APSC 278 Little Last Minute Things

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1 Chemistry Stuff

1.1 Primary Bonds

1.1.1 Ionic Bonds

- Between metal and nonmetal
- Strongest bonds
- bonds are nondirectional

1.1.2 Covalent Bonds

- Between atoms of similar electronegativity
- bonds are directional

1.1.3 Metalic Bonds

- Forms electron cloud where electrons can move freely

1.2 Secondary Bonds

1.2.1 Vanderwaal Bonding

This is when the electrons all move to one side of an atom creating a small dipole

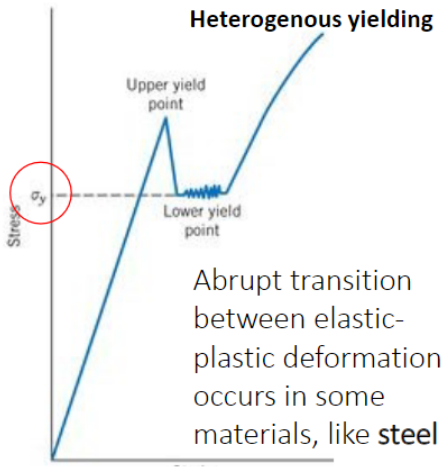
1.2.2 Hydrogen Bonding

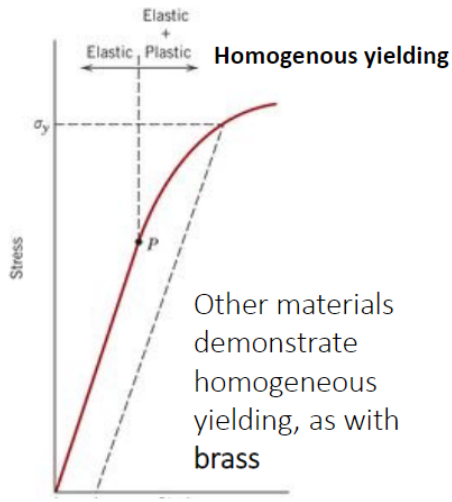
Happens with H, O, and N molecules. Creates a strong dipole interaction

2 Mechanical Properties of Materials

Definitions:

- Young's Modulus E:
  Stress over strain in the elastic region
  $$E = \frac{\sigma}{\varepsilon}$$
- Modulus or Resilience (MOR):
  Energy that can be completely recovered. The area of a stress-strain curve in the elastic region.
  $$MOR = \frac{\sigma_y^2}{2E}$$
- True Stress/Strain:
  The instantaneous stress/strain
- Engineering stress/strain:
  The stress/strain compared to the initial area
- Poisson's Ratio ν:
  How much the material stretches in the horizontal directions when submitted to an axial load.
  $$\nu = -\frac{\varepsilon_{\parallel}}{\varepsilon_{\perp}}$$
- Shear Modulus G:
- Yield Strength σ_{YS}:
  When the material starts to leave the elastic region
- Plastic deformation:
  Permanent (irreversible) deformation where the material doesn't fully recover.
- Heterogeneous and homogeneous yielding:





- Ultimate Tensile Strength σ_{UTS}:
  The maximum possible stress felt by the material. Marks the onset of necking

- Work hardening:
  When the material is in the plastic region before ultimate tensile stress.
  The increase in stress required to continue deformation beyond the elastic limit

$$\sigma_T = K\varepsilon_T^n$$

  gives the true stress which can be used up to the point of necking.

- Necking:
  When the material starts to get skinny. After σ_{UTS} and before ε_{UTS}
  Caused by cavitation of pores in the material that result in less load bearing area.

- Ductility (strain to failure) ε_{UTS}:
  Amount of deformation a material will tolerate before failure (in percentage)

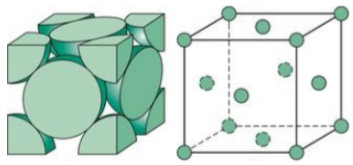
$$D = \frac{A_0 - A_f}{A_0} = \frac{L_f - L_0}{L_0}$$

- Toughness K_{IC}:
  The total amount of energy that can be absorbed by a material before failure (total area under stress/strain curve)
  More carbon makes materials stronger but more brittle (lower ductility)

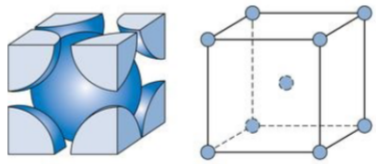
- Hardness R_i:
  A material's resistance to localized plastic deformation.
  Hardness values are relative (to be compared only between the same testing method)

3 Crystal Structure and Strengthening Methods

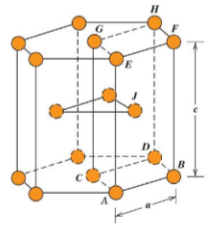
3.1 Crystal Structures



Face centered cubic (FCC)



Body centered cubic (BCC)



Hexagonal close packed (HCP)

- Crystaline material:
  atoms arranged in a repeating array, and exhibit long range order
- Cyrstal structure:
  Specific spatial arrangement of atoms in crystalline solids
- Crystal morphology:
  Shape and size of the crystals or grains
- Number of atoms per unit cell:
  - FCC: 4
  - BCC: 2
  - HCP: 6
- Coordination number:
  Number of nearest neighbour or touching atoms in a structure
  - FCC: 12
  - BCC: 8
  - HCP: 12
- Close packed directions:
  directions within the unit cell with highest linear density of atoms
- Atomic packing factor:
  volume of atoms in a unit cell per volume of a unit cell
  - FCC: 0.74
  - BCC: 0.64
  - HCP: 0.74

- Theoretical density:
  Mass of atoms in unit cell per volume of unit cell.
  The theoretical density is always higher than the real density because of imperfections.

$$\rho_{Th} = \frac{nA_i}{V_c N_A}$$

  where n is number of atoms, A_i is weight of atoms, V_c is volume of unit cell, and N_A is avagadro's number

- Anisotropic:
  Having different material properties in different directions

- Isotropic:
  Matrial properties are the same in all directions

- Planar density:
  Number of atoms in a plane per unit area

3.2 Dislocations and Strengthening

- Imperfections
  All crystals have an equilibrium concentration of vacancies:

$$N_v = Ne^{-\frac{Q_v}{RT}}$$

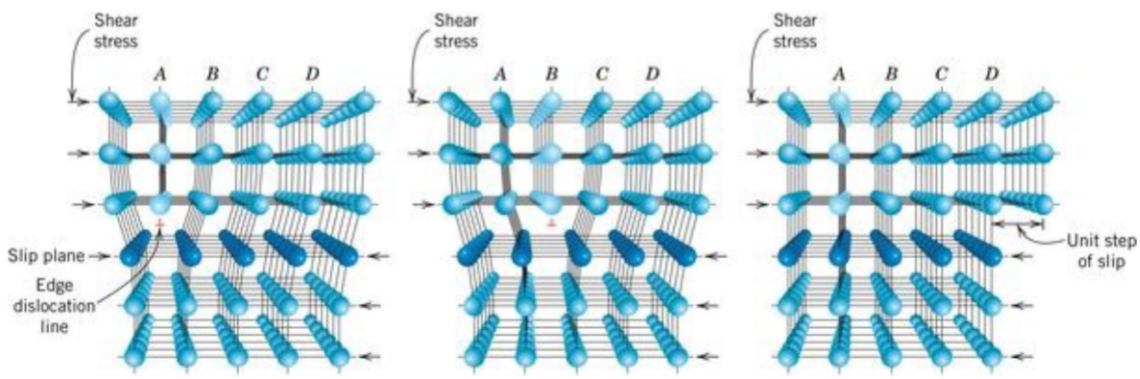
  where N_v is number of vacancies per unit volume and N is number of atoms per unit volume. Q_v is activation energy for vacancy formation and R is Boltzmann's constant.

- Diffusion
  The process in which atoms move within a solid.
  Atoms will move from a high density to a low density area to obtain lower energy configurations.

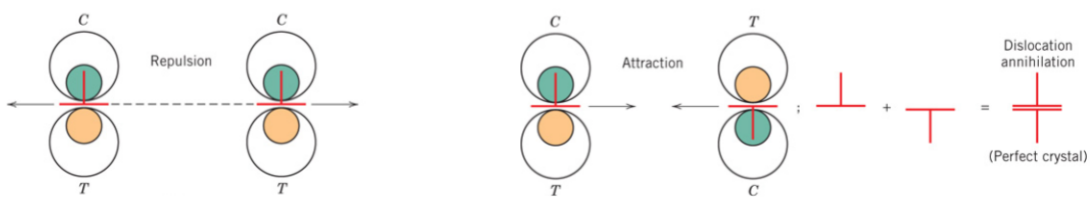
- Dislocations:
  Linear crystalline defects whose motion gives rise to plastic deformation in crystalline materials

- Slip:
  The process by which plastic deformation is produced by dislocation movement

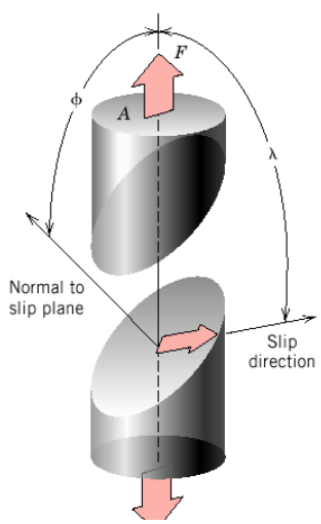
Dislocations:



A dislocation will form and area of compressive stress (C) and an area of tensile stress (T) within the material. These ares will react with each other similar to charges.



- Slip Systems:
  describes the preferred plane (slip plane) and direction (slip direction) for dislocation movement
  It is such atomic distortion in minimized with dislocation movement



- Resolved shear stress:

$$\tau_R = \sigma \cos\phi \cos\lambda$$

  where σ is the applied stress

- slip occurs along this slip system when the critical resolved shear stress is reached, which is a material property that indicates when yielding occurs

$$\sigma_y = \frac{\tau_{crss}}{(\cos\phi\cos\lambda)_{max}}$$

  where τ_{crss} is the critical resolved shear stress

- Polycrystalline materials are stronger than crystalline materials because they are less prone to fail in a particular direction

- Hall Petch equation:
  Relates grain size (d) to yield strength

$$\sigma_y = \sigma_0 + k_y d^{-1/2}$$

- Alloys:

- Substitutional solute:
  alloy atom has similar size as host atom, and replaces them in the crystal structure

- Interstitial solute:
  alloy atom is smaller than host atom, and fits into spaces (interstices) between host atoms

- Substitutional atoms impose lattice strain that impede dislocation motion

- Work hardening involves increase in dislocation density and dislocation-dislocation interaction

- The degree of strain hardening is often expressed as percent cold work

$$CW = \frac{A_0 - A_d}{A_0}$$

  where A_d is the area of the deformed sample

- Methods that hinder dislocation motion strengthen the material
  These include:
  - Grain size reduction
  - solid solution strengthening
  - Work hardening

- Homologous temperature: the ratio of the deformation temperature to melting temperature (in Kelvin)

$$T_H = \frac{T_{\text{deformation}}}{T_{\text{melting point}}}$$

- Hot working:
  pure metals: $T_H > 0.4$
  alloys: $T_H > 0.6$

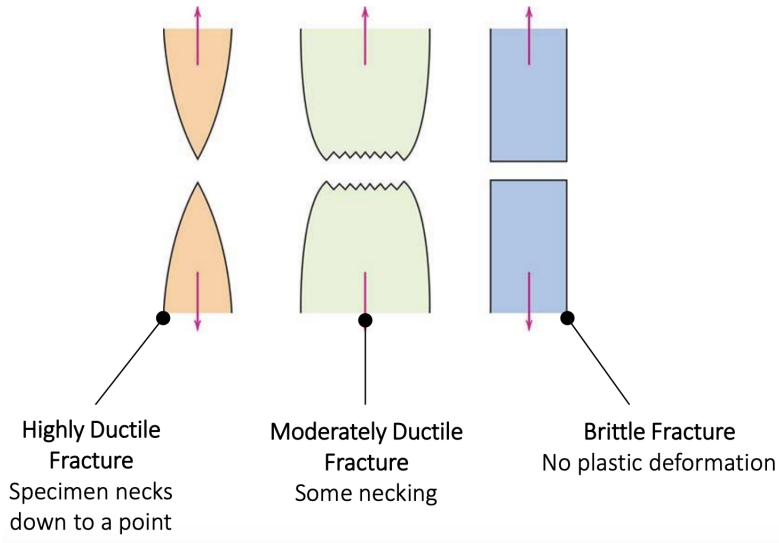
- Cold working increases strength and decreases ductility.
  σ_y and σ_{UT} both increase but get closer together. The material becomes more brittle

