Mat E 272

Final Exam Review Topics

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Callister: chapters 8 – 19

Chapter 8 – Failure Mechanisms

I. Fracture

Definition: Fracture is a separation of an object into two or more pieces in response to active stresses below the melting temperature of the material.

Two steps in the process of fracture:

- Crack initiation
- Crack propagation

Simple fracture may occur by one of two methods, ductile or brittle

Dependent upon the plastic deformation of the material
Properties which influence the plastic deformation of a material:

- Modulus of elasticity
- Crystal structure
- Temperature (for many BCC metals and alloys)

Brittle fracture

- Absence of plastic deformation
- **Little or no plastic deformation and low energy absorption before failure.**
- A rapid propagation of cracks through a stressed material.
- The cracks usually travel so fast that you can't tell when the material is about to break
- little or no plastic deformation before failure
- Crack propagation is spontaneous and rapid
- propagation is perpendicular to the direction of the applied stress, forming an almost flat fracture surface
- Crack is *unstable*, since it continues to grow without the aid of additional stresses

This is the worst type of fracture because you can't repair visible damage in a part or structure before it breaks:

Ductile fracture:

- characterized by the occurrence of necking
- fracture produces a "cup-and –cone" structure
- most common form of ductile fracture
- Involves a substantial amount of plastic deformation and energy absorption before failure.
- **The fracture process usually consists of several stages:**
  (a) Initial necking
  (b) Cavity formation
  (c) Cavities form a crack
  (d) Crack propagation
  (e) Final shear
  occurs at an angle of 45°, where shear stress is at a maximum

Ductile vs. Brittle Fracture

- **"Brittle fracture" and "ductile fracture" are general terms describing two opposite extremes of the fracture spectrum.**
- **What are the factors that make a material lean toward one type of fracture as opposed to the other type?**

- **The first and foremost factor is <u>temperature</u>.**
    - higher temperatures → yield strength is lowered and the fracture is more ductile in nature
    - lower temperatures → yield strength is greater while the fracture is more brittle in nature
    - At moderate temperatures (with respect to the material) the material exhibits characteristics of both types of fracture.
    - Thus, temperature determines the amount of brittle or ductile fracture that can occur in a material (mainly in BCC, HCP but not so much for FCC).
- **Another factor is dislocation density.**
    - The higher the dislocation density, the more brittle the fracture will be in the material.
    - Recall how dislocations interact; as dislocation density increases due to applied stresses above the yield point, it becomes increasingly difficult for the dislocations to move because their strain fields interact with each other.
    - A material that already has a high dislocation density can only deform but so much before it fractures in a brittle manner.
- **The third factor is grain size.**
    - As grains get smaller, fracture becomes more brittle.
    - This phenomena is due to the fact that in smaller grains, dislocations have less space to move before they hit a grain boundary.
    - When dislocations can not move very far before fracture, then plastic deformation decreases. Thus, the material's fracture is more brittle.

II. Crack Initiation and Propagation

- **Cracks usually initiate at some point of <u>stress concentration</u>**
    - Typical culprits include scratches, fillets, threads, and dents
    - Pre-existing internal cracks play a major role
- **Crack propagation occurs in two stages:**
    - **<u>Stage I</u>**: propagates slowly along crystallographic planes of high shear stress and may constitute either a large or small fraction of the fatigue life of a specimen
    - **<u>Stage II</u>**: the crack growth rate increases and changes direction, moving perpendicular to the applied stress

Crack propagation across grain boundaries is known as <u>transgranular</u>, while propagation along grain boundaries is termed <u>intergranular</u>

- **Transgranular fracture:**
    - The fracture travels <u>through the grain</u> of the material.
    - The fracture changes direction from grain to grain due to the different lattice orientation of atoms in each grain.

- when the crack reaches a new grain, it may have to find a new path or plane of atoms to travel on because it is easier to change direction for the crack than it is to rip through.
- Cracks choose the path of least resistance. You can tell when a crack has changed in direction through the material, because you get a slightly bumpy crack surface.

- **Intergranular fracture**

  - The crack path follows the grain boundaries, and not through the actual grains.
  - Usually occurs when the grain boundary is weak and brittle
    - i.e., cementite in Iron grain boundaries.

III. Fracture Mechanics

- **Use of fracture analysis to determine the critical stress at which a crack will propagate and lead to failure**
- **The stress at which fracture occurs is termed fracture strength**
  - For a brittle elastic solid the theoretical fracture strength is around E/10, where E is the modulus of elasticity
  - This strength is a function of the cohesive forces between the atoms
  - Experimental values lie between 10 and 1000 times below this value
  - This is due to the presence of small flaws occurring throughout the material, referred to as **stress raisers** (Griffith theory of fracture).
- **If one assumes that the crack is elliptical with it's long axis perpendicular to the applied stress, the maximum stress at the crack tip is:**

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

σ_o is the nominal applied tensile stress
ρ_t is the radius of curvature of the crack tip
a is the length of a surface crack (becomes $a/2$ for an internal crack)

