Molecules and Materials

Last Updated: August 23, 2024

Contents

Notes based off of the textbook Materials Science and Engineering: An Introduction. MSE course was taught by professor Hattrick. Unless otherwise specified, all images are from the textbook.

1 Introduction

Solid materials are grouped into 3 different basic categories: metals, ceramics, and polymers. A Composite is made with materials from two or more groups.

1.1 Metals

- Composed of one or more metallic elements on the periodic table (ex. iron, aluminum, copper).

- Relatively dense, stiff, strong, and ductile compared with the other material groups.

- Many unlocalized electrons.

- Good conductors of electricity and heat.

- Not transparent.

- Can be magnetic.

1.2 Ceramics

- Compounds between metallic and nonmetallic elements which are most frequently oxides, nitrides, and carbides (ex. aluminum oxide, silicon dioxide, concrete, glass, clay).

- Relatively stiff, strong, hard, and brittle.

- Good insulators of heat and electricity.

- Relatively more resistant to high temperatures and harsh environments.

- May be transparent or opaque.

- May have magnetic properties.

1.3 Polymers

- Large molecular structures which are often chainlike in nature that often have a backbone of carbon atoms (ex. polyethylene, nylon, polyvinyl chloride).

- Not very dense.

- Extremely ductile.

- Unreactive and chemically inert.

- Low electrical conductivities and nonmagnetic.

- May decompose.

2 Atomic Structure and Intermolecular Bonding

2.1 Fundamental Concepts

- **Atomic Number (Z)** - The number of protons in the element.

- **Isotopes** - Atoms of the same element with different atomic masses.

- **Atomic Weight** - Weighted average of the atomic masses of the atom's naturally occurring isotopes.

- **Atomic Mass Unit (amu)** - $\frac{1}{12}$ the weight of carbon 12 which is 1.660×10^{-27} kg. 1 amu per atom is equivalent to 1 g per mole.

- **Mole** - 6.022×10^{23} (Avogadro's number) atoms or molecules.

- In wave mechanics, every electron in an atom is characterized by four parameters called **quantum numbers**:

  - **Principal Quantum Number** (n) - The energy level of the electron (1, 2, 3, 4) or (K, L, M, N).

  - **Angular Momentum Quantum Number** (l) - The shape of the electron's orbital (0, 1, 2, 3, ..., $n-1$) or (s, p, d, f).

  - **Magnetic Quantum Number** (m_l) - The number of electron orbitals for each subshell ($-l, -l+1, \ldots, 0, \ldots, l-1, l$).

  - **Spin Quantum Number** (m_s) - The direction of the electron's spin ($\pm\frac{1}{2}$).

Table 2.1 Summary of the Relationships among the Quantum Numbers n, l, m_l and Numbers of Orbitals and Electrons

Value of n	Value of l	Values of m_l	Subshell	Number of Orbitals	Number of Electrons
1	0	0	$1s$	1	2
2	0	0	$2s$	1	2
	1	−1, 0, +1	$2p$	3	6
3	0	0	$3s$	1	2
	1	−1, 0, +1	$3p$	3	6
	2	−2, −1, 0, +1, +2	$3d$	5	10
4	0	0	$4s$	1	2
	1	−1, 0, +1	$4p$	3	6
	2	−2, −1, 0, +1, +2	$4d$	5	10
	3	−3, −2, −1, 0, +1, +2, +3	$4f$	7	14

Source: From J. E. Brady and F. Senese, *Chemistry: Matter and Its Changes,* 4th edition, 2004. Reprinted with permission of John Wiley & Sons, Inc.

- **Pauli Exclusion Principle** - Each electron state can hold no more than two electrons that must have opposite spins.

- **Ground State** - When all the electrons occupy the lowest energy levels.

- **Electron Configuration** - The manner in which these states are occupied.

- **Valence Electrons** - Electrons which occupy the outermost electron shell (specified by principle quantum number).

2.2 Periodic Table

- **Electronegativity** - The ability of an atom to attract electrons to itself.

2.3 Primary Interatomic Bonds

There are three primary types of bonds found in solids: ionic, covalent, and metallic.

The net force F_N between two atoms is the sum of the attractive force F_A and the repulsive force F_R.
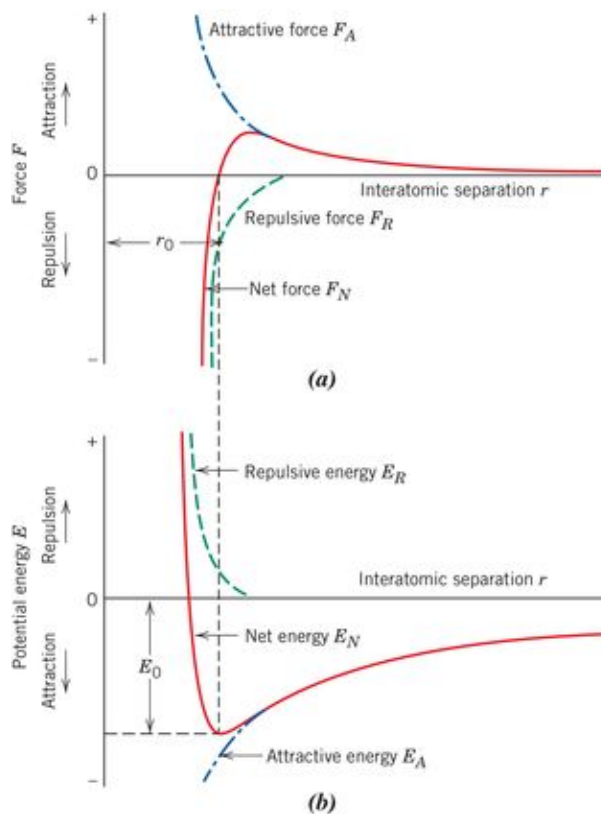

Figure 1: Graph of force versus distance.

- The slope of a stiff material at r_0 would be quite steep.

- A deep and narrow trough would normally correlate with a low coefficient of thermal expansion.

$$F_N = F_A + F_R \tag{1}$$

2.3.1 Ionic Bonds

- Always found in compounds composed of both metallic and non-metallic elements.

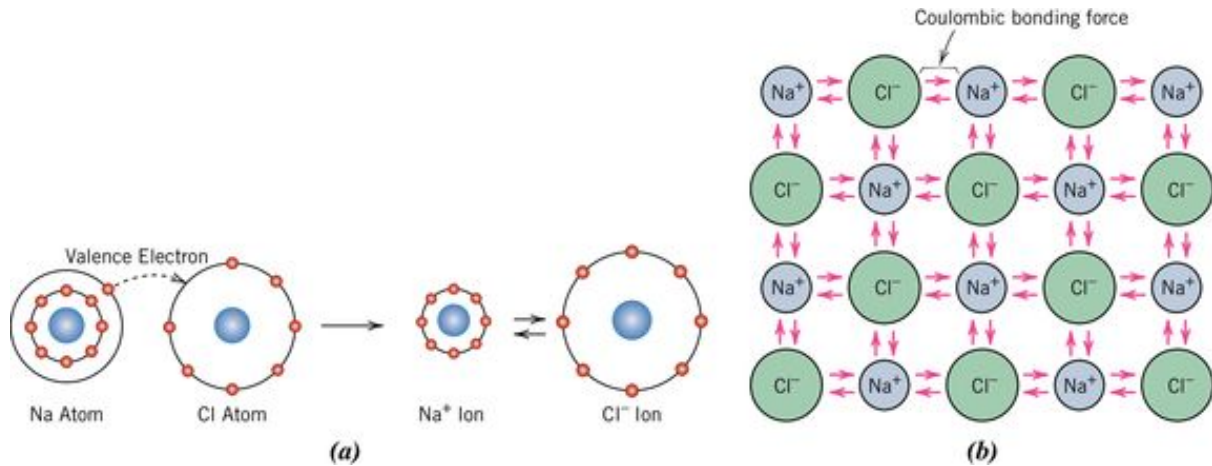- Metallic atoms give their valence to the nonmetallic atoms.

Figure 2: Ionic bonding in sodium chloride (Source: All images are from the textbook).

- The attractive bonding forces are coulombic: the positive and negative ions attract each other.

- The attractive energy E_A and attractive force F_A are determined by the equations

$$E_A = -\frac{A}{r} \tag{2}$$

$$F_A = \frac{dE_A}{dr} \tag{3}$$

$$A = \frac{|Z_1||Z_2|e^2}{4\pi\varepsilon_0} \tag{4}$$

  - $|Z_1|$ and $|Z_2|$ are absolute values of the valences for the two ion types.
  - e is the electronic charge (1.602×10^{-19} C)
  - r is the interatomic distance
  - ε_0 is the permittivity of a vacuum (8.85×10^{-12} F/m).

- Ionic bonding is nondirectional as the magnitude of the bond is same in all directions around an ion.

- Found most in ceramic materials.

2.3.2 Covalent Bonding

- Found in materials whose atoms have small differences in electronegativity.

- Each atom shares electrons.

- Covalent bonds are direction meaning that it may only exist in the direction between one atom and another.

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- It is difficult to predict the mechanical properties of covalently bonded materials.
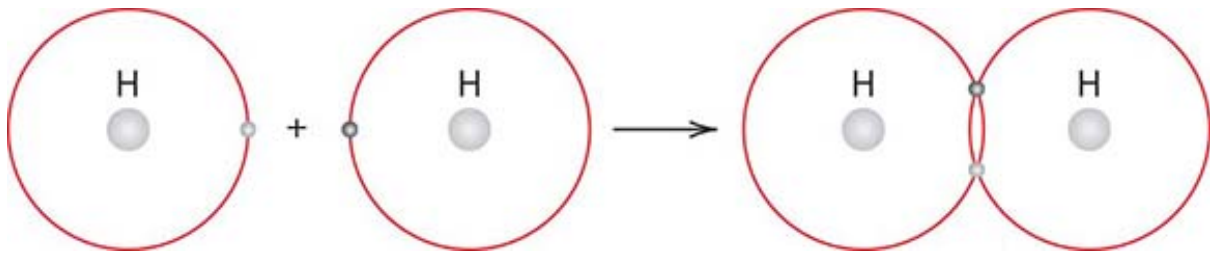

Figure 3: Covalent bonding between atoms of hydrogen.