- work hardening increases the internal energy in a material

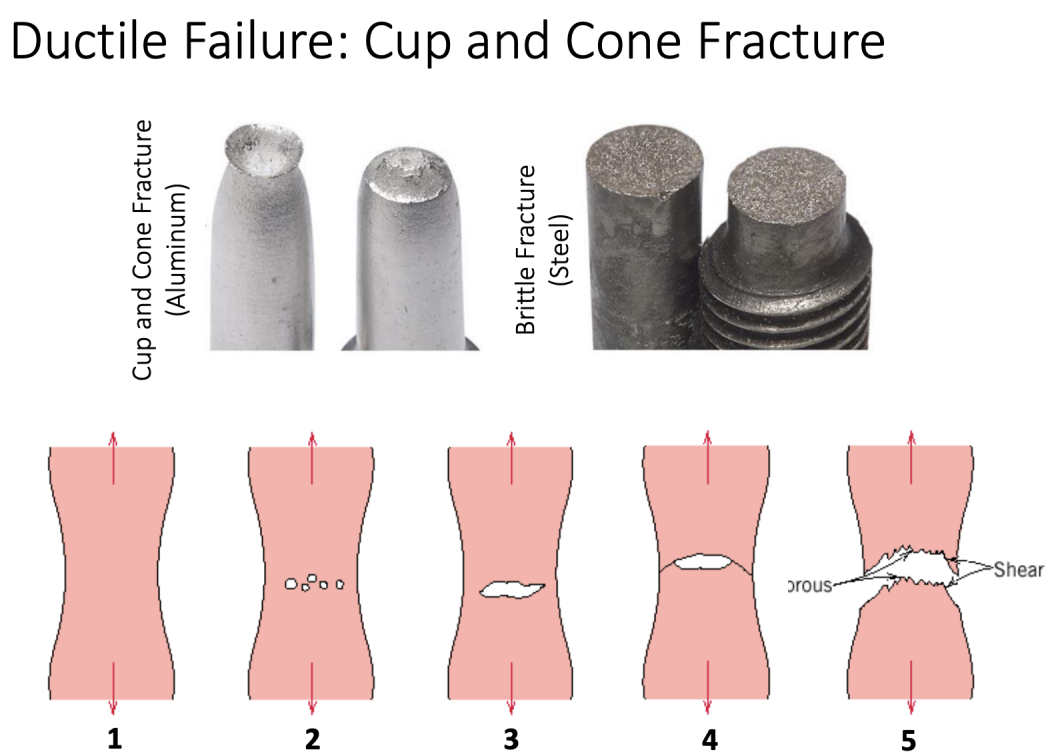
- Annealing heat treatment can reverse the effects of work hardening

4 Material Failure

4.1 Fracture



Ductile Failure:



1. Necking begins when the UTS is exceeded
2. Cavities previously present in material are enlarged

3. Cavities coalescence to form crack
4. Crack propagates
5. When the applied stress can no longer be sustained, fracture occurs

Fracture Characteristics:

	Ductile Fracture	Brittle Fracture
Toughness	High	Low
Extent of plastic deformation	Extensive	Little to none
Appearance of fracture surface	Dull and fibrous	Shiny and crystalline
Morphology	• Dimples (microscopic) • Cup and cone • Evidence of shear (failure along paths of maximum shear)	• Flat surface • Evidence of cleavage of grains • Chevron and fan-shaped patterns

4.1.1 The Many K's

Fracture Toughness (K_C)

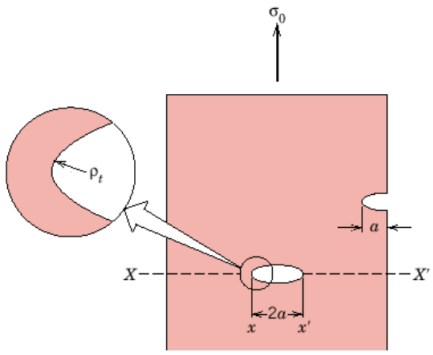
- A measure of a material's resistance to brittle fracture when a crack is present
- Fracture toughness decreases with increasing yield strength
- We can compute K using a formula for a given scenario. If $K > K_C$ then the crack will propagate

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

Stress Concentration Factor (K_t)

- Maximum stress: $\sigma_m = 2\sigma_0(\frac{a}{\rho_t})^{1/2}$
  - σ_0 = nominal stress (at position far removed from crack)
  - σ_m = maximum stress (at crack tip)
  - ρ_t = radius of curvature at the crack tip

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



- **For internal crack, length is $2a$. For edge crack, the length is a**

Sources of stress concentration:

- mechanical surface damage
- residual stress from manufacturing
- corrosion pitting
- sharp corners (design)

Griffith Theory of Brittle Fracture
When a crack propagates

- There is a release of elastic strain energy
  - $\Delta E_{\text{strain energy}} = \frac{\sigma^2}{2E}(V)$ is the energy released per unit thickness when a crack propagates a distance a
- Energy is consumed to extend the crack
  - $\Delta E_{\text{surface}} = 2\gamma_s a(l)$ is the surface energy required per unit thickness to extend a crack from 0 to a

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

where γ_s is the specific surface energy and σ_c is the critical stress for crack propagation in a brittle material.

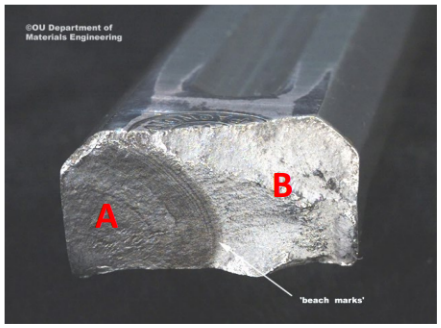
4.2 Fatigue

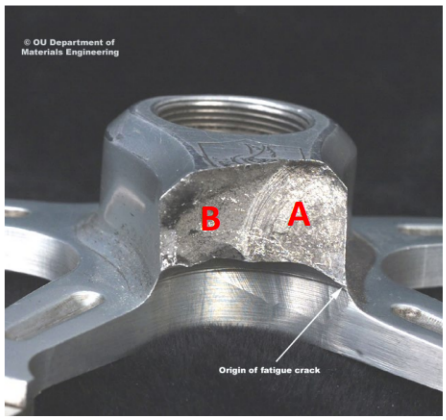
- Failure at stress levels below yield or tensile strength of the material
- Occurs after a long time of cyclic loading

Fatigue Failure:

- Requires tensile stresses
- Failure occurs when crack grows to critical length (when K_C is exceeded)
- Single largest cause of failure

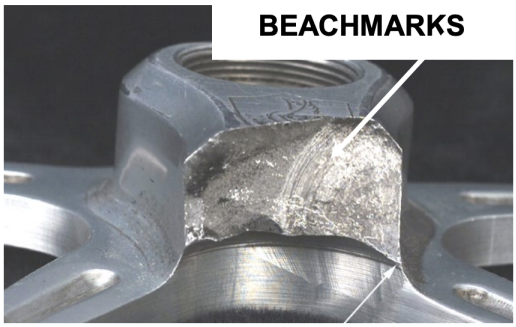
4.2.1 Cyclic Loading

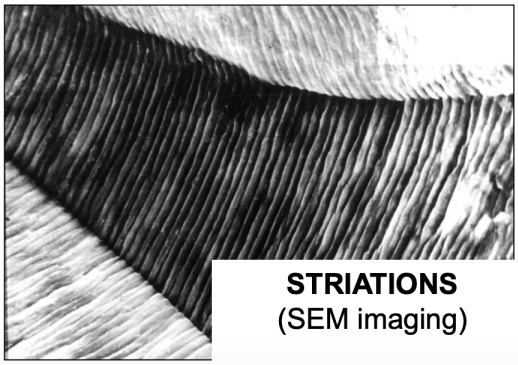




Diagnosis

- **Beachmarks**: found where crack propagation occurred (**A**); beachmark spacing is indicative of the rate of crack propagation
- Rapid failure occurred in the rugged section (**B**)
- Crack initiated at a location of maximum bending moment at the tensile side (later investigation identified initiation from a machining mark)
- Rapid failure occurred when part could no longer withstand bending moment applied



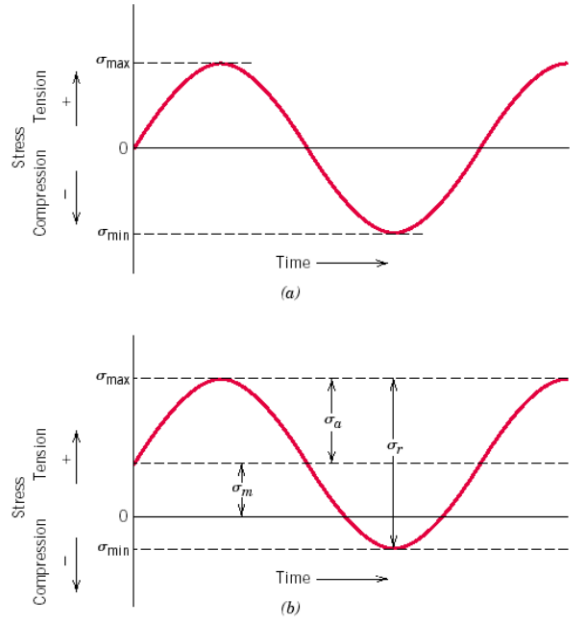


Features of fatigue fracture

Beachmarks: <u>macro-scale</u> features usually associated with periodic start-up of machinery; they do not reflect load cycles, but indicate rate of crack propagation

Striations: <u>micro-scale</u> features indicating crack origin and growth characteristics; indicative of load cycles

Characterization of Fatigue Loading



Mean Stress

$$\sigma_m = \frac{\sigma_{\max} + \sigma_{\min}}{2}$$

Stress Range

$$\sigma_r = \sigma_{\max} - \sigma_{\min}$$

Stress Amplitude

$$\sigma_a = \frac{\sigma_{\max} - \sigma_{\min}}{2}$$

Stress Ratio $$R = \frac{\sigma_{\min}}{\sigma_{\max}}$$

Materials Engineering

S-N Curves:
S is the stress amplitude and N is the number of cycles until failure.
A *fatigue limit* is the stress amplitude at which fatigue failure does not occur. (Flat part of an SN curve)

4.2.2 Factors Affecting Fatigue Life

Shot Peening:
This is when you shoot a bunch of itty bitty particles at the surface

- Residual compressive stresses are generated on the surface of a metal by shooting hard particles at it
- Residual compressive stresses delay crack initiation

Case Hardening:
This is when you harden the outside surface of a material while the inside stays all nice and tough (high K_C)

- A carbon- or nitrogen-rich surface is created through atomic diffusion by exposing the metal to a carbon or nitrogen-rich atmosphere at a high tempature

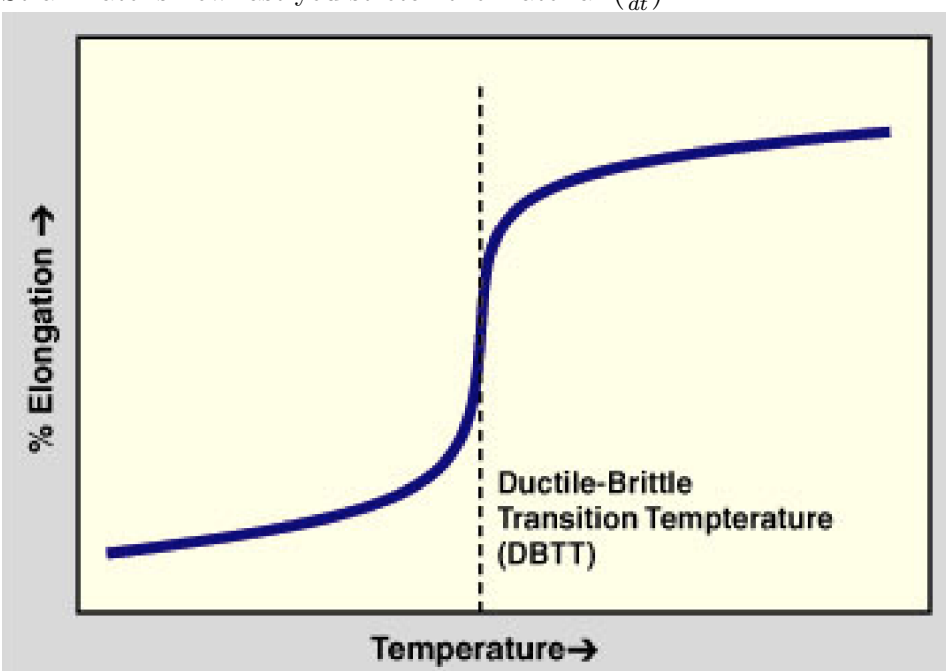
Three measures that can be taken to increase the resistance to fatigue of a metal alloy:

- Shot-peening

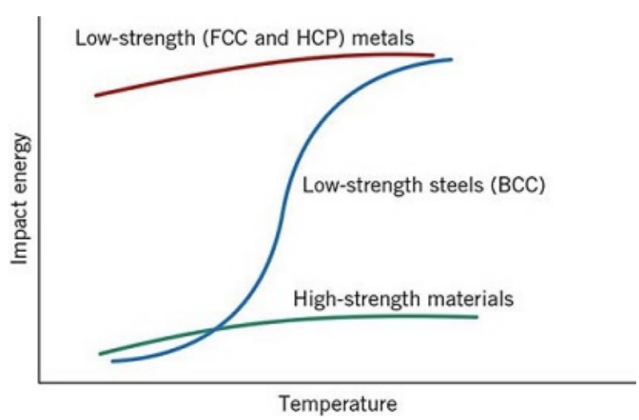
- Removing any sharp-corners
- Removing as many internal defects as possible

4.3 Ductile-Brittle Transition

The drastic reduction in ductility of a material within a temperature range.
Increasing strain rate makes the material behave brittle over a wider range of temperatures.
Strain rate is how fast you stretch the material $\left(\frac{d\epsilon}{dt}\right)$



Many metals do not exhibit ductile-brittle transitions.

