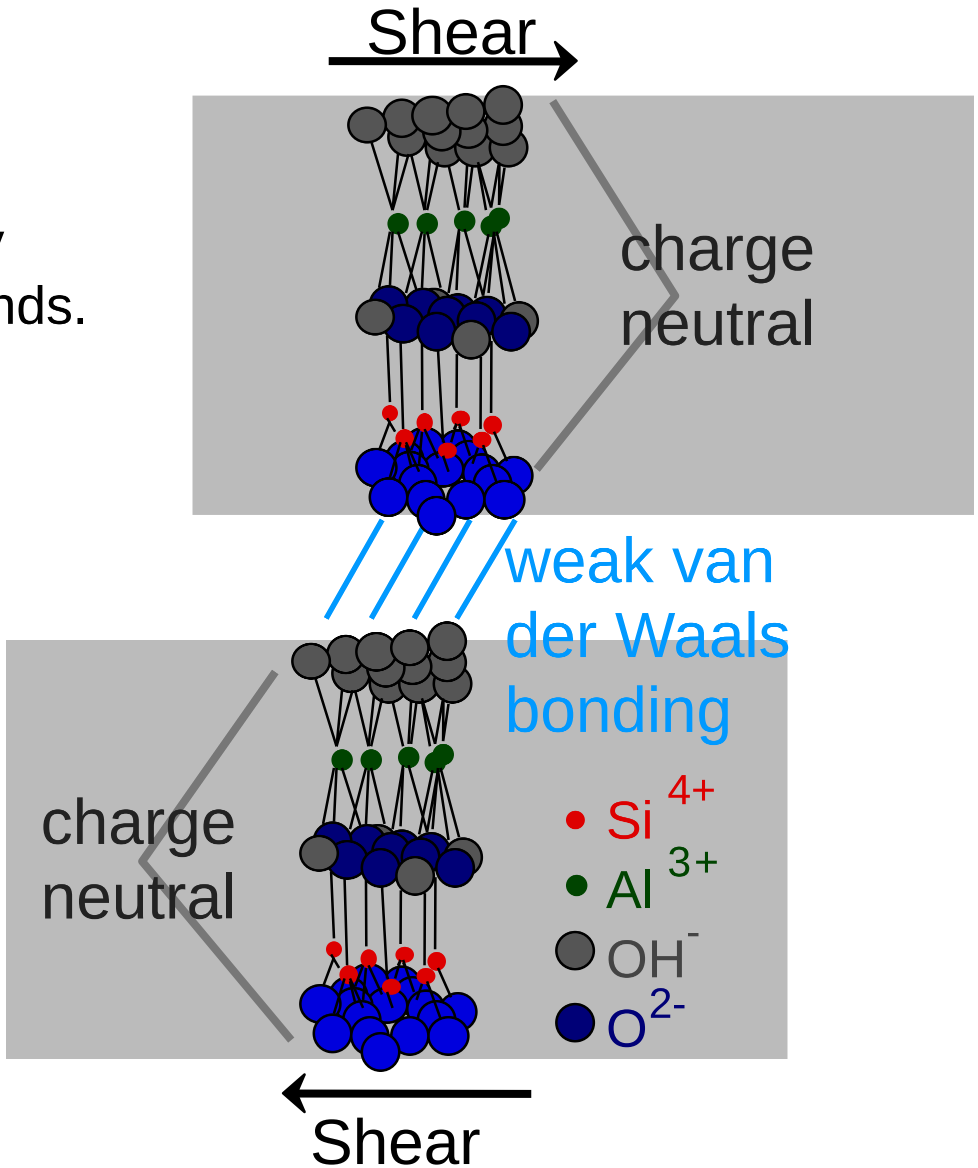



- Dry and fire the component.

