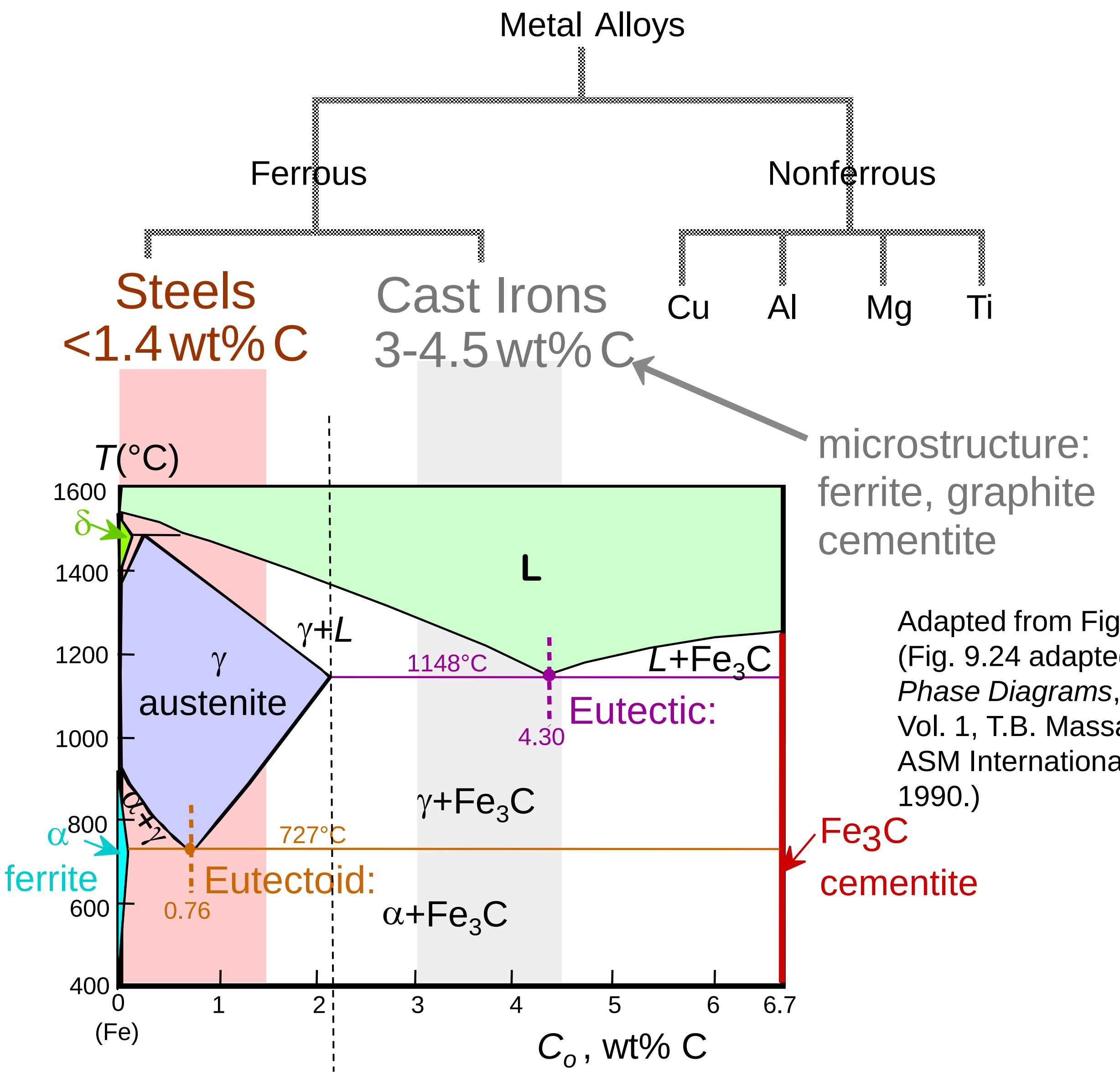
Chapter 11-13: Metal Alloys and Ceramics Applications and Processing

ISSUES TO ADDRESS...

- How are metal alloys classified and how are they used?
- What are some of the common fabrication techniques?
- How can properties be modified by post heat treatment

- Structures of ceramic materials
- Point defects, impurities, types of ceramic
- Processing and applications

Taxonomy of Metals



microstructure: ferrite, graphite cementite

Adapted from Fig. 11.1, *Callister 7e*.

Adapted from Fig. 9.24, *Callister 7e*. (Fig. 9.24 adapted from *Binary Alloy Phase Diagrams*, 2nd ed., Vol. 1, T.B. Massalski (Ed.-in-Chief), ASM International, Materials Park, OH, 1990.)

Steels

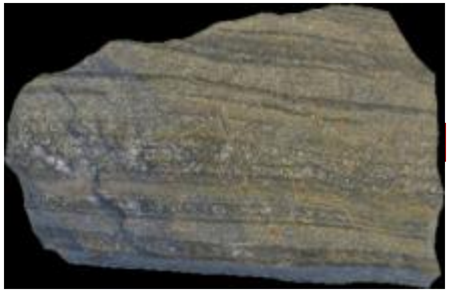
- Low Alloy
  - low carbon <0.25 wt% C
  - Med carbon 0.25-0.6 wt% C
  - high carbon 0.6-1.4 wt% C
- High Alloy

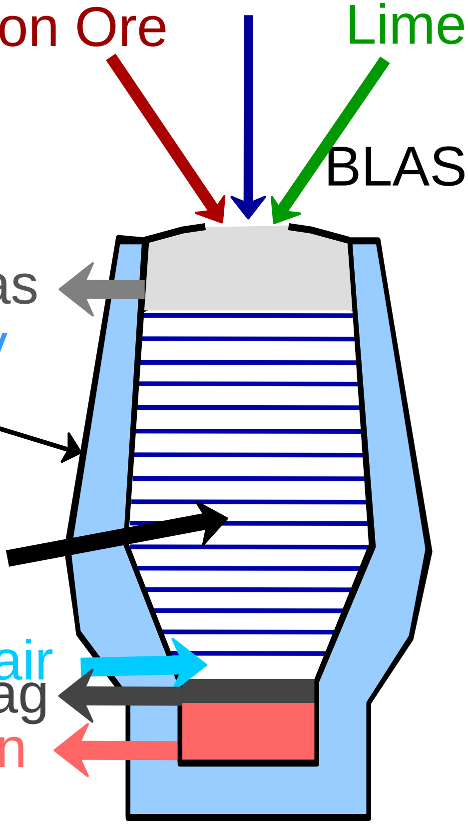
	low carbon		Med carbon		high carbon		High Alloy
Name	plain	HSLA	plain	heat treatable	plain	tool	austenitic stainless
Additions	none	Cr,V Ni, Mo	none	Cr, Ni Mo	none	Cr, V, Mo, W	Cr, Ni, Mo
Example	1010	4310	1040	4340	1095	4190	304
Hardenability	0	+	+	++	++	+++	0
TS	-	0	+	++	+	++	0
EL	+	+	0	-	-	--	++
Uses	auto struc. sheet	bridges towers press. vessels	crank shafts bolts hammers blades	pistons gears wear applic.	wear applic.	drills saws dies	high T applic. turbines furnaces V. corros. resistant

→ increasing strength, cost, decreasing ductility

Based on data provided in Tables 11.1(b), 11.2(b), 11.3, and 11.4, *Callister 7e*.

Refinement of Steel from Ore





Coke

Iron Ore

Limestone

BLAST FURNACE

gas

refractory vessel

layers of coke and iron ore

air

slag

Molten iron

heat generation

$$C + O_2 \rightarrow CO_2$$

reduction of iron ore to metal

$$CO_2 + C \rightarrow 2CO$$

$$3CO + Fe_2O_3 \rightarrow 2Fe + 3CO_2$$

purification

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CaO + SiO_2 + Al_2O_3 \rightarrow \text{slag}$$

http://www.youtube.com/watch?v=i6BIyQJZdTg

Ferrous Alloys

Iron containing – Steels - cast irons

Nomenclature AISI & SAE

10xx	Plain Carbon Steels
11xx	Plain Carbon Steels (resulfurized for machinability)
15xx	Mn (10 ~ 20%)
40xx	Mo (0.20 ~ 0.30%)
43xx	Ni (1.65 - 2.00%), Cr (0.4 - 0.90%), Mo (0.2 - 0.3%)
44xx	Mo (0.5%)

where xx is wt% C x 100

example: 1060 steel – plain carbon steel with 0.60 wt% C

Stainless Steel -- >11% Cr

Cast Iron

- Ferrous alloys with > 2.1 wt% C
  - more commonly 3 - 4.5 wt%C
- low melting (also brittle) so easiest to cast

- Cementite decomposes to ferrite + graphite

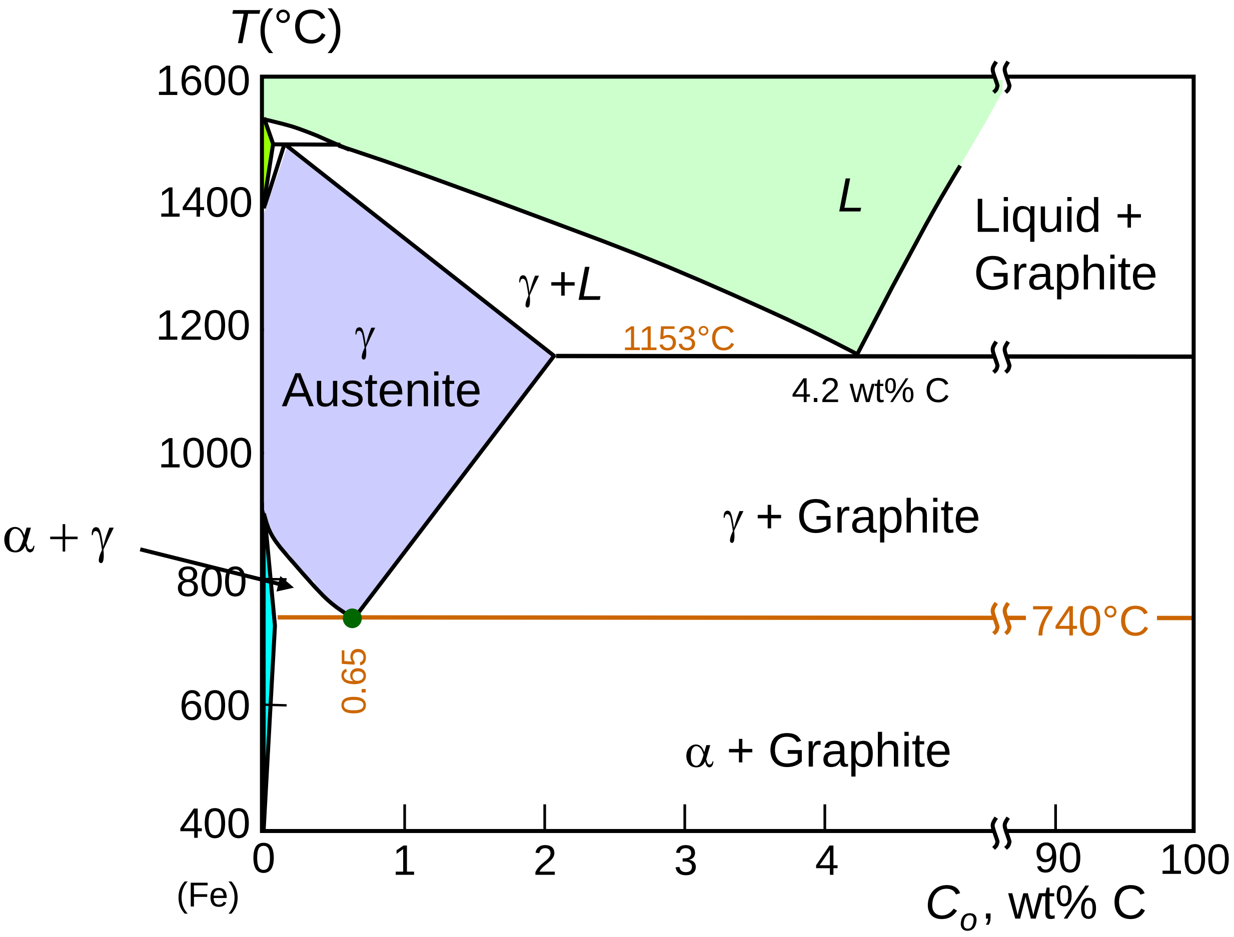
$$Fe_3C \rightarrow 3\ Fe\ (\alpha) + C\ (\text{graphite})$$

  - generally a slow process

Fe-C True Equilibrium Diagram

Graphite formation promoted by

- Si > 1 wt%
- slow cooling



Adapted from Fig. 11.2,*Callister 7e*. (Fig. 11.2 adapted from *Binary Alloy Phase Diagrams*, 2nd ed., Vol. 1, T.B. Massalski (Ed.-in-Chief), ASM International, Materials Park, OH, 1990.)

Types of Cast Iron

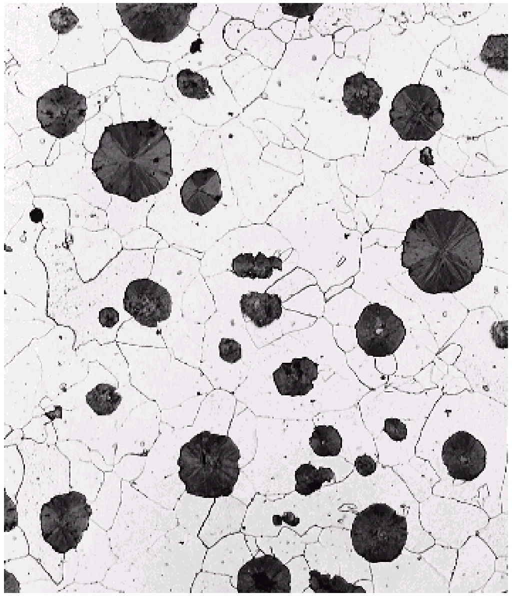
Gray iron

- graphite flakes
- weak & brittle under tension
- stronger under compression
- excellent vibrational dampening
- wear resistant

Adapted from Fig. 11.3(a) & (b), *Callister 7e*.

Ductile iron

- add Mg or Ce
- graphite in nodules not flakes
- matrix often pearlite - better ductility



