

Bonding Forces and Energies

$$F_{\text{net}} = F_R + F_A$$

$$E_{\text{net}} = E_R + E_A$$

Quantifying Atomic Packing

$$V_{\text{atoms}} = (\# \text{atoms}) \times 4/3\pi R^3$$

$$V_{\text{cell}} = a^3$$

$$\text{APF} = V_{\text{all atoms}} / V_{\text{unit cell}}$$

$$a_{\text{SC}} = 2R$$









$$a_{\text{BCC}} = 4R / \sqrt{3}$$

$$a_{\text{FCC}} = 2\sqrt{2}R$$

$$\text{HCP: } c/a = 1.63$$

HCP (Close-Packed): ABABAB

FCC (Close-Packed): ABCABCABC

Crystal Structure	Details					
	Structure (Hard Sphere Model)	Reduced Sphere Unit Cell	Atoms / Unit Cell	$a = f(R)$	Atomic Packing Factor	Coordination Number
Simple Cubic			1	$a = 2R$	0.52	6
Body Centered Cubic			2	$a = \frac{4R}{\sqrt{3}}$	0.68	8
Face Centered Cubic			4	$a = 2\sqrt{2}R$	0.74	12
Hexagonal Close Packed			6	$a = 2R$ $c = 1.63a^*$ <i>*ideal</i>	0.74	12

Density

$$P = (n/V_c)(A/N_A)$$

(atoms/volume)(mass/atom)

FCC → BCC : P decreases, stretches

BCC → FCC : P increases, shrinks

X-Ray Diffraction

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

$$a = d\sqrt{(h^2 + k^2 + l^2)}$$

Vacancies

$$N_V = N \exp(-Q_V / kT) \text{ or } N \exp(-Q_V / RT)$$

$$C_{\text{wt}\%} = m_1 / \sum n_i \times 100$$

$$C_{\text{at}\%} = (n_m)_1 / \sum (n_m)_i \times 100$$

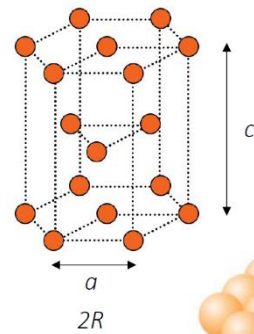
$$X_V = N_V / N$$

Fick's First Law

$$J = -D \times (dc / dx)$$

Diffusion Coefficient

$$D = D_0 \exp(-Q_d / RT)$$

HCP:

Ideally, $c/a = 1.63$
But not always.

Crystallinity:

$$\% \text{crystallinity} = P_c(P_s - P_a) / P_s(P_c - P_a) \times 100$$

P_c = density of crystalline polymer

P_s = density of specimen

P_a = density of amorphous polymer

Stress and Strain Formulas**Engineering Normal Stress:**

$$\sigma = F_x / A_o$$

Engineering Strain:

$$\varepsilon = \Delta L / L_o$$

Shear Stress:

$$\tau = F_x / A_y$$

Shear Strain:

$$\gamma = \Delta x / y = \tan \theta$$

Elastic Deformation:**Tension/Compression:** $\sigma = E\varepsilon$ **Shear:** $\tau = G\gamma$ **Shear/Elastic related via:** $E = 2G(1+\nu)$ **Poisson's Ratio:**

$$\nu = \varepsilon_x / \varepsilon_z = \varepsilon_y / \varepsilon_z$$

Percent Elongation:

$$\frac{l_f - l_o}{l_o} \times 100$$

Percent Reduction in Area:

$$\frac{A_o - A_f}{A_o} \times 100$$

Modulus of Resilience:

$$\frac{\sigma_y^2}{2E}$$

Hall-Petch Equation: Grain Strength:

$$\sigma_{yield} = \sigma_o + k_y d^{-0.5}$$

d = average grain diameter**k, σ_o** = constants**Yield Strength**

$$\sigma_y = \sigma_o + k_s \sqrt{C}$$

C = solution concentration**Cold Working %CW:**

$$\frac{A_o - A_f}{A_o} \times 100$$

Critical Length

$$a_c = \frac{1}{\pi} \times \left(\frac{K}{Y\sigma} \right)^2$$

$$K = Y\sigma\sqrt{\pi \times a}$$

K = Fracture Toughness**Y** = Shape Factor**a** = Crack Size**Diameter of Cylindrical Rod**

$$d = \sqrt{\frac{4Fl_o}{\pi E \Delta l}}$$

Initial Length

$$l_o = \frac{E \Delta L A_o}{F}$$

In Brittle Materials:

$$K = \sqrt{2\gamma E}$$

$$a = \frac{2E\gamma}{\pi\sigma^2} \quad a = \frac{2EG}{\pi\sigma^2} \quad \text{length} = a/2$$

 γ = Surface Energy

$$l_f = l_o(1 + \varepsilon)$$

$$M = A l_p$$

$$E_c = E_f V_f + E_m V_m$$

$$\sigma = \alpha_l E \Delta T$$

Electrical and Thermal Equations**Resistivity (ρ)**

$$\rho = \frac{RA}{l} \quad R = \frac{L}{\sigma A}$$

Conductivity (σ)

$$\sigma = \frac{1}{\rho}$$

Current Density (J)

$$J = \sigma E$$

Electric Field (E)

$$V = \frac{E}{l}$$

Fermi energy $E_f \rightarrow$ energy of the last (highest) filled state at OK

Electron Motion

$$V_d = \mu_e E$$

V_d = Drift velocity

μ = Electron mobility (m^2/Vs)

E = Electric field

$$\rho_{total} = \rho_t + \rho_i + \rho_d$$

$$\rho_t = \rho_0 + aT$$

$$\rho_i = A c_i (1 - c_i)$$

C_i is the impurity concentration as atomic fraction. A is a composition-independent constant. Is a dependant on both the impurity and host metals.

