Lecture 2: Atomic Structure

2.1   Motivation

Material properties are dictated by their atomic structure; both the types of atoms and the arrangement of atoms or molecules. Other factors that affect this are defects and impurities, or grain size. All of these can change material prioerties. The structure of materials depends heavily on the processing conditions.

Multiple length scales are critical in engineering. The structures at different scales affect different kinds of properties (e.g. tensile strength and Young's modulus are determined at the atomic level, while ductility is determined at the scale of micrometers or millimeters - confirm.) Mechanical (strength, ductility), electrical (resistivity), thermal (heat conduction) and optical (transmittance) properties can all be influenced by atomic structure.

Using the wrong materials, or processing them incorrectly, has led to a number of disasters. Excessive stress, corrosive environments, incorrect structures from improper alloying or heat treatment, or embrittlement can all be catastrophic problems with materials in engineering. Concorde, WTC, Columbia, WW2 Liberty Ships.

2.2   Atomic Structure

2.2.1   Bohr model of the atom

Electrons are assumed to revolve around a nucleus (of protons and neutrons) in discrete orbitals, and the position of an electron is entirely determined by its orbital. This is slightly wrong, as it does not account for the particle-wave duality of electrons. The quantum mechanical model better explains the states available to each electron in an orbital. The quantum mechanical model provides a wavefunction for the position of an electron; rather than assuming an electron will definitely be at a certain place, it gives a continuous probability distribution of its location.

2.2.2   QM Model

Electrons behave like particles in that they scatter off objects and have momentum ($p = hk/2\pi$), but they behave like waves in that they are spread out in space, they can interfere with each other to form standing waves, and their energy and momentum depend on their wavelength. Electrons are best described by energy waves with a specific amplitude and wavelength, which may be found by solving Schrodinger's equation. The solutions are categorized as quantum numbers: n, l, m, and spin.

2.2.3 Quantum Numbers

2.2.3.1 n

The allowed values of n are 1, 2, 3 and so on. It is roughly associated with the electron's energy, and indicates how far from the nucleus the electron is (what electron shell is it in)

2.2.3.2 l

This is the angular momentum, and it has allowed values 0 to (n - 1). It is related to the shape and angular momentum of the electron in its orbit. l is usually represented as a letter (s = shape -¿ 1, p = principal -¿ 3, d = diffuse -¿ 5, f = fundamental -¿ 7), each corresponding to a number of energy states

2.2.3.3 m

This is the magnetic quantum number. It can take on $2l + 1$ distinct values, from $-l$ to $+l$ inclusive. This describes the spatial orientation of the electron, and directly represents the number of energy states for each subshell. It describes how the angular momentum splits under an applied magnetic field (verify).

2.2.3.4 m_s

This is the spin of the electron, which can be $\frac{-1}{2}$ or $\frac{1}{2}$.

The Pauli Exclusion Principle states that no two electrons can have the same four quantum numbers.

2.2.4 Electron Properties

Electrons have discrete energy states (are quantized) and tend to apply the lowest available energy states. The first few electrons in an atom have the following properties:

n	l	m	m_s
1	0	0	1/2
1	0	0	-1/2
2	0	0	1/2
2	0	0	-1/2

For degenerate levels such as 2p, each orbital is filled with one electron before electrons are paired up.

We can fully specify the electron configuration of an element by writing the n and l of each one with a superscript indicating how many electrons have these property. For example, S has a configuration of $1s^2 2s^2 2p^6 3s^2 3p^4$.

Electrons are filled up in an order to maximize the total spin, in the order indicated by the arrows here:
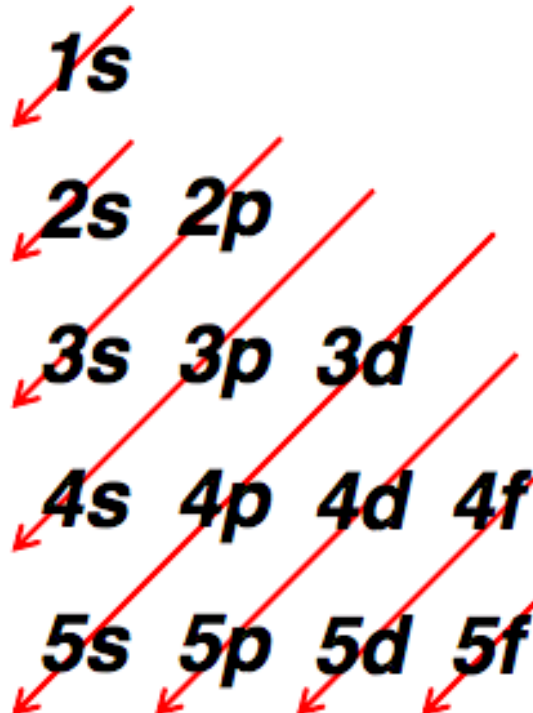
Electron filling rules:

s – orbitals ➜ 1 state / 2 electrons
p – orbitals ➜ 3 states / 6 electrons
d – orbitals ➜ 5 states / 10 electrons
f – orbitals ➜ 7 states / 14 electrons

Maximize total spin

1s

2s 2p

3s 3p 3d

4s 4p 4d 4f

5s 5p 5d 5f

2.3   The Periodic Table

The periodic table is arranged according to the order of electrons in the outermost shell. The alkaline metals have one electron in the s-orbital (Li, Na, K, Rb) and they have shared properties such as high reactivity because of it. Alkaline earth metals have two s electrons; chalcogens have a filled s orbital and four p electrons; halogens have five p electrons, and those with a partially-filled d orbital are the transition metals.

Noble gases have stable electronic configurations, with complete s and p subshells. Therefore, they tend to be inert. Elements without stable configurations can gain or lose an electron to obtain a stable state.

The properties that determine how easy it is to do this are the *ionization potential* or ionization energy, the energy required to take an electron out to vacuum (by convention, positive), and the *electron affinity*, the energy required to place an electron in an atom from vacuum (by convention, negative). The atom's electronegativity is a measure of how likely an atom is to take or give up an electron, and it is defined simply as

$$\chi = \frac{IP + EA}{2} \tag{2.1}$$

When two atoms are brought together, the one with the higher χ will have a higher electron density around its nucleus. A larger $\Delta\chi$ means a more ionic bond.

As a result of this, some trends emerge on the periodic table: the ionization energy increases moving left to right, and decreases top to bottom.
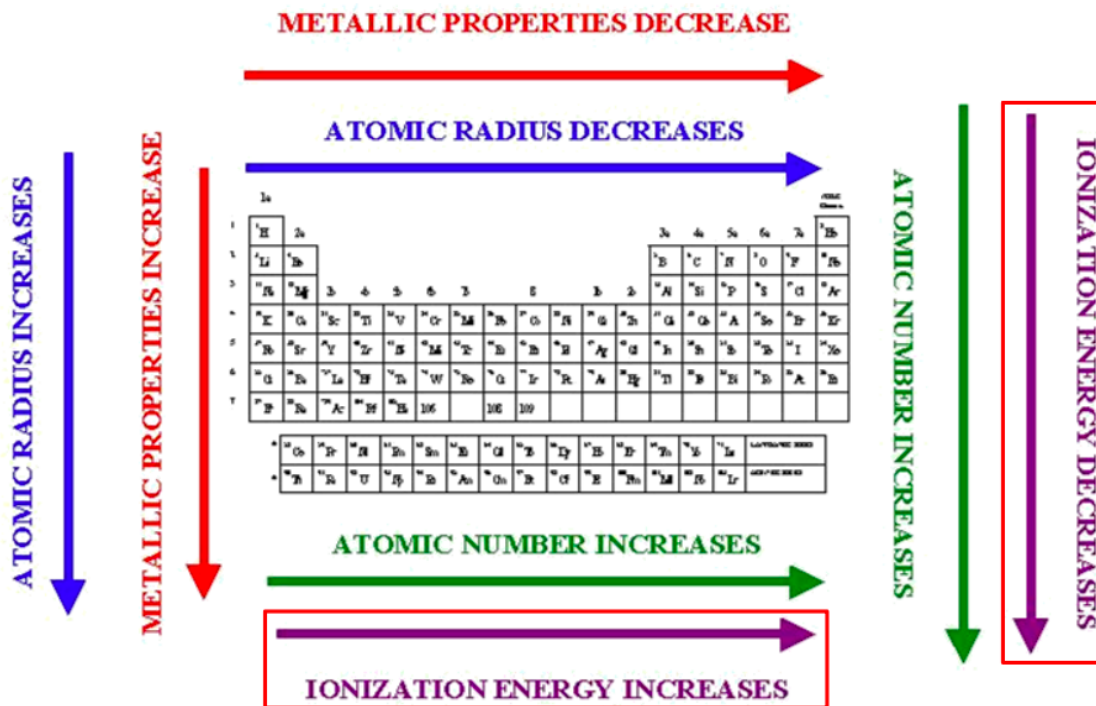
2.4 Factors that affect bonding

Bonding is affected by the relative energies of the valence electrons and the lowest available states (based on IP, EA, and χ), the number of valence electrons, and the symmetry of the valence orbitals.

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Lecture 3: Interatomic Bonding	
Lecturer: Lane Martin *August 27* *Aditya Sengupta*	

3.1   Ionic Bonding

Elements on the left of the periodic table tend to give up electrons (low electronegativity), and on the right they tend to acquire electrons (high electronegativity). An ionic bond is a transfer of electrons between two atoms of these types. A large difference in electronegativity is required. For example, Na can bond with Cl this way; Na gives up one electron and Cl accepts it.

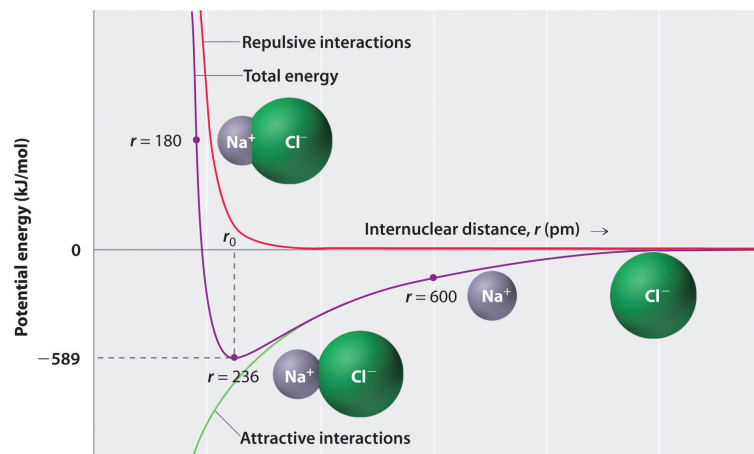The electric energy between these two is:

$$E_A = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r} \tag{3.1}$$

Since $z_1 = 1$ (Na) and $z_2 = -1$ (Cl), this is negative:

$$E_A = -\frac{e^2}{4\pi\varepsilon_0 r} = -\frac{A}{r} \tag{3.2}$$

Atoms do not collapse on themselves as a result of this, as there is also a repulsive term proportional to $1/r^n$.

We want to create an energy balance of attractive and repulsive terms to create a stable system.

3.2 Covalent Bonding

This involves electrons being shared. The system's energy is lowered overall by creating a bond in which both atoms have a completely filled shell rather than a half-filled shell.

covalent bond - two electrons being shared by two atoms (a carbon and a hydrogen atom)
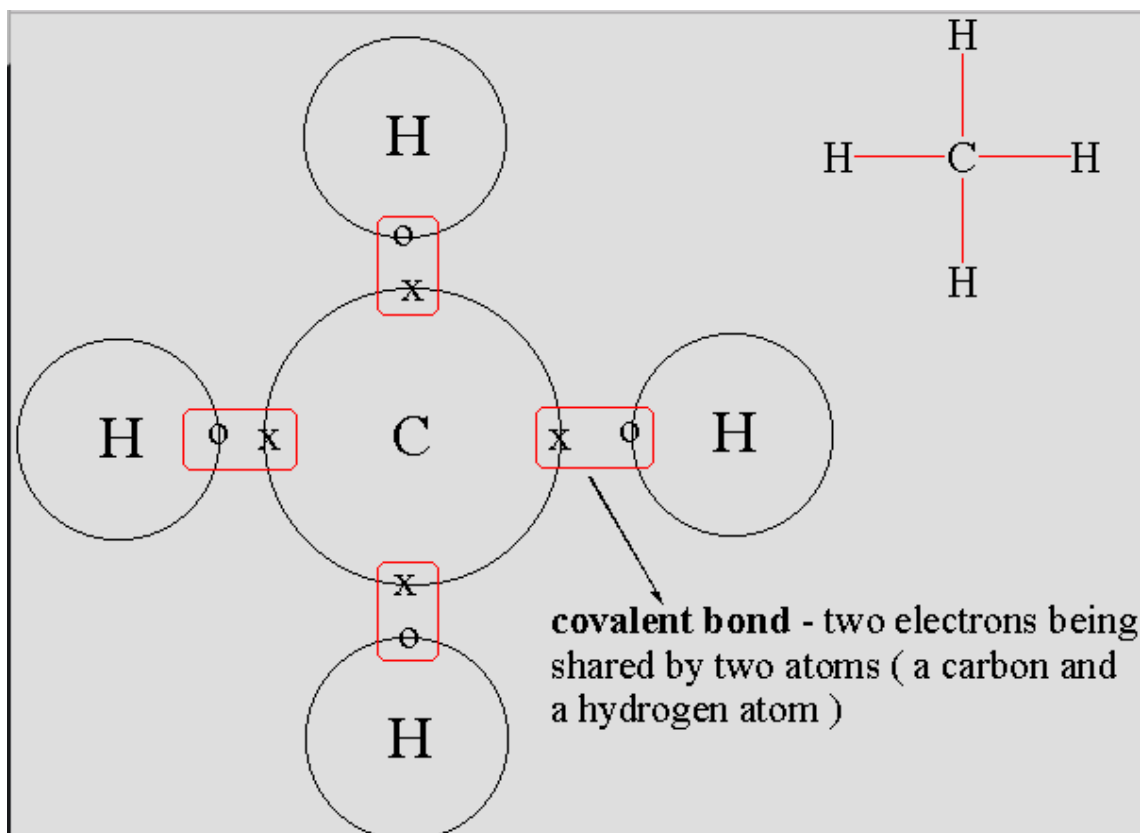
3.2.1 Hybridization

Sometimes the electrons being shared will not come from the same subshell; in this case, in order to make the molecule symmetric and reduce total energy overall, the shared electrons will join hybridized orbitals. An electron from an s subshell and one from a p orbital will hybridize to form an sp orbital. One s and three p can make an sp^3 orbital.
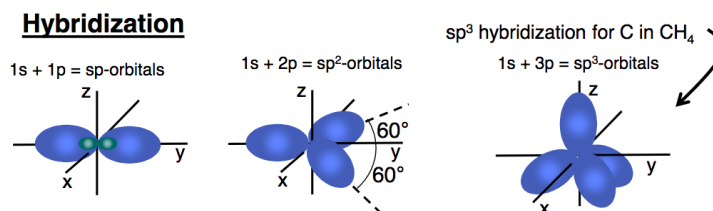
3.3 Metallic Bonding

This is the primary bond for metals and their alloys. It usually takes place when the atoms have a large atomic radius and small ionization potential. Since ionization energy increases moving to the right on the periodic table, low-IP atoms are more likely to be metals. In this bond, metals attract electrons from a śeaóf valence electrons and bond with them.

3.4 Ionicity

All the properties of materials are largely determined by the nature of bonding (type, and strength) between the constituent atoms.

Most bonds between types of atoms are not entirely ionic, entirely covalent, or entirely metallic. This formula lets you calculate the ionic character of a bond:

$$\% ioniccharacter = 1 - e^{-0.25(\chi_A - \chi_B)^2} \tag{3.3}$$

If %IC is close to 1, the material is likely to be an ionic ceramic, a complex salt, etc. If it is closer to 0, it may be a transition metal, alloy, or alkali metal. This is a spectrum, moving from ionic to covalent to metallic. Generally, a larger electronegativity difference makes the bond more ionic.

3.5 Secondary Bonds

3.5.1 Van der Waals Bonds

These arise from dipole-dipole interaction: a secondary bond between molecules with permanent dipole moments. For example, in hydrogen chloride, weaker secondary bonds are created by the dipole moment.

3.5.2 Dipole/induced-dipole interactions

This is a secondary bond between molecules, in which if a momentary dipole arises due to the probability distribution of electrons, it can induce a dipole in a neighbouring species, creating a temporary bond.

(remember definitions of IP, EA, e-, etc)

3.6 Properties from Bonding Curve

Melting temperature can be inferred from the bond curve; the lower the equilibrium point, the more difficult it is to break the bond, and therefore the higher the melting temperature. T_m is larger if E_0 is larger.

The sharper the curve is, the higher the elastic modulus. Elastic modulus/Young's modulus determines how much the material can be stretched before it cannot return to equilibrium; if the curvature is large, the elastic modulus is large.

The thermal expansion coefficient is related to how asymmetric the bonding curve is; heat makes the atoms oscillate, so if it is symmetric it will be less likely to expand. If it is asymmetric, it will expand much farther with the same amount of input heat energy.

3.7   Preview of Next Lectures

- Define terminology: lattice, basic atoms, crystal structure, unit cell

- Describe hard-sphere packing

The energy of a system is minimized by a close-packed crystal structure of atoms or molecules. Crystal structures are characterized by high density and regular spacing.

Some structures have little global structure. They have complex structures, rapid cooling, and no periodic packing. These are called *amorphous*.

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Lecture 4: Crystal Structures

Lecturer: Lane Martin *29 August* *Aditya Sengupta*

4.1 Unit Cells

A unit cell is the basic structural unit of a crystal structure. Its geometry and atomic positions define the crystal structure. A unit cell is the smallest component; when repeated and translated, it eventually forms the whole crystal. More than one unit cell can be chosen for a given crystal, but by convention, we choose the one with the highest symmetry.

A space lattice is an infinite array of mathematical points. Each point has identical surroundings to all the others. This is an ideal, not a physical, concept. To create a crystal structure, we apply a *basis* or *motif* to the lattice. Therefore the periodic arrangement of atoms in a crystal can be described completely by a lattice and an atom decoration on that lattice.

Lattice points do not necessarily always lie at the center of atoms. Polonium is the only element with a simple cubic structure, in which the atoms and the lattice points do line up, but every other element is more complicated.

To define unit cells, we need some way of describing 3D space. We set unit vectors $\vec{a}, \vec{b}, \vec{c}$. These are not necessarily mutually perpendicular; by convention, the angle between $\vec{a}$ and $\vec{b}$ is γ, between $\vec{b}$ and $\vec{c}$ is α, and between $\vec{c}$ and $\vec{a}$ is β.

This gives us 7 crystal classes:

Crystal System	Axial Relationships	Interaxial Angles
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^o$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^o, \gamma = 120^o$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^o$
Trigonal/Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^o$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^o$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^o \neq \beta$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^o$

There are several types of unit cells: primitive cells contain only one point, face-centered cells contain atoms centered on all the faces of the cell, body-centered cells contain an atom at the body center, and end-centered cells contain atoms on the sides or ends of the cell. Combining these with the 7 crystal classes gives us 14 Bravais lattices. Combining these 14 with all possible symmetry elements, e.g. rotations, translations, mirrors, glides gives us 230 space groups.

4.2 Analyzing Crystal Structures

Atoms can be shared between unit cells. For example, a vertex atom is on the corner of 8 unit cells, so it counts as $\frac{1}{8}$ of an atom for each of those unit cell.

- Edge atoms are shared between 4 unit cells → 1/4 atom per cell

- Face atoms are shared between 2 unit cells → 1/2 atom per cell

- Body atoms are not shared → 1 atom per cell

The coordination number is the number of nearest neighbors any atom in the crystal structure. What we usually want to know about the crystal structure of a material falls into one of these categories:

- basic structural parameters

- atoms per unit cell

- volume per cell

- atomic packing factor

- closed-packed direction

- linear densities in certain directions

- planar density of a given plane

Generally, we want to relate the cube side length a to the packing of ideal spherical atoms of radius R.