  - Note that as the ratio (a/ρ) becomes smaller, the stress around the tip increases and exceeds the applied stress
  - The effect is most pronounced for short, sharp cracks
  - **Fracture will occur when the stress level exceeds this maximum value .**

- **The stress concentration factor, K, is given by**

$$K = \frac{\sigma_m}{\sigma_o} = 2\sqrt{\frac{a}{\rho_t}},$$

and gives the degree to which an applied load is amplified at the tip of a crack

Griffith theory:

- all brittle materials contain small cracks and flaws
- these flaws act as stress risers, increasing the local applied stress around sharp corner or discontinuities

- fracture occurs when the local stress exceeds the material's cohesive strength.
- **Describes crack propagation in brittle materials containing internal flaws**
- **The critical stress required for crack propagation in a brittle material is given by:**

$$\sigma_c = \left(\frac{2E\gamma_s}{\pi a} \right)^{1/2}$$

  - E = modulus of elasticity
  - γ_s= specific surface energy
  - (creation of nascent surfaces requires energy)
  - a = half the length of an internal crack
- **Applies only in cases where there is no plastic deformation present.**
  - A similar expression is obtained for ductile materials

IV. Fracture Toughness:

- Stresses near the crack tip of a material can be characterized by the stress intensity factor (or stress concentration factor), K,
- A critical value of K exists, similar to the value σ_c, known as fracture toughness given by:

$$K_c = Y\sigma\sqrt{\pi a}$$

σ is the critical stress for crack propagation, a is the crack length, and Y is a dimensionless parameter that depends on both the crack and specimen geometries (=a/W).

- **fracture toughness is a property that describes a material's resistance to brittle fracture when a crack is present**
- **Plain-strain fracture toughness, K_{Ic} depends on temperature, strain rate, and microstructure**
  - *Increases as grain size decreases*
  - *Decreases with increasing strain rate*
  - *Decreases with decreasing temperature….*

How do we characterize fracture?

Charpy Impact test

Procedure:

1. A notched bar-shaped specimen is clamed in the holder
2. The weight is released from a known height
3. After breaking the specimen, the pendulum swings on, reaching a height (lower than the initial height)
4. The difference in potential energy of the pendulum gives the energy required to break the specimen

DBT (Ductile-to-Brittle Transformation):

DBT is a consequence of slower dislocation mechanics in BCC metals compared with FCC.

- a large number of structural steels are included in the BCC classification category
- DBTT can fall between -100°C (-148 °F) and +100°C (212 °F), depending on composition
- Cold water temperatures, about 35 degrees Fahrenheit, can cause certain steels to crack in a brittle manner, like glass, instead of the normal ductile, twisting, tearing manner.

V. Fatigue:

Definition: Nucleation and growth of cracks in a material undergoing time-varying loading (at levels <u>below</u> the yield strength)

Estimated to be responsible for ~ 90% of all failures in metals

- **As a result of fatigue, materials can fracture at stress levels well below yield strength.**
- Fatigue is insidious
- Little, if any, large-scale plastic deformation before failure
- Types of fatigue loading:

  I. Reversed stress cycle:
  II. Repeated stress cycle:
  III. Random stress cycle:

Chapter 9 - Phase Diagrams

II. Introduction

A. Terminology

1. Phase - a homogeneous portion of a system that has uniform chemical and physical characteristics - i.e., the same crystal structure throughout with no *discontinuous* changes in composition or dimensions
2. Component - the chemical elements (or occasionally compounds) which compose an alloy
3. Solvent - the component of a solution present in the greatest amount
4. Solute - the component of a solution present in a minor amount (note that the distinction between solute and solvent is sometimes blurred)
5. Solubility Limit - the maximum concentration of solute which can be dissolved in a solvent
6. Equilibrium - a system in its most stable or lowest energy configuration - reaching equilibrium may take a very long time

B. Sugar - Water Phase Diagram

III. Solid State Phase Diagrams

A. Binary Isomorphous Systems (Cu-Ni)

1. Contain a single solid phase
2. Melting point range for all but pure components
3. Phase compositions in 2 phase regions - given by solubility limits of each phase
4. Phase amounts in 2 phase regions - given by position along tie line
5. Inverse Lever Arm Rule
    a. **Amount of given phase proportional to the length of tie line on opposite side of line**
    b. **Calculated from phase compositions at solubility limits and composition of overall alloy**
6. Equilibrium melting and solidification
7. Non-equilibrium solidification
    a. **Coring - varying composition of solid phase(s)**
    b. **Suppression of melting point**
8. Mechanical properties
    a. **Solid solution strengthening due to solute addition**
    b. **Ductility reduction usually (but not always) occurs with strengthening**

