Science And Technology of Materials

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1 GENERAL OVERVIEW, CLASSIFICATION OF MATERIALS, CRYSTALLINE STRUCTURES, DEFECTS

1.1 METALS AND ALLOYS

- Conductors for heat and electricity
- Are prepared by melting and can be machined
- Usually solid at room temperature
- Can form alloys
- They have corrosion and oxidation issues
- Density is typically in the range of 2.7 to $8g/cm^3$
- Metallic bonds consist of atoms sharing delocalized valence electrons among all others
- Alloys are classified according to their majority element (eg. Iron-based alloys, copper-based alloys etc)
- Each nucleus is bound to others by the global electric field, but it is not bound to a particular other atom, and neither are the delocalized electrons
- Metals are not transparent
- Mobile electrons make them good thermal and electrical conductors
- High plasticity (tendency to deform due to non-directional character) and high toughness (resistance to crack propagation and mechanical shocks)
- Bonding strength (BS) affects hardness (H) and melting point (MP)

1.2 CERAMICS

- Compounds (oxides, carbides, nitrides etc) with density ranging between 3 and 5 g/cm^3
- Hard and brittle: hard to machine
- Insulators
- High melting point
- Prepared by sintering or other; never melting

1.3 GLASSES

- Prepared by melting of oxides
- Hard, brittle and can only be deformed at suitable temperatures. Cannot be machined
- Insulators
- Density of about $2.5g/cm^3$

1.4 IONIC COMPOUNDS

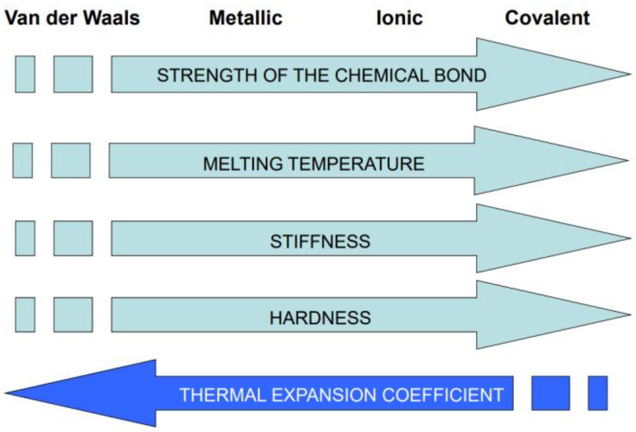
- Composed of metals (electropositive) and non-metals (electronegative) ions with different sizes
- Bonds are created by attractive interactions between oppositely charged ions
- Total charge of a crystal is zero
- Some frequencies of visible light can interact with electrons involved in ionic bonds, so they can be partially transparent and coloured
- Insulators when solid but can be conductors when dissolved
- High melting point and low to mid density

1.5 COVALENT STRUCTURES

- Covalent bonds are highly directional
- Transparent and colourless
- Low electrical conductivity
- High melting properties
- Low density
- High hardness and brittle

1.6 POLYMERS

- Organic macro-molecules, natural or synthetic
- Prepared by organic synthesis
- Low density ($< 1g/cm^3$)
- Easy to machine
- Insulators
- Low thermal and mechanical properties
- Covalent + Van der Waals bonds
- Some can conduct electricity with the use of doping
- Most cannot sustain high temperatures, show low mechanical resistance and are flexible because of the presence of weak secondary bonds (Van der Waals)
- Bond Comparisons:



1.7 COMPOSITES

- Two phases: matrix and second phase
- Are classified according to the matrix, which can be
  - Metal matrix composites
  - Polymer matrix composites
  - Ceramic matrix composites
  - Glass and glass-ceramic matrix composites
- Can also be classified according to second phase morphology
  - Fiber reinforced composites
  - Particle reinforced composites
- Second phase can be metal, polymer, ceramic, glass

1.8 STRUCTURE OF MATERIALS

- Materials can generally be:
    - Monoatomic gases
        - No order
        - E.g. Argon gas
    - Amorphous materials
        - only short-range order
        - E.g. Glass, plastic
    - Liquid crystals
        - Long- and short-range order
        - Eg LCD polymers
    - Crystalline Materials
        - Single crystals (e.g. silicon, GaAs) and polycrystalline (e.g. metals, alloys and most ceramics)
        - Short- and long-range order
    - Semi-crystalline
        - E.g. Some polymers, glass-ceramics
- Amorphous structures do not have a defined melting temperature, but undergo progressive softening
    - Crystalline structures have a melting temperature, which is directly proportional to bond strength
    - However, small nanoparticles (Smaller than 10nm) will melt at a lower temperature

1.9 CRYSTALLINE STRUCTURES

- Atoms/ions/molecules (particles from now on) are in ordered positions called crystalline cells
- Particles are at equilibrium position between attraction and repulsion
    - Bond length or bond distance (usually 0.1-0.26nm at room temperature without external forces)
- When describing a crystalline cell, we use a, b, c for cell parameters and α, β, γ for cell angles
- a, b, c vary with temperature (T) and applied forces.
    - At $0K$ they are at equilibrium distance. Increasing T causes thermal expansion, then melting
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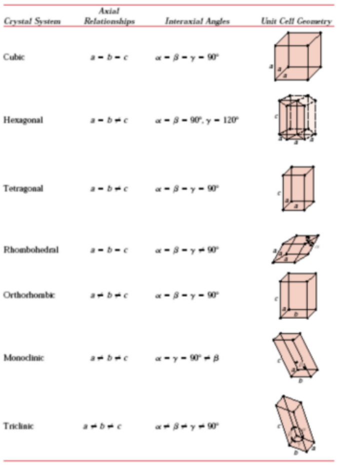
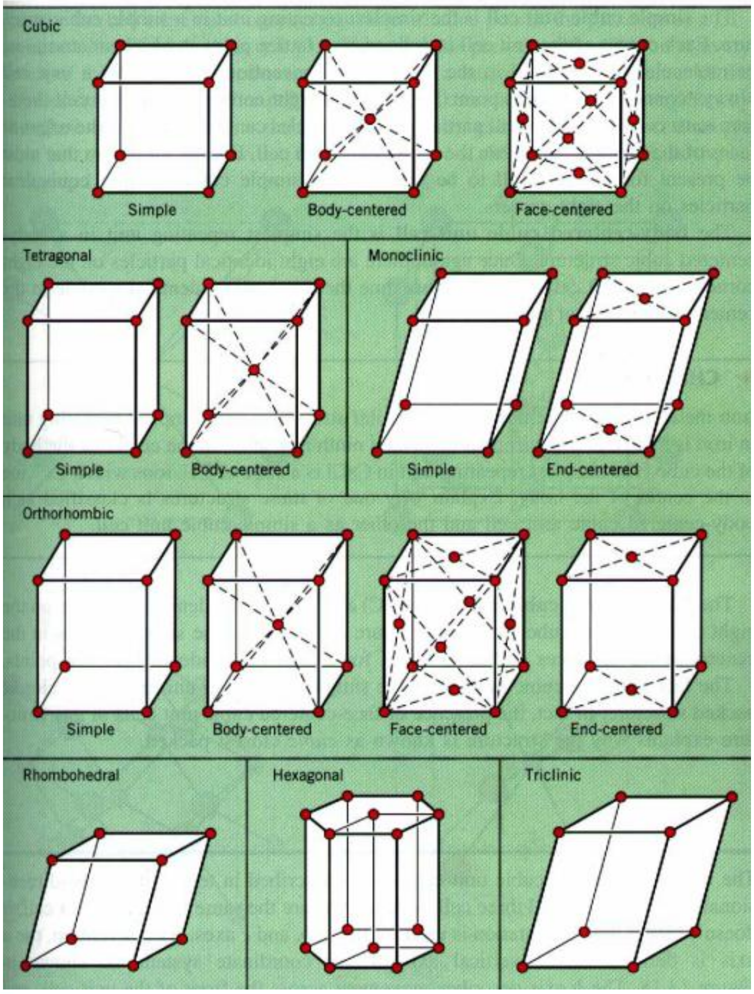


Crystal System	Axial Relationships	Interaxial Angles	Unit Cell Geometry
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	

- Bravais' Lattice Cells:



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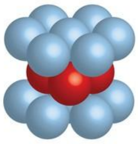

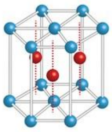

hexagonal (hcp)

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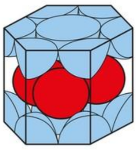
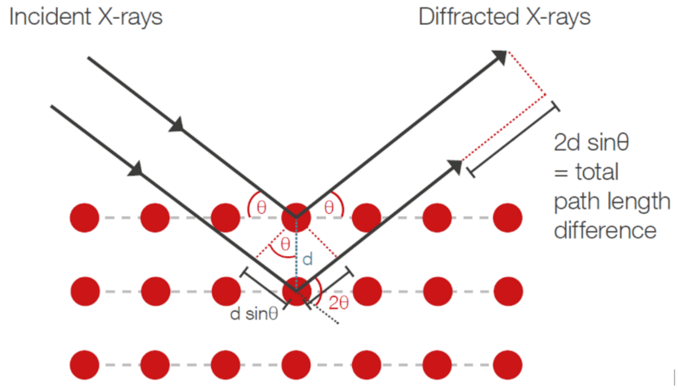


- (Hexagonal Compact/HC cell)

1.10 X-Ray Diffraction (XRD)

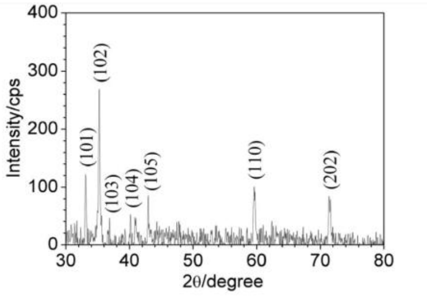
- Method used to identify crystal structures



-
- Bragg's law:

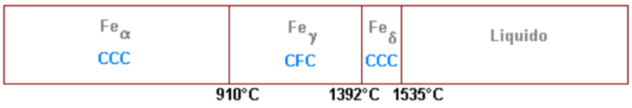
$$n\lambda = 2d\sin\theta$$

  - $n \in \mathbb{Z}^+$
  - d is the spacing between diffracting planes
  - θ is the angle of incidence



- Fig. 3 XRD pattern of the in situ synthesized SiC NWs.
- Interplanar distance d depends on lattice parameters and miller indices h, k, l. For a cubic cell:

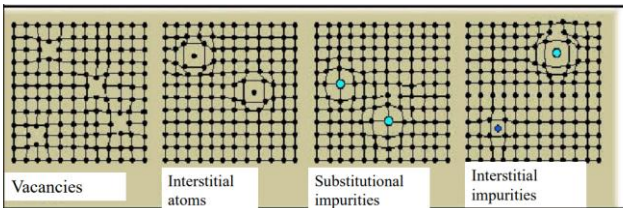
$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

- Allotropy or polymorphism is the change of crystalline structure during heating (as a solid)
  - 

1.11 DEFECTS

- Crystalline structures are not completely ordered. There are lattice defects
  - Zero-dimensional defects (point defects)
  - Monodimensional defects
  - Bidimensional defects
  - Three-dimensional defects
- Lattice defects influence:
  - Physical properties (e.g. density)
  - Mechanical properties (e.g. strength)
  - Technological properties (e.g. cold working ability, conductivity, resistance to corrosion)

1.11.1 Point Defects

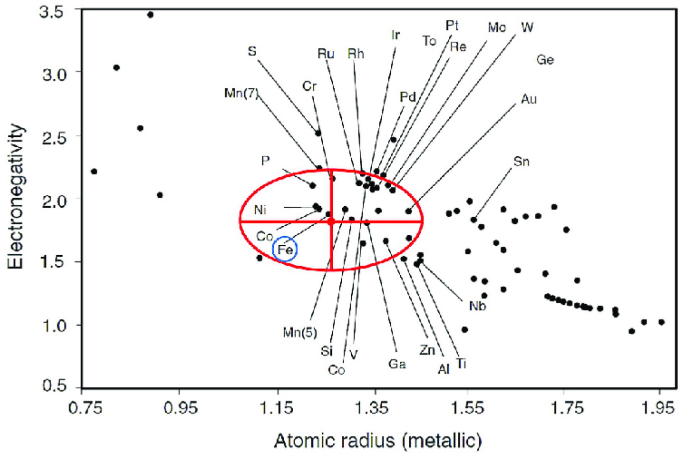
- Point defects can be:
  - Vacancies
  - Interstitial atoms
  - Substitutional atoms
  - Defects in ionic solids ("Couple")
- 

- Point defects will cause a stress inside the crystal

- Vacancies are caused by impurities, presence of elements with different oxidation numbers (valences), solidification process, or vibrations induced by T
  - Vacancy concentration is given by Arrhenius' Law:

    $$\frac{N_V}{N_{TOT}} = Ce^{-\frac{E_V}{KT}}$$

    - N_V: equilibrium number of vacancies
    - N_{TOT}: Total number of atomic sites
    - C: constant
    - E_V: Energy required for the formation of a vacancy
    - $K = 1.38 \times 10^{-23} m^2 kg s^{-2} K^{-1}$: Boltzmann Constant
- Interstitial atoms do not occupy nodes, and there is a limit of solubility related to the maximum amount of stress accepted by the crystal
  - If the limit is surpassed, a second phase is formed rather than a solid solution
- Substitutional atoms add compressive stress if bigger than host atoms, or tensile stress if smaller
  - They can be ordered (forming an ordered solid solution) or random
    - Ordered structures will get destroyed at high temperatures
- There are two main types of ion defects:
  - Frenkel defect: An ion creates a vacancy and moves into an interstitial position
  - Schottky defect: 1 anion vacancy + 1 cation vacancy
  - Both types increase electrical conductivity
- Defects make alloying possible and substitutional impurities are necessary for charge movement in semiconductor science
- For two metals to "blend" and form a substitutional solid solution they must follow all four "Humme-Rothery Rules, which are:
  - The difference in atomic radii must be less than 15%
  - Both metals must have the same crystal structure (e.g. FCC, BCC etc.)
  - Their electronegativity must be similar ($\Delta E < 0.4$ for partial solubility and $\Delta E < 0.2$ for full solubility. Usually)
  - A metal prefers to dissolve another metal of the same or higher valency. If their valencies are different, the electron sea that holds the structure together gets much harder to maintain.
    - Same valency means that percentage of each metal does not matter: the solution will form
    - Different valency means that solubility can be possible but is limited.
    - Examples:
      - Copper and nickel (Both +2) can form alloys of 99% Copper and 1% Nickel just like they can form alloys of 1% Copper and 99% Nickel.
      - Copper (+2) and Silver (+1) have limited solubility, since they follow the other 3 rules, but their valencies are different. So proportions of each are limited.
- Darken-Gurry Map can help figure out what metals can form solid solutions with others