4.2.1 Atomic Packing Factor

This is defined as

$$APF = \frac{\text{Vol. of atoms in unit cell}}{\text{Vol. of unit cell}} \tag{4.1}$$

This is some ratio of used to total space. It is independent of atomic radius. For example, APF for the simple cubic structure is 0.52. We can do much better than this. For example, in three dimensions, we can layer atoms so that one layer fits into the free space left by the one below it.

4.2.2 Body-Centered Cubic Crystal Structure

This has a close-packed structure of atoms at the corners as well as one at the center. The length along a diagonal is $4R$, which is $\sqrt{2}a$ when projected onto the diagonal of a square. Geometry tells us that the relation between a and R is

$$a = \frac{4R}{\sqrt{3}} \tag{4.2}$$

From this, we can find the volume of the unit cell in terms of R:

$$V_{unitcell} = a^3 = \frac{64R^3}{3\sqrt{3}} \tag{4.3}$$

$$APF = \frac{8/3\pi R^3}{64R^3/(3\sqrt{3})} = 0.68 \tag{4.4}$$

The coordination number is 8; each center atom has 8 neighbours at the corners.

4.2.3 Face-Centered Cubic Crystal Structure

As above, we can find a relationship between a and R when we have atoms on each face:

$$a = 2\sqrt{2}R \tag{4.5}$$

The coordination number here is 12, as there are 4 neighbors in each of 3 planes. We can repeat the volume ratio calculation and get 0.74 for APF here.

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Lecture 5: Crystal Structures and Coordinate Systems

Lecturer: Lane Martin   *August 31*   *Aditya Sengupta*

5.1 Hexagonal Close-Packed Crystal Structure

This is similar to FCC, with the difference being that HCP repeats the first layer's structure in the third layer, instead of a third unique layer type as in FCC. Both have the same packing factor, as all atoms are packed as densely as possible.

5.2 Point Coordinates

To define a point in a unit cell, we can use a slight variation on Cartesian coordinates, in which x, y, and z are expressed as fractions of the magnitude of unit vectors. This is done because the directions are not necessarily orthogonal.

To define a vector, we start at the origin, and determine the length of the vector projection in each of the 3 axes in units or fractions of a, b, and c. We reduce these to the smallest integer values. These are then denoted as three values enclosed in square brackets. Negative directions are indicated with bars over the number.

Families are defined by the modes of symmetry available to a specific geometry, e.g. the cubic family is characterized by complete rotational symmetry (at 90 degree rotations).

5.3 Lattice planes

Lattice planes are important for determining crystal structure via diffraction (measuring d between parallel lattice planes), for plastic deformation (occurs because of atoms slipping past each other in a crystal) and to quantify transport properties. Therefore, it is important that we know how to designate planes. To do this, we do the following:

1. Take the reciprocals of the lengths at which the plane intersects each plane.

2. Find the LCM that converts all reciprocals to integers.

3. Enclose the new triple in parentheses to form the Miller Index of the plane.

If the plane passes through the origin, either construct a parallel plane translated, or choose another origin at the corner of the adjacent unit cell. Now, the plane either intersects or is parallel to each axis.

5.4 Densities in Materials

1. Crystal density: units of mass per volume (g/cm^3)

2. Linear density: number of atoms per unit length (cm^{-1})

3. Planar density: number of atoms in a unit plane (cm^{-2})

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Lecture 6: Crystalline Solids

Lecturer: Lane Martin	*5 September*	*Aditya Sengupta*

(implement guest lec)

6.1   Densities in Materials

Density can refer to the crystal density (3D) of a material, which has units of mass per volume, the linear density (number of atoms per unit length) or the planar density (atoms per unit area).

The linear density is defined as the number of atoms centered on a direction vector divided by the length of the direction vector. For example, the density of an FCC crystal along [1 1 0] is $\frac{1}{2R}$; along [1 1 0], there are 2 atoms along a length of 4R. Only atoms that are fully bisected by the given vector maybe included.

The planar density is defined as the number of atoms centered on a given plane, divided by the area of the plane. For example, the planar density on the (1 1 0) plane of an FCC crystal is $\frac{1}{4\sqrt{2}R^2}$, as there are 2 complete atoms in the plane (1/4 of 4 corner atoms and 1/2 of 2 side atoms), over an area of $2\sqrt{2}R \times 4R$

6.2   X-Ray Diffraction to Determine Crystal Structure

The ways light interacts with a crystal can tell us about its structure. In some cases, light can strike the first layer of atoms, or the second, or it may pass through undiffracted. The governing law here is $n\lambda = 2d\sin\theta$, where λ and d are of comparable lengths. Since the atomic spacing is on the order of angstroms, light is too large to show all the information that it is possible to gain with this methods. Therefore we can use x-rays to do this instead.

To measure diffraction effects, we send x-rays in at an incident angle 2θ, and measure the resulting intensity.

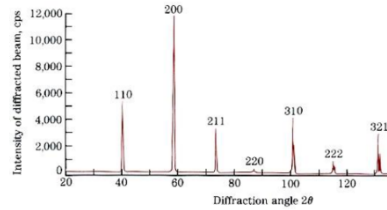## 6.3   Crystal Structure and Planar Distances

Let h, k, l be the Miller indices of the planes of atoms that scatter. Then, different conditions on these indices can yield constructive interference (reflections) or destructive interference (none).

Bravais	Constructive	Destructive
BCC	h + k + l = Even	h + k + l = Odd
FCC	(h, k, l) all odd/all even	(h, k, l) not all odd/all even
HCP	h + 2k $\neq$ 3n, n $\in$ N, l odd	Not that

Allowed Diffraction Peaks   Berkeley
                                          UNIVERSITY OF CALIFORNIA
                                          MATERIALS SCIENCE & ENGINEERING

Self-Assessment:
From what crystal structure is this?

(h k l)	$h^2+k^2+l^2$	h+k+l	h,k,l all even or odd?
100	1	1	No
110	2	2	No
111	3	3	Yes
200	4	2	Yes
210	5	3	No
211	6	4	No
220	8	4	Yes
221	9	5	No
300	9	3	No
310	10	4	No
311	11	5	Yes
222	12	6	Yes
320	13	5	No
321	14	6	No

h + k + l = even and gave the labels on
graph above, so crystal is BCC.

6.4   Ionic Crystals

An ionic crystal is one with significant ionic character. They consist of an anion (negative) and cation (positive), in which the cation is usually smaller due to anions having larger electron clouds.

Most ionic crystals can be considered to be close-packed structures of anions, with cations in the interstitial sites. The interstitial sites can have various shapes based on the method of packing. For example, in FCC, interstitial sites have eight edges surrounding them, so they are octahedral sites.

In HCP, there are six octahedral sites, and twelve tetrahedral sites. (Look at slides again for this) Rock salt places its cations in the octahedral sites.

6.5   Charge Neutrality

The net charge in ionic crystals must be 0. For example, if Ca^{2+} combines with F^-, the resulting formula must be CaF_2. They fall into a stable configuration when anions surrounding a cation are all in contact with the cation.

The coordination number of an ionic crystal scales with $\frac{r_{cation}}{r_{anion}}$.

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Lecture 7: Ionic Crystals

Lecturer: Lane Martin   *7 September*   *Aditya Sengupta*

7.1   Coulombic Interaction

In ionic solids, all the atoms are point charges which have interactions according to Coulomb's law:

$$E_C = \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 r} \tag{7.1}$$

In an ionic solid, we can model an individual atom's Coulombic interactions with its nearest neighbours:

$$E = -\frac{6e^2}{r} + \frac{12e^2}{2r} - \frac{8e^2}{\sqrt{3}r} + \ldots E = -M\frac{e^2}{r} \tag{7.2}$$

M is a constant, the same for each different crystal structure type.

If all terms are attractive, the crystal cannot be in equilibrium. Therefore we modify the formula:

$$E = -M\frac{e^2}{r} + B\frac{e^2}{r^n} \tag{7.3}$$

At an equilibrium distance r_0, energy is at a minimum. We get

$$U = -\frac{MN_A Z_1 Z_2 e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right) \tag{7.4}$$

n here is the Born exponent, which describes the repulsion that prevents core electron interpenetration. It is equal to the average of the n for the cation and anion, which correspond to noble gases; $He = 5, Ne = 7, Ar = 9, Kr = 10, Xe = 12$.

U is the molar lattice energy.

7.2   Crystal Types

Given the radii of the cation and anion of a crystal, and the ratio of cations to anions (from the formula) we can predict the coordination number of the crystal. From this, we can infer the unit cell type.

For example, NaCl has a radius ratio of 0.564, which yields a coordination number of 6. This tells us that NaCl has this structure:
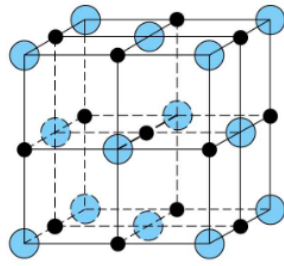
FIGURE 12.2 A unit cell for the rock salt, or sodium chloride (NaCl), crystal structure.

ROCK SALT STRUCTURE

We can extend this to make cool structures!

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Lecture 8: Defects

Lecturer: Lane Martin *September 10* *Aditya Sengupta*

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Defects can disrupt the long-range structure of a system, creating things like silicon glass by filling the interstitial sites of silicon dioxide with sodium. The change between crystalline and non-crystalline SiO_2, however, does not significantly change the electrical characteristics. Long-range order is not what determines electrical resistivity and band gap.

Allotropes are different structures for the same substance. They are usually seen in elemental solids such as carbon. Carbon can form diamond (a variant of zinc blende, with covalent bonding) or graphite (more stable at STP, better electrical conductivity, also with covalent bonding, and layers of hexagonally arranged carbon atoms with each atom bond), which are allotropes. Carbon nanotubes are one of these, in which carbon sheets are "rolled up" to make long structures with great material strength.

8.1 Defects

Defects come in several flavours:

- Zero dimensional (point defects) such as vacancies, interstitial atoms

- One dimensional (linear defects) such as imperfections in stacking layers

- Two dimensional (planar defects) such as surfaces, grain boundaries

- Three dimensional (volume defects) such as second phases, voids.

Defects can be difficult to study because they can be so small; zero-dimensional defects can be the size of an angstrom. However, they are probably the most important part of MSE. By introducing defects or impurities, mechanical properties (structural strength) can be improved such as with metal alloys, electrical properties (metal conductivity through defects, semiconductor conductivity through doping) changed, and so can optical properties.

8.1.1 Point Defects

These are mostly vacancies, the absence of atoms from lattice sites. They cause missing bonds, so it costs energy to create them. They form when the required activation energy is less than the ambient energy due to room temperature:

$$N_s = Ne^{-\frac{Q_s}{kT}} \tag{8.1}$$

where N_s is the number of vacancies, N is the total number of lattice sites, and Q_s is the activation energy. kT is the inverse of the energy derivative of the natural log of the number of microstates available to the system, or the temperature scaled by the Boltzmann constant if you're being boring.

A point defect can also be an extra atom placed in between lattice sites, which is referred to as a *self-interstitial*. Self-interstitials are usually not as probable as vacancies, because the activation energy is higher; a self-interstitial causes a lattice to bend sufficiently to include another atom of the same type as the lattice.

Because ambient conditions provide some activation energy for defects, perfect crystals to create are impossible at STP.

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Lecture 9: Point Defects

Lecturer: Lane Martin   *12 September*   *Aditya Sengupta*

Calculate the equilibrium number of vacancies for a cubic centimeter of copper at 1000ºC.

Regular unit conversion using mass and Avogadro's number tells us $N = 7.963 \times 10^{22}$. Then,

$$N_v = N\exp\left(-\frac{Q_v}{kT}\right) = 2.1834 \times 10^{19} \tag{9.1}$$

If this specimen is cooled to $300K$, $N_v = 6.11568 \times 10^7$ (same procedure). Rapid cooling will create almost the same change.

Increasing T auses the surfaces of atoms to grow, because the equilibrium vacancy concentration increaess via atom motion from the crystal to the surface.

Point defects are also possible in ionic solids, as long as charge neutrality is maintained. If an an anion vacancy is created, a cation must also be removed to maintain electronic neutrality, A Frenkel defect is a cation vacancy with a cation interstitial (not necessarily adjacent), and a Schottky defect is a cation vacancy with an anion vacancy.

In the limit of a small number of impurities, we can consider them to be point defects. When there is a large number, consider them a solution: a homogeneous distribution of impurities (a solute) within the crystal structure of the host (a solvent). If an impurity B is added to a host A, we either have a solid solution of B in A (which can be either a substitutional alloy, where B fills the A vacancies, or an interstitial alloy, where B is an interstitial to A) or a solid solution plus particles of a new phase, which can lead to a different composition altogether.

The solubility of a substitutional solution depends on:

1. Atomic size factor (better solubility if atomic radii are within 15%)

2. Crystal structure (host and impurity atoms should have the same crystal structure)

3. Electronegativity (difference should be small - otherwise, intermetallic compounds rather than solutions)

4. Valence (same valence is preferred)

Observing these through experimentation led to the Hume-Rothery Rules for Mixing (empirical guidelines, not a strict set of rules)

1. If the size difference of atoms $\frac{r_{solute} - r_{solvent}}{r_{solvent}} > 0.15$, lattice distortions (local lattice strain) are too big, solid solution is not favoured. But still possible.

2. For appreciable solubility, the crystal structure of metals must be the same.

3. The more electropositive one element is and the more electronegative the other, the more likely intermetallic compounds are; low ΔE favours a solid solution.

4. A metal will dissolve another metal of higher valence more than one of lower valence. "Higher in lower alright, lower in higher, it's a fight".

The composition of A in B is usually specified either by a weight percentage, or an atomic percentage:

$$wt\% = \frac{m_A}{m_A + m_B} \times 100\% \tag{9.2}$$

$$at\% = \frac{n_A}{n_A + n_B} \times 100\% \tag{9.3}$$

Kroger-Vink notation representations of point defects can be useful for bookkeeping (although not too necessary for the course). A negative charge is $'$, a positive charge is $\cdot$, V is a vacancy, e is an electron, h is a hole. The species of interest is written, with the site it's occupying as a right-side subscript. A vacancy in Na corresponds to $Na_{Na} \rightarrow V'_{Na} + 1h^{\cdot}$, for example.

9.1 Line Defects

These are things like dislocations (linear defects around which atoms are misaligned).

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Lecture 10: Linear and Planar Defects

Lecturer: Lane Martin *14 September* *Aditya Sengupta*

10.1 Linear Defects

10.1.1 Line/Edge dislocation

An edge dislocation is the presence of an additional partial plane of atoms along (conventionally) the end of a line that characterizes that dislocation (the dislocation line). It is denoted by $\perp$, or the flipped version of it, pointing to the extra half-plane.

10.1.2 Screw dislocation

This occurs when there is a shear between two layers: the bottom layer is pulled away from the structure, and the top layer is pushed in towards the structure. The shift is one atomic distance.
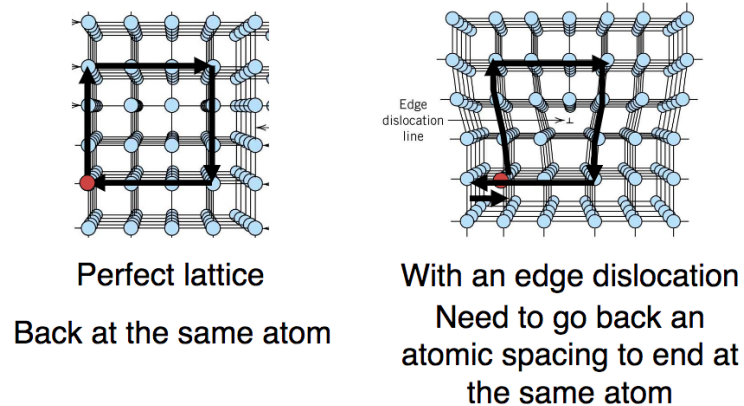
10.1.3 Mixed Edge/Screw Dislocation

This is a mixture of the two.

10.2 Burgers Vector, Imaging Defects

The Burgers vector is a way of characterizing a defect. If the vector is perpendicular to the structure, it is an edge dislocation; if it is parallel, it is a screw dislocation; if in between, it is a mixture. The magnitude indicates the degree of deformation. When going around in a loop around the defect (e.g. up, left, down, and right the same number of atoms along the lattice), the displacement between the end point and the start point after going in an apparent loop is the Burgers vector. The Burgers vector has a magnitude given by

$$\frac{a}{2}|uvw| \tag{10.1}$$

where a is the lattice parameter, and $|uvw|$ represents the slip direction which is also the close-packing direction.

Perfect lattice

Back at the same atom

With an edge dislocation

Need to go back an atomic spacing to end at the same atom

We can observe dislocations by direct imaging. They can actually improve mechanical properties by a process known as "work hardening", essentially adding a deformation to increase the resistance to future deformations.

10.3 Planar Defects

Any surface of a material is a defect, because surface atoms are in higher energy states than internal atoms. This is because they lack some of the bonds due to nearest neighbours not being present, therefore there is some latent energy on the surface. This surface energy can be tapped so that the materials are used as catalysts. A catalyst increases the rate of a chemical reaction without being consumed. Active sites on catalysts are normally surface defects.

10.3.1 Grain Boundaries

These are 2D defects that separate small grains. In a single crystal, the periodic arrangement of atoms is perfect, but a mismatch in the faces leads to a grain boundary. The higher the angle of the grain boundary, the greater the defect. A small angle grain boundary (e.g. a tilt boundary) can be considered to be an array of edge dislocations. An array of screw dislocations leads to a twist boundary (0 or parallel misalignment).

Small angle grain boundary such as
this tilt boundary can be considered
as an array of edge dislocations

Array of screw
dislocations lead to a
twist boundary → 0°
misalignment or parallel
misalignment
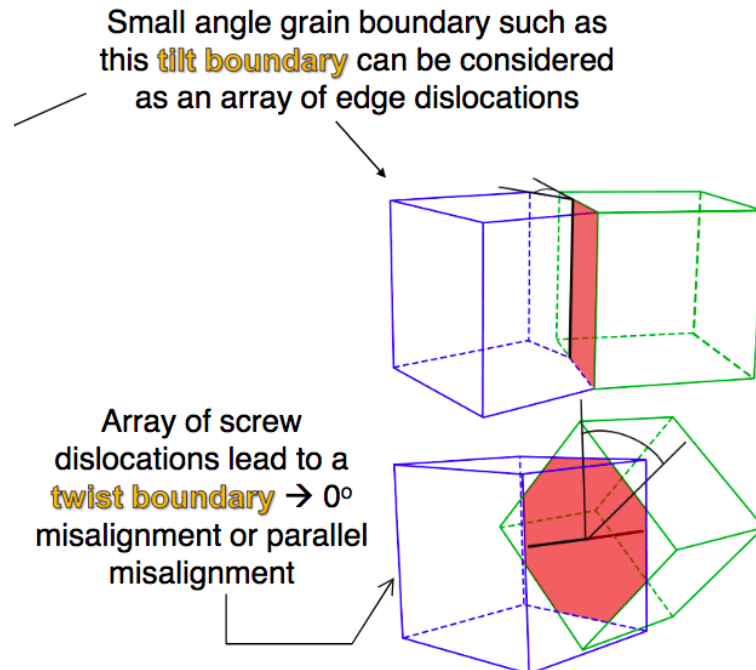
A twin boundary is a special misalignment in which atoms on one side of the boundary mirror those on the other side. Mechanical twins are produced by shear force (in BCC and HCP), and annealing twins are produced by heat treatment (in FCC).

10.3.2   Effects of Grain Boundaries

Grain boundaries change mechanical properties (make fractures likely, interrupt the movement of dislocations), electrical properties (good place to scatter or inhibit the motion of electrons). They are also sites for atom diffusion. Grain boundaries can be directly imaged.

Another fault in materials can be due to a deviation in the stacking sequence of atomic planes. This can convert an FCC to an HCP structure, which may alter the material's properties. Stacking faults look almost exactly like twins under an electron microscope.