# Features of a Slip

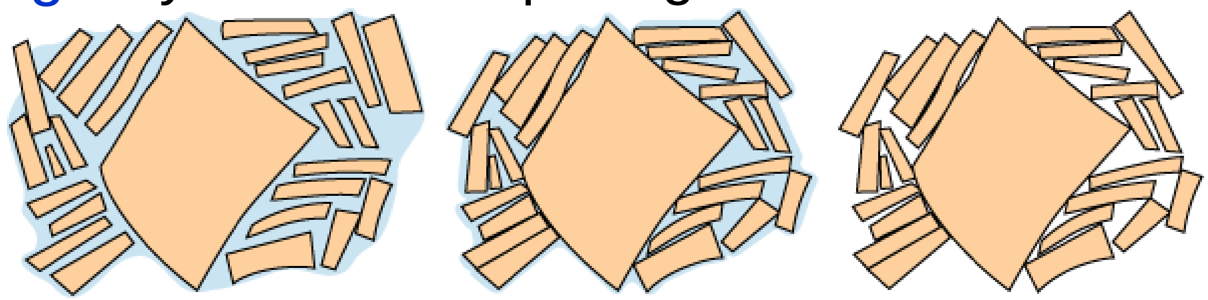
- Clay is inexpensive.
- Adding water to clay
  - allows material to shear easily along weak van der Waals bonds.
  - enables extrusion.
  - enables slip casting.

- Structure of Kaolinite Clay :
  (고령토)



# Drying and Firing

- Drying: layer size and spacing decrease.

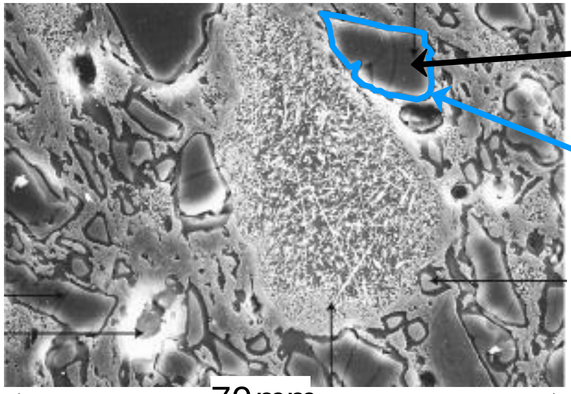


wet slip partially dry "green" ceramic

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

- Firing:
  - $T$ raised to 900~1400°C
  - vitrification : liquid glass forms from clay and flows between $SiO_2$ particles. Flux melts at lower $T$.

micrograph of porcelain



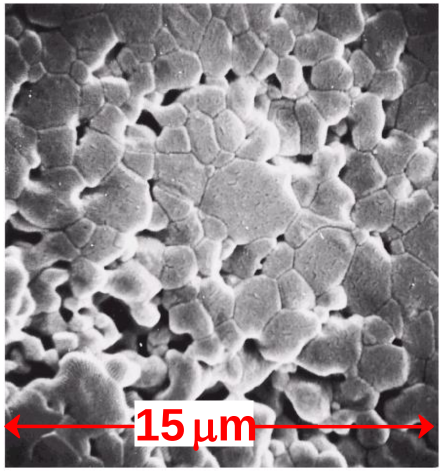
# Ceramic Fabrication Methods (3)

GLASS FORMING | **PARTICULATE FORMING** | CEMENTATION

Sintering: useful for both clay and non-clay 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