In general:

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

μ_e : Electron mobility μ_h : Hole mobility
 e = charge of electron or hole = 1.6×10^{-19} C

For intrinsic semiconductors, since # of holes (p) = # of electrons (n):

$$\sigma = n_i |e| (\mu_e + \mu_h)$$

Intrinsic carriers:

$$n_i = n_o \exp\left(-\frac{E_g}{2kT}\right)$$

Extrinsic carriers (n-type):

$$n = n_{Do} \exp\left(-\frac{E_D}{kT}\right)$$

Extrinsic carriers (p-type):

$$p = p_{Ao} \exp\left(-\frac{E_A}{kT}\right)$$

n-Type Mobility

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

p-Type Mobility

$$\sigma = p |e| \mu_h$$

Heat Capacity

$$C = \frac{\Delta Q}{\Delta T} \times \frac{1}{m}$$

T in K

m in kg

Heat Loss

$$Q = \frac{KA\Delta T}{(\text{thickness } "L")}$$

$$\text{Heat Flux} = -K \left(\frac{dT}{dx} \right)$$

k = Thermal Conductivity

$$\Delta T \alpha_L = \frac{\Delta l}{l_o}$$

$$\Delta T \alpha_v = \frac{\Delta V}{V_o}$$

$$\varepsilon^{th} = \frac{\Delta l}{l_o}$$

Only for Rapid Temperature Changes

$$\sigma_T = E \alpha_l (T_o - T_1)$$

Thermal Shock Resistance

$$TSR = \frac{\sigma_f k}{E \alpha_l}$$

$$\text{Heat Loss} = (\text{Flux})(\text{Area})$$

Fick's First Law

$$J = -D \left(\frac{dC}{dx} \right)$$

D = Diffusion Coefficient

Atomic Structure and Bonding

Arrangement of atoms and their bonding will affect the material's properties.

At R_0 (equilibrium atomic bond length):

$$F_n = 0$$

E_n = minimum (equilibrium bond energy)

Lower bond energy = lower melting temperature.

Low energy \rightarrow Gas phase

Medium energy \rightarrow Liquid phase

High energy \rightarrow Solid phase

Steeper curve around R_0 leads to an increase in the modulus of elasticity (stiffness).

Broad and asymmetrical curve \rightarrow Higher thermal expansion coefficient.

Primary Bonding

1. Ionic:

Transfer electrons from metallic to non-metallic.

Low-electronegativity: Net positive charge

Higher-electronegativity: Net negative charge.

This causes coulombic attraction.

Non-directional. Like-ions cannot be adjacent. High bond energy. High melting point. Very strong; hard but brittle. Electrically and thermally insulating.

2. Covalent:

Form for atoms with small differences in electronegativity.

Atoms share electrons. **Directional.** Organic chemistry and polymer science and semiconductor science depend on covalent bonding.

Properties vary; some have high melting

points, other low. Electrically insulating or semiconducting.

3. Metallic:

Occurs for metallic elements and alloys.

Valence electrons form a "sea". Non-valence electrons and nuclei form ion core.

Non-directional. Melting point can vary as bonding strength varies. Ductile. Good electrical and thermal conductors.

Secondary Bonding

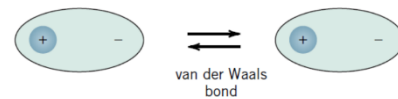
Very weak compared to primary bonds.

Secondary bonds are always present but can be overshadowed by primary bonds.

1. van der Waals:

Arise from dipoles.

Coulombic attractions.



Fluctuating dipole: Caused by temp fluctuations in electrons around nucleus or in molecule.

Permanent dipole: Caused by asymmetry in the distribution of positively and negatively charged regions in a molecule (polar/non). Attract neutral molecules to one another.

2. Hydrogen bonding:

A special type of permanent dipole is formed when hydrogen is covalently bonded to highly electronegative elements.

The H nucleus serves as a bare proton capable of strong attraction.

- Ionic Bond
- Covalent Bond
- Metallic
- Hydrogen Bond
- Van der Waals is the weakest

Structure of Crystalline Materials

Amorphous materials:

Glass, polymers

No periodic packing

Atomic arrangement: Random

Order: Short range

Crystalline materials:

Ceramics and metals

Periodic arrangement

Atomic arrangement: Regular

Order: Long range

	Crystalline	Amorphous	Mixed
Metals	usually (e.g. steel, brass)	rarely (e.g. metallic glass)	never
Ceramics	often (e.g. alumina)	often (e.g. soda glass)	often (e.g. silicon nitride)
Polymers	never ("crystalline" polymers always partly amorphous)	usually (e.g. polyethylene)	sometimes (e.g. nylon)

Crystal Structure: Matter in which atoms, ions, or molecules are spatially arranged.

Crystalline Materials: Atoms arranged into a periodic array. Repeat unit called "unit cell". Repeated pattern called "crystal lattice".

Unit cell: Basic structural unit or building block of a crystal. Defines the geometry and atom positions. Smallest volume that represents the structure and symmetry. Repeated to make any size crystal.

Lattice constant (a): Distance between unit cell corners. Refer to equations above.