2.3.3 Metallic Bonding

- Found in metals and their alloys.
- Valence electrons are allowed to drift throughout the entire material.
- The free electrons shield the positively charged ion cores from the repulsive electrostatic forces.
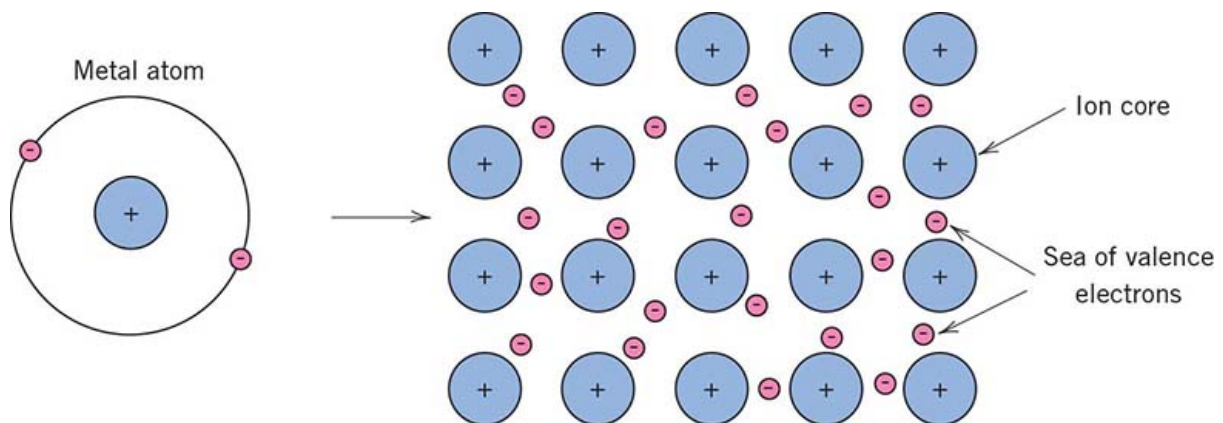- Nondirectional in character.

Figure 4: Illustration of metallic bonding.

2.4 Secondary Bonding or van der Waals Bonding

- Secondary bonds are weaker than primary bonds. Secondary bonds arise from the interaction of **dipoles**.
- **Intramolecular** - The forces that hold atoms together in a molecule.
- **Intermolecular** - The forces that hold molecules together in a material.
- There are three types of secondary bonds:
    - **Dipole-Dipole** - The attraction between the positive end of one polar molecule and the negative end of another polar molecule.
    - **Dipole-Induced Dipole** - The attraction between the positive end of a polar molecule and the negative end of a nonpolar molecule.
    - **Dispersion Forces** - The attraction between the electrons of one nonpolar molecule and the nucleus of another nonpolar molecule.
- **Hydrogen Bonding** - A special type of dipole-dipole interaction that occurs between hydrogen and an electronegative atom (F, O, N).

2.5 Mixed Bonding

- The percent ionic character of a bond between elements A and B may be approximated by the expression

$$\%IC = 100\% \left(1 - e^{-\frac{1}{4}(X_A - X_B)^2}\right) \tag{5}$$

where X_A and X_B are the electronegativities of elements A and B, respectively.

3 The Atomic Structure of Crystalline Solids

- **Crystalline Material** - A material whose atoms are arranged in a periodic array.

- **Amorphous Material** - A material whose atoms are randomly arranged.

- **Polycrystalline** materials are composed of many small crystals or grains.

- **Crystal Structure** - The manner in which atoms, ions, or molecules are spatially arranged.

- **Unit Cell** - The smallest repetitive volume which contains the complete lattice pattern of a crystal.

- The number of atoms per unit cell can be calculated by the equation

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8} \tag{6}$$

where N_i is the number of interior atoms, N_f is the number of face atoms, and N_c is the number of corner atoms.

- **Lattice** - A three-dimensional array of points coinciding with atom positions.

3.1 Metallic Crystal Structures

- **Coordination Number** - The number of nearest neighboring atoms to any atom.

- **Atomic Packing Factor (APF)** -

$$APF = \frac{\text{Volume of atoms in unit cell}}{\text{volume of unit cell}} \tag{7}$$

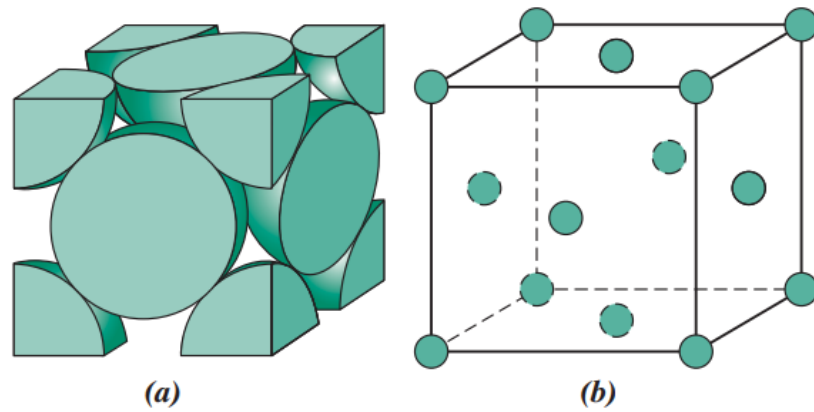### 3.1.1 Face-Centered Cubic (FCC) Structure

Figure 5: The hard-sphere unit cell representation and a reduced unit cell representation of the FCC crystal structure.

- $a = 2R\sqrt{2}$

- Coordination number: 12

- 4 atoms per unit cell.

- APF: 0.74

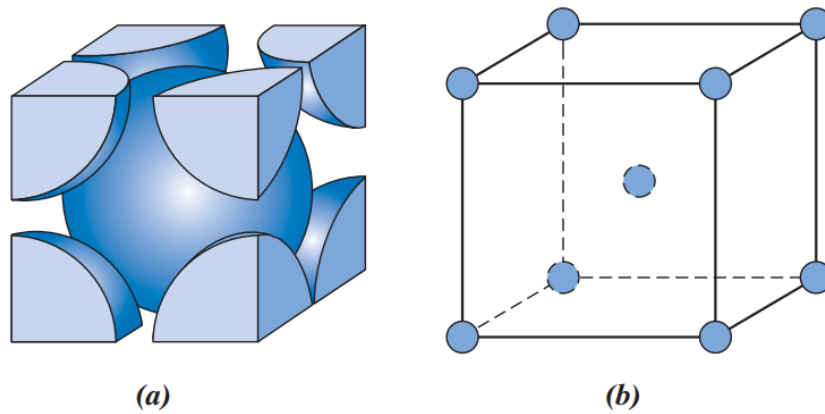### 3.1.2 Body-Centered Cubic (BCC) Structure

Figure 6: The hard-sphere unit cell representation and a reduced unit cell representation of the BCC crystal structure.

- $\sqrt{3}a = 4R$

- Coordination number: 8

- 2 atoms per unit cell.

- APF: 0.68

3.1.3   Simple Cubic (SC) Structure

Figure 7: The hard-sphere unit cell representation and a reduced unit cell representation of the SC crystal structure.

- $a = 2R$

- Coordination number: 6

- 1 atom per unit cell.

- APF: 0.52

- The only simple-cubic element is polonium which is considered to be a metalloid.
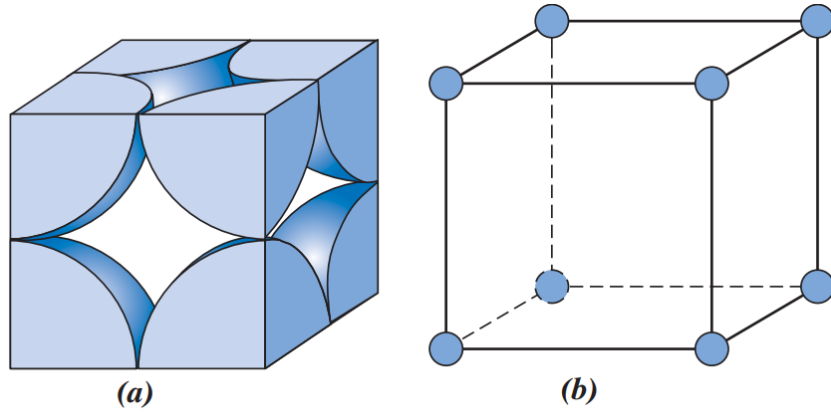
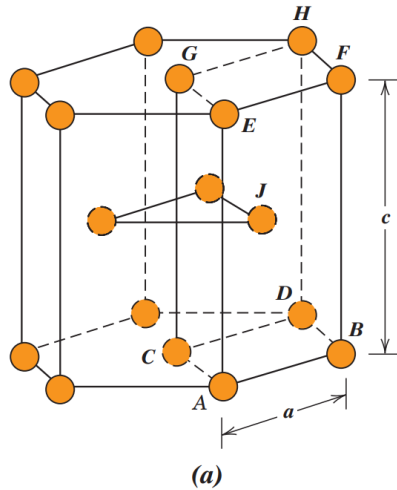### 3.1.4   Hexagonal Close-Packed (HCP) Structure

Figure 8: The hard-sphere unit cell representation and a reduced unit cell representation of the HCP crystal structure.

- $a = 2R$

- Coordination number is 12.

- 6 atoms per unit cell.

- APF: 0.74

3.2   Density Calculations

For metallic solids, the density can be calculated as follows:

$$\rho = \frac{nA}{V_C N_A} \qquad (8)$$
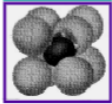
where n is the number of atoms per unit cell, A is the atomic weight in grams per mole, V_C is the volume of the unit cell in m^3 per unit cell, and N_A is Avogadro's number in atoms per mole.

3.3   Polymorphism and Allotropy

- **Polymorphism** - The ability of a solid material to exist in more than one form or crystal structure.

- **Allotropy** - Polymorphism in elemental solids.

3.4   Ceramic Crystal Structures

- Bonding can be ionic or covalent in character.

Figure 9: The geometries of these structures are determined by the ratio of the cation to anion radii.

3.4.1 AX Structures

(a) A unit cell for the rock salt, or sodium chloride (NaCl), crystal structure.