Types of Cast Iron

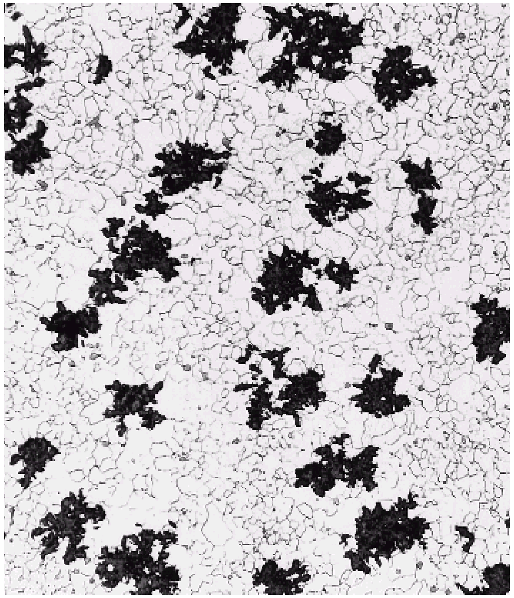
White iron

- <1wt% Si so harder but brittle
- more cementite

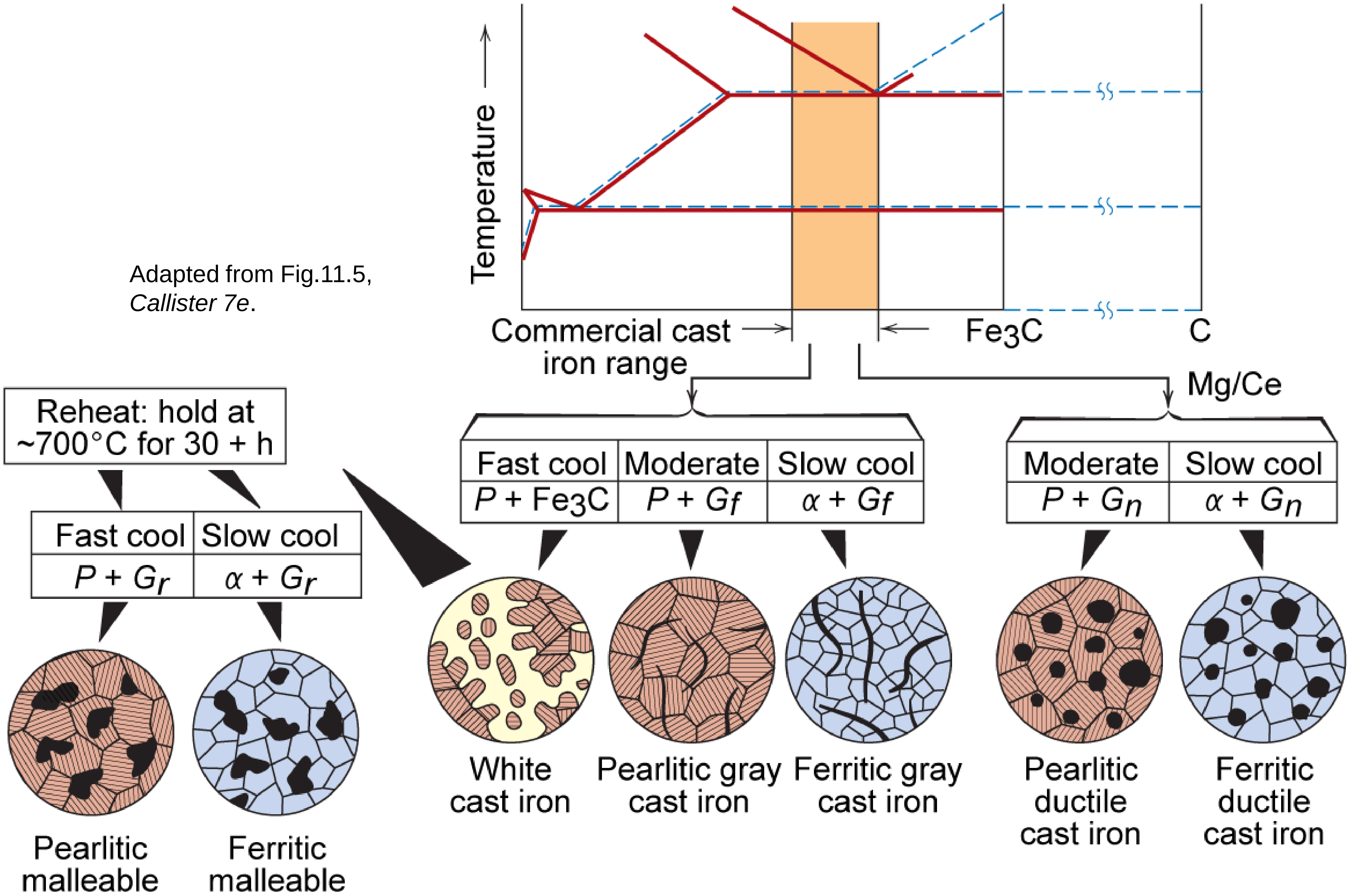
Adapted from Fig. 11.3(c) & (d), *Callister 7e*.

Malleable iron

- heat treat at 800-900ºC
- graphite in rosettes
- more ductile



Production of Cast Iron



Adapted from Fig.11.5, *Callister 7e*.

Limitations of Ferrous Alloys

1) Relatively high density
2) Relatively low conductivity
3) Poor corrosion resistance

Nonferrous Alloys

NonFerrous Alloys

- Cu Alloys

Brass: Zn is subst. impurity (costume jewelry, coins, corrosion resistant)

Bronze : Sn, Al, Si, Ni are subst. impurity (bushings, landing gear)

Cu-Be: precip. hardened for strength

- Al Alloys

-lower ρ: 2.7g/cm^3

-Cu, Mg, Si, Mn, Zn additions

-solid sol. or precip. strengthened (struct. aircraft parts & packaging)

- Mg Alloys

-very low ρ: 1.7g/cm^3

-ignites easily

-aircraft, missiles

- Ti Alloys

-lower ρ: 4.5g/cm^3 vs 7.9 for steel

-reactive at high *T*

-space applic.

- Noble metals

-Ag, Au, Pt

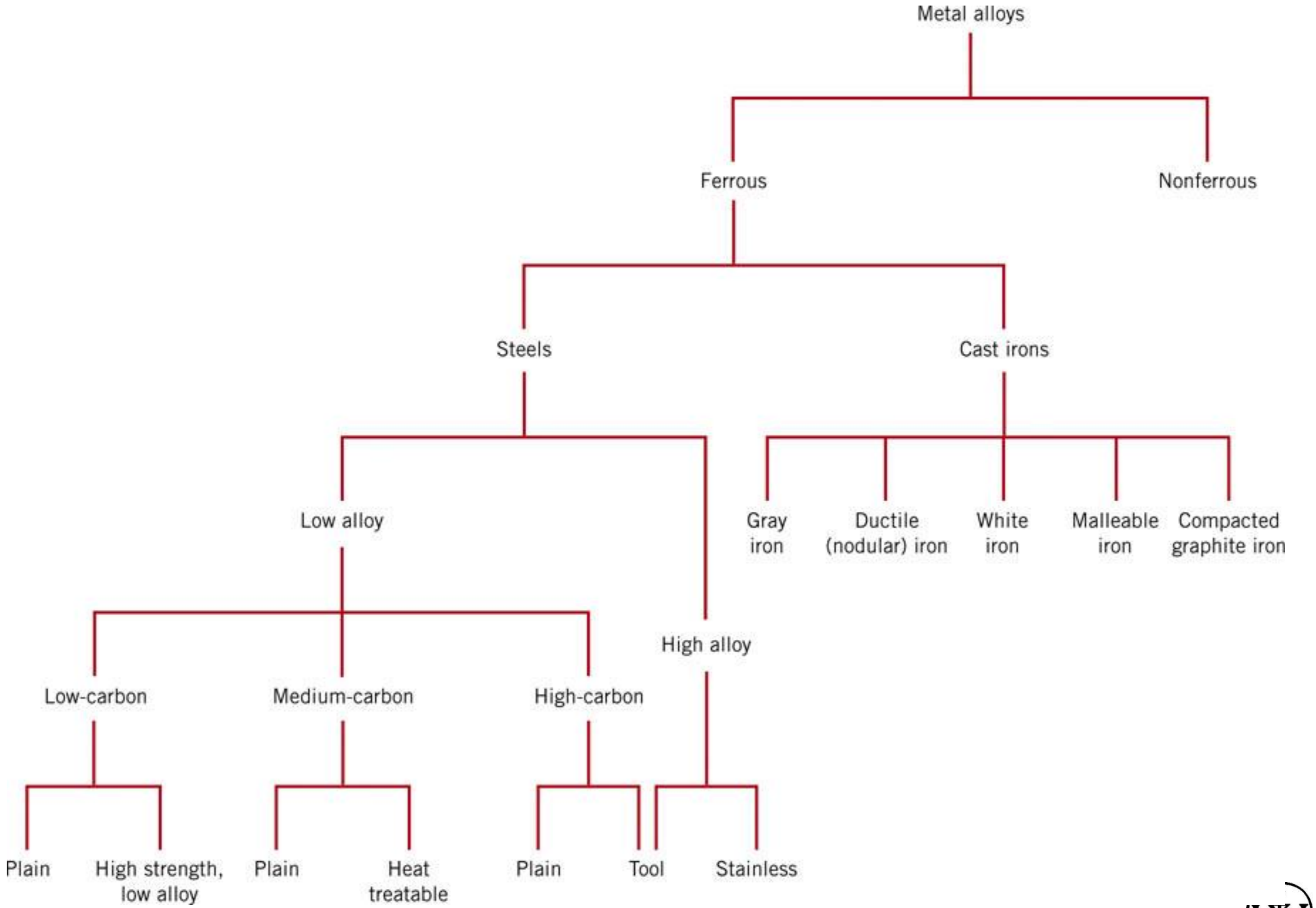
-oxid./corr. resistant

- Refractory metals

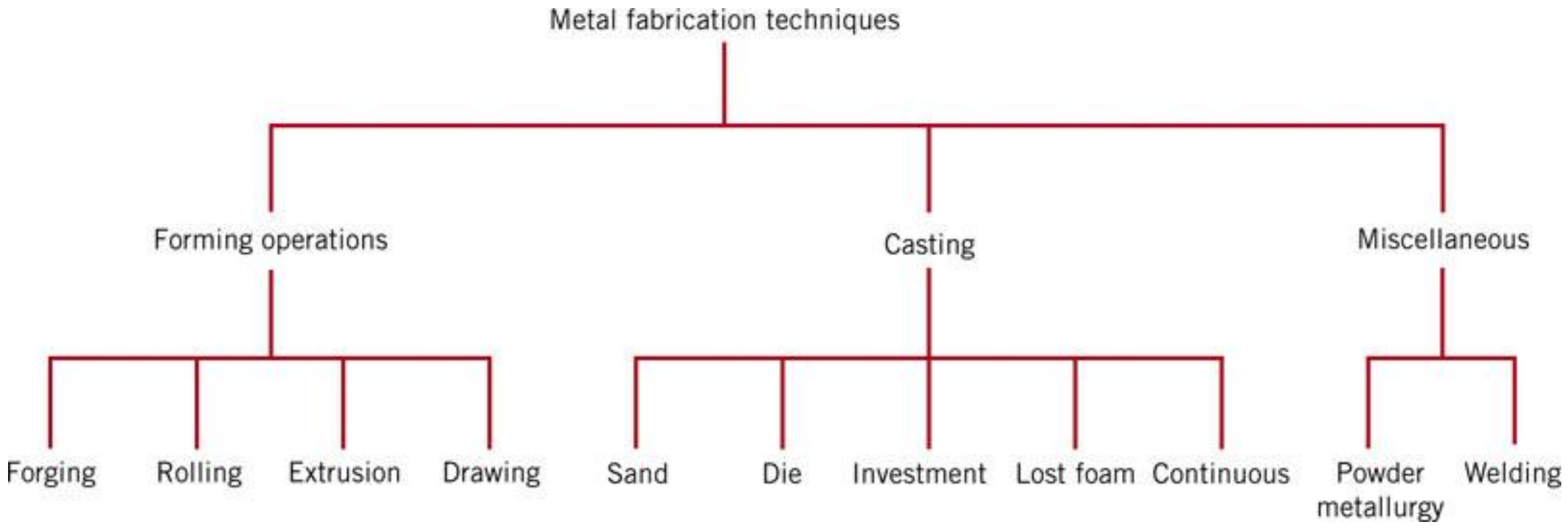
-high melting *T*

-Nb, Mo, W, Ta

Based on discussion and data provided in Section 11.3, *Callister 7e*.



- Metal alloys
  - Ferrous
    - Steels
      - Low alloy
        - Low-carbon
          - Plain
          - High strength, low alloy
        - Medium-carbon
          - Plain
          - Heat treatable
        - High-carbon
          - Plain
          - Tool
      - High alloy
        - Tool
        - Stainless
    - Cast irons
      - Gray iron
      - Ductile (nodular) iron
      - White iron
      - Malleable iron
      - Compacted graphite iron
  - Nonferrous


Metal fabrication techniques
Forming operations
Casting
Miscellaneous
Forging
Rolling
Extrusion
Drawing
Sand
Die
Investment
Lost foam
Continuous
Powder metallurgy
Welding

Metal Fabrication

- How do we fabricate metals?
  - Blacksmith - hammer (forged)
  - Molding - cast

- Forming Operations
  - Rough stock formed to final shape

<u>The shape of a metal piece is changed by plastic deformation</u>

Hot working vs. Cold working

Hot working

- *T* high enough for recrystallization
- Larger deformations possible
- Deformation energy are less
- some surface oxidation.

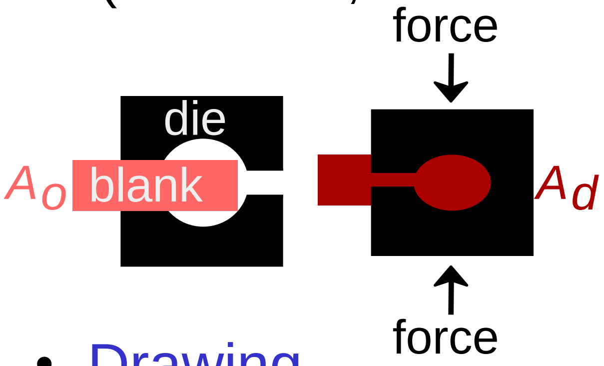
Cold working

- well below T_m
- the strain hardens
- smaller deformations
- high quality surface finish

Metal Fabrication Methods - I

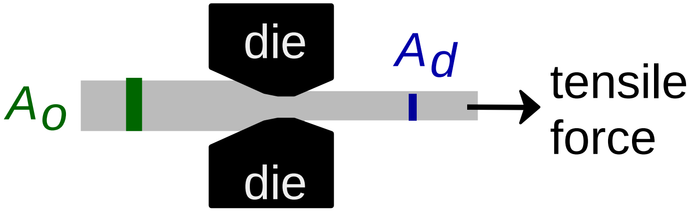
FORMING CASTING JOINING

- Forging (Hammering; Stamping)
  (wrenches, crankshafts)



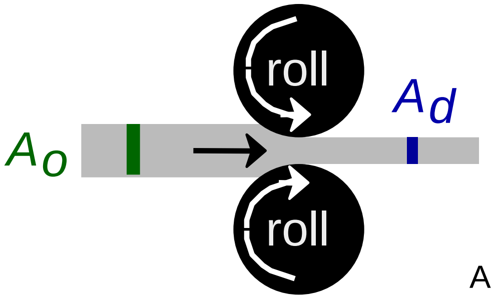
often at elev. *T*

- Drawing
  (rods, wire, tubing)



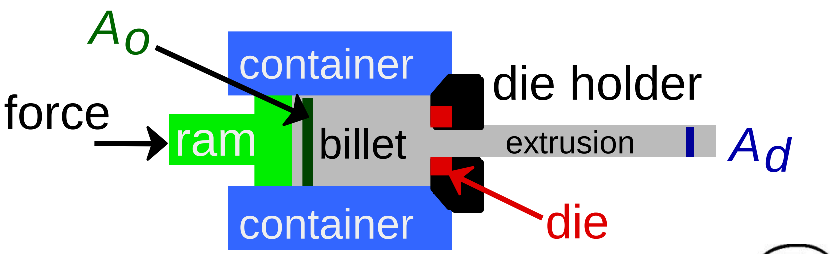
die must be well lubricated & clean

- Rolling (Hot or Cold Rolling)
  (I-beams, rails, sheet & plate)



Adapted from Fig. 11.8, *Callister 7e*.