Metallic Crystals:

1. SC - Rare (Atoms at corners)

Not close-packed

2. FCC (Atoms at corners, center, and faces)

Examples: Cu, Al, Ag, Au, γ Fe

Close-packed

Stacking of planes: ABCABCABC

3. BCC (Atoms at corners and center)

Not close-packed

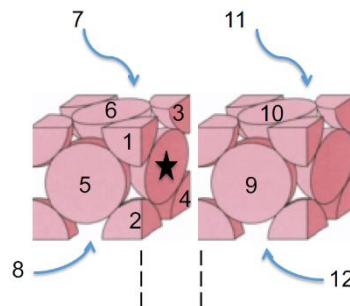
Examples: α Fe, Cr, W, Mo

4. HCP

Examples: Ti, Mg, Zn, Zr

Stacking of planes: ABABAB

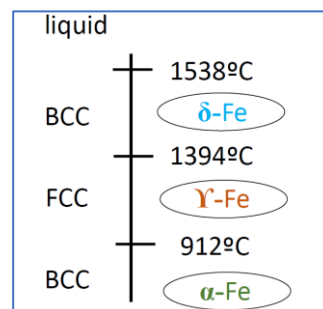
Coordination Number: Number of nearest neighbours for each atom.



Polymorphism:

Some materials contain two or more distinct crystal structures for the same material; polymorphs/allotropes.

The crystal structure that the material adopts depends on the temperature and pressure.



Points, Planes, Directions

Anisotropy: The properties of materials differ depending on the direction in which measurements are taken. Ex: Graphite/Mica *Conductivity, elastic modulus, and index of refraction* generally depend on direction.

Isotropy: Materials where the measured properties are independent of the direction of measurement. Known as being isotropic. Anisotropic means they are dir. dependent.

As structural symmetry *decreases*, anisotropy *increases*.

Miller Indices:

Points: q,r,s

Planes: (hkl)

Direction: [uvw]

In cubic materials, direction is normal to the plane.

Defects in Crystalline Materials

0D: Point Defects

Critical for allowing the microstructure of the material to evolve.

Vacancies:

A lattice position that is vacant because the atom is missing. The fraction of vacancies in metallic crystals at its melting temp is 10^{-4} .

Interstitials:

An atoms that occupies a place outside the normal lattice position. It may be the same element (self-interstitial), or a different element (alloying element or impurity).

Substitutional atom:

Literally a different atom in place of the solvent atom.

Thermodynamics of Vacancies

Systems tend towards minimal enthalpy (H) and maximum entropy (S).

A perfect crystal only has one atomic configuration ($S=0$) [no defects].

Vacancies give rise to many atomic configurations

> If n vacancies are added to a lattice:

$$> n \uparrow \Rightarrow H \uparrow \Rightarrow S \uparrow \Rightarrow G \downarrow$$

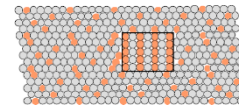
> Vacancies are created until G is at a minimum.

Increasing the temperature causes a surface island of atoms to grow. Island grows/shrinks to maintain equilibrium vacancy concentration in the bulk.

Solute atom: Atom which is different than the host atom (solvent). Sometimes referred to as “impurities”.

Alloys

An alloy is a homogeneous mixture or solid solution of two or more metals in which the impurities (solutes) have intentionally been added to provide specific properties.



Second phase particle
--different composition
--often different structure & properties

Solubility of Substitutional Solute Elements:

- i) Atomic size factor – Should be similar
- ii) Crystal structure – Should be the same
- iii) Electronegativity – Should be similar
- iv) Valences

Mechanisms of Diffusion:

For an atom to diffuse/migrate from one lattice site to another;

- i) There must be an empty adjacent site
- ii) The atom must have sufficient energy

Interstitial Diffusion:

Easier than vacancy diffusion since they are smaller and there is plenty of vacant space for them to occupy/move to.

Diffusion is generally faster in BCC crystals than FCC.

Activation Energy for Diffusion:

An atom's energy is lowest when in lattice position.

Atoms squeeze through gaps – a thermally activated process (faster at high T).

Diffusion faster for:

- Open crystal structures
- Lower melting T materials
- Materials with secondary bonding
- Smaller diffusing atoms

Rate of Diffusion: Depends on concentration of vacancies and the rate of jumping.

1D: Line Defects

Dislocations: Crystal planes move across one another, atoms “move”, and produce plastic deformation. Thermodynamically unstable. Dislocations always increase the energy of the crystal.

2 types: Edge, Screw (can have mix)

Most dislocations will disappear at high enough temperatures.

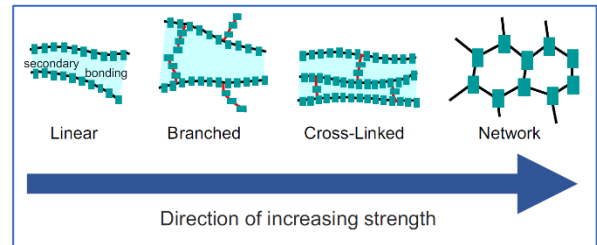
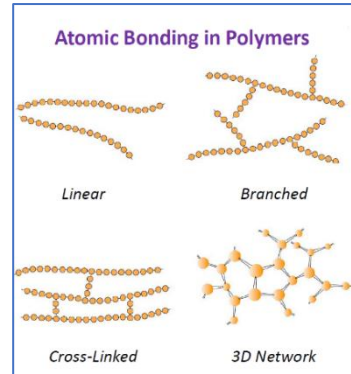
Edge: An extra half-plane of atoms in the material. The Burgers vector and the dislocation line are perpendicular. Edge dislocations move by breaking and remaking atomic bonds. Moves parallel.