- Coordination # Cation: 6
- Coordination # Anion: 6
- Anion Packing: FCC
- Atoms per Unit Cell: 4
- $a = 2(r_{anion} + r_{cation})$
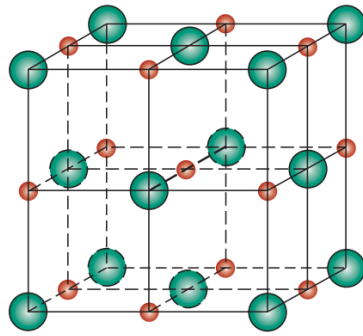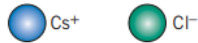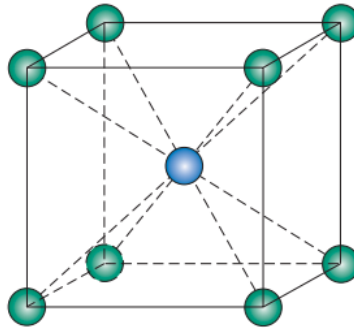
(b) A unit cell for the cesium chloride (CsCl) crystal structure.

- Coordination # Cation: 8
- Coordination # Anion: 8
- Anion Packing: SC
- Atoms per Unit Cell: 1
- $a = 2r_{anion}$
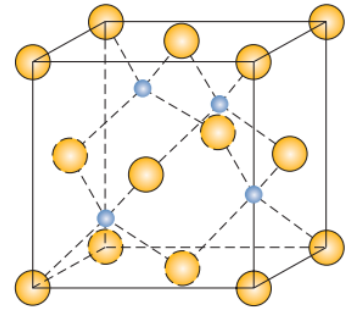
(c) A unit cell for the zinc blende (ZnS) crystal structure.

- Coordination # Cation: 4
- Coordination # Anion: 4
- Anion Packing: FCC
- Atoms per Unit Cell: 4
- $a = 2\sqrt{2d^2(1 - \cos 109.5°)}$

3.4.2 AX_2, ABX_3, and AB_2X_4 Structures
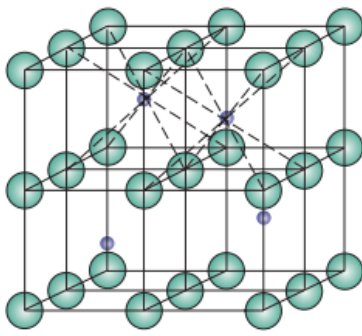
(a) A unit cell for the fluorite (AX_2) crystal structure.

- Anion Packing: SC
- Coordination # Cation: 8
- Coordination # Anion: 4
- Formula Units per Unit Cell: 4
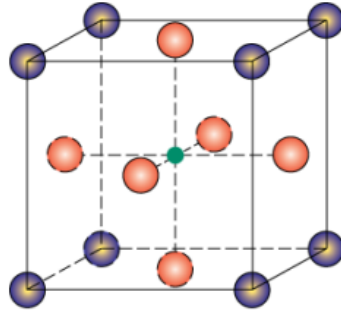
(b) A unit cell for the perovskite (ABX_3) crystal structure.

- Anion Packing: FCC
- Coordination # Cation: 12 (A), 6(B)
- Coordination # Anion: 6
- Formula Units per Unit Cell: 1
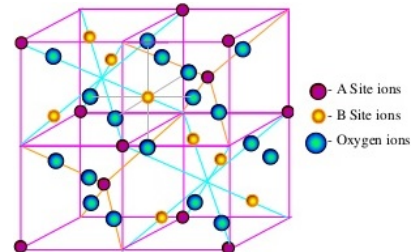
(c) A unit cell for the spinel (AB_2X_4) crystal structure.

- Anion Packing: FCC
- Coordination # Cation: 4(A), 6(B)
- Coordination # Anion: 8
- Formula Units per Unit Cell: 8

3.4.3 Density

$$\rho = \frac{n' \left(\sum A_C + \sum A_A \right)}{V_C N_A} \tag{9}$$

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- n' is the number of formula units per unit cell.

- $\sum A_C$ is the sum of the atomic weights of the cations.

- $\sum A_A$ is the sum of the atomic weights of the anions.

3.4.4 Silicate Ceramics

- Silicates are amorphous materials (low density) made up of silicon and oxygen.

- Polymorphs of silica include quartz, cristobalite, and tridymite.

- High melting temperature from strong S-O bonds.

- Glass is noncrystalline and made of SIO_4^{4-} tetrahedral units.

3.4.5 Polymorphic Forms of Carbon
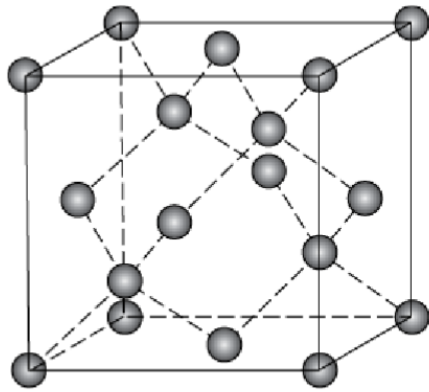
Fig. 3.17, *Callister & Rethwisch 5e.*

(a) Diamond has an FCC structure with additional atoms at 1/4th the distance along the body diagonals. There are 8 carbon atoms per unit cell.
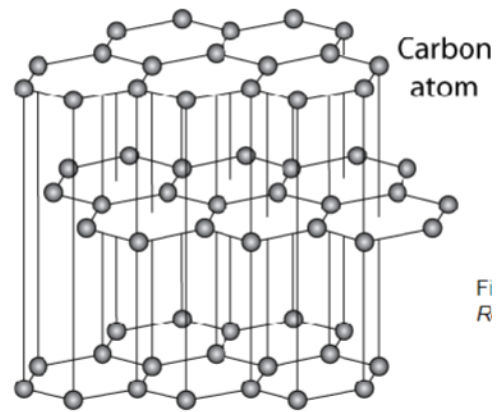
(b) Graphite is made up of parallel hexagonal planes which are held together by van der Waals forces and slide over each other easily.

3.5 Crystal Systems

- **Lattice Parameters** - The three edge lengths a, b, and c, and the three interaxial angles α, β, γ.

- There are seven different combinations of a, b, c, α, β, and γ each of which represents a distinct **crystal system**.
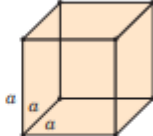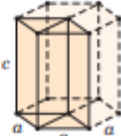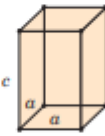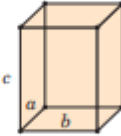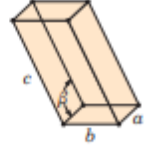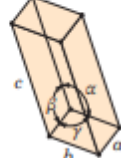
Crystal System	Axial Relationships	Interaxial Angles	Unit Cell Geometry
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	
Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	

Figure 13: The seven different crystal systems.

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3.6 Point Coordinates and Directions
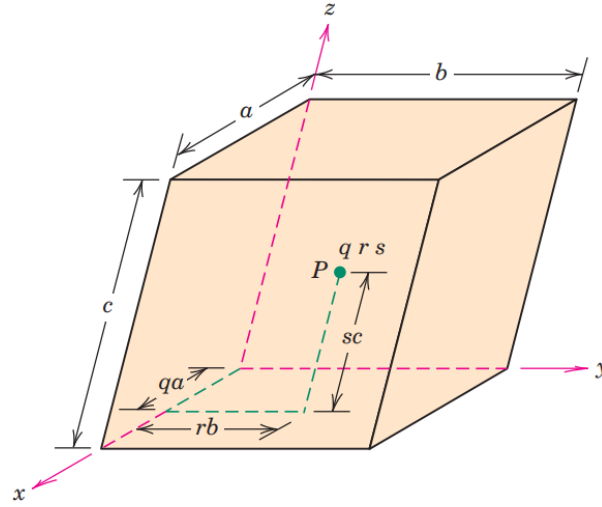
Figure 14: Point indices q,r, and s are fractional multiples of a, b, and c which are the unit cell lengths.

- Directional indices are found by subtracting the head point coordinate by the tail point coordinate.

- Indices are reduced to the smallest integer values, and negative indices are represented by an overbar.

- Indices are enclosed in square brackets(ex. [111]).

3.6.1 Linear Density

$$LD = \frac{\text{number of atoms in a direction vector}}{\text{length of the direction vector}} \tag{10}$$

3.7 Crystallographic Planes

- Miller Indices are used to represent crystallographic planes.

- Example: Determine the miller indices for the following plane:
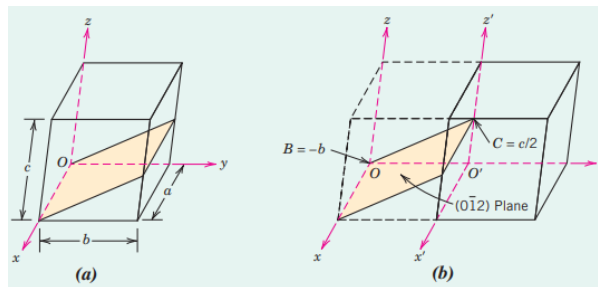
- Origin needs to be shifted as show in diagram (b) to O' since O intersects the plane.

-

$$h = \frac{1a}{\infty a} = 0 \tag{11}$$

$$k = \frac{1b}{-b} = -1 \tag{12}$$

$$l = \frac{1c}{c/2} = 2 \tag{13}$$

- The miller indices are $(0\bar{1}2)$.

3.7.1 Planar Density

$$PD = \frac{\text{number of atoms in a plane}}{\text{area of the plane}} \tag{14}$$

3.8 Single and Polycrystalline Materials

- **Single Crystal** - When the periodic and repeated arrangement of atoms is perfect and extends throughout the entirety of the specimen without interruption.

- **Polycrystalline** - When a material is composed of many small crystals or grains.

- **Grain Boundaries** - The region where two grains meet.

3.9 Anisotropy

- **Isotropic** - A material that has the same properties in all directions.

- **Anisotropic** - A material that has different properties in different directions.

4 Imperfections in Solids

4.1 Point Defects
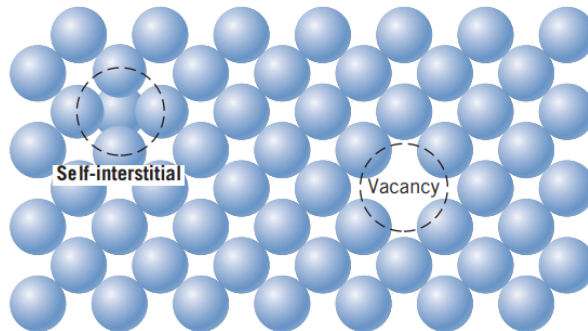
Figure 15: The two different types of point deflects: self-interstitial and vacancy.