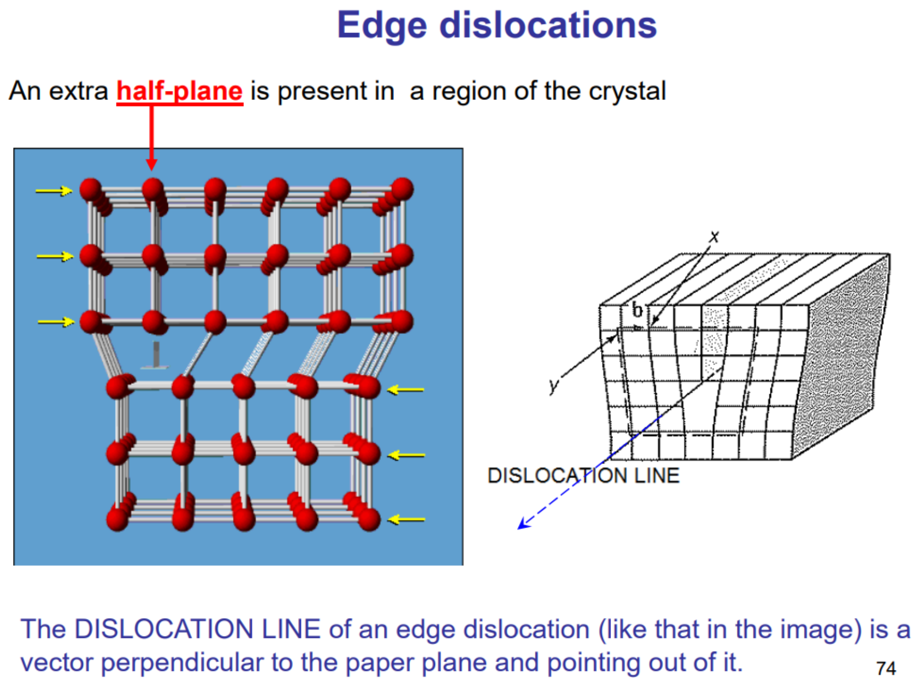


- Metals are plotted on the atomic radius-electronegativity scatter map, and an ellipse is drawn around the first metal in the alloy. The height is ± 0.4 electronegativity units and the width is about 15% of the radius. Metals inside the ellipse are likely to mix well

- For interstitial alloys, only small atoms can enter a metallic cell as interstitial defects and are at most 10% of composition (limit for carbon in iron is about 2%, so the number varies)

1.11.2 Linear Defects

- Dislocations can e seen as irregular lines on the cross-section of a material at very high magnifications. They cause distortion of the crystal around a row of atoms
- They are produced during solidification and during plastic deformation
- They are usually present in commercial materials
- Real dislocations are quite irregular and complex in shape, but we can separate them into:
  - Edge/linear
  - Screw
  - Real dislocations have both edge and screw components (So they are mixed)



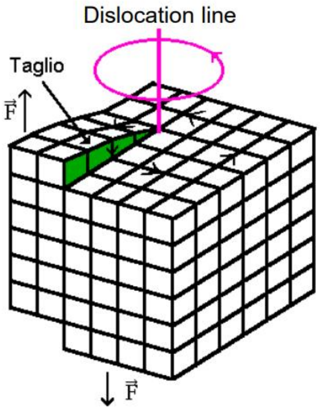
Edge dislocations

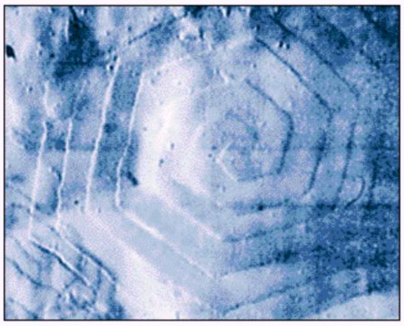
An extra **half-plane** is present in a region of the crystal

The DISLOCATION LINE of an edge dislocation (like that in the image) is a vector perpendicular to the paper plane and pointing out of it.

Screw dislocations

A screw dislocation does not include an extra plane: the planes perpendicular to the dislocation line show small distortion and they trace a **spiral path** around the dislocation line.





Superficie di un cristallo organico: in evidenza la spirale dovuta all'accrescimento del cristallo per la presenza di una dislocazione a vite.

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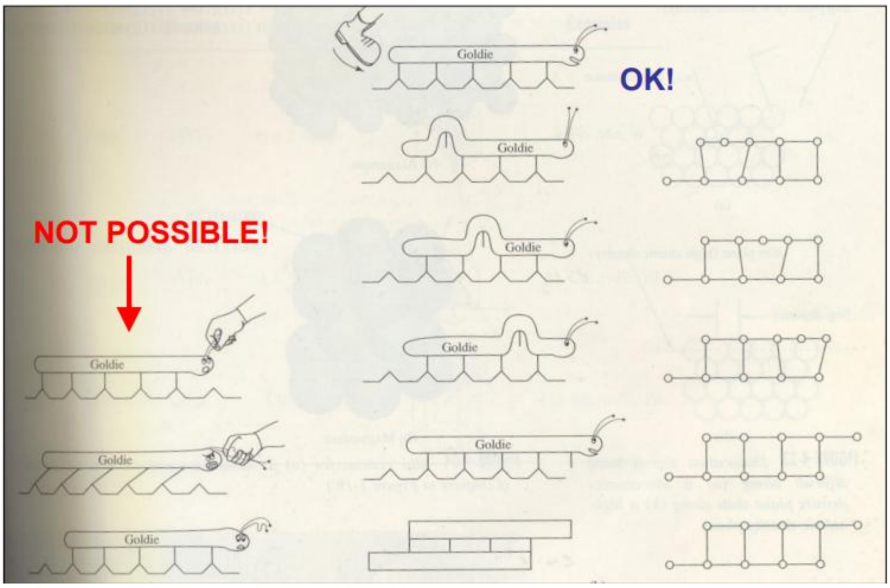
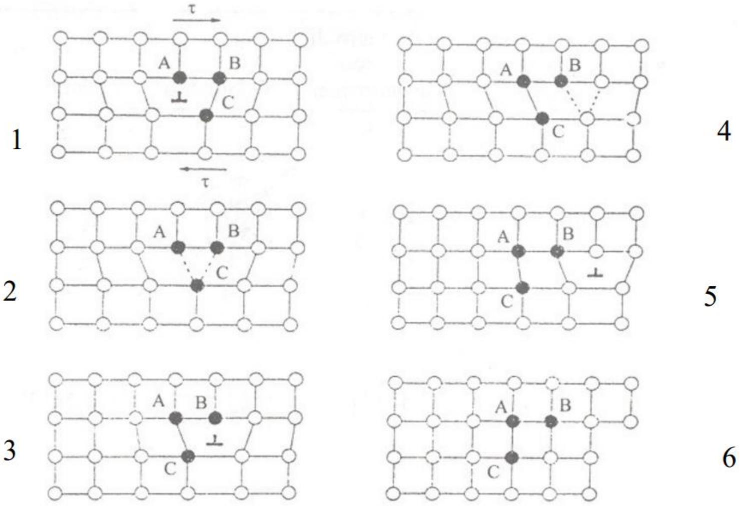
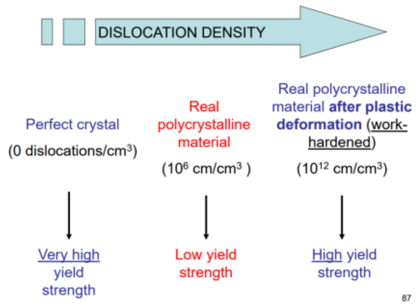
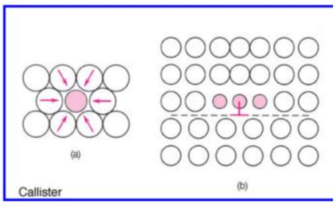
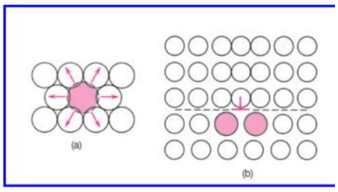
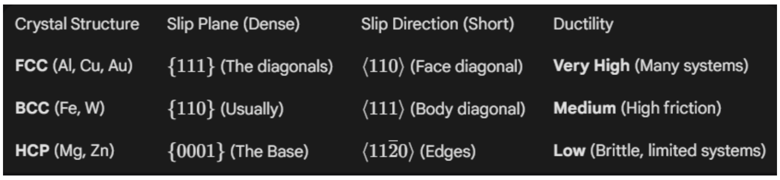
- Visualization for how dislocation move:
  - 

  - 

- Dislocations allow for plastic deformation to take 0.01-1% the force of deforming a perfect crystal, since in a perfect crystal deformation would require breaking many more bonds at once.
- Dislocation (And therefore plastic deformation) begins when yield strength has been reached
- Plastic deformation refers to irreversible deformation or changes in shape. This is because stress applied causes dislocation motion which do not revert when the stress is removed.
  - Elastic deformation is the opposite – a temporary change in shape. No dislocations
- Movement of dislocations generates new dislocations.
  - A dislocation forest is then produced, limiting further movement of dislocations
  - There also is repulsion between stress fields generated by the dislocations, further impeding movement
    - Yield strength (and therefore resistance to further deformation) increases
- Hardening is obtained during deformation of a metallic materials by increasing the number of dislocations
  - Before deformation, there are about $10^6 cm$ of dislocation per cm^3
  - After deformation, there are about 10^{12}.
  - There are too many dislocations, so they interfere, leading to increased strength and reduced ductility
  - 

- Dislocations create stress fields (Compression when there are extra half-planes, Tension otherwise).
- Impurities migrate to these fields to lower energy, "pinning" the dislocation (Strengthening).
- Same-sign dislocations repel (Work Hardening).
- Opposite-sign dislocations annihilate (Recovery/Annealing).
- How alloying can increase dislocations:
  - 



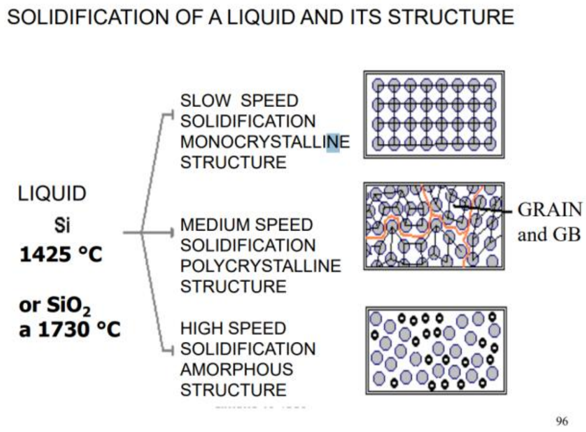
- Dislocations are “lazy”. They only move on the "smoothest" floors.
  - High Density Plane (The Smooth Floor): When atoms are packed tight, the surface is flatter. Dislocations glide easily. (This is where slip happens).
  - Low Density Plane (The Bumpy Road): When atoms are spread out, there are deep holes between them. Dislocations get stuck. (Slip does NOT happen here).
- 

Crystal Structure	Slip Plane (Dense)	Slip Direction (Short)	Ductility
FCC (Al, Cu, Au)	$\{111\}$ (The diagonals)	$\langle 110\rangle$ (Face diagonal)	**Very High** (Many systems)
BCC (Fe, W)	$\{110\}$ (Usually)	$\langle 111\rangle$ (Body diagonal)	**Medium** (High friction)
HCP (Mg, Zn)	$\{0001\}$ (The Base)	$\langle 11\bar{2}0\rangle$ (Edges)	**Low** (Brittle, limited systems)

1.12 COMPARING SOLIDS

- In ionic solids, there are no preferred sliding directions
  - When a dislocation occurs, equal-charge ions overlap and repel, leading to crystal fracture
    - Ionic crystals are brittle
- In covalent solids (e.g. diamond, SiC) directional bonding is unfavourable to dislocation motion
  - Therefore, covalent solids are brittle materials
- In metallic solids, motion occurs smoothly, so they have significant plastic deformation ability

1.13 CRYSTALLINE STRUCTURES



- Crystal structures can be:
  - Monocrystals: crystalline cells are oriented in the same way (Produced with slow solidification)
    - E.g. silicon for microelectronics, with about 10 defects/cm^2
  - Polycrystals: Crystalline cells are oriented in the same way ONLY inside the same grains (Produced with fast solidification)
- Larger grains have greater resistance to creep deformation
- Jet engine fan blades (E.g. in commercial turbofan engines) use monocrystalline nickel-based superalloys to provide great strength at very high temperatures.
  - A superalloy is one that provides huge creep resistance, even at high temperatures (Close to melting point). They also resist corrosion very well.

    - Some nickel superalloys such as gamma prime (Ni_3Al) actually get more resistant as it gets hotter (up to about 800°C)
- Grain boundaries separate grains, and in a 3D view they are surfaces
    - Grain boundaries are not precise lines, but have a thickness of about 2-5 atomic diameters and are a “transition area” between two grains
- For lower temperatures ($T < 0.5T_m$), finer grains provide better strength.
    - At higher temperatures, larger crystals are better
    - 

Feature	Low Temp (Car Chassis)	High Temp (Jet Engine Blade)
Dominant Enemy	Dislocation Motion (Slip)	Grain Boundary Sliding (Creep)
Role of Boundaries	**Barriers** (Stop movement)	**Lubricants** (Facilitate sliding)
Ideal Structure	**Fine Grains** (Hall-Petch)	**Single Crystal** (No boundaries)
Material Example	High-Strength Steel	Nickel Superalloy

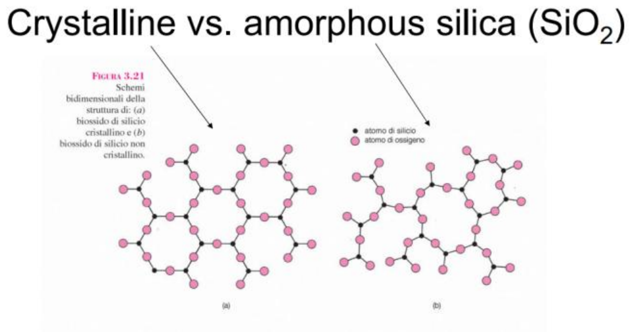
- Grain boundaries are more chemically reactive in comparison to grains since they have a higher energy state
- Grains can also be found in ceramics
- For ceramic crystals (such as silica), monocrystalline structures tend to be transparent, while polycrystalline structures are more opaque due to refraction occurring over and over

1.14 3D DEFECTS

- When making an interstitial solid solution, if we go above solubility limit, we get a second phase forming. This is a type of 3D defect.
    - This is because the second phase has a lower energy state than if it was dissolved.
- Pores and cavities can strongly decrease mechanical, electrical and optical properties of materials
- Cracks also decrease mechanical properties, leading to catastrophic failure (fracture) of the material
    - Especially in ceramics
- Lattice distortions create stress fields that oppose plastic deformation
    - Yield strength is increased

1.15 AMORPHOUS MATERIALS

- Disordered structure with no melting point
    - They instead have a variation in viscosity with temperature
- Glasses and many polymers are amorphous
- They have short range order (few nm)
- They are formed with rapid cooling, giving the material no time to form crystals