B. Binary Eutectic Systems
(Eutectic - having a low melting point)

1. Eutectic point (invariant point) - melting at a specific temperature
2. Three phases in equilibrium at eutectic point compositions and temperature
3. L → a + b
    a. **Written as a cooling reaction**
    b. **Phase compositions and temperatures included**
4. Terminology
    a. **Terminal solid solutions - phases containing the pure components**
    b. **Hypoeutectic - having a composition less than eutectic**
    c. **Hypereutectic - having a composition greater than eutectic**
    d. **Proeutectic phases - form before (higher T) eutectic**
    e. **Liquidus - line above which all of alloy is liquid**
    f. **Solidus - line below which all of alloy is solid**
    g. **Solvus - boundaries between solid phase regions**
5. Eutectic microstructures
    a. **Eutectic alloys - often lamellar**

   b. **Precipitation from terminal solid solutions**
   c. **Hypo- and Hypereutectic alloy structures**

C. Phase Diagrams with Intermediate (or Intermetallic) Phases

1. Phases present other than terminal solid solutions
   a. **Intermediate phases - solid solutions at intermediate compositions**
   b. **Intermetallic compounds - stoichiometric phases with very small range of solubility**
2. Eutectoid reaction (Eutectic like)
   a. **a → b + γ**
   b. **Cools from one solid phase to two different solid phases**
3. Peritectic reaction
   a. **a + L → b**
   b. **Cools from a mixture of liquid and a solid phase to a different solid phase**
4. Peritectoid reaction
   a. **a + b → γ**
   b. **Cools from a mixture of two solid phases to a different solid phase**
5. Congruent transformations
   a. **L → a or a → b**
   b. **A transformation with no change in composition of the phases**

IV. Iron-Carbon Alloys (Fe-Fe_3C phase diagram)

A. Phases

1. Ferrite - α iron
2. Austenite - γ iron
3. Delta ferrite - δ iron
4. Cementite (Iron Carbide) - Fe_3C

B. Invariant reactions

1. Eutectic transformation - L → γ + Fe_3C
2. Eutectoid transformation - γ → α + Fe_3C
3. Peritectic transformation - δ + L → γ

C. Eutectoid microstructures

1. Pearlite from eutectoid composition alloy
2. Hypoeutectoid alloys - proeutectoid ferrite
3. Hypereutectoid alloys - proeutectoid carbide
4. Rapidly cooled alloys
   a. **Bainite**
   b. **Martensite**

Chapter 10 - Phase Transformations

V. Nucleation and Growth Transformations

A. Nucleation time - slow transformation as nuclei form
B. Growth time - rapid growth initially followed by slowing growth (Fig 10.1)
C. Rate of reaction generally taken as $r = 1/t_{0.5}$
D. Nucleation process - fastest when old phase(s) most unstable
E. Growth rate - fastest at higher temperatures (diffusion)
F. Reactions on heating - faster as T increases
G. Reactions on cooling
1. Nucleation faster as T decreases
2. Growth rate faster as T increases

VI. Fe-Fe_3C Transformations

A. Pearlite transformation
1. Rate increases as T decreases - down to about 550 □ C
2. Higher nucleation rate at lower T gives finer Pearlite
3. Isothermal Transformation Diagrams - transformation from austenite to ferrite and carbide when held at constant T

B. Bainite transformation
1. Homogeneous nucleation at lower T produces Bainite
2. Transformation rate decreases as T decreases due to slower growth
3. Rapid cooling required to form Bainite

C. Spheroidite production
1. Coarse carbide particles in a ferrite matrix
2. NOT produced directly from austenite
3. Reheating of some other ferrite and carbide structure to coarsen carbides

D. Martensite
1. Rapid cooling of austenite to temperature where austenite is very unstable but transformation rate to ferrite and carbide is very slow
2. Body centered tetragonal lattice produced (BCC ferrite with supersaturation of carbon)
3. Athermal transformation - not time dependent
4. Degree of transformation dependent on temperature (M_s & M_f)

E. Tempered Martensite
1. Produced by reheating of Martensite
2. Martensite transforms to very fine ferrite and carbide
3. Structure similar to Bainite but easier to produce
4. Potential for warping and cracking in quench

F. Proeutectoid phase formation
1. Phases form only at higher temperatures where diffusion is fast
2. Proeutectoid ferrite for hypoeutectoid alloys
3. Proeutectoid carbide for hypereutectoid alloys

VII. Isothermal Transformation Diagrams

A. Applicability
1. Describes <u>only</u> the transformation of austenite when held at a fixed temperature
2. After austenite has been transformed, IT diagram no longer applies
3. Reheating will <u>not</u> reverse the transformation
4. IT diagrams apply to
   a. a specific alloy composition
   b. a specific austenitizing temperature and time
   c. a specific austenite grain size

B. Plain Carbon Steel Alloys

1. Eutectoid Steel IT
    - **a. Pearlite produced at higher temperatures - becomes finer as transformation T decreases**
    - **b. Bainite produced at medium temperatures - becomes finer as transformation T decreases**
    - **c. Martensite produced when quenched**
2. Hypoeutectoid Steel IT
    - **a. Proeutectoid ferrite produced if transformed above or just below eutectoid T**
    - **b. At lower T's, no proeutectoid regions**
3. Hypereutectoid Steel IT
    - **a. Proeutectoid carbide produced if fully austenitized and transformed above or just below eutectoid T - NOT desirable**
    - **b. At lower T's, no proeutectoid regions**
4. Martensite transformations
    - **a. M_s & M_f decrease as carbon content increases**
    - **b. Higher carbon gives more strained M lattice**