Math is coming. (Yay)

Diffusion is the transport of mass or materials by atomic motion. This can occur in gases and liquids via Brownian motion (not being covered), and in solids via vacancy diffusion or interstitial diffusion.

An example of a process using diffusion is case hardening, in which carbon atoms are diffused into iron atoms at the surface. This results in a case that is hard to deform (carbon atoms prevent plane shearing) and hard to crack (the surface is in compression). Another process that uses diffusion is doping, which is used in semiconductors; rich layers of P on the surface of silicon, when heated, causes doped semiconductor regions.

Diffusion is bidirectional; one material diffusing into a second one means the same will happen in reverse. This creates a concentration gradient, in which atoms move from high to low concentration. Self-diffusion, in which atoms within one material exchange positions, is also possible.

How does this motion happen? For diffusion to occur, the adjacent site needs to be empty (a vacancy or interstitial), and there must be sufficient available energy for bonds to be broken and lattice distortion overcome. This leads to two major mechanisms, in which atoms adjacent to a vacancy move into it (vacancy diffusion) or in which small atoms that were interstitial impurities change interstitial sites (interstitial diffusion). This is faster than vacancy diffusion; generally, smaller species can diffuse faster.

11.1 Diffusion Model

We are interested in mathematically modelling diffusion flux. Over an area A, over a time t, if a net M atoms pass through then the flux is $\frac{M}{At}$. In general,

$$J = \frac{1}{A}\frac{dM}{dt} \tag{11.1}$$

Flux can be measured for vacancies, host atoms, and impurity atoms. Diffusion can be modelled in general as bidirectional outward flux, which follows a concentration gradient; atoms flow from higher to lower concentrations. This gives us Fick's first law.

$$J_x = -D\frac{dC}{dx} \tag{11.2}$$

MSE 45: Properties of Materials **Fall 2018**

Lecture 12: Exam Review

Lecturer: Lane Martin *September 21* *Aditya Sengupta*

12.1 Chapter 1

Definitions of materials science, materials engineering. Materials tetrahedron - performance, structure, processing in engineering, structure, properties, processing in science.

Three major classes of materials - metals, ceramics, polymers. Mostly we're discussing metals and ceramics. Should know what it is that defines a material to be a metal vs a ceramic, at an atomic structure level. If we stack things together, why will we get a metal, etc.

There are six important properties of solid materials - mechanical, electrical, magnetic, thermal, optical, and chemical deterioriation.

12.2 Chapter 2

We looked at the strcture of the atom, and the trends in IP, EA, c, etc. We also looked at the types of bonding - ionic, covalent, metallic, secondary. What are the implications for the properties if a certain type of bond is used?

Quick recap of Bohr vs QM model of the atom. What are the differences? Characterizing electrons via quantum numbers - n (orbital), l (angular momentum), m (magnetic), m_s (spin). Pauli exclusion. Can use that to fill the shells of real atoms. Order in which they're added is along diagonals; 3p then 4s, 3d then 4p then 5s, etc. Stable electronic configurations have complete s and p subshells, and are usually inert.

Electronegativity is a measure of how likely an atom is to take up or give up an electron. (IP+EA)/2. Based on that, understand the trends in the periodic table.

Ionic bonding, typically between + and - ions. Electron transfer, large electronegativity difference. Coulombic interaction based. Use that to characterize system energy, get $-A/r + B/r^n$. Gives you a bonding curve, from which lots of information can be extracted.

Covalent bonding - sharing of electrons, incomplete transfer of electrons. Happens when electronegativies are the same or comparable.

Metallic bonding - metal ion cores pair with a sea of valence electrons. Primary bonds for metals and their alloys. Large R and small electronegativity.

Every bond is somewhere between ionic and metallic (covalent in the middle). Percent ionic character = $1 - exp(0.25(\chi_a - \chi_b)^2)$ (χ are electronegativities).

12.3   Chapter 3

Metal and Ceramic Structures. How do macroscopic properties and microscopic properties relate? Lattice, basis, crystal structure, unit cell, coordination number. Describe hard sphere packing, define densities in different dimensions.

The unit cell - smallest component of the crystal that can be stacked together (with only translational motion) to reproduce a whole crystal.

Crystal structure built from an infinite array of mathematical points (a lattice) decorated by a basis/motif. This describes the periodic arrangement of atoms in a crystal. To do this we can define a unit cell geometrically, with parameters $a, b, c, \alpha, \beta, \gamma$. In general there aren't any relationships between these. We can come up with 7 crystal classes based on similarities/differences between these parameters. Know the seven. 14 Bravais lattices based on the types of unit cell each one can have - primitive, body-centered, face-centered, side-centered.

Use these unit cells for analysis - can relate lattice constants to radii. Atoms per unit cell, volume, APF, densities, close-packed directions. We know how to do all of these. It's all geometry. Put down the standard a = kR equations for BCC, FCC, etc.

BCC - a = 4R/sqrt(3). At/u = 2, coord number = 8, APF = 0.68 FCC - a = 2sqrt(2)R. At/u = 4, coord number = 12, APF = 0.74, stacking ABCABC...

Draw out the close-packing layers with top-down view if stuck.

Difference between HCP and FCC. Know that HCP exists and how it relates to FCC, but probably not much about HCP.

How to define point coordinates? How far along each unit vector (vector corresponding to each lattice parameter).

Crystallographic direction - start at origin, determine length of projection in each of 3 axes, reduce to lowest integers, enclose in square brackets. Negative with bar.

Planes - take reciprocal of intersection points, find LCM to convert all to integers. Find out how to draw/understand a plane from Miller indices, how to make a Miller index from a drawing.

Densities - can make them on multiple dimensions.

How do we find out about crystal structure? Diffraction. Bragg's law, diagram. Unless otherwise specified, n = 1. Remember 2 theta.

In the second part of the structure chapter, we started to deal with crystal structures consisting of multiple possible atoms. Should know where tetrahedral and octahedral voids are. Cation/anion radius ratio gives a likely coordination number. Table is given on the exam.

In ionic solids, we can add up all the Coulombic interactions and get a Madelung constant.

12.4   Chapter 4

Defects - can happen in each dimension (0, 3).

Vacancies - missing atoms from lattice sites. There are $N_v = N exp(-Q/kT)$ of them. Alloys are also interstitial defects - either mix Cu substitutionally in Ni, or C in the interstitials of Fe.

H-R Guides for Mixing.

What's a Burgers vector

MSE 45: Properties of Materials	**Fall 2018**
Lecture 13: Diffusion I	
Lecturer: Lane Martin　　　　　*26 September*　　　　　*Aditya Sengupta*	

Diffusion is a process by which atoms of one type are transported through another type of material. This can take the form of interdiffusion, vacancy diffusion, or interstitial diffusion in solids, and Brownian motion in liquids or gases. Diffusion is important for the creation of various kinds of materials, such as steel; iron is hardened by diffusing carbon atoms into it at its surface. This leads to improved mechanical properties. The carbon atoms take up interstitial sites on the surface of iron. This makes the creation of dislocations by applying a shear on the surface-level planes more difficult, as the carbon atoms lock them in place (C interstitials between the layers of Fe make relative motion difficult). The additional carbon interstitials also place the surface in compression, which makes it less brittle. Diffusion is also used in the creation of semiconductors. To create an n-type semiconductor, Si is doped with P (an element with a higher number of valence electrons - specifically, it is *pentavalent* - that can give a free electron to the surface) in order to increase conductivity in specific regions. This is done by placing the phosphorus on the surface of the silicon, and heating it to cause diffusion at a measurable rate.

Consider atoms going through a plane. There is a net number of atoms going through it per unit time, which is a net flux.

Flux can be measured for vacancies, host atoms, and impurity atoms. The net flow of atoms is caused by a system wanting to increase its own entropy. It is governed by Fick's first law. Assume a dilute intersitial solid solution, with parent atoms (A) in a cubic lattice and solute atoms (B) in the interstices without distortion. Assue the solution is sufficiently dilute that every interstitial atom is surrounded by 6 vacant interstitial sites. The concentration of B atoms varies in one dimension (x) and B atoms can diffuse throughout the material to make concentration uniform throughout. Diffusion can then be modelled as a set of random processes.

13.1　Mathematical Model

Consider atoms going through a plane. There is a net number of atoms going through it per unit time, which is a net flux. Specifically, if we have n_R atoms moving from left to right and n_L atoms moving from right to left, each with mass m_a, we can say the flux is the mass flow per unit area and unit time:

$$J = \frac{(n_R - n_L)m_a}{At} \tag{13.1}$$

We can make this into a differential expression in the total net mass flow over a small time period:

$$J = \frac{1}{A}\frac{dM}{dt} \tag{13.2}$$

J has units of kg/m²s.

Net flux is caused by a difference in the concentration profile; specifically, it follows the negative of the concentration gradient, $J_x \propto -\frac{dC}{dx}$. We can put in a proportionality constant to get Fick's first law:

$$J_x = -D\frac{dC}{dx} \tag{13.3}$$

Flux can be measured for vacancies, host atoms, and impurity atoms. The net flow of atoms is caused by a system wanting to increase its own entropy.

Assume a dilute interstitial solid solution, with parent atoms (A) in a cubic lattice and solute atoms (B) in the interstices without distortion. Assue the solution is sufficiently dilute that every interstitial atom is surrounded by 6 vacant interstitial sites. The concentration of B atoms varies in one dimension (x, without loss of generality) and B atoms can diffuse throughout the material to make concentration uniform throughout. Diffusion can then be modelled as a set of random processes.

At plane 1, let there be n_1 B atoms per m^2, and at plane 2, let there be n_2 B atoms per m^2. Flux from 1 to 2 in one second is given by an expression linear in n_i. Since the net flux is from left to right, we can say

$$J_B = \frac{1}{6}\Gamma_B(n_1 - n_2) \tag{13.4}$$

$$\tag{13.5}$$

(rest of the derivation to be added later; it's supposed to be in the lecture notes but $i\ t\ i\ s\ n\ '\ t$)

The diffusion coefficient can be found using the usual Arrhenius equation.

13.2 Types: Interdiffusion and Self-Diffusion
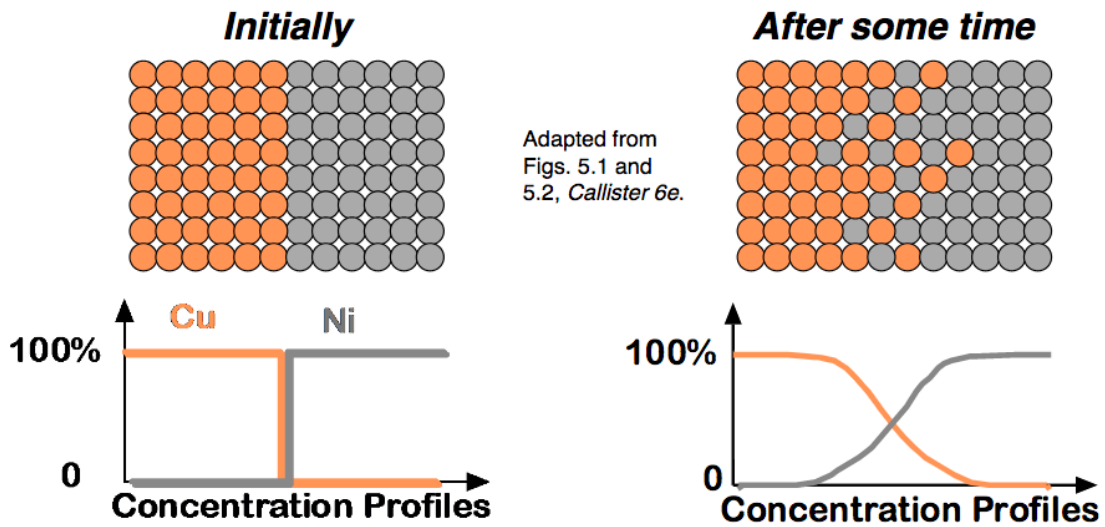
13.2.1 Interdiffusion

In interdiffusion, atoms of one type diffuse into the bulk of the other element present, and the reverse also happens at the same time. Based on this phenomenon, we can say that atoms tend to move from regions of high concentration to those of low concentration.

13.2.2 Self-Diffusion

In self-diffusion, atoms of one type exchange positions within a crystal. If we note the positions of specific atoms at a certain time, and observe those atoms at later times, they may have changed position. For atoms to migrate within an elemental solid, there must be a vacant site available, and there must be sufficient available energy to break the bonds holding the atom in place and to resist lattice distortions. There are two major mechanisms by which this can happen: vacancy diffusion and interstitial diffusion.

13.2.2.1 Vacancy Diffusion

This occurs when an atom is adjacent to a vacant lattice site and moves into it. Vacancy diffusion requires first that the moving atom breaks its bonds with its surrounding atoms. Then, it must overcome the lattice distortions due to the vacancy, "pushing back" the surrounding atoms that have moved towards the vacant space to compensate for the absence of an atom. After this, the atom can move into the vacant site.

Initially

After some time

Adapted from
Figs. 5.1 and
5.2, *Callister 6e.*

Cu   Ni

100%

0

Concentration Profiles

100%

0

Concentration Profiles

13.2.2.2 Interstitial Diffusion

This occurs when an interstitial atom moves from one interstitial site to another. This mostly occurs with smaller atoms that can be impurities in a larger crystal structure, such as carbon, hydrogen, and oxygen. Interstitial diffusion is faster than vacancy diffusion for this reason; having smaller atoms move is faster. Additionally, there are many more interstitial sites available than vacancies in a crystal.

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Lecture 14: Diffusion II

Lecturer: Lane Martin　　　　　　　*28 September*　　　　　　　*Aditya Sengupta*

Smaller things diffuse into larger things even at moderately higher temperatures.

14.1 Example of using Fick's first law

By diffusing H_2 through a palladium sheet, it can be purified. Compute the number of kilograms of hydrogen that pass per hour through a 6mm thick sheet of palladium with an area of $0.25m^2$ at 600°C.

Assume $D = 1.7 \times 10^{-8} m^2/s, C_H = 2.0 kg/m^3, C_L = 0.4 kg/m^3$, and that steady state conditions have been achieved.

$$J = -D\frac{\partial C}{\partial x} = -d\frac{\Delta C}{\Delta x} \tag{14.1}$$

$$M - -DAt\frac{\Delta C}{\Delta x} \tag{14.2}$$

Numbers tell us that M $= 4.1 \times 10^{-3}\frac{kg}{h}$.

14.2 Steady-State Diffusion

Fick's first law holds in the case of steady-state diffusion, where the concentration profile is time-invariant (more specifically, where $\frac{dC}{dt} = 0$). At steady-state, we can therefore say that the rate of diffusion in one direction is exactly equal and opposite that in the other direction. If there is a net flux in one direction (e.g. atoms entering the region in the +x direction), there must be an equal and opposite flux as well (e.g. atoms exiting the region in the +x direction). We can therefore apply Fick's first law to this situation:

$$J_x = -D\left(\frac{dC}{dx}\right) \tag{14.3}$$

$$J_{x,left} = J_{x,right} \tag{14.4}$$

$$\therefore \left(\frac{dC}{dx}\right)_{left} = \left(\frac{dC}{dx}\right)_{right} \tag{14.5}$$

In the limit where the size of the region in the x direction goes to 0, we know that the concentration gradient to its left and right must be equal. Therefore, the concentration gradient does not vary with position: $\frac{d}{dx}\frac{dC}{dx} = 0$.

This linearity in the steady-state case allows us to simplify problems involving diffusion. Let there be two elements at concentrations C_1 and C_2, at positions x_1 and x_2. Because of the constant slope, we can easily find $\frac{dC}{dx}$:

$$\frac{dC}{dx} \approx \frac{\Delta C}{\Delta x} = \frac{C_2 - C_1}{x_2 - x_1} \tag{14.6}$$

from which we can find the rate of diffusion based on the diffusion constant, which comes out of the Arrhenius equation $D = D_0 e^{-\frac{Q_d}{k_B T}}$. This tells us the rate of diffusion is dependent on temperature exponentially.

The rate of diffusion is also dependent on crystal structures; atoms can more easily diffuse through more open structures, even if the more closed structures are at higher temperatures.

14.3   Example Problems: Steady-State Diffusion

14.3.1   Example 1

If butyl rubber gloves, 0.04cm thick, are used to handle methylene chloride (diffusion coefficient of these two is $110 \times 10^{-8} cm^2/s$) with surface concentrations $C_1 = 0.44g/cm^3$ and $C_2 = 0.02g/cm^3$, find the steady-state rate of diffusion of methylene chloride into butyl rubber.

$$J = -D\frac{dC}{dx} = -110 \times 10^{-8} cm^2/s \times \frac{0.02g/cm^3 - 0.44g/cm^3}{0.04cm} = 1.16 \times 10^{-5}\frac{g}{cm^2 s} \tag{14.7}$$

14.3.2   Example 2

At 300° C, the diffusion coefficient and activation energy for Cu in Si are $7.8 \times 10^{-11} m^2/s$, and $41.5kJ/mol$ respectively. What is the diffusion coefficient at 350° C?

$$D(T) = D_0 e^{-\frac{Q_d}{k_B T}} \tag{14.8}$$

$$\ln D(T) = \ln D_0 - \frac{Q_d}{R}\frac{1}{T} \tag{14.9}$$

$$\tag{14.10}$$

We can substitute in two different temperatures T_1 and T_2 to this relation,

$$\ln D_2 = \ln D_0 - \frac{Q_d}{R}\frac{1}{T_2} \tag{14.11}$$

$$\ln D_1 = \ln D_0 - \frac{Q_d}{R}\frac{1}{T_1} \tag{14.12}$$

$$\therefore \ln \frac{D_2}{D_1} = \frac{Q_d}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{14.13}$$

We can exponentiate both sides and therefore find D_2 in terms of D_1,

$$D_2 = D_1 e^{\frac{Q_d}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \tag{14.14}$$

Substitute in the known values of D_1, Q_d, R, T_1, T_2 (while changing the temperatures to Kelvin) to get

$$D_2 = 15.7 \times 10^{-11} m^2/s \tag{14.15}$$

14.4 Life is Complicated

Fick's first law is a linear approximation that does not necessarily hold. It works in the case of steady-state diffusion, where the relative concentrations of the elements stay the same even after diffusion. This does not really work, since we don't have infinite quantities of everything with which to maintain a steady state. We can look at transient diffusion by considering concentration as a function of x and t, which gives us Fick's second law:

$$\frac{dC}{dt} = D\frac{\partial^2 C}{\partial x^2} \tag{14.16}$$

We can get this by taking the first derivative of Fick's first law with respect to x:

$$\frac{dJ}{dx} = -\frac{d}{dx}\left(D\frac{dc}{dx}\right) \tag{14.17}$$

Also, applying conservation of mass:

$$-\frac{dC}{dt} = -\frac{J_r - J_i}{dx} = \frac{dJ}{dx} \tag{14.18}$$

This tells us that the fluxes to the left and right are directly related to the change in concentration over time. Substituting this into the x derivative of Fick's law from above, we get

$$\frac{dC}{dt} = D\frac{d^2 C}{dx^2} \tag{14.19}$$

This is a partial differential equation, which means boundary conditions are required to solve it. (Fun fact: this is exactly the same setup as the heat equation, where the first derivative of a quantity in time is directly proportional to its second derivative in space.) For example, consider the case of copper diffusing into a bar of aluminium (assumed to be a semi-infinite solid). We know that at $t_0, C = C_0$ inside the bar of aluminium. At $t > t_0, C(x = 0) = C_s$ (some known concentration of copper), and $C(x = \infty) = C_0$ (an infinite-length bar will have no copper diffusion at an infinite distance away from the copper source).

Solutions exist only when the boundary conditions are physically meaningful. Generally, if we assume these boundary conditions are that a solid is semi-infinite has its surface concentration held constant at C_0 and has some other species diffuse into it at concentration C_s, we can make a generalized solution to the partial differential equation defined by Fick's second law:

$$\frac{C(x,t) - C_0}{C_s - C_0} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right) \tag{14.20}$$

Solutions to the transient equation are usually of the form of error functions $erf(z) = \frac{2}{\sqrt{\pi}}\int_0^z e^{-y^2}dy$. In general, this function is not integrable, but using numerical approximation methods we know standard values of this integral, which can be looked up in a table.