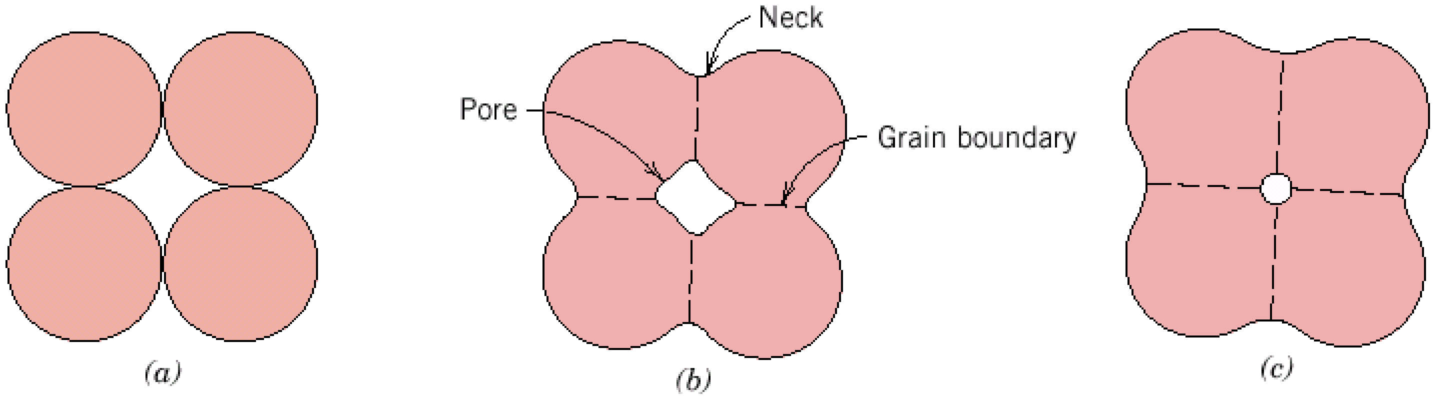
# Powder Pressing

- 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



# Tape Casting

- **Thin sheets of green ceramic cast as flexible tape**
- **Used for integrated circuits and capacitors**
- **Cast from liquid slip (ceramic + organic solvent)**