C. Alloy Steels

1. Alloying elements used to slow transformations (more diffusion required)
2. Pearlite transformation slowed more than bainite
3. Slower cooling and bainite formation possible

VIII. Continuous Cooling Transformation Diagrams

A. CCT diagrams shifted to right and down from IT diagrams

B. Represent more realistic cooling in manufacturing

IX. Mechanical Behavior

Effect of carbon content on mechanical properties

1. Higher C - higher strength and hardness
2. Higher C - lower ductility and toughness

B. Effect of microstructure on mechanical properties

1. Finer distribution of carbide - higher strength and hardness
2. Finer distribution of carbide - lower ductility and toughness

Chapter 11 - Thermal Processing of Metal Alloys

X. Annealing– heating followed by slow cooling

- ***A. Process Annealing***
  1. Heating to reduce effects of cold work
  2. Recrystallization anneal
- ***B. Stress Relief Annealing***
  1. Low temperature anneal to reduce internal stresses
  2. Recrystallization does NOT occur
- ***C. Ferrous Alloys (Steels)***
  1. Critical temperatures (solvus lines)
     - **a. A_1 – lower critical temperature (eutectoid temperature) below which ferrite and carbide are stable**
     - **b. A_3 – upper critical temperature above which austenite is found and below which proeutectoid ferrite is stable**
     - **c. A_{cm} – upper critical temperature above which austenite is found and below which proeutectoid carbide is stable**
  2. Full annealing – slow cooling to achieve near equilibrium
     - **a. Heat to 15-40□ C above A_3 (hypoeutectoid) or A_1 (hypereutectoid) until in equilibrium (usually about 1 hr at temperature)**
     - **b. Slow cool (furnace cool) to produce coarse pearlite and proeutectoid phase**
  3. Normalizing – faster cooling to achieve finer and more homogeneous structure
     - **a. Heat to 55-85□ C above A_3 or A_{cm} to produce homogeneous austenite**
     - **b. Air cool to produce fine pearlite with little or no proeutectoid phase**
  4. Spheroidizing – heat to soften steel
     - **a. Heat to just below A_1 and hold there for approximately 24 hours**
     - **b. Coarse carbides in a ferrite matrix produced**

XI. Hardening Processes for Steels

- ***A. Form Martensite by austenitizing followed by rapid cooling***
- ***B. Hardenability***
  1. Describes how easily a steel can be quenched to form martensite
     - **a. High hardenability – can form martensite with a relatively slow cooling rate**
     - **b. Low hardenability – requires a very fast cooling rate to produce martensite**
  2. NOT the same as hardness
- ***C. Jominy End-Quench Test***
  1. Used to measure hardenability
  2. Steel is quenched from one end of a bar with varying cooling rates along the length of the bar
  3. Flat(s) ground (while preventing structure changes from grinding)
  4. Hardness measurement every 1/16" for ½ inch and every 1/8" for 1½" distance from quenched end (DQE)
  5. Hardenability curve (HRC vs. DQE) shows depth of hardening
  6. Relation of DQE to cooling rate
  7. Maximum hardness based on C content
  8. Hardenability based on diffusion rate (due to alloying)
  9. Higher carbon content gives higher hardenability
  10. Hardenability a range of values due to alloy variations
  11. "H" grade steels guaranteed to produce narrow band of hardenability
- ***D. Effects of Sample Size and Geometry, Quench Medium***
  1. Size effects for round bars
  2. Medium effects

a. **Water**
b. **Oil**
c. **Air**

E. Tempering

1. Effects of tempering temperature – hardness reduced with higher temperatures, very sensitive to temperature
2. Effects of tempering time – hardness reduced with longer times but effects are small

XII. Precipitation (Age) Hardened Alloys

A. Second phase precipitates upon cooling from a solid solution

1. Phase diagram must have high solid solubility at elevated temperature
2. Solubility must decrease significantly at lower temperatures

B. Processing

1. Solution heat treating
   a. **Alloy heated to elevated temperature to produce solid solution**
   b. **Quenched to room temperature to preserve supersaturated solid solution**
2. Precipitation process
   a. **Alloy raised to temperature where diffusion will allow second phase (precipitate) to form**
   b. **Precipitation temperature may be at room temperature in some alloys**
   c. **Stages of precipitation**
      1. Solid solution
      2. Coherent precipitate
      3. Incoherent precipitate – second phase
      4. Overaged precipitate
3. Effects of aging temperature
4. Combined strain hardening and age hardening
   a. **Ordinarily cold worked in solution treated condition**
   b. **Cold work after aging may lead to cracking**