Suppose it is desired that a specific concentration C_1 is achieved in an alloy at a specific x; then, we can apply the solution derived above:

$$-\frac{C_1 - C_0}{C_s - C_0} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right) = const \tag{14.21}$$

$$\frac{x}{2\sqrt{Dt}} = const \tag{14.22}$$

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Lecture 15: Diffusion III

Lecturer: Lane Martin *1 October* *Aditya Sengupta*

$$\frac{C_x - C_0}{C_s - C_0} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right) \tag{15.1}$$

For a concentration drop of $\frac{0.3-0.1}{0.9-0.1} = 0.25$, we can look up the value in the erf table for 0.75, and get

$$\frac{x}{2\sqrt{Dt}} = 0.814 \implies t = 1.13 \times 10^5 s \tag{15.2}$$

for a given D that characterizes the system (and was likely given in the problem).

15.1 Example Problems: Transient Diffusion

15.1.1 Example 1

Copper diffuses into a bar of aluminium. 10 hours at 600º C gives a certain desired $C(x)$. How many hours would it take to get the same $C(x)$ if the process were carried out at 500º C? $D_{500} = 4.8 \times 10^{-14} m^2/s$, $D_{600} = 5.3 \times 10^{-13} m^2/$.

We know that

$$\frac{C(x,t) - C_0}{C_s - C_0} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right) \tag{15.3}$$

Since the left hand side remains the same, because the only starting condition that changes is the temperature, we can set the right hand sides equal for the two cases:

$$1 - erf\left(\frac{x}{2\sqrt{D_{500}t_{500}}}\right) = 1 - erf\left(\frac{x}{2\sqrt{D_{600}t_{600}}}\right) \therefore D_{500}t_{500} = D_{600}t_{600} \tag{15.4}$$

$$t_{500} = \frac{5.3 \times 10^{-13}}{4.8 \times 10^{-14}} \times 10h = 110.4h \tag{15.5}$$

15.1.2 Example 2

During a steel carburization process at 1000º C, there is a drop in carbon concentration from 0.5 at% to 0.4 at% between 1 mm and 2 mm from the surface (γ-Fe at 1000º C).

Estimate the flux of carbon atoms at the surface given: $D_o = 2.3 \times 10 - 5m^2/s$ for C diffusion in γ-Fe, $Q_d = 148kJ/mol$, $\rho_{\gamma-Fe} = 7.63g/cm^3$, and $A_{Fe} = 55.85g/mol$. If we start with $C_o = 0.2$ wt% and $C_s = 1.0$ wt%, how long does it take to reach 0.6 wt% at 0.75 mm from the surface for different processing temperatures?

15.2 Coulombic Interactions

Inter-ionic attractions and repulsions affect diffusion. Smaller cations will usually diffuse faster, but analogous to charge neutrality required for defect formation, each ion will need a counter charge to move with it. This can take the form of a vacancy, impurity, a free electron or a hole. Weaker bonds are better for faster diffusion.

15.3 Phase Diagrams

A phase is a homogeneous portion of a system that has uniform physical and chemical characteristics. Phase diagrams are plots of various quantities (pressure/temperature, temperature/concentration, etc) over which areas on the graph represent various phases. Most phase diagrams in this class will stay at constant pressure.

We can determine phase composition in a 2-phase region by noting where the tie line (hold temperature constant, vary composition) intersects the liquidus and solidus lines, i.e. where the line crosses the phase boundaries. We can then read off the compositions at the boundaries. The tie line, in general, connects the phases that are in equilibrium with each other. It can also be called an isotherm.

To determine the phase amount in the 2-phase regions, we can find a mass percentage from an atomic percentage as we've been doing before. Let the starting concentrations in the liquid phase be C_o, let the liquidus line/tie line concentration be C_l, and let the same quantity at the solidus line be C_s. Then the mass fraction of the liquid phase is

$$W_l = \frac{C_s - C_o}{C_o - C_l} \tag{16.1}$$

and for the solid phase

$$W_s = \frac{C_o - C_l}{C_s - C_o} \tag{16.2}$$

This tells us that W_l (ratio) of the mass at this intermediate composition is liquid, and W_s is solid.

We can analyze the impact of these partial phases on the microstructures. In equilibrium cooling, the material is cooled very slowly so that phase equilibrium can be maintained during the cooling process. At high temperatures, the material starts as a homogeneous liquid, then the liquidus line is reached. The α phase begins to nucleate, and we have a partial phase as determined by the composition and mass fraction. The cooling curve here follows the tie line, being briefly almost completely flat. After a certain point, the solidus line is reached and the cooling curve returns to the usual expected value.

However, in real life, we don't cool at equilibrium because that is painfully slow. We want to cool a sample at a high rate relative to the rate of diffusion. When we do this, we get a cored structure, where the C_s changes as we solidify; initially, there is a high concentration at the center, and as the radius around which solidification is occurring increases, the concentration reduces. Although on average (by conservation of mass) the composition is the same either way, the distribution of the smaller element (say Ni) will change, with the first α to solidify having a greater concentration than the average, and the last α to solidify having a lower concentration than the average.

The eutectic point is where the two liquidus lines corresponding to the α and β phases meet. The eutectic is an invariant point. The eutectic reaction goes from a liquid at high temperatures to the two solids α and β, or vice versa.

MSE 45: Properties of Materials	**Fall 2018**

Lecture 17: Phase Diagrams II

|		
Lecturer: Lane Martin	*5 October*	*Aditya Sengupta*

On the eutectic phase diagram, suppose we go through a temperature transition (cooling). We go from a liquid to a homogeneous mixture of α and β, which has a lamellar or layered structure.

17.1 Real Life Is Sad

There are two types of phase transformations: congruent ones, in which there is no change in composition upon transformation, and incongruent ones, in which at least one of the phases goes through a composition change. Intermediate or intermetallic compounds are an example of an incongruent phase transformation, consisting of discrete metal compounds rather than solutions; they have a distinct chemical formula. Their phase diagram can be considered to be two simpler phase diagrams put together.
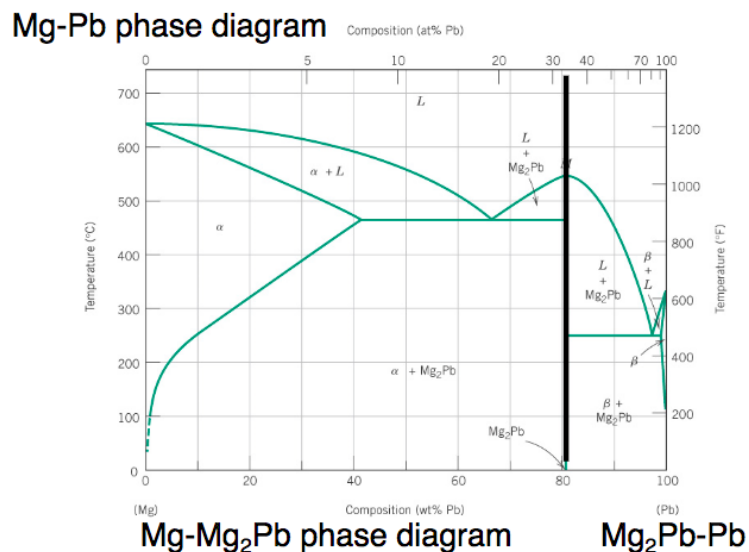
Sometimes, intermediate solid solutions have phase diagrams that don't mix as well, making intermediate phases. These translate to intermediate regions on a phase diagram.
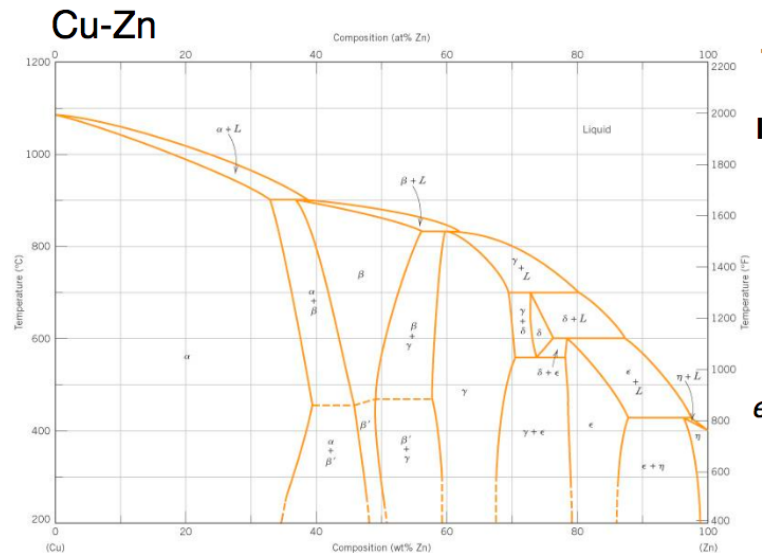
These intermediate phases can be classified into two major types of reactions; eutectoid and peritectic. Eutectoid reactions are characterized by one solid phase turning into two other solid phases upon cooling (this is reversible), and peritectic reactions have one solid phase transforming into a liquid and different solid phases upon heating (this is reversible too).

Ceramics can also have phase diagrams, which can be simple, or *incredibly complicated*. In general, they have three axes, represented as a sort of vector field or a colour map along the three sides of an equilateral triangle.

17.2 Gibbs phase rule

$$P + F = C + N \tag{17.1}$$

The number of phases present plus the degree of freedom (number of externally controllable parameters: T, P, C) is equal to the number of components plus the number of non-compositional variables (temperature and pressure).

Consider a Cu-Ag phase diagram. This gives us $C = 2$, $N = 1$ as temperature is the only external variable, $P = 2$ as there are two phases present. Therefore the degree of freedom is 1. When only one phase is present, the degree of freedom is 2. The degree of freedom is the number of variables required to fully define a system. At the maximum degrees of freedom, such as at a eutectic point, everything about the system needs to be defined.

This is a good point to point out the difference between a eutectoid point and a eutectic point. A eutectic point is a minima, in terms of concentration, of the temperature of the liquid phase; moving to the left or to the right at this point would move the material into either of two solid phases. A eutectoid point is ne at which the material undergoes a eutectoid transition, that is, one in which one solid phase transitions into two or more solid phases.

The Gibbs phase rule can be very simply applied. Consider this example (from homework):

7. (9 pts.) In the figure below is the pressure–temperature phase diagram for H_2O. Apply the Gibbs phase rule at points A, B, and C; that is, specify the number of degrees of freedom (or the number of externally controllable variables that need be specified to completely define the system) at each point. Clearly define all variable and the values for each variable.
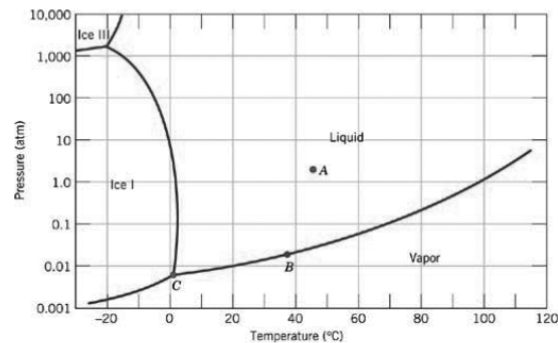

C is the number of components; in this case, only $H_2 O$ is present, so C = 1. There are two non-compositional variables (pressure and temperature), so N = 2. Therefore P + F = 3.

At point A, P = 1 due to one phase being present, so F = 2. At point B, P = 2 due to two phases being present, so F = 1. At point C, P = 3 due to three phases being present, so F = 0.
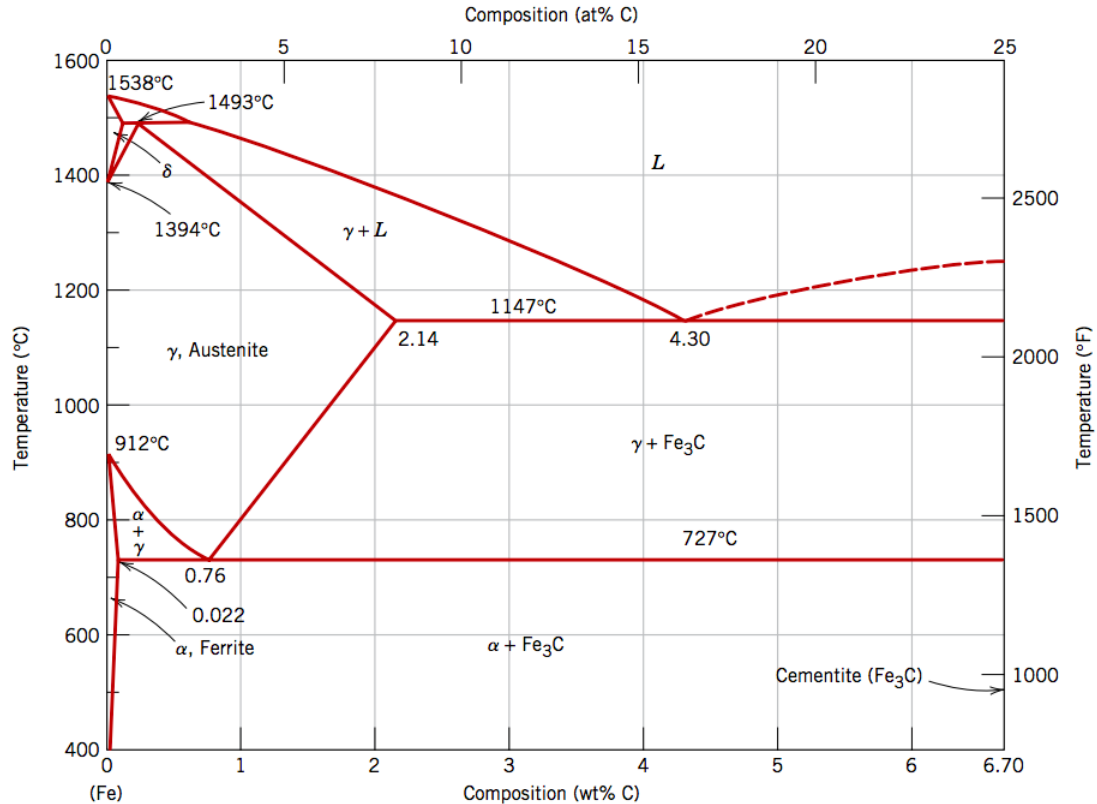
(To do: add something motivating the Gibbs phase rule. Why is it important that there is a degree of freedom at a point)

17.3 The Iron-Carbon System

Iron has three distinct solid phases based on its temperature:
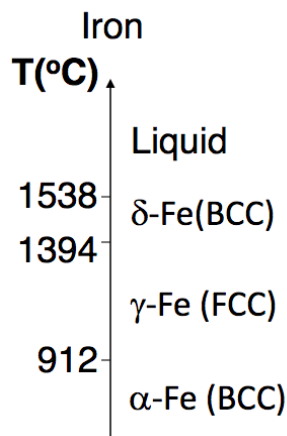
The α phase of iron or of an iron-carbon mixture with concentration less than that of Fe_3C is referred to as *ferrite*, and the γ phase is called *austenite*.

The FCC γ phase has the highest carbon concentration without having an Fe$_3$C component, at 2.14% as can be read off the graph (at that concentration and around 1100°C). This is a higher concentration than the BCC α phase, at only 0.022% wt C. This makes sense because of FCC's closer packing, meaning more interstitial sites for carbon atoms. (citation needed).

At the eutectoid point, the following reaction takes place:

$$\gamma(0.76wt\%C) \rightleftharpoons \alpha(0.022wt\%C) + Fe_3C(6.7wt\%C) \tag{17.2}$$

This changes the γ phase to a lamellar structure, consisting of austenite surrounding α phase ferrite strands; this is the characteristic structure of pearlite. The layered structure forms for the same reason as the eutectic structure (which may be why they're named similarly).

17.3.1   Hypoeutectoid Alloys

Below the eutectoid composition, proeutectoid ferrite is eventually formed along with the eutectoid structure. At the start, γ Fe is present at high temperature; as this is cooled at a composition less than the eutectic point, the iron passes through the left side of the point, with a phase composition of $\alpha + \gamma$. Here, the α phase nucleates at the boundaries of the γ phase. As the temperature is reduced, the eutectoid isotherm is crossed, forcing the rest of the γ phase into the eutectoid structure. Therefore the final result is some fraction pearlite and some fraction proeutectoid ferrite (the nucleated α phase at the boundaries).

17.3.2 Hypereutectoid Alloys

Above the eutectoid composition, proeutectoid cementite is eventually formed along with the eutectoid structure. This comes from the same logic as the hypoeutectoid case, with cementite (Fe_3C) forming at the boundaries of the γ phase.

In both cases, the ratio of the proeutectoid component to the eutectoid can be found using the tie line.

> **MSE 45: Properties of Materials** **Fall 2018**
>
> ## Lecture 18: Phase Diagram Wrap-Up, Phase Transformations
>
> *Lecturer: Lane Martin* *October 8* *Aditya Sengupta*

By adding different alloying elements, the eutectoid temperature can be dramatically increased or decreased. The composition at which the eutectoid is can also change based on the concentration of alloying elements. This is useful processing information that can be used to control the microstructure.

18.1 Phase Transformations

Transformations on a phase diagram are not instantaneous.

Phase transformations have two steps: nucleation, in which nuclei or seeds act on templates on which crystals grow, and growth, in which the nucleated species grow until a new equilibrium is attained in the system. For the nucleus to form, the rate of addition of atoms to the nucleus must be faster than the rate of loss. The driving force to nucleate increases as we increase ΔT, so there are two major paradigms for nucleation: supercooling at eutectoid/eutectic transformations, and superheating at peritectic transformations. Small supercooling corresponds to a slow nucleation rate, few nuclei, and large crystals; large supercooling corresponds to a rapid nucleation rate, many nuclei, and small crystals.

Kinetics is the study of reaction rates of free transformations. To determine this, we measure the degree of transformation as a function of time. That'd be nice, if we knew what the degree of transformation was. There are many ways to find this, such as via X-ray diffraction, measurements of electrical conductivity, or measurements of the propagation of sound waves.

Nucleation comes in two types: homogeneous, in which nuclei form in the bulk of liquid metal (although this requires considerable supercooling between 80 and 300 degrees C), and heterogeneous, which is much easier, in which nuclei form on the mold wall or impurities in the liquid phase. This only requires slight supercooling, between 0.1 and 10 degrees C.

In solid state reactions, the factor hindering nucleation is the surface energy, which grows proportional to r^2. Once the new surface has been grown, nucleation is energetically favourable because bulk energy takes over.

