Materials Notes
ASEN 1022

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March 13, 2016

2   Atomic Bonding

Frequency of Isotopes

$$n_{\text{total}} = an_1 + bn_2 \qquad\qquad 1 = a + b$$

Solve for a or b in the right equation, sub into the left equation.

Forces

Coulombic Attraction

$$F_c = \frac{-K}{a^2}$$

where $K = k_0(Z_1 q)(Z_2 q)$

Repulsive Force

$$F_R = \lambda e^{\frac{-a}{r}}$$

The net bonding force is $F = F_c + F_R$. The equilibrium bond length a_0 occurs at the point where the forces balance.

Bonding Energy

Bonding energy E is related to the bonding force through the differential expression

$$F = \frac{dE}{da}$$

The equilibrium bond length occurs at a minimum in the energy curve, where the force equals zero.

$$F = 0 = \left(\frac{dE}{da}\right)_{a=a_0}$$

It follows that a_0 is the sum of two atomic radii:

$$a_0 = r_{Na^+} + r_{Cl^-}$$

Coordination Number

Coordination number determines the number of atoms that can be packed around a central atom.

Radius ratio is calculated as $\frac{r}{R}$, where r is the radius of the smaller ion, and R is the radius of the larger.

Covalent Bonds

To determine the reaction energy, take the final bond energy from the new bonds formed, and subtract the initial energy of the bonds being broken.

Example: Length of a polyethylene molecule, $(C_2H_4)_n$, where $n = 500$.
Bond length $l = (C--C \text{ bond length}) \times \sin(\frac{109.5^\circ}{2})$
Total length $L = 500 \times 2 \times l$

Bonding Energy Curve

Common way to describe the curve is

$$E = -\frac{K_A}{a^6} + \frac{K_R}{a^{12}}$$

Take the derivative and set equal to zero, solve for a to find the equilibrium bond length.

3   Perfect Crystalline Structures

Seven Crystal Systems, can be stacked together in the 14 *Bravais Lattices*.

Edge Length(a), Atomic Radius(r) and atoms/unit		
Crystal Structure	**a vs. r**	**Atoms/Unit cell**
bcc	$a = \frac{4r}{\sqrt{3}}$	2 atoms/unit
fcc	$a = \frac{4r}{\sqrt{2}}$	4 atoms/unit
hcp	$a = 2r$	2 atoms/unit

Triangles in $\mathbb{R}^3$

For a triangle with vector sides u and v originating at one vertex, the area can be written as

$$A = \frac{1}{2}|u \times v|$$

Diffraction

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

Where d is spacing between adjacent crystal planes, θ is the angle of scattering, λ is the radiation wavelength, $n \in \mathbb{Z}$.

Interplanar Spacing

Cubic:

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

Where a is the side length of a unit cell, and h, k, l come from miller indices of the plane.

Hexagonal:

$$d_{hkl} = \frac{a}{\sqrt{\frac{4}{3}(h^2 + hk + k^2) + l^2(\frac{a^2}{c^2})}}$$

Where a and c are the lattice parameters.

4 Crystal Defects and Noncrystalline Structure- Imperfection

4.1 Solid Solutions

Can think of metal alloys as solid solutions. Called a *substitutional solid solution* because some atoms are swapped for others in the lattice sites. Only occurs when these rules are met:

4.1.1 Hume-Rothery Rules

1. Less than about 15% difference in atomic radii.

2. The same crystal structure

3. Similar electronegativities (within 15%)

4. The same valence ($2^+, 3^-$, etc.)

$$\%\text{Difference} = \frac{R - r}{R} \times 100$$

If one or more rule is violated, only partial solubility is possible. Solutions can either be *random solid solutions*, (differing particles randomly mixed in) or *ordered solid solutions*. (Where different particles take the face positions of an *fcc* lattice, for example.)

4.1.2 Interstitial Solid Solutions

Interstitial solid solutions occur when one atom is way smaller than the others, and can fit into the gaps in the lattice structure.

Ideally an interstitial atom would just be touching the other atoms in the structure. This ideal radius can be calculated:

$$r_{interstitial} = \frac{1}{2}a - R$$

Where a is the length of the unit-cell edge, and R is the radius of a larger atom.

Net charge of the substance must remain the same: to add 2 Al^{3+} ions, 3 Mg^{2+} ions must be removed. This leads to points in the structure with no ions present.