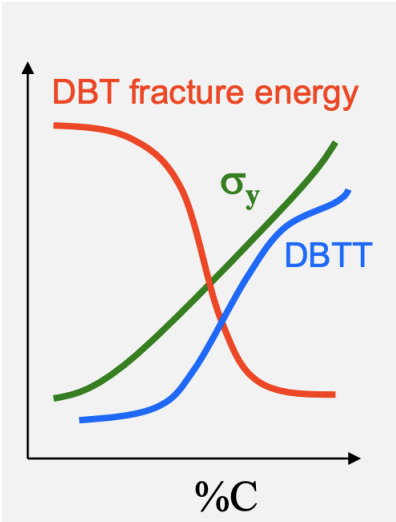


- FCC and HCP metals, and high-strength materials do not demonstrate DBT

IMPORTANT:

- Ductile failure is a result of dislocation movement, whereas brittle fracture occurs as a result of crack propagation

4.3.1 Impact of Carbon Content

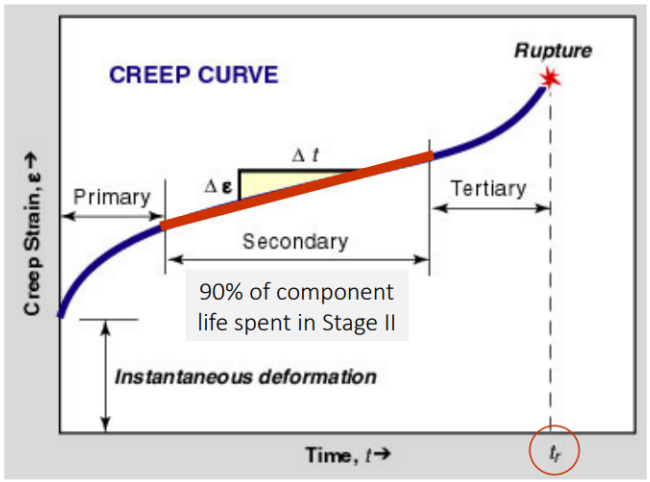


Increasing the carbon content increases yield strength, DBTT, and decreases DBT fracture energy.

4.4 Creep

Creep is time-dependent and permanent deformation of materials subjected to a constant load at elevated temperatures

- For metals, creep is observed at temperatures above $0.4T_m$
- There are three regimes:
  - Primary creep
  - Secondary (steady-state) creep
  - Tertiary creep (rupture)
- Metals with high melting temperature, high elastic modulus and large grain size demonstrate greater resistance to creep
- Large grains result in smaller surface area for grain boundary sliding (sliding occurs at high temperature and strain, ie. Creep)



1. **Primary or instantaneous creep:** continuously decreasing creep rate due to strain hardening
2. **Secondary or steady state creep:** constant creep rate ε_s due to balancing of strain hardening and recovery; longest stage
3. **Tertiary creep:** acceleration of creep rate until rupture at t_r

As stress and/or temperature increase, the material will fail quicker

4.5 Corrosion

Driving force of corrosion is a reduction in energy. Oxidation is thermodynamically favourable (large release of energy).

What is required for corrosion to occur?

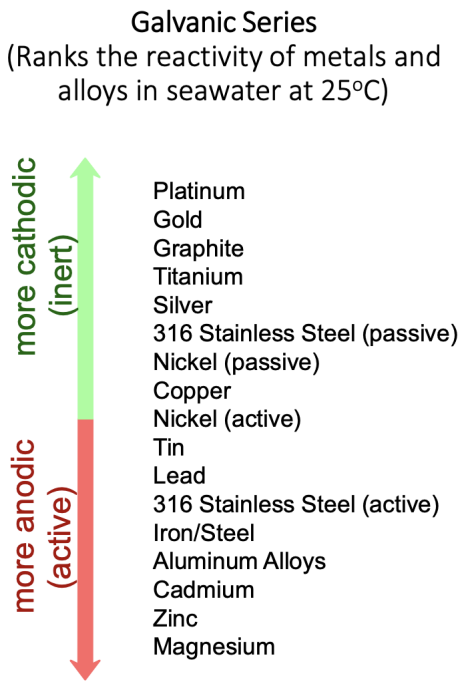
- Reduction in energy (thermodynamic driving force)
- Water or moisture to act as a medium for ion conduction and ionic transport
- Source of oxidant (normally O2, sometimes sulfur)
- Mass transport of oxidant to the metal surface

4.5.1 Stress Corrosion

- Corrosion can promote crack propagation in components under stress
- Ex: a bent steel bar in seawater. Metal oxide can form at the crack tip or crack vicinity and contribute to crack propagation

4.5.2 Galvanic Corrosion

- Occurs when two different metals or alloys are electrically coupled while exposed to an electrolyte
- The more reactive metal is **oxidized** and acts as the **anode**; it corrodes. The less reactive metal is **reduced** and acts as the **cathode**; it is protected.



- Lists metals and alloys
- Values measured experimentally
- Accounts for effects of passive films, oxidation kinetics, and the environment

Corrosion Protection for Metals:

1. Self-driven formation of a protective oxide
   - Formation of a protective oxide outer layer that limits oxygen transport to the interior
   - Forms only for certain metals such as stainless steel, some aluminium alloys and titanium
2. Physical barriers (paint, noble coating)
   - Uses a less chemically active metal layer than the main metal
   - Acts as a physical barrier to inhibit contact with water and oxygen
3. Sacrificial or cathodic protection
   - Uses a more chemically active metal layer than the main metal
   - The sacrificial coating acts as the anode, and corrodes while the main metal stays intact
   - Prone to physical or chemical damage, like paint or film
4. Change environmental factors
   - Reduce temperature
     slows kinetics of oxidation and reduction

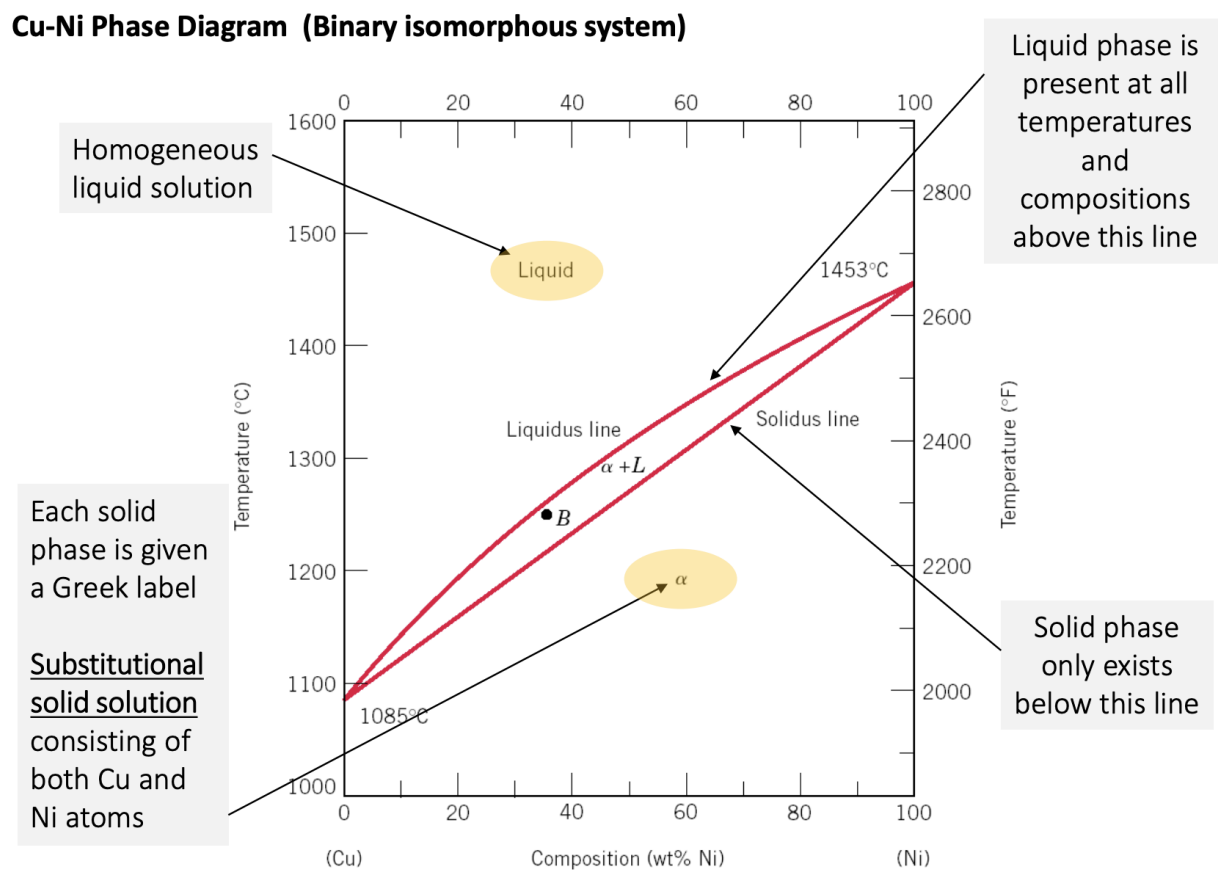
- Remove reactants
  such as removing O_2 gas to create a more reducing environment
- Add inhibitors
  e.g. coolant additives in automotive cooling systems (radiators) provide corrosion prevention in addition to protection against freezing

5 Engineering Microstructure

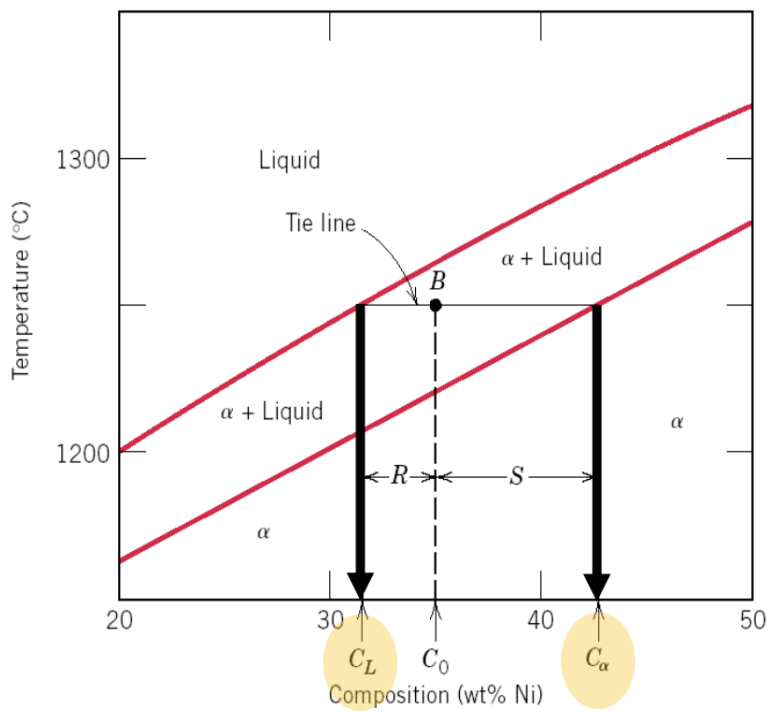
5.1 Phase Diagrams

- **Phase:** A homogeneous portion of a system that has uniform physical and chemical characteristics (ex: liquid, gas, different structural forms of solids with same composition)

5.1.1 Binary Isomorphous Diagrams (Ni-Cu System)



Determination of Phase Composition:



- To determine composition of a two-phase region with C_0, draw a horizontal line through a point of interest that intersects with the neighbouring phase boundaries (this is called a **tie line**)
- Intersection of the tie line and the phase boundaries gives the composition of respective phases
- For example, for the graph above, the liquid phase is 32 wt % Ni and the alpha solid phase is 43 wt% Ni

Determination of Phase Fractions:
Use **Lever Rule**:

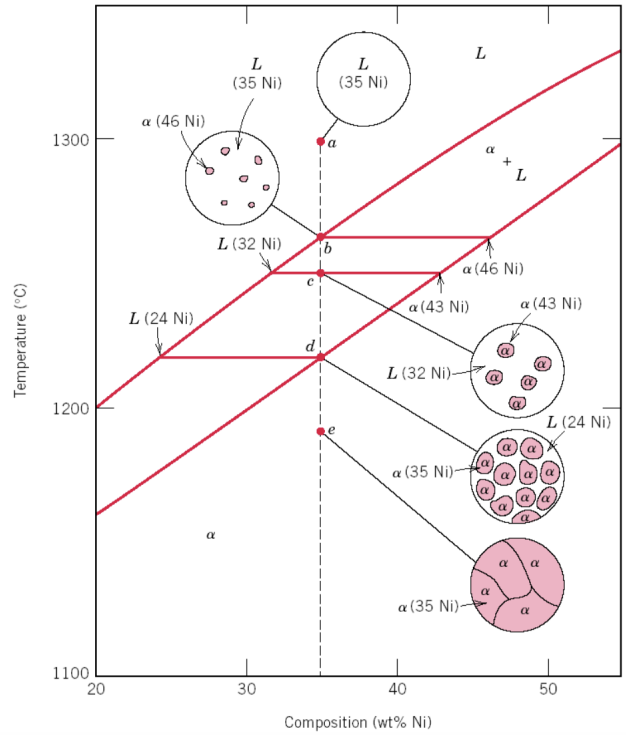
- Mark intersection of tie line with phase boundaries
- The mass fraction of a phase is the length of the tie line on the **OPPOSITE** side of the overall composition point vs. the overall tie line length