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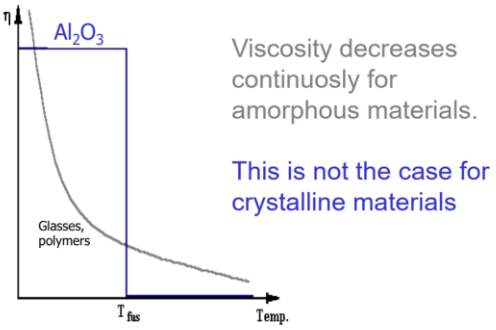
- They are not thermodynamically stable:
    - They become crystalline if properly heated
    - They are therefore high-energy
- Viscosity is a measure of resistance to flow
    - Unit is “Poise” ($10Poise = 1Pa\ s = 1Nm^{-2}s$)
    - Symbol generally is η



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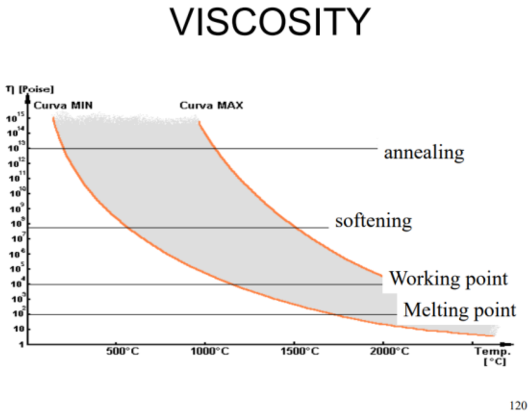
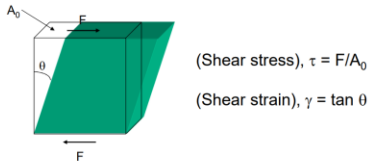
- For silicate glasses:



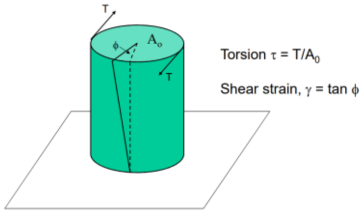
    -
    - The graph shows min and max because not all types of glass are the same.
    - Annealing happens at around $10^{13}Poise$
    - Softening happens at around $10^{7.6}Poise$
    - Working point happens at around $10^{4}Poise$
    - Melting point happens at about $10^{2}Poise$
- A metallic glass is formed when a metal or alloy is solidified very fast, creating an amorphous metal
    - They have high corrosion resistance since there are no grain boundaries to “eat through”

2 MECHANICAL PROPERTIES OF MATERIALS (PART 1)

- Stress (σ) is measured in Newtons per meter (Nm^{-2}) or often $MPa = Nmm^{-2}$ (Megapascal). It can be
    - Tensile
    - Compressive
    - Bending
    - Shear
-
$$\sigma = \frac{F}{A_0}$$
- Strain (ε) is the deformation. It is dimensionless (percentage)
$$\varepsilon = \frac{l - l_0}{l_0} = \frac{\Delta l}{l_0}$$
- 

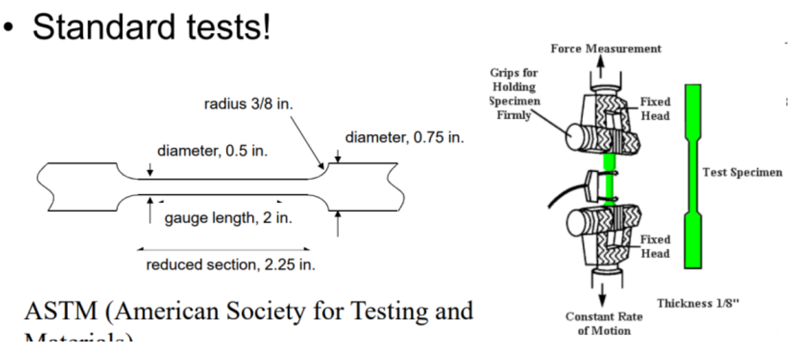
(Shear stress), $\tau = F/A_0$

(Shear strain), $\gamma = \tan\theta$

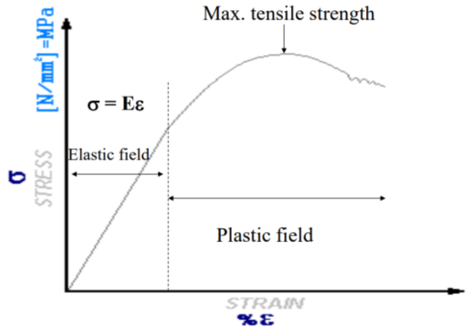
- 

Torsion $\tau = T/A_0$

Shear strain, $\gamma = \tan\phi$

- 
• Standard tests!

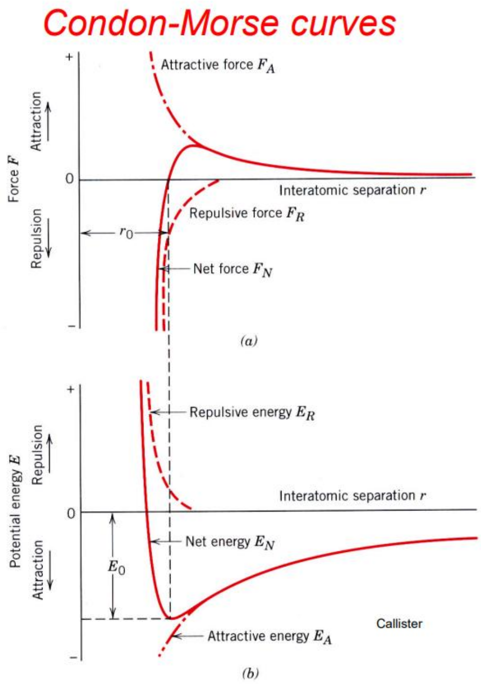
ASTM (American Society for Testing and Materials)

- For most materials, Hooke's Law applies
$$\sigma = E\varepsilon$$
$$[E] = MPa$$
    - Where E is Young's Modulus (Or elastic modulus)
- 

- $E_{ceramics} > E_{metals} \gg E_{polymers}$
  - Or better:

$$E_{CovalentSolids} > E_{CrystallineOxides} > E_{Glasses} > E_{Metals} \gg E_{Polymers}$$

- $E \propto \text{Atomic bond energy}$
- No fracture of bonds in elastic field. Bond length is increased though, which is reversible



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  - The above graph shows relation between interatomic separation and the force applied between two atoms. Equilibrium is reached when net energy is minimized, and net force is therefore zero.
  - $E \propto \frac{dF}{dr}$
  - Weaker bonds will have lower forces.
- Generally, as elastic modulus increases, we can expect an increase in melting temperature
- Amorphous structures show lower E than crystalline ones
- Elastic modulus is not related to movement of dislocations, since dislocations affect plastic deformation
- In the elastic region:

$$E = \frac{d\sigma}{d\varepsilon}$$

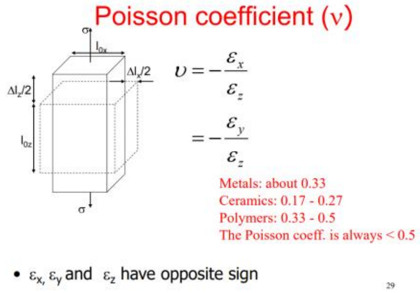
- Tensile tests require:
  - Sample preparation
  - Destruction of the sample
  - The material to not be brittle
- Sonic tests can also be used. This involves tapping a sample and studying the sound emitted to determine E:

$$E = 0.9465 \frac{\Gamma \nu^2 L^4 \rho}{t^2}$$

  - Where:
    - Γ: Shape constant

        - ν: Resonant frequency
        - L: Sample length
        - ρ: Material density
        - t: Sample thickness
- Elastic modulus decreases with temperature increases
- When we have solid solutions, we take a weighted average based on volumetric fraction of the composition:

$$E_C = \sum_{n=1}^{N} E_n f_{vn}$$

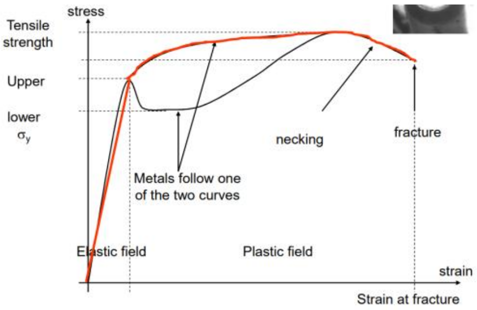
- 

  Poisson coefficient (ν)

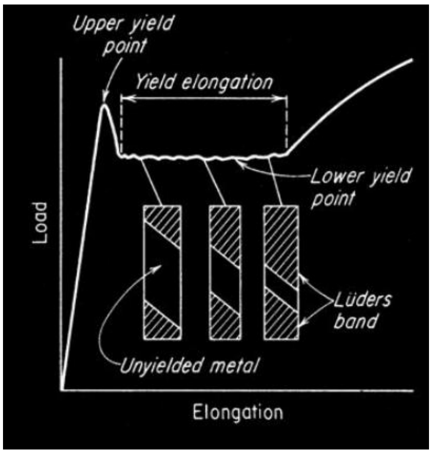
  $$\upsilon = -\frac{\varepsilon_x}{\varepsilon_z} = -\frac{\varepsilon_y}{\varepsilon_z}$$

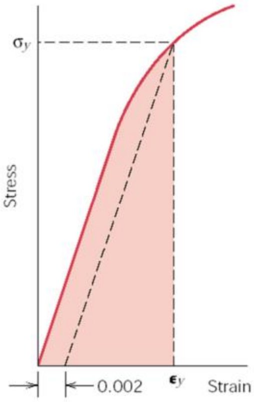
  Metals: about 0.33
  Ceramics: 0.17 - 0.27
  Polymers: 0.33 - 0.5
  The Poisson coeff. is always < 0.5

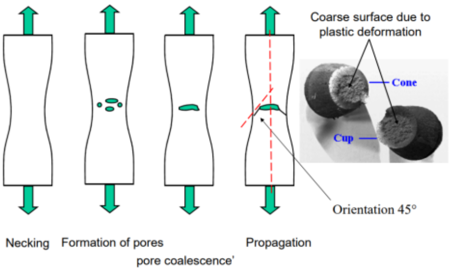
  - ε_x, ε_y and ε_z have opposite sign

- For some materials, E is not constant throughout the elastic regime, so it must be calculated locally
    - This is non-linear elasticity, or in some cases it can show anelastic behaviour, where time is required to recover from deformation (some polymers show this)
- When $\varepsilon > 0.002$ (approximately), Hooke's Law no longer applies
    - Bonds start breaking, and we have plastic deformation
    - The boundary between the two is defined as yield strength or limit of proportionality
    - 

    - The black line happens with low-carbon steel (for example). Up to a certain point, dislocations are pinned, therefore blocking dislocation movement up to the upper yield point. Then, dislocations are freed from the pins and start moving with less force required (lower yield point). (Lower yield point is usually what we care about)
    - In the lower yield point, we get "Lüders Bands": bands of yielded metal which propagate as it gets stretched. These bands do not all form at the same time, which is why the lower yield point is not a smooth, flat line:

        - 

- To calculate yield strength for the other type of curve (the red one on top), we draw a line which starts at 0.2% strain which is parallel to the real stress-strain. Where the two curves intersect, we have our yield strength:
    - 

- Dislocations lower yield strength
- BCC and FCC have at least 12 sliding planes while HCP has a maximum of 6. Therefore FCC and BCC metals are ductile with large plastic deformation, while HCP metals are more brittle
- Strain which is permanent after a stress is applied is called permanent deformation, while the recovered strain is called elastic recovery
- Necking is the reduction of cross-sectional area of an object due to stress causing rearrangement of the structure. This causes further deformation to be easier
    - After necking, ductile fracture occurs and one side of the fracture looks like a cup and the other like a cone. It is a fibrous (rough) fracture. This happens in stages:
        - Necking
        - Formation of pores
        - Pore coalescence (Pores merge into one big pore)
        - Propagation at 45° from direction of tensile stress
        - 

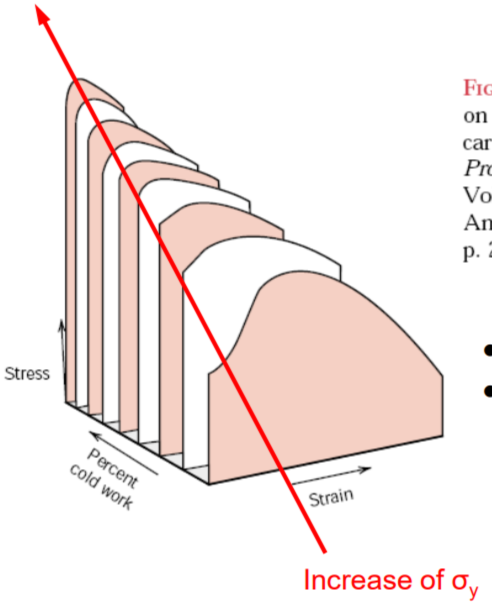
- Brittle materials (Such as ceramics, glasses, brittle alloys, brittle polymers and brittle composites) have no or limited plastic deformation before fracture.
    - These undergo brittle fracture. The fracture will be flat rather than look like cup and cone.
    - Fracture follows crystalline planes for mono-crystalline materials (cleavage) and follows an intergranular structure for poly-crystalline materials
- Methods to modify plastic properties (Generally, making dislocations harder means increased strength:
    - Smaller grains mean stronger materials
        - Can be modified via thermal treatment
    - Solid solutions can make the material stronger
    - Second phases as well
        - Undissolved particles can cause ring dislocations around them (This is called the “Orowan Mechanism”. Effectiveness of this depends on the number of these particles rather than their mass/volume
    - Work hardening (create many dislocations such that they can’t move)
        - The material undergoes several loading-unloading cycles to create many dislocations
    - Monocrystals (There are no dislocations that cause motion)
- Hall-Petch Law:

$$\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}}$$

    - σ_y is the yield strength
    - d is the grain diameter
    - k_y is the locking parameter (value dependant on each material)
    - σ_0 mono-crystal yield strength
- Ramberg-Osgood Law (plastic field):

$$\sigma = H\varepsilon^n$$

    - H is the strength coefficient (Unit is MPa)
    - n is the work hardening exponent. High value means that it will harden faster



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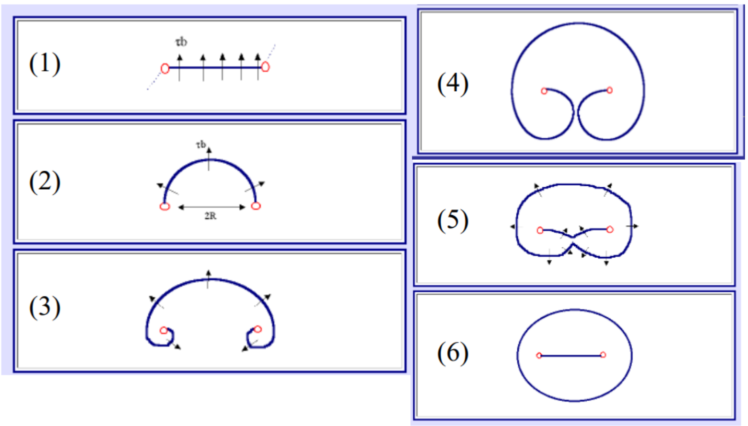
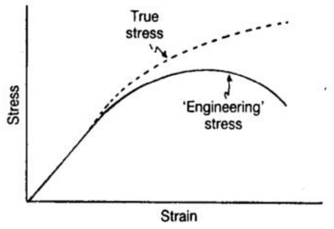
- How one dislocation can “reproduce” during bending:



- Stress is inversely proportional to dislocation spacing or directly proportional to the square root of dislocation density

3 MECHANICAL PROPERTIES PART 2

- Until now, we considered the “Engineering Stress”, which is the force over the initial area. This is not what happens since area varies with force due to necking, so the true stress is higher than what we calculate:



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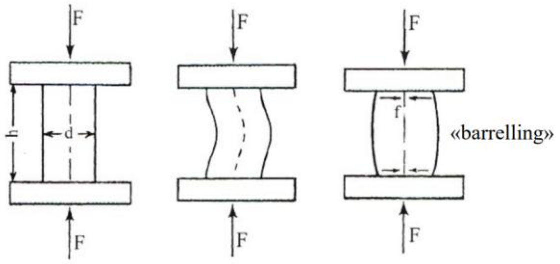
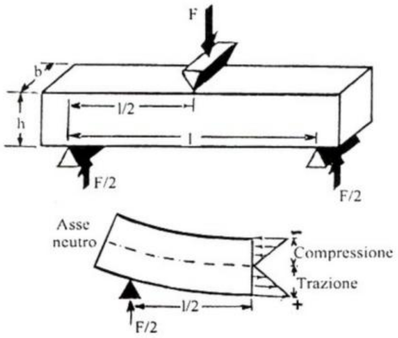
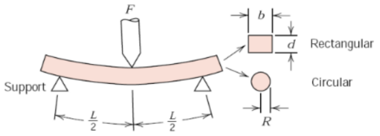
- In a stress-strain curve, the “ultimate tensile strength” or simply “tensile strength” is the maximum point on the graph.
- Maximum elongation is the highest strain before fracture
- Compression tests are used mainly for brittle materials. An issue with this is that the test overestimates compressive strength, since the combination of compression and torsion/bending will weaken the material, leading to a lower REAL strength.



- Bending or flexural test



- 

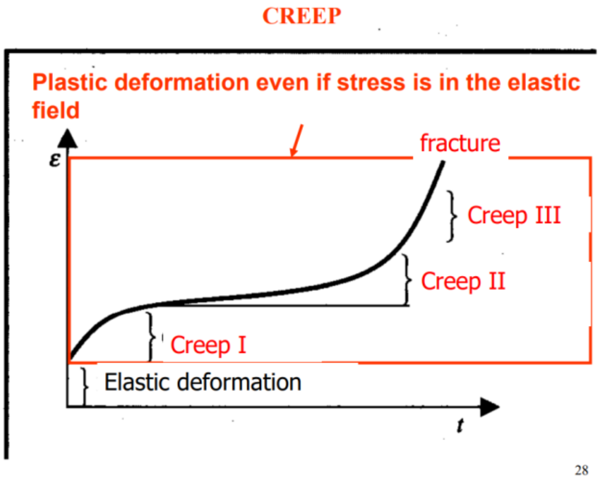
σ = stress = $\frac{Mc}{I}$

where M = maximum bending moment
c = distance from center of specimen to outer fibers
I = moment of inertia of cross section
F = applied load

	M	c	I	σ
Rectangular	$\frac{FL}{4}$	$\frac{d}{2}$	$\frac{bd^3}{12}$	$\frac{3FL}{2bd^2}$
Circular	$\frac{FL}{4}$	R	$\frac{\pi R^4}{4}$	$\frac{FL}{\pi R^3}$

-

- The above test is a 3-point bending test. 4-point and 4-point asymmetrical tests can also be performed.



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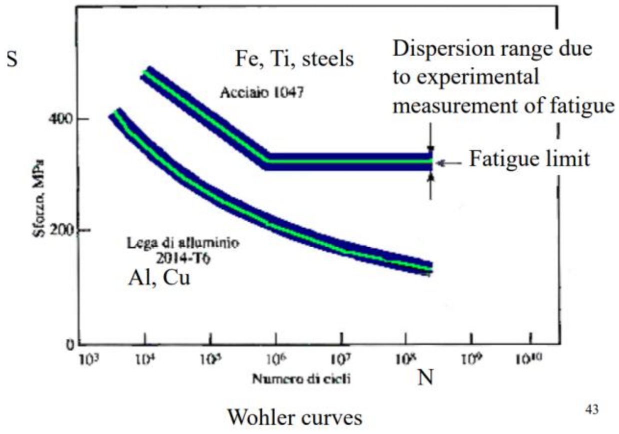
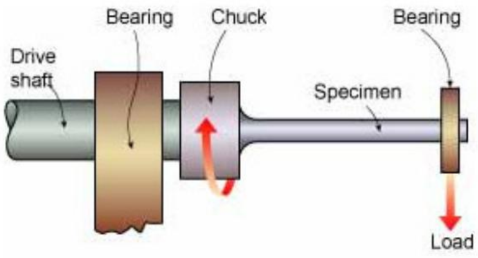
    - Creep happens when under constant load can lead to plastic deformation (while in the elastic field), progressive to fracture. The process is thermally activated and accelerated.
    - Where it happens approximately:
        - Metals: $T > 0.3T_m$
        - Ceramics: $T < 0.6T_m$
        - Amorphous materials: $T > T_{glass}$
- For a creep test, a constant force is applied to a sample, and strain is recorded against time.
- Usually, we have three stages to creep:
    - Primary creep
        - We have elastic + plastic deformation, where plastic deformation is favoured by dislocation movement. The rate of deformation progressively decreased
    - Secondary creep
        - Deformation rate is low and mostly constant
    - Tertiary creep
        - At grain boundaries there are cracks and voids, which propagate and cause material rupture
- For secondary creep:

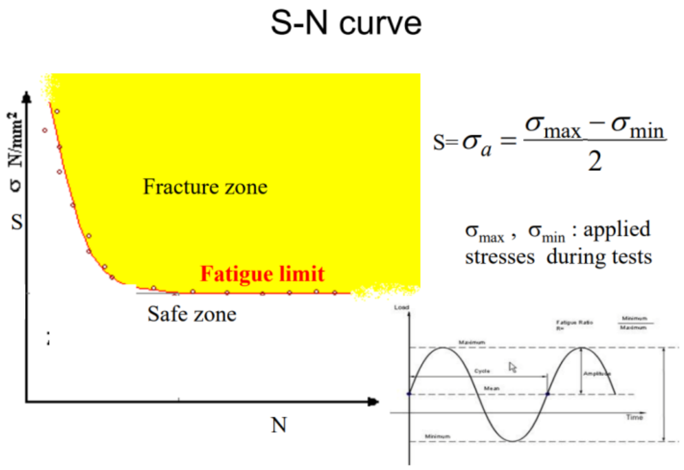
$$\frac{d\varepsilon}{dt} = \dot{\varepsilon}_{ss} = C\sigma^n e^{-\frac{E_{CR}}{RT}} = A\sigma^n$$

    - C: constant depending on materials
    - n: coefficient depending on materials
    - E_{CR}: Activation energy
    - R: Perfect gas constant
    - T: Test temperature
- In tertiary creep, voids form internally on grain boundaries. These will then link and merge, leading to creep failure
- To reduce creep:
    - High T_m and E_{CR}
    - Large grains and monocrystals
    - Solid solutions

    - Precipitates
    - Second phases
- Wohler Curve or S-N curves:
    - 

    - It shows the number of cycles of loading-unloading until failure for each stress value.
- The above phenomenon is fatigue:
    - Failure due to cyclical loading
    - Main mechanical failure of materials
    - Failure happens at stress lower than σ_R or σ_Y
    - It leads to catastrophic failure of materials (also for ductile materials)
    - Fatigue tests ensure material capabilities
    - Fatigue limit is used
- Rotating bending test is used to see what happens when a load is applied to a rotating shaft. The load is perpendicular to rotation
    - 

    - Very time consuming



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

σ_{max} , σ_{min} : applied stresses during tests

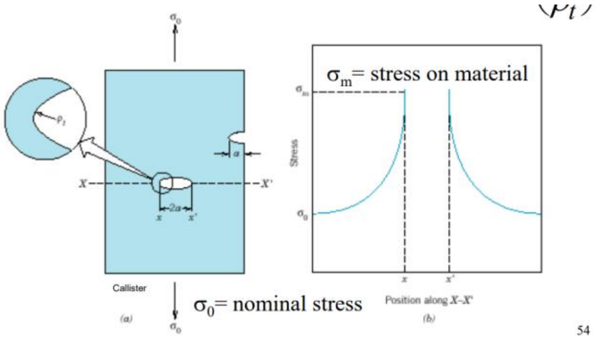
-

- Fatigue resistance is stress necessary to fracture the material after a given number of cycles
- Fatigue life is number of cycles to fracture the material at a given load
- Ductile fracture shows slow crack propagation (i.e. stable propagation)
  - Brittle fracture shows quick crack propagation (i.e. unstable propagation) and catastrophic failure
- Around cracks, local stress σ_m is higher than nominal stress σ_0
  - A critical defect is a crack that is barely large enough to cause material failure (beyond this point, the crack propagates at the speed of sound, which is $\sim 5000 ms^{-1}$ in steel)
  - For an elliptical crack of minor radius ρ and major radius a,

$$K = \frac{\sigma_m}{\sigma_0} = 2\sqrt{\frac{a}{\rho}}$$

$$\Rightarrow \sigma_m = 2\sigma_0\sqrt{\frac{a}{\rho}}$$

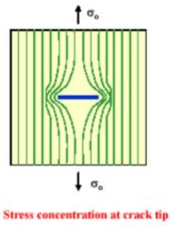
    - Where K is called the stress intensity factor

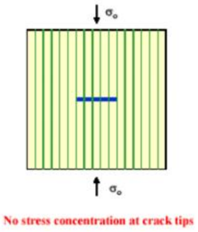


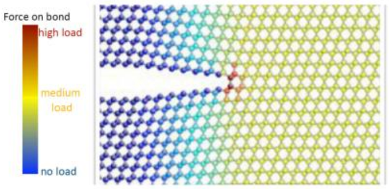
  -
  - If plastic deformation is possible, ρ can increase, and as a result, σ_m decreases. Otherwise, catastrophic failure occurs
- σ_c is "critical stress" (sometimes it is referred to as σ_f):
  - The point where if $\sigma > \sigma_c$, there is crack propagation
  - We can then define:

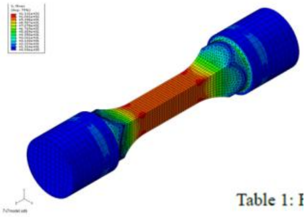
$$K_{Ic} = Y\sigma_c\sqrt{\pi a}$$
$$[K_{Ic}] = MPa\, m^{0.5}$$

    - Where K_{Ic} is called the "fracture toughness". It is a material property. The higher it is, the tougher the material is
    - a is the half-crack size (minor radius)
    - Y is a geometric parameter
- Weibull Statistics say:
  "The PROBABILITY of fracture is linked to the dimensional distribution of the defects in the material volume and to the probability of finding cracks of certain dimensions in a sample"
  - This means that larger samples are more likely to fail under the same load, since they have a higher chance of containing defects of critical size
  - This is the scale effect
  - An example of a glass slab having around 100Mpa tensile strength while glass fibres it can get up to 1000MPa
- Mechanical strength depends on the weakest element

- 

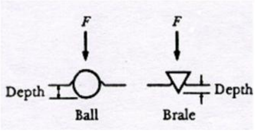
  Stress concentration at crack tip
  

  No stress concentration at crack tips
  

- To increase material’s fatigue resistance, we can use coatings or other surface strengthening methods
- Note that features such as threads on a screw act as fractures and therefore decrease the component’s strength
- Finite Element Analysis (FEA) is a software used to calculate the strength of a component
  - 

- Hardness is a measure of a material’s resistance to localized compressive stress due to indentation (Can be H or HB)

$$H = \frac{F}{A}$$

  - Hardness tests are done by applying a load using an indenter to the surface of the material. We then remove the load and measure the dent that has been left
  - The indenter is usually a sphere or pyramid (ball or brale)
  - 

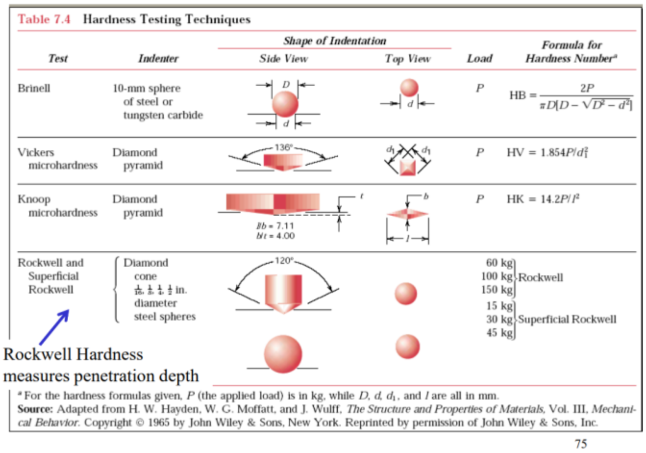
  - H can be expressed as GPa or sometimes as the depth of the indentation (mm or μm)
  - 

Table 7.4 Hardness Testing Techniques

Test	Indenter	Shape of Indentation: Side View	Shape of Indentation: Top View	Load	Formula for Hardness Number[a]
Brinell	10-mm sphere of steel or tungsten carbide	D d	d	P	$\text{HB} = \frac{2P}{\pi D[D - \sqrt{D^2 - d^2}]}$
Vickers microhardness	Diamond pyramid	136°	d_1 d_1	P	$\text{HV} = 1.854P/d_1^2$
Knoop microhardness	Diamond pyramid	t $l/b = 7.11$ $b/t = 4.00$	b l	P	$\text{HK} = 14.2P/l^2$
Rockwell and Superficial Rockwell	Diamond cone $\frac{1}{16}, \frac{1}{8}, \frac{1}{4}, \frac{1}{2}$ in. diameter steel spheres	120°		60 kg, 100 kg, 150 kg: Rockwell 15 kg, 30 kg, 45 kg: Superficial Rockwell	

Rockwell Hardness measures penetration depth

[a] For the hardness formulas given, P (the applied load) is in kg, while D, d, d_1, and l are all in mm.