4.1.3 Non-Stoichiometric Compounds

Iron Oxide, $Fe_{1-x}O$ with $x \simeq .05$ is an example of a *nonstoichiometric compound*, since it has both Fe^{2+} and Fe^{3+} ions occupying the cation sites. Ideally there would be an equal amount of Fe^{2+} and O^{2-}.

4.2 Point Defects

4.2.1 Schottky Defect

- A pair of oppositely charged ion vacancies.

- Ensures local charge neutrality

4.2.2 Frenkel Defect

- Vacancy-interstitialcy combination

- One slot with a vacancy, one slow with two ions crammed in.

4.3 Linear Defects

Also known as *dislocations*, given the symbol $\perp$. $\perp$ represents an extra half-plane of atoms.

4.3.1 Burgers Vector

The Burgers Vector b is the displacement vector to close a stepwise loop around the defect. In a perfect crystal, the loop stop and start at the same place. The vector represents the magnitude of the defect.

The magnitude of b in simple metal structures is the repeat distance along the highest atomic density direction.

4.3.2 Edge Dislocation

Dislocation line runs along the edge of an extra row of atoms. In this case the Burgers vector is perpendicular to the dislocation line.

4.3.3 Screw Dislocation

Comes from the spiral stacking of crystal planes around the dislocation line. Burgers vector is parallel to the dislocation line.

The two above are the perfect extremes, many are mixed variants of the two. Burgers vector will neither be parallel or perpendicular to the dislocation line.

4.4 Planar Defects

4.4.1 Twin Boundary

Separates two crystalline regions that are structurally mirror images.

4.4.2 Hirth-Pound Model

Elaborate ledge system instead of smooth planes.

Grain Boundaries are the most important here, which is the region between two adjacent single crystals or grains.

4.5 Tilt Boundary

Occurs when two adjacent grains are titled a few degrees relative to each other. Includes a few isolated edge vacancies. Regions will consist of regions of good correspondence, separated by *grain-boundary dislocations*, a type of linear defect.

Distance between isolated edge dislocations is given by $D = \frac{b}{\theta}$, where b is the length of the Burgers vector, and θ is the tilt between adjacent crystal sheets.

It's useful to have an index of grain size, typically use *grain-size number*, G.

$$N = 2^{G-1}$$

Where N is the number of grains observed in an area of 1 in.^{2} (645 mm^2) on a photomicrograph taken at $100\times$ magnification.

Can also count the number of grains per unit length n_L of a random line drawn across a micrograph. Average grain diameter d is given by

$$d = \frac{C}{n_L M}$$

Where M is the magnification, and C is some constant greater than 1. Typically 1.5 is adequate.

4.6 Noncrystalline Solids: Three-Dimensional Imperfections

4.6.1 Zachariasen Model

Illustrates the important features of oxide glass structures. (Recall: Glass refers to a noncrystalline structure that shares characteristics of a ceramic.) *Short Range Order (SRO)* is maintained, in that the the building blocks still retain their shape. However, the *Long range order (LRO)*, or crystallinity is lost in the glass.

4.6.2 Bernal Model

Produced by drawing lines between the centers of adjacent atoms. The resulting polyhedra are irregular in shape and lack any repitition in stacking arrangements. Some evidence for *medium range order (MRO)*, which has effects over the range of a few nanometers, and can introduce structure on a very small scale.

5 Diffusion

Boltzmann's Constant

$$k = 1.381 \times 10^{-23} \frac{m^2 kg}{s^2 K} = 8.617 \times 10^{-5} \frac{eV}{K}$$

Ideal Gas Constant

$$R = 8.314 \frac{J}{\text{mol} \cdot K}$$

5.1 Thermally Activated Processes

Typically processes increase in rate with temperature. "Rate" $= k$.

$$\text{rate} = Ce^{\frac{-Q}{RT}}$$

Where C is a **preexponential constant**, independent of temperature. Q is the **activation energy**, R is the universal gas constant, and T is the absolute temperature.

To solve for Q: Take two different temperatures and rates, then divide one by the other. C cancels, solve for Q.

Arrhenius Equation

$$\ln(\text{rate}) = \ln C - \frac{Q}{R}\frac{1}{T}$$

Making a semi-log plot of $\ln(\text{rate})$ vs $\frac{1}{T}$ creates a straight line plot of rate data with slope $\frac{Q}{R}$. $\mathcal{Y}$ intercept is $\ln C$.