W_L *and* W_α is the mass fraction of liquid and α-solid, respectively

$$W_L = \frac{S}{R+S} = \frac{C_\alpha - C_0}{C_\alpha - C_L}$$

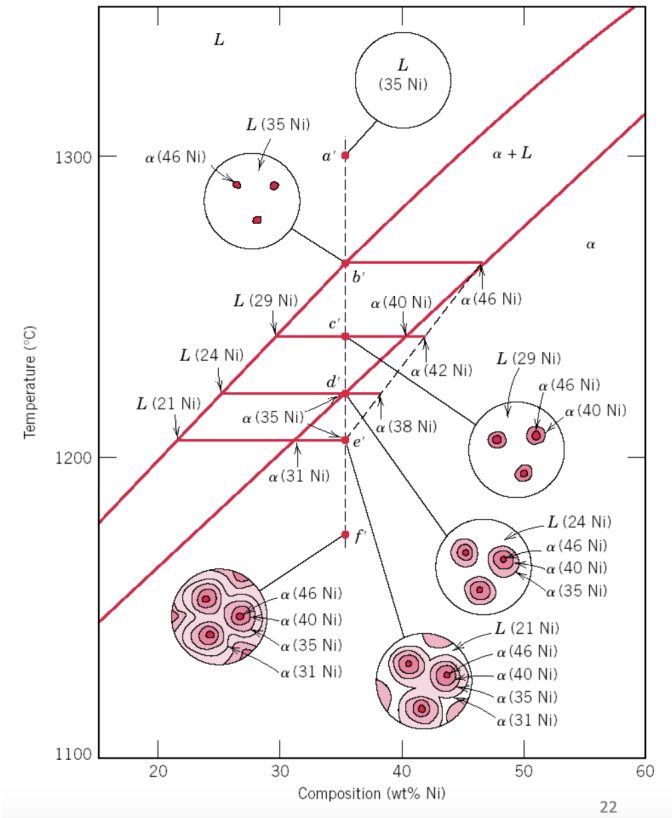
$$W_\alpha = \frac{R}{R+S} = \frac{C_0 - C_L}{C_\alpha - C_L}$$

Microstructural Changes in Equilibrium Cooling



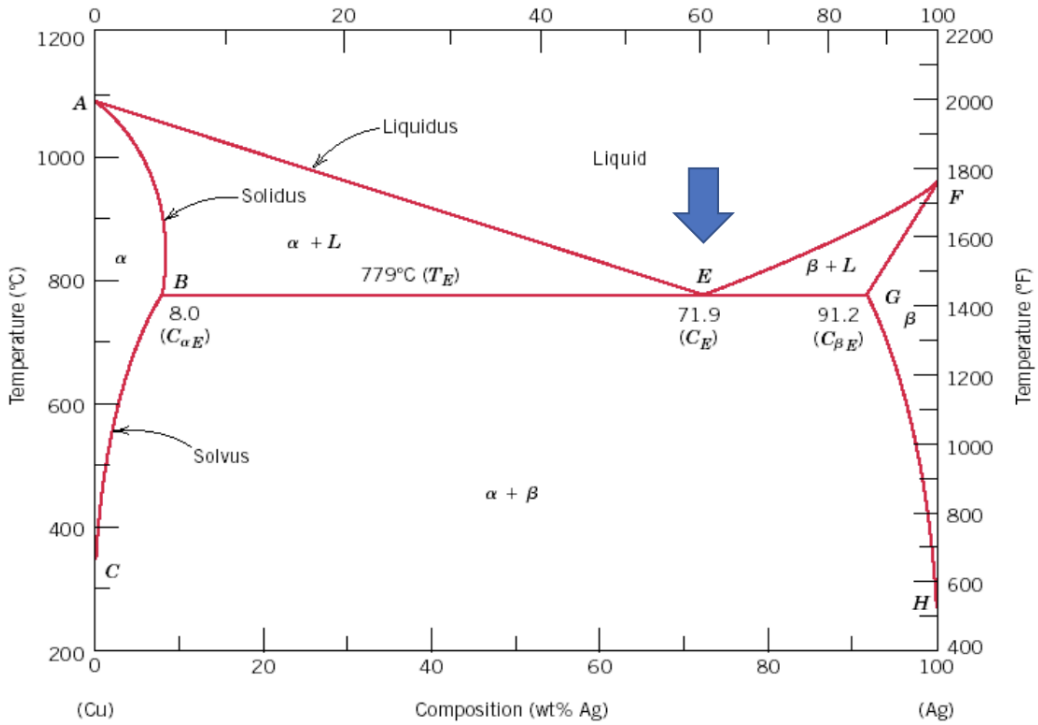
- Assumes "infinite diffusion" which means that mass is redistributed instantaneously (obviously not true)
- Use Lever Rule

Microstructural Changes in Non-Equilibrium Cooling



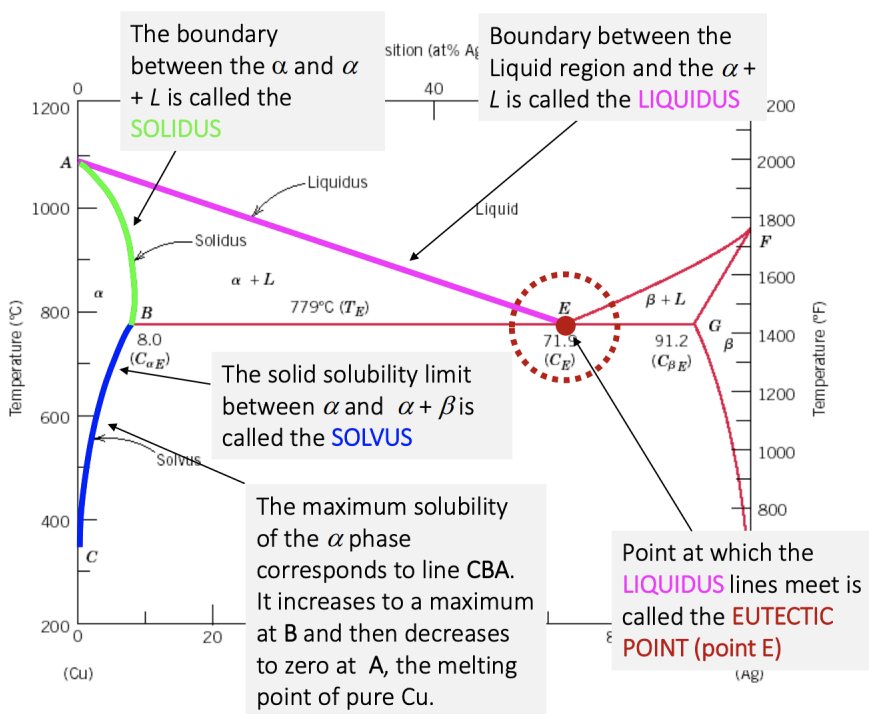
- No or very little diffusion in solid, but instantaneous diffusion in liquid
- No or little compositional changes in solid over time
- As a result, solids are non-uniform and have cored structures

5.1.2 Binary Eutectic System (Cu-Ag System)



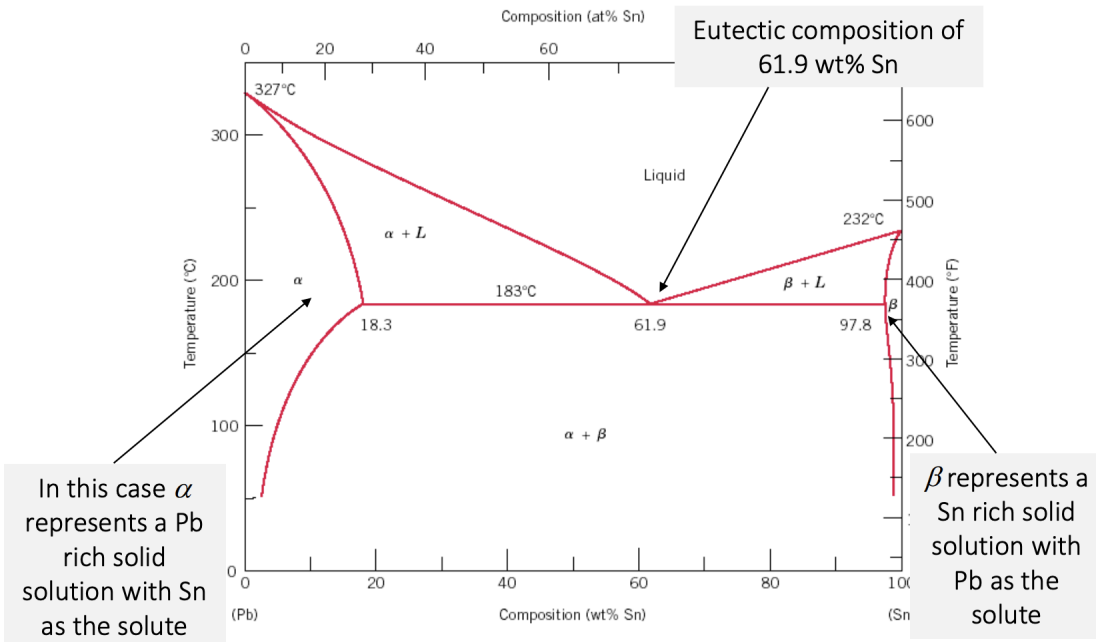
ls

A **eutectic system** is a mixture of chemical compounds or elements that have a single chemical composition that solidifies at a lower temperature than any of its constituents



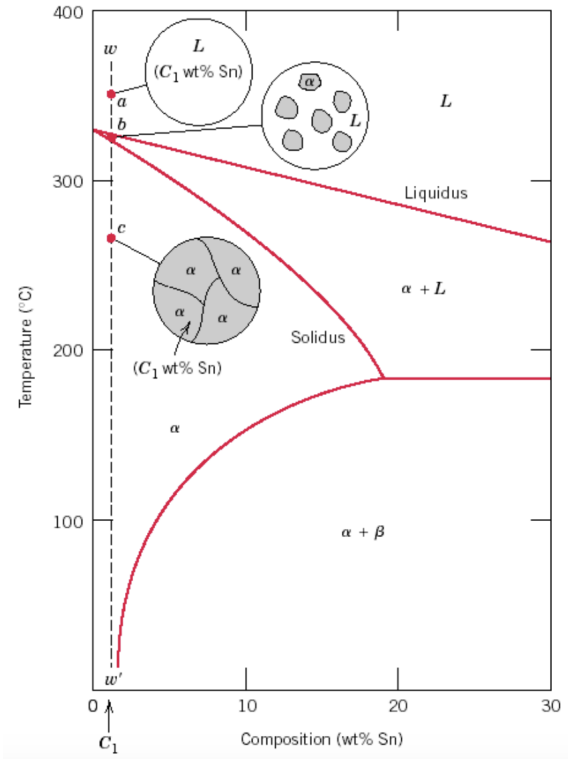
3 phases exist in equilibrium at the **eutectic point** (α, β and L).

5.1.3 Binary Eutectic System (Pb-Sn System)



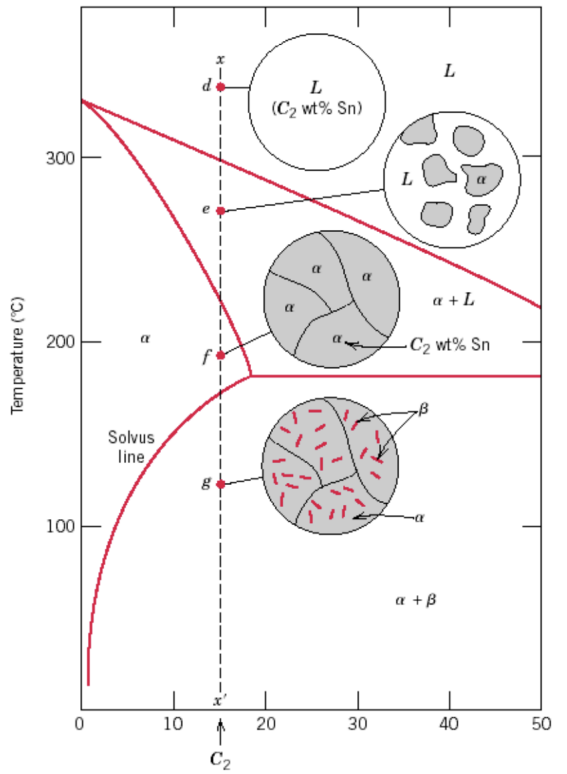
5.1.4 Microstructural Development in Eutectic Alloys

Region C_1: Compositions remaining entirely in α-phase upon cooling



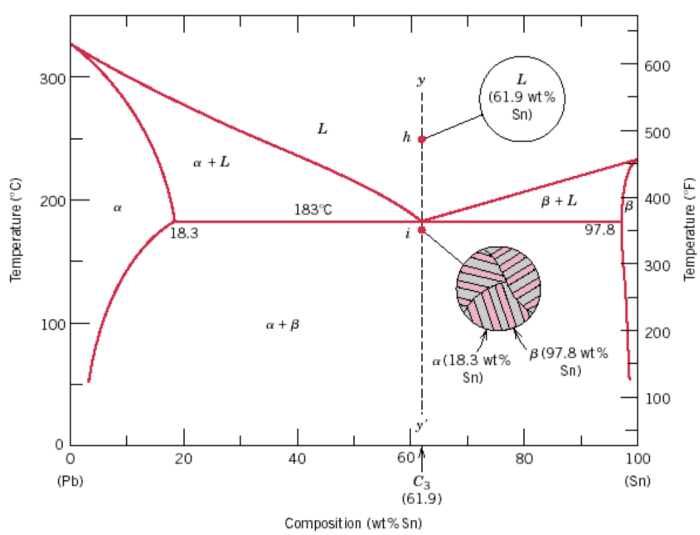
- Results in a polycrystalline alloy of uniform composition. A Pb-rich alloy with 0-2 wt% Sn
- No compositional changes will occur when further cooled