Screw: When the lattice has sheared. Burgers vector and dislocation line are parallel. Moves perpendicularly.

2D: Planar Defects

Boundaries are 2D defects that separate regions of a material. Boundary regions have different structure as compared to the bulk.

Atom on a surface plane have more energy than interior atoms. Dangling bonds have excess energy. To reduce this energy, materials try to reduce the surface area.

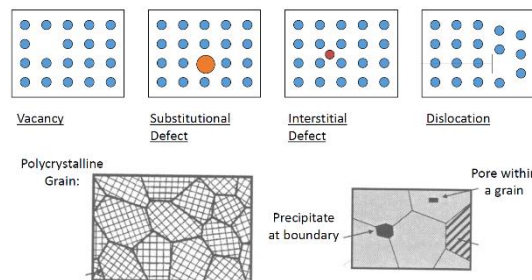


Grain boundaries: Most solids are polycrystalline – contain many grains. Mirrored grains are called twins, with a twin boundary separating them (shear forces/heat treatments, straight lines in a micrograph). Twin boundaries have a lower energy than free surfaces.

Stacking faults: When planes are stacked out of order.

3D: Bulk/Macroscopic Defect

Yield Strength: Ceramics > Metals > Polymers = Composites



Characterization

Microscopy: Used to image the bulk material (metal/glass/polymer).

In metals: Optical Microscopy reveals the

different microstructures of the material, while Electron Microscopy reveals the defects in the crystal lattice. Optical also lets us see grain boundaries and twin planar defects. Electron lets us probe lattice parameters, interplanar spacing, and stacking faults.

Amorphous SolidsF

Lacking crystalline structure.

Polymers: Composed of hydrocarbons.

Repeat Unit: Structural entity repeated along the polymer chain. Isotropic.

Ethylene is the *monomer* of polyethylene.

While majority of polymers are anamorphous, it's possible to have semi-crystalline polymers with regions of order. Rarely 100% crystalline. Less complex polymers can align and orient to crystallize more easily. Crystalline structure is complex and often chain-folded.

Thermoplastics: Little cross-linking, require heat to form, retain shape when cool, soften with heating, Linear.

Thermosets: Large cross-linking (10-50%), form into a permanent shape, "set" by chemical reaction, DO NOT soften with heating.

Deformation of Semi-crystalline Polymers:

1. Deformation begins in the amorphous region, sliding of the polymer chain occurs
2. Crystalline blocks rotate, and then segment
3. Amorphous regions stretch out

Molecular Weight (MW): Mass of a mole of chains. Impacts the melting temperature and glass transition temperature and the viscosity properties.

T_g = Temperature at which an amorphous material transitions from brittle "glassy" state to a more fluid and viscous state. Lower than melting temperature. Viscous deformation occurs above this temperature, while elastic deformation occurs below this temperature.

Glass is an amorphous material. Unlike metals and some ceramics, its atoms are locked into an unordered pattern by cooling it rapidly – it does not have time to form a crystalline structure.

Phase Diagrams

Phase diagrams describe the conditions (temperature, pressure, composition) under which a phase is stable and at equilibrium conditions. If the material is not at equilibrium, you can have like liquid water at -15 C (have like smooth container surfaces). The boiling point of water is a function of pressure.

Phase: A region of a substance that is:

1. Uniform in chemical composition
2. Physically distinct
3. Mechanically separable

Physically and/or chemically distinct regions in the material.

- 1 phase: White Gold (Au, Ag, Ni, Alloy)

- 2 phase: Ice in water (solid + liquid H_2O)

Component: A chemically distinguishable constituent of a substance. The elements that are mixed to make the alloy.

The **composition** is the concentration of each component present in an alloy.

Equilibrium: The lowest energy state of a system (striving towards equilibrium)

Solid Solution: A solid in which the two or more components are compatible and form a single phase.

	1 phase	2 phases
1 component	Pure water Diamond	Ice water
2 components	Brass (Cu, Zn alloy)	Saturated salt water ($\text{NaCl}_{(s)} + \text{H}_2\text{O}_{(l)}$)
3 components	White gold (Au, Ag, Ni alloy)	Snowflake obsidian (SiO_2 , MgO , Fe_3O_4)

Solubility Limit: The maximum concentration of solute atoms that may dissolve in the solvent, at a specific temperature, to form a solid solution. Adding solute past this limit yields another solid solution (different crystal structure) or compound that has a different composition. Volume is not conserved when you add shit.

Two Types of Binary Phase Diagrams:

1. Complete solubility of two components (isomorphous)
 - Similar crystal structure, atomic radii, electronegativity
2. Limited solubility of two components (eutectic)

Type 1: Isomorphous Phase Diagrams

Identifying Phases Present

Locate the temperature-composition point and see which phases are listed within the region

Compositions of Phases

If one phase is present, it is the same composition as the overall composition of the alloy.

If two phases are present, follow the horizontal to both phase lines and see what the composition of each is at that point on the phase line.

Relative Amounts of Phases

Lever rule; one side of the tie line, over the entire length of the tie line give you the relative amount of the opposing phase. So if solid is to the left of the point, the amount on the right of the point corresponds to the solid.

Type 2: Binary Eutectic Phase Diagrams:

Binary eutectic happens when 2 elements completely dissolve into each other in a liquid state, but only partially dissolve into each other as a solid state.

Eutectic Solid – Consists of the lamellae of A and B

Eutectic A – Lamellae of A

Eutectic B – Lamellae of B

Phase Transformations

Kinetics of Solid-State Reactions

Most reactions involve nucleation and growth: Nucleation is an incubation process (involves time), and growth is limited by the diffusion process (also takes time).