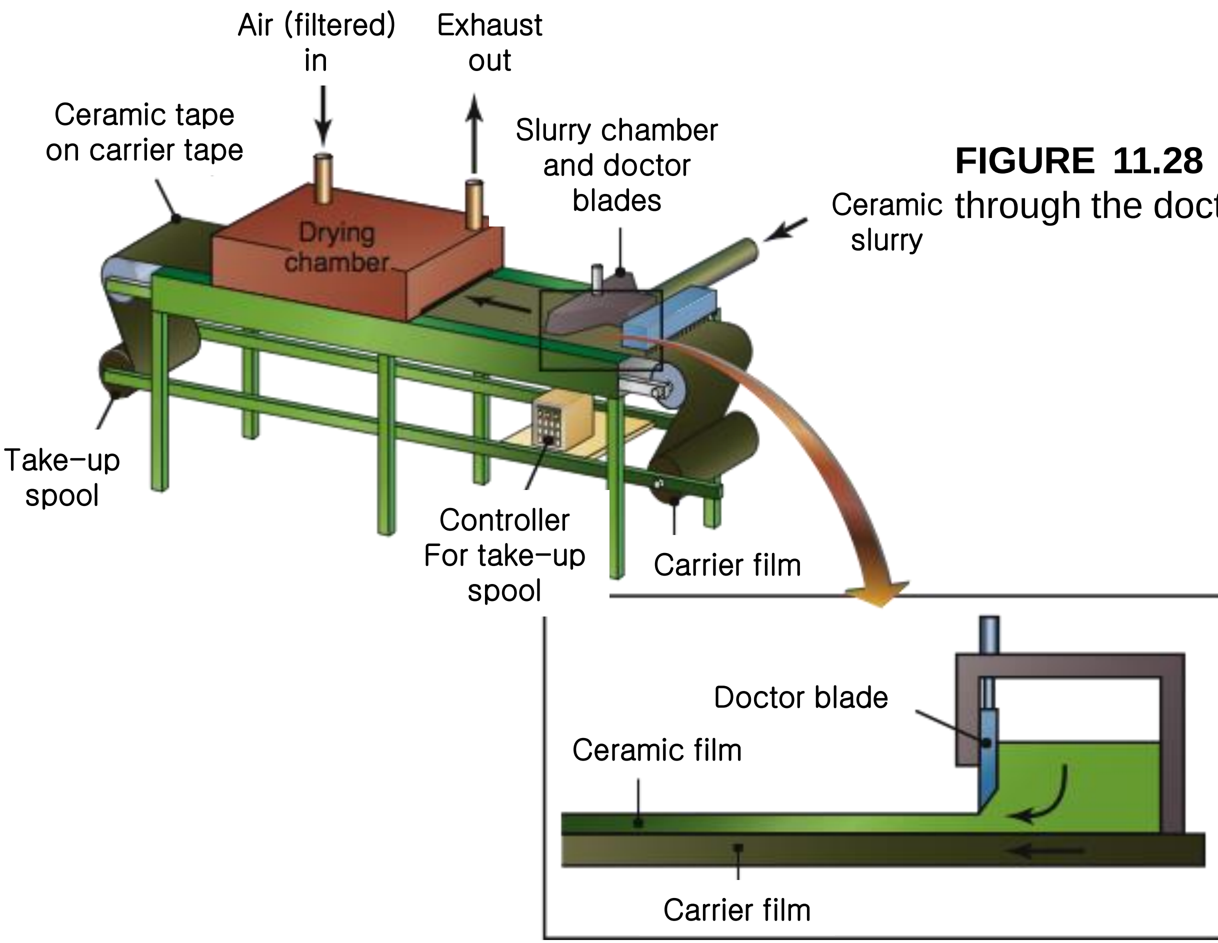



**FIGURE 11.28** Production of ceramic sheets through the doctor-blade process.

# Ceramic Fabrication Methods (4)

GLASS FORMING | PARTICULATE FORMING | **CEMENTATION**

- Produced in extremely large quantities.
- Portland cement:
  - mix clay and lime bearing materials
  - calcination (heat to 1400°C)
  - primary constituents:
    - tri-calcium silicate
    - di-calcium silicate
- Adding water
  - produces a paste which hardens
  - hardening occurs due to hydration (chemical reactions with the water).
- Forming: done usually minutes after hydration begins.

# Properties of ceramics

**TABLE 11.7**

**Approximate Range of Properties of Various Ceramics at Room Temperature**

| Material | Symbol | Transverse Rupture Strength (MPa) | Compressive Strength (MPa) | Elastic Modulus (GPa) | Hardness (HK) | Poisson's Ratio ($\nu$) | Density (kg/m$^3$) |
|---|---|---|---|---|---|---|---|
| Aluminum oxide | $Al_2O_3$ | 140–240 | 1000–2900 | 310–410 | 2000–3000 | 0.26 | 4000–4500 |
| Cubic boron nitride | cBN | 725 | 7000 | 850 | 4000–5000 | – | 3480 |
| Diamond | – | 1400 | 7000 | 830–1000 | 7000–8000 | – | 3500 |
| Silica, fused | $SiO_2$ | – | 1300 | 70 | 550 | 0.25 | – |
| Silicon carbide | SiC | 100–750 | 700–3500 | 240–480 | 2100–3000 | 0.14 | 3100 |
| Silicon nitride | $Si_3N_4$ | 480–600 | – | 300–310 | 2000–2500 | 0.24 | 3300 |
| Titanium carbide | TiC | 1400–1900 | 3100–3850 | 310–410 | 1800–3200 | – | 5500–5800 |
| Tungsten carbide | WC | 1030–2600 | 4100–5900 | 520–700 | 1800–2400 | – | 10,000–15,000 |
| Partially stabilized zirconia | PSZ | 620 | – | 200 | 1100 | 0.3 | 5800 |

*Note*: These properties vary widely, depending on the condition of the material.