- Extrusion
  (rods, tubing)



ductile metals, e.g. Cu, Al (hot)

Metal Fabrication Methods - II

FORMING CASTING JOINING

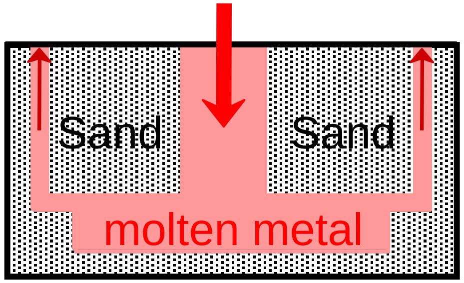
- Casting- mold is filled with metal
  - metal melted in furnace, perhaps alloying elements added. Then cast in a mold
  - most common, cheapest method
  - gives good production of shapes: large or complicated shapes
  - weaker products, internal defects
  - good option for brittle materials

Metal Fabrication Methods - II

FORMING CASTING JOINING

- Sand Casting

(large parts, e.g.,auto engine blocks,fire hydrants, large pipe fittings)



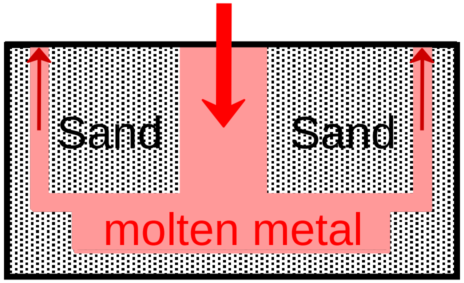
- trying to hold something that is hot
- what will withstand >1600ºC?
- cheap - easy to mold => sand!!!
- pack sand around form (pattern) of desired shape

Metal Fabrication Methods - II

FORMING CASTING JOINING

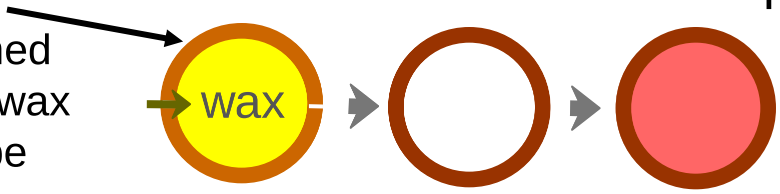
- Sand Casting

  (large parts, e.g., auto engine blocks)



- Investment Casting

  (low volume, complex shapes e.g., jewelry, turbine blades)


plaster die formed around wax prototype

Investment Casting (lost-wax)

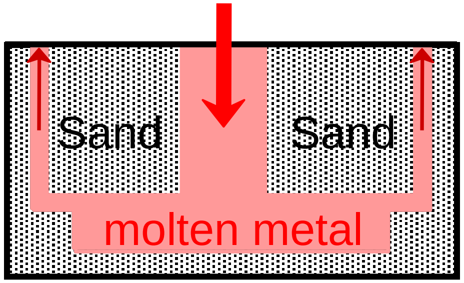
- pattern is made from paraffin or wax.
- mold made by encasing in plaster of paris
- melt the wax & the hollow mold is left
- pour in metal

Metal Fabrication Methods - II

FORMING | **CASTING** | JOINING

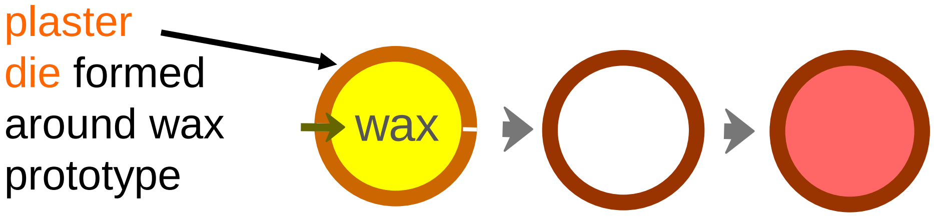
- Sand Casting

  (large parts, e.g., auto engine blocks)



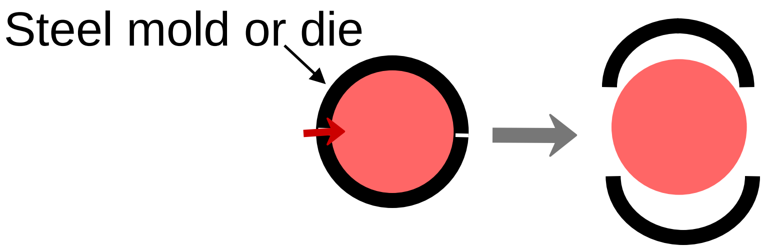
- Investment Casting

  (low volume, complex shapes e.g., jewelry, turbine blades)



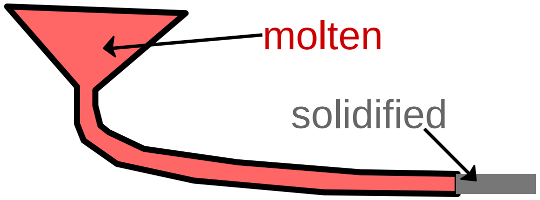
- Die Casting

  (high volume, low T alloys)



- Continuous Casting

  (simple slab shapes)

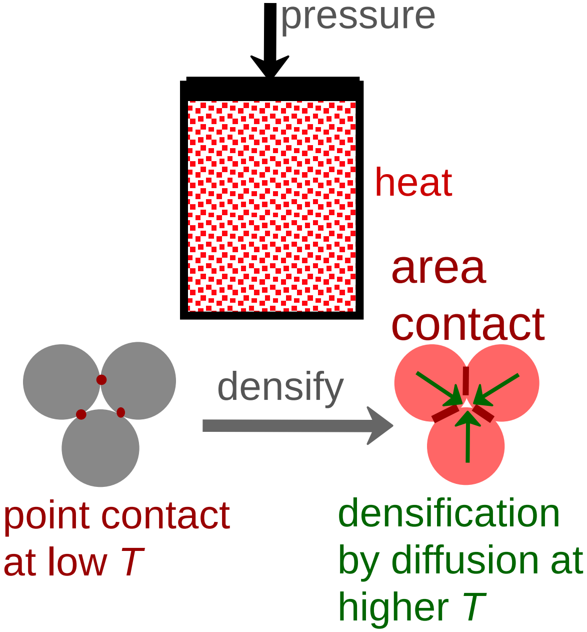


Metal Fabrication Methods - III

FORMING CASTING JOINING

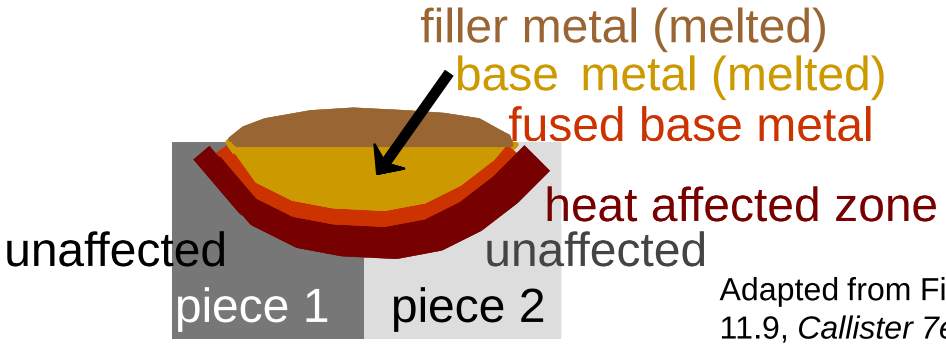
- Powder Metallurgy

(materials w/low ductility or high melting temperature)



- Welding

(when one large part is impractical)



Adapted from Fig. 11.9, *Callister 7e*. (Fig. 11.9 from *Iron Castings Handbook*, C.F. Walton and T.J. Opar (Ed.), 1981.)

- Heat affected zone:

(region in which the microstructure has been changed).

Gas and arc welding, or Laser beam welding

Thermal Processing of Metals

Annealing: Heat to T_{anneal}, then cool slowly.

Types of Annealing

- **Stress Relief**: Reduce stress caused by:
  - -plastic deformation
  - -nonuniform cooling
  - -phase transform.

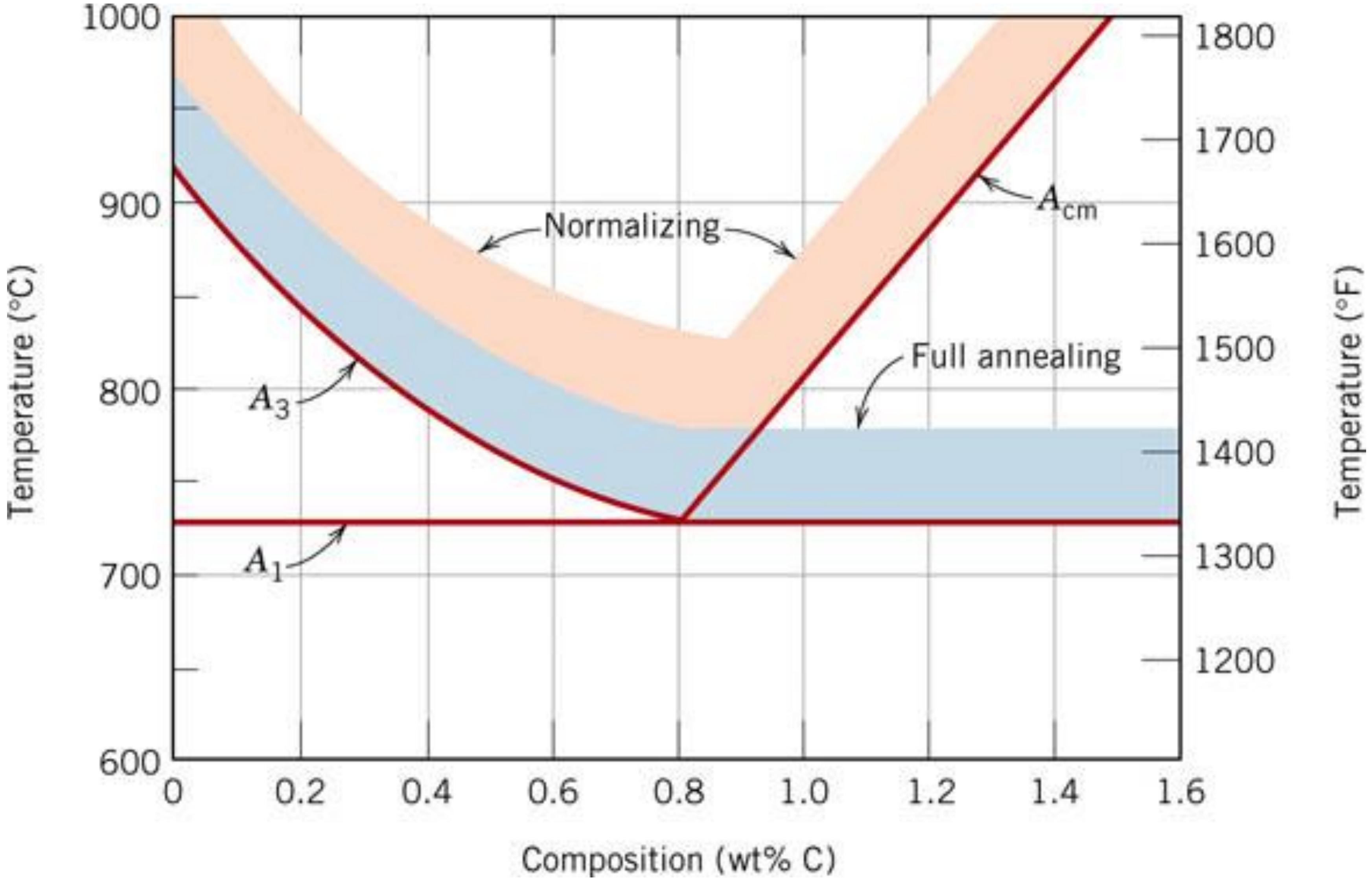
- **Spheroidize** (steels): Make very soft steels for good machining. Heat just below T_E & hold for 15-25 h.

- **Full Anneal** (steels): Make soft steels for good forming by heating to get γ, then cool in furnace to get coarse P.

- **Process Anneal**: Negate effect of cold working by (recovery/ recrystallization)

- **Normalize** (steels): Deform steel with <u>large</u> grains, then normalize to make grains small.

Based on discussion in Section 11.7, *Callister 7e*.

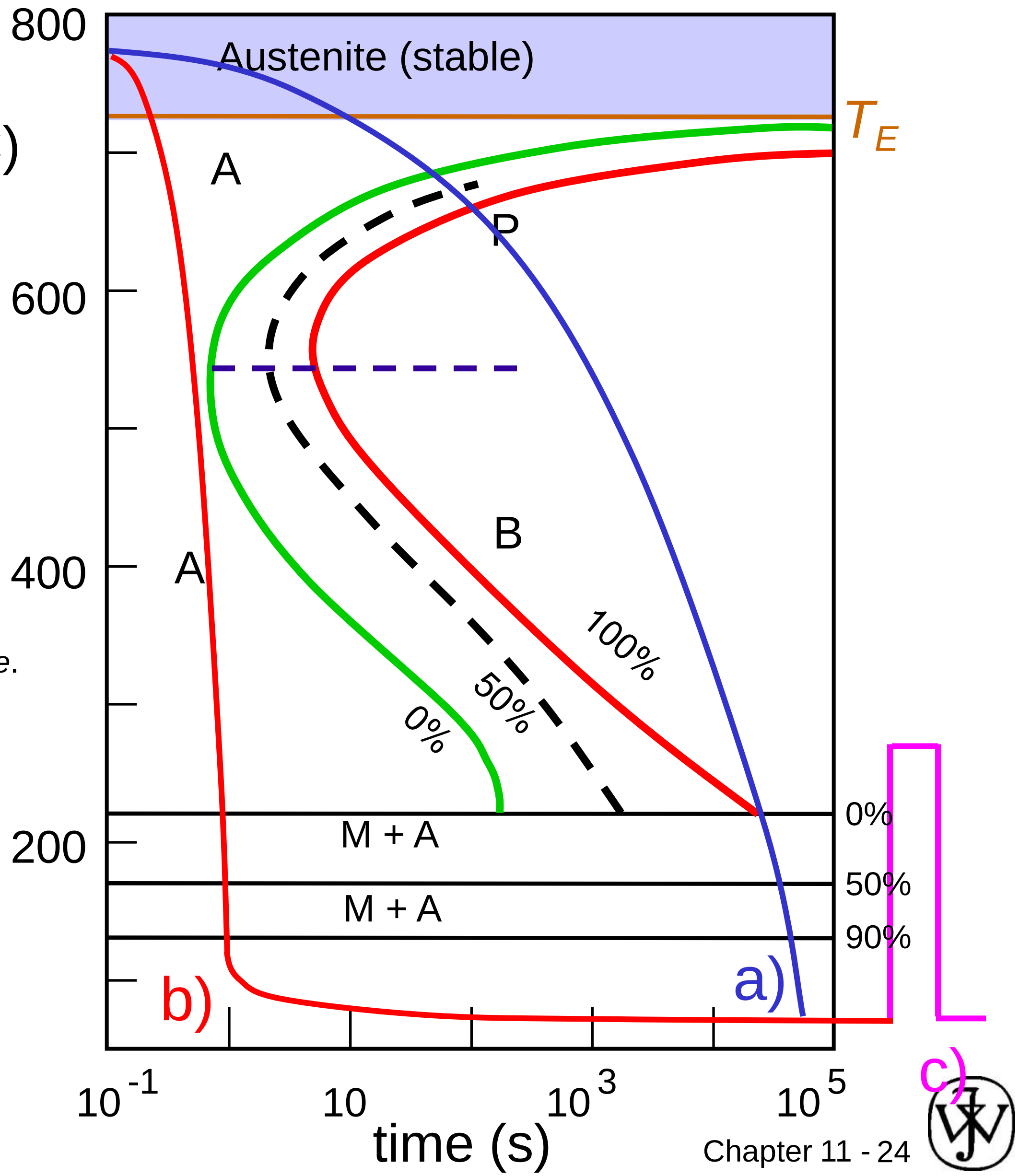

1000
900
800
700
600
1800
1700
1600
1500
1400
1300
1200
Temperature (°C)
Temperature (°F)
Normalizing
Full annealing
A_{cm}
A_3
A_1
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
Composition (wt% C)

Heat Treatments

a) Annealing

b) Quenching

c) Tempered Martensite



Adapted from Fig. 10.22, *Callister 7e*.

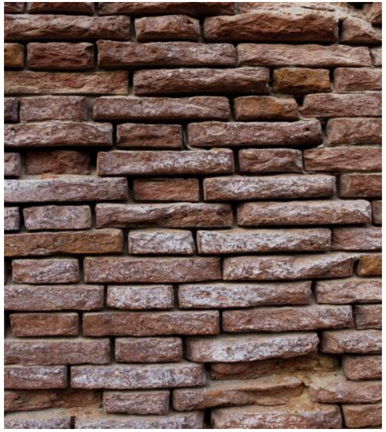
Summary-metal alloy

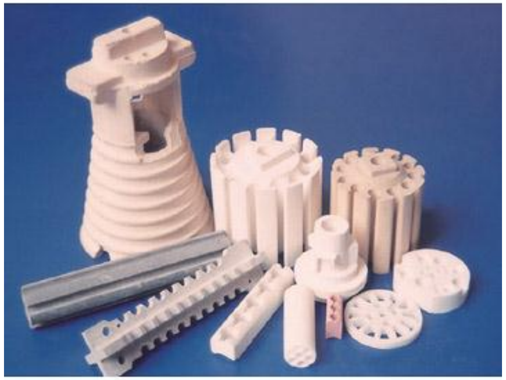
- Steels: increase *TS*, Hardness (and cost) by adding
  --C (low alloy steels)
  --Cr, V, Ni, Mo, W (high alloy steels)
  --ductility usually decreases w/additions.
- Non-ferrous:
  --Cu, Al, Ti, Mg, Refractory, and noble metals.
- Fabrication techniques:
  --forming, casting, joining.
- Thermal treatment

Ceramics

Traditional ceramics: china, porcelain, bricks, tiles, glass, etc.

Quaternary clay in Estonia.