Transformation is temperature dependant.

Martensitic Transformation: Is not thermally activated. Diffusionless. Transformation occurs at high speed.

Independent of time – depends ONLY on temperature.

Metastable vs Equilibrium States

True equilibrium states are rarely achieved.
Supercooling/heating – cooling/heating past a phase transition temperature without the occurrence of a transformation.

Mechanical Behaviour of Materials

Stress and Strain

Stress – Means force ($\text{N/m}^2 = \text{Pa}$)

Strain – Displacement ($\text{m/m} = \text{unitless}$)

A material will strain in response to a stress:

Non-permanent strain = **elastic**

Permanent strain = **plastic**

Elastic Behaviour of Materials

For elastic deformation, stress and strain are proportional.

Modulus of Elasticity (E) (Young's Modulus)

Ratio of stress to strain (slope). Measure of the **stiffness** of a material.

Van der Waals < Metallic < Covalent

$E_{\text{ceramic}} > E_{\text{metal}} > E_{\text{polymer}}$

Shear Modulus (G): Similar but for shear stress/strain

Poisson's Ratio (V): Measures the lateral contraction during simple tension and compression.

Metals = 0.33

Ceramics = 0.25

Polymers = 0.40

Auxetics are materials that have a negative Poisson's ratio. When stretched, they become thicker perpendicular to the applied force. High fracture resistance and energy absorbing properties. No squish=0.

Plastic Behaviour of Materials

Plastic deformation is permanent or non-recoverable. The response can be ductile or brittle. It's permanent because you are breaking and forming new bonds.

Yield Strength

Yielding – The onset of plastic deformation

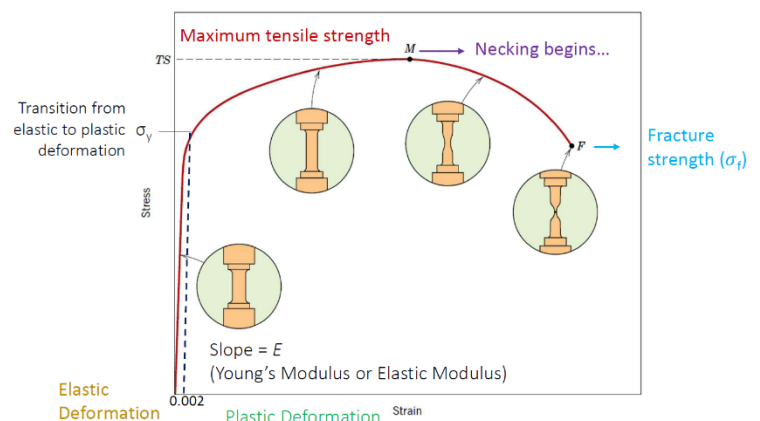
Yield Strength (σ_y): The stress required to produce a very specific amount of plastic strain; a strain offset of 0.002 (0.2%) is commonly used. MPa.

Large variation between materials.

Ceramics > Metals > Polymers

Work Hardening

Hardening – An increase in yield strength due to plastic deformation. Significantly effected by temperature and composition.



Ductility

How much a material plastically deforms before it fractures. May be expressed as percent elongation (%EL) or percent reduction in area (%RA) from a tensile test.

A material that experiences very little/no plastic deformation up to fracture is termed brittle. A crack happens if strain energy released > free surface energy created.

Toughness

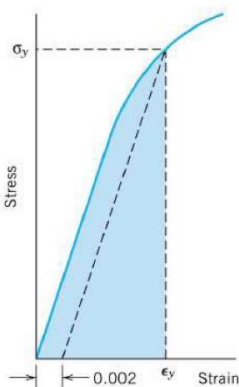
Energy required to fracture a unit volume of material. Area under stress-strain curve.

Energy Storage and Resilience

Resilience: the capacity of a material to absorb energy when it is deformed elastically and then, upon unloading, can recover this energy. That means there must be energy stored in the solid.

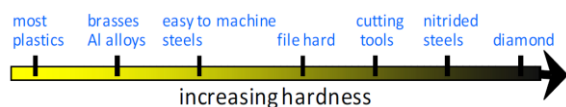
Modulus of Resilience (U_r): The strain energy per unit volume (J/m^3).

The area under the engineering stress-strain curve up to the point of yielding.



Hardness

A measure of a material's resistance to local plastic deformation, i.e. permanent indentation on the surface.



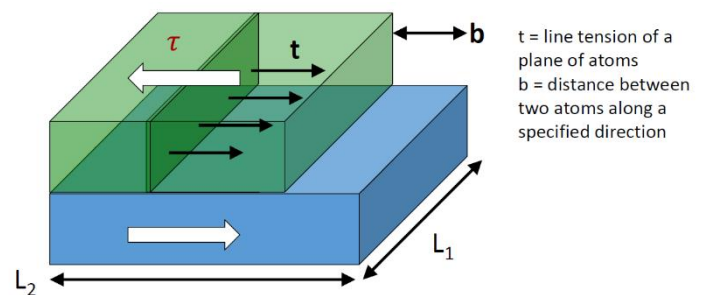
Summary:

- Ceramics have high strength but very fragile.
- Metals have properties that are a good compromise between strength and ductility
- Polymers are weak at low temperatures, and very ductile at high temperatures.
- Although E is basically constant for the type of material, all other properties are dependent on microstructure

Mechanical Behaviour of Materials – Mechanisms

Perfect crystals are very strong because we have to break all bonds simultaneously for plasticity. Real crystals have defects (dislocations) and so plastically deform at lower stress.