- The equilibrium number of vacancies N_v for a given quantity of materials in per meters cubed is given by the equation

$$N_v = N e^{-\frac{Q_v}{kT}} \tag{15}$$

where N is the number of atomic sites per cubic meter, Q_v is the energy required to form a vacancy in joules per mole or eV per atom, k is the Boltzmann constant 1.38×10^{-23} J/atomK or 8.62×10^{-5} eV/atomK, and T is the temperature in kelvins.

- N can be calculated by the equation

$$N = \frac{N_A \rho}{A} \tag{16}$$

where N_A is Avogadro's number, ρ is the density of the material, and A is the atomic weight.

4.1.1 Imperfections in Ceramics
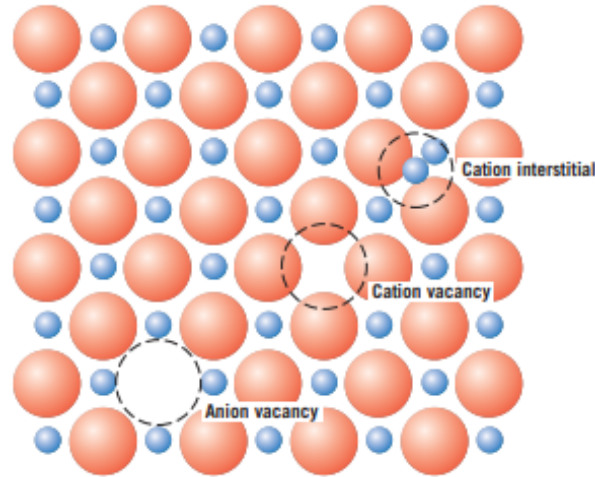
Figure 16: The two different types of point defects in ceramics.

- Charge balance is maintained (electroneutrality).

- **Frenkel Defect** - A cation vacancy and a cation interstitial.

- **Schottky Defect** - A cation vacancy and an anion vacancy.

- **Stoichiometric** - A state for ionic compounds where the ratios of cations and anions is the same as predicted by the chemical formula.

- For Frenkel defects, the number of cation vacancies is equal to

$$N_v = N e^{-\frac{Q_{fr}}{2kT}} \tag{17}$$

where N is the number of lattice sites, Q_{fr} is the energy required to form each Frenkel defect, k is the Boltzmann constant, and T is the temperature in kelvins.

4.2 Impurities in Solids

- **Solvent** is the element or compound present in the greatest amount.

- **Solute** is the element or compound present in a minor concentration.

- There are two types of impurity point defects: **substitutional**(solute replaces solvent atoms) and **interstitial**(solute atoms are in between solvent ones).

- The conditions for the formation of substitutional solid solutions can be expressed as four Hume-Rothery rules:

  - **Atomic Size Factor**: Appreciable quantities of a solute may be accommodated in this type of solid solution only when the difference in atomic radii between the two atom types is less than about $\pm 15\%$. Otherwise, the solute atoms create substantial lattice distortions and a new phase forms.

- – **Crystal Structure**: For appreciable solid solubility, the crystal structures for metals of both atom types must be the same.
  - – **Electronegativity Factor**: The more electropositive one element and the more electronegative the other, the greater the likelihood that they will form an intermetallic compound instead of a substitutional solid solution.
  - – **Valences**: Other factors being equal, a metal has more of a tendency to dissolve another metal of higher valency than to dissolve one of a lower valency.

- Aliovalent - Having a different valence.
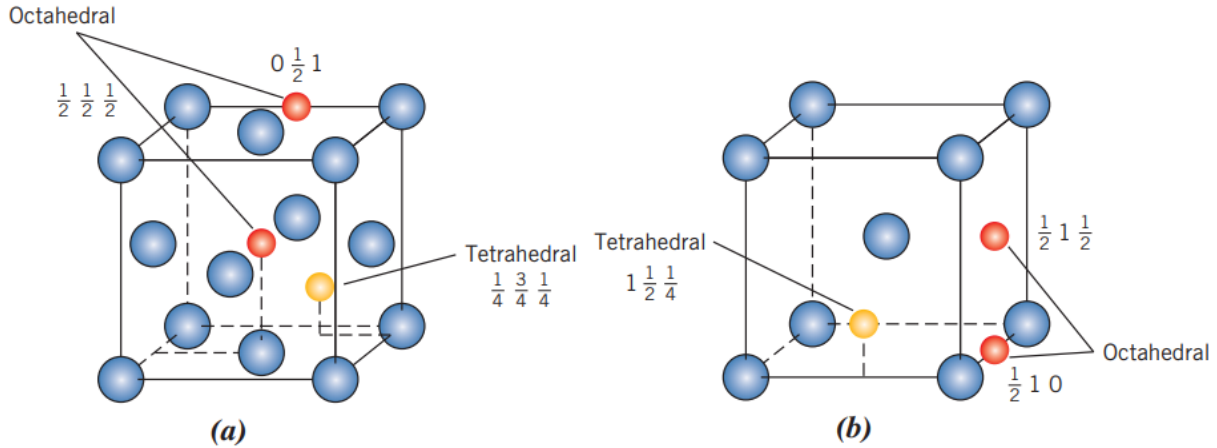
Figure 17: The two most common types of interstitial sites are the octahedral and tetrahedral sites. (a) FCC (b) BCC

4.3 Specification of Composition

- The weight percent can be defined as

$$C_1 = \frac{m_1}{m_1 + m_2} \times 100. \tag{18}$$

- The atomic percent can be defined as

$$C_1' = \frac{n_1}{n_1 + n_2} \times 100. \tag{19}$$

- The weight percent can be converted to atomic percent by the equation

$$C_1' = \frac{C_1 A_2}{C_1 A_2 + C_2 A_1} \times 100. \tag{20}$$

- The atomic percent can be converted to weight percent by the equation

$$C_1 = \frac{C_1' A_1}{C_1' A_1 + C_2' A_2} \times 100. \tag{21}$$

4.4   Line Defects
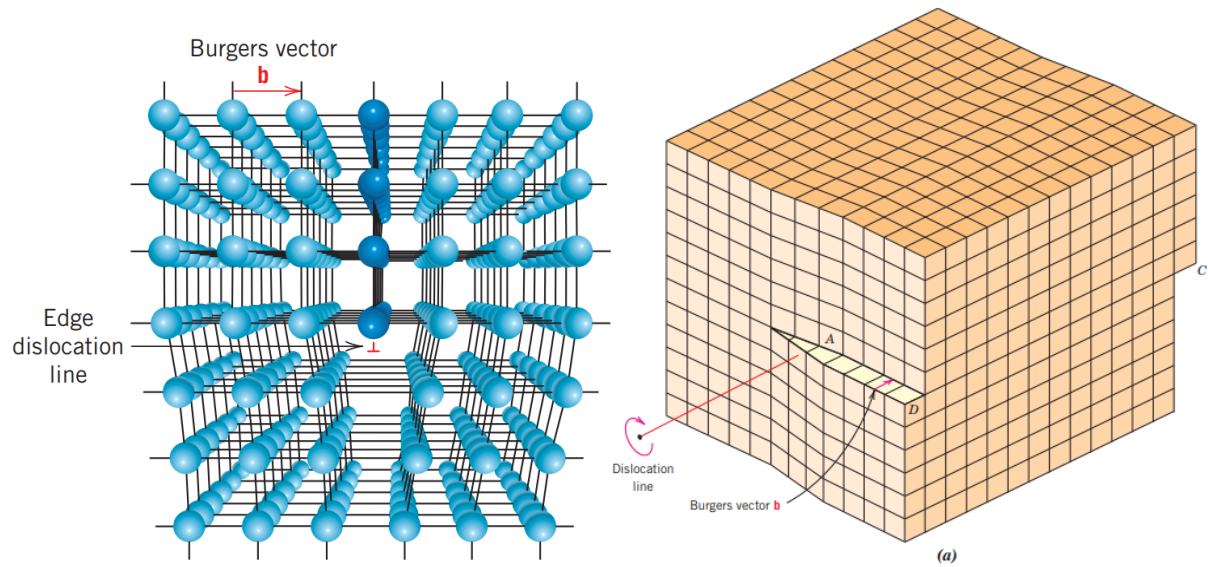
(a) Edge dislocations occur when an extra half-plane terminates within the crystal.

(b) Screw dislocations may be thought of as being formed by a shear stress.

Figure 18: The **dislocation line** is the line formed the end of the extra half-plane of atoms. The magnitude and direction of the lattice distortion can be expressed as a **Burgers vector**.

- Most dislocations are a combination of edge and screw dislocations (mixed dislocation).

4.5   Plane Defects

- Five types of 2D boundaries include **external surfaces** (where the crystal structure terminates), **grain boundaries**, **phase boundaries**, **twin boundaries**, and **stacking faults**.
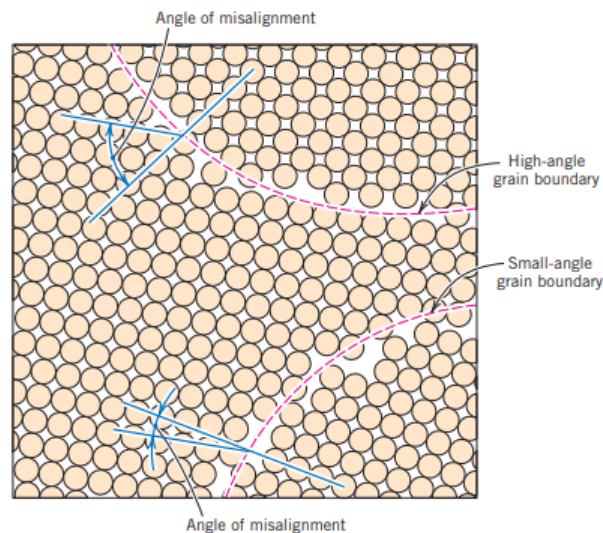
Figure 19: The grain boundary can be described as the boundary separating two small grains or crystals having different crystallographic orientations in polycrystalline materials.

- Phase boundaries exist in multiphase materials, in which a different phase exists on each side of the boundary.
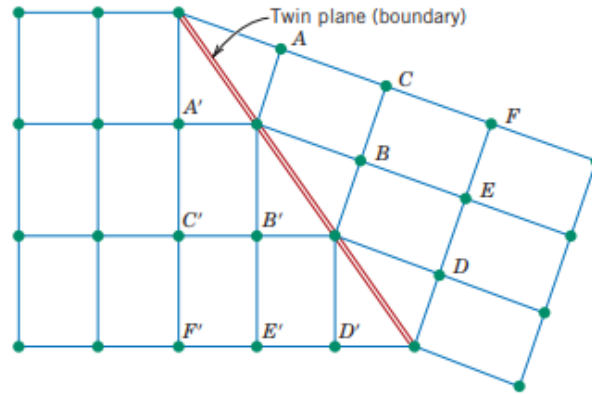
Figure 20: A twin boundary is a special type of grain boundary across which there is a specific mirror lattice symmetry.