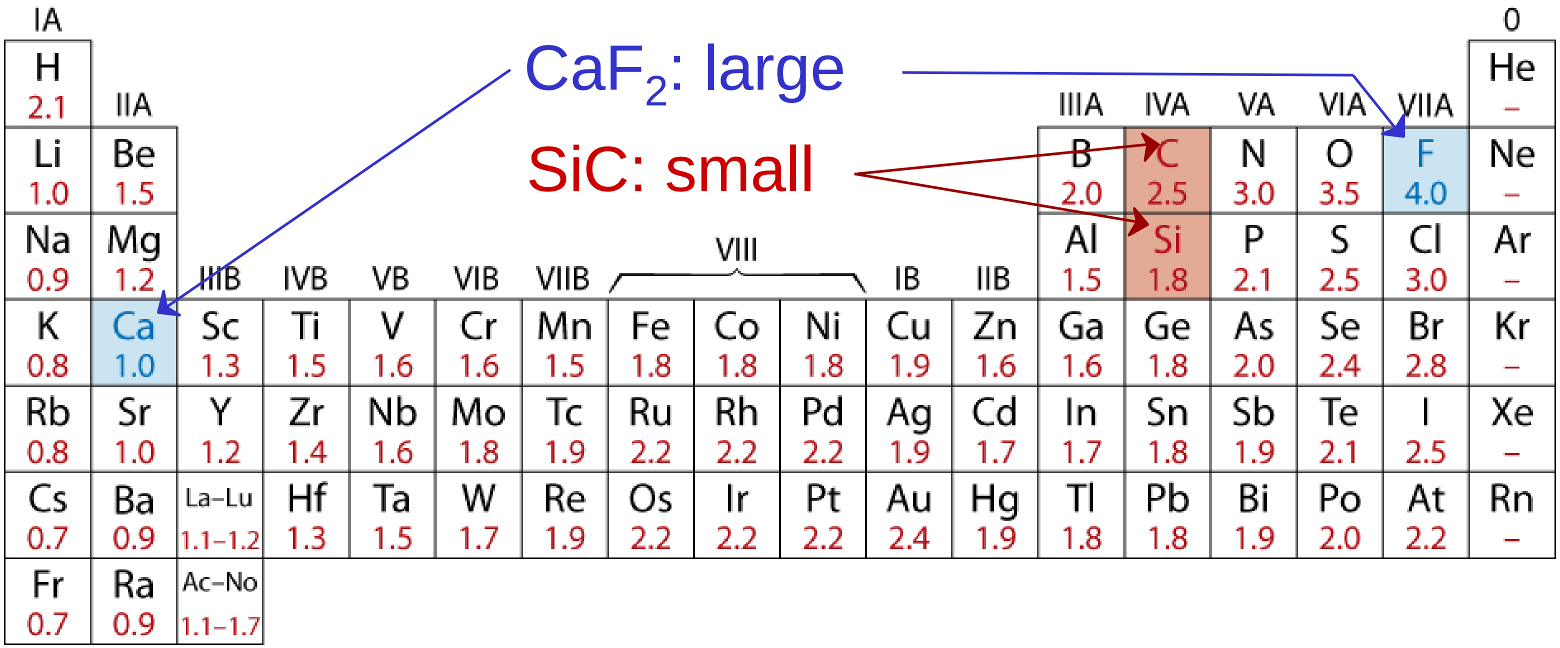


Ceramic Bonding

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

$$\% \text{ ionic character} = \{1 - \exp[-(0.25)(X_A - X_B)^2]\} \times 100$$

- Large vs small ionic bond character:



CaF_2: large

SiC: small

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
H 2.1																	He –
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne –
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar –
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr –
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe –
Cs 0.7	Ba 0.9	La–Lu 1.1–1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn –
Fr 0.7	Ra 0.9	Ac–No 1.1–1.7															

Adapted from Fig. 2.7, *Callister 7e.*

Most ceramics are compounds between metallic and nonmetallic elements

Ionic Crystals

Note: larger anion radius

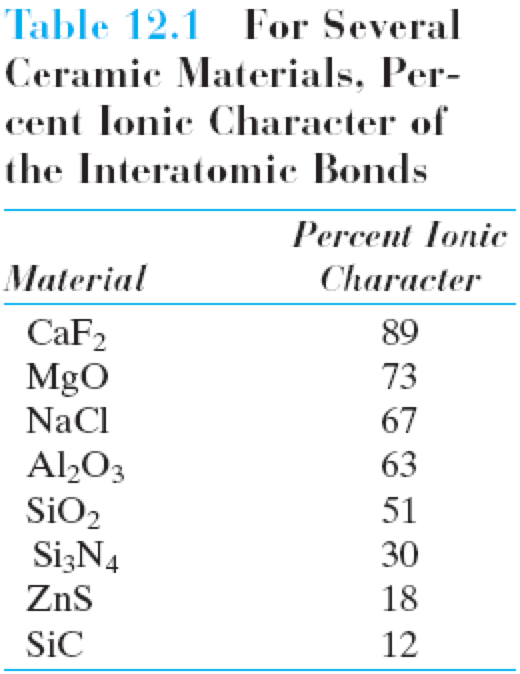


Table 12.1 For Several Ceramic Materials, Percent Ionic Character of the Interatomic Bonds

Material	Percent Ionic Character	Cation Radius (nm)	Anion Radius (nm)
CaF_2	89	0.100	0.133
MgO	73	0.072	0.14
$NaCl$	67	0.102	0.182
Al_2O_3	63	0.053	0.140
SiO_2	51	0.040	0.140
Si_3N_4	30		
ZnS	18		
SiC	12		

Cations: metallic ions, positively charged
Anions: nonmetallic ions, negatively charged

Crystal structure
- The magnitude of the electrical charge on each of the component ions
- The relative sizes of the cations and anions

Most ionic crystals can be considered as close-packed structure of anions with cations in the interstitial sites.

Ceramic Crystal Structures

Oxide structures

- oxygen anions much larger than metal cations
- close packed oxygen in a lattice (usually FCC)
- cations in the holes of the oxygen lattice

Site Selection

Which sites will cations occupy?

1. Size of sites
   - does the cation fit in the site

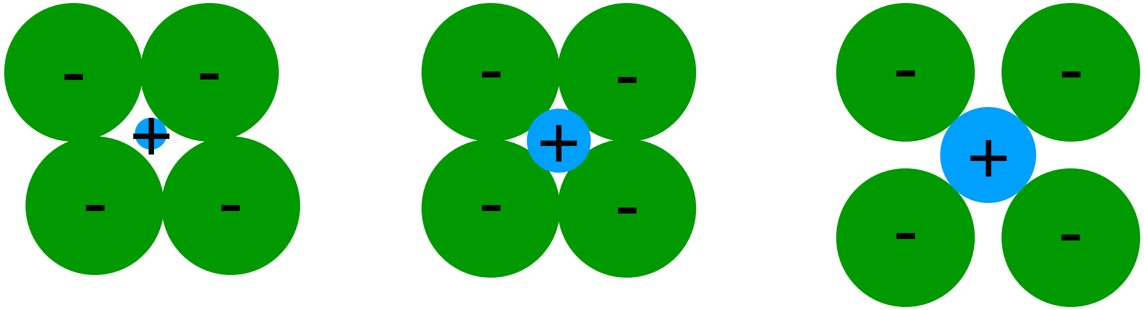
for each cation prefers to have as many nearest-neighbor anion; the anions also desire a maximum number of cation nearest neighbors.

2. Stoichiometry
   - if all of one type of site is full, the remainder have to go into other types of sites.
3. Bond Hybridization

Ionic Bonding & Structure

1. Size - Stable structures:

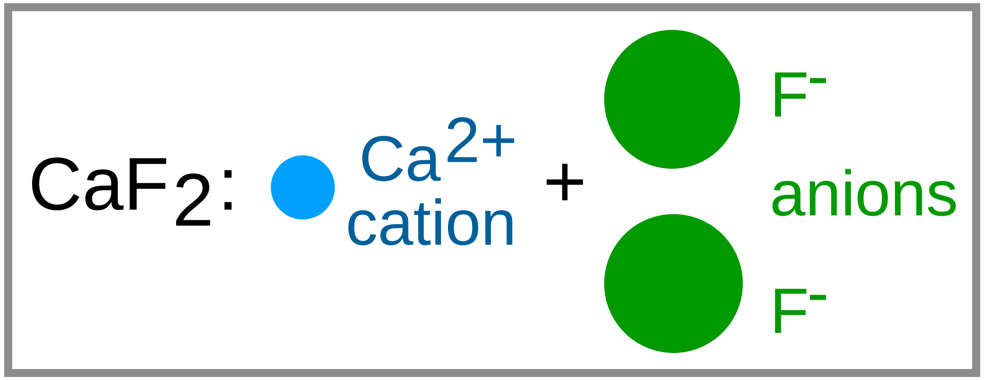
--maximize the # of nearest oppositely charged neighbors.



unstable stable stable

Adapted from Fig. 12.1, *Callister 7e.*

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



CaF_2: Ca^{2+} cation + F^- F^- anions

--General form: A_mX_p

m, p determined by charge neutrality

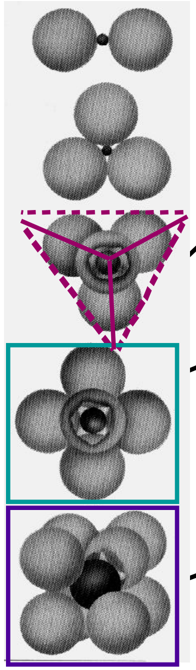
Coordination # and Ionic Radii

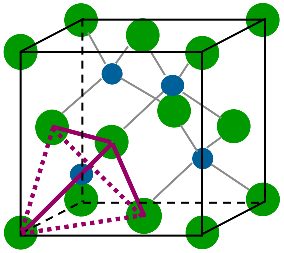
- Coordination # increases with $\frac{r_{cation}}{r_{anion}}$

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

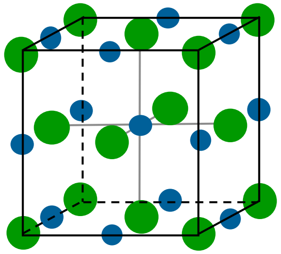
Adapted from Table 12.2, *Callister 7e.*





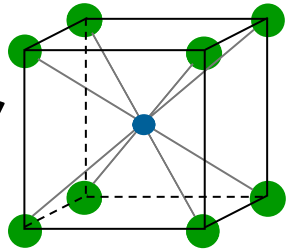
ZnS (zincblende)

Adapted from Fig. 12.4, *Callister 7e.*



NaCl (sodium chloride)

Adapted from Fig. 12.2, *Callister 7e.*



CsCl (cesium chloride)

Adapted from Fig. 12.3, *Callister 7e.*

Cation-anion stable configuration

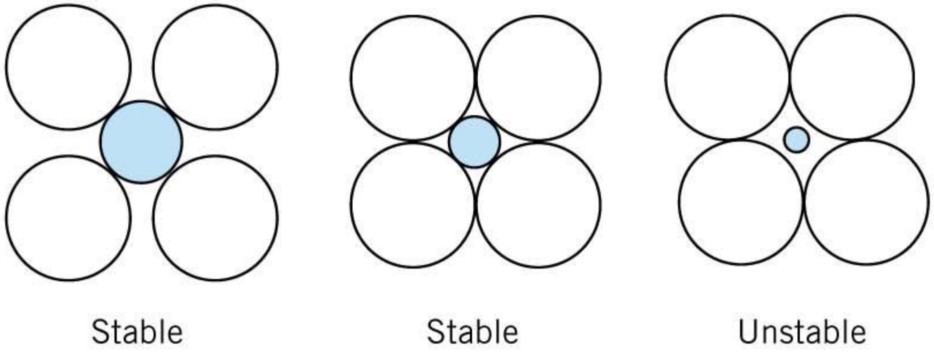
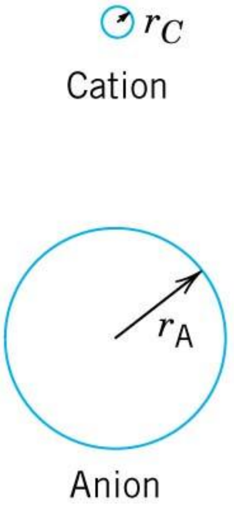
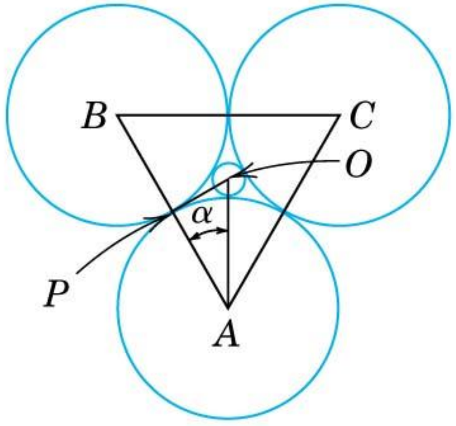


FIGURE 12.1 Stable and unstable anion–cation coordination configurations. Open circles represent anions; colored circles denote cations.

e.g. computation of minimum $\frac{r_C}{r_A}$ for a 3-coordinate

when $\cos\alpha = \frac{r_A}{r_A + r_C}$





Rewrite as

$$\frac{r_C}{r_A} = \frac{1}{\cos\alpha} - 1$$

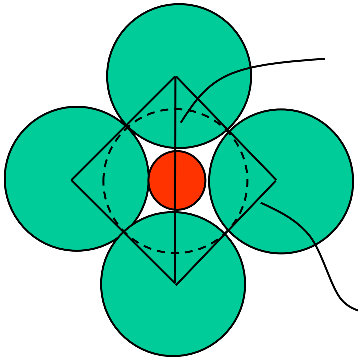
With α = 30°

Minimum ratio for 3-coordinate →

$$\frac{r_C}{r_A} = 0.155$$

Cation Site Size

- Determine minimum r_{cation}/r_{anion} for O_H site (C.N. = 6)



$$2r_{anion} + 2r_{cation} = \sqrt{2}a$$

$$a = 2r_{anion}$$

$$2r_{anion} + 2r_{cation} = 2\sqrt{2}r_{anion}$$

$$r_{anion} + r_{cation} = \sqrt{2}r_{anion} \qquad r_{cation} = (\sqrt{2} - 1)r_{anion}$$

$$\boxed{\frac{r_{cation}}{r_{anion}} = 0.414}$$

Site Selection II

2. Stoichiometry
    - If all of one type of site is full, the remainder have to go into other types of sites.

Ex: FCC unit cell has 4 O_H and 8 T_D sites.

If for a specific ceramic each unit cell has 6 cations and the cations prefer O_H sites

4 in O_H

2 in T_D

Site Selection III

3. Bond Hybridization – significant covalent bonding
   - the hybrid orbitals can have impact if significant covalent bond character present
   - For example in SiC
     - $X_{Si} = 1.8$ and $X_C = 2.5$

$$\%\, ionic\, \text{character} = 100\{1\text{-}\exp[-0.25(X_{Si} - X_C)^2]\} = 11.5\%$$

- ca. 89% covalent bonding
- both Si and C prefer *sp*^{3} hybridization
- Therefore in SiC get T_D sites

Example: Predicting Structure of FeO

- On the basis of ionic radii, what crystal structure would you predict for FeO?

Cation	Ionic radius (nm)
Al^{3+}	0.053
Fe^{2+}	0.077
Fe^{3+}	0.069
Ca^{2+}	0.100
Anion	
O^{2-}	0.140
Cl^{-}	0.181
F^{-}	0.133

- Answer:

$$\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{0.077}{0.140}$$

$$= 0.550$$

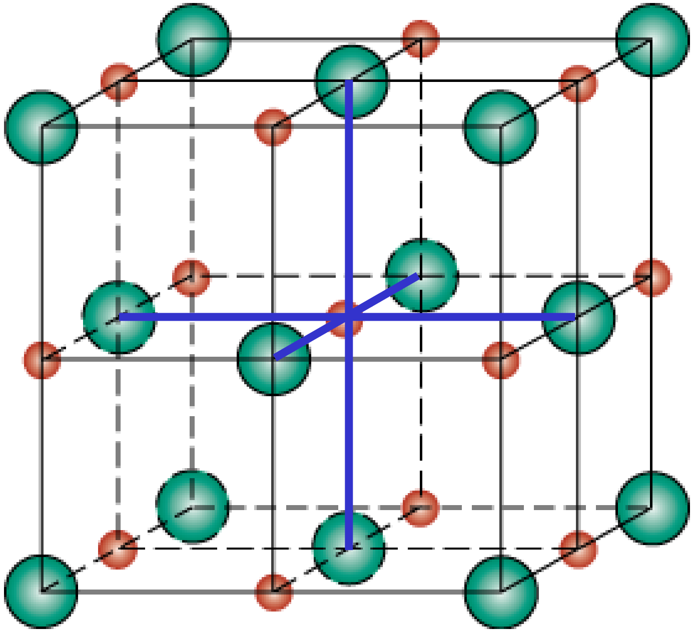
based on this ratio,
--coord # = 6
--structure = NaCl

Data from Table 12.3, *Callister 7e.*

Rock Salt Structure

Same concepts can be applied to ionic solids in general.