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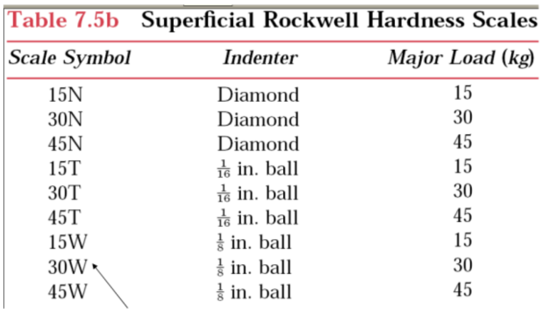
- 

  Table 7.5b Superficial Rockwell Hardness Scales

Scale Symbol	Indenter	Major Load (kg)
15N	Diamond	15
30N	Diamond	30
45N	Diamond	45
15T	$\frac{1}{16}$ in. ball	15
30T	$\frac{1}{16}$ in. ball	30
45T	$\frac{1}{16}$ in. ball	45
15W	$\frac{1}{8}$ in. ball	15
30W	$\frac{1}{8}$ in. ball	30
45W	$\frac{1}{8}$ in. ball	45

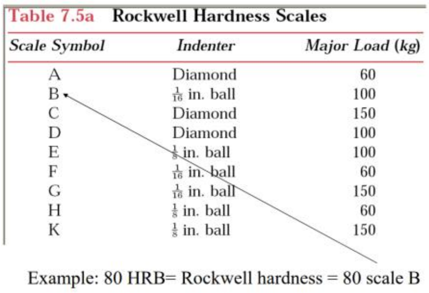
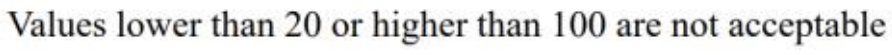
  

  Table 7.5a Rockwell Hardness Scales

Scale Symbol	Indenter	Major Load (kg)
A	Diamond	60
B	$\frac{1}{16}$ in. ball	100
C	Diamond	150
D	Diamond	100
E	$\frac{1}{8}$ in. ball	100
F	$\frac{1}{16}$ in. ball	60
G	$\frac{1}{16}$ in. ball	150
H	$\frac{1}{8}$ in. ball	60
K	$\frac{1}{8}$ in. ball	150

  Example: 80 HRB= Rockwell hardness = 80 scale B

- 

  Values lower than 20 or higher than 100 are not acceptable
  - Usually scale B (HRB) and scale C (HRC) are used
  - With unacceptable values we mean that we should use a harder or softer scale to get a useful result
- Hardness test is not destructive, so it is usually more used than the tensile strength test

- We can use hardness test to approximate ultimate tensile strength:

$$TS \approx 3.45 \times HB$$

  - Where TS is the tensile strength in MPa, and HB is the Brinell Hardness Number (Hardness)

- For Vicker's micro-hardness on brittle materials:

$$K_{Ic} = 0.016 F_H \sqrt{\frac{E}{HV\, c^3}}$$

  - Where E is Young's modulus

- Toughness is related to the energy absorbed up to fracture:

$$= \int \sigma \, d\varepsilon$$

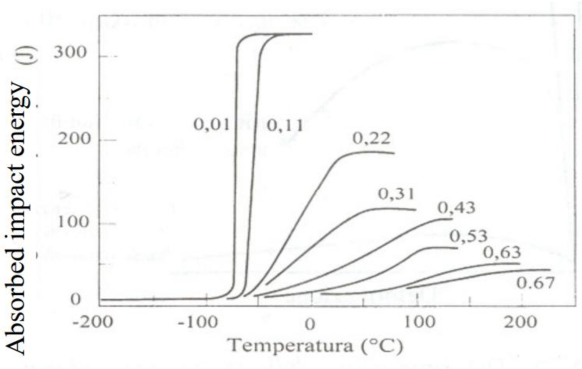
  - Unit is Jm^{-3} or Nm^{-2}, Pa

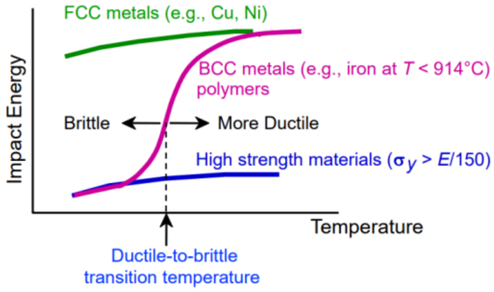
- Fracture elastic energy or resilience modulus:

$$U_r = \int_{\varepsilon_0}^{\varepsilon_y} \sigma \, d\varepsilon$$

  - Integral is taken over the elastic field

- For steel, the carbon density can help determine where the ductile to brittle transition is in temperature. Low-carbon steel creates soft and weak steel, but which is very tough.
  - Low temperatures make steel brittle

- 

- 

- “CHARPY tests” are done to find these results

4 THERMAL PROPERTIES OF MATERIALS

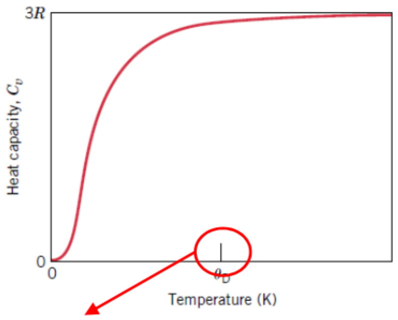
- Thermal properties are responses to heat
    - Heat capacity
    - Thermal conductivity
    - Thermal expansion
    - Thermal stresses
- Heat is transferred via free electrons and vibrational waves
- Due to chemical bonds, atoms are not independent, and therefore exchange heat via vibrational waves quantized via phonons. (Just like light is quantized by photons and gravity is quantized via gravitons)
    - The speed of propagation is equal to the speed of sound in the material
- In real crystals, amplitude of vibration is typically much smaller than lattice spacing
- As heat increases, it is the amplitude of vibration that increases
    - Interatomic distance also increases → Thermal expansion
    - Atomic, ionic and molecular vibrations increase
    - Atomic vibration within molecules increases
    - Rotation of molecules are affected
- Heat capacity (in JK^{-1}):

$$C = \frac{dQ}{dT} = \frac{\Delta E}{\Delta T}$$

- Specific heat (in $JK^{-1}kg^{-1}$):

$$c = \frac{1}{m}\frac{dQ}{dT} = \frac{C}{m}$$

    - We have 2 different types of specific heat:
        - c_p: is measured with constant external pressure
        - c_V: measured with constant volume
    - Usually, $c_p > c_V$ but at room temperature, $c_p \approx c_V \approx c$
- Heat capacity increases as T increases (it is not constant) at relatively low temperatures



DEBYE TEMPERATURE
(below room temperature for many solid materials)

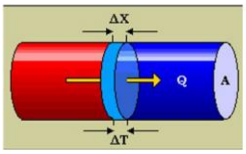
- Atomic or molecular heat is like specific heat, but in $J\ mol^{-1}K^{-1}$
    - For most solids, atomic heat ≈ $25J\ mol^{-1}K^{-1}$
    - Also depends on temperature for low T

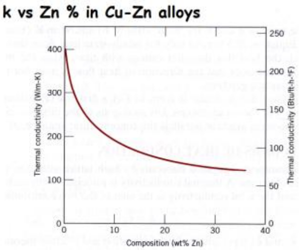
4.1 THERMAL CONDUCTIVITY

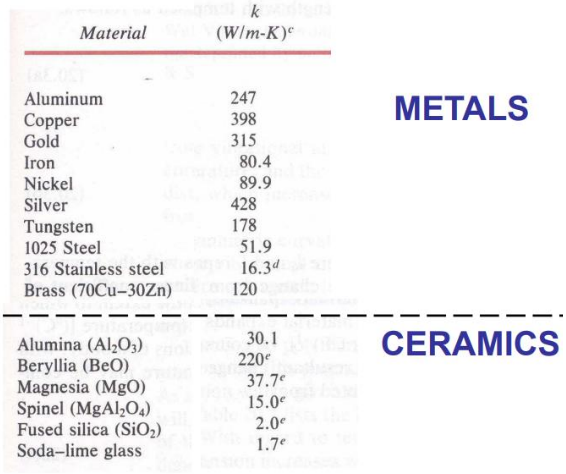
- The ability for a material to transfer thermal energy

- Thermal power:

$$Q = kA\frac{\Delta T}{\Delta x}$$

    - k: Thermal conductivity coefficient
        - $k = k_l + k_e$
        - Total conductivity = lattice vibration conductivity (via phonons) + electron conductivity (via kinetic energy transfer)
        - $[k] = Wm^{-1}K^{-1}$
    - A: cross-sectional area
    - Δx: thickness of volume in between the two parts of different temperature
    - 

- Free electrons are mainly used in metals, while phonons are predominant in ceramics
- $k_{polymers} \ll k_{glass} < k_{ceramics} < k_{metals}$
    - No crystalline lattice means lower conductivity.
        - Also porous materials are less conductive
        - In polymers, heat is partially dissipated by vibration of long polymer chains
- k depends on T
    - Random thermal agitation increases with higher T, disturbing propagation of phonons, so k_l
    - Electron motion is not significantly affected by T, so k_e doesn't change much
- Steel has high k and high c
- 

    - Note that the above is NOT a linear relation, and therefore not a simple weighted average
- For polymers, $k \approx 0.3Wm^{-1}K^{-1}$
    - 

Material	k (W/m-K)^c
METALS	
Aluminum	247
Copper	398
Gold	315
Iron	80.4
Nickel	89.9
Silver	428
Tungsten	178
1025 Steel	51.9
316 Stainless steel	16.3^d
Brass (70Cu–30Zn)	120
CERAMICS	
Alumina (Al_2O_3)	30.1
Beryllia (BeO)	220^e
Magnesia (MgO)	37.7^e
Spinel ($MgAl_2O_4$)	15.0^e
Fused silica (SiO_2)	2.0^e
Soda–lime glass	1.7^e

    - $k_{air} = 0.02Wm^{-1}K^{-1}, k_{FoamGlass} = 0.04Wm^{-1}K^{-1}$

    - For aerogel, k is lower than in air, since pore size in aerogel is lower than free mean path for air molecules, so heat transfer is less effective in aerogels than in air (convection)
- Some ceramics have high k:
    - Atoms with similar mass
    - High E
    - Low defects
    - Simple crystalline cell (e.g. cubic)
- For some materials, such as graphite, k depends on the direction of heat transfer. For the example of graphite:
    - Within a single plane, k is high (tight covalent bonds), while across planes it is low (weak Van der Waals forces)
- Grain size affects thermal conductivity:

$$k^{-1} \propto d^{-\frac{1}{2}}$$

    - Large grains = better conductivity

4.2 THERMAL EXPANSION

- $\Delta L \approx \alpha L_0 \Delta T$
    - $\varepsilon_t = \frac{l - l_0}{l_0} = \alpha \Delta T$
    - α is the thermal expansion coefficient
- Higher T means more vibration, increasing bond length and leading to macroscopic expansion
- $\alpha_{polymers} \gg \alpha_{metals} > \alpha_{ceramics}$
    - 

Metals	$\alpha \approx 5\text{-}25\ 10^{-6}\ K^{-1}$
Ceramics	$\alpha \approx 0.5\text{-}15\ 10^{-6}\ K^{-1}$
Polimers	$\alpha \approx 50\text{-}400\ 10^{-6}\ K^{-1}$

    - α slightly varies with T
    - Silica crystals are an outlier, with $\alpha = 4 \times 10^{-7} K^{-1}$
- Strong bonds mean lower α
- α changes with the crystal structure (Same element, but different BCC, FCC etc)
- Impurities can change α. For example, adding fibres to polymers will decrease it.
- Thermally induced stress:

$$\sigma = E\varepsilon = \frac{E\Delta l}{l_0} = E\alpha\Delta T$$

- For stress at the interface between two solids having different α:

$$\sigma = \frac{E_M E_C}{E_M + E_C} \Delta T (\alpha_M - \alpha_C)$$

    - E: Young's modulus (M=Metal, C=Ceramic)
- Thermal shock resistance:

$$TSR \approx \frac{\sigma_f k}{E\alpha}$$

    - σ_f: flexural strength
- For ductile materials, thermal stress can induce plastic deformation (unavoidable)
- For brittle materials, thermal stress can lead to fracture. Can be avoided by:
    - Changing chemical composition (e.g. adding other oxides in glasses)
    - Second phase with different α
    - Pores

5 PHASE DIAGRAMS

- A phase is a homogeneous portion of a system with uniform chemical and physical characteristics.
    - A chemical element or compound can exist as different phases:
        - Liquid water, water vapor, ice, Fe_α, Fe_γ
- Monophasic systems have only one phase
- Biphasic systems have two different phases:
    - Aggregation state (e.g. liquid + solid)
    - Composition (e.g. oil + water)
    - Crystalline structure (e.g. $Fe_\alpha + Fe_\gamma$)
- Phase diagrams show T on the y-axis and composition (wt.%) on the x-axis.
    - Wt.% is percentage **MASS**
- Phase diagrams are valid when thermodynamic equilibrium is reached (energy is minimized and therefore slow cooling was used)
- In single component phase diagrams, instead of wt.% we use pressure
    - In binary phase diagrams, we usually only consider solids and liquids, so p is not significant
- Gibbs' Rule (aka. Phases Rule)

$$V = C - f + n$$

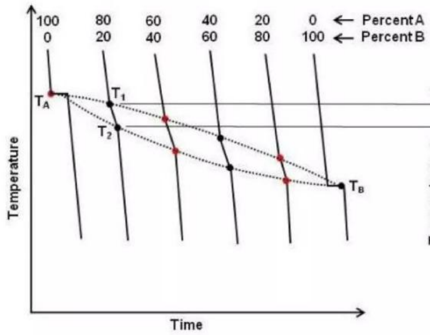
    - V: Number of variables that can change
    - C: Number of components (parts with the same phase)
    - f: number of phases
    - n: number of physical parameters (p, T)
    - Since we set p as constant, we can rewrite as:

$$V = C - f + 1$$

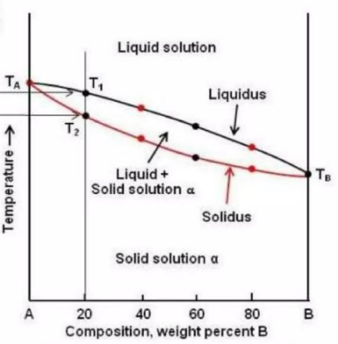
    - Or in binary systems:

$$V = 3 - f$$

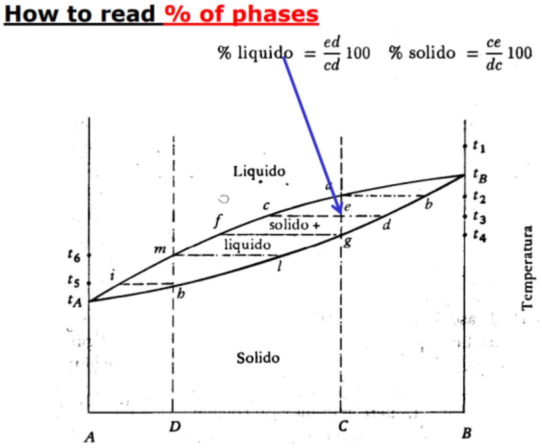
- Cooling curves are graphical plots of phases of elements on temperature against time
    - The resulting phase during solidification is different for various alloy composition
    - Most common are for:
        - Pure metals
        - Alloys (binary)
        - Eutectic binary alloy
        - Off-eutectic binary alloy
    -