- Stacking faults occur when there is an error in the planar stacking sequence of atoms in a crystal.

4.6 Microscopic Techniques

- **Optical Microscopy** - Utilizes optical and illumination systems.

- **Electron Microscopy** - Utilizes a beam of electrons to create an image. Transmission electron microscopes passes an electron beam through the specimen. Scanning electron microscopes reflects electrons off the surface of the specimen.

- **Scanning Probe Microscopy** - Utilizes a probe to scan the surface of a specimen.

4.7 Grain Size

- There are two primary ways of determining grain size. The first is by the linear intercept method.
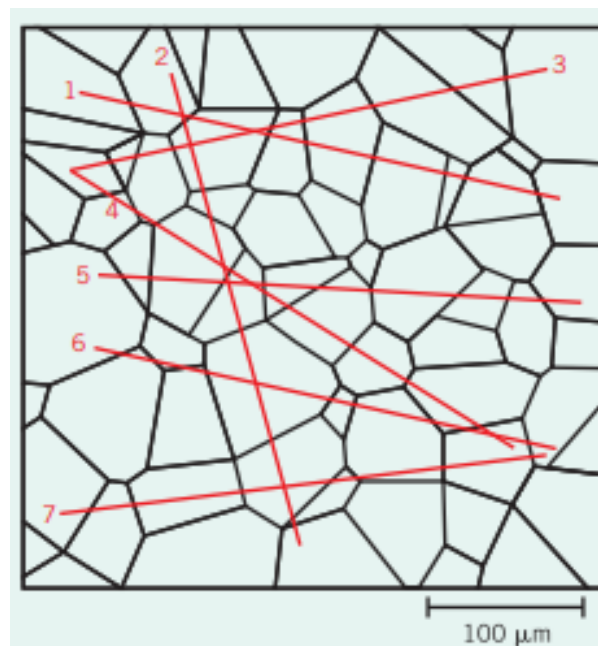
Figure 21: The linear intercept method.

The mean intercept length $\bar{l}$ can be calculated by the equation

$$\bar{l} = \frac{L_T}{PM},$$

(22)

where L_T is the total length of lines, P is the number of intercepts, and M is the magnification.

- The second method is by comparison. If G is the grain size number, an n is the average number of grains per square inch at a magnification of 100, then

$$n = 2^{G-1}.$$

(23)

5 Mechanical Properties of Metals

5.1 Fundamentals of Stress and Strain
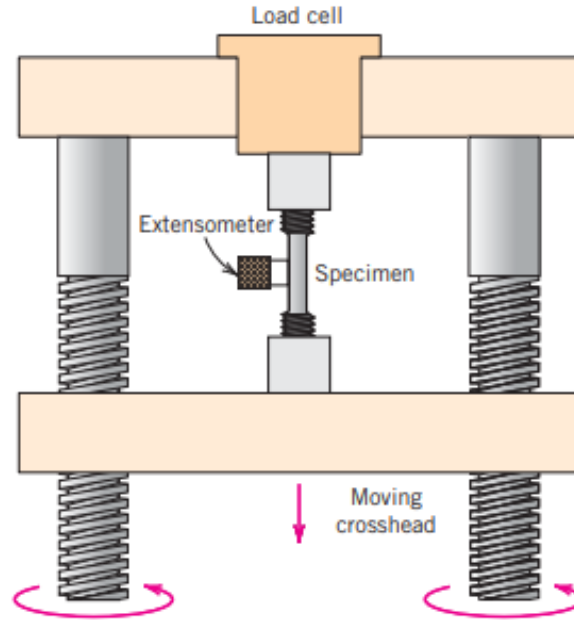
Figure 22: The following setup can be used to test for stress and strain.

$$\sigma = \frac{F}{A_0} \qquad\qquad\qquad \text{Stress} \qquad (24)$$

$$\varepsilon = \frac{\Delta L}{L_0} \qquad\qquad\qquad \text{Strain} \qquad (25)$$

$$\tau = \frac{F}{A_0} \qquad\qquad\qquad \text{Shear} \qquad (26)$$

$$E = \frac{\sigma}{\varepsilon} \qquad\qquad\qquad \text{Young's Modulus} \qquad (27)$$

$$\gamma = \frac{\Delta x}{y} = \tan\theta \qquad\qquad\qquad \text{Shear Strain} \qquad (28)$$

$$G = \frac{\tau}{\gamma} \qquad\qquad\qquad \text{Shear Modulus} \qquad (29)$$

$$\nu = -\frac{\varepsilon_y}{\varepsilon_z} \qquad \text{Poisson's Ratio (Ratio of the lateral and axial strains)} \qquad (30)$$

$$K = \frac{P}{\frac{\Delta V}{V_0}} \qquad\qquad\qquad \text{Elastic Bulk Modulus} \qquad (31)$$

$$G = \frac{E}{2(1+\nu)} \qquad\qquad\qquad \text{Shear Modulus Relationship} \qquad (32)$$

$$K = \frac{E}{3(1-2\nu)} \qquad\qquad\qquad \text{Bulk Modulus Relationship} \qquad (33)$$

- Plastic deformation is permanent while elastic deformation is temporary.

- For metals, maximum tensile strength occurs at the onset of necking.

- Yield strength is the stress at which a material begins to deform elastically.

5.2   Ductility

- Ductility is a measure of the degree of plastic deformation that has been sustained at fracture.

- It may be expressed as either percent elongation or percent reduction in area.

-
$$\%EL = \frac{L_f - L_0}{L_0} \times 100 \qquad\qquad (34)$$

  where L_f is the fracture length and L_0 is the original length.

-
$$\%RA = \frac{A_0 - A_f}{A_0} \times 100 \qquad\qquad (35)$$

  where A_f is the fracture area and A_0 is the original area.

5.3   Resilience and Toughness

- Resilience is the ability of a material to absorb energy when it is deformed elastically.

- It is measured by the area under the stress-strain curve.

$$U_r = \int_0^{\varepsilon_y} \sigma \, d\varepsilon \qquad\qquad (36)$$

- Toughness is the ability of a material to absorb energy without fracturing.

5.4   True Stress and Strain

- True stress can be related with engineering stress by the equation

$$\sigma_T = \sigma(1 + \varepsilon). \tag{37}$$

- True strain can be related with engineering strain by the equation

$$\varepsilon_T = \ln(1 + \varepsilon). \tag{38}$$

- The region of the true stress-strain curve after the onset of plastic deformation can be modeled by the equation

$$\sigma_T = K\varepsilon_T^n \tag{39}$$

where K is the strength coefficient and n is the strain-hardening exponent.

5.5   Hardness

- Hardness is a measure of a material's resistance to localized plastic deformation.

- A higher hardness is equivalent to a higher resistance to deformation and increased wear resistance.

5.6   Flexural Strength

- For a rectangular cross-section the flexural strength can be calculated by the equation

$$\sigma_f = \frac{3FL}{2bd^2}. \tag{40}$$

- For a circular cross-section the flexural strength can be calculated by the equation

$$\sigma_f = \frac{FL}{\pi r^3}. \tag{41}$$

5.7   Plastic Deformation in Ceramics

- Crystalline Ceramics deform like metals by the motion of dislocations.

- Noncrystalline ceramics deform by viscous flow. The rate is proportional to the applied stress. The equation for viscosity is

$$\eta = \frac{\tau}{dv/dy} \tag{42}$$

where τ is the shear stress, dv/dy is the change in velocity perpendicular and away from the plates.

5.8   Porosity of Ceramics

- Porosity P can be related with the modulus of elasticity E by the equation

$$E = E_0(1 - 1.9P + 0.9P^2) \tag{43}$$

where E_0 is the modulus of elasticity of the nonporous material.

- Porosity is deleterious to flexural strength since pores reduce the cross-sectional area, and they also act as stress concentrators.

$$\sigma_{fs} = \sigma_0 e^{-nP} \tag{44}$$

6 Dislocations Mechanisms

- **Slip** - The process by which plastic deformation is produced by dislocation motion.

- **Dislocation Density** - The number of dislocations per unit volume.

- **Slip System** - The combination of a slip direction and a slip plane.

Metals	*Slip Plane*	*Slip Direction*	*Number of Slip Systems*
Face-Centered Cubic			
Cu, Al, Ni, Ag, Au	{111}	$\langle 110 \rangle$	12
Body-Centered Cubic			
α-Fe, W, Mo	{110}	$\langle 111 \rangle$	12
α-Fe, W	{211}	$\langle 111 \rangle$	12
α-Fe, K	{321}	$\langle 111 \rangle$	24
Hexagonal Close-Packed			
Cd, Zn, Mg, Ti, Be	{0001}	$\langle 11\bar{2}0 \rangle$	3
Ti, Mg, Zr	{10$\bar{1}$0}	$\langle 11\bar{2}0 \rangle$	3
Ti, Mg	{10$\bar{1}$1}	$\langle 11\bar{2}0 \rangle$	6

Figure 23: Slip systems for metals.

6.1 Deformation by Slip

- For a single crystal, the resolved shear stress can be calculated by the equation

$$\tau_R = \sigma \cos \phi \cos \lambda \tag{45}$$

where σ is the applied tensile stress, ϕ is the angle between the tensile axis and the slip plane normal, and λ is the angle between the tensile axis and the slip direction.

- $\cos \phi \cos \lambda$ is called the Schmid factor.

- The critical resolved shear stress can be calculated by the equation

$$\sigma_y = 2\tau_{\text{crss}}, \tag{46}$$

and it occurs when $\phi = \lambda = 45°$.

- For polycrystalline materials, the orientation of slip planes vary.