Example: NaCl (rock salt) structure



Adapted from Fig. 12.2, *Callister 7e.*

● Na^+ $r_{Na} = 0.102$ nm

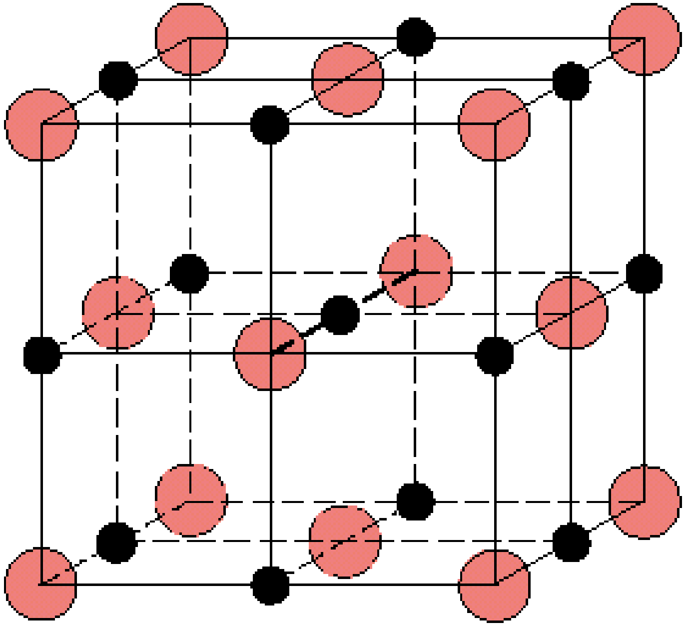
● Cl^- $r_{Cl} = 0.181$ nm

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

$\therefore$ cations prefer O_H sites

MgO and FeO

MgO and FeO also have the NaCl structure



Adapted from Fig. 12.2, *Callister 7e.*

🔴 O^{2-} $r_O = 0.140$ nm

● Mg^{2+} $r_{Mg} = 0.072$ nm

$r_{Mg}/r_O = 0.514$

$\therefore$ cations prefer O_H sites

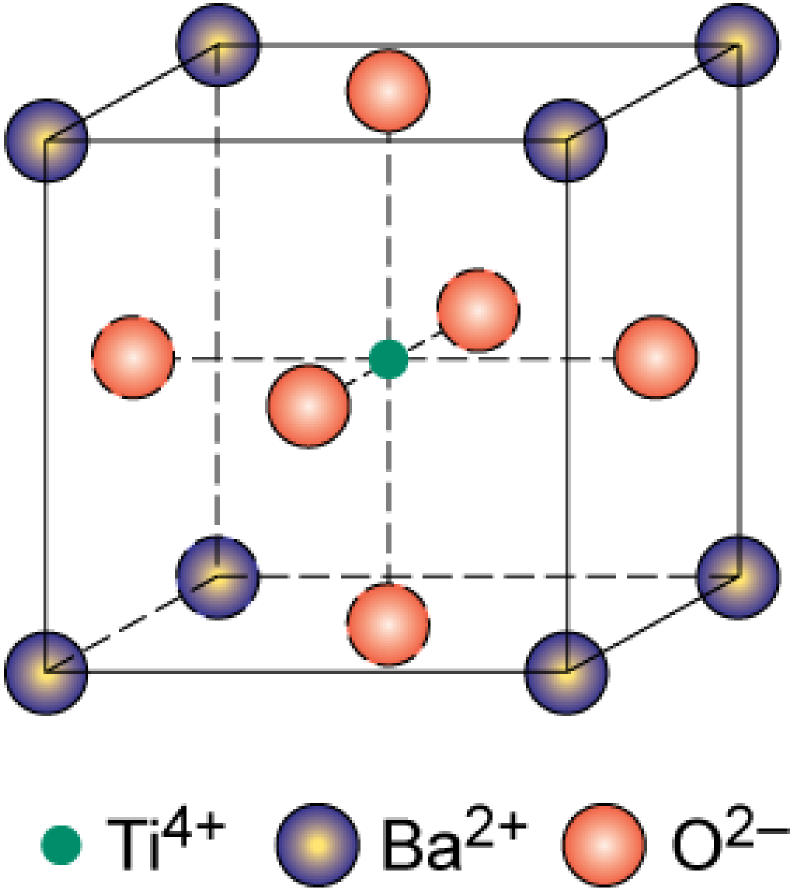
So each oxygen has 6 neighboring Mg^{2+}

ABX_3 Crystal Structures

- Perovskite

Ex: complex oxide

$BaTiO_3$



Adapted from Fig. 12.6, *Callister 7e.*

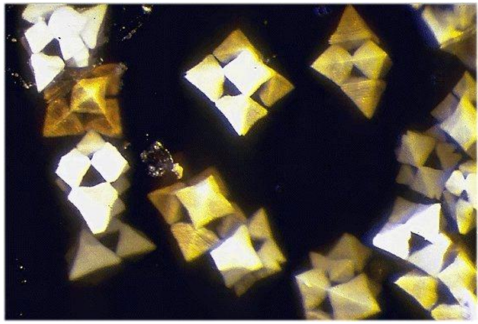
Mechanical Properties

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

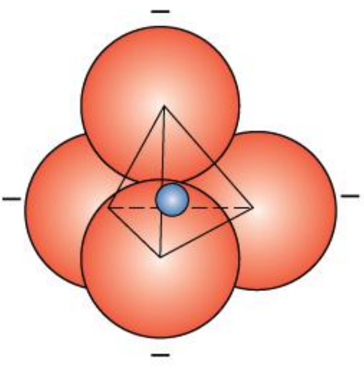
- Consider method of deformation
  - – slippage along slip planes
    - in ionic solids this slippage is very difficult
    - too much energy needed to move one anion past another anion

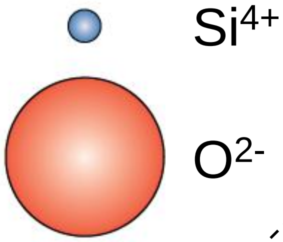
Silicate Ceramics

Most common elements on earth are Si & O

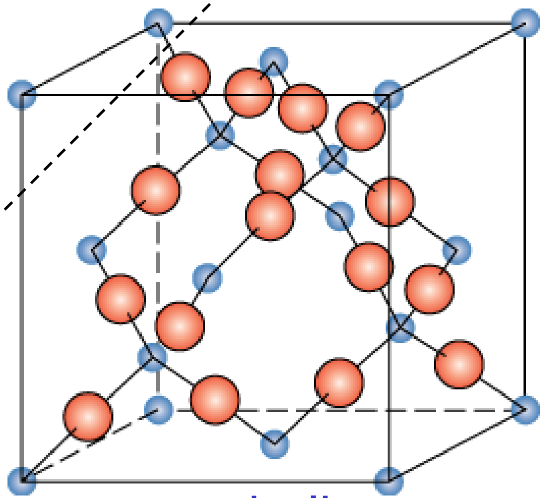


SiO_4^{4-} tetrahedron



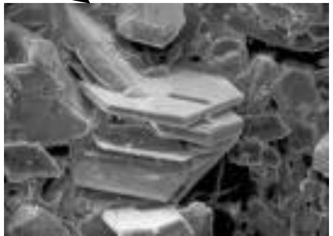


Adapted from Figs. 12.9-10, *Callister 7e.*



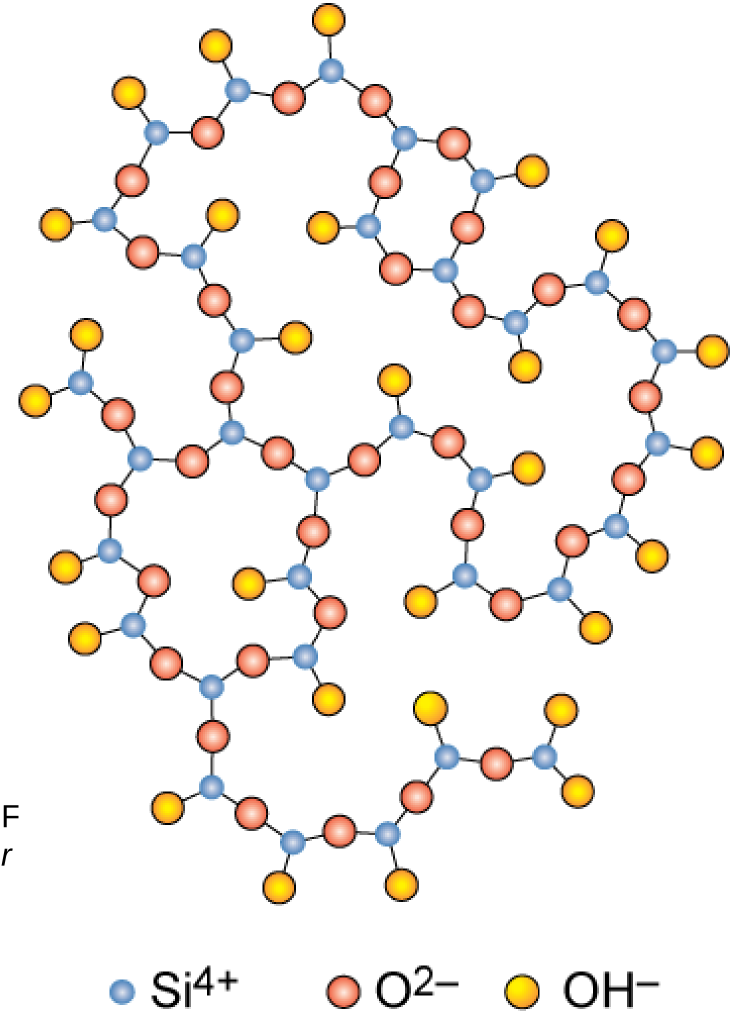
crystobalite

- SiO_2 (silica) polymorphic crystalline structures are quartz, crystobalite, & tridymite
- The strong Si-O bond leads to a strong, high melting material (1710ºC)



Amorphous Silica

- Silica gels - amorphous SiO_2
  - – Si^{4+} and O^{2-} not in well-ordered lattice
  - – Charge balanced by H^+ (to form OH^-) at “dangling” bonds
    - very high surface area > 200 m^2/g
  - – SiO_2 is quite stable, therefore unreactive
    - makes good catalyst support



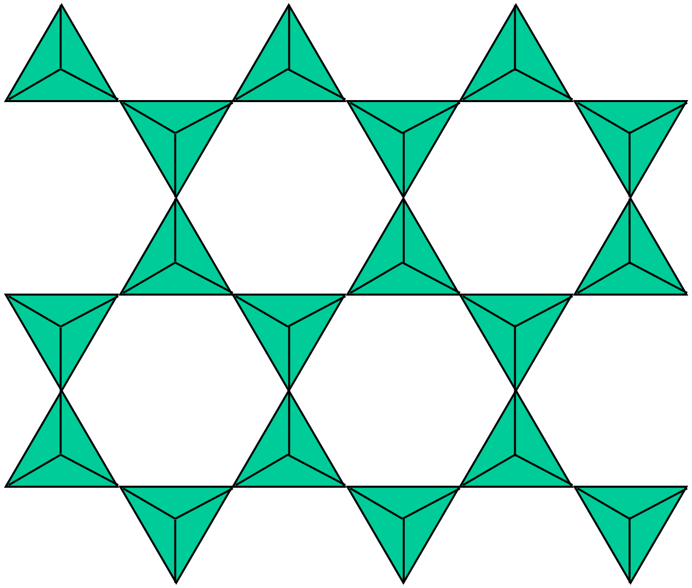
Adapted from F 12.11, *Callister*

Silica Glass

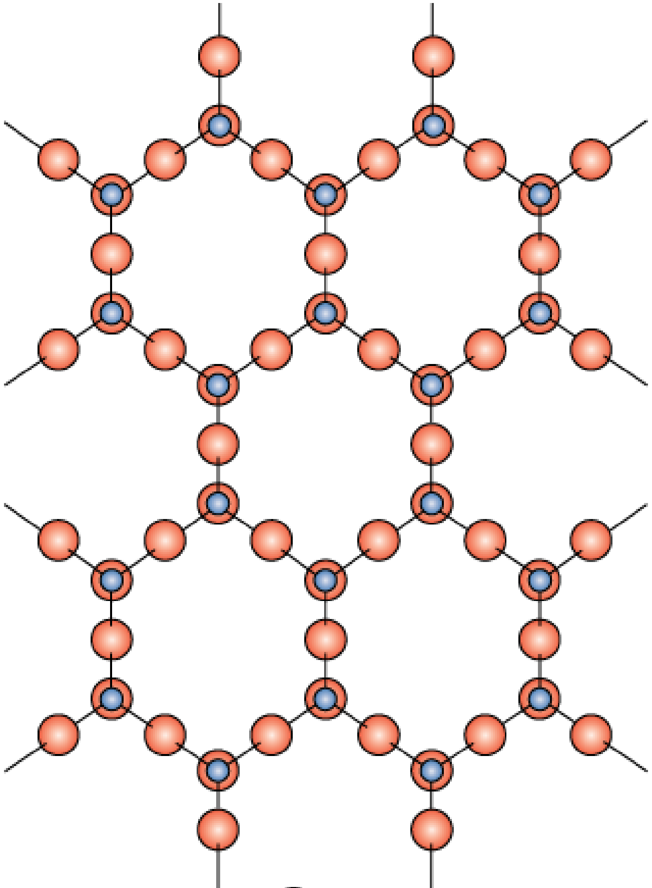
- Dense form of amorphous silica
  - Charge imbalance corrected with “counter cations” such as Na^+
  - Borosilicate glass is the pyrex glass used in labs
    - better temperature stability & less brittle than sodium glass
    - In addition to the quartz, sodium carbonate, and calcium carbonate traditionally used in glassmaking, boron is used in the manufacture of borosilicate glass. Typically, the resulting glass composition is about 70% silica, 10% boric oxide, 8% sodium oxide, 8% potassium oxide, and 1% calcium oxide (lime).
    - Borosilicate glass begins to soften around 821 °C

Layered Silicates

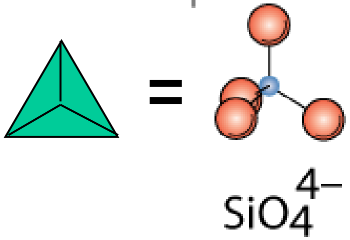
- Layered silicates (clay silicates)
  - SiO_4 tetrahedra connected together to form 2-D plane