Series of cooling curves for different alloys in a completely soluble system both in the liquid and solid states

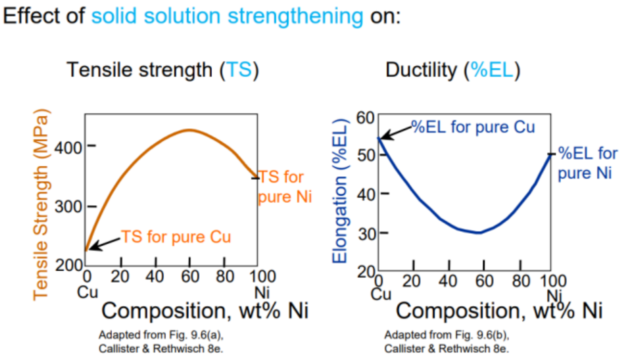


Phase diagram of two metals completely soluble in the liquid and solid states

- 

How to read % of phases

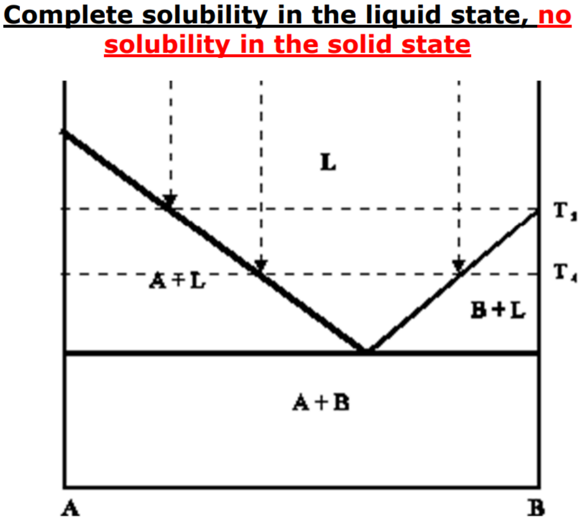
$$\% \text{ liquido } = \frac{ed}{cd}100 \quad \% \text{ solido } = \frac{ce}{dc}100$$

- 

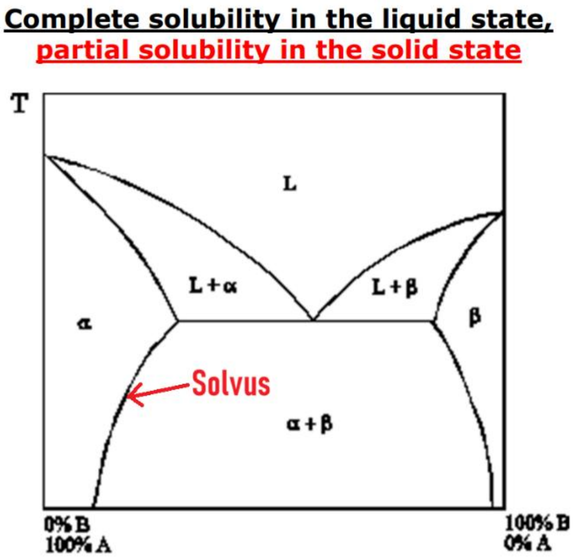
Effect of solid solution strengthening on:

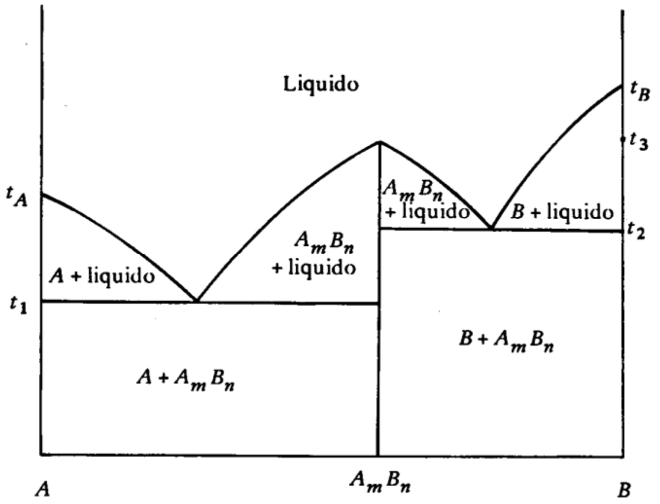
Adapted from Fig. 9.6(a), Callister & Rethwisch 8e.

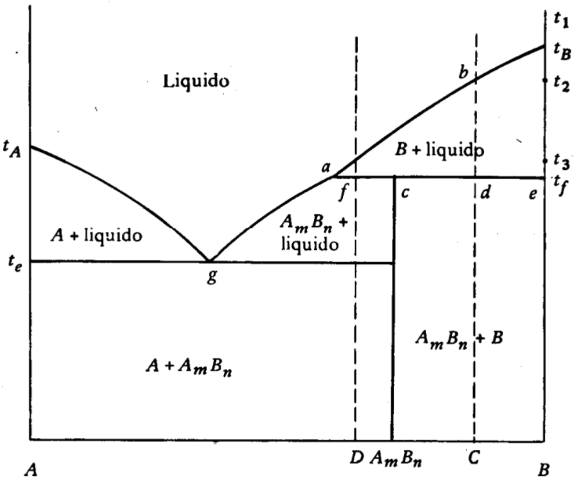
Adapted from Fig. 9.6(b), Callister & Rethwisch 8e.

- A eutectic reaction is one that melts all at the same temperature, with no intermediate “pasty” stage
  - $L \leftrightarrow \alpha + \beta$
  - No intermediate $L + \beta$ or $L + \alpha$ part
- In a eutectic system, there is always a specific composition (eutectic composition) that freezes at a lower temperature than any other
  - At this point, both phases melt/form at the same temperature
  - $(wt\%, T)$ is the eutectic point
- 

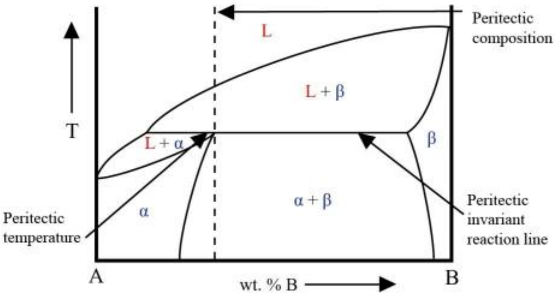
Complete solubility in the liquid state, no solubility in the solid state

- 

- 

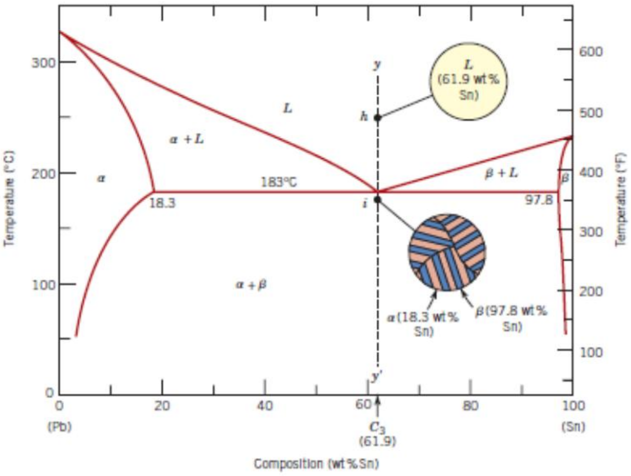
  - In this case, we have complete solubility in the liquid state, but no solubility in the solid state
  - A_mB_n represents a phase where A, B can ONLY mix at a specific ratio (e.g. 1:1, 1:3, 2:3 etc.) It acts as its own metal
  - Congruent melting (melting into the same chemical composition)
- 

  - Same as previous, but non-congruent melting

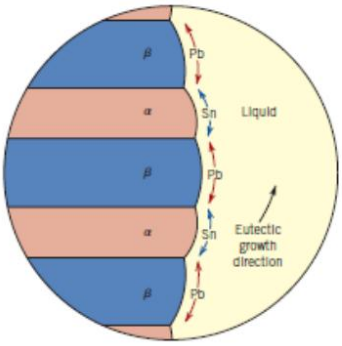


-
  - Peritectic reaction
  - $L + \delta \rightarrow \gamma$
    - When a liquid solidifies, it converts the phase of the whole system δ into another phase γ as it does.

Figure 9.13 Schematic representations of the equilibrium microstructures for a lead–tin alloy of eutectic composition C_3 above and below the eutectic temperature.

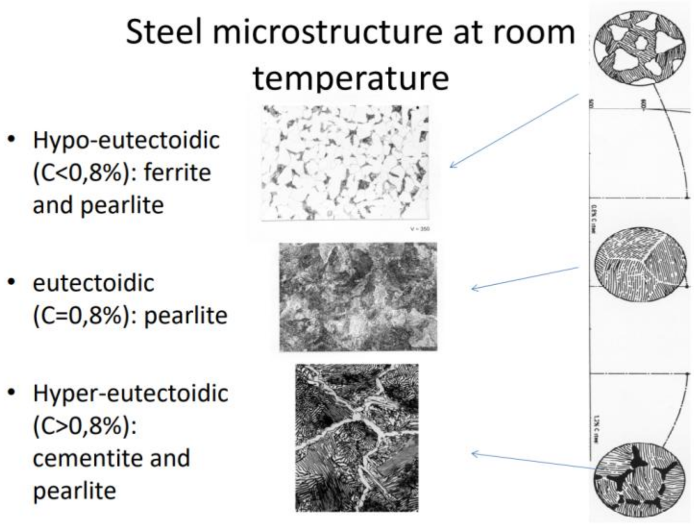


-
  - For eutectic reactions, notice the band formations in the solid state



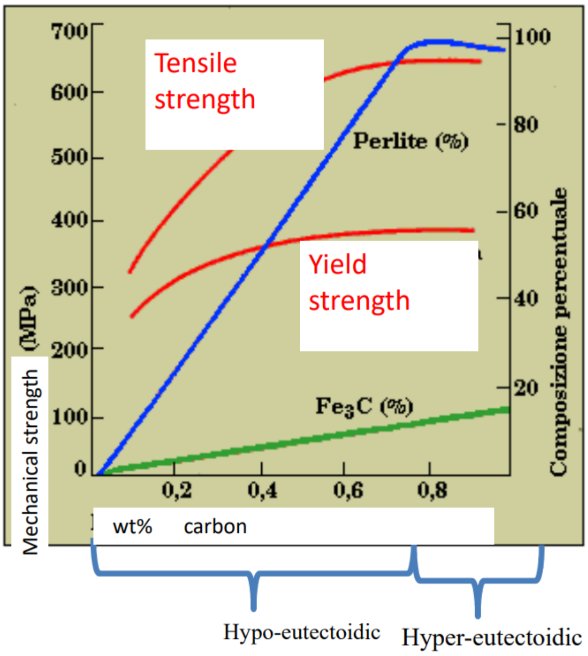
  -

6 PHASE DIAGRAM EXAMPLES



Steel microstructure at room temperature

- Hypo-eutectoidic (C<0,8%): ferrite and pearlite
- eutectoidic (C=0,8%): pearlite
- Hyper-eutectoidic (C>0,8%): cementite and pearlite



6.1 STEELS

Pearlite is a form of steel with optimal strength and ductility for many applications: It is alternate layers of ferrite and cementite.

Microstructure of pearlite formed at different isothermal T:

If > T → coarse pearlite (> diffusion)

If < T → fine pearlite (< diffusion)

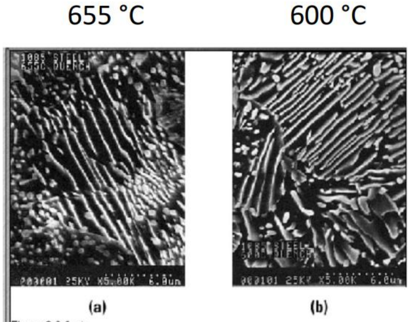


Figure 6.3.2a-b
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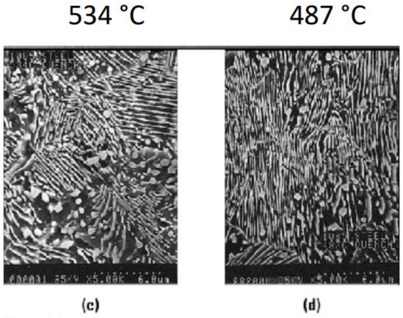

Figure 6.3.2c-d
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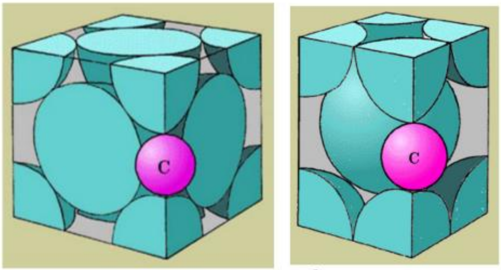
Above, pearlite is formed by heating at high temperatures (about 900°C) and then cooled at the labelled temperatures. When particles have more energy, they will move to form larger clumps.

When pearlite is formed just below eutectic temperature ($\sim 700°C$ for about 24hrs) it forms globular pearlite or spheroidite. This creates large grains of cementite in a ferrite solid solvent. It is the most ductile granular steel due to the large grains and low grain boundary density.



Austenite → Martensite

Martensite is extremely hard and fragile due to the higher concentration of carbon with respect to other steels such as austenite. The carbon contrasts motion of dislocations. The material is formed via polymorphic transformation of austenite with the addition of extra carbon.

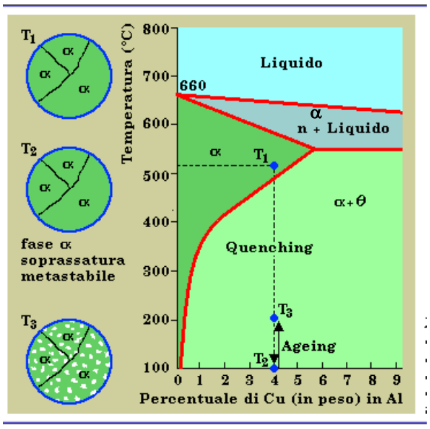
Tempered martensite (aka sorbite) a matrix of ferrite with fine particles of cementite. Similar to spheroidite but it has finer particles and is formed via heat treatment of martensite.

6.2 AL-CU ALLOYS

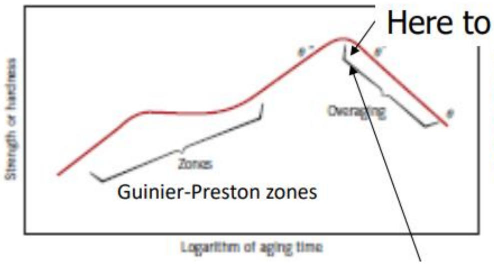
Aluminium is very soft, but adding a small amount of copper can make it harder. Precipitation hardening is the process of:

- Heating $Al + Cu$ until they perfectly dissolve.
- The alloy is then quenched (rapidly cooled) creating a high-energy state where the solution is supersaturated with copper, which could not escape since there was no time during cooling.
- The material is then heated slightly and aged (waiting) allowing the θ phase ($CuAl_2$) to form grains within the aluminium α phase, hardening it.