Chapter 12 - Metal Alloys

XIII. Fabrication Processes

A. Forming Operations

1. Cold working - deformation at temperature where a deformation structure is created
2. Hot working - deformation at temperature where dynamic recrystallization can occur
3. Forging - forcing metal to take the shape of a die by applying high pressure
4. Rolling - passing metal through restricted rollers to reduce thickness and/or produce a shape
5. Extrusion - pushing metal through a restricted opening to change its dimensions and/or shape
6. Drawing - pulling metal through a die to change its dimensions and/or shape

B. Casting Operations

1. Sand casting - pouring molten metal into a cavity formed by packing sand around a pattern
2. Die casting - forcing molten metal under pressure into a permanent cavity in a metal mold
3. Investment casting (lost wax process) - pouring molten metal into a cavity created by a wax pattern surrounded by a ceramic shell
4. Continuous casting - casting of a continuous 'ingot' strand - not normally used to produce a finished product

C. Powder Metallurgy

1. Powdered metal compacted under high pressures to produce a 'green' compact
2. Green compact is sintered (heated) to produce fusion of the metal powder

XIV. Ferrous Alloys

A. Steels - up to approximately 1.4 % C

1. Low alloy
    - **a. Low carbon < 0.25 % C**
        1. Plain carbon
            - *a. Low carbon steels - not heat treatable for higher strength (except by carburizing or other surface treatment)*
            - *b. Inexpensive and easily formable*
        2. High strength low alloy (HSLA)
            - *a. Small amounts of alloying elements to increase strength*
            - *b. Improved corrosion resistance*
            - *c. Higher cost*
    - **b. Medium carbon 0.25 to 0.60 % C**
        1. Plain carbon
            - *a. Difficult to harden except for small parts*
        2. Low alloy
            - *a. Alloying elements added to improve hardenability*
            - *b. Generally quenched and tempered or cooled to form bainite*
    - **c. High carbon > 0.60 % C**
        1. Plain carbon
            - *a. Low cost tool steels*
            - *b. Hardened only by severe quenching*
            - *c. Soften easily in high speed cutting*
        2. Alloy tool steels
            - *a. Alloying elements added to form stabile carbides*
            - *b. Hardened by moderate quenching*

c. *Hold edge at high speeds*

2. High alloy
   - **a. Stainless steels**
     1. Austenitic
        - *a. FCC stabilized by Ni and/or Mn additions*
        - *b. Not hardenable*
     2. Ferritic
        - *a. BCC stabilized by Cr additions*
        - *b. Low carbon, not hardenable*
     3. Martensitic
        - *a. FCC and BCC lattices possible*
        - *b. C sufficient to form martensite*
     4. Precipitation Hardenable (PH)
        - *a. Alloy precipitate formed*
        - *b. Not hardenable by eutectoid transformation*

B. Cast Irons - carbon content in eutectic region

1. Gray Iron

a. 2.5 - 4.0 wt. % C and 1.0 to 3.0 wt. % Si
b. Graphite flakes form on solidification
   Sharp tips act as stress concentrators
c. High damping capability
d. Weak in tension
e. Alloy matrix
   1. ferrite
   2. pearlite

2. Ductile (Nodular) Iron

a. Graphite spheres form on solidification
b. Additions of Mg or Rare Earths to change surface tension of C
c. More ductile than gray iron
d. Alloy matrix
   1. ferrite
   2. pearlite
   3. martensite (tempered)

3. White Iron

a. Based on metastable Fe-Fe_3C phase diagram
b. Low Si (<1%) and moderate C to alloy metastable Fe-Fe_3C alloy
c. High hardness and wear resistance, quite brittle

XV. Nonferrous Alloys

A. Copper and Alloys

1. Copper (nominally pure)
   a. High conductivity
   b. Soft and malleable
2. Brass
   a. Cu-Zn alloys
   b. a -brasses
      1. single phase FCC lattice
      2. soft and ductile
   c. b -brass
      1. mixture of a and b ' (ordered b phase) phases
      2. heavily strengthened by presence of hard b ' phase
3. Bronze
   a. Cu alloyed with Sn, Al, Si and/or Ni

b. Strong with good corrosion resistance

4. Precipitation hardened Be-Cu alloys
    a. High strength and tough
    b. Reasonably good conductors
    c. Electrical contacts and springs
    d. High strength tools and parts

B. Aluminum and Alloys

1. Wrought alloys
    a. Designed to be formed by working processes
    b. Heat treatable alloys can form a precipitate
    c. Non-heat treatable alloys strengthened by solid solution only
2. Cast alloys
    a. Designed to be formed only by casting - generally brittle if deformed
    b. Heat treatable alloys are precipitation hardened
3. Temper designations
    a. Describe heat treatment/cold work processes
    b. F- as fabricated
    c. H - strain hardened
    d. O - annealed (softened)
    e. T - hardened - various subtypes indicating combinations of cold work and aging

C. Other Nonferrous Alloys

1. Magnesium alloys
    a. Used for their light weight
    b. Chemically reactive, corrode easily

2. Titanium alloys
    a. High strength, low weight alloys
    b. Corrosion resistant
    c. High cost

3. Refractory metals
    a. High strength strongly bonded metals
    b. Temperature resistant, but oxidize readily at high temperatures
    c. Used primarily as alloying elements

4. Superalloys
    a. Alloys based on Fe, Ni or Co
    b. High strength, corrosion resistance and temperature resistance
    c. Often include 10 or more other alloying elements

5. Noble metals
    a. Expensive, corrosion resistant metals such as Au, Ag, Pd, Pt, etc.
    b. Used for jewelry, catalysts, etc.