- $(Si_2O_5)^{2-}$
- So need cations to balance charge

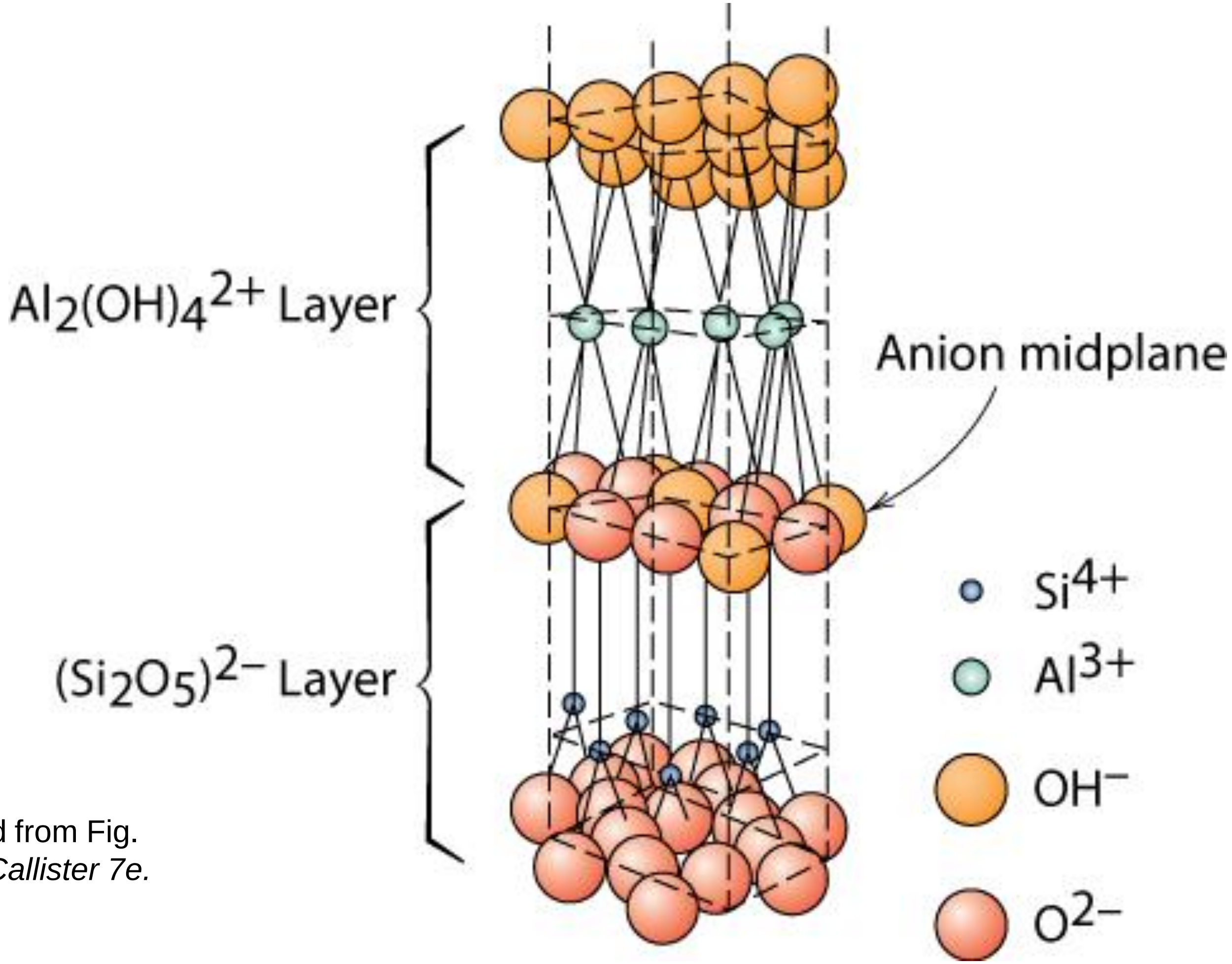


Adapted from Fig. 12.13, *Callister 7e.*



Layered Silicates

- Kaolinite clay alternates $(Si_2O_5)^{2-}$ layer with $Al_2(OH)_4^{2+}$ layer



Adapted from Fig. 12.14, *Callister 7e.*

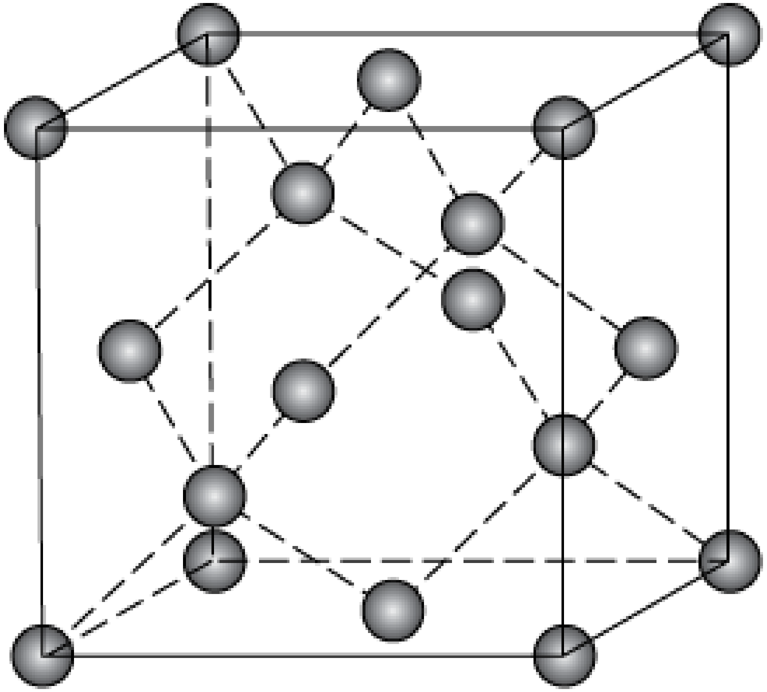
Note: these sheets loosely bound by van der Waal’s forces

Layered Silicates

- Can change the counterions
  - this changes layer spacing
  - the layers also allow absorption of water
- Micas $KAl_3Si_3O_{10}(OH)_2$
  - smooth surface for AFM sample holder
- Bentonite
  - used to seal wells
  - packaged dry
  - swells 2-3 fold in H_2O
  - pump in to seal up well so no polluted ground water seeps in to contaminate the water supply.

Carbon Forms

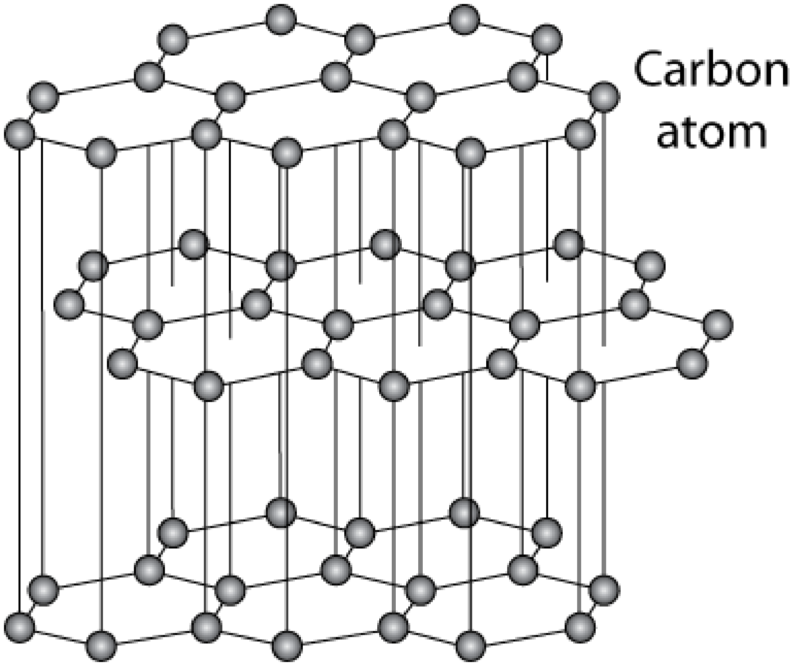
- Carbon black – amorphous – surface area ca. 1000 m^2/g
- Diamond
  - tetrahedral carbon
    - hard – no good slip planes
    - brittle – can cut it
  - large diamonds – jewelry
  - small diamonds
    - often man made - used for cutting tools and polishing
  - diamond films
    - hard surface coat – tools, medical devices, etc.



Adapted from Fig. 12.15, *Callister 7e.*

Carbon Forms - Graphite

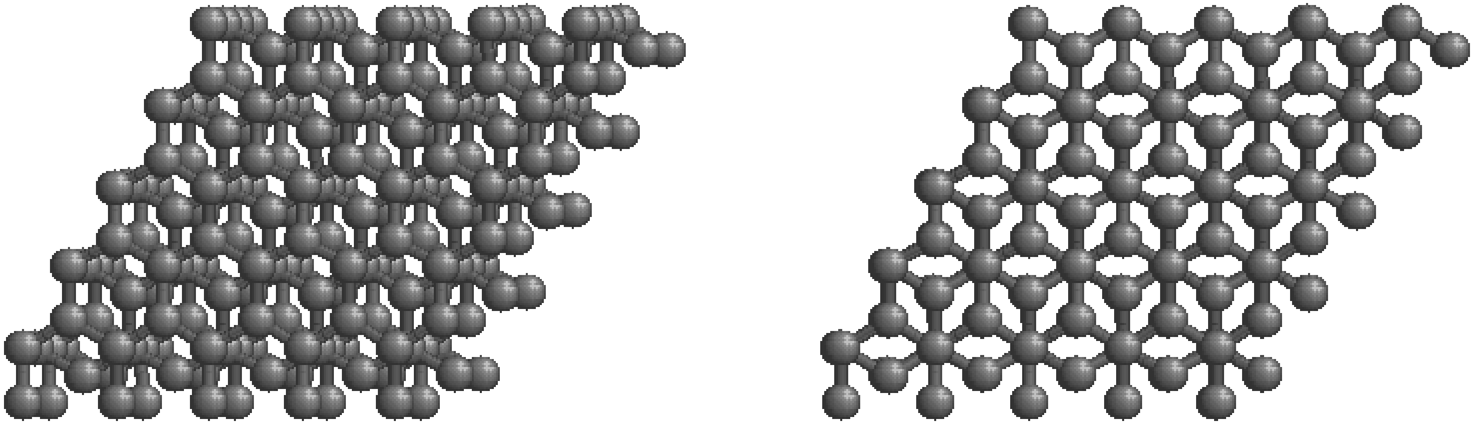
- layer structure – aromatic layers

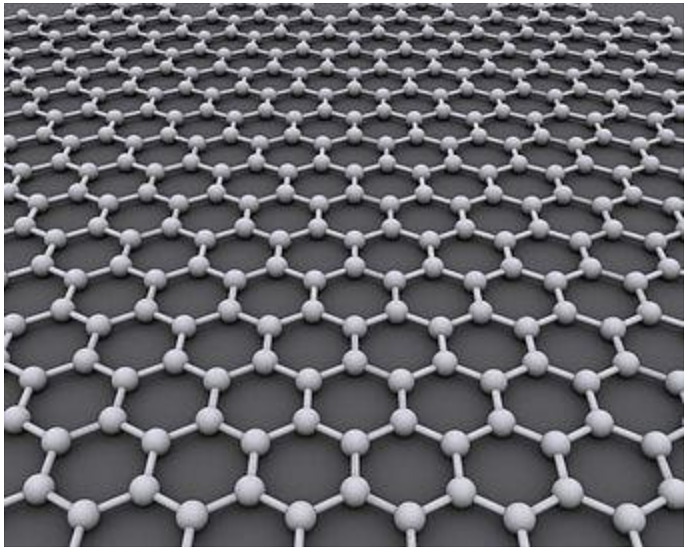


Adapted from Fig. 12.17, *Callister 7e.*

  - weak van der Waal's forces between layers
  - planes slide easily, good lubricant

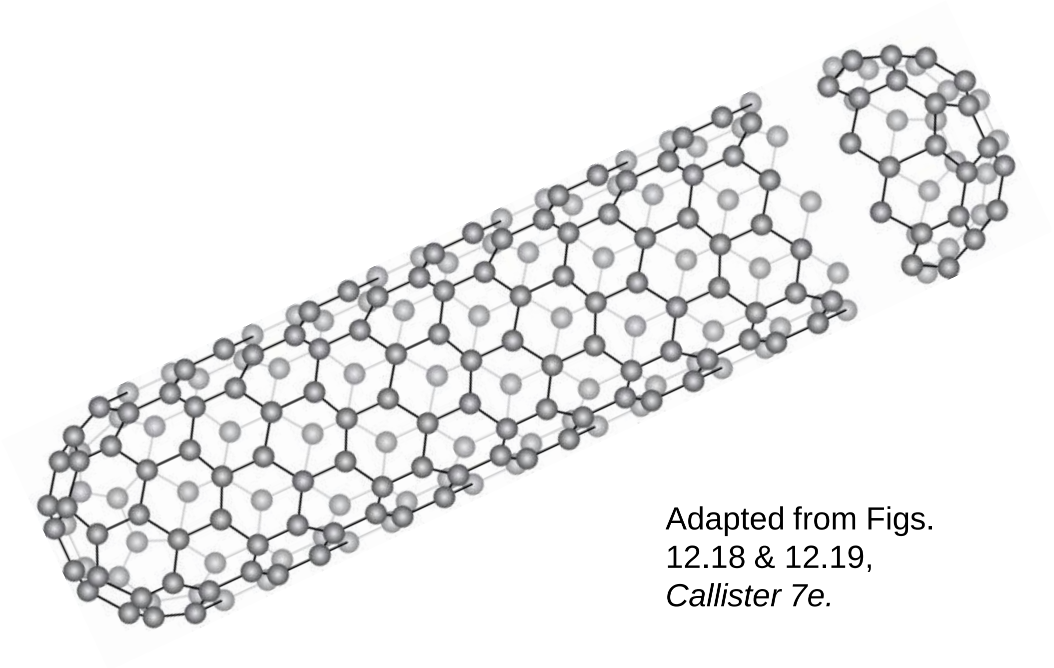
Carbon Forms - Graphite

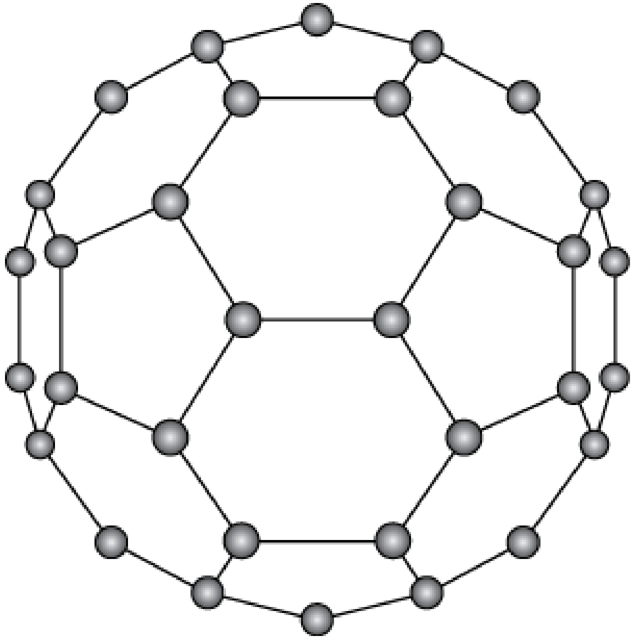




Carbon Forms – Fullerenes and Nanotubes

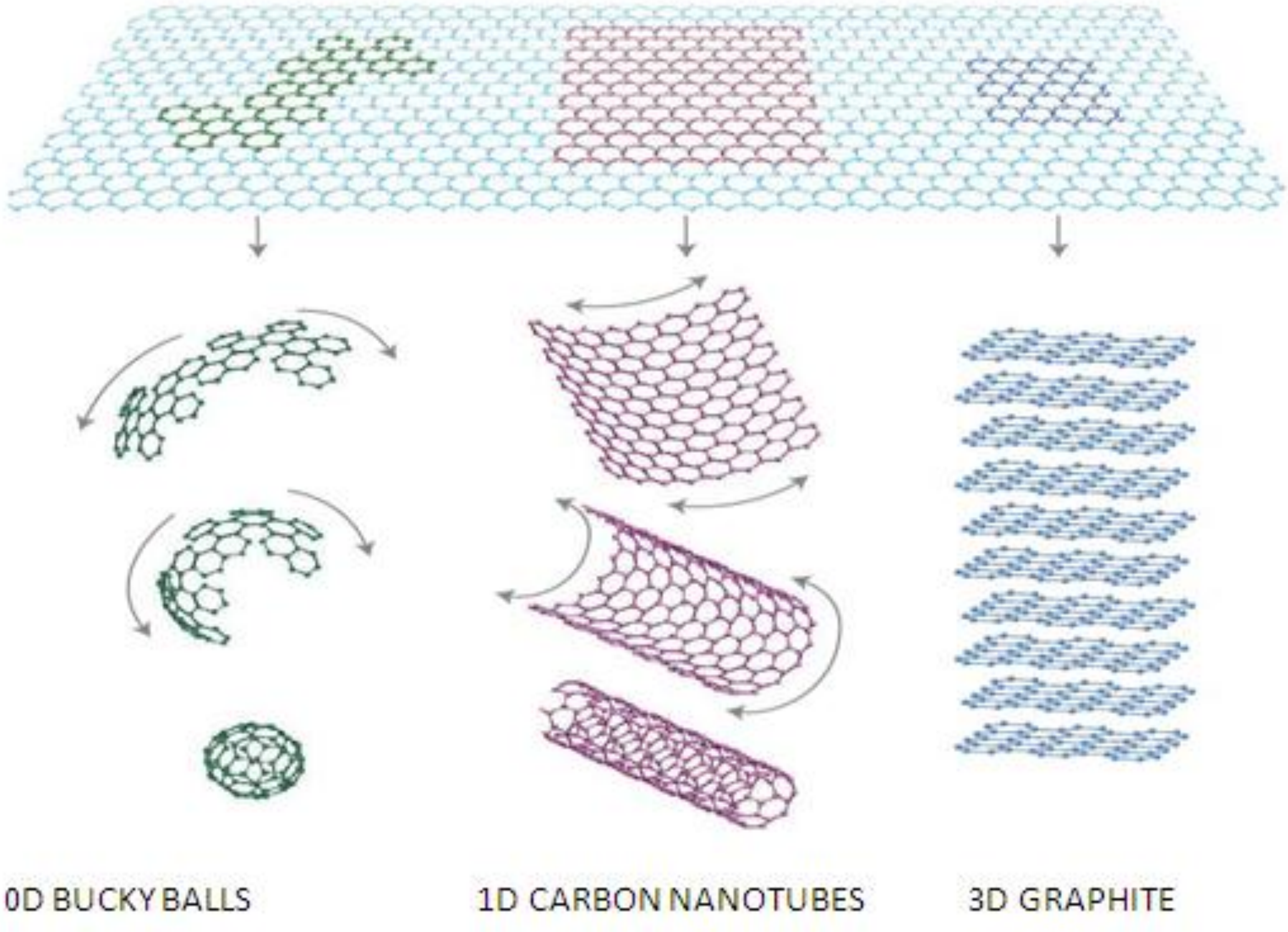
- Fullerenes or carbon nanotubes
  - wrap the graphite sheet by curving into ball or tube
  - Buckminister fullerenes
    - Like a soccer ball C_{60} - also C_{70} + others





Adapted from Figs. 12.18 & 12.19, *Callister 7e.*

Graphene



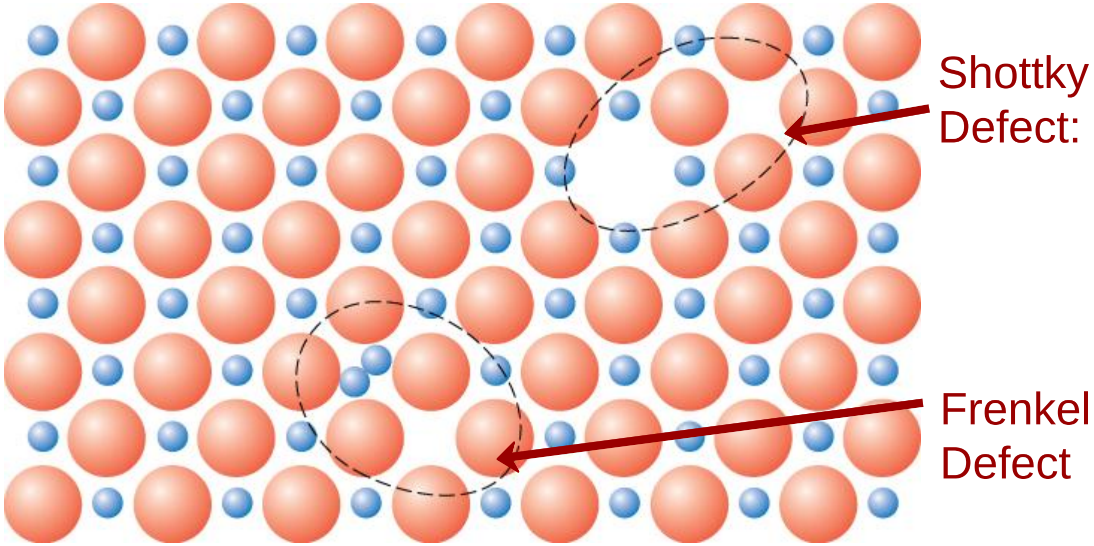
Defects in Ceramic Structures

- Frenkel Defect

  --a cation is out of place.