Region C_2: Starts in α-region, but crosses the solvus line



- Upon crossing the solvus line, the α solid solubility is exceeded
- Small β particles form and will grow on cooling

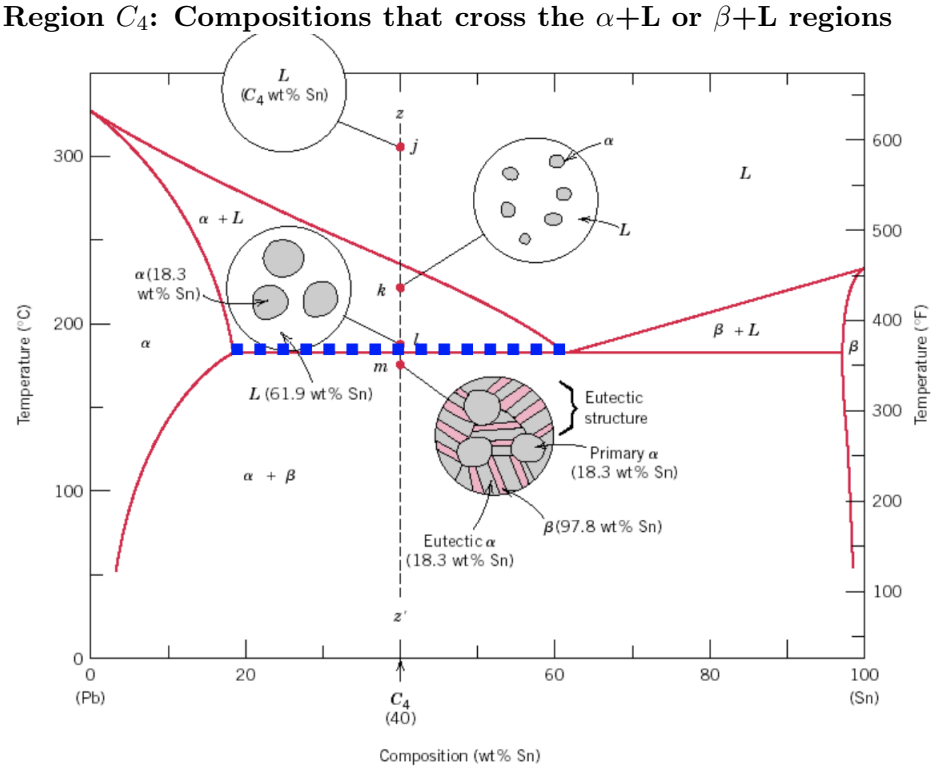
Region C_3: Eutectic composition



- Rapid transition from liquid phase to α and β phases when eutectic temperature is reached

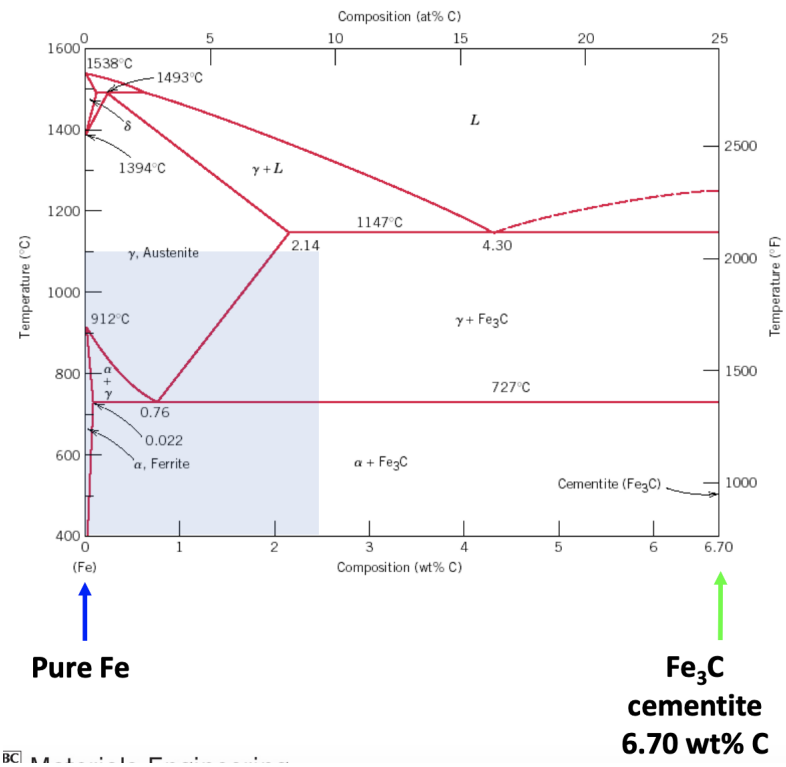
- Redistribution of Rb and Sn occurs by atomic diffusion
- Resultant microstructure consists of fine alternating layers of α and β phases known as **lamellae**
- Because the phase transformation has to occur quickly, diffusion occurs over short distances, resulting in a fine lamellar microstructure
- With further cooling, microstructure experiences only minimal changes
- Mass fraction of beta phase increases ever so slightly, with a corresponding slight decrease in alpha solid

Region C_4: Compositions that cross the α+L or β+L regions



Below the eutectic temperature, α phase will be present in two forms:

- As α' particles formed during cooling through α+L region, also called **primary** α
- In the eutectic structure; the α phase in the eutectic structure is referred to as **eutectic** α

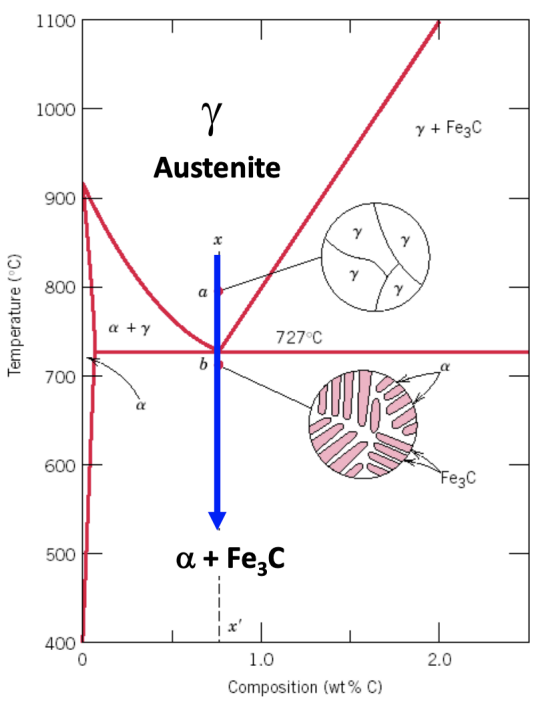


The Fe-Fe_3C Phase Diagram

This portion of the Fe-C diagram is sufficient to describe all of the steels and cast irons used today.

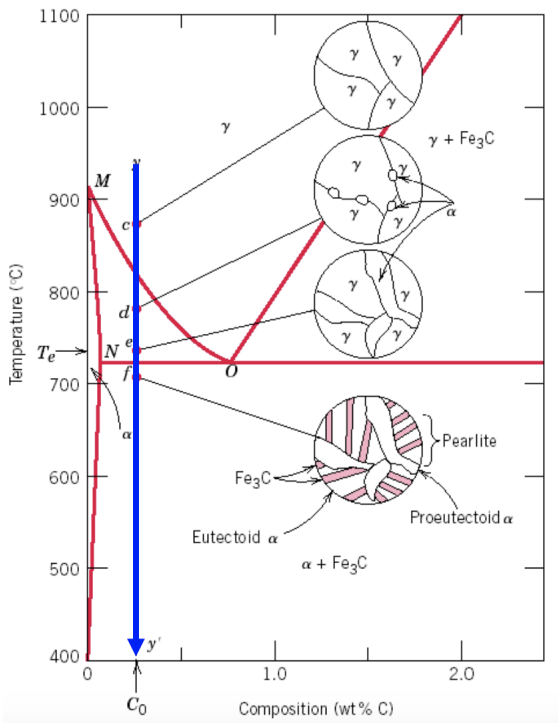
- At 6.70 wt%C cementite (Fe3C) is formed, which is hard, brittle and not used on its own

Development of Pearlite Microstructure



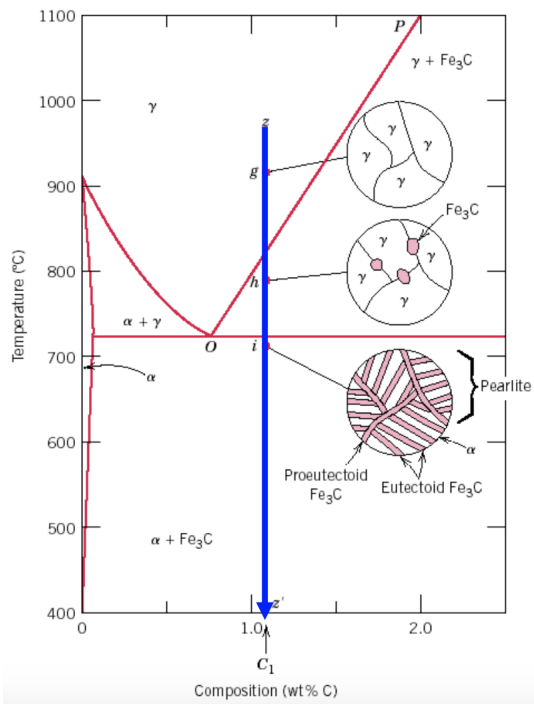
- Equilibrium cooling from the γ region through the eutectoid composition yields pearlite ($\alpha + Fe_3C$)
- Lamellar microstructure is formed because phase transformation occurs instantaneously over short diffusional distances
- Mechanical properties are in between the soft, ductile ferrite (α) and the brittle, hard cementite

Equilibrium Cooling in Hypo-Eutectoid (0.002-0.76 wt%) Steel Alloy



- Upon cooling, solid austenite (γ) enters a two-phase region of $\alpha + \gamma$ (pro-eutectoid ferrite + austenite)
- The pro-eutectoid ferrite forms at γ grain boundaries
- Below the eutectoid isotherm, the remaining austenite transforms to pearlite
- Final microstructure consists of pro-eutectoid ferrite and pearlite

Equilibrium Cooling in Hyper-Eutectoid (0.76-2.14 wt%) Steel Alloy



- Upon cooling, solid austenite (γ) enters a two-phase region of $Fe_3C + \gamma$ (pro-eutectoid cementite + austenite)
- The pro-eutectoid cementite phase forms along the γ grain boundaries
- Below eutectoid isotherm, remaining austenite transforms to pearlite
- Final structure is comprised of pro-eutectoid cementite and pearlite

5.1.5 Mechanical Properties of Steel

The mechanical properties of steel are largely dictated by carbon content and microstructural transformations upon cooling.

Examples of ways to change external heat transport:

Cooling method	Relative cooling rate
Furnace cooled	Slow
Air cooled	Moderate
Oil quenched	Fast
Water quenched	Very fast

Note: the practical rates achieved will be dependent on section thickness (internal heat transport)

5.2 Heating and Quenching and Stuff

Quenching and tempering of steel diagram:

1. Austenitize

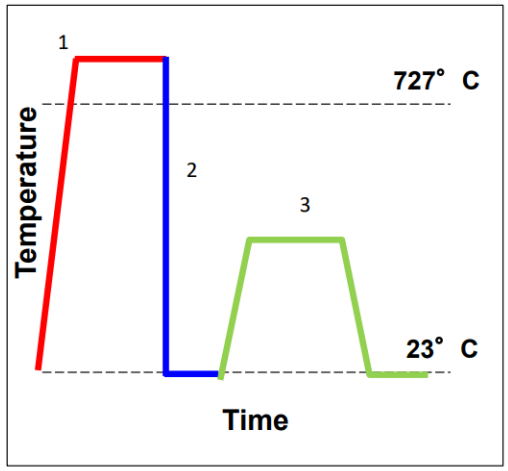
- Heat to a temperature region where 100% Austenite is formed
- Hold to allow complete transformation

2. Quench

- Use water or oil to rapidly cool
- Form non-equilibrium, hard microstructures

3. Temper

- Reheat to 200 - 550° C
- Decreases hardness, regain some ductility



Bainite

- Carbon must diffuse to form pearlite layers
- If the sample is quenched to a sufficiently low temperature (high cooling rate) there is little time for diffusion to occur
- Instead of lamellae, new structures with thin needles of Fe_3C in a ferrite matrix will form
- Bainite forms when quenched to a temperature between $210 - 520°C$

Martensite

- If cooled VERY rapidly (such as by quenching into water), there is no time for diffusion and martensite is formed
- Formed by a diffusionless process
- A supersaturated and unstable structure
- The hardest, strongest (high yield strength) and most brittle microstructure in steel
- Tempering involves reheating to moderate temperatures after quenching to regain ductility and toughness

The microstructures in order from lowest to highest ductility are

1. Martensite
2. Spheroidite
3. Tempered martensite

4. Fine pearlite
5. Coarse pearlite

6 Polymers

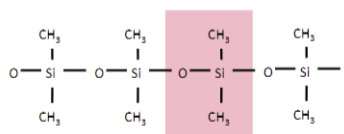
6.1 Chains and Molecules

Defining characteristics of polymers:

- Lightweight ($\rho = 0.9 - 3$ g/cm^3)
- Low elastic modulus (in bulk form)
- Low strength (in bulk form)
- Low fracture toughness (K_{IC})
- Good ductility and specific toughness
- Highly formable
- Chemistry is well-understood and manipulatable

Polymers are differentiated by their side groups and/or backbone chain.
Many properties of polymers are linked to the polymer chain length and molecular weight.