- In deformation by rolling, grains are elongated in the rolling direction.
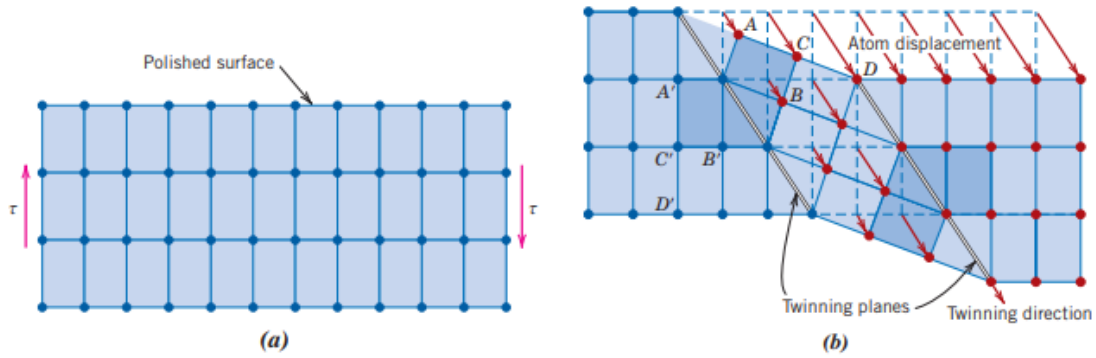
6.2 Deformation by Twinning

Figure 24: Twinning results in atomic displacements such that a mirror image of the lattice structure is produced.

Table 1: Slip vs Twinning

Slip	Twinning
Crystallographic orientation stays the same.	Crystallographic orientations are different across twin boundaries.
Occurs in distinct atomic spacing multiples.	The atomic displacements are less than the interatomic separation
Occurs in FCC metals or at high temperatures and low loading rates	Occurs in BCC or HCP metals at low temperatures and high loading rate.
Relatively large plastic deformations.	Relatively small plastic deformations

7 Strengthening Mechanisms

7.1 Grain Size Reduction

- Grain boundaries act as barriers to dislocation motion because the two grains are of different orientation and the atomic disorder within a grain boundary results in a discontinuity of slip planes.

- The yield strength varies with grain size according to the equation

$$\sigma_y = \sigma_0 + kd^{-1/2} \tag{47}$$

where d is the average grain diameter.

7.2 Solid-Solution Strengthening

- Alloying a metal with impurity atoms is called solid-solution strengthening.

- Small substitutional impurities introduce compressive strains

- Large substitutional impurities introduce tensile strains

- This may cancel out the tensile and compressive strains located along the slip line.

- Alloys are usually stronger than pure metals.

7.3   Strain Hardening

- Strain hardening also known as cold work is the increase in strength and hardness that results from plastic deformation.

- Percentage cold work can be calculated by the equation

$$\%CW = \frac{A_0 - A_d}{A_0} \times 100 \tag{48}$$

  where A_0 is the original cross-sectional area and A_d is the final cross-sectional area.

- The dislocation density increases which is why cold work strengthens the material. The motion of a dislocation is hindered by the presence of other dislocations.

7.4   Annealing Treatment

- The processes of strain hardening can be reverted by two different processes that occur at elevated temperatures: recovery and recrystallization, which may be followed by grain growth.

- Tensile strength decreases and ductility increases.

7.4.1   Recovery

- Some stored internal strain energy is relieved by atomic diffusion.

- There is some reduction in the number of dislocations.

- The electrical and thermal conductivity is recovered to its precold-worked state.

7.4.2   Recrystallization

- The recrystallization temperature is the temperature at which recrystallization reaches completion in 1 hour.

- Grains with high strains are replaced with new, unstrained grains.

- The metal becomes more ductile.

- There is a significant reduction in the number of dislocations.

- All the internal strain energy is relieved.

- Processes carried out at temperatures above the recrystallization temperature is a process termed hot working.

7.4.3   Grain Growth

- After recrystallization is complete, the strain-free grains will continue to grow if the metal specimen is left at elevated temperatures.

- Large grains will grow at the expense of smaller grains.

- Grain diameter varies with time t according to the equation

$$d^n - d_0^n = Kt \tag{49}$$

  where d_0 is the initial grain diameter.

8 Fractures

8.1 Brittle Fracture

- Brittle fraction takes place without any appreciable deformation and by rapid crack propagation.

- **Transgranular Fracture** - Fracture cracks pass through the grains.

- **Intergranular Fracture** - Fracture cracks pass along the grain boundaries.

8.2 Fracture Mechanics

- If it is assumed that a crack is similar to an elliptical hole through the plate. The maximum stress at the crack tip may be approximated by,

$$\sigma_m = 2\sigma_0 \left(\frac{a}{\rho_t} \right)^{1/2}, \tag{50}$$

  where σ_0 is applied tensile stress, a is the length of the surface crack or half the length of an internal crack, and ρ_t is the radius of curvature at the crack tip. Fracture toughness is defined as

$$K_c = Y\sigma_c\sqrt{\pi a} \tag{51}$$

  where σ_c is the critical stress for crack propagation, Y is a parameter which depends on both crack, specimen sizes, geometries, the manner of load application, etc., and a is the surface crack length.

- **Plane Strain** - There is no strain component perpendicular to the front and back faces.

8.3 Impact Testing

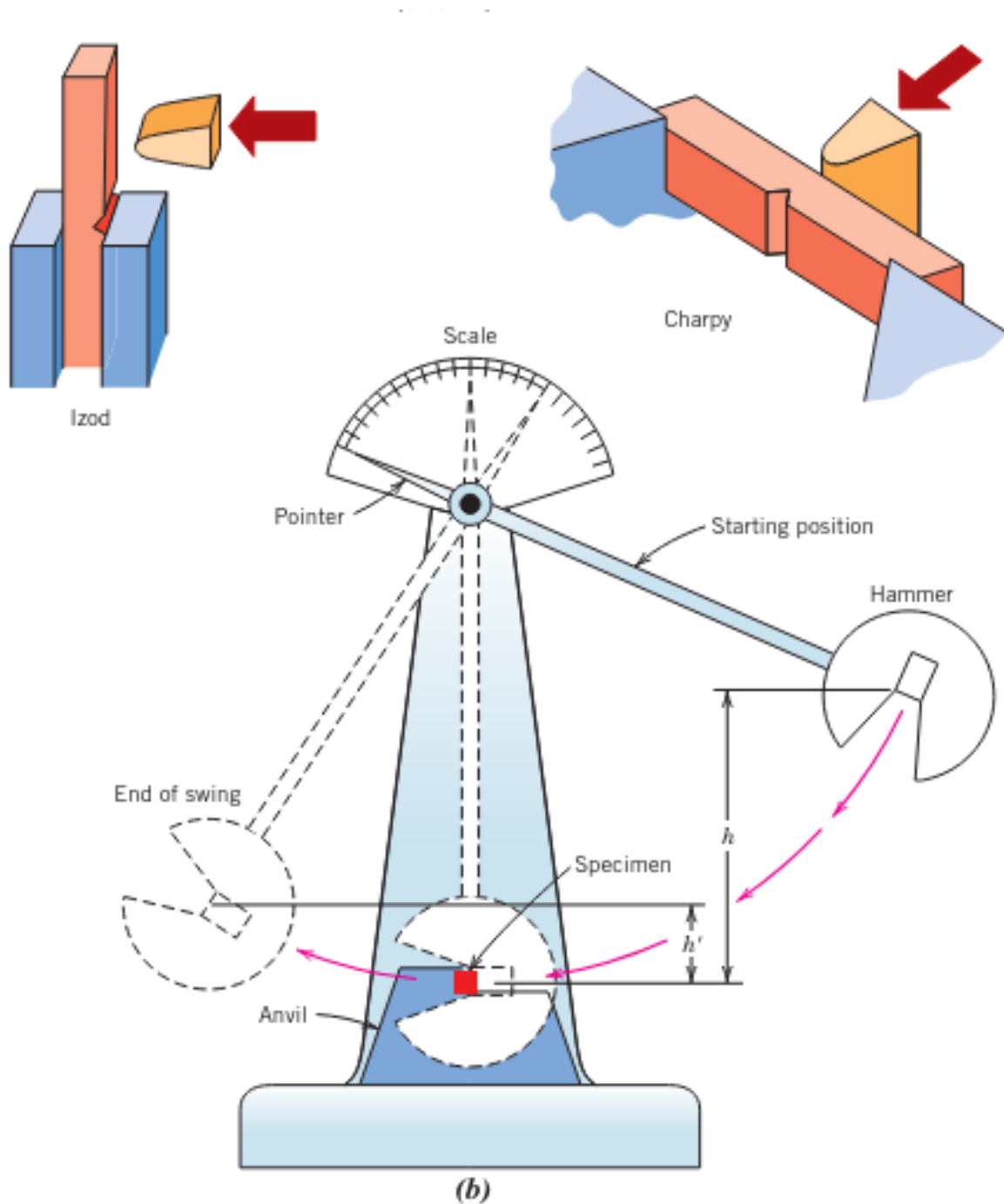- The Charpy and the Izod tests are used to measure impact energies.

Figure 25: The specimen is positioned at the base as shown. Upon release, a knife edge mounted on the pendulum strikes and fractures the specimen at the notch, which acts as a point of stress concentration for this high-velocity impact blow.

- One of the primary uses of impact testing is to determine the ductile-to-brittle transition temperature.

- At high temperatures, impact energy is high corresponding to a ductile mode of failure, and at low temperatures, the material is brittle.

8.4   Cyclic Stresses

- **Fatigue** - The failure of a material due to fluctuating stresses.

- Several parameters characterize the fluctuating stress cycle: the stress amplitude σ_a, the mean stress σ_m, the stress ratio $R = \sigma_{\min}/\sigma_{\max}$, and the stress range σ_r.

- A stress amplitude (S) vs. number of cycles to failure (N_f) curve can be used to determine the **fatigue strength** of a material defined as the stress level at which failure occurs after a specified number of cycles.

- **Fatigue Life** - The number of cycles to failure at a specified stress level.