Chapter 13 – Ceramics

I. Ceramic Structures

D. Ionic ceramics

1. Ionic character based on difference in electronegativity
2. Charge neutrality required
3. Coordination number based on radius ratios of ions
4. AX Crystals
    a. **Rock salt (NaCl) CN = 6**
    b. **CsCl CN = 8**
    c. **ZnS CN = 4**
5. A_mX_p Crystals
   CaF_2
6. $A_mB_nX_p$ Crystals
   $BaTiO_3$

E. Silicate ceramics

1. Tetrahedral bonding - highly covalent
2. Crystalline SiO_2
3. Silica glasses - amorphous

F. Carbon polymorphs

1. Diamond - cubic crystal
2. Graphite - ordered structure in 2-D layers
3. Fullerenes - "buckyballs" - complex 3-D structures

II. Defects in Ceramics

G. Schottky defect - ion pair vacancy

H. Frenkel defect - cation vacancy/cation interstitial pair

I. Vacancies in crystals with polyvalent ions
e.g., FeO with Fe^{+2} and Fe^{+3}

J. Interstitial solute

K. Substitutional solute

Phase Diagrams

Usually based on pseudo-binary systems (each end member itself a compound, not a pure element)

Same rules and terminology applies as for binary metal phase diagrams

III. Mechanical Behavior

L. Flexure testing

M. Brittle fracture

N. Viscous flow in amorphous ceramics (creep)

Chapter 15 - Polymer Structures

I. Hydrocarbons and Polymers

O. Saturated Hydrocarbons (C_nH_{2n+2})

1. Covalent bonds in molecules
2. Weak van der Waals bonds between molecules
3. Melting point and strength increase with molecule size

P. Isomers - same chemical formula but different structure

II. Thermoplastic vs. Thermosetting

Q. Thermoplastic polymers

1. Large molecules bonded to each other with weak bonding forces
2. Soften on heating

R. Thermosetting polymers

1. 3-D network of strong (usually covalent) bonds throughout polymer structure
2. Smaller molecules may be trapped in the 3-D network
3. Will NOT soften on heating once 3-D structure is created

III. Common Polymers

S. Vinyls

1. Polymers based on mer C_2H_3X
2. Polyethylene
3. Polyvinyl chloride
4. Polypropylene
5. Polystyrene

T. Vinylidenes - Polymethyl methacrylate

U. Teflon - PTFE

V. Bakelite (Phenyl-formaldehyde) - thermoset

W. Other thermoplastics

1. Nylon 6,6
2. PET
3. Polycarbonate

IV. Polymerization

X. Monomer - basic building block of the polymer

Y. Mer - the smallest repeating unit of a polymer

Z. Addition polymerization

1. Active radical (such as HO·) breaks bond in monomer
2. Active site breaks bond in additional monomer and adds it to chain

V. Molecular Weight

AA. ***Polymer properties partially based on average molecular weight***

BB. ***- the number average molecular weight***

$$\overline{M_n} = \sum x_i M_i$$

CC. - the weight average molecular weight

$$\overline{M_w} = \sum w_i M_i$$

D. - Degree of polymerization - average number of mers per molecule

VI. Polymer Structures

DD. 'Random walk' arrangement for linear polymer mers able to rotate freely

EE. Branched polymers

FF. Crosslinked polymers (vulcanized)

GG. Network polymers (thermosets)

HH. Isomers

1. Stereoisomers - same bonds but different positioning of side groups on adjoining mers
    - **a. isotactic**
    - **b. atactic**
    - **c. syndiotactic**
2. Geometrical isomers - side groups bonded to same atoms but different positions within the mer
    - **a. cis-isoprene**
        1. natural rubber
        2. elastic material due to 'arched' mer
    - **b. trans-isoprene**
        1. gutta percha
        2. hard brittle material due to linear mer

II. Copolymers - more than one mer in a linear polymer

1. Random - random arrangement of mers in chain
2. Alternating - alternating arrangement of mers in chain
3. Block - blocks of each type of mer in chain
4. Graft - backbone of one mer and chains of other mer grafted into backbone

JJ. Crystallinity

1. Mers must have a regular arrangement in linear chain
2. Regions of crystallinity - never completely a crystal

Chapter 18 – Oxidation and Corrosion

I. Basic Concepts

a material is oxidized if its atoms lose electrons and is reduced if its atoms gain electrons.