Mer units: Mer units are the repeating units of a long polymer chain



Polydimethylsiloxane (PDMS, Silicone)

6.1.1 Molecular Weight

There are typically 2 ways of defining molecular weight:

1. Number-average molecular weight:
   determined from a histogram of the number of chains within a given size interval.

$$\overline{M}_n = \sum x_i M_i$$

2. Weight-average molecular weight:
   determined from a histogram of the total mass of the chains within the given size interval.

$$\overline{M}_w = \sum w_i M_i$$

M_i is the mean molecular weight of the size interval, i
x_i is the number fraction of chains within the size interval i
w_i is the weight fraction of molecules within the size interval i

Note that in all cases the weight-average molecular weight will be higher than the number-average.

$$\boxed{\overline{M}_w > \overline{M}_n}$$

6.1.2 Degree of Polymerization (DP)

DP represents the average number of mer units in a chain.

$$DP = n_n = \frac{\overline{M}_n}{m}$$

where m is the molecular weight of one mer unit.

Higher DP means:

- Higher melting points
- Higher stiffness
- Higher strength

6.1.3 Branching

- side-branched chains connected to main ones
- results from side reactions that occur during synthesis
- chain packing efficiency is reduced, lowers polymer density
- polymers that form linear structures may also be branched
- chains pack poorly so it has less strong intermolecular forces, resulting in a lower tensile strength and increased ductility

Crosslinking:

- adjacent linear chains strongly joined to one another
- achieved during synthesis or by a non-reversible chemical reaction
- often accomplished by additive atoms or molecules that are covalently bonded to the chains
- many rubber elastic materials are irreversibly crosslinked (called vulcanization)

6.2 Bulk Properties

6.2.1 Polymer Crystallinity

- Metals are typically 100% crystalline
- However, polymers can be partially crystalline, ranging from entirely amorphous (noncrystalline) to almost completely crystalline
- For a given composition and molecular weight, increased crystallinity increases the density of a polymer due to increased packing

In amorphous polymers:

- Strong covalent bonds form the polymer chain backbone
- There is extensive van der Waals interactions between chains holding the polymer strands together, but with no long-range order

Polymers can exhibit different degrees of crystallinity and packing
Factors that inhibit crystal formation:

- Bulky side groups
- Branching
- Atacticity (random distribution of sidechain locations)
- Random arrangement of mers in copolymers

Crystallinity affects the following properties:

- Melting temperature
- Strength
- Stiffness
- Density (ie. greater packing of polymer chains)
- Resistance to softening (polymer can be used at higher temperatures)

The mechanical behavior of polymers is highly sensitive to:

- rate of deformation (strain rate)
- temperature
- environment (organic solvents, water)

Effect of strain rate on mechanical properties of a polymer:
Increasing the strain rate:

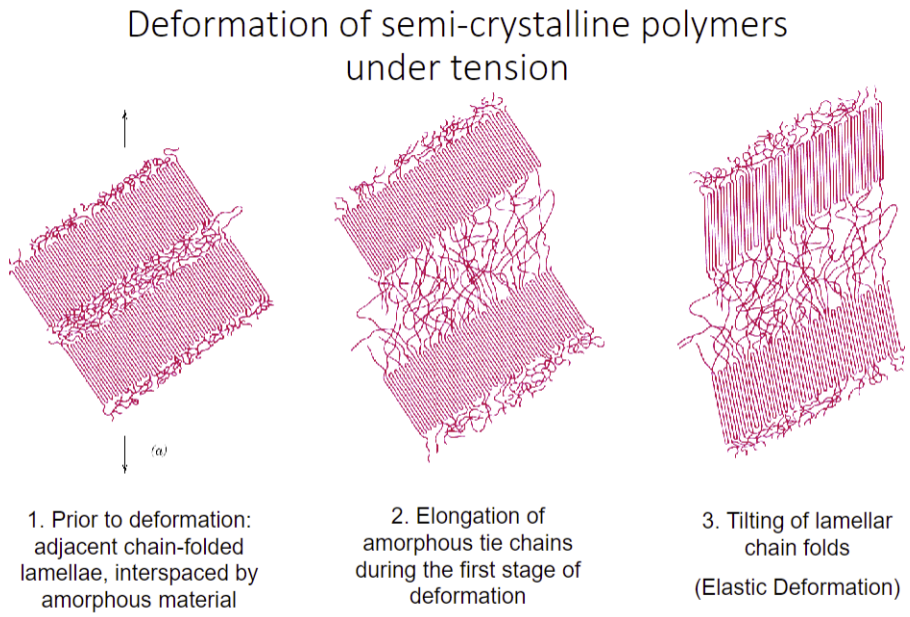
- Increases the elastic modulus (stiffness)

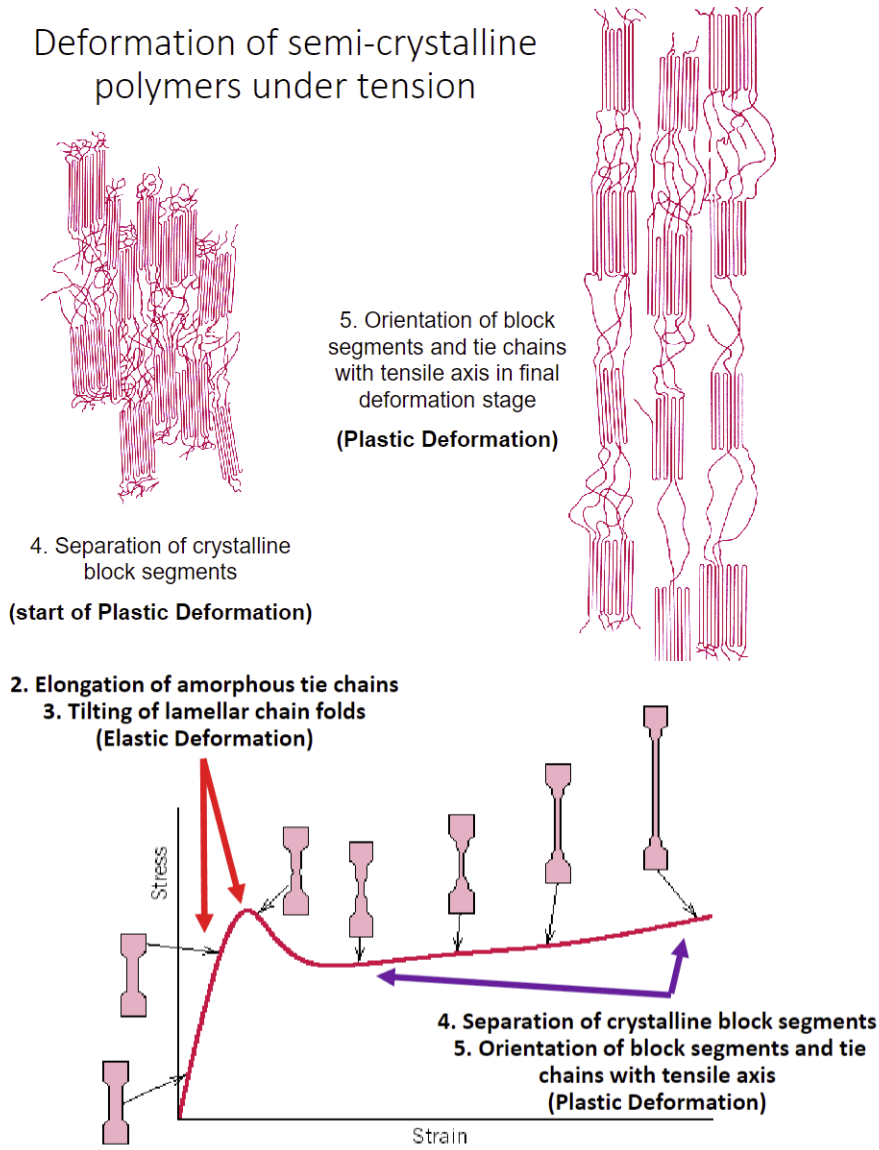
- Decreases ductility
- Increases the ultimate tensile strength

Three types of general stress-strain behavior for polymers:

- Brittle
- Plastic
- Highly elastic

The brittle and plastic behaviors are similar to metals, however, the highly elastic behavior is only characteristic of some polymers, not metals or ceramics.





6.2.2 Thermoplastics, thermosets, and elastomers

Thermoset:

- decomposes upon heating and does not become softer
- These polymers are formed by curing (i.e. hardening) a soft solid or viscous liquid material
- During curing, the addition of catalysts and/or heat result in crosslinking of polymer chains, so that chains cannot freely flow or move
- Characteristics
  - Strong and stiff

  - Can be used at higher temperature (although will decompose at high temperature)
  - More chemically inert

Thermoplastic:

- becomes more pliable or moldable upon heating
- Any resin which can be melted by heat and cooled without appreciable change in properties
- Polymer chains are not interconnected by covalent bonds, but held by weak secondary bonds
- Characteristics
  - Less strong and stiff
  - Cannot be used at high temperatures (will melt instead of decompose)
  - Formable via injection molding, vacuum forming and extrusion

Elastomers:

- can withstand large elastic strains at ambient temperatures
- May be lightly crosslinked for stability
- Most elastomers are also thermoset plastic (i.e. cannot heat and melt most elastomers)
- Modulus of elasticity is small

In its unstressed state, elastomers are amorphous, and composed of molecular chains that are highly twisted, kinked and coiled. When a tensile load is applied, there is partial uncoiling, untwisting and straightening of chains in direction of stress. Upon release of stress, entropy increase restores the chains original conformations

6.2.3 Polymer Manufacturing

Polymer additives are chemicals that improve the ductility of polymers and prevent degradation.

Types of polymer additives:

- Plasticisers: increase flexibility, ductility, and toughness in brittle plastics (often liquids with low molecular weights, fitting between large polymer chains)
- Stabilizers: counteract the deterioration of plastics (protect against UV degradation, heat and flame deterioration, or oxidation of bonds)

Health concerns of polymer additives:

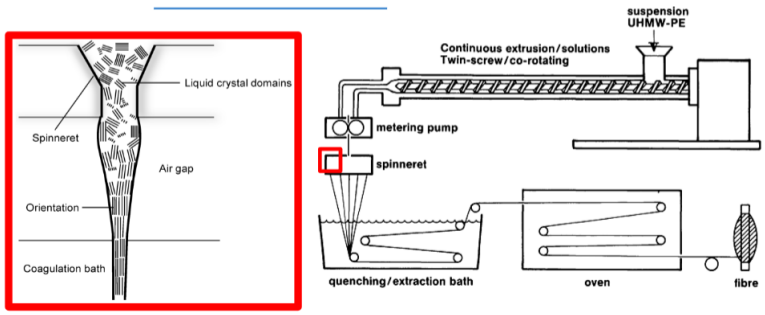
- Possible endocrine disruptor (interfere with the body's natural hormones)
- May cause cancer or developmental disturbances

Air Entrainement **(THINK CROCS!!!!!!):**

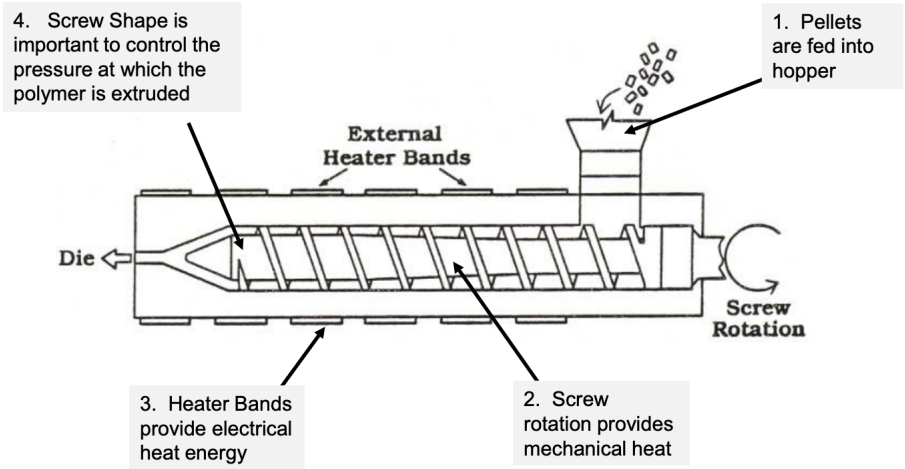
- Air bubbles introduced into polymer to form **expanded polymers or foam**
- Achieved using either: (1) a blowing agent that which expands and creates gas bubbles when heated or (2) dissolved gas in molten plastic under high pressure that form bubbles as pressure is released