Maxwell-Boltzmann Distribution

$$\mathcal{P} \propto e^{\frac{\Delta E}{kT}}$$

Where $\mathcal{P}$ is the probability of finding a molecule at an energy ΔE greater than the average energy characteristic of a particular temperature, T. The energy barrier must be overcome by thermal activation.

Above equation was developed for gasses, holds true for solids too. Often requires several steps; slowest step will be the rate-limiting step.

5.2 Thermal Production of Point Defects

Point defects occur as a result of thermal vibration of the atoms in a crystal structure.

$$\frac{n_{\text{defects}}}{n_{\text{sites}}} = Ce^{\frac{-E_{\text{defect}}}{kT}}$$

Where $\frac{n_{\text{defects}}}{n_{\text{sites}}}$ is the ratio of point defects to ideal crystal-lattice sites, C is a preexponential constant, E_{defect} is the energy needed to create a single point defect, k is Boltzmann's constant, and T is the absolute temperature.

E depends on the type of defect being considered.

Concentration of vacancies:

$$\frac{n_v}{n_{\text{sites}}} = Ce^{\frac{-E_v}{kT}}$$

Where E_v is the energy of formation of a single vacancy.

$$\ln\frac{n_v}{n_{\text{sites}}} = \ln C - \frac{-E_v}{kT}$$

5.3 Point Defects and Solid-State Diffusion

Molecules from areas of high concentration to areas of low concentration. **Vacancy migration** moves particles along vacancies. Material flows opposite direction from vacancy. Particles can "Randomly Walk" in any direction with equal probability, but the difference in concentration tends to produce a net flow from areas of high concentration to areas of low concentration.

Fick's First Law

$$J_x = -D\frac{\delta c}{\delta x}$$

Where J_x is the flux, of the diffusing species due to a **concentration gradient** $\frac{\delta c}{\delta x}$. The proportionality coefficient D is called the *diffusion coefficient* or *diffusivity.*

Fick's Second Law

$$\frac{\delta c_x}{\delta t} = \frac{\delta}{\delta x}\left(D\frac{\delta c_x}{\delta x}\right)$$

For most problems it can be assumed that D is independent of c, leading to the simplified version:

$$\frac{\delta c_x}{\delta t} = D\frac{\delta^2 c_x}{\delta x^2}$$

Solutions take the form

$$\frac{c_x - c_0}{c_s - c_0} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Where c_0 is the initial bulk concentration of the diffusing species, and 'erf' refers to the **Gaussian Error Function**. *Gaussian Error Function:*

$$\text{erf}(z) \equiv \frac{2}{\sqrt{\pi}}\int_0^z e^{-t^2}\,dt$$

Linear Interpolation Formula

$$\begin{bmatrix} x_1 & y_1 \\ x_2 & y_2 \\ x_3 & y_3 \end{bmatrix}, \mathbf{y_2} = \frac{(x_2 - x_1)(y_3 - y_1)}{(x_3 - x_1)} + y_1, \ \mathbf{x_2} = \frac{(y_2 - y_1)(x_3 - x_1)}{(y_3 - y_1)} + x_1$$

Arrhenius for Diffisivity Data

$$D = D_0 e^{\frac{-q}{kT}}$$

D is the diffusion coefficient, in $\frac{m^2}{s}$

D_0 is the maximum diffusion coefficient at ∞ temperature

q is the activation energy for defect motion. and $q = E_{\text{defect}} + E_{\text{defect motion}}$

or

$$\boxed{D = D_0 e^{\frac{-Q}{RT}}}$$

Q is activation energy per mole of diffusing species

5.4 Steady-State Diffusion

Concentration Gradient

See Fick's 1$^{\text{st}}$ law.

$$\frac{\delta c}{\delta x} = \frac{\Delta c}{\Delta x} = \frac{c_h - c_l}{0 - x_0} = -\frac{c_h - c_l}{x_0}$$

5.5 Alternate Diffusion Paths

Up until now just considered volume diffusion, but diffusion can be much easier along a grain boundary. Surface diffusion is even easier.

$$Q_{\text{volume}} > Q_{\text{gran boundary}} > Q_{\text{surface}}$$

and

$$D_{\text{volume}} < D_{\text{gran boundary}} < D_{\text{surface}}$$

6 Mechanical Behavior

6.1 Stress Versus Strain

Metals

Engineering Stress:

$$\sigma = \frac{P}{A_0}$$

P is the load on the original sample.