Net energy ΔG is

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma \tag{18.1}$$

$$\tag{18.2}$$

Take an r derivative to find a critical radius,

$$\frac{4}{3}\pi(\Delta G_v)3r^2 + 4\pi\gamma(2r) = 0 \tag{18.3}$$

$$r_c = -\frac{2\gamma}{\Delta G_v} \tag{18.4}$$

$$\Delta G(r_c) = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} \tag{18.5}$$

This tells us how the nuclei will change size. Define $\Delta G_T = \Delta G_S + \Delta G_V$, (surface and volume free energy changes). Graphing the surface and volume energy changes, as well as the total energy changes, demonstrates that a phase transformation is energetically favourable after this critical radius, that is, after the energy barrier of the material has been overcome:
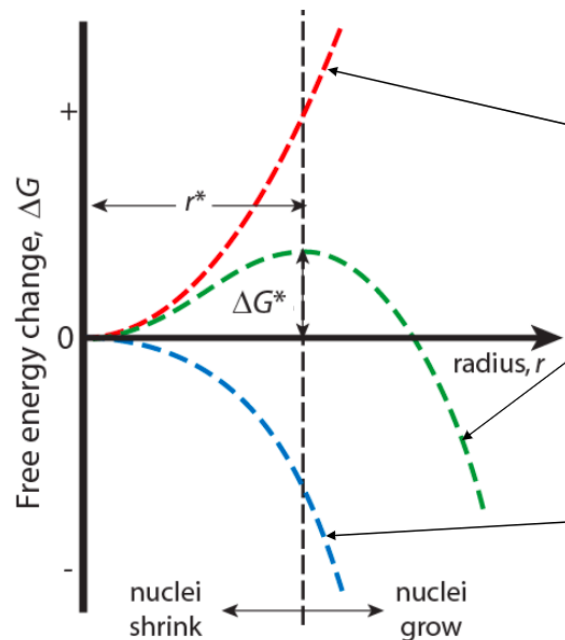
We can rewrite the total energy in terms of the heat of fusion (energy released upon solidification),

$$\Delta G_v = \frac{\Delta H_f(T_m - T)}{T_m} \tag{18.6}$$

With this definition, we can find the critical radius,

$$r_c = -\frac{2\gamma}{\Delta H_f}\left(\frac{T_m}{T_m - T}\right) \tag{18.7}$$

and therefore the energy barrier in terms of heat of fusion,

$$\Delta G^* = \frac{16\pi\gamma^3}{3\Delta H_f^2} \left(\frac{T_m}{T_m - T}\right)^2 \tag{18.8}$$

As temperature decreases, both r_c and ΔG^* become smaller, which makes a phase transformation more energetically favourable. Liquid instability is present at lower temperatures for this reason.

Diffusion is also a significant effect; faster diffusion between phases leads to more collisions between atoms. The frequency of atoms sticking together is directly related to diffusion. This manifests itself in that its frequency is proportional to the Arrhenius expression, as usual. Combining the liquid instability and the effects of diffusion,

$$\frac{dN}{dt} = Kn * v_d = K \left(exp\left(\frac{-\Delta G^*}{kT}\right) exp\left(\frac{-Q_d}{kT}\right) \right) \tag{18.9}$$

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Lecture 19: Phase Transformations II

Lecturer: Lane Martin   *10 October*   *Aditya Sengupta*

Tip from the iClicker questions: If a pearlite structure were slowly heated to just below the eutectoid temperature for 100 hours, the microconstituents would coarsen.

19.1 Phase Transformation Rates

$$n* \propto exp\left(-\frac{\Delta G^*}{kT}\right) \tag{19.1}$$

$$v_d \propto exp\left(-\frac{Q_d}{kT}\right) \tag{19.2}$$

These are the separate expressions for liquid instability and diffusion rate that we combined last time into a rate of nucleation. Now we can look at the growth phase.

In growth, nuclei increase in size. Halfway through growth, a maximum rate is reached, after which the amount unconverted is less so the rate slows down. This is described by the Avrami equation,
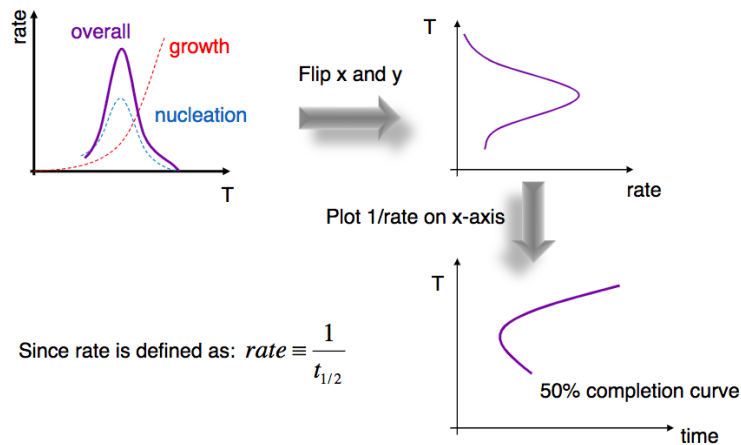
$$y = 1 - exp(-kt^n) \tag{19.3}$$

Typically, we characterize this by the maximum rate, which is achieved this average point.

The rate of growth has temperature dependence, which follows (you guessed it) the Arrhenius equation. We can use this curve, combined with the nucleation curve, to characterize the overall rate of a transformation.

An initial rapid temperature change (quick cooling) followed by an isothermal process can be characterized by an isothermal transformation diagram, which is a concentration/time graph. These allow us to make TTT (Time-Temperature-Transformation) plots; these are graphs of temperature over time, on which the different curves characterize transformations from 0% to 100% completion. We get these by flipping the isothermal transformation diagram (swapping the axes, then vertically flipping it).

Recall rates as function of T...

Flip x and y

Plot 1/rate on x-axis

Since rate is defined as: $rate \equiv \dfrac{1}{t_{1/2}}$

50% completion curve

For example, consider pearlite formation. For this to happen, α and cementite have to both be nucleated. To do this, an Fe- and C-rich region must be created. (something more here? I had a point but it's only in what he said, not the slides.) If the initial quenching goes to a higher temperature, the microstructure is coarser, and if it goes to a lower temperature, the microstructure is finer. The lower the temperature we go to, the faster nucleation happens.

Other steel microstructures - we can get microstructures that don't exist in equilibrium. Bainite is needles or plates consisting of cementite and ferrite that are much finer than the already-fine pearlite. Martensite is formed when steel is quenched rapidly enough to prevent carbon diffusion, and makes a body-centered tetragonal structure. To make martensite, quenching has to be so fast that carbon diffusion is not appreciable. This transformation happens roughly at the speed of sound. Spheroidite is formed when pearlite or bainite structures are heated below the eutectoid temperature for an extended period of time.

19.2   Examples

Consider an iron-carbon alloy of eutectoid composition that starts at 760° C. Specify the nature of the final microstructure (micro-constituents and approximate percentages) given the following heat treatments:

(add in the slide)

1. Rapidly cool to 350° C, hold for $10^4 s$, quench to room temperature. In this case, we get pure bainite.

2. Rapidly cool to 250° C, hold for $10^2 s$, quench to room temperature. In this case, we get pure martensite.

3. Rapidly cool to 650° C, hold for 20s, cool to 400° C, hold for $10^3 s$ quench to room temperature. In this case, we get 50% bainite and 50% pearlite, because the pearlite transformed in the first step is not changed by the A-B transformation.

TTT diagrams at different compositions are a thing. We can move to a hypereutectoid composition, which provides new curves on our temperature/time plot.

We also have to keep in mind that cooling from one temperature to another that is not room temperature (i.e. cooling that is not quenching) is rarely discrete. We need to describe a continuous cooling transformation. A whole bunch of curves are shifting and changing in space.

Lecture 19-2

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### Lecture 20: Phase Transformations, Mechanical Properties

| *Lecturer: Lane Martin* | *15 October* | *Aditya Sengupta* |

20.1 Continuous Cooling

We can draw transformation curves for systems, which are straightforward at constant temperatures. At nonconstant temperatures, the slope is a bit sharper. We can draw different TTT curves for this nonconstant temperature, the curves are shifted down and to the right. This is now a continuous cooling transformation (CCT) diagram. We can read microstructures off the CCT diagram in the same way as the TTT one. Usually, no bainite is formed in continuous cooling.
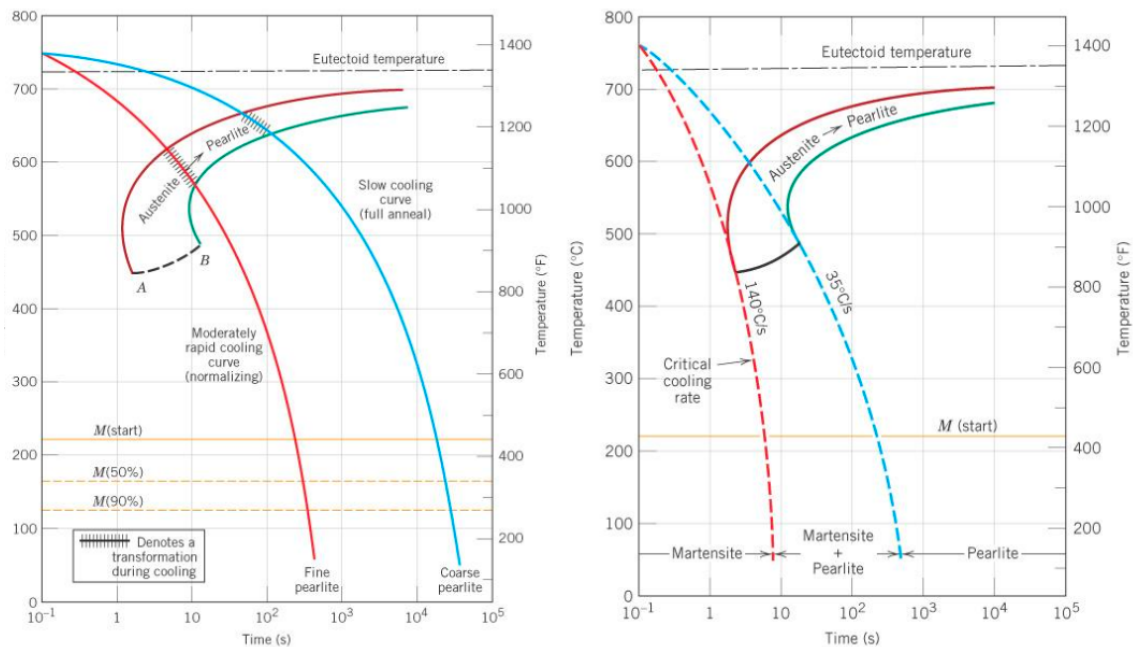

Martensite is the most resistant to deformation by surface indentation among martensite, spheroidite, coarse and fine pearlite. This is because martensite has a finer cementite microstructure, which makes it more difficult to move defects around.

20.2 Mechanical Behaviour Under Phase Transitions

In a regime with pearlite and ferrite (more carbon content on the x-axis), there is an increase in the tensile strength, yield strength, and Brinell hardness, due to an increased amount of cementite. The ductility decreases with this increase in strength. The processing also affects properties; a fast quench leads to high strength but low ductility, and a slow quench has the reverse. With increased percent Fe_3C, the Rockwell hardness goes up and levels off, but the tensile and yield strengths can drop fast.

There are general trends in steels, that are much better described in the slides than I can do:
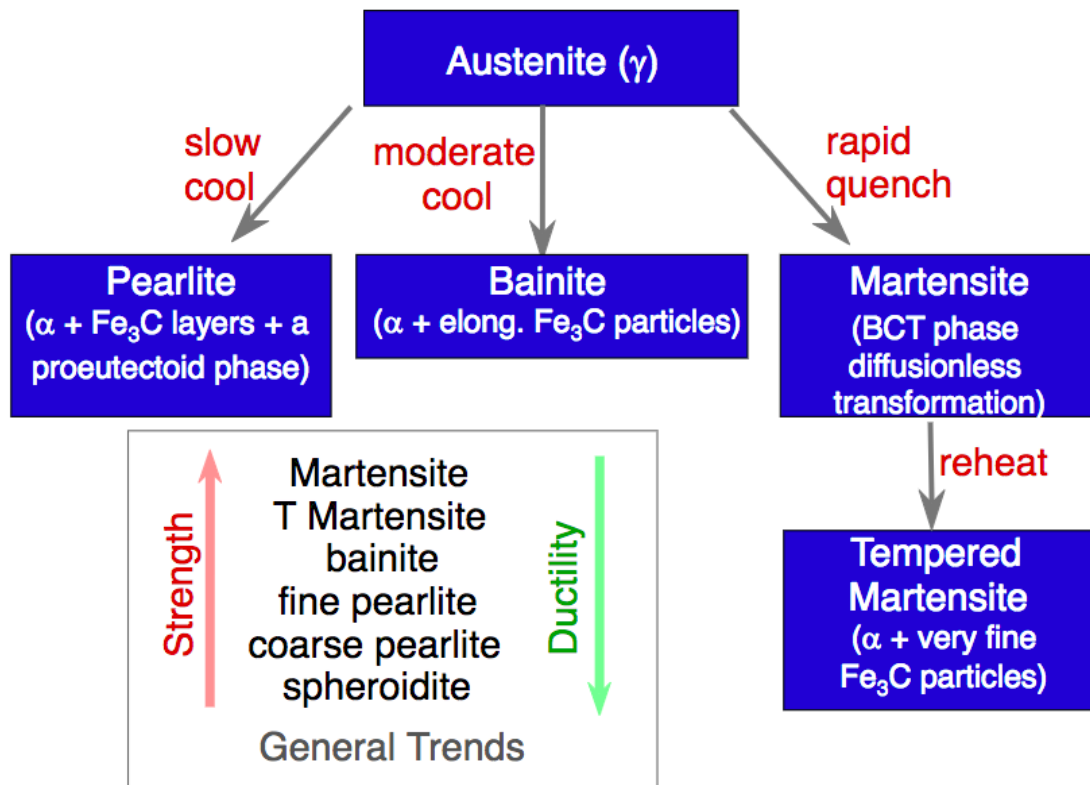
Shape-memory alloys are an example of a phase transformation in action. Following deformation, these materials have the ability to return to their pre-deformed size and shape upon application of heat. They can recover significant deformations in this way, just by heating it up and having it undergo a phase transformation. An application of these is for stents, devices to open up arteries. These cannot be inserted directly into the artery easily, so they are compressed and inserted, whereupon body heat drives it through a phase transformation which lets it pop open.

20.3   Phase Transformations, Summary

Know:

- Kinetics of solid-state reactions (what is the Avrami equation, what are nucleation and growth, how do surface and volume energies affect nucleation, how do we characterize reaction rates)

- Isothermal transformations

- TTT plots and relations to reaction rates (what is the composition of a sample that undergoes a specific set of temperature transitions over specific times)

- Microstructures of Fe-C systems under different cooling conditions (all the different constituents - fine and coarse pearlite, bainite, spheroidite, martensite)

- CCT plots (see TTT)

- Effects of processing on mechanical properties (e.g. fine pearlite has the best strength and worst ductility)

- Phase transformations in polymers - how are they different from metals

20.4   Mechanical Properties of Materials

These are important because if you neglect them people die, or worse, get sued.

Stress σ is pressure due to an applied load. The application of stress causes strain ε, the response of a material due to stress such as physical deformation.

$$\sigma = \frac{F}{A} \tag{20.1}$$

$$\varepsilon = \frac{l_i - l_o}{l_0} = \frac{\Delta l}{l_o} \tag{20.2}$$

A material can be in four different types of stress: tension, when it undergoes outward axial forces (is pulled); compression, when it undergoes inward axial forces (is pushed); shear, when it undergoes transverse linear forces; and torsion, when it is twisted. Materials do not have the same response to both tension and compression in general, even though it may seem from the bonding curve that its response would be symmetric in the direction of axial force. This is due to extrinsic defects; if a crack is present in the material, applying tension makes the crack grow, and applying compression does not act on the crack. Cables are placed under simple tension, drive shafts are placed under simple torsion, and bridges undergo simple compression. More complicated states of stress include biaxial tension, such as a pressurized tank, or hydrostatic compression, such as an object underwater.

We can define engineering stress and engineering strain, which are the idealized stress and strain using the above formulas. These are different from true stress and true strain, which take into account the time-varying physical shape and size of a material sample. In compression, everything works the same, except with opposite signs; by convention, stress and strain are negative in compression. In shear, the pure shear stress is $\tau = \frac{F}{A_o}$ and the pure shear strain is $\gamma = \tan\theta$ where θ is an angular deformation.

Stress-strain curves for a system can be derived using tensile test machines, which use load cells to apply specific values of stress and measure the corresponding strain. Typical tensile specimens are structured like dog bones, in which the middle section has a smaller diameter. This creates a greater value of stress over the region of interest.

When stress is first applied, the material first responds elastically, like stretching a spring (which is an intermolecular bond). This could be linear or nonlinear, but it is necessarily reversible.

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Lecture 21: Mechanical Properties, II

Lecturer: Lane Martin   *17 October*   *Aditya Sengupta*

Linear elastic deformation obeys Hooke's law,

$$\sigma = E\varepsilon \tag{21.1}$$

which indicates direct proportionality between stress and strain, with proportionality constant E, the elastic modulus. The slope of the stress-strain plot, which is determined by the elastic modulus, depends on the bond strength of the material; weaker bonds correspond to smaller elastic moduli.

Ceramics have more elastic than plastic behaviour. Neither glass nor alumina undergo plastic deformation. (Elastic porosity?) In general, the Young's modulus (elastic modulus) for ceramics is higher than that for metals, which in turn is higher than for polymers. Other than the elastic moduli, materials have an elastic shear modulus G with the direct proportionality stress-strain relationship $\tau = G\gamma$, which comes from putting the material in torsion, and an elastic bulk modulus K which comes from placing the material under pressure. There is direct proportionality between pressure and the change in volume, $P = -K\frac{\Delta V}{V_0}$. For isotropic materials, relationships can be drawn between these and the elastic modulus:

$$G = \frac{E}{2(1+\nu)} \tag{21.2}$$

$$K = \frac{E}{3(1-2\nu)} \tag{21.3}$$

where ν is the Poisson ratio, describing the relationship between width and axial strain:

$$\nu = -\frac{\Delta w/w}{\Delta l/l} = -\frac{\varepsilon_L}{\varepsilon} \tag{21.4}$$

This has a negative sign because a positive axial strain corresponds with a negative width strain to roughly conserve volume, and vice versa. Metals have $\nu \approx 0.33$, ceramics have $\nu \approx 0.25$, and polymers have $\nu \approx 0.4$. The Poisson ratio as a whole has a range $-1 \leq \nu \leq \frac{1}{2}$.

In three dimensions, stress has three components, which can be decomposed into one component σ_1 along the loading and two components σ_2, σ_3 perpendicular to it. Therefore the total linear strain in the x direction due to an applied stress with those three components is

$$\varepsilon_1 = \frac{1}{E}\left(\sigma_1 - \nu(\sigma_2 + \sigma_3)\right) \tag{21.5}$$

In a uniaxial tensile test, $\sigma_1 = \sigma_2 = 0$, therefore we get the simple relationships $\varepsilon_3 = \frac{\sigma_3}{E}$ and $\varepsilon_1 = \varepsilon_2 = -\nu\varepsilon_3$.

For a material under hydrostatic pressure, the stress from all directions is equal, so

$$P = \frac{\sigma_1 + \sigma_2 + \sigma_3}{3} = \frac{\sigma_{tr}}{3} \tag{21.6}$$

$$\varepsilon_1 = \frac{1}{E}\left((1+\nu)\sigma_1 + 3\nu P\right) \tag{21.7}$$

For volumetric strain,

$$\frac{\Delta V}{V} = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 = (1 - 2\nu)\frac{\sigma_3}{E} = 3(1 - 2\nu)\frac{P}{E} \tag{21.8}$$

which can be used to calculate the bulk modulus:

$$K = \frac{E}{3(2\nu - 1)} \tag{21.9}$$

(I think lecture notes are off by a minus sign)

21.1 Plastic Deformation

Plastic deformation occurs after the elastic region of deformation, when a force large enough to cause planes of atoms to shear is applied. This ensures that even after unloading, the material will not revert to its earlier state. This is a permanent deformation, with atoms breaking bonds to form new ones. In metals, this typically happens at around 0.5% strain.
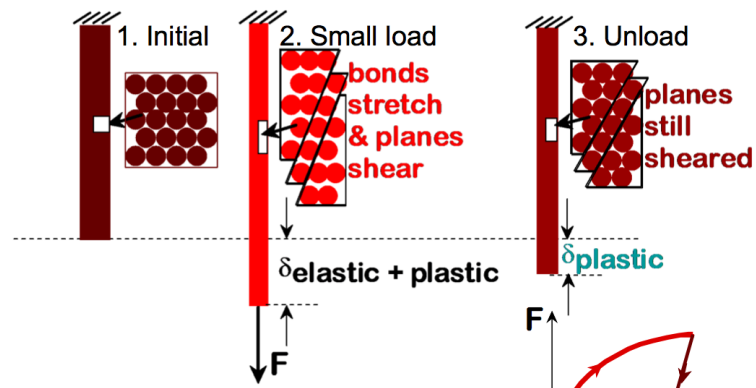
Plastic behaviour can be modelled as linear elastic with some specific offset for the plastic deformation:

(left out the bit about tensile testing machines, not important I think)

The yield strength of the material is the strength required to produce a very slight yet specified amount of plastic deformation. To find it, we use the *strain offset* method; starting from a strain of 0.002, draw a line parallel to the elastic region. The point at which the line and the stress-strain curve intersect is the yield strength σ_y

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MSE 45: Properties of Materials **Fall 2018**

Lecture 22: Mechanical Properties, III

Lecturer: Lane Martin *19 October* *Aditya Sengupta*

Most materials are not volume-conserving.