6.2.4 Forming and Molding Methods

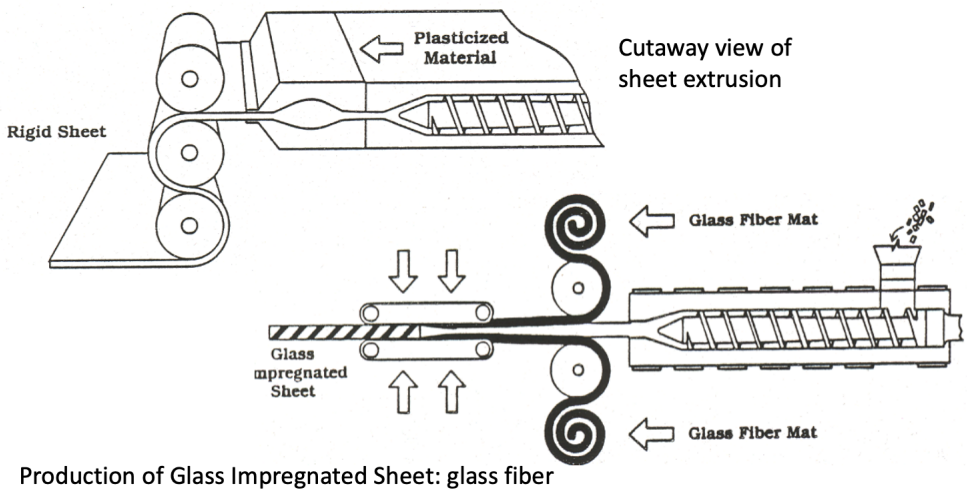
The technique used to form a polymer depends on: whether it is thermoplastic or thermosetting, final geometry and size.
Themoplastic materials are normally fabricated at elevated temperatures, with application of pressure to shape the material.
Thermoset materials are often formed with reliance on gravity and surface tension to pour into molds or act as a coating
Various methods are available to produce individual pieces with custom features:

- **Fibers**
  - Conditioning polymers to increase strength
  - Drawing (stretching) polymers to align the polymer chains in one direction
  - Results in very strong, stiff polymer fibers
  - Ultra-high molecular weight polyethylene after drawing is known as SPECTRA or DYNEEMA, and can be used in bullet proof vests, climbing rope, etc.
  - 

- **Extrusion of Thermoplastics**
  - Squeezing, pressing or pushing a material through a die to form a product with a consistent cross-sectional profile



- Extrusion of thermoplastic sheets (including glass impregnated sheet):



Production of Glass Impregnated Sheet: glass fiber sheets are introduced to upper and lower surfaces of extruded sheet before applying pressure

- **Blown Film Extrusion**
  - For thermoplastics
  - Using air pressure instead of a solid mold allows for precise control of very thin film production

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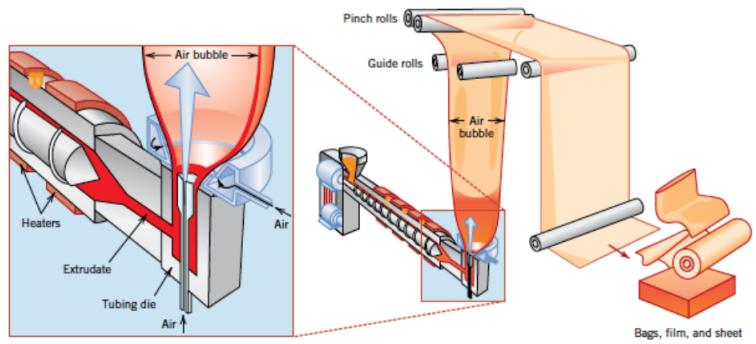

- **Blow Moulding**
  - For thermoplastics

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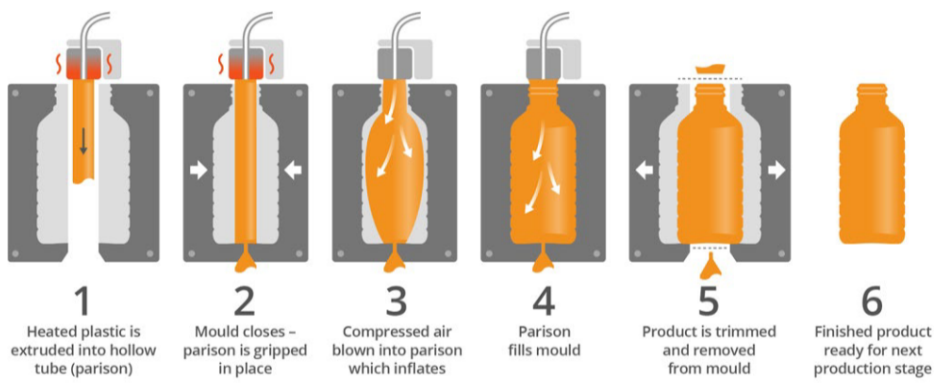
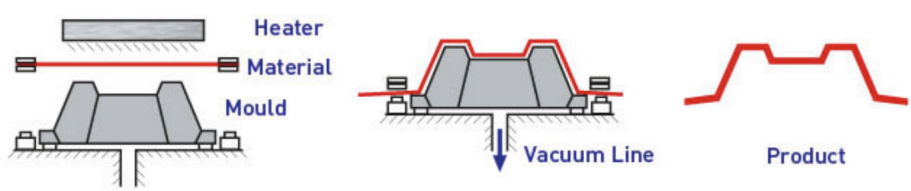
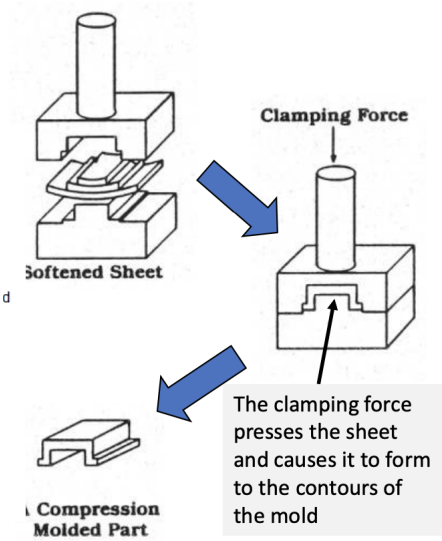


- **Vacuum Forming**
  - For thermoplastic sheets
  - Sheet of plastic heated to a high temperature, stretched onto a mould with a vacuum applied to force the sheet against the mould
  - <u>Limitations:</u> cannot form around holes or surfaces that go beyond 90 degrees to the vertical



- **Compression Moulding**
  - Can be used for both thermoplastics and thermosets
  - Polymer is heated and compressed between moulds

- Lower pressure than for injection moulding so less expensive



- **Injection Moulding**
  - In injection molding:
    1. Polymer granules are heated until molten
    2. Compressed by a ram or a screw
    3. Injected into a cold, split mold under pressure
    4. The molded polymer is cooled below T_g
    5. The mold opens and the product is ejected
  - Excess material is often pumped into the mold to compensate for contraction
  - Cycle time can be seconds or up to 5 minutes, depending on part size (far more expensive than vacuum or compression molds)

Molding method	Important notes
Blow Molding	• Produces thin uniform films, bags and other end products formed after film is produced
Vacuum Forming	• Yields lowest level of detail • Formed from sheet stock • Low cost of equipment
Compression Molding	• More detail than vacuum forming • Much lower cost than injection molding dies
Injection Molding	• Highest level of detail • Highest expense for fabrication

7 Ceramics and Cement! Like modern art pottery! AND CONCRETE!!!!!!!!!!

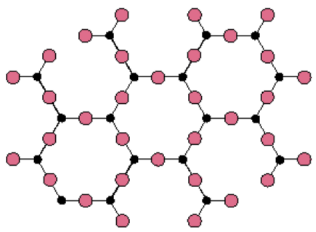
7.1 Glass and pottery!

Ceramics (POTTERY YAYYYY!):

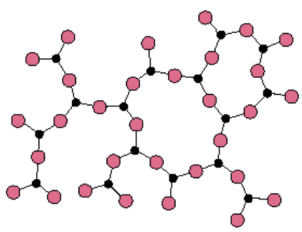
- Compounds of metallic and non-metallic elements
- Interatomic bonds can range from entirely ionic to entirely covalent
- Regular crystalline structure with long range order

GLASS:

- Same constituents and local bonds as ceramics, but are non-crystalline (amorphous) and have no long-range order



Schematic material of ceramic material with crystalline structure



Schematic material of glass with non-crystalline structure

Advantages of ceramics:

- Pottery!
- High melting point (excellent thermal insulator)
- High creep resistance
- High elastic modulus
- High hardness
- High wear resistance
- Excellent compressive strength
- Chemically inactive (often resistant to most acids, alkalis and organic solvents)
- High electrical resistivity

Disadvantages:

- Low density
- Low ductility (very brittle!)

- Low fracture toughness

High strength of ceramics due to restricted dislocation movement:

- Dislocation movement hardest for covalent bonds, and also hard for ionic bonds (which are both in ceramics)
- Dislocation movement is a lot easier in metals because all atoms are electrically neutral, and electrons can move freely

Fracture strength is related to flaws in the specimen
Fracture strength in ceramics is often much lower than predicted by interatomic bonding forces, and is due to the presence of flaws

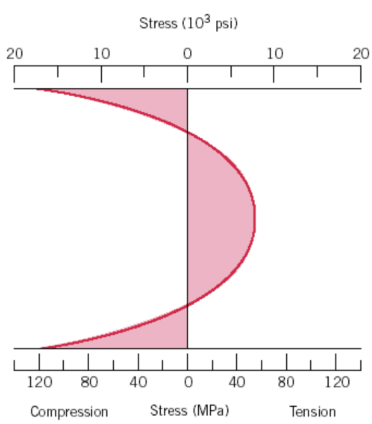
Strength of glass fibers:

- Strength of ceramic fibers can be very high (5000 MPa), because small fibers have a low probability of containing a large flaw
- With these structures, the experimental tensile strength can actually exceed the compressive strength

7.1.1 Glass Tempering

Tempered Glass:

- Outer surfaces have compressive stresses, while the interior is left in tension
- Material stores elastic energy that must be overcome before the material fractures
- Release of energy causes glass to shatter in small pieces



3-Step Heat Treatment for Glass Tempering:

1. Heat to temperature just below the softening point
2. Quench the surface in an inert gas (e.g. N2 gas) so that surface cools while interior stays hot
3. Allow center to cool to room temperature

7.1.2 How To Make Ceramics (Basically Pottery!)

- Powder
  Mill (grind) and screen constituents to obtain desired particle size
- Form
  Press or cast the powder into the desired shape (resulting part is still soft and pliable)
- Dry
  Drive out excess water before firing
  - As water is removed, inter-particle spacing decreases, resulting in overall shrinkage
  - Drying too rapidly can cause warping or cracking
- Fire!!!!!
  for clay-based aggregates, firing at a high temperature causes either vitrification or sintering
-
  - Vitrification: Liquid glass forms, which can flow between SiO 2 particles and make the part strong and waterproof by filling voids
  - Sintering: When firing a piece below the melting temperature (no liquids are formed), the particles coalesce due to an overall reduction in surface area - gaps between particles are reduced

7.2 CONCREEEEEEETE!!!!!!!!!!!!!! (and cement :))

We love concrete :) THE MAIN COURSE HAS ARRIVED EVERYONE!!!!!!!
BUT WHAT IS CONCRETE?!

Concrete:

- A composite material consisting of aggregate particles bound together in a solid body by cement
  - **Cement:** A ceramic that by a chemical reaction binds particulate aggregates into a cohesive structure
  - **Aggregate:** Granular material which provide the majority of the volume of concrete (sand, gravel). It is used as filler, providing dimensional stability and wear resistance.
  - **Reinforced Concrete:** Concrete that includes a third reinforcing material (usually steel)

Advantages of concrete

- Economical
- On-site fabrication
- Durable
- Fire resistant

Disadvantages

- Low ductility
- Low strength-to-weight
- Low tensile strength
- Associated with large carbon footprint

Properties of Concrete:

- Similar compressive strength to wood, about 10x less than steel
- It is about 10x stronger in compression than in tension

Hoover Dam Case Study Conclusions:

- The lower the water content in the cement mixture, the less shrinkage and potential for crack formation
- Concrete is strongest in compression: when cured in compression, concrete is strengthened
- Cement hardens by chemically reacting with water, which is an exothermic reaction

Hydraulic vs. Non-hydraulic Concrete:

- Hydraulic concrete hardens by reacting with water
- The difference from currently used concrete (Portland cement) lies in the use of volcanic ash from Pozzuoli, instead of cement as binder
- Used by the Romans!