9 Material Selection

1. Determine objective (ex. Minimize mass, minimize cost)

2. Identified fixed variables and constraints.

3. Determine free variables.

4. Solve for the free variables in terms of the constraints.

5. Substitute the free variables into the objective function.

6. Separate the variables into 3 categories: [Functional][Geometric][Material].

7. Your MPI would be the variables in the materials' category.

10 Phases

10.1 Binary Isomorphous Phase Diagrams

- Binary phase diagrams consist of two components. In this case, we'll consider two alloys.
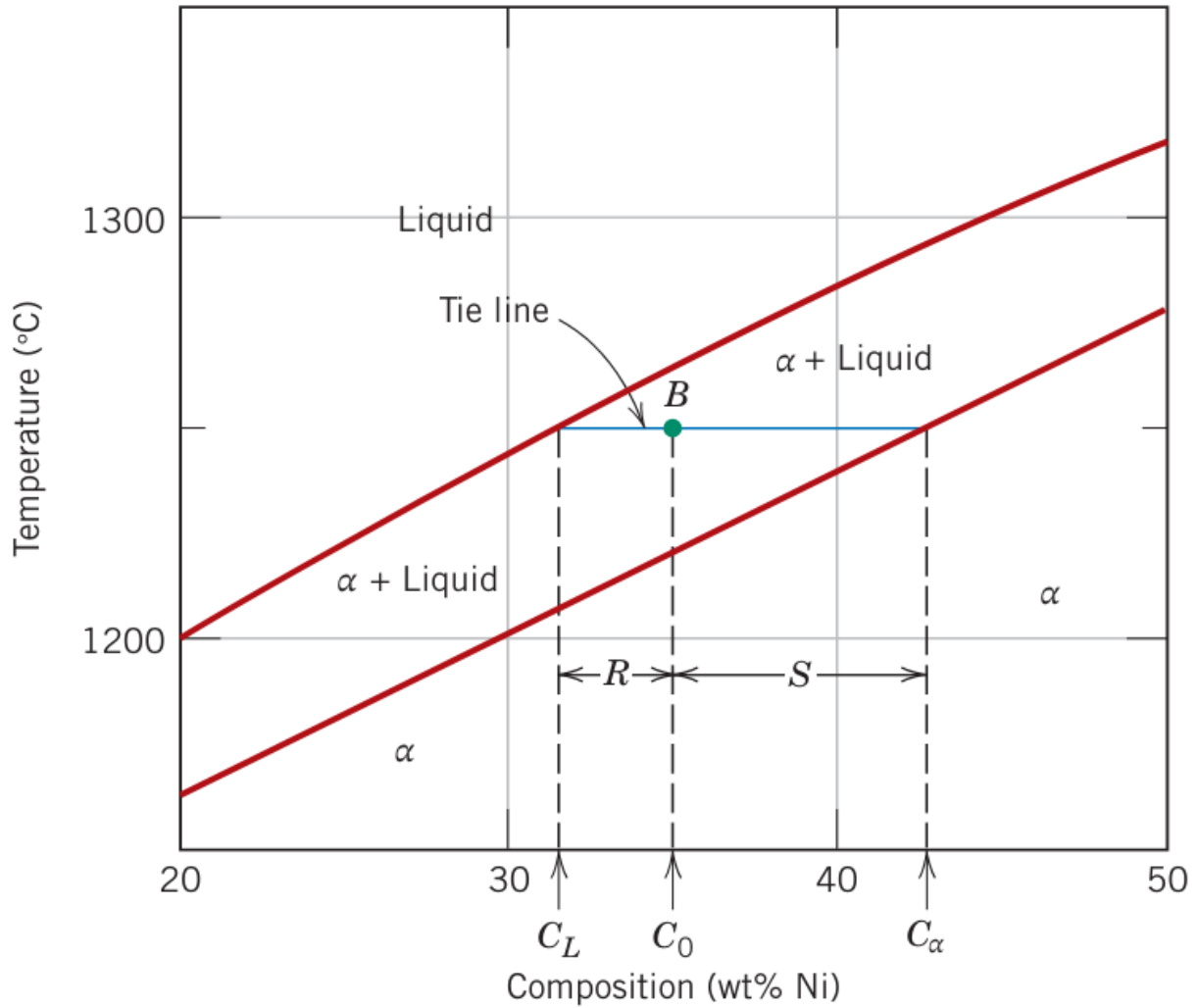
Figure 26: The binary phase diagram for the copper nickel system.

- As shown in the diagram above, the copper nickel system is **isomorphous** since it consists of a solid α phase and a liquid L phase.

- In between the two phases is we can draw a horizontal line called the **tie line** to determine the percent weight composition of each phase.

- For example, the amount of solid copper at point B can be calculated as

$$C_B = \frac{R}{R+S} \tag{52}$$

10.2 Binary Eutectic Phase Diagrams

- A eutectic phases diagram is similar to an isomorphous phase diagram but with an extra phase β.
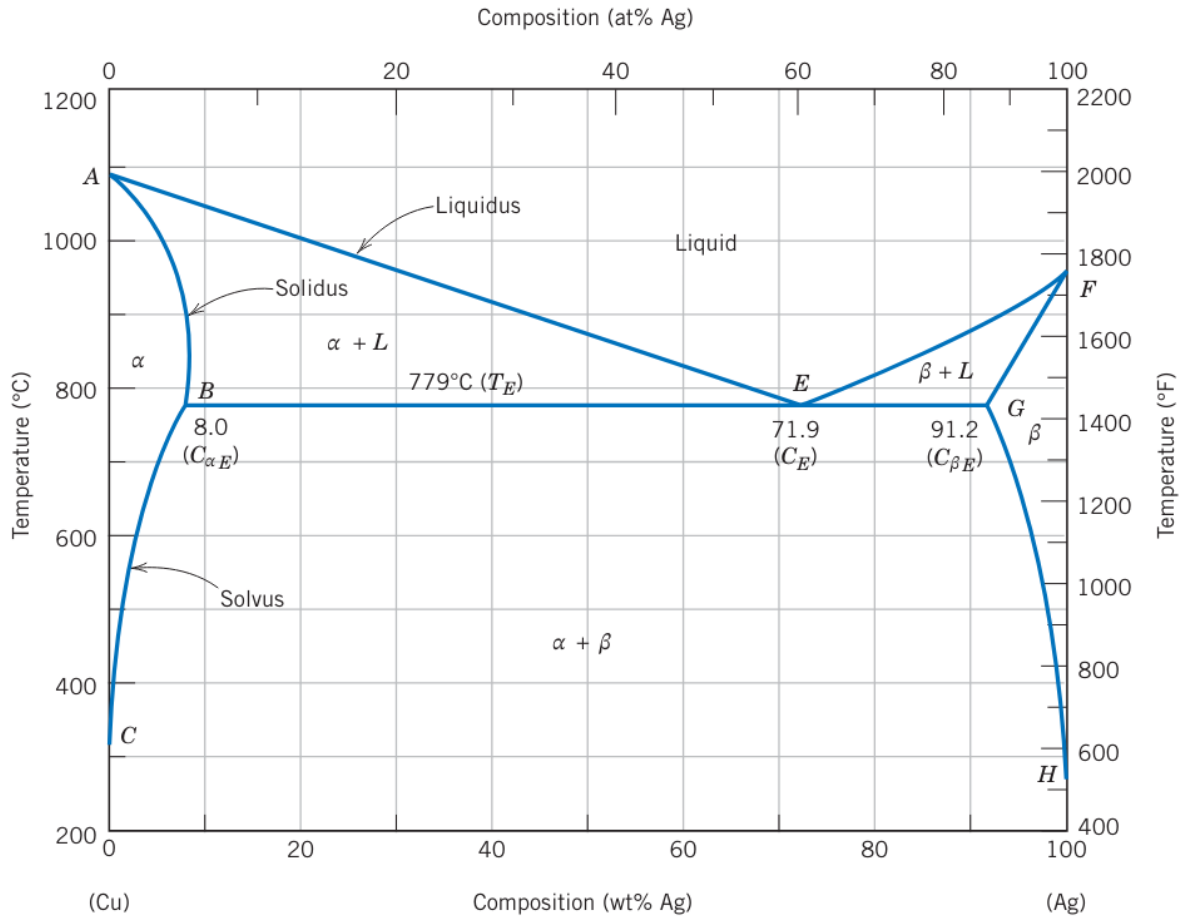
Figure 27: The copper-silver phase diagram.

- As shown in the copper-silver phase diagram above, the α phase has silver as the solute while the β phase has copper as the solute.

- **Eutectic Reaction** - One liquid phase will transform into two solid phases when cooled. In the diagram above, this may occur at point E.

- **Eutectoid Reaction** - One solid phase transforms into two other solid phases.

- **Peritectic Reaction** - One solid phase transforms into a liquid phase and a different solid phase.

10.3 Gibbs phase rule

- Gibbs phase rule states that

$$P + F = C + N \tag{53}$$

where P is the number of phases, F is the number of degrees of freedom, C is the number of components, and N is the number of non-compositional variables (Variables not % weight in the diagram).

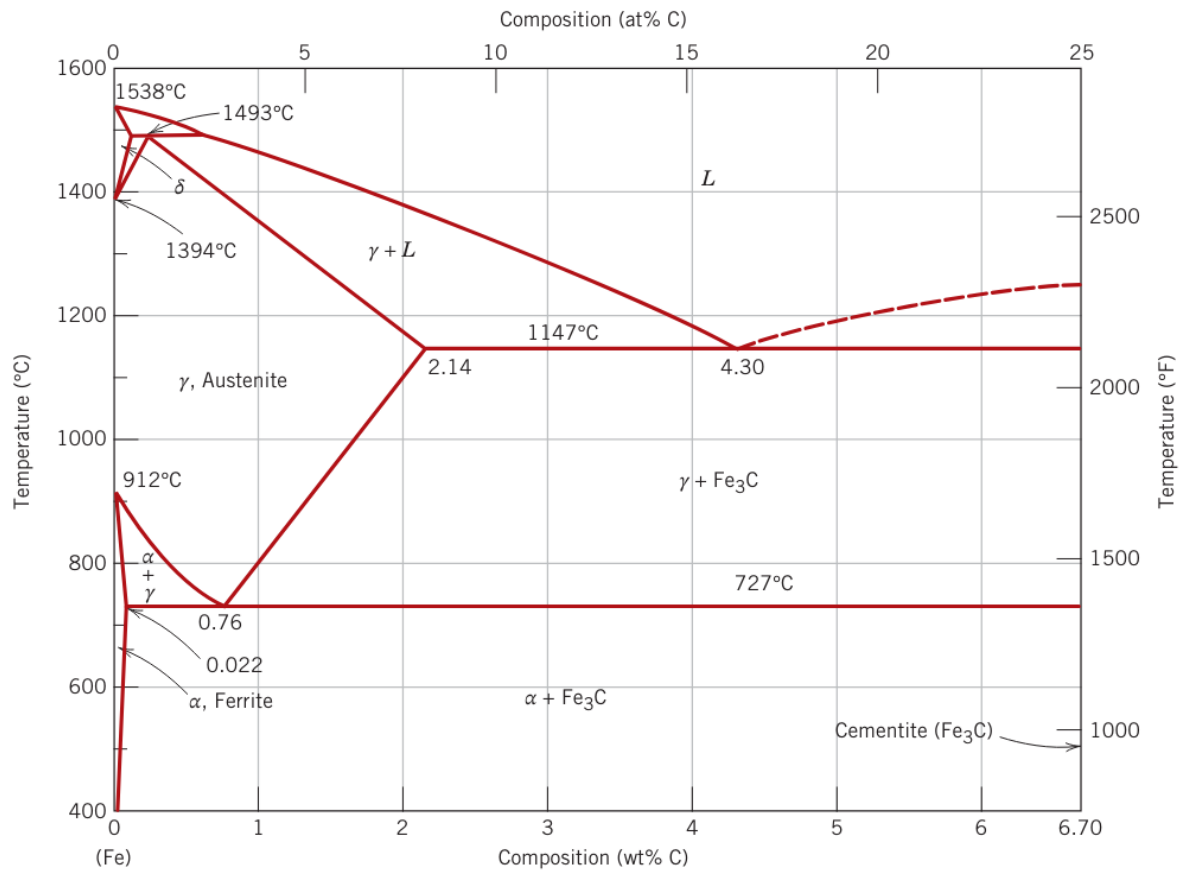## 10.4　The Iron-Iron Carbide Phase Diagram

Figure 28: The iron–iron carbide phase diagram.