A_0 is the original cross sectional area

Engineering Strain

$$\epsilon = \frac{l - l_0}{l_0} = \frac{\Delta l}{l_0}$$

l is the gage length at a given load

l_0 is the original length.

Elastic Deformation is temporary, and is fully recovered when load is removed.

Plastic Deformation is permanent, although a small elastic portion may be recovered.

Plastic Region is the non-linear portion generated once the total strain exceeds elastic limits.

Yield Strength is defined as the intersection of the deformation curve with a straight line parallel to the elastic portion, and offset .2% on the strain axis. Yield strength represents the stress necessary to generate .2% of deformation.

Young's Modulus, or Modulus of Elasticity

The linearity of the stress-strain plot is a graphical statement of the linearity of *Hooke's Law*:

$$\sigma = E\epsilon$$

E is the modulus, which represents the stiffness.

Specific Strenth or Strength-to-weight ratio is often preferred in aerospace applications.

Residual Stress is defined as the residual stress remaining after loads are removed.

Tensile Strength or *Ultimate Tensile Strength* is the maximum stress.

Strain Hardening is the term for increasing strength with increasing deformation.

True Stress

$$\sigma_T = K\epsilon_T^n$$

σ_t is the true stress

ϵ_T Is the true strain

K, n are constants with values given for a metal or alloy

Ductility is quantified as the percent elongation at failure: $100 \times \epsilon_{\text{failure}}$. Opposite of ductile is brittle. $(\epsilon_{\text{failure}} - \epsilon_{\text{recovery}}) \times 100$

Toughness is the combination of strength and ductility.

Upper Yield Point is the transition from elastic region, followed by a non-homogeneous deformation that begins at a point of stress concentration. (Often where the specimen is gripped)

Lower Yield Point is the end of the ripple pattern, beginning of general plastic deformation.

Poisson's Ratio

$$v = -\frac{\epsilon_x}{\epsilon_z}$$

ϵ_x, ϵ_z are the strain in the x and z directions.

Shear Stress:

$$\tau = \frac{P_s}{A_s}$$

P_s is the load on the sample

A_s is the area of the sample parallel to the applied load.

Shear stress produces an angular displacement:

$$\gamma = \tan \alpha$$

γ is the shear strain

α is the angular displacement.

Shear Modulus, or Modulus of Rigidity (G)

$$G = \frac{\tau}{\gamma}$$

The shear modulus G and the elastic modulus E are related for small strains by Poisson's ratio:

$$E = 2G(1 + v)$$

Ceramics and Glasses

Modulus of Rupture

$$\mathbf{MOR} = \frac{3FL}{2bh^2}$$

F Is the applied force

b, h, L are dimensions defined in the figure below.

Griffith Crack Model

Assumes that there will be numerous elliptical cracks at the surface and/or interior. The highest stress at the tip of such a crank is σ_m.

$$\sigma_m \simeq 2\sigma \left(\frac{c}{\rho}\right)^{\frac{1}{2}}$$

σ is the applied stress

c is the crack length

ρ is the radius of the crack tip

Polymers

The *flexural strength* is equivalent to the modulus of rupture defined for ceramics. The *flexural modulus* is:

$$E_{\text{flex}} = \frac{L^3 m}{4bh^3}$$

m is the slope of the tangent to the initial straight-line portion of the load deflection curve. Others defined above.

Dynamic Modulus of Elasticity:

$$E_{\text{dyn}} = CIf^2$$

C is a constant defined by specific test geometry

I is the moment of inertia of the beam and weights

f is the frequency of vibration for the test

6.2 Elastic Deformation

Fundamental mechanism at play here is the stretching of atomic bonds. For elastic deformation, compressive and tensile forces often behave similarly.

6.3 Plastic Deformation

Works better with existing deformations and imperfections. The theoretical *critical shear stress* is roughly one order of magnitude less than the bulk *shear modulus, G.*

Slipping along a plane in the crystal structure is more difficult as the atomic step distances are increased. Increased dislocations *hinder* further dislocations, which is why cold-working a metal can increase the strength.

Dislocation slips are easier along slip planes with higher atomic density, because the "road" is smoother. The number of slip systems dramatically alter the ductility of the material; materials with a greater number of slip systems are far more ductile.