Oxidation: a loss of one or more valence electrons , viz.
$M \rightarrow M^{(n+)} + (n)e^-$ (this occurs at the metal-scale interface)

Reduction: a gain of one or more valence electrons, (usually to form an ion)
$\frac{1}{2}O_2 + (n)e^- \rightarrow O^{(n)-}$ (this occurs at the scale-gas interface)

Most metals form stable oxide compounds when exposed to air
- oxides are usually more stable than pure metals

II. Oxidation Fundamentals

Types of oxidation:

1) Unprotective ("bad" oxidation)

A porous oxide film (like a sponge) forms on the surface of a metal, and because of the porosity, molecular oxygen penetrates to the metal surface. There, it reacts with the metal to form more oxide, the process continuing until all of the original metal is consumed.

oxygen (gas) is available (and consumed) at a constant rate

linear growth rate law. $y = c_1 t + c_2$

2) Protective ("good" oxidation)

A non-porous oxide film forms on the surface of a metal; because it is not porous, oxygen ions can only react with metal ions through *diffusion* (there is no direct penetration route). Hence, the growth rate decreases as the scale thickness increases

transport of metal and/or oxygen ions is by diffusion through the scale.

parabolic growth rate law $y^2 = c_4 t + c_5$

3 cases of protective oxidation:
1) metal ions diffuse through the scale; react at scale-gas interface
2) oxygen ions diffuse through the scale; react at scale-metal interface
3) both ions diffuse through the scale; react within the film

Pilling-Bedworth Ratio

the degree to which an oxide coating is likely to be protective is given by the "Pilling-Bedworth" ratio: $R = \frac{\left(\frac{A_o}{d_o}\right)}{\left(\frac{A_m}{d_m}\right)} = \frac{A_o d_m}{A_m d_o}$

where A_o and A_m are the atomic weights of the oxide and metal, respectively, and d_o and d_m correspond to the density of each. Physically, the P-B ratio gives the oxide volume produced per unit volume of metal consumed.

P-B < 1: porous and non-protective

1 < P-B < 2: protective

P-B > 2: non-porous but subject to large compressive stresses leading to *spalling*

III. Corrosion Fundamentals

Corrosion is the dissolution of a metal into an aqueous environment

The anode is the metal that dissolves, or corrodes (by giving up electrons) in an *anodic reaction*:

The cathode is the metals that accepts electrons from the anode and neutralizes the cations in a *cathodic reaction*:

If 2 metals are in contact (either by way of an electrolytic solution or by a wire), they will exchange electrons, according to their electronegativity difference.

There will be a net flow of electrons from the more electropositive (anode) to the electronegative (cathode) metal

Tables have been constructed listing the relative tendency for electron transfer between pairs of metals in their respective electrolytic solutions, and the respective voltages. This is called the standard EMF series.

If metal "A" falls below metal "B" on this list, "A" will most likely corrode and eventually disintegrate when electrically connected to "B"

If dissolved oxygen is present in an aqueous solution, the cathodic reaction becomes:

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

In other words, electrons from the anode combine with water and dissolved oxygen to form hydroxyl ions.
The hydroxyl ions react with the iron cations to form *ferric hydroxide*, $Fe(OH)_3$ a.k.a. **RUST**, which becomes an insoluble product

IV. Preventative Methods

Oxidation prevention: addition of an element that will form a dense, coherent oxide layer in which the mobility of both ions and electrons is low.

Example: addition of Cr to steel. Typically, *stainless steels* contain from 11 to 25 wt. % Cr; the Cr forms a Cr_2O_3 oxide scale which protects the bulk of the steel from subsequent oxidation.

Methods of reducing or avoiding the effects of corrosion:

1) **Avoid galvanic couples such as zinc and iron pipe connections**

2) **Avoid "duplex" microstructures (when possible)**
   dissimilar metals can exhibit galvanic effects (corrosion). This can also happen on a microscopic scale, within a material.

3) **Avoid heavily cold-worked regions where localized stress regions become anodic (differential cold-work)**

4) **Adopt cathodic protection methods**

5) **Galvanic protection (sacrificial anode)**

6) **Be aware of microstructural changes resulting from welding (weld decay)**

Chapter 19 - Electrical Properties

I. Electrical Conductivity

II. Ohm's Law – V = I R

III. Resistivity (Conductivity) –

IV. $$\rho = \frac{1}{\sigma} = \frac{RA}{l}$$

V. *Conduction by* electrons *or by* ions

I. Band Structures in Solids

II. Discrete energy levels in isolated atoms
III. Energy bands for valence electrons as the atoms come close together and bond
IV. Valence band - energy band containing valence electrons in lowest energy state
V. Conduction band - energy band with next highest energy levels beyond valence band - no electrons at lowest energy state
VI. Fermi energy - highest filled energy state at 0K (lowest energy state)
VII. Energy band gap - energy difference between energy of highest energy electron at 0K and the next empty state