Lattice strain, zones of compression and tension, are created around the dislocation.



Force applied in shear:	$\tau L_1 L_2$	[N]
Work done due to disc. motion:	$\tau L_1 L_2 \times b$	[J]
Line Tension opposing motion:	t	[N/m]
Work resisting motion:	$(t \times L_1) L_2$	[J]

t/b is the critical shear stress. If $T > t/b$, the dislocation will move.

Dislocation Motion

Covalent bonding – motion hard (directional bonding)

Ionic bonding – motion hard (must retain charge neutrality)

Metals – motion easiest (non-directional, close-packed)

Slip Systems

Dislocations do not move with the same ease on all crystallographic planes and in all crystallographic directions.

There is typically a preferred plane where motion is easiest (require the least stress).

Slip plane: The most dense plane having the highest planar atomic density.

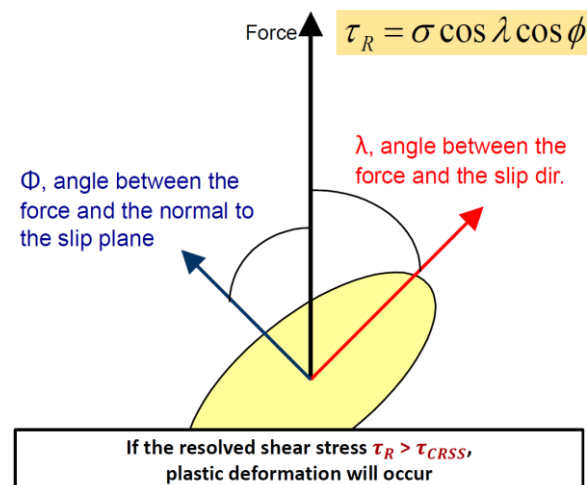
Slip direction: The most closely packed direction, i.e. having the highest linear atomic density, within the slip plane.

Collectively called “Slip System”

Slip in Crystals

Single Crystals – Each step (shear band) results from the generation of many dislocations

Polycrystalline Materials – Grain orientations with respect to applied stress are random. Dislocation motion occurs along the slip systems in the direction with highest resolved shear stress.



Summary

Plastic deformation occurs at lower strength than the theoretical strength to break bonds

- Crystal lattice contains defects (dislocations)
- Dislocations move along a plane of atoms
- Dislocations are easy to move in shear
- No matter the load, there will always be a crystallographic plane of atoms that experiences shear loading
- The preferred atomic plane / direction for deformation is called a slip system

Strengthening of Materials

To strengthen crystalline materials, make it harder for dislocations to move. Increasing strength = almost always decreases ductility

Strengthening by Grain Size Reduction

Dislocations can't move across a grain boundary

- Dislocations have to change their direction of motion
- The greater the crystallographic mis-orientation, the more difficult the dislocation movement
- Atomic disorder results in discontinuity of slip planes

Fine-grained materials have greater amount of grain boundary area; materials with smaller grain size are stronger than those with large grain size.

Grain size reduction improves strength and toughness.

If we keep decreasing the grain size, we get *nano-grained materials* (lots of strength)

Solid Solution Strengthening

Strengthening of metals by adding solute atoms (i.e. alloying) (Substitutional or interstitial elements)

Mechanism: Impurity atoms cause lattice strains. These strains repel dislocations and make dislocation motion more difficult. Solute and host atoms are not the same size.

Precipitate Strengthening

A dislocation can easily move through an un-deformed crystal. The addition of small and hard second phase particles (precipitates) will act as an “obstacle course” to slow dislocation motion. By quenching, then reheating an alloy, precipitates will form within the grains.

Particles influence dislocation motion in two ways:

- They act as obstacles to motion (like an obstacle course)
- When dislocations are pinned at two ends by particles, dislocations multiply in what is called a Frank Read source

Work Hardening

The motion of dislocations is hindered by presence of other dislocations.

A ductile metal becomes harder and stronger as it is plastically deformed, because the number of dislocations increases and thereby their mobility decreases. Dislocation density increases with deformation.

Cold Working is deforming (straining) a material at low temperatures.

As cold working is increased:

- Yield strength (σ_y) increases.
- Tensile strength (σ_{UTS}) increases.
- Ductility (%EL or %AR) decreases.

Cold working a material (forging, rolling, extruding, drawing) will change the microstructure significantly.

Cold working a material may distort the shape of the grains

- They can become elongated in the direction of strain
- This can lead to anisotropy in yield strength and ductility (directional dependence after working)

Polymers

Dislocations do not play a role in the strength amorphous solids. Instead, the relative slippage of two segments of a polymer chain controls strength.

Annealing

Overview: Deforming a polycrystalline metal leads to:

- Change in grain shape and dimension
- Increase in dislocation density
- Increase in energy stored as strain energy

Cold-worked metals can be undone by a heat treatment called annealing.