- Shottky Defect

  --a paired set of cation and anion vacancies.

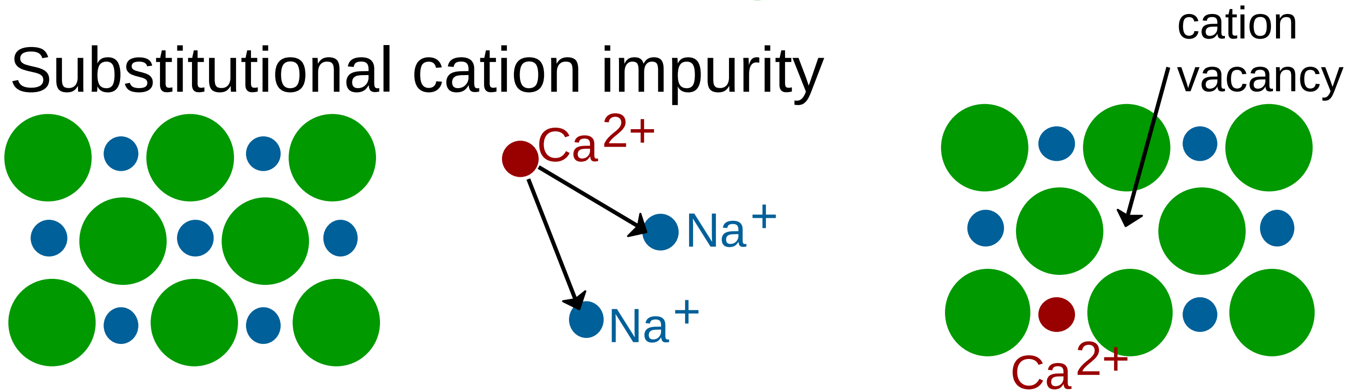


Adapted from Fig. 12.21, *Callister 7e.* (Fig. 12.21 is from W.G. Moffatt, G.W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*, John Wiley and Sons, Inc., p. 78.)

- Equilibrium concentration of defects $\sim e^{-Q_D / kT}$

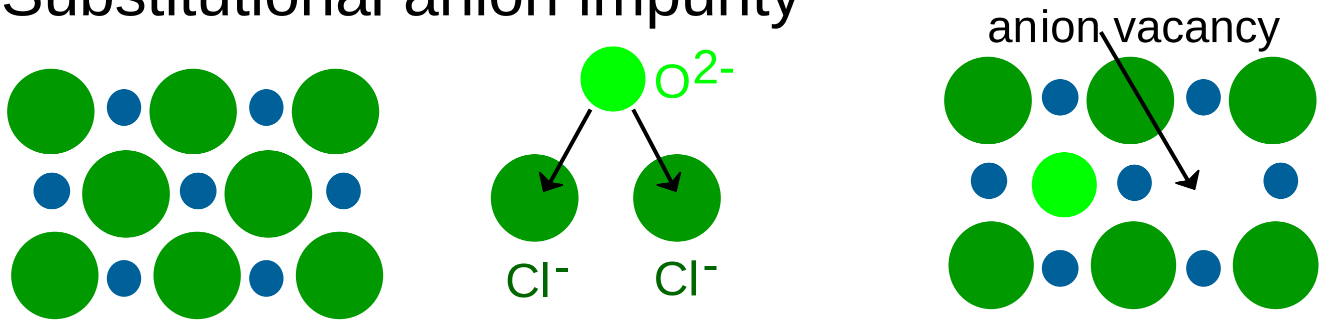
Impurities

- Impurities must also satisfy charge balance = Electroneutrality
- Ex: NaCl Na^+ ● Cl^- ●
- Substitutional cation impurity



initial geometry Ca^{2+} impurity resulting geometry

- Substitutional anion impurity



initial geometry O^{2-} impurity resulting geometry

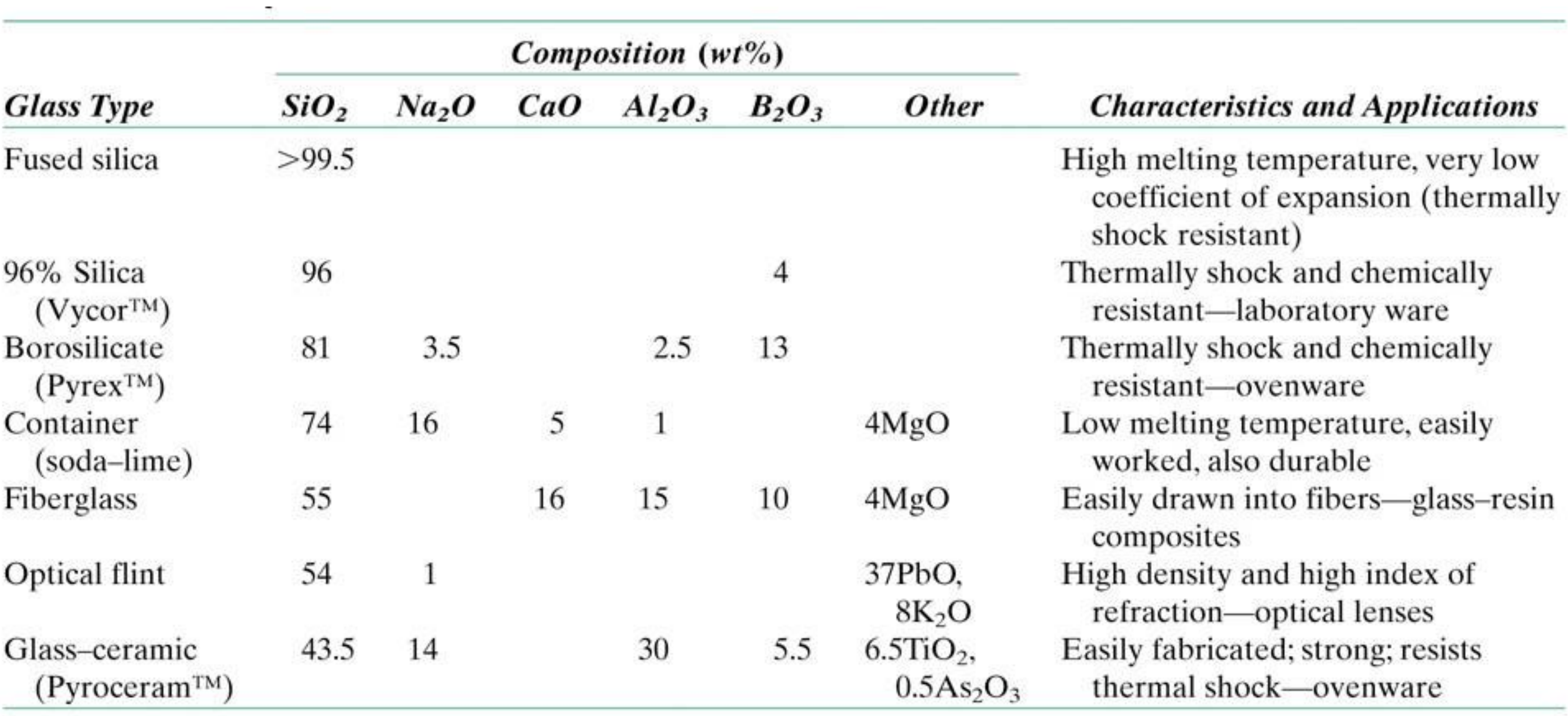
Application-classification of Ceramics

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

Adapted from Fig. 13.1 and discussion in Section 13.2-6, *Callister 7e.*

- Properties:
  - -- T_m for glass is moderate, but large for other ceramics.
  - -- Small toughness, ductility; large moduli & creep resist.
- Applications:
  - -- High *T*, wear resistant, novel uses from charge neutrality.
- Fabrication
  - -- some glasses can be easily formed
  - -- other ceramics can not be formed or cast.

Compositions and characteristics of some of the common commercial gasses



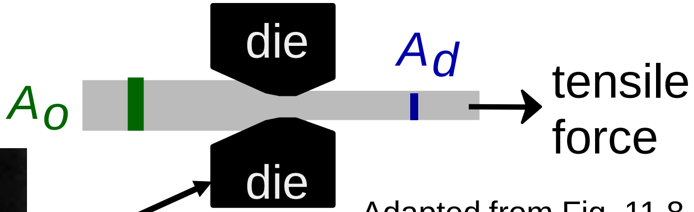
	Composition (wt%)						
Glass Type	***SiO_2***	***Na_2O***	***CaO***	***Al_2O_3***	***B_2O_3***	***Other***	***Characteristics and Applications***
Fused silica	>99.5						High melting temperature, very low coefficient of expansion (thermally shock resistant)
96% Silica (Vycor™)	96				4		Thermally shock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

- •Optical transparency
- •Relative ease to fabricate

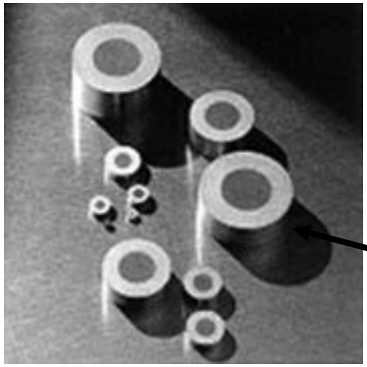
Application: Die Blanks

- Die blanks:
  - -- Need wear resistant properties!

SiC, WC, Al_2O_3, silica sand, etc

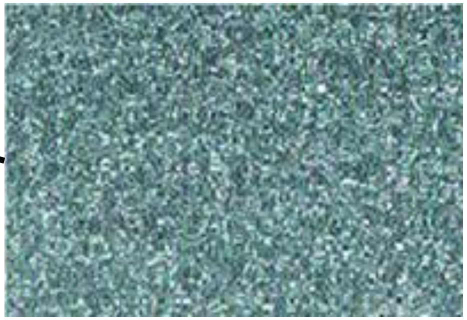


Adapted from Fig. 11.8 (d), *Callister 7e*.



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.

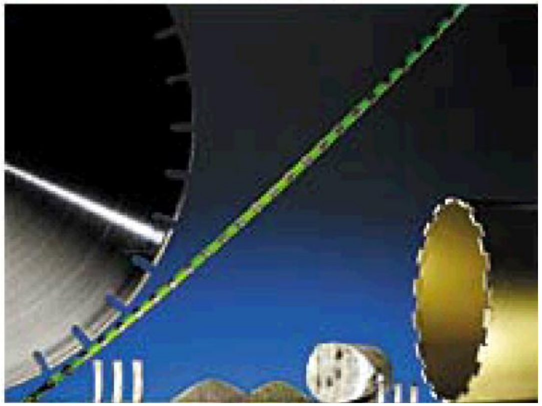


Courtesy Martin Deakins, GE Superabrasives, Worthington, OH. Used with permission.

Application: Cutting Tools

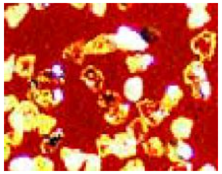
- Tools:
  - -- for grinding glass, tungsten, carbide, ceramics
  - -- for cutting Si wafers
  - -- for oil drilling
- Solutions:
  - -- manufactured single crystal or polycrystalline diamonds in a metal or resin matrix.
  - -- optional coatings (e.g., Ti to help diamonds bond to a Co matrix via alloying)
  - -- 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

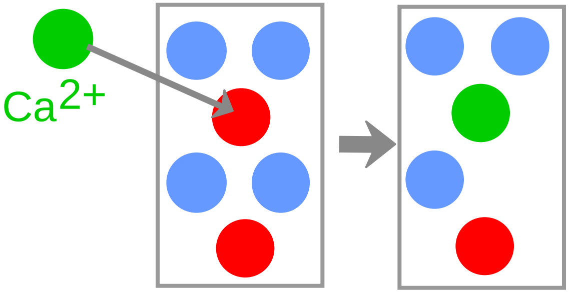
- Example: Oxygen sensor ZrO_2
- Principle: Make diffusion of ions fast for rapid response.
- Approach:

  Add Ca impurity to ZrO_2:

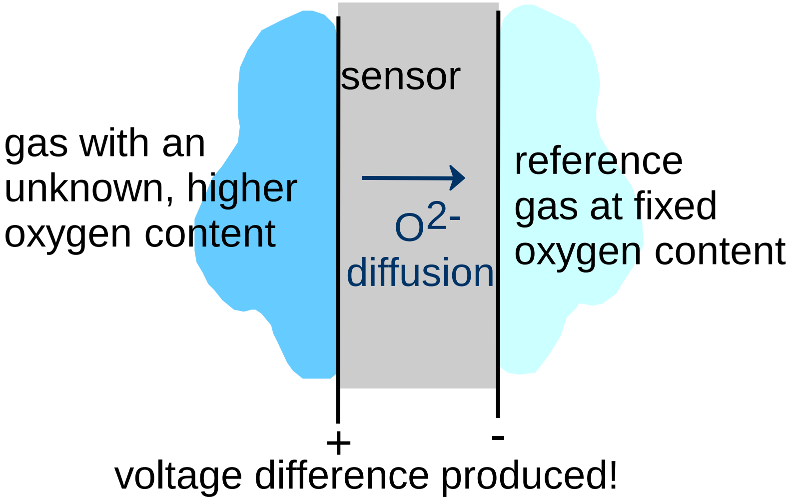
  -- increases O^{2-} vacancies

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

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



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



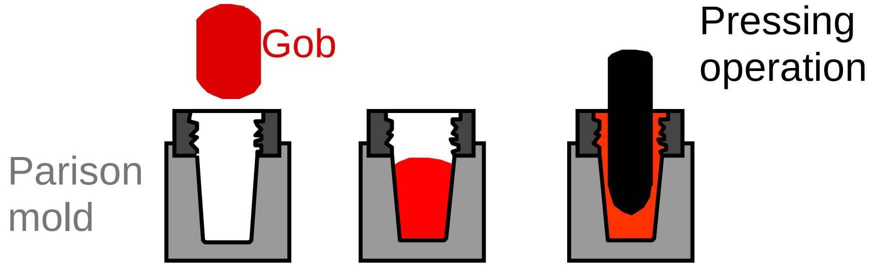
Ceramic Fabrication Methods-I

GLASS FORMING

PARTICULATE FORMING

CEMENTATION

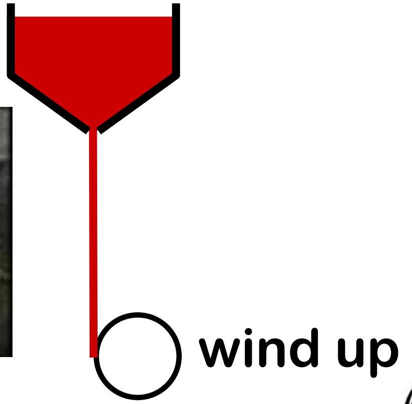
- Pressing:



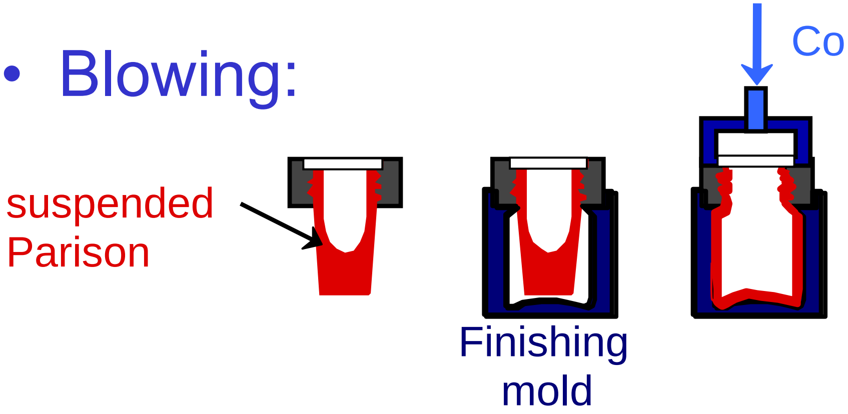
plates, dishes, cheap glasses

--mold is steel with graphite lining

- Fiber drawing:



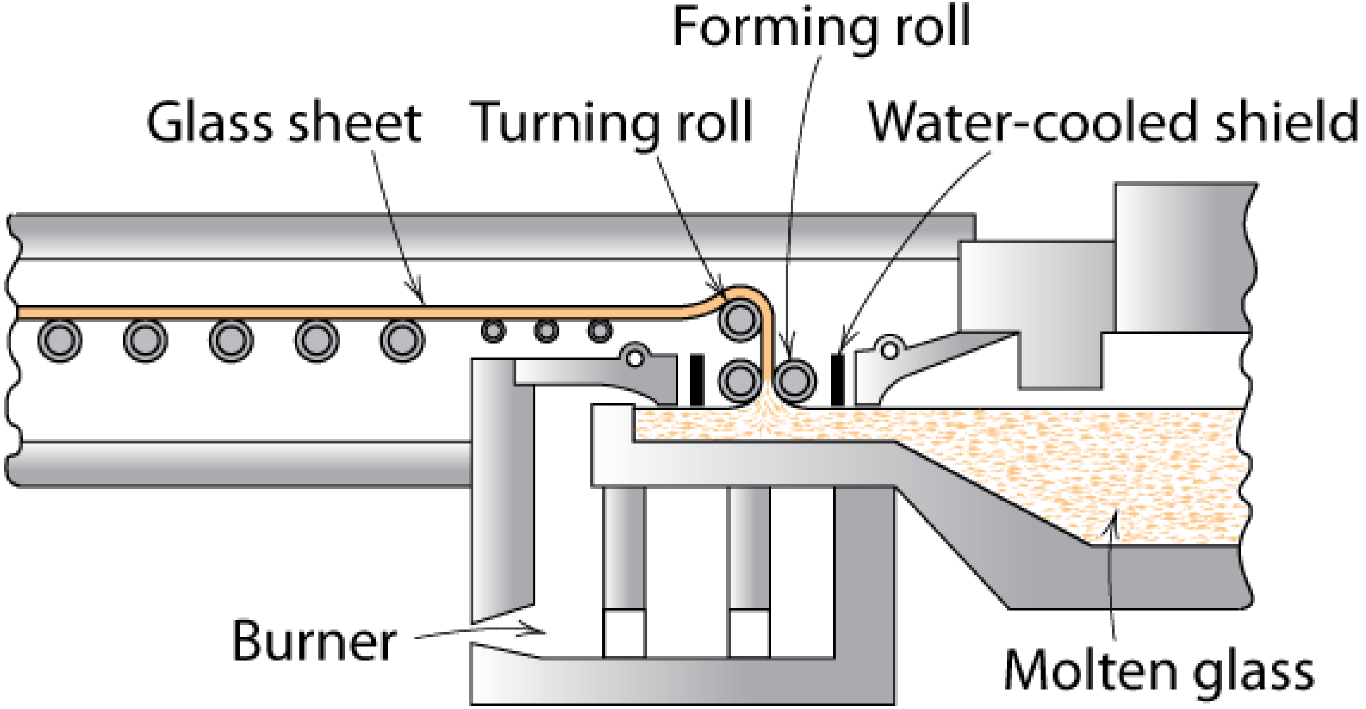
- Blowing:



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.*

http://www.istockphoto.com/file_closeup/?id=2889395&refnum=1088283

Ceramic Fabrication Methods-IIA

GLASS FORMING

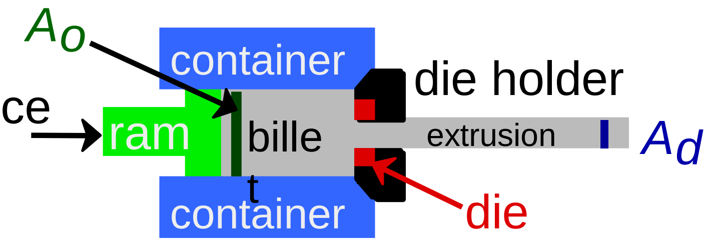
PARTICULATE FORMING

CEMENTATION

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

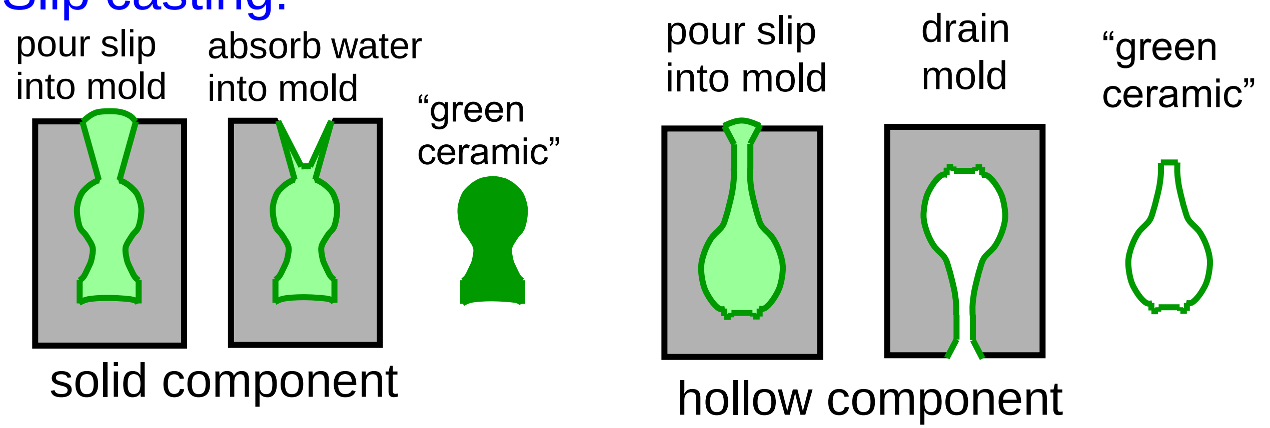
--Hydroplastic forming:

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



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

--Slip casting:

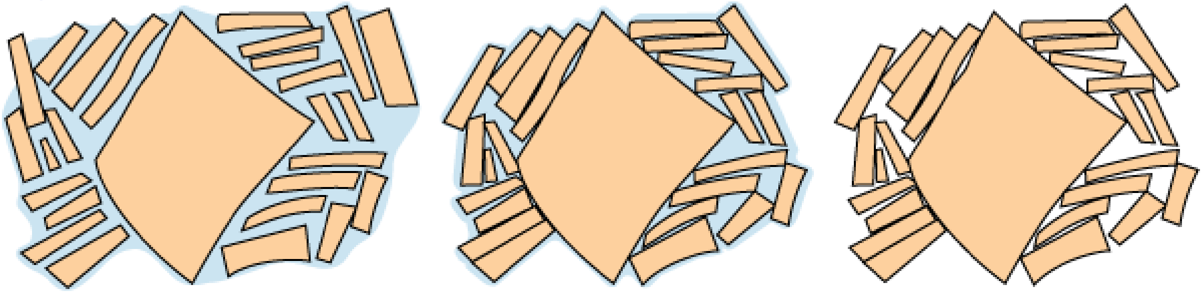


Adapted from Fig. 13.12, *Callister 7e*. (Fig. 13.12 is from W.D. Kingery, *Introduction to Ceramics*, John Wiley and Sons, Inc., 1960.)

- Dry and fire the component

Drying and Firing

- Drying: layer size and spacing decrease.



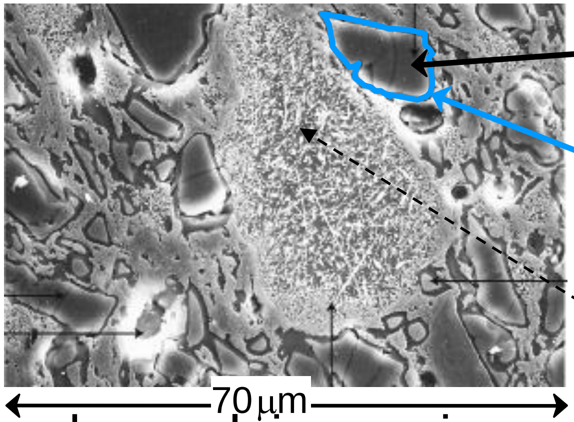
wet slip partially dry "green" ceramic

Adapted from Fig. 13.13, *Callister 7e*. (Fig. 13.13 is from W.D. Kingery, *Introduction to Ceramics*, John Wiley and Sons, Inc., 1960.)

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



SiO_2 particle (quartz)

glass formed around the particle

Mullite needles

Fired porcelain specimen

Adapted from Fig. 13.14, *Callister 7e*. (Fig. 13.14 is courtesy H.G. Brinkies, Swinburne University of Technology, Hawthorn Campus, Hawthorn, Victoria, Australia.)

Ceramic Fabrication Methods-IIB

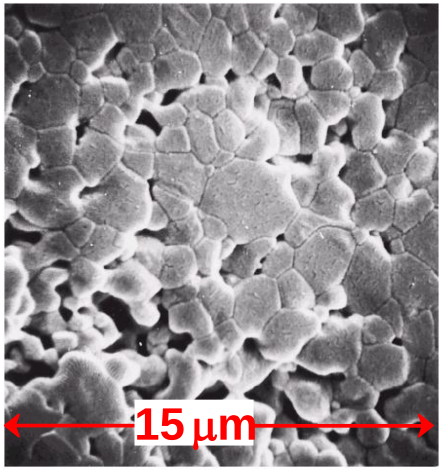
GLASS FORMING

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.



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

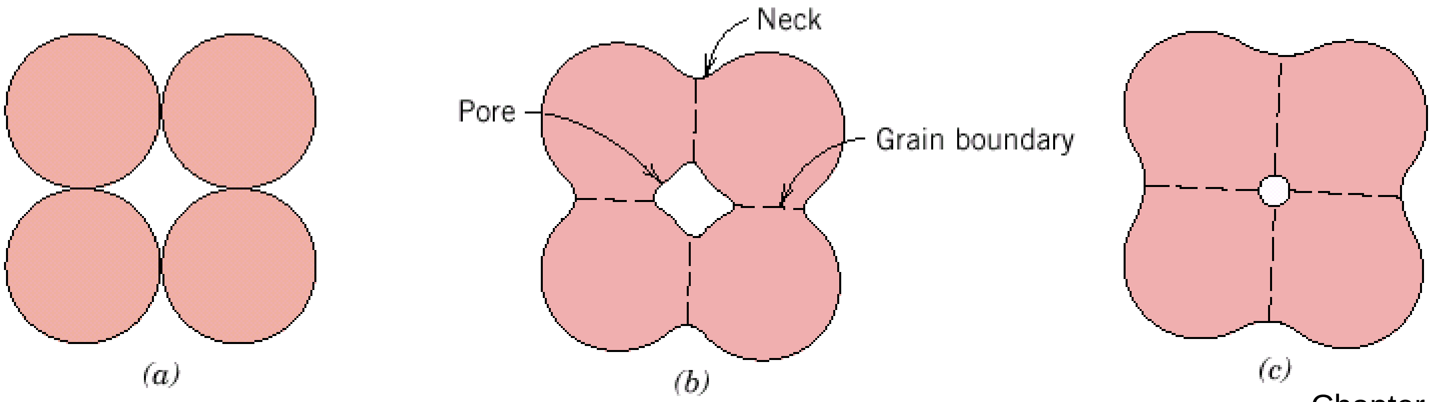
- add processing aids to help form neck
- little or no plastic deformation

Uniaxial compression - compacted in single direction

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

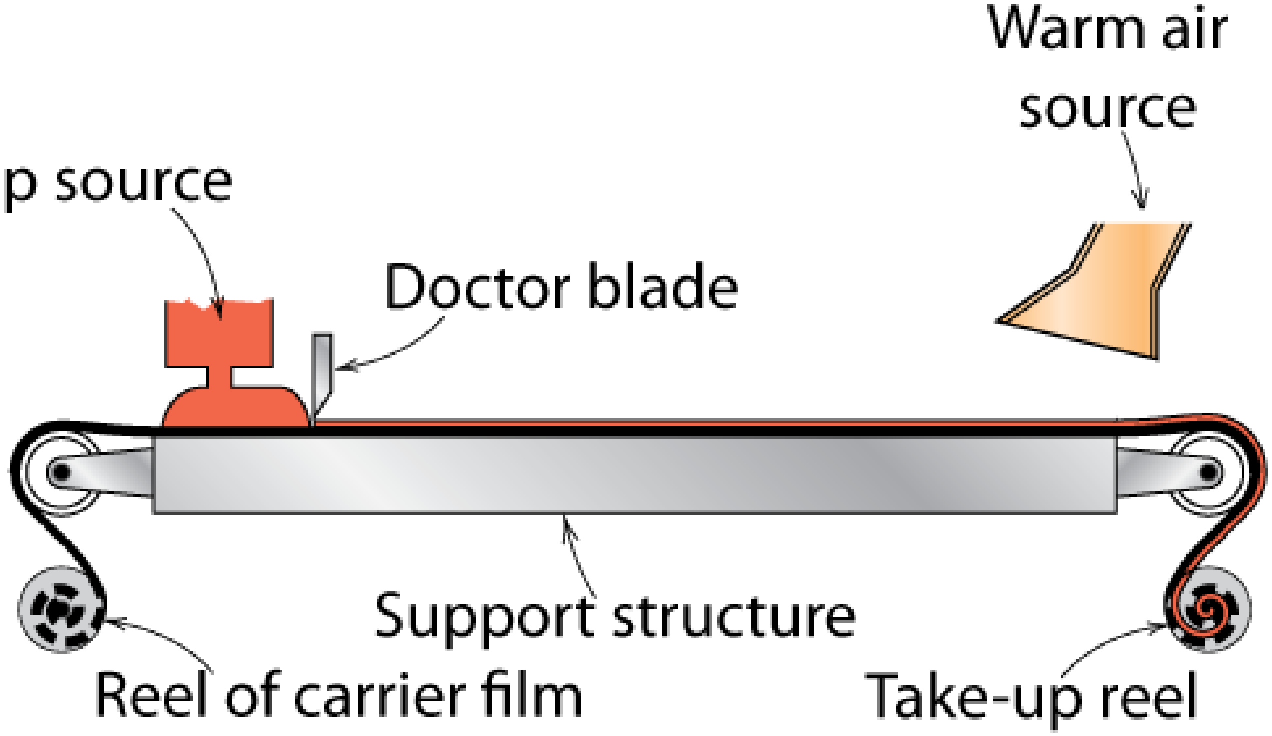
Hot pressing - pressure + heat

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



Tape Casting

- thin sheets of green ceramic cast as flexible tape
- 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

- Produced in extremely large quantities.
- Portland cement:
  - -- mix clay and lime bearing materials
  - -- calcinate (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.

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

Summary-2

- Ceramic materials have covalent & ionic bonding.
- Structures are based on:
  - -- charge neutrality
  - -- maximizing # of nearest oppositely charged neighbors.
- Structures may be predicted based on:
  - -- ratio of the cation and anion radii.
- Defects
  - -- must preserve charge neutrality
  - -- have a concentration that varies exponentially w/*T*.
- Room *T* mechanical response is elastic, but fracture is brittle, with negligible deformation.
- processing and application