The yield point phenomenon occurs when the elastic-plastic transition is abrupt. To analyze this, no offset method is required. The lower yield point is taken as σ_y, the averaged stress over the lower part of the plastic regime (since this is less sensitive to testing methods). The jagged curve that is averaged at the lower yield point occurs when the solute binds dislocations and dislocations proceed to unbind. The yield strength follows the same trend as Young's modulus, with ceramics greater than metals which are greater than polymers.

22.1   Ultimate Tensile Strength

This is the maximum possible engineering stress in tension. In metals, this occurs when necking starts (where the cross-sectional area decreases causing stress buildup); in ceramics, this is when crack propagation starts. In polymers, this occurs when polymer backbones are aligned and are about to break.

Past the UTS point, the material is not becoming weaker; rather, necking causes a smaller cross-sectional area. But because of the engineering stress being independent of the change in geometry, the stress seems to go down, even though the actual area by now is less. We can introduce true stress and true strain to fill in this gap,

$$\sigma_T = \frac{F}{A_i} \tag{22.1}$$

$$\epsilon_T = \ln \frac{l_i}{l_0} \tag{22.2}$$

Before necking, engineering and true stress are related as follows:

$$\sigma_T = \sigma(1 + \epsilon) \tag{22.3}$$

$$\epsilon_T = \ln(1 + \epsilon) \tag{22.4}$$

These are derived as follows. For true stress as a function of engineering stress:

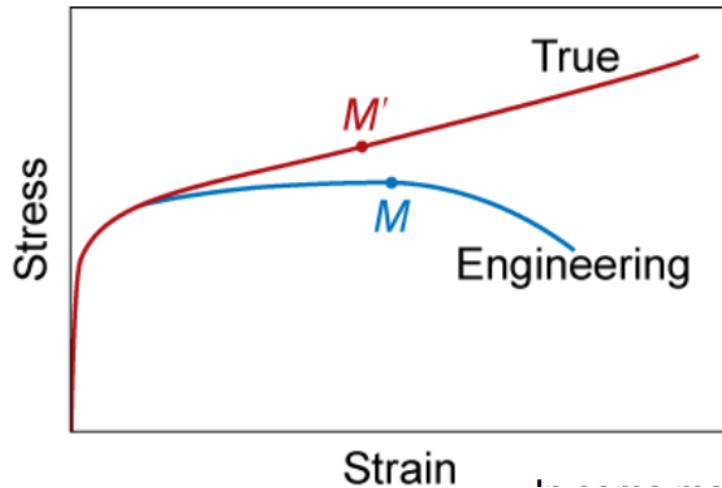$$\sigma_{\text{true}} = \frac{P}{A_i} = \frac{P}{V} l_i = \frac{P}{A_0} \frac{l_i}{l_0} = \sigma_e \left(1 + \frac{\Delta l_i}{l_0}\right) = \sigma_e \left(1 + \epsilon_e\right) \tag{22.5}$$
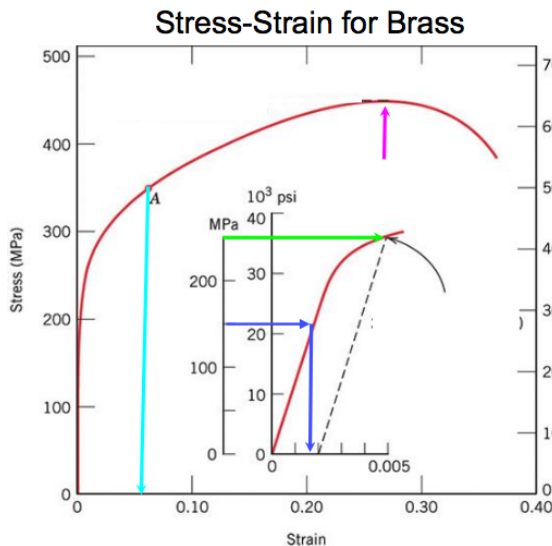
and true strain as a function of engineering strain:

$$\epsilon_{\text{true}} = \frac{\Delta l_i}{l} = \int_{l_0}^{l_f} \frac{dl}{l} \tag{22.6}$$

$$\epsilon_{\text{true}} = \ln l\,|_{l_0}^{l_f} = \ln\frac{l_f}{l_0} = \ln\left(1 + \frac{\Delta l}{l_0}\right) = \ln(1 + \epsilon_e) \tag{22.7}$$

Note that this derivation assumes conservation of volume.

An example problem and solution that I was too lazy to transcribe is shown here:

Stress-Strain for Brass

- Gauge is 250 mm (10 in) in length and 12.8 mm (0.505 in) in diameter.
- Subject to tensile stress of 345 MPa (50 ksi)

- Young's Modulus, E   (bond stretch)

$$E = \frac{\sigma_2 - \sigma_1}{\varepsilon_2 - \varepsilon_1} = \frac{(150-0)MPa}{0.0016-0} = 93.8\,GPa$$

- Offset Yield Strength, YS   (plastic deformation)

$$YS = 250\ MPa$$

- Max. Load from Tensile Strength TS

$$F_{max} = \sigma_{TS} A_0 = \sigma_{TS}\pi\left[\frac{d_0}{2}\right]^2$$

$$= 450MPa\left(\frac{12.8x10^{-3}m}{2}\right)^2 \pi = 57{,}900N$$

- Change in length at Point A, $\Delta l = \varepsilon l_0$

$$\Delta l = \varepsilon l_0 = (0.06)250\ mm = 15\ mm$$

22.2 Ductility

Ductility is a measure of the degree of plastic deformation that has been sustained at the fracture point. Ductile materials can tolerate large plastic deformations, and brittle ones cannot. Ductility can be measured by a percentage elongation or a percentage reduction in area; these are given by the following expressions:

$$\%EL = \frac{l_f - l_0}{l_0} \times 100\% \quad \%A = \frac{A_0 - A_f}{A_0} \times 100\% \tag{22.8}$$

Since crystal slip does not change material volume, these two are usually comparable. Typically materials are considered brittle if %EL < 5% and ductile if %EL > 5%.

Most metals are ductile at room temperature, but can become brittle at lower temperatures. This is because the dislocations cannot easily move at lower temperature.

22.3 Resilience and Toughness

Resilience is the capacity of the material to absorb energy when deformed elastically and recover all of it when unloaded. It is approximated as the area under the elastic stress-strain curve,

$$U_r = \int_0^{\varepsilon_y} \sigma d\varepsilon = \int_0^{\varepsilon_y} E\varepsilon d\varepsilon = E\frac{\varepsilon_y^2}{2} = \frac{\sigma_y \varepsilon_y}{2} = \frac{\sigma_y^2}{2E} \tag{22.9}$$

Toughness is the energy to break a unit volume of material, or absorb energy to fracture. It is the approximate area under the stress-strain curve:

$$U_T = \int_0^{\varepsilon_f} \sigma d\varepsilon \tag{22.10}$$

Brittle fracture: elastic energy
Ductile fracture: elastic + plastic energy
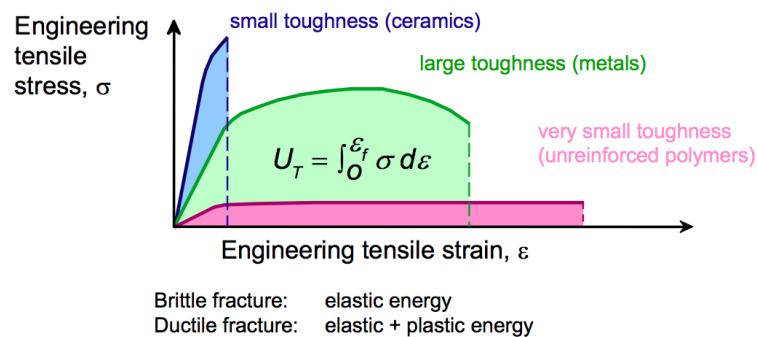
Materials undergo elastic recovery after plastic deformation, which can be exploited to increase their yield strength. This is called *work hardening*, *strain hardening*, or *cold working* a material.

MSE 45: Properties of Materials   **Fall 2018**

Lecture 23: Dislocations and Strengthening Mechanisms, I

Lecturer: Lane Martin   *22 October*   *Aditya Sengupta*

Studying how to increase the strength of materials requires knowledge of several different aspects of materials science. Dislocations are especially important to strengthening, as they cause rows of applied forces which potentially strengthen a material all at once.

Slip is defined as plastic deformation induced in a material by the motion of dislocations, and the slip plane is the crystallographic plane on which the dislocation line traverses. Based on these definitions, we can say that a dislocation moves along a slip plane in a slip direction perpendicular to the dislocation line. The slip direction is the same as the direction of the Burgers vector.

23.1   Dislocation Interaction

Dislocations move much more easily in metals than in ceramics. This is because metals do not have directional bonding, whereas covalent and ionic ceramics are directionally specific. Metals have close-packed directions along which slip takes place, with a higher dislocation density. By contrast, the dislocation density is much less in ceramics.

The presence of dislocations puts strain on the lattice. Edge dislocations create tensile and compressive stresses on the lattice; an increased density just above the dislocation point creates compressive stress, and the decreased density creates tensile stress just below the dislocation point. Screw dislocations cause pure shear strain.

Edge dislocations can interact, which creates stress fields that add like electric charges: like ones (in terms of orientation) repel, and opposite ones attract. Like dislocations repelling means if two dislocation atoms oriented the same way are adjacent to one another, they create a greater net compressive force in the direction of both dislocations and a greater net tensile force in the other direction; between the dislocation atoms, there is a repulsion due to these similarly oriented forces. If oppositely oriented dislocations combine, the compressive and tensile forces destructively add in both positions, creating a perfect crystal. There is no net strain from the missing half row of atoms. Dislocations can pile up, creating a "traffic jam", when up against an obstacle such as a grain boundary or twin. This creates a greater stress in the direction leading away from the obstacle.

Edge dislocations can interact at an angle; at small angles, the similarly oriented like dislocation atoms still repel one another. However, with different slip planes and an angle greater than 45 degrees, like dislocations start to attract. The final configuration that is stable in a collection of similarly oriented dislocation atoms is a *low-angle grain boundary*. Similarly, when dislocation atoms have opposite orientation, the unlike dislocation atoms still attract one another. At angles greater than 45 degrees, however, opposites end up repelling.

23.2   Slip Systems

A slip system is the combination of a slip plane and a slip direction. In metals, the slip plane is the most close-packed plane, as introducing defects pushes the lattice along the direction of close-packing. For example, in FCC, the slip plane is (111) and the three other unique planes in that family. Although there

are 8 close-packed planes in the FCC lattice, 4 are parallel to the other 4. Flip all the minus signs in a plane in the (111) family and the resultant plane is parallel to the original. Within each plane, there are 3 directions; one along each face whose diagonal is on the slip plane.
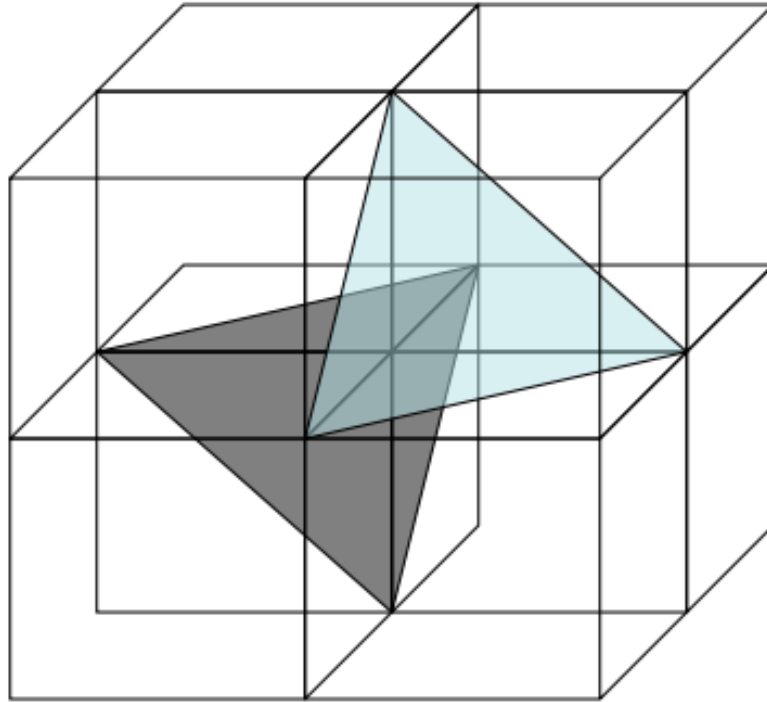
FCC and BCC have many more slip systems than HCP, which corresponds to the metals having HCP structures being less ductile.

In single crystals, slip cannot be analyzed as a phenomenon arising from atomic dislocations. Instead, a slip direction and a slip plane are specified with angles, which allows the shear stress for any arbitrary slip system to be calculated.

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Lecture 24: Dislocation and Strengthening Mechanisms, II

Lecturer: Lane Martin *24 October* *Aditya Sengupta*

Even with a pure tensile stress in a material, a shear component may also exist, depending on the geometry of the crystal and the planes and slip directions. The resolved shear stress is given by

$$\tau_R = \sigma \cos \phi \cos \lambda \tag{24.1}$$

where ϕ and λ are the characterizing polar-coordinate angles in the crystal; λ is the angle between the applied stress and the slip direction, and ϕ is the angle between the applied stress and the normal of the slip plane. $\cos \phi \cos \lambda$ is called the Schmid factor. There are multiple slip planes and slip directions, so the resolved shear stress can be found by taking the angles that give the maximum shear stress. This can come out of geometry, by first projecting onto a plane that is along the slip direction that is ϕ from the coordinate system which gives a new area $A_s = A_0 / \cos \phi$. We get

$$\tau_R = \frac{F_s}{A_s} = \frac{F \cos \lambda}{A_0 / \cos \phi} = \sigma \cos \lambda \cos \phi \tag{24.2}$$

There are three vectors associated with a slip system: the applied stress, the normal to the slip plane, and the direction of the actual slip. Say there's an FCC material. The slip plane is (111) because that's the close-packed plane for FCC. The slip direction is the close-packed direction, which is in the $\langle 110 \rangle$ family - this includes [110], [101], [011], [$\bar{1}$ $\bar{1}$ 0], [$\bar{1}$ 1 0], and so on. $\langle 111 \rangle$ is the perpendicular direction to the [111] plane. So, for an arbitrary state of stress, the Schmid factor can be calculated by taking dot products.

Generally, one slip system is most favourably oriented. To account for this, we introduce a quantity called the critical resolved shear stress, τ_{CRSS}, which is the minimum shear stress required to initiate slip. Dislocation motions takes place when $\tau_R > \tau_{CRSS}$. An applied stress σ_y is related to τ_{CRSS} as follows,

$$\sigma_y = \frac{\tau_{CRSS}}{(\cos \phi \cos \lambda)_{\max}} \tag{24.3}$$

24.1 Example Problems

Determine the Schmid factor for an FCC single crystal oriented with its [100] parallel to the loading axis.

We determine that the slip plane is [111], and the slip direction is [1$\bar{1}$0]. We can find angles by taking dot products: between the slip plane and loading, the cosine of the angle is $\frac{1}{\sqrt{3}}$, and between the dislocation and loading, the cosine of the angle is $\frac{1}{\sqrt{2}}$. So the Schmid factor is 0.409.

24.2 Deformation by Twinning, Polycrystalline Material

(TBD: deformation by twinning. Understand it and write about it)

Polycrystalline materials are in general stronger than single crystals. Grains elongate in the direction of stress, but grain boundaries remain intact. If a roll of tantalum is machined and fired at a target, its deformation on the impacted end can be seen. This shows the anisotropic deformation of materials. (relevance?)

24.3   Methods of Strengthening

24.3.1   Grain Size Reduction

Grain boundaries are barriers to slip. The bigger the misorientation between the two grains, the stronger the barrier is for slip. A dislocation may easily cross a small-angle boundary, but this is not the case for large angles. Smaller grain sizes also present more barriers to slip. Grain size may be controlled by a solidification process and by plastic deformation followed by appropriate heat treatment. This is described by the Hall-Petch equation:

$$\sigma_y = \sigma_0 + k_y d^{-1/2} \tag{24.4}$$

Basically, this says that if grain size is down, strength is up. This is good for grain sizes ranging from 1mm to 1μm, but below that, the equation says the strength should go to infinity. This does not square with experimental data. A number of different mechanisms have been proposed for why this happens, such as dislocation-based, diffusion-based, grain boundary shearing-based, and two-phase based.

The pileup of dislocations at grain boundaries is a hallmark mechanism of the Hall-Petch relationship. Once grain sizes drop below the equilibrium between dislocations, this is no longer necessarily valid.

24.3.2   Via Solid Solutions

Impurity atoms can distort the lattice and generate stresses. This stress can produce a barrier to dislocation motion. A small impurity generates local stresses, and stresses can concentrate at dislocations. Small and large substitutional impurities both create stress concentrations at diagonally opposite lattice points opposing dislocation motion.

24.3.3   Strengthening via Alloying

Small impurities tend to concentrate at dislocations, to reduce the mobility of the dislocation. This helps to increase strength. Large amounts of impurities concentrate around dislocations, on their low density site (where tensile stress is created), to lock them into place and prevent further dislocation motion. Alloying increases the tensile strength and yield strength of the material, but reduces the ductility, so strengthening comes with a tradeoff.

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Lecture 25: Strengthening

Lecturer: Lane Martin *26 October* *Aditya Sengupta*

25.1 Strengthening Methods, Contd.

25.1.1 Strengthening via Precipitation

Aluminium alloys are strengthened by precipitation. Hard precipitates (small, with different phase micro-constituents) are difficult to shear (this can be seen in the case of ceramics in metals, such as with silicon carbide in aluminium or iron), so they can pin dislocations in place, strengthening the material.

25.1.2 Strengthening via Strain Hardening

This is also called *cold working* because the material is deformed at a low temperature. For metals, this deformation usually takes place at room temperature. The degree of cold-working is characterized by the change in cross-sectional area of the material. Strain hardening works because dislocations entangle with one another during cold-working, which makes further dislocation motion difficult.

This method has the result of increasing dislocation density by orders of magnitude, from around 10^3mm^{-2} to around 10^9mm^{-2}, although heat treatment brings the density down to around 10^6mm^{-2}. The yield stress increases with increasing ρ_d. Overall, with increasing cold work, yield and tensile strength both increase as ductility reduces.

It is important to know how to manage tradeoffs based on graphs of elongation/area reduction change with amount of cold work along with graphs of yield and tensile strength.

25.2 Temperature Dependence of $\sigma - \varepsilon$ Behaviour

With increasing test temperature, yield and tensile strength reduce while the amount of elongation increases. On a microscopic level, this is because the increasing temperature helps the motion of dislocations. This is why heating reverses the effects of cold working. The effects of heating (annealing) take place in three stages: recovery, recrystallization, and grain growth.

25.2.1 Recovery

The stored strain energy due to the locking of dislocations is relieved because of the temperature increase, because increased temperature means increased diffusion. The dislocation density is thus reduced. Since dislocation atoms diffuse from higher to lower concentrations, they meet and annihilate with the oppositely oriented dislocations, creating a perfect plane out of the previous half-plane.

25.2.2   Recrystallization

A new set of crystals or grains are formed, which have small dislocation densities and small average sizes. They consume cold-worked or deformed crystals until no cold-worked crystals remain. This leads to a reduction in the material's strength and hardness, and an increase in ductility. This happens over relatively short time-scales, in a matter of seconds.