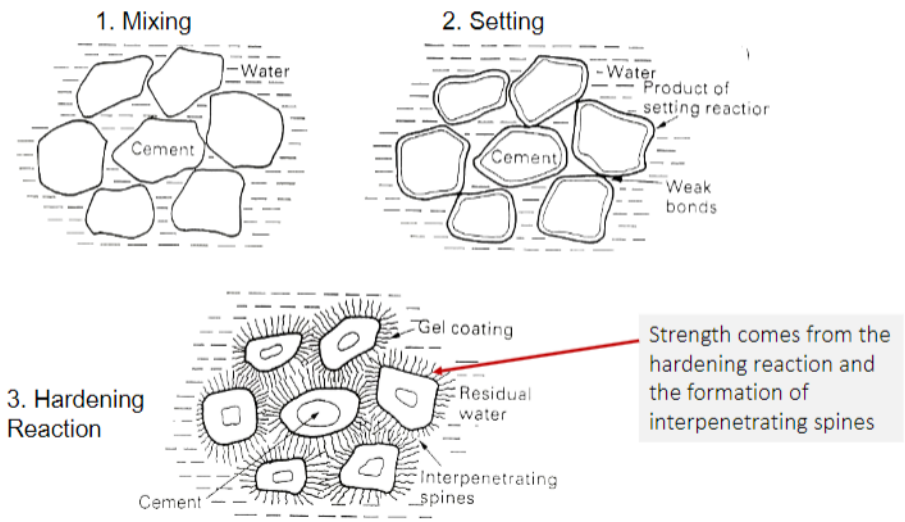
The Kiln:

- Thermally insulated chamber to produce high temperatures for hardening, drying and chemical reactions
- The direct flame and gases from combustion heats the raw meal to 1500°C to complete the chemical reaction, producing clinker (waste from concrete production)
- Produces a lot of carbon dioxide

Hydration of Portland Cement (Modern Cement):

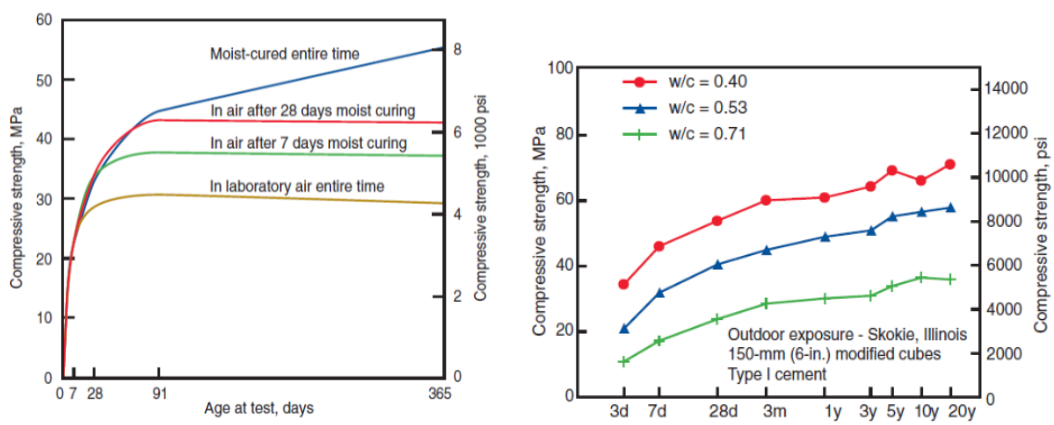
- Hydraulic cements harden by chemical reaction with water, and NOT by drying
- The reaction is exothermic, and heat is released
- Gypsum is added to slow the chemical reaction, so that there is time for placing and working the cement

- Two sets of reactions take place during hydration
  1. Setting (0 – 4 hours)
  2. Hardening (4 hours – years)



The water to cement ratio affects mechanical properties of cement:

- Too little water and cement powder is left unreacted, compromising mechanical properties
- Too much water beyond a threshold, and unreacted water gives rise to cracks once evaporated



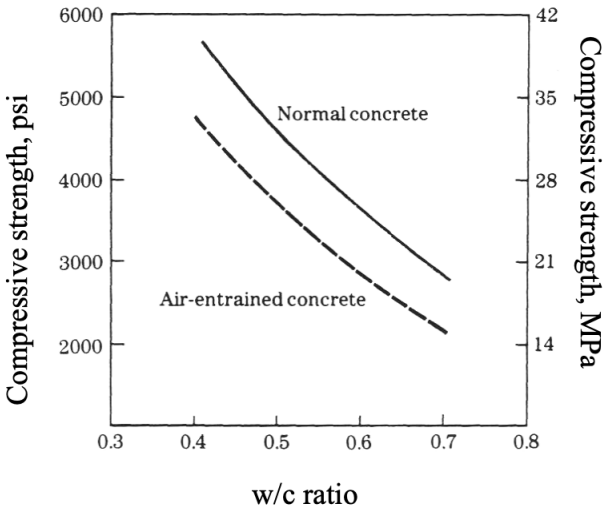
The following can be altered in concrete production:

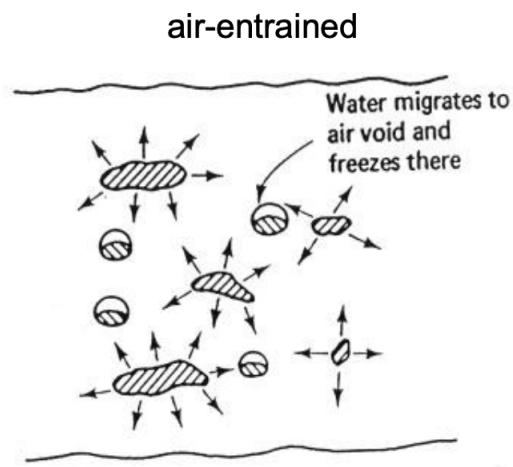
- Water content
- Air Entrainment
- Mechanical reinforcement (steel rebar, fibers)

Air Entrainement:

- Introduces thousands of microscopic air bubbles into concrete

- Decreases strength, but increases the ability of cement to withstand freeze-thaw cycles





Reinforcing Concrete With Steel:

- Reinforcing steel bar is commonly called rebar
- Rebar has a patterned surface morphology to help create a good bond with concrete and transfer the load to the steel
- Rebar is placed in regions of high tensile stress in the concrete, resulting in a strong composite structural material
- Failure typically occurs when concrete detaches from the rebar, such as due to corrosion of steel

8 Composites

Composites are materials with more than 1 phase present, each of which are chemically dissimilar and separated by a distinct interface.
Composites may have the following benefits:

- Low density
- High stiffness
- Small coefficient of thermal expansion
- Fatigue and impact resistant
- Corrosion resistance

Structure of Composites:

- They are composed of two distinct phases, (1) the **matrix** and (2) the **reinforcing phase**
- The most common composite structure is composed of fibre (reinforcing phase) and polymer (matrix)

8.1 Fiber-Based Composites

- Usually combinations of fibres made from ceramic, polymer, or glass embedded in a polymer matrix
- Typically 40-60% fiber by volume
- Characteristic "weave" pattern (e.g. carbon fibre), or less organized fibre patterns with randomized cut fibres (e.g. fibreglass-based chairs)
- **Advantages**: good combination of stiffness, density and fracture toughness.
- **Disadvantages**: often expensive, may be difficult to process, and often difficult to detect damage (cracks). Ideally suited to withstand tension, not compression.

Properties of the Matrix in Composites:

- Typically low density, relatively ductile materials
- Matrix must bind to fiber very well since it transmits external loads to the fibers, while carrying only a small fraction of the load itself
- It separates the fibres and stops cracks from propagating directly from fibre to fibre
- Ex: polyesters, vinyl esters, polyimides

Properties of Fibre Materials:

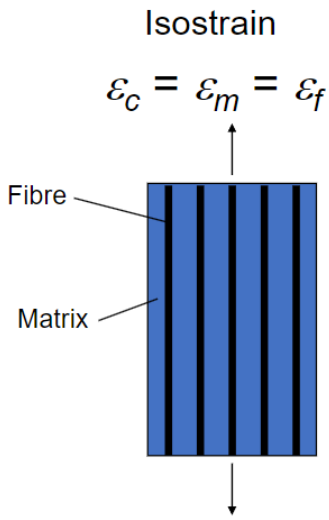
- High strength of fibres is achieved due to low probability of flaws in individual fibres
- Carbon fibers have high specific modulus and specific strength compared to all fibre materials. It is a semi-crystalline version of carbon
- Example of common fibres: glass (fiberglass), carbon, Spectra (polyethylene), Kevlar

8.1.1 Upper and Lower Bounds of Performance for Fiber Composites

- Long fiber composite materials are highly *anisotropic* (mechanical behavior is direction-dependent)
- The extreme cases are represented by fibers that are arranged at 0 and 90 degrees to the tensile force
- We can use two cases to determine the upper and lower bounds of fiber-based composites, and see how they vary based on the amount of fibre vs. matrix in the material:

*subscript c refers to composite, subscript m refers to matrix, and subscript f refers to fiber

Isostrain Analysis



- Isostrain represents the ideal arrangement, as the composite structure has been optimized for loading direction
- This represents the *upper bound* for overall performance
- Assume that under load: $\varepsilon_c = \varepsilon_m = \varepsilon_f$
- The total load is the load carried by the fibers plus the load carried by the matrix

$$F_c = F_m + F_f$$

$$\sigma_c A_c = \sigma_m A_m + \sigma_f A_f$$

- Therefore

$$\sigma_c = \sigma_m \frac{A_m}{A_c} + \sigma_f \frac{A_f}{A_c}$$

- Since the length of the fibres and matrix are the same, we can replace the area fraction with the volume fraction (V_f, and V_m are the volume fraction of fiber and matrix, respectively)

$$\sigma_c = \sigma_m V_m + \sigma_f V_f$$

- In isostrain, the stiffness of the overall material is determined by the stiffness and volume fractions of the fibre and matrix

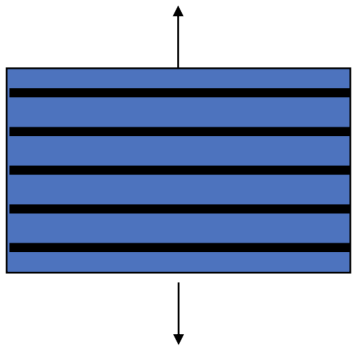
$$E_c = E_m V_m + E_f V_f$$

Isostress Analysis

- Fibers are oriented perpendicular to the force
- *Lower-bound* of performance (worst-case for composite)

Isostress (layers)

$\sigma_c = \sigma_m = \sigma_f$



- Under that load, each layer experiences the same stress

$$E_c = \frac{E_m E_f}{E_m V_f + E_f V_m}$$

We can examine the ratio of the load carried by the fibers versus the load carried by the matrix portion of the composite:

In **isostress conditions** ($\sigma_c = \sigma_m = \sigma_f$)

$$\frac{F_f}{F_m} = 1$$

All of the fibre and matrix layers experience the same force, and therefore the same stress

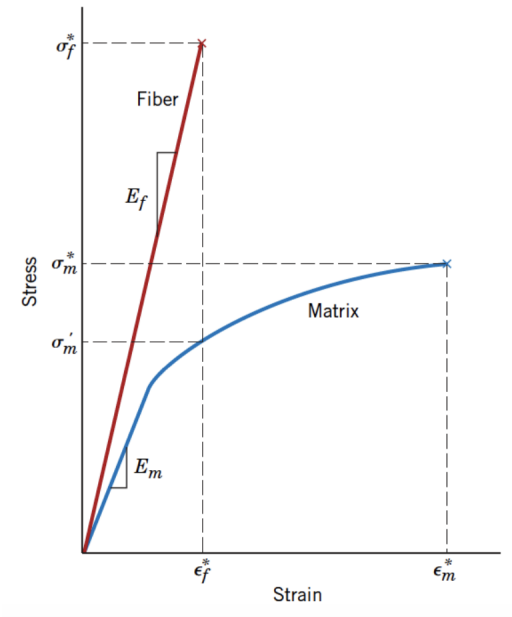
In **isostrain conditions** ($\varepsilon_c = \varepsilon_m = \varepsilon_f$)

$$\frac{F_f}{F_m} = \frac{\sigma_f A_f}{\sigma_m A_m} = \frac{\sigma_f V_f}{\sigma_m V_m} = \frac{\varepsilon_f E_f V_f}{\varepsilon_m E_m V_m} \Rightarrow \frac{F_f}{F_m} = \frac{E_f V_f}{E_m V_m}$$

Fiber Orientation and Length:

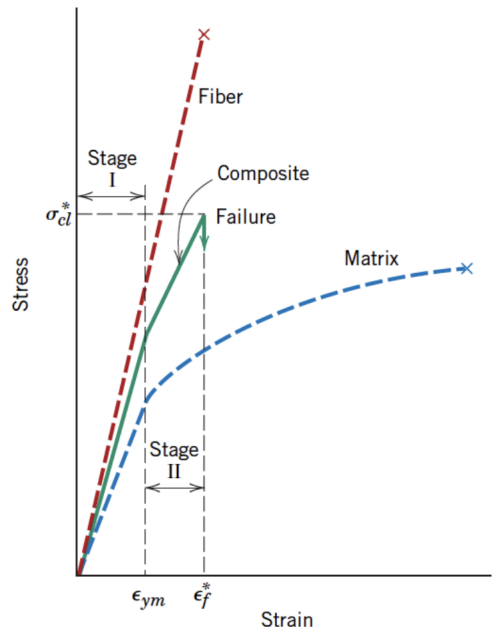
- Longer fibers all oriented in the direction of tension lead to best performance

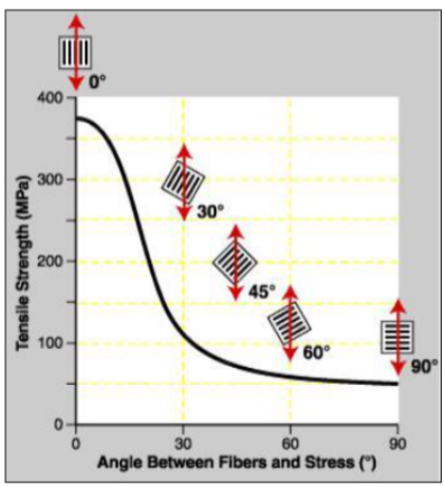
Stress-Strain Behaviour of Aligned Fibre Composites: For fibers aligned parallel to the loading axis, we can represent the stress-strain behaviour of the fibre and matrix schematically:



Material with these fibres and matrix will exhibit a uniaxial stress-strain response:

- **Stage I:** both fibres and matrix deform elastically
- **Stage II:** the matrix starts to yield as the fibres continue to deform elastically
- Going from Stage I to Stage II, the proportion of load carried by the fibres increases
- Composite failure begins when the fibres start to fracture
- These fractured fibres are capable of sustaining a smaller load as the matrix is plastically deformed



Effect of Orientation on Strength of Composites

- When fibres are oriented in the direction of the tensile force (0°), the tensile strength is determined predominantly by the fibre tensile strength
- When fibres are oriented perpendicular to tensile force (90°), the weakest link is the strength of the matrix: $(\sigma_c)_{max} = (\sigma_m)_{UTS}$