We can define the "resolved shear stress", τ which is the actual stress operating on the slip system.

$$\tau = \sigma \cos(\lambda) \cos(\phi)$$

Where $\sigma = \frac{F}{A}$

A value of τ great enough to produce slip by dislocation motion is called the *critical resolved shear stress*, and is given by

$$\tau_c = \sigma_c \cos(\lambda) \cos(\phi)$$

6.4 Hardness

The *hardness test* is a relatively simple alternative to the tensile test from earlier. Often use the "Brinell Hardness Number" to express the hardness, given by

$$BHN = \frac{2P}{\pi D[D - \sqrt{D^2 - d^2}]}$$

P is the load

D is the sphere diameter (mm)

d is the indent diameter (mm)

6.5 Creep and Stress Relaxation

Creep can be defined as plastic deformation occurring at high temperature under constant load over a long period.

Primary Stage is characterized by a decreasing strain rate. Relatively rapid increase in length.

Secondary Stage is characterized by straight-line, constant-strain-rate data.

Tertiary Stage strain rate increases due to an increase in true stress. The comes from a cross-sectional area reduction.

Can view the steady-state creep rate $\dot{\epsilon}$ with activation energy Q:

$$\dot{\epsilon} = Ce^{\frac{-Q}{RT}}$$

Can also characterize *stress relaxation*, similar to a rubber band. Use relaxation time τ defined as the time necessary for the stress σ to fall to $\frac{1}{e}$ of the initial stress σ_0.

$$\sigma = \sigma_0 e^{\frac{-t}{\tau}}$$

or

$$\frac{1}{\tau} = Ce^{\frac{-Q}{RT}}$$

Simplified Form

$$\ln\left(\frac{K_1}{K_2}\right) = \frac{Q}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

6.6 Viscoelastic Deformation

Viscous behavior of glasses can be defined by the "viscosity", η.

$$\frac{F}{A} = \eta\frac{dv}{dx}$$

Inorganic Glasses

$$\eta = \eta_0 e^{\frac{Q}{RT}}$$

Region	η Values
Melting Range	50-500
Working Range	$10^4 - 10^8$
Softening Point	$10^{7.6}$
Annealing Range	$10^{12.5} - 10^{13.5}$
Annealing Point	$10^{13.4}$

Organic Polymers

Modulus of Elasticity is usually plotted instead of viscosity for organic polymers.

7 Thermal Behavior

7.1 Heat Capacity

Heat Capacity, C is defined as the amount of heat required to raise the material's temperature by $1°$ K.

$$C = \frac{Q}{\Delta T}$$

With Q being the amount of heat necessary to produce temperature change ΔT.

Common alternative is the specific heat, which uses a basis of unit mass:

$$c = \frac{q}{m\Delta T}$$

There are two ways to measure heat capacity– holding constant volume C_v or constant pressure C_p. C_p is always greater than C_v, but the difference is minor for most solids at room temperature or below.

Interestingly, C_v rises very sharply from 0 K as $C_v = AT^3$. Above a Debye temperature θ_D the value of C_v levels off at approximately $3\ R$, where R is the universal gas constant. θ_D is often less than room temperature, and for many solids $C_v \approx C_p$, so we have a good rule of thumb.

7.2 Thermal Expansion

Increase of temperature leads to greater vibrations in the atoms, which causes the material to expand. The overall dimension of a material in a given direction, L, will increase with the temperature T. This is reflected by the linear coefficient of thermal expansion, α.

$$\alpha = \frac{\mathrm{d}L}{L\mathrm{d}T}$$

It it worth noting that $[\alpha] = \frac{mm}{mm \cdot °C}$

7.3   Thermal Conductivity

We can define thermal conductivity, k, by Fourier's Law:

$$k = -\frac{\dfrac{dQ}{dt}}{A\dfrac{dT}{dx}}$$

Where $\frac{dQ}{dt}$ is the rate of heat transfer across an area A, due to a temperature gradient $\frac{dT}{dx}$. $[k] = \frac{J}{s \cdot m \cdot K}$.

For steady state heat conduction through a flat slab, we can simplify the above by replacing the differentials with a change Δ.

7.4   Thermal Shock

Thermal shock is defined as the fracture of a material after a sudden change in temperature (usually rapid cooling).

$$\epsilon = \alpha \Delta T$$

Then apply $\sigma = E\epsilon$