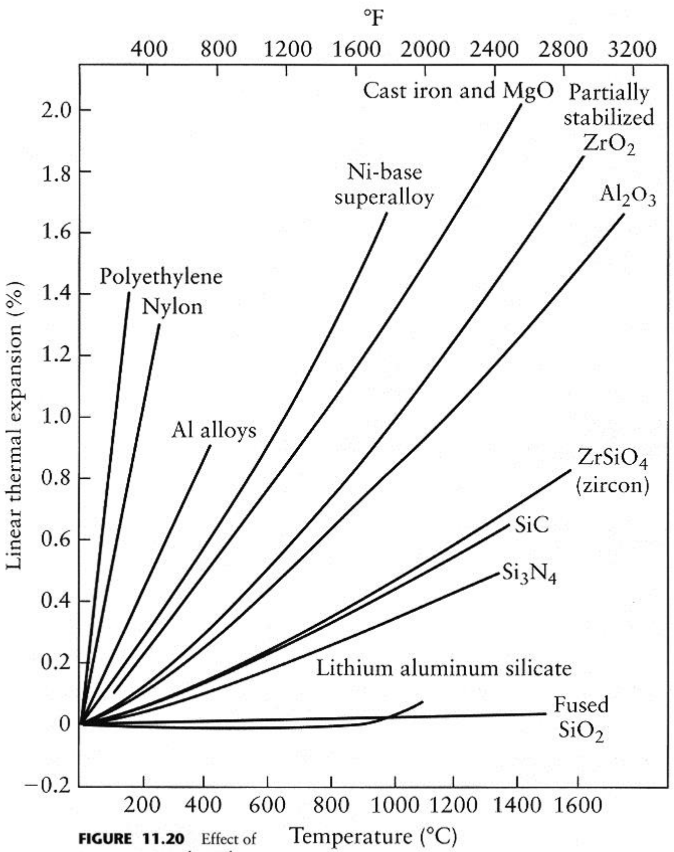
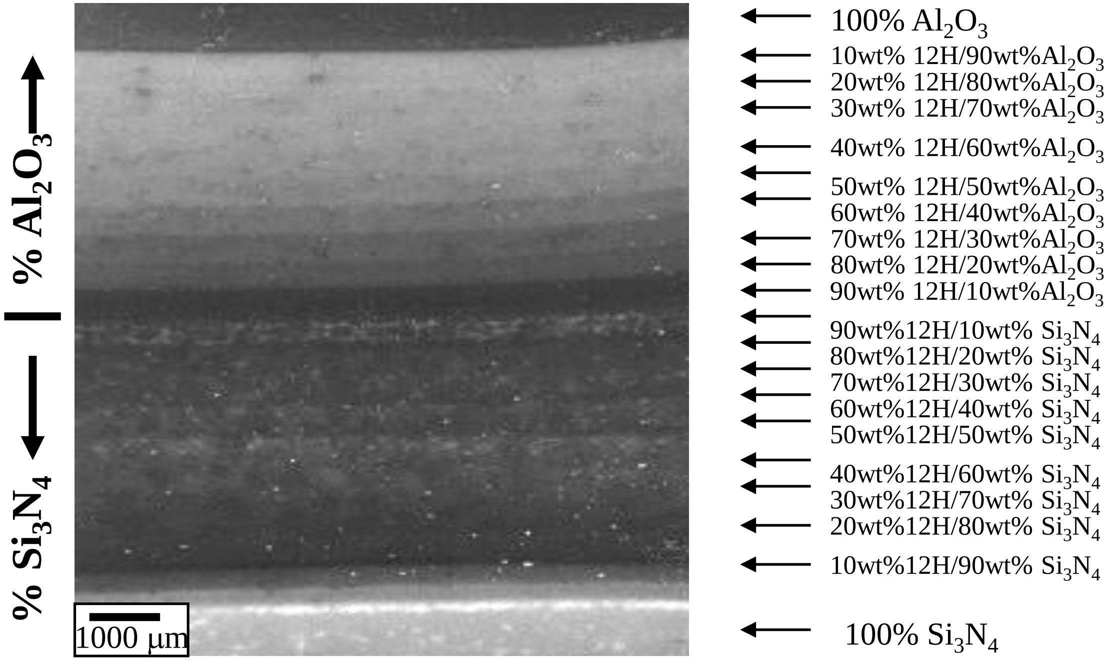
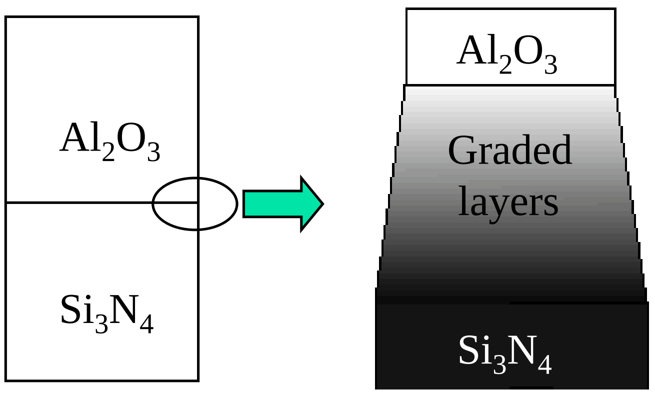
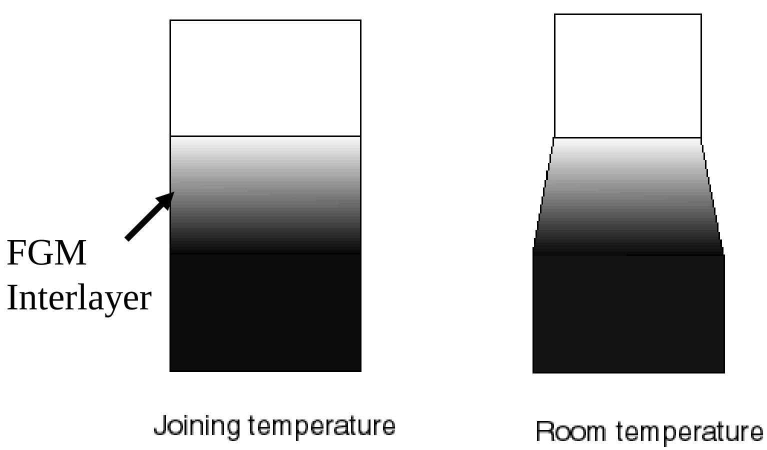