Precipitation hardening for Al-Cu alloys



It is important to not over-age the material:



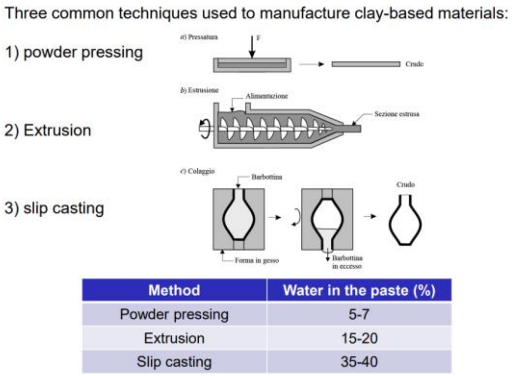
Here to maximize mechanical strength

Guinier-Preston zones

and hardness as a function of the logarithm of aging time at constant temperature during the precipitation heat treatment.

7 CERAMICS

- Very strong directional bonds
- No free electrons
- Good compressive strength but poor tensile strength
- Fragile, but high hardness
- Good heart resistance
- Good thermal and electrical insulation
- Good chemical inertia (resistance to acids and bases)
- Poor resistance to thermal shock
- Cycle of production of ceramics:
    - Minerals
    - Chemical process
    - Powders
    - Crushing, milling, sieving
    - Moulding
    - “Green” (compacted particles)
    - Sintering
    - Optional surface treatment
- Moulding methods for clay-based materials:



Three common techniques used to manufacture clay-based materials:

Method	Water in the paste (%)
Powder pressing	5-7
Extrusion	15-20
Slip casting	35-40

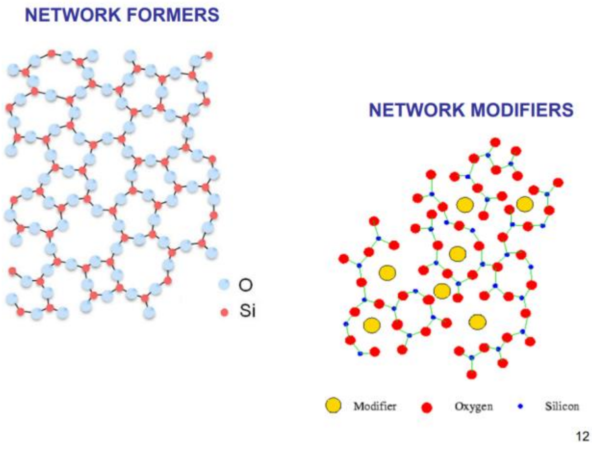
- Sintering temperature for clay-based materials is above 1000°C.
    - Sintering is the process of compacting a powder into a solid at high temperature and pressure
    - Sintering aids can be used to form a stronger material. This is called vitrification. The sintering aids is a liquid glass that fills in gaps between grains
- Sintering causes the overall shape to shrink (since it is compacted)

8 GLASS

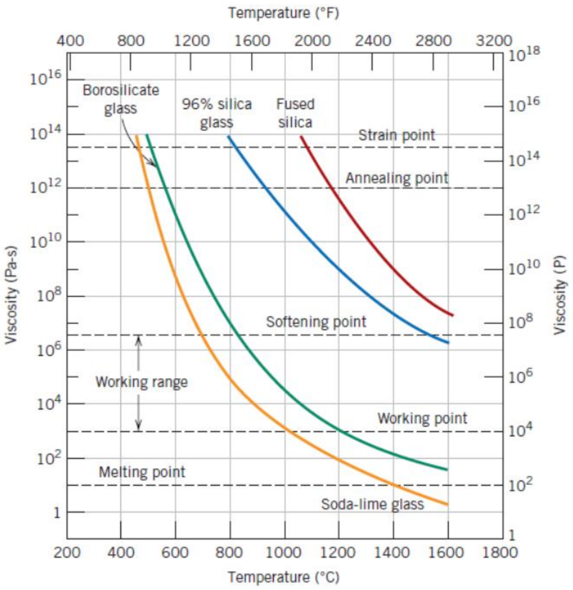
- Amorphous, disordered structure
    - No long-range atomic order
    - Short-range order
- No definite melting point
    - There is a glass transition temperature T_g above which glass progressively softens
    - We define T_m as “liquid temperature” above which it behaves as a stable liquid

$$T_g \approx \frac{2}{3} T_m$$

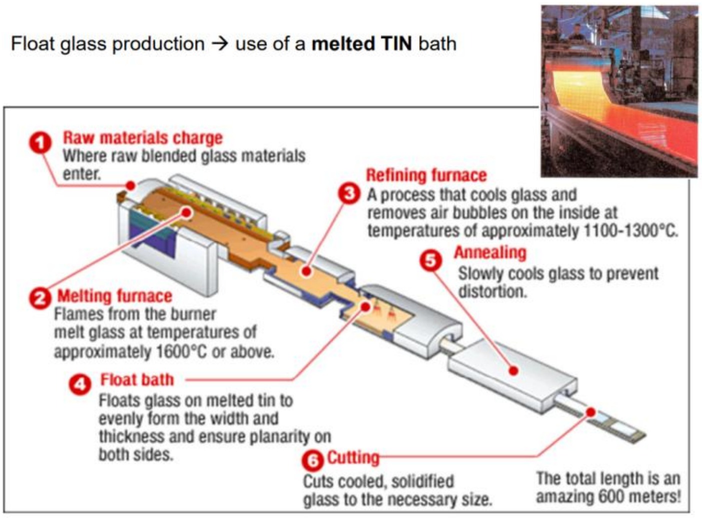
- The definition of a glass is any substance that can turn into an amorphous state
    - Ceramics (inorganic oxides, inorganic fluorides, inorganic chalcogenides)
    - Metals (cooling speed $> 10^7 Ks^{-1}$
    - Organic compounds
    - All polymers
    - Some native elements like S, Se, P
- Since amorphous structures are thermodynamically metastable (not stable), they slowly rearrange into crystalline structures (can take thousands of years at room temperature)
    - This can be accelerated by thermal treatment, $T < T_m$)
    - This rearrangement is called devitrification
- Glasses formally belong to the class of ceramic materials. Ceramics are:
    - Fully crystalline
    - Glasses
    - Glass-ceramics (multiple crystalline phases are embedded in an amorphous glass
- Glass often contains multiple compounds
    - Network formers: oxides able to form the glass (e.g. SiO_2, B_2O_3)
    - Network modifiers: Not able to form the glass. They break bonds by having their cations incorporated in the glass, lowering viscosity of the material
    - Intermediates: They can be substituting atoms and stabilize the network



-
- The typical method for glass production is melting-quenching:
    - Reagents are mixed in a crucible, melted and moulded with rapid cooling
    - The glass can be pressed, blown or drawn in fibres



-
- Industrial method for glass production:



Float glass production → use of a **melted TIN bath**

① **Raw materials charge** Where raw blended glass materials enter.

② **Melting furnace** Flames from the burner melt glass at temperatures of approximately 1600°C or above.

③ **Refining furnace** A process that cools glass and removes air bubbles on the inside at temperatures of approximately 1100-1300°C.

④ **Float bath** Floats glass on melted tin to evenly form the width and thickness and ensure planarity on both sides.

⑤ **Annealing** Slowly cools glass to prevent distortion.

⑥ **Cutting** Cuts cooled, solidified glass to the necessary size.

The total length is an amazing 600 meters!

    -
- We can use different chromophore ions to create coloured glass
- Glasses are brittle, and perform better under compression than tension
    - Properties greatly depend on glass composition
- General features:
    - Density of about $2.5 g/cm^3$
    - Hardness of about 6 Mohs
    - $E = 75GPa$
    - $\sigma_c = 1000MPa$
    - $\sigma_t = 40MPa$ (can get up to 200 for special glasses)
    - $TEC = 9 \times 10^{-6} K^{-1}$
    - Low thermal conductivity
    - Low thermal shock resistance for common glass, but good for silica glass
    - Refractive index: $n = 1.5$
- Most common glasses are silica-soda-lime glasses ($SiO_2 - Na_2O - CaO$)
    - Low cost
    - Easy manufacturing
    - Good resistance to devitrification and stability in water

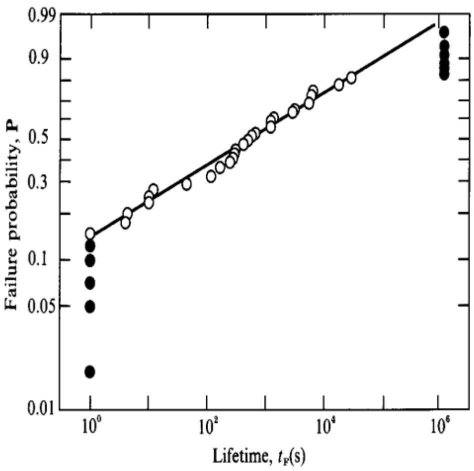
  - Silica increases durability
  - Poor heat resistance
- Armoured glass is made by inserting a metal net within the planes, allowing for flame propagation delay in case of a fire, since if the glass were to shatter, it would remain in position for longer, preventing the fire from spreading as fast
- In tempered glass, compressive forces act near the surface, and tensile forces in the core to increase mechanical resistance (e.g. for impacts)
  - Chemically tempered glass involves adding K^+ ions which substitute Na^+ ions. Due to potassium being larger it causes compressive strength near the surfaces.
- Multilayered glass also increases strength
- Foamed glass (or cellular glass) is used for thermal and acoustic insulation
  - Cellular, waterproof and gas-proof structure
  - Low density, high chemical stability
  - Satisfactory mechanical performance
  - Has many pores
  - (FOAMGLASS is commercial name)
  - Cheap, easy to process and eco-friendly

The mechanical strength of glasses and many ceramics tends to progressively decrease over time

• After a certain time, glass breaks due to a static stress which is lower than the expected one.

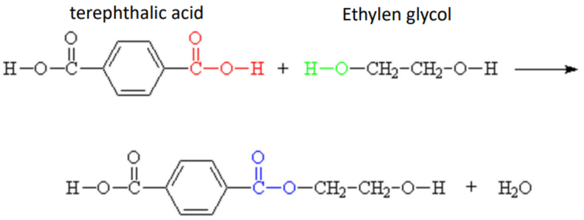
• Thus: the defect population evolves with time

This is a phenomenon known as **static fatigue**.

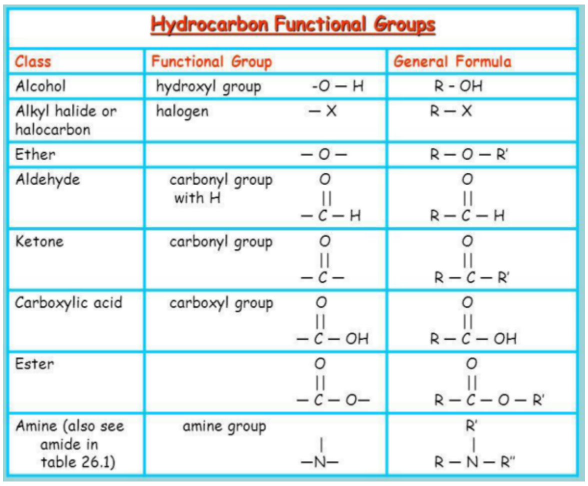


-
- Water can damage glass by breaking bonds and forming cracks

9 POLYMERS

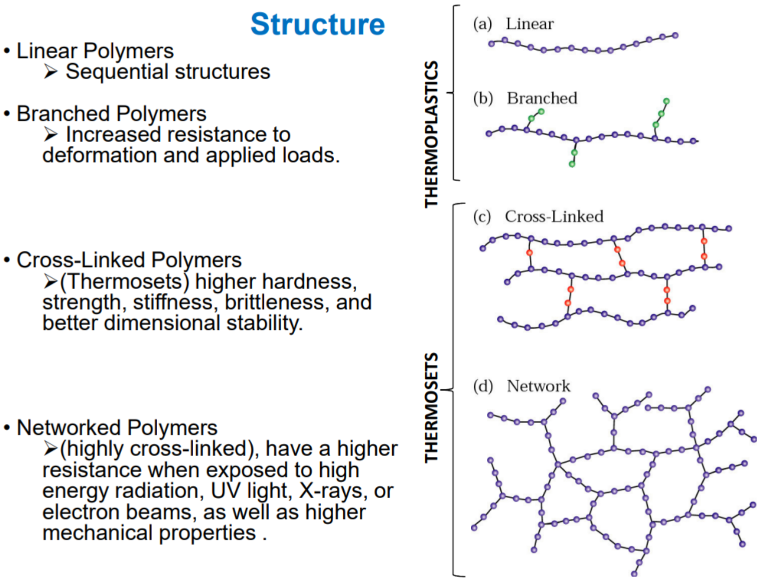
- Polymers (chains of monomers which form macromolecules) can be natural (e.g. polyisoprene) or synthetic (e.g. PTFE)
- Usually chains of C and H, but other structures can also exist, such as silicon-based polysiloxanes (silicones) which have a -Si-O-Si-O-Si- structure.
- Features of polymers
    - Low cost
    - Low electrical and thermal conductivity
    - Low density
    - High stress-to-weight ratio
    - Resistance to chemical corrosion
    - Noise reduction
    - Can be easily coloured
    - Easy to manufacture
    - Minimal surface treatments required
    - Many forms available
    - Additives can be added easily
    - Low mechanical properties
    - Low thermal resistance
    - Flammable
    - Damage due to visible light and UV over time
- Polymerization is the process of combining many monomers into covalently bonded chains
- Addition polymers are ones composed of alkane-derived monomers, due to the C=C bond which can break and form chains
- Condensed polymers are produced by functional group transformation
    - Combines two different monomers and creates a byproduct (such as water)
    - 

    - Condensation polymers form more slowly than addition monomers and often require heat
- Molecular weight distribution is the distribution of the molecular weight of all chains in a plastic.
- Degree of polymerization is the length of a polymer chain