Annealing (thermally activated) Process

1. Recovery (dislocations annihilate)

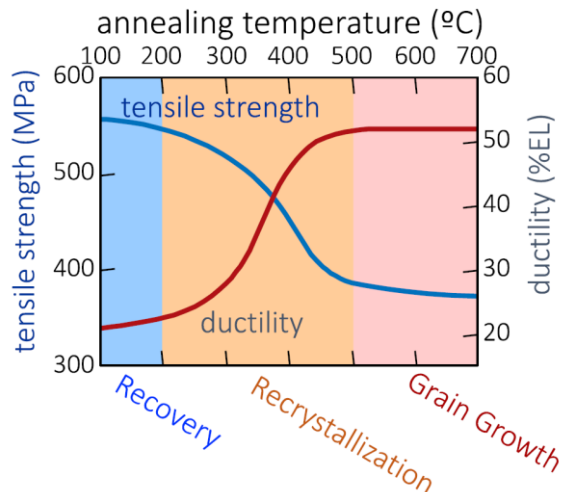
- Small decrease in strength/hardness
- Small increase in ductility
- Grains are mostly unchanged
- Some internal strain energy is relieved
- Electrical/thermal conductivity restored

2. Recrystallization (new strain-free grains nucleate)

- Decrease in strength/stress/Elec Resist
- Ductility is restored
- New grains form
- Temperature and time dependant
- Relatively high strain energy state
- Dislocation density decreases

3. Grain Growth (larger grains grow at the expense of smaller ones)

- Grain size increases
- Small decrease in strength
- Does not need to be preceded by recovery/recrystallization
- Reduction in total energy



It's All About Reducing Energy:

Recovery: The combination and annihilation of dislocations...reduces the energy associated with dislocations (strain-energy)

Recrystallization: The new strain free grains...have lower energy than deformed grains

Grain Growth: Larger grains have lower surface-to-volume ratio thus...reducing the energy stored in grain boundaries (surface-energy)

Electrical Conduction

Electronic: Flow of electrons, dominates

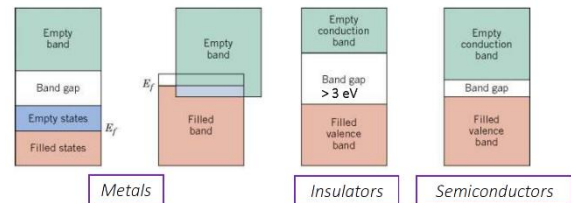
Ionic: Diffusion of charged ions, liquids

Valence Band: Occupancy is based on the outermost shells of the atoms. These will interact at close range (as interatomic distance decreases).

Conduction Band: range of electron energies where an atom is free from bonding with its atom to move freely within the atomic lattice. Free electrons are in the conduction band.

A material being a conductor or insulator depends on the outermost shell of its atoms.

- If a band is partially full or bands overlap → conductor
- If the valence band is full and the conduction band is empty → insulator or semiconductor



Conduction in Metals

- Electrons are excited into one of the empty and available energy states above E_f
- There are vacant energy states adjacent to the highest filled state at E_f , therefore little energy is required to promote electrons to empty states
- Electric field provides sufficient energy.

Electron Mobility

When an electric field is applied, free electrons accelerate in the opposite direction to the field.

Frictional forces counter this acceleration, which are a result of scattering electrons by imperfections in the crystal lattice including:

- Impurity atoms
- Vacancies
- Interstitial atoms
- Dislocations
- Thermal vibrations

Scattering:

- Electron loses kinetic energy
- Electron changes direction of motion
- Scattering causes resistance to passage of electric current

Electrical Resistivity of Metals

Depends on:

- Temperature
- Composition
- Degree of cold work (dislocation density)
- The total resistivity is the sum of each

Conduction in Semiconductors and Insulators

In semiconductors and insulators, no available empty states are adjacent to the filled valence band.

The energy required to promote an electron to the conduction band equals band gap energy. Energy is usually from a nonelectrical source (heat, light, etc.)

- If $E_g > 3 \text{ eV} \rightarrow$ insulator
- If E_g is smaller \rightarrow semiconductor

The number of excited electrons into the conduction band depends on E_g and temperature. $E_g \uparrow = \sigma \downarrow$ at a given T .

Intrinsic Semiconductors

- Band gap typically $< 2\text{eV}$
- At $T = 0\text{K} \rightarrow$ conductivity $= 0$

At $T > 0\text{K}$, heat helps electrons jump over the band gap: creation of electron-hole pairs.

For every electron excited into the conduction band, a hole is left behind

- Positively charged relative to the electron ($+1.602 \times 10^{-19}\text{C}$)
- A vacant electron state in the valence bond

Intrinsic Conductivity

2 types of charge carriers:

- Free electrons (n : number of electrons/ m^3)
- Holes (p : number of holes / m^3)

Importance of Material Purity:

Commercial semiconductors are all extrinsic: Behaviour doesn't come from random impurities, but the intentional addition of dopants.

Depending on the dopants, an extrinsic semiconductor will be:

- n-type: negative charge carrier (excess of electrons)
- p-type: positive charge carrier (excess of holes)

The conductivity of semiconductors is much less than that of metals.

Semiconductors can be either:

- Intrinsic: Electrical behaviour is dependent on the properties of the pure material. Only Si and Ge are pure.
- Extrinsic: Electrical behaviour is dictated by impurity/solute atoms, also known as dopants (Check lecture 12 for examples)

n-Type Extrinsic Semiconductor

If we bond a 5-valence with a 4-valence, only 4/5 valence are going to participate in bonding. The extra electron is very loosely bound and can easily be broken off. This extra electron sits at a donor state below the conduction band. No hole is created in the valence band.

Electron Bonding Energy corresponds to the energy required to excite an electron from impurity state to a state within the conduction band.

$E_D \ll E_g$ (band gap energy)

At room temp, many donors are promoted

- Very few electron-hole pairs
- $n \gg p$

Only electron mobility is considered.

Position of donor state depends on temp and donor concentration

P-Type Extrinsic Semiconductors

If we add 3-valence to 4-valence, one covalent bond is deficient by one electron. Can be thought of as a hole that is weakly bonded to the impurity atom. The hole may trade spots with an electron from an adjacent bond. Impurity atom introduces an acceptor state in the band gap, just above the valence band. Thermal excitation of a

valence electron into this acceptor state creates a hole in the valence band.