25.2.3   Grain Growth

At times longer than a few seconds, larger grains consume small grains to reduce the grain boundary area and therefore the energy. Grain growth is characterized by the following general equation,

$$d(t)^n = d_0^n + K_0 t e^{-Q/kT} \tag{25.1}$$

Overall, the process of annealing reduces hardness and strength in favour of ductility across all three phases, but mostly in recrystallization. The following diagram characterizes this:
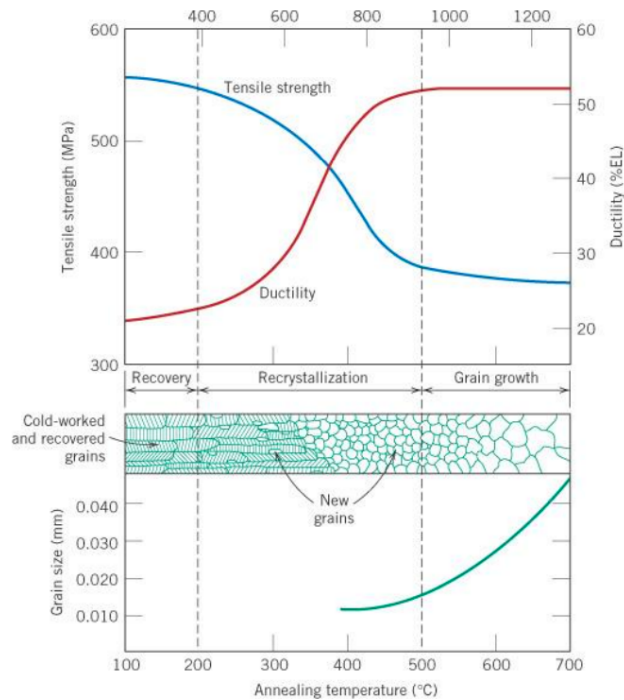
Repeatedly cold-working and annealing a material can help to maintain material properties within tolerable ranges, making gradual changes to both parameters in one direction each at a time until an end state is reached. (Problems on this based on ductility/cold-working and yield-or-tensile-strength/cold-working graphs will be relevant.)

25.3   Deformation in Ceramics

Ceramics do not undergo plastic deformation as easily as metals. It is more difficult for dislocations to move and there are fewer of them to begin with in crystalline ceramics. In ionic ceramics, there is electronic repulsion between atoms that makes dislocation motion difficult; in covalent ceramics, bonds are relatively strong, there are a limited number of slip systems, and dislocation structures can be complicated. Noncrystalline ceramics undergo plastic deformation by viscous flow as in liquids.

MSE 45: Properties of Materials **Fall 2018**

Lecture 26: Failure, I and II

Lecturer: Lane Martin   *29 October, 31 October*   *Aditya Sengupta*

Failure comes in three forms: fracture, fatigue, and creep. It is important to understand all of these to know how to mitigate them in engineering design. Failure can be mitigated through materials selection, processing, and design safety.

26.1 Fracture

Fracture is the phenomenon of separation of a material into two or more components in response to an imposed stress. There are two major types of fracture: ductile and brittle. While brittle fracture is relatively quick, making a clean break all at once, ductile fracture starts with the formation of small cavities in the material, which coalesce under further stress to form a crack that eventually propagates to separate the material. This creates a fibrous interface between the two sections that split due to ductile failure.

The degree of ductility decreases with a reduction in temperature, to the point that it becomes more brittle at some low temperatures. This is the ductile-to-brittle transition. In order to avoid failure, materials should have a ductile-to-brittle transition that is not close to the ambient or operating temperatures.

Ceramics usually undergo brittle fracture, as they do not undergo appreciable plastic deformation before fracturing; they fail catastrophically without warning, like me on this midterm. They undergo rapid crack propagation, typically in a direction perpendicular to the applied stress. Fracture crack propagation in ceramics comes in two types: transgranular, i.e. passing through grains, or intergranular, propagating along grain boundaries.

Fracture due to intergranular (between grains) crack propagation normally occurs after processes that weaken or make more brittle the grain boundaries. For most brittle materials, cracks propagate in a transgranular (across grains) fashion, by successive breakage of atomic bonds along specific planes. This is called cleavage.

Brittle fracture surfaces are studied (this subfield is called fractography) normally using scanning electron microscopy. This is used to study the cause of failure in engineering structures, and to study models of crack growth. Cracks grow fast in real materials, to the point that the tensile strength of perfect materials can be up to 100 times that of real-life materials. This is because flaws in a material cause premature failure. Larger samples have more potential flaws, and are also more likely to have flaws of a certain critical size.

(MacGyver: arrest cracks by drilling into the wing)

26.2 Real Life is Sad

This difference between real and ideal fracture strength can be described by the stress concentration factor,

$$K_t = \frac{\sigma_m}{\sigma_0} = 2\sqrt{\frac{a}{\rho_t}} \tag{26.1}$$

where σ_m is the maximum stress that can be applied, σ_0 is the magnitude of the applied stress, a is the crack length, and ρ_t is the radius of curvature at the crack tip.

Large values of K_t, over around 3, promote failure. If a crack is unavoidable, its length should be minimized and its radius of curvature maximized. This is where MacGyver comes in. Surface cracks are worse; if a crack is present at a sharp corner, the chances of failure are increased.

Stress concentrations can be observed using photoelasticity, an experimental method where a material looks like it does in FEA. Photoelasticity gives an accurate depiction of stress concentrations even around sharp corners.

26.3   Griffith's Criteria for Fracture and Failure

1. Material failure will not occur from a crack if it is parallel to a longer crack.

2. Material failure will not occur from cracks that are parallel to applied stress.

The longest crack present in a material that has the greatest angle relative to the applied stress is the failure mode of that material. Since fast fracture occurs when $K \geq K_c$ (sequence breaking? K_c hasn't yet been discussed), the largest and most stressed cracks grow first.

The critical stress for crack propagation can be described mathematically,

$$\sigma_c = \left(\frac{2E(\gamma_s + \gamma_p)}{\pi a} \right)^{1/2} \tag{26.2}$$

where E is the elastic modulus, γ_s is the specific surface energy, and γ_p is the plastic deformation energy. These terms come out of the fact that for a crack to propagate, enough stress must be applied to both overcome the surface energy and cause plastic deformation. Highly ductile materials do not have the surface energy factor, and highly brittle materials do not have the plastic deformation factor.

26.4   Fast Fracture

Fast fracture is a term given to a phenomenon in which a flaw (such as a crack) in a material expands quickly, and leads to catastrophic failure of the material. The stress acting on a material at fast fracture does not have to be the material's yield stress.

From the above expression for σ_c, we can get

$$\sigma_c \sqrt{\pi a_0} = \sqrt{E G_c} = \text{const} \tag{26.3}$$

The right-hand factor is a constant because it is entirely dependent on overall material properties. This leads to a definition of the resistance of a material to brittle fracture, its fracture toughness K_c:

$$K_c = Y \sigma_c \sqrt{\pi a_0} \tag{26.4}$$

where Y is a factor covering the crack orientation and how the load is applied (factors which can be understood qualitatively through Griffith's criteria).

For thin materials, K_c depends on the thickness; as thickness increases, the fracture toughness tends to the so-called *plane strain fracture toughness* K_{Ic} (K one c):

$$K_{Ic} = Y\sigma\sqrt{\pi a} \tag{26.5}$$

For an infinite plate, $Y = 1$, and for a semi-infinite plate, $Y = 1.1$.

This allows us to mathematically describe the conditions for fast fracture. Fast fracture occurs when $\sigma_m \geq \sigma_c$ or $K \geq K_c$. Given that $K = \sigma\sqrt{\pi a}$, we can say that fast fracture occurs either when a material containing cracks of size a is subjected to some critical stress, or when at a fixed stress cracks grow to some critical a_c.

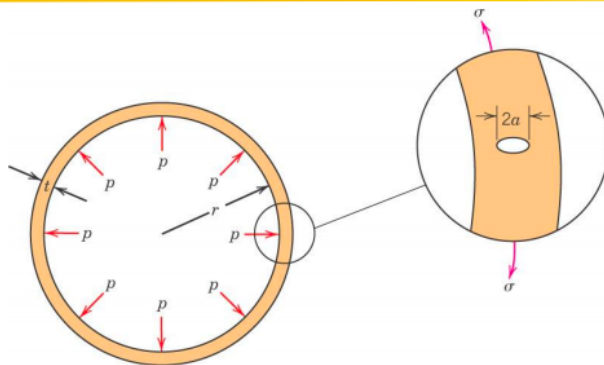To design against crack formation and propagation, the fact that the largest and most stressed cracks grow first should be taken into account. There are two cases: either the maximum crack size dictates the maximum allowable stress, or vice versa:

$$\sigma_{design} < \frac{K_c}{Y\sqrt{\pi a_{max}}} \tag{26.6}$$

$$a_max < \frac{1}{\pi}\left(\frac{K_c}{Y\sigma_{design}}\right)^2 \tag{26.7}$$

Too lazy to transcribe this next bit:

Design Example: Gas Tank

Spherical gas/fluid tank under pressure p

Circumferential wall stress:

$$\sigma = \frac{pr}{2t}$$

Two possible designs for safety:

A) Plastic distortion before leaking (*i.e.*, the mechanical deformation before a leak occurs)
   - Calculate relative maximum critical crack length where plastic deformation occurs before catastrophic crack propagation for 1040 Steel, Ti alloy and Stainless steel

B) Leak-before-break (*e.g.*, to prevent pressure build-up leading to explosion). Achieved when $a_c = t$ (*i.e.*, complete opening before crack propagation)
   - Calculate the relative maximum pressure for same 3 materials as A

Transformation toughening can also be used to arrest crack propagation. When the stress field of a crack is sufficient to cause a phase transformation to a different, stable, solid phase, the new phase may apply its own compressive force that pinches the crack closed.

26.5 Fatigue

(which is how I'm feeling after typing all these up after the lectures)

Fatigue is failure under cyclic loading. By loading a material repeatedly even well below the yield point of the material, the material can fail over time. This causes 90% of mechanical engineering failures.

The key parameters in stress are S, the stress amplitude, and σ_m, the mean stress. Fatigue failure involves crack initiation (almost always on the surface), incremental crack propagation with each cycle, and final failure after the crack reaches a critical size.

Fatigue loading could have equal tensile and compressive components, could be asymmetric with respect to zero stress, or could just be asymmetric.

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Lecture 28: Failure, III

Lecturer: Lane Martin *2 November* *Aditya Sengupta*

(to take notes for the past few lectures)

28.1 Too many [coo]Ks

The stress concentration factor $K_T = \frac{\sigma_m}{\sigma_0} = 2\sqrt{\frac{a}{\rho}}$ is different from the fracture toughness $K_c = Y\sigma_c\sqrt{\pi a}$, which is the total amount of energy the system can absorb before fracture, where Y is a shape prefactor; the plane strain fracture toughness is a subclass of this for which $Y = 1$.

28.2 Fatigue continued

The fatigue limit is the stress level below which fatigue failure will not occur. The largest value of fluctuating stress that will not cause failure for infinite cycles. This is not present in nonferrous metals. The fatigue strength is the stress level at which failure will occur for some specific number of cycles; the fatigue life is the number of cycles to cause failure at a specific stress level.

If we were able to examine the crack length at each cycle of stress, we would be able to plot a as a function of N, and quantify $\frac{da}{dN}$. For a smaller stress, the curve moves to the right, requiring more cycles to produce an equivalent a. The curves are roughly exponential; this relationship allows us to define the crack propagation rate at any fixed point. More formally than "roughly exponential", we can say

$$\frac{da}{dN} = A(\Delta K)^m \tag{28.1}$$

or

$$\log\left(\frac{da}{dN}\right) = m\log\Delta K + \log A \tag{28.2}$$

With the definition of $\Delta K = Y\Delta\sigma\sqrt{\pi a}$, we can say

$$N_f = \frac{1}{A\pi^{m/2}(\Delta\sigma)^m}\int_{a_0}^{a_c}\frac{da}{Y^m a^{m/2}} \tag{28.3}$$

We can predict the cycles to failure.

Fatigue life can be improved by imposing a compressive surface stress to suppress crack growth, either by mechanical "shots" or by carburizing with a carbon-rich gas. It can also be improved by removing stress concentrators, polishing surfaces to remove surface cracks, and/or by optimizing processing conditions to minimize defects.

28.3 Creep

Creep is time-dependent permanent deformation due to static mechanical stress, usually at elevated temperatures. This is undesirable, and it limits the lifetime of materails. A creep test can be run on any materials, by applying a constant stress at a constant temperature and measuring the deformation over time.

Creep falls into three regions in the creep strain/time curve; primary (with decreasing slope due to strain hardening), secondary (which is steady state), and tertiary (with increasing slope up until rupture). At steady state, we can say

$$\dot{\varepsilon}_s = K_1 \sigma^n \tag{28.4}$$

Temperature dependence is predictable,

$$\dot{\varepsilon}_s = K_1 \sigma^n \exp\left(\frac{-Q_c}{RT}\right) \tag{28.5}$$

Creep can be mitigated by first knowing the possible mechanisms, as each one has a characteristic stress/creep-rate curve. These mechanisms can be vacancy diffusion induced by stress, grain boundary diffusion and sliding, and dislocation motion. Creep can be solved by using single crystals (which is impractical) or at least increasing the grain size, or by hardening the material with solid solutions or precipitation hardening.

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Lecture 29: Electrical Properties of Materials

Lecturer: Lane Martin   *5 November*   *Aditya Sengupta*

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29.1 Electrical Conduction

Ohm's Law is the most basic principle of how electrical conduction works. It states that the voltage drop between two points is equal to the current between them, multiplied by the resistance R, introduced as a proportionality constant that turns out to be dependent on materials and dimensions.

$$V = IR \tag{29.1}$$

The material properties can be isolated in the quantity ρ, which is referred to as the resistivity, by the following relation:

$$\rho = \frac{RA}{l} \tag{29.2}$$

where l is the path length, and A the cross-sectional area. The material's conductivity is defined as

$$\sigma = \frac{1}{\rho} = \frac{l}{RA} \tag{29.3}$$

This is analogous to the flow of water in a pipe.

29.2 Electronic Structure

At a microscopic level, a material's electronic properties are determined by its band structure. Energy exists in discrete levels in an atom. In molecules consisting of several atoms, these energy levels split to produce a number of molecular orbitals. In aggregate materials, with on the order of 10^{20} molecules, the discretization of energy levels matters less and less until a continuous band of energy is reached in solids. Some energy levels, however, contain no orbitals, and these are referred to as *band gaps*. Other than in the band gaps, in the energy bands, energy forms a near continuum.

Electrons move from the valence band to the conduction band by absorbing energy in some form. This can happen by photon absorption or thermal transfer. If an electron gains enough energy to overcome the band gap, it moves to the conduction band. A material is a metal, insulator, or semiconductor based on its bond structure and the development of its electronic band structure. This can be quantified mainly in the band gap energy. If the gap is small, electrons can easily cross and conduction is easily allowed; these are metals. If the gap is moderate, some electrons can cross and conduction is somewhat restricted; these are

semiconductors. If the gap is large (greater than 3 eV), electrons cannot cross and conduction is not allowed; these are insulators.

The Fermi energy of a system refers to the difference between the highest and lowest single-particle states in a system at 0K. There are lots of different energy states available to an electron in the valence band, some of which will allow it to cross over into the conduction band. The Fermi level is the statistical equilibrium point between electrons and holes. In an intrinsic semiconductor, the n-p ratio is 1:1, which gives us a Fermi level halfway between the valence and conduction bands. n-type semiconductors have a higher Fermi level, closer to the conduction band, and p-type semiconductors have a lower Fermi level, closer to the valence band. The Fermi level reflects where the energy of an electron averages out, a weighted average of the possible energy levels.

At a more advanced level, free electrons are fermions that obey Fermi-Dirac statistics, which has a probability distribution that looks kind of like an Arrhenius relationship but not really:

$$f(E) = \frac{1}{e^{\frac{E - E_m}{kT}} + 1} \tag{29.4}$$

and the Fermi level is the energy level at which $f(E) = \frac{1}{2}$. The Fermi level is, physically, the highest energy that is occupied by electrons at 0 K.

Metals can have either overlapping band structures or partially filled band structures. Thermal energy excites electrons from their valence states to the adjacent empty higher energy states; in overlapping structures, there is no jump to the conduction band, whereas in partially filled structures, the first empty states are in the valence band, and the next ones are in the conduction band after an energy gap.
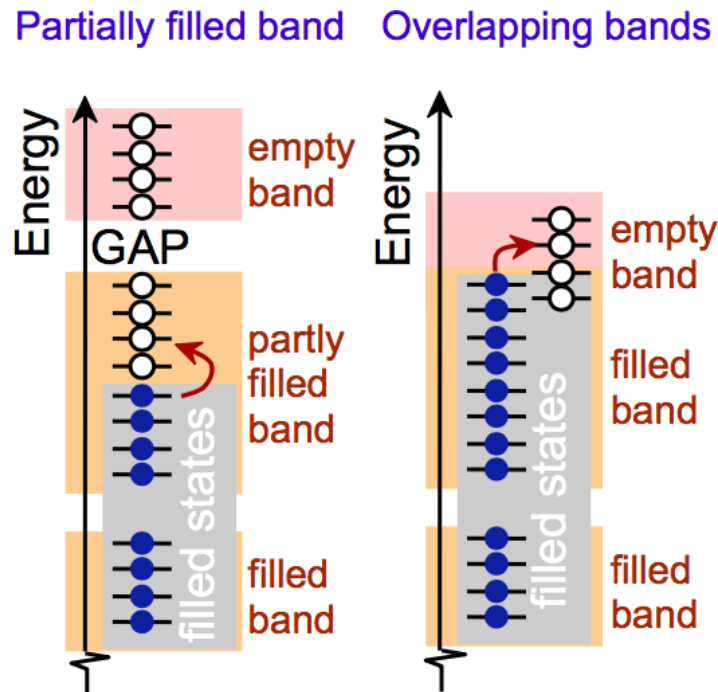
Real band structures are strange and involve plots of Greek letters against energies. These Greek letters

specify a direction in momentum space. Exciting an electron with only photons lets it move in energy space, and with thermal energy it can move in momentum space.

In metals, the presence of impurities increases the resistivity, because the presence of grain boundaries, dislocations, impurity atoms and vacancies all work to scatter electrons and therefore impede conduction. Resistivity also increases with temperature, and the degree of cold-working. Overall, the resistivity of a metal sample can be broken down into

$$\rho = \rho_{thermal} + \rho_{deformation} + \rho_{impurity} \tag{29.5}$$

Given the yield strength or some physical parameter of a known binary alloy, we can find the relative concentrations of the two components, and look up the corresponding resistivity.

Semiconductors and insulators have completely filled valence bands, and to fill the higher energy states, the electrons must cross the band gap, as only metals have the partially filled structure.

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MSE 45: Properties of Materials **Fall 2018**

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Lecture 30: Midterm 2 Review

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Lecturer: Lane Martin   *7 November*   *Aditya Sengupta*

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30.1 Chapter 5: Diffusion

What is it, what does it happen, how is it affected by conditions, how can we exploit or stop it?

Types: inter- and self-. Interdiffusion is one material diffusing into another and vice versa along a concentration gradient. Atoms move from high to low concentration. Diffusion of A in B and B in A don't have to happen at the same rate. Also, vacancy diffusion - an atom adjacent to a vacant lattice site moves into it. First, bonds with neighbouring atoms are broken, then slide in.

Interstitial diffusion is also a thing, where interstitial particles migrate from one interstitial site to another. This is mostly for small atoms that can be interstitial impurities (H, C, N, O). This is faster than vacancy diffusion as it's smaller stuff moving.