- 

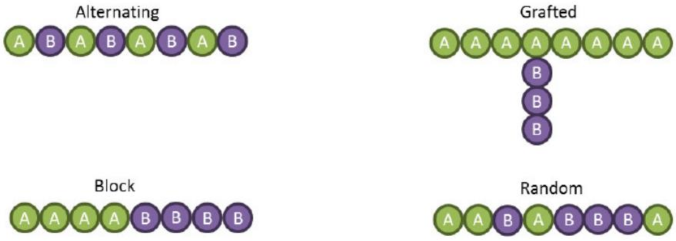
Hydrocarbon Functional Groups

Class	Functional Group		General Formula
Alcohol	hydroxyl group	$-O-H$	$R-OH$
Alkyl halide or halocarbon	halogen	$-X$	$R-X$
Ether		$-O-$	$R-O-R'$
Aldehyde	carbonyl group with H	$-\overset{\overset{O}{\|}}{C}-H$	$R-\overset{\overset{O}{\|}}{C}-H$
Ketone	carbonyl group	$-\overset{\overset{O}{\|}}{C}-$	$R-\overset{\overset{O}{\|}}{C}-R'$
Carboxylic acid	carboxyl group	$-\overset{\overset{O}{\|}}{C}-OH$	$R-\overset{\overset{O}{\|}}{C}-OH$
Ester		$-\overset{\overset{O}{\|}}{C}-O-$	$R-\overset{\overset{O}{\|}}{C}-O-R'$
Amine (also see amide in table 26.1)	amine group	$-\overset{\|}{N}-$	$R-\overset{\overset{R'}{\|}}{N}-R''$

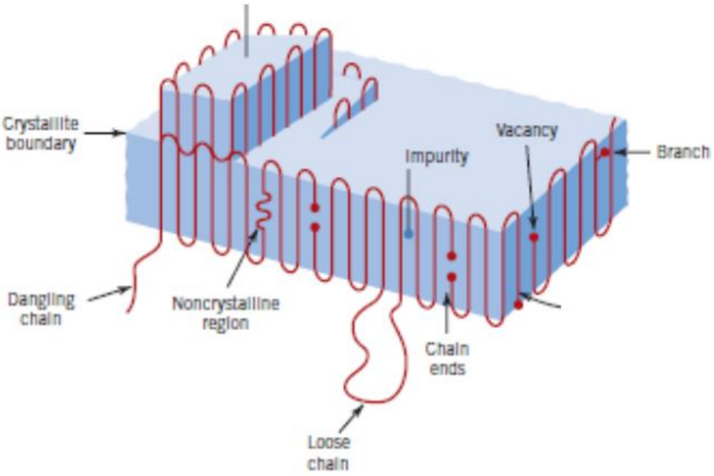
- 

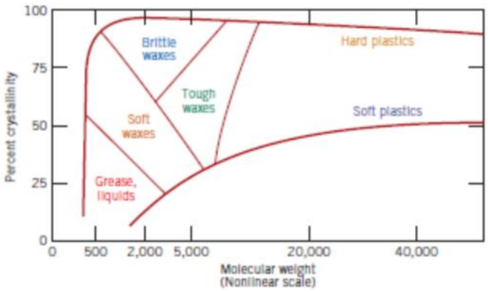
Structure

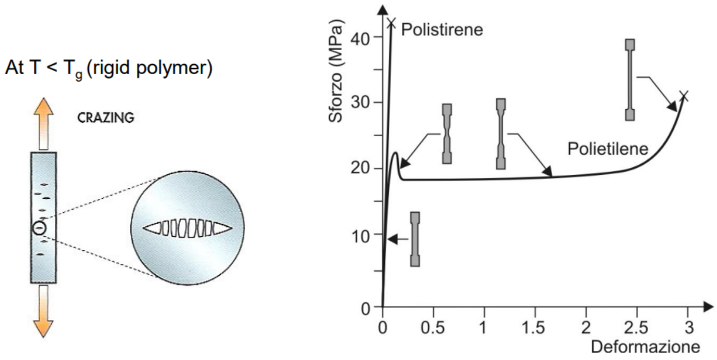
- Linear Polymers
  - Sequential structures
- Branched Polymers
  - Increased resistance to deformation and applied loads.
- Cross-Linked Polymers
  - (Thermosets) higher hardness, strength, stiffness, brittleness, and better dimensional stability.
- Networked Polymers
  - (highly cross-linked), have a higher resistance when exposed to high energy radiation, UV light, X-rays, or electron beams, as well as higher mechanical properties .

- Copolymers contain two types of polymers while terpolymers contain three
  - 

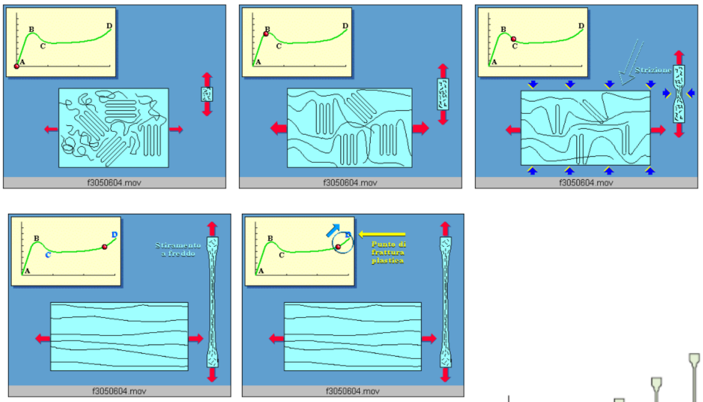
- Polymers can be amorphous (no order) or semi-crystalline (have crystallites: regions of crystalline structure)
  - Crystallinity can be increased by decreasing solidification rate
- When polymer sections form crystalline structures, they look like this (folded-chain model):

    - 

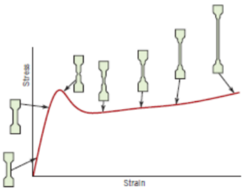
- Higher crystallinity means a harder and more brittle polymer
    - 

- Thermoplastics will melt if heated up (can be recycled) while thermosets will not (they will eventually burn rather than melt. They therefore are not recyclable. This happens due to cross-links between chains)
- Elastomers are linear polymers with a low number of bridging bonds. This gives it excellent elastic deformation (up to 800%)
- Polymers can have two types of stress-strain behaviours:
    - 

    - When $T < T_g$, cracks form since the polymer is rigid and brittle. Applying more pressure leads to catastrophic failure (the process is called crazing).
    - When $T > T_g$ it is semi-crystalline and flexible. It shows elastic behaviour until the upper yield point, where necking occurs. Once the whole sample is stretched, the pressure required to stretch it further increases until failure.



Thermoplastic polymers



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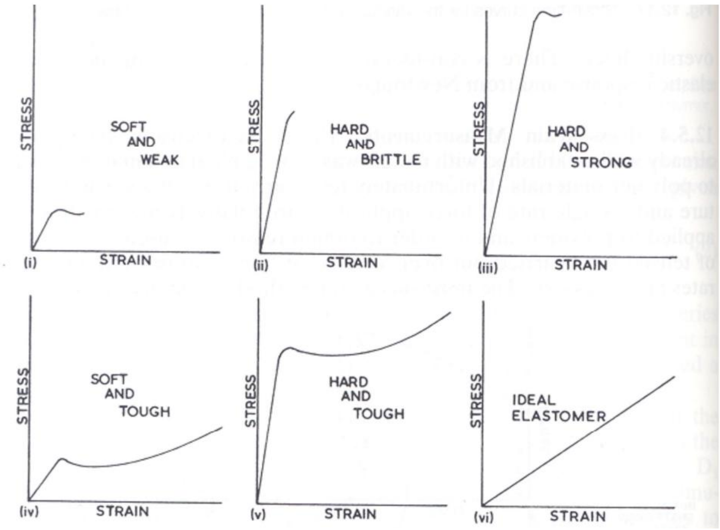
  - 

  - Increased temperature makes a polymer tougher

Thermoplastic materials processing technologies:

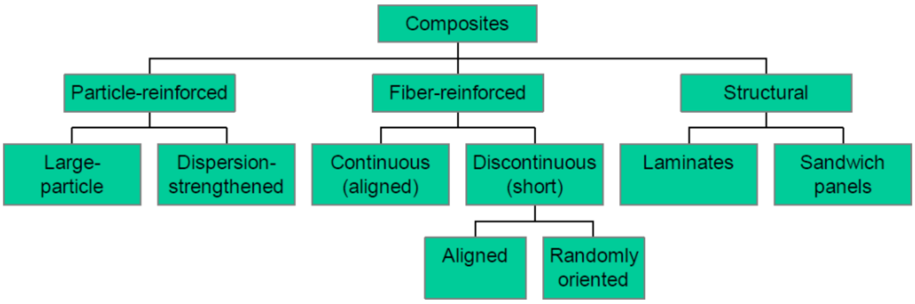
- Molding, injection
- Thermoforming
- Extrusion
- Calendaring
- Blowing

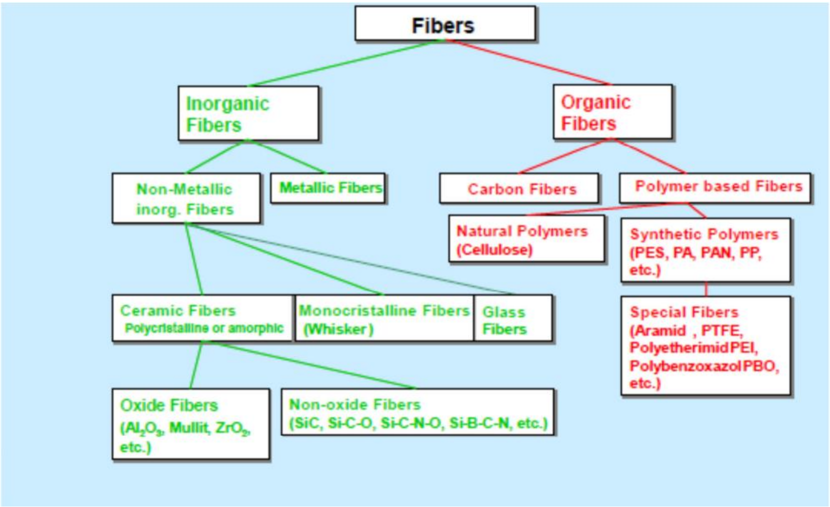
Processing technologies of **thermosetting** materials:

- Injection molding + transfer (for polymer-matrix composites)
- Compression
- Pultrusion (for polymer-matrix composites)
- Rotational molding

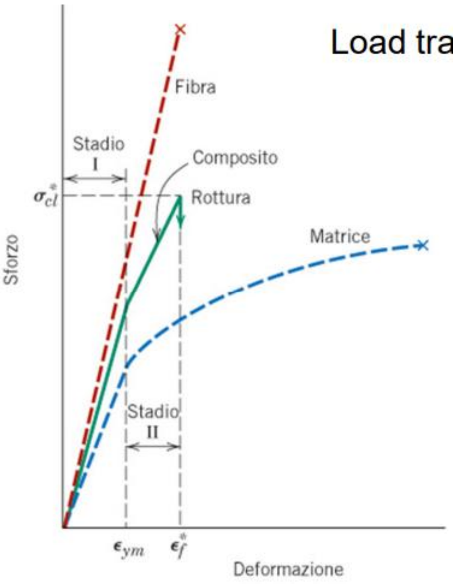
-
- Flame retardants can help increase thermal resistance

10 COMPOSITES

- A composite material is a combination of chemically distinct insoluble phases
- Can be classified by their matrix material:
  - Metal matrix composites (MMC)
    - Soft and flexible matrix
    - High strength and stiffness reinforcement
    - Strong reinforcement-matrix bond
    - Can be dispersion strengthened alloys, regular particulate composites or long fibre reinforcements
  - Ceramic matrix composites (CMC)
    - Soft and flexible matrix
    - High strength and stiffness reinforcement
    - Strong reinforcement-matrix bond
  - Polymer matrix composites (PMC) or organic matrix composites (OMC)
    - Hard and brittle matrix
    - Reinforcement must have high tensile strength to stop crack growth
    - Weak reinforcement-matrix bonds
- 

- 

- Reinforcement mechanism due to fibre:



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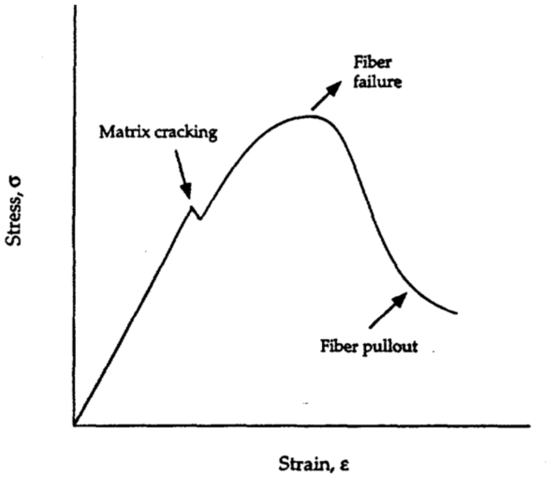
- Debonding (pull-out) is when fibres can move (slightly) within the matrix.
    - This helps by absorbing energy when cracks expand, preventing the whole object from shattering.



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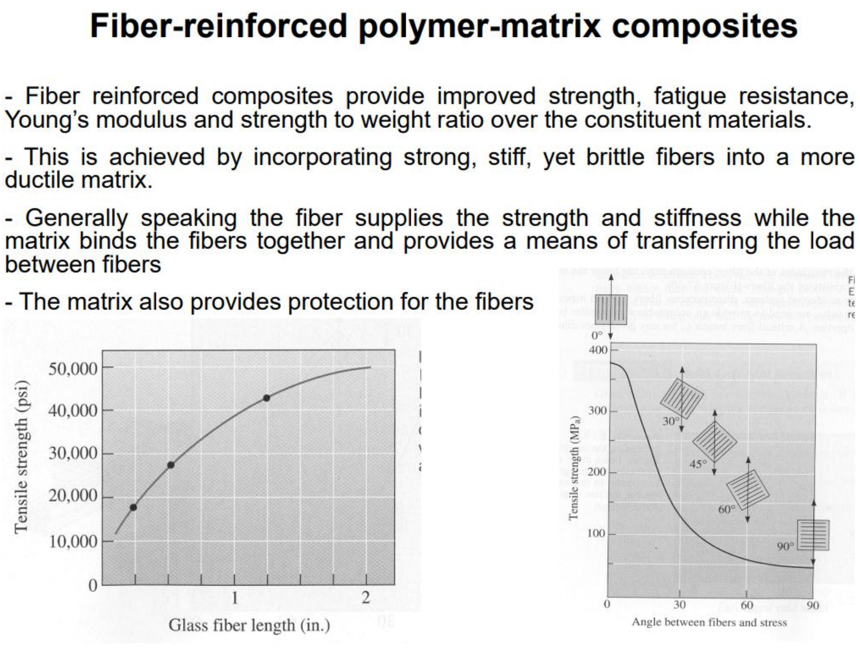

Fiber-reinforced polymer-matrix composites

- Fiber reinforced composites provide improved strength, fatigue resistance, Young's modulus and strength to weight ratio over the constituent materials.

- This is achieved by incorporating strong, stiff, yet brittle fibers into a more ductile matrix.

- Generally speaking the fiber supplies the strength and stiffness while the matrix binds the fibers together and provides a means of transferring the load between fibers

- The matrix also provides protection for the fibers

-

- We can estimate the properties of the composite using a simple lerp function based on volume fraction
    - The exception is with elastic modulus perpendicularly to fibre direction:

$$\frac{1}{E_c} = \frac{f_f}{E_f} + \frac{f_m}{E_m}$$