The only charge carrier produced is the hole in the valence band. A free electron is not created in the conduction band.

$E_A \ll E_g$

Room temp; many acceptor states are filled.

$p \gg n$

Holes are the majority carriers, only hole mobility is taken into consideration.

Temperature Dependence of Semiconductivity (Intrinsic)

- Concentration of carriers will increase with temperature → More thermal energy available to excite electrons.

At intermediate temperatures:

- Carrier concentration depends mostly on dopant concentration
- Intrinsic excitations are negligible
- Known as **extrinsic region** (or saturation/exhaustion region)

At very low temperatures:

- Thermal energy insufficient to excite electron movement from donor states or into acceptor states. Known as **freeze-out**

At high temperatures:

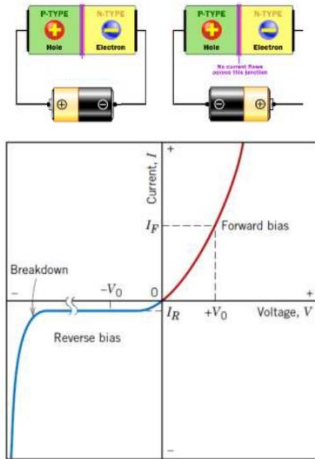
- Intrinsic excitations become significant, and state to dominate. **Intrinsic region**

Solid State Devices

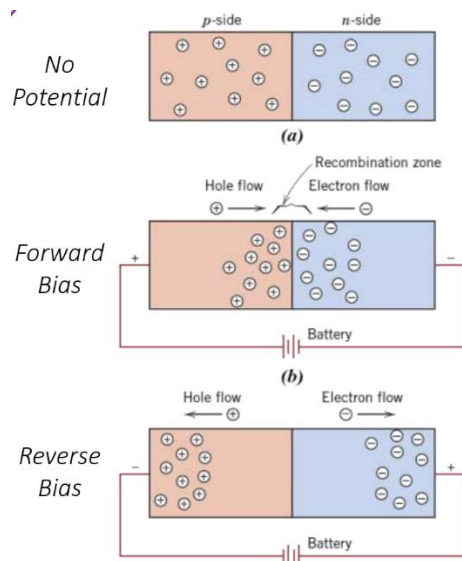
Diode

- P- and n- type regions in contact
 - P-n junction
- Device is a single crystal with different dopants

- The behaviour of the junction depends on the direction of the bias voltage
 - Forward bias: Low resistance
 - Reverse bias: Insulator, Rectifier



Current-voltage characteristics of a p-n junction



Forward Bias: New electrons and holes are injected into the device at the end contacts.
Reverse Bias: Depleted region behaves as an intrinsic semiconductor (drops by a factor of 10^7)

Transistor

Same principles as the p-n junction, but more complicated

Two major types of transistors:

- Junction Transistor
 - MOSFET (metal-oxide field effect transistor)
- Transistors can amplify a signal, or act as a switch.
 - The two states of a transistor (conducting/non-conducting) allows for binary information to be represented.
 - Arithmetic computing operations

Thermal Properties

Specific Heat Capacity: Represents the amount of energy required to produce a unit temp rise in a unit mass of material. Has units $J/(kg\ K)$ or Molar: $J/(Mole\ K)$.

Materials gain thermal energy by increasing the vibrational energy of the atoms.

Below the Debye Temp, C_V is temp dependent, while above this Temp, it is temp independent.

Thermal Conductivity

Heat transported from high to low temperature regions of a substance.

In solids, heat is conducted by:

- > Lattice vibrations (phonons)
- > Movement of free electrons

$$K = K_{\text{lattice}} + K_{\text{electrons}}$$

Usually one predominates:

- > Metals: Free electrons
- > Ceramics: Phonons
- > Polymers: Vibrational + Rotational

Coefficient of Thermal Conductivity (K)

Property that describes a material's ability to transport heat across a temperature gradient.

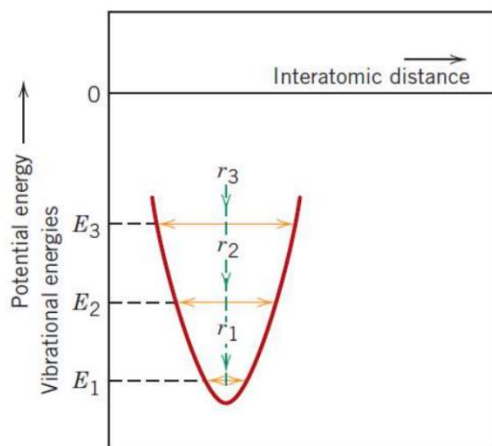
Coefficient of Thermal Expansion (α)

Thermal expansion effects in solids is generally small. Materials expand at different rates.

In many materials, the value of α_L is anisotropic. When the thermal expansion is isotropic, $\alpha_v = 3\alpha_L$

Thermal expansion is reflected at the atomic level as an increase in the equilibrium distance between two atoms.

Thermal expansion is due to the asymmetric curvature of this potential energy trough (NOT the increased atomic vibrational amplitudes with rising temperature)



Thermal expansion is important in bi-metallic strips.

Thermal expansion results in deformation, and thermal-mechanical stresses within solids. Thermal stresses can build in a solid when it is subject to changes in temperature.

Temperature gradients cause different parts of an object to expand by different amounts.

The capacity of a material to withstand failure due to a sudden change in temp is described by its Thermal Shock Resistance.