- **Pearlite** forms at the Eutectoid of the iron-iron carbide phase diagram.

- **Proeutectoid Cementite**- forms before the eutectoid reaction.

11　Polymers

- Polymers with the same molecular formula but different structures are called isomers.

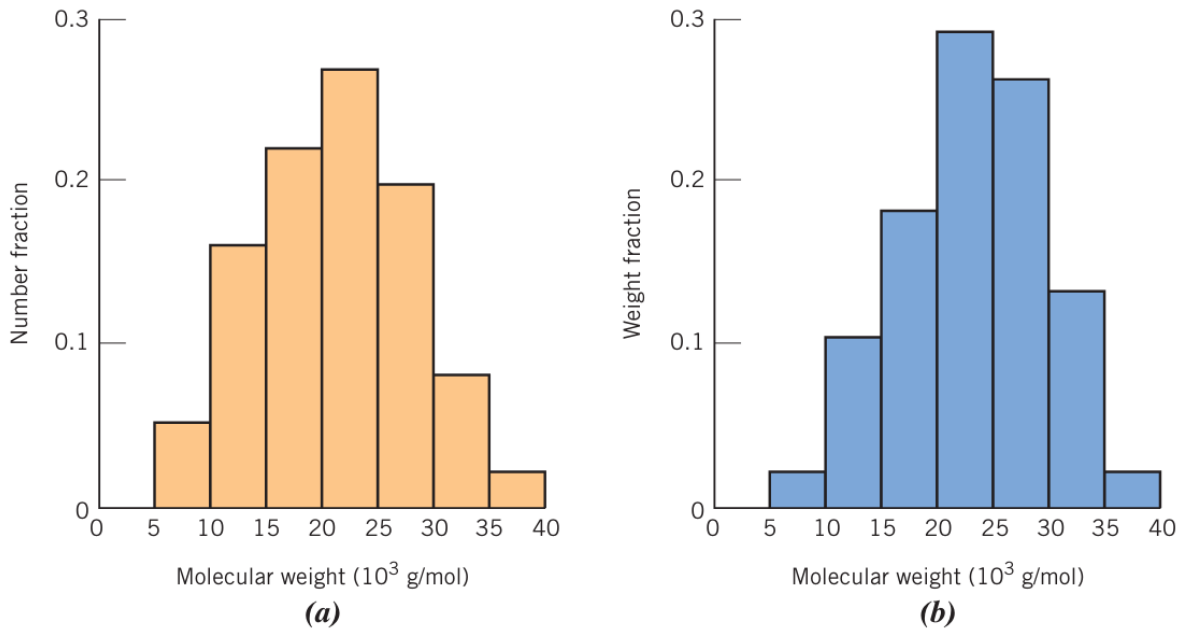## 11.1 Calculating Polymer Weight

Figure 29: Polymer weight distributions can be defined based on the number fraction or the weight fraction.

- The number average molecular weight can be calculated by the equation

$$\bar{M}_n = \sum x_i M_i \tag{54}$$

  where x_i is the number fraction of the polymer and M_i is the mean molecular weight of the size range.

- Likewise, the weight average molecular weight can be calculated by the equation

$$\bar{M}_w = \sum w_i M_i \tag{55}$$

  where w_i is the weight fraction of the polymer.

- The degree of polymerization is based off of the number average molecular weight.

$$DP = \frac{\bar{M}_n}{m} \tag{56}$$

  where m is the molecular weight of the repeating unit.
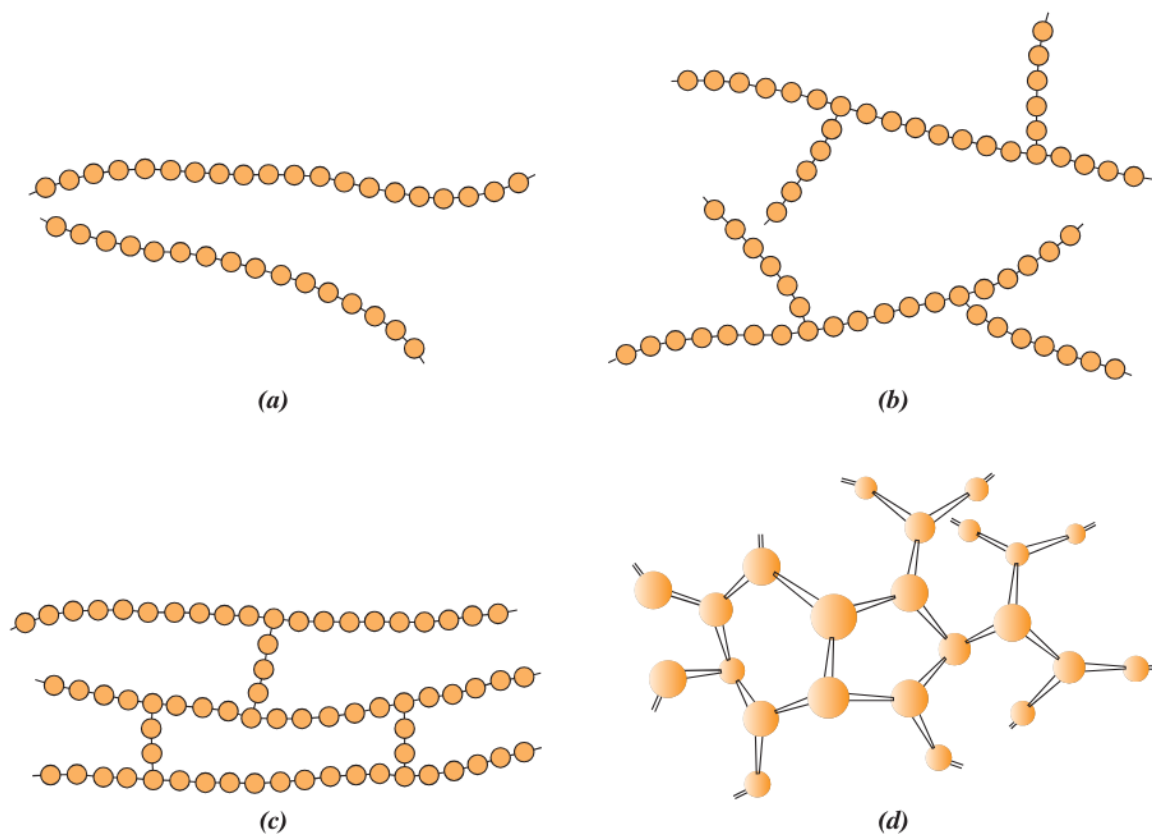
11.2   Polymer Structure

Figure 30: Schematic representations of (a) linear, (b) branched, (c) crosslinked, and (d) network (three-dimensional) molecular structures.

11.3   Molecular Configurations

- **Stereoisomerism** - The atoms are connected in the same order but differ in spatial arrangement.
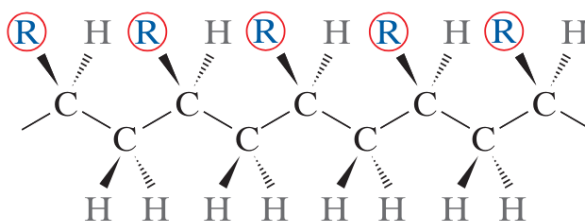- The following are some examples of one stereoisomer.

Figure 31: Isotactic configuration - all the R groups on the same side.
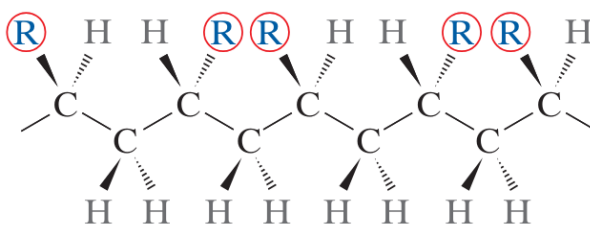

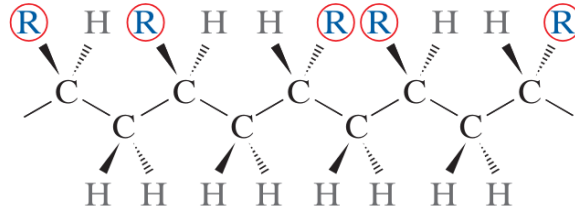Figure 32: Syndiotactic configuration - The R groups alternate sides.

Figure 33: Atactic configuration - The R groups are randomly positioned.

- **Geometric Isomerism** - A type of stereoisomer which forms from restricted rotation of a double bond. Can be either cis or trans.

11.4 Polymer Crystallinity

- Polymers are rarely 100% crystalline.

- The degree of crystallinity can be calculated by the equation

$$\%\text{Crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100 \tag{57}$$

where ρ_c is the density of the crystalline polymer, ρ_s is the density of the polymer specimen, and ρ_a is the density of the amorphous polymer.

12 Electrons

- **Fermi Energy** - The energy corresponding to the highest filled state at 0 K is called the Fermi energy.

- **Band Gap** - The energy difference between the highest filled state and the lowest unfilled state.

- Frequency is given by the equation

$$f = \frac{c}{\lambda}. \tag{58}$$

- Energy is given by the equation

$$E = hf \tag{59}$$

where h is Planck's constant.

- A photon is able to jump the band gap if its energy is greater than the band gap.