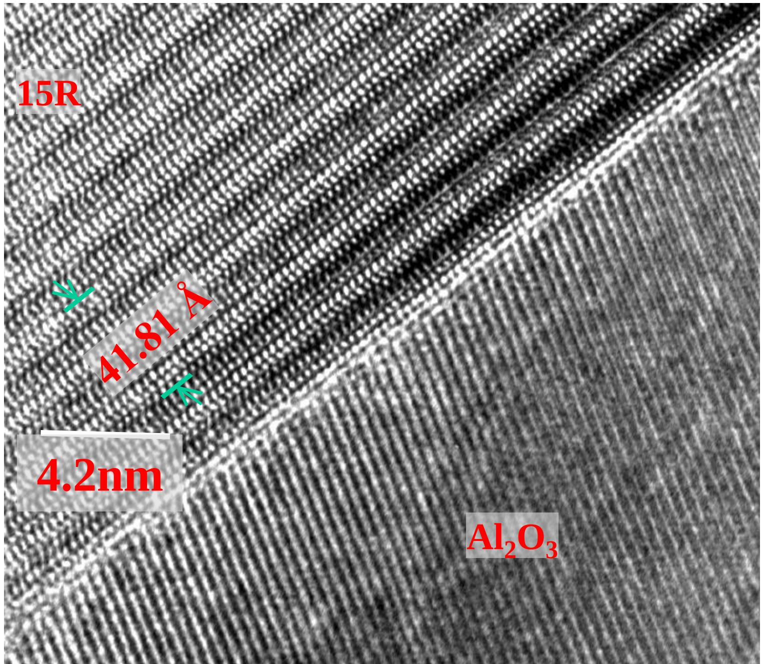

**FIGURE 11.20** Effect of temperature on thermal expansion for several ceramics, metals, and plastics. Note that the expansions for cast iron and for partially stabilized zirconia (PSZ) are within about 20%.