III. Conduction Models

Metallic Materials

3. Very small energy band gap - highest filled state and next state adjacent to each other
4. Partially filled valence band
5. Overlapping valence and conduction bands

Insulators

6. Strong ionic or covalent bonding holds electrons tightly
7. Large energy band gap between filled valence band and conduction band
8. High amount of activation energy required to boost electron from valence to conduction band

Semiconductors

9. Weaker covalent bonding
10. Small energy band gap between filled valence band and conduction band
11. Small amount of activation energy required to boost electron from valence to conduction band

Mobility

12. Ability of an electron to move under the force of an applied electric field

$$\mu_e = \frac{v_d}{E}$$

13. Conductivity given by number of carriers, charge of carrier and mobility of carrier –

$$\sigma = n|e|\mu_e$$

KK. Electrical Resistivity

1. Metallic materials
    - **a. Temperature effects**
        1. Resistivity increases with temperature

2. Change approximately **linear** for metals in normal temperature range of application –

$$\rho_t = \rho_0 + aT$$

b. Alloying effects

1. Adding alloying elements to a pure material increases resistivity
2. Multiphase materials have net resistivity approximately proportional to resistivity and amount of each phase

c. Deformation effects - Cold work increases resistivity due to distorted lattice

IV. Semiconduction

LL. Intrinsic Semiconduction

1. Conduction due to excitation of valence electrons into conduction band
2. Equal number of electron carriers in conduction band and empty sites (holes) in valence band
3. Hole - treated as a positive carrier with charge magnitude same as electron (electrons actually move)

$$\sigma = n|e|\mu_e + p|e|\mu_h$$

4. Conductivity due to sum of conductivity of electrons and holes - where n = p for intrinsic conduction

MM. Extrinsic Semiconduction

1. Conduction ***primarily*** due to either electrons or holes
2. n-type extrinsic semiconduction
   a. Addition of impurity with extra valence electron
   b. Donor electron will have energy close to conduction band

$$\sigma \cong n|e|\mu_e$$

   c. n >> p at operating temperatures,
3. p-type extrinsic semiconduction
   a. Addition of impurity with one less valence electron
   b. Acceptor site will have energy close to valence band

$$\sigma \cong p|e|\mu_h$$

   c. p >> n at operating temperatures,

NN. Effects of Temperature on Conduction

1. Electron mobility decreases with temperature
2. Number of carriers increases with temperature in a semiconductor
3. Intrinsic semiconductors
   a. Equal numbers of n and p carriers
   b. Carriers increase faster than mobility decreases
4. Extrinsic semiconductors
   a. p-type semiconductors
      1. more holes than electrons
      2. saturation level for normal operation
   b. n-type semiconductors
      1. more electrons than holes
      2. exhaustion level for normal operation

V. Semiconductor Devices

OO. Diodes

1. p-n junction
2. movement of charge carriers from junction leads to rectification
   a. forward bias - carriers pushed to junction region and combine

b. reverse bias - carriers pulled away from junction - few carriers to combine and carry current

3. I-V characteristics of a diode
   a. large forward current
   b. small reverse current
   c. breakdown at high reverse voltages

PP. Transistors

1. Bipolar Junction Transistors (BJT's)
   a. 3 semiconducting regions - NPN or PNP
   b. emitter-base junction forward biased
   c. base-collector junction reverse biased
   d. pnp operation
      1. narrow base region allows holes to pass from emitter to collector through the base
      2. small base-emitter current controls larger emitter-collector current
   e. npn operation
      1. narrow base region allows electrons to pass from emitter to collector through the base
      2. small base-emitter current controls larger emitter-collector current
2. Metal Oxide Silicon Field Effect Transistor (MOSFET)
   a. single charge carrier active but controlled by a narrow channel which carriers must pass through
   b. very small gate current can control large source-drain current (high input impedance)
   c. p-channel FET
      1. positive charge on gate will reduce hole carriers in p-type Si
      2. negative charge on gate will allow passage of holes
   d. n-channel FET
      1. negative charge on gate will reduce electron carriers in n-type Si
      2. positive charge on gate will allow passage of electrons

XVI. Conductivity in Ceramics and Polymers

A. Ionic Ceramics

1. Conduction primarily due to ion motion
2. Generally insulating materials until at or near melting

B. Polymers

1. Generally insulating due to covalently bonded electrons
2. Conduction possible by doping with appropriate compounds (sometimes filled with conducting elements)

XVII. Dielectric Behavior

A. Dielectric Materials - insulators with internal dipoles capable of aligning with an external field

B. Capacitance

1. Relative ability of a device to store charge
   $C = Q/V$ (units of farads or coulombs/volt)
2. Parallel plate capacitor
   $C = e (A/l)$
   a. e is the permittivity of the material between the plates
   b. A is the area of the plates
   c. l is the distance between the plates
3. Permittivity
   a. in a vacuum - $e_0 = 8.85 \times 10^{-12}$ F/m
   b. relative permittivity (dielectric constant) - $e_r = e / e_0$

c. dielectric strength - resistance to breakdown in presence of an electric field