Can describe this mathematically,

$$J_x = -D\frac{dC}{dx} \tag{30.1}$$

The steeper the concentration profile, the greater the flux. Fick's first law says the flux is proportional to the concentration gradient, with diffusion rate being time-independent. This equation describes steady-state diffusion.

$$\frac{dC}{dx} \approx \frac{C_2 - C_1}{x_2 - x_1} \tag{30.2}$$

Temperature dependence is described by an Arrhenius relationship,

$$D = D_0 \exp\left(-\frac{Q_d}{RT}\right) \tag{30.3}$$

Should be able to look at paired systems - carbon in α iron, vs iron in γ iron, and tell which ones have faster diffusion rates. Based on packing factor and size of diffusing factor. Less open structures diffuse slower even at higher temperatures.

In the non steady-state case, we describe diffusion by Fick's second law,

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{30.4}$$

which has a solution given by the error function,

$$\frac{C(x,t) - C_0}{C_s - C_0} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \tag{30.5}$$

Diffusion is faster for open crystal structures, lower melting T materials, materials with secondary bonding, smaller diffusing atoms, and lower density materials, and slower for all the opposite ones.

30.2 Chapter 9: Phase Diagrams

A phase is a homogeneous portion of a system with some uniform physical and chemical characteristics. The most common phase diagrams are pressure-temperature or temperature-concentration, should be able to read multiple kinds. The components of a phase diagram (elements or compounds being mixed) combine to make phases.

Equilibrium is the minimum energy state for a given T, P and composition; implicitly, we're talking about equilibrium phases when we draw a phase diagram. These are time independent. Assume P is atmospheric if not given.

Some examples of phase diagrams: the binary isomorphous system, composition - Ni in Fe vs temperature. There's a central region in that phase diagram with $L + \alpha$. To find the fractional parts of each phase, the phases on the left and right, draw the tie line and see where intersections happen and apply the lever rule (basically conservation of mass). Phase diagrams will be complicated. Yay.

Can get information on the microstructure from a phase diagram; precipitation of a solid as a liquidus line is crossed, which happens throughout the intermediate region, and it finishes solidifying at the solidus line to get a characteristic microstructure. If this is not done at equilibrium, i.e. if it's done faster, we see coring: layers of high composition at the centers of circles, moving out gives lower compositions.

Binary eutectic systems - eutectic means easily melted. Should know how to read those phase diagrams and know what a eutectic is. Should be able to analyze microstructures in binary eutectics. We should know what happens when a material has the eutectic composition, or what happens when it is either hypo or hyper eutectic. Has a tendency to form lamellar or layered structures. Why isn't it just two discrete portions for the two parts of the mix?

Know how to find an amount of a proeutectic phase relative to the total phase in the system. Should be able to understand position on the phase diagram and type of microstructure based on knowing whether you have a hyper or hypo eutectic sample. Both have the same global structure, with some proeutectic smooth portions among the lamellar eutectic.

Congruent transformations undergo no change in composition; melting is congruent along lines on the temp-composition phase diagrams. In incongruent transformations, at least one phase undergoes a composition change, e.g. melting along a curve on the phase diagrams.

Intermetallic compounds with a formula $A_x B_y$, not a solution, can be described by phase diagrams; put two diagrams back to back, and consider each one to be a type of eutectic. Intermediate solid solutions are also possible; these are solid solutions that don't extend to pure components on the phase diagrams. There are a lot more intermediate phases, but you can still deal with those using the tie line and the lever rule.

Other types of reactions: eutectoid and peritectic. Eutectoid is solid cooling to two solids, and peritectic is solid heating to solid plus liquid. (Eutectic is liquid cooling to two solids)

Pseudobinary phase diagrams, such as of ceramics, can be dealt with using the same methods, the only difference being that the composition axis is scaled differently; amount of one thing to amount of another thing.

Gibbs Phase Rule, $P + F = C + N$. Understand what all of them are, and what it means to have a degree of freedom. P is the number of phases present, F is degree of freedom, C is number of components, and N = 2. (number of non-compositional variables: for everything we'll deal with, this is temperature and pressure).

The iron-carbon system is important. There's a lot of stuff that goes on in the part of the phase diagram we see, that goes up to 6.7% C. Can apply tie lines, lever rules, fractions of phases, etc. to the iron-carbon system; should know what the phases are, because each one has a special name that gets confusing fast. The basics are: the γ phase, austenite, has low carbon content and is FCC (those two are related), the α phase, ferrite, has very low carbon content because it becomes cementite or an inter-phase mix of the two at higher carbon content.

30.3   Chapter 10: Phase Transformations

Phase transformations take place in two steps, nucleation and growth. Nuclei act as templates for crystal growth, and growth then proceeds until equilibrium is attained. The driving force to nucleate has to increase with increasing ΔT. Small supercooling and large supercooling have (something I missed). Nucleation can be homogeneous, where nuclei form in the bulk of liquid metal and require lots of supercooling, or heterogeneous, at a surface, which is easier because only slight supercooling is required.

We can describe the net energy,

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma \tag{30.6}$$

and derivatives give us the critical radius,

$$r_c = -\frac{2\gamma}{\Delta G_v} \tag{30.7}$$

Kinetics can be described by rewriting the energy in terms of the heat of fusion (energy released upon solidification). Rate of nucleation is dependent upon liquid instability and diffusion. Growth rate is described by the Avrami equation, $y = 1 - \exp(-kt^n)$, and grain growth has temperature dependence described by an Arrhenius relationship.

An overall rate of transformation can be derived from all this, which allows us to plot a TTT diagram - Time-Temperature-Transformation. This helps us characterize the microstructure, the reaction rate to a specific percentage, etc. Most of the time, cooling is continuous, not a jump discontinuity, so when T varies during the transformation, we get a CCT diagram. We can use both of those to our advantage.

Overall, there are some trends in steel. The new things here are bainite and martensite, which both come from rapid cooling/quenching.

30.4   Chapter 6: Mechanical Properties

Foundational concepts: stress and strain. How are they related, how to find them. Four kinds of stresses: tension, compression, shear, torsion. For elastic deformation, we have Hooke's law, which is direct proportionality between stress and strain, but things aren't nice. This comes in two forms: plastic deformation, and the Poisson ratio, a measure of how not volume conserving a material is.

$$\nu = -\frac{\Delta w/w}{\Delta l/l} \tag{30.8}$$

Metals are around 0.33, ceramics around 0.25, polymers around 0.4.

Plastic deformation can be characterized by the 0.2% strain offset method. Going through the stress strain curve, the next thing after the yield point (inflexion between elastic and plastic) is the ultimate tensile strength, where the change in the geometry of the system overcomes the stress, i.e. we see a reduction in engineering stress. This reduction in cross-sectional area is called necking. At the end of the stress-strain curve, we get fracture. Engineering and true stress and strain are related by $\sigma_T = \sigma(1+\varepsilon)$, and $\varepsilon_T = \ln(1+\varepsilon)$.

Ductility can be characterized by the percentage reduction in area or increase in length; if more than 5%, it's generally called ductile. Resilience - amount of elastic deformation and recovery possible, toughness - amount of energy absorbed before fracture. Ceramics are tested using a three-point bending test, flexural strength is a thing. There is a correlation between Rockwell hardness and toughness of a material.

Keep in mind factors of safety, $\sigma_{work} = \sigma/FoS$.

30.5   Chapter 7: Dislocation and Strengthening

Based on dislocation motion, we can characterize the compressive and tensile strain fields they induce, causing "traffic jams" - interactions between dislocations, having them line up, etc., to increase the strength. These create a grain boundary in a material. Slip happens in the close-packed planes and close-packed directions of a material. How do you end up with 12 unique slip systems for a material? In single crystals, shear stress resolvs geometrically as described by the Schmid factor $\cos\phi\cos\lambda$, by $\tau_R = \sigma\cos\phi\cos\lambda$.

We can cover a number of strengthening mechanisms, but we're out of time. Should know about grain size reductions, solid solutions, and a couple other things.

30.6   Chapter 8: Failure

At the far end of the stress-strain diagram, there are many kinds of failure, such as ductile and brittle. Ductile failure has tiny flaws that lead to catastrophic failure in the end. Cracks in materials can propagate differently, within and across the grains, creating different kinds of fracture surfaces. Flaws can cause stress inside a material, so stress can be concentrated as given by a proportionality factor $K_t = 2\sqrt{\frac{a}{\rho_t}}$. This factor depends on crack length and radius.

Fatigue - should know what it is, should know that even by applying less than the yield stress a material can fail. Should know how to mitigate it. Should understand what creep is, that it has three regimes and what's happening in each, how it evolves with temperature, and how to mitigate that too.

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Lecture 31: Semiconductor Systems

Lecturer: Lane Martin   *14 November*   *Aditya Sengupta*

Insulators have a wide band gap, across which few electrons can be excited across it. Semiconductors have a narrower band gap, less than 2-3 eV, but still sufficient not to excite all the electrons and cause full conduction. There are two types of electronic charge carriers in semiconductors: free electrons, which are excited to the conduction band, and holes, which are positive charges left behind by the vacant electron state in the valence band. These move at different speeds under a potential, characterized by their drift velocity.

Intrinsic semiconductors are group IV materials such as silicon and germanium. Semiconductors can also be made out of compounds, such as III-V compounds (GaAs, InSb) and II-VI compounds (CdS, ZnTe). The wider the electronegativity difference between the elements, the wider the energy gap.

In an intrinsic semiconductor such as Si, valence electrons surround atoms of silicon in a covalent manner. When an electric field is applied, an electron-hole pair is created; the electron moves towards the positive and the hole towards the negative end of the applied potential. The electrical conductivity is given by

$$\sigma = n|e|\mu_e + p|e|\mu_h \tag{31.1}$$

where μ_e is electron mobility, μ_h is hole mobility, n is a number of electrons per unit volume and p is a number of holes per unit volume. In intrinsic semiconductors, $n = p$ is guaranteed because electrons and holes are always guaranteed to exist in pairs, but in extrinsic semiconductors, this may not be the case.

Carrier mobility characterizes how quickly an electron/hole can move through a metal or semiconductor under an electric field. The mobility is defined as μ where $v_{drift} = \mu E$. It has units of $cm^2/(V \cdot s)$. Conductivity is proportional to mobility and to carrier concentration; conductivity could come from a small number of highly mobile electrons, or from a large number of not very mobile electrons. Many things can impact semiconductor mobility; essentially anything that can scatter electrons.

The above relation can be used to calculate a number of charge carriers per cubic meter. We find that GaAs has on the order of 10^{24} charge carriers, while Si has only 10^{16}. This is despite both being intrinsic semiconductors, having the same effective charge, etc. The difference arises from the band gap. The band gap for Si is 1.1eV, and for GaAs is 1.4eV. This means GaAs is a direct gap semiconductor, and Si is an indirect gap semiconductor. This low conductivity of Si is a problem. Therefore, to make it more conductive, Si can be doped; impurities that introduce excess electrons or holes can be added.

An n-type semiconductor is doped with a penta- or hexavalent atom such as phosphorus to make $n >> p$; a p-type semiconductor is doped with a di- or trivalent atom such as boron to make $p >> n$. Doped systems have much higher conductivity curves. After a "freeze-out" zone of low temperature in which electrons cannot be excited, the extrinsic conduction becomes much higher than the intrinsic site, because imperfection sites lower the activation energy to produce mobile electrons that can cross the gap.

The Hall effect can be used to characterize a semiconductor as n- or p-type. This is done by applying a magnetic field perpendicular to the direction of motion of a charged particle, and measuring the induced Hall voltage. The sign of this voltage indicates which type of carrier is found. Specifically, the Hall voltage is given by

$$V_H = \frac{R_H I B}{d} \tag{31.2}$$

where R_H is a material proportionality constant, related to the number of electrons by

$$R_H = \frac{1}{n|e|} \implies |R_H| = \frac{\mu}{\sigma} \tag{31.3}$$

A p-n rectifying junction, which allows the flow of electrons only in one direction, is an example of a device that can be made using semiconductor properties. This can be placed in forward bias, in which carriers flow through p-type and n-type regions, holes and electrons recombine at the p-n junction, and current is allowed to flow; or in reverse bias, in which that doesn't happen and current doesn't flow. Another example is a junction transistor, in which two p components are sandwiched between an n base. A MOSFET, which has two p-type dopant regions connected by a thin channel of the same dopant, all on an n-type substrate, is also important. Conduction can be turned on and off by applying a forward or reverse voltage. The carriers in the channel can be completely depleted by applying an external bias, forbidding conduction.

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| ## Lecture 32: Electrical Properties, III |
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| *Lecturer: Lane Martin*   *26 November*   *Aditya Sengupta* |
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32.1 Charge Displacement Processes

What happens to materials without a lot of mobile charges when it is placed under an electric field? These materials are called *dielectrics*. When we apply an electric field to an ideal dielectric there is no long-range charge motion, but there is local rearrangement of the charge in the system such that the dielectric acquires a dipole moment and is said to be polarized. An electric dipole is two equal and opposite point charges separated by a distance δx, and the dipole moment is a vector with its positive sense from negative to positive charge, $p = Q\delta x$. A polarized material consists of individual dipolar units, whose end faces carry surface charges $+\sigma p$ and $-\sigma p$.

The structure of a capacitor is like this, with an E between and normal to two parallel plates, with surface charge density σ and separated by vacuum. This gives us $E = \sigma/\varepsilon_0$. With a dielectric, the parallel plate charge is partially due to a dielectric: $E = (\sigma_T - \sigma_p)/\varepsilon_0$. The total charge density σ_T is the magnitude of the electric displacement vector, $D = \varepsilon_0 E + P$. In the case of linear dielectric, P is proportional to E. This case is fairly common and is represented by $P = \chi_E \varepsilon_0 E$, where χ_E is electric susceptibility, which is a dimensionless rank-2 tensor.

This allows us to write

$$D = \varepsilon_0 E + \chi_E \varepsilon_0 E = (1 + \chi_E)\varepsilon_0 E \tag{32.1}$$

Since D is the total charge density, we can say

$$\frac{Q_T}{A} = (1 + \chi_E)\varepsilon_0 \frac{V}{h} \tag{32.2}$$

This allows us to define the capacitance of the capacitor, its ability to store electric energy, as

$$C = \frac{Q_T}{V} = (1 + \chi_E)\varepsilon_0 \frac{A}{h} \tag{32.3}$$

which allows us to define the permittivity of a dielectric as a multiplier on the permittivity of free space, $\varepsilon = (1 + \chi_E)\varepsilon_0$. The relative permittivity or dielectric constant of a material is $\frac{\varepsilon}{\varepsilon_0}$.

When we apply an electric field to a system, we have different possible responses in a material. All materials undergo atomic polarization under an electric field, which causes a small displacement of the electrons relative to the nucleus. This is active up to frequencies around $10^{15} - 10^{17}$ Hz. Ionic polarization, the relative displacement of cations and anions, is also possible. These are optical lattice vibrations, active up to around $10^{13} - 10^{14}$ Hz. Dipolar or molecular polarization is a third type. This is the reorientation of polar

molecules in an applied field. This is roughly equivalent to diffusional exchange of atoms over a few atomic distances. This process is relatively slow, occuring for frequencies less than 10^8 Hz. Finally, there is space charge polarization, which is the transport of charge carriers until they strike a potential barrier such as a grain or phase boundary. This only contributes to dielectric effects at frequencies on the order of 10^2 Hz.

Connections can be made between the macroscopic properties of materials, such as the index of refraction, and the above effects. For example, for a non-magnetic dielectric, $n = \sqrt{\varepsilon_r}$. This is only valid when the same types of polarization are present when measuring ε_r and n. For example, this is the case in diamond and silicon.

There are 32 crystal classes, of which 11 possess centers of symmetry, which means they have no polar properties. The remaining 21 show polar effects when put under stress.

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Lecture 33: Electrical Properties, IV

Lecturer: Lane Martin	*28 November*	*Aditya Sengupta*

A uniform application of stress on one of the 11 centrosymmetric crystal types results in a small movement of charge symmetrically distributed about the center of symmetry. An application of electric field produces a strain, but this strain is unchanged when the field is reversed. This tells us the effect is quadratic in nature. This is called *electrostriction*.

Of the remaining non-centric classes, 20 exhibit electrical polarity when subjected to a stress. This effect is linear; if the stimulus is reversed, then the response also reverses. This is called the *piezoelectric effect*. Piezoelectricity works in reverse too: applying voltage induces a change in the dimensions of the materials. Piezoelectricity has applications in ultrasound and sonar.

Put another way, a piezoelectric is material that changes its polar configuration under pressure which changes the distribution of charge density on the surface, creating a potential difference on the surface. If you apply pressure, you get voltage. A ferroelectric is a piezoelectric material with an initial spontaneous dipole moment.

Polar crystals have spontaneous polarization, which cannot be detected by charges on the surface of the crystal, because the depolarizing field can be balanced by free charge within the crystal. 10 of the remaining crystal classes have this characteristic, of a polar axis causing spontaneous polarization. In general, spontaneous polarization is temperature dependent. Its existence can be investigated using the flow of charge to and from the surfaces under a change in temperature.

Pyroelectricity arises from this temperature dependence. It is shown by ferroelectrics. A change in polarization in a solid is accompanied by a change in surface charges, which can be detected by an induced current in an externally connected circuit. This external circuit neutralizes the surface charges if connected for a long enough time, because of the electrical conductivity of the material. This neutralization occurs after $t = \rho \varepsilon_r \varepsilon_0$.

The pyroelectric effect can be described by the electrical displacement applied to a polar material:

$$D = \varepsilon_0 E + P_{total} = \varepsilon_0 E + (P_s + P_{induced}) \tag{33.1}$$

wich can be differentiated with respect to temperature, assuming a temperature-invariant electric field, to get

$$\frac{\partial D}{\partial T} = \frac{\partial P_s}{\partial T} + E \frac{\partial \epsilon}{\partial T} \tag{33.2}$$

which gives us

$$p_g = p + E \frac{\partial \epsilon}{\partial T} \tag{33.3}$$

In this equation, p, which is defined as $\frac{\partial P_s}{\partial T}$, is the pyroelectric coefficient, and p_g is the *generalized* pyroelectric coefficient.

The polarization vector is the pyroelectric coefficient times the change in temperature. The pyroelectric coefficient has three components, $\Delta P_i = p_i \Delta T$ for $i = 1, 2, 3$.

The $E \frac{\partial \epsilon}{\partial T}$ component can contribute to the pyroelectric coefficient in all dielectrics, whether or not they are polar. Temperature coefficients of permittivity of ferroelectric/polar materials are high, therefore their contribution can be close to the intrinsic pyroelectric effect. Since pyroelectric materials are polar and piezoelectric, they undergo strain due to thermal expansion, resulting in additional contribution.

There is a threshold temperature above which ferroelectric materials are highly polar, called the Curie temperature. Materials lose their permanent magnetism and have this replaced by an induced magnetism; they go from being ferroelectric to paraelectric. This transition can be complicated; it involves going from a low-temperature tetragonal, orthorhombic, etc. structure to a high-temperature cubic structure. A material can undergo multiple structural transitions at multiple temperatures.

An induced electric field causes polarization in ferroelectrics in a nonlinear fashion to make a hysteresis loop, like observed in ferromagnets. Similarly to a Carnot cycle, in which work is derived from heat as input to a system, work can be derived through changes in polarization caused by a changing electric field. This is called an Ericsson cycle [citation needed].

A ferroelectric can switch between two stable states by applying an electric field. In this way, a ferroelectric has "memories".

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Lecture 34: The End

Lecturer: Lane Martin	*30 November*	*Aditya Sengupta*

34.1 Magnetic Properties - The Highlights

Magnetism comes from electronic motion and electronic spin. There are four types of responses: ferromagnetic systems have long-range parallel alignment of the atomic moment that results in a net magnetization even if there isn't an external field. Ferrimagnets have two types of magnetic moment, aligned antiparallel to one another. There is still a net magnetic moment in one direction, so it still looks like a ferromagnet. Antiferromagnets have magnetic dipoles that are aligned antiparallel; paramagnets are weakly positive, diamagnets are weakly negative.

Sorry, I've got a lab report. That's not exactly a dramatic ending to this document. Bye!