# FGM (Functionally Graded Material)



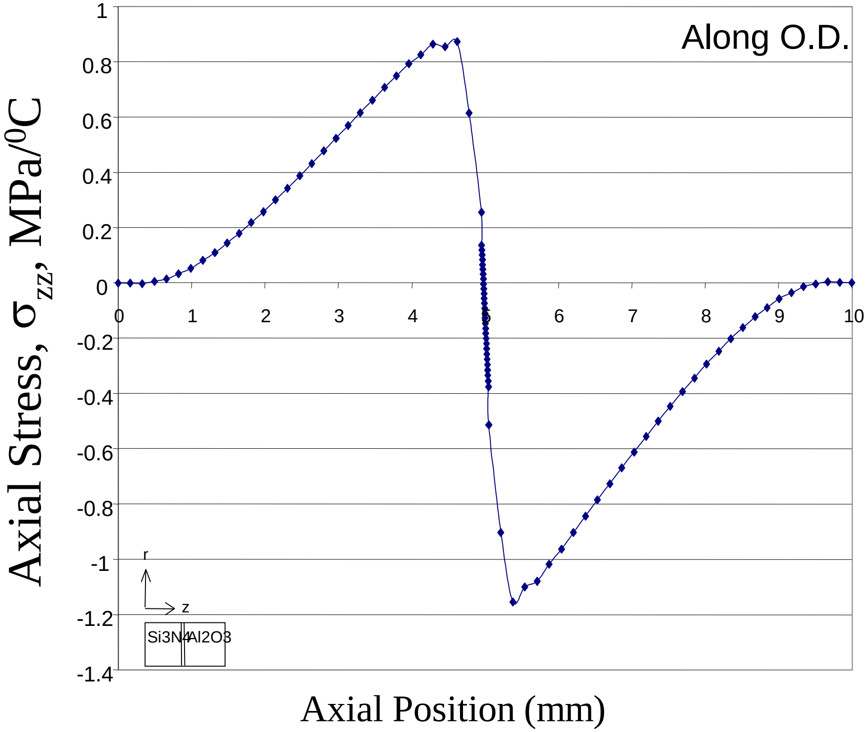



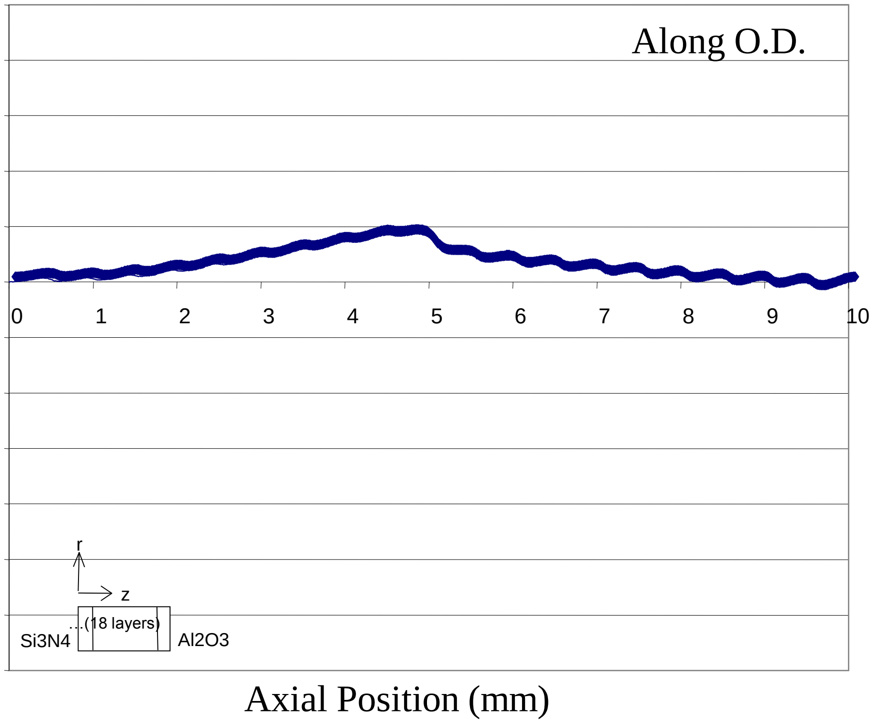



# Residual stresses calculation of FGM joint

**$Si_3N_4$ 5mm, Sialon 0.1mm, $Al_2O_3$ 5mm**




**20 layer, $Si_3N_4 \rightarrow Al_2O_3$, 0.5 mm each**




- Significant reduction in residual stresses confirms experiment (Lee *et al.*, Acta Mat. (2001))