Material science

Chapter 1. INRODUCTION

1 .1 Historical Perspective

Materials are so important in the development of civilization that we associate Ages with them. In the origin of human life on Earth, the Stone Age, people used only natural materials, like stone, clay, skins, and wood. When people found copper and how to make it harder by alloying, the Bronze Age started about 3000 BC. The use of iron and steel, a stronger material that gave advantage in wars started at about 1200 BC. The next big step was the discovery of a cheap process to make steel around 1850, which enabled the railroads and the building of the modern infrastructure of the industrial world.

1.2 Materials Science and Engineering

Understanding of how materials behave like they do, and why they differ in properties was only possible with the atomistic understanding allowed by quantum mechanics, that first explained atoms and then solids starting in the 1930s. The combination of physics, chemistry, and the focus on the relationship between the properties of a material and its microstructure is the domain of Materials Science. The development of this science allowed designing materials and provided a knowledge base for the engineering applications (Materials Engineering).

Structure:

- At the atomic level: arrangement of atoms in different ways. (Gives different properties for graphite than diamond both forms of carbon.)
- At the microscopic level: arrangement of small grains of material that can be identified by microscopy. (Gives different optical properties to transparent vs. frosted glass.)

Properties are the way the material responds to the environment. For instance, the *mechanical, electrical and magnetic* properties are the responses to mechanical, electrical and magnetic forces, respectively. Other important properties are *thermal* (transmission of heat, heat capacity), *optical* (absorption, transmission and scattering of light), and the *chemical stability* in contact with the environment (like corrosion resistance).

Processing of materials is the application of heat (heat treatment), mechanical forces, etc. to affect their microstructure and, therefore, their properties.

1.3 Why Study Materials Science and Engineering?

- To be able to select a material for a given use based on considerations of cost and performance.
- To understand the limits of materials and the change of their properties with use.
- To be able to create a new material that will have some desirable properties.

All engineering disciplines need to know about materials. Even the most "immaterial", like software or system engineering depend on the development of new materials, which in turn alter the economics, like software-hardware trade-offs. Increasing applications of system engineering are in materials manufacturing (industrial engineering) and complex environmental systems.

1.4 Classification of Materials

Like many other things, materials are classified in groups, so that our brain can handle the complexity. One could classify them according to structure, or properties, or use. The one that we will use is according to the way the atoms are bound together:

Metals: valence electrons are detached from atoms, and spread in an 'electron sea' that "glues" the ions together. Metals are usually strong, conduct electricity and heat well and are opaque to light (shiny if polished). Examples: aluminum, steel, brass, gold.

Semiconductors: the bonding is covalent (electrons are shared between atoms). Their electrical properties depend extremely strongly on minute proportions of contaminants. They are opaque to visible light but transparent to the infrared. Examples: Si, Ge, GaAs.

Ceramics: atoms behave mostly like either positive or negative ions, and are bound by Coulomb forces between them. They are usually combinations of metals or semiconductors with oxygen, nitrogen or carbon (oxides, nitrides, and carbides). Examples: glass, porcelain, many minerals.

Polymers: are bound by covalent forces and also by weak van der Waals forces, and usually based on H, C and other non-metallic elements. They decompose at moderate temperatures (100 – 400 C), and are lightweight. Other properties vary greatly. Examples: plastics (nylon, Teflon, polyester) and rubber.

Other categories are not based on bonding. A particular microstructure identifies **composites,** made of different materials in intimate contact (example: fiberglass, concrete, wood) to achieve specific properties. **Biomaterials** can be any type of material that is biocompatible and used, for instance, to replace human body parts.

1.5 Advanced Materials

Materials used in "High-Tec" applications, usually designed for maximum performance, and normally expensive. Examples are titanium alloys for supersonic airplanes, magnetic alloys for computer disks, special ceramics for the heat shield of the space shuttle, etc.

1.6 Modern Material's Needs

- Engine efficiency increases at high temperatures: requires high temperature structural materials
- Use of nuclear energy requires solving problem with residues, or advances in nuclear waste processing.
- Hypersonic flight requires materials that are light, strong and resist high temperatures.
- Optical communications require optical fibers that absorb light negligibly.
- Civil construction – materials for unbreakable windows.
- Structures: materials that are strong like metals and resist corrosion like plastics.

Chapter 2. ATOMIC STRUCTURE AND BONDING

2.2 Fundamental Concepts

Atoms are composed of electrons, protons, and neutrons. Electron and protons are negative and positive charges of the same magnitude, 1.6×10^{-19} Coulombs.

The mass of the electron is negligible with respect to those of the proton and the neutron, which form the *nucleus* of the atom. The unit of mass is an atomic mass unit (amu) = 1.66×10^{-27} kg, and equals 1/12 the mass of a carbon atom. The Carbon nucleus has Z=6, and A=6, where Z is the number of protons, and A the number of neutrons. Neutrons and protons have very similar masses, roughly equal to 1 amu. A neutral atom has the same number of electrons and protons, Z.

A mole is the amount of matter that has a mass in grams equal to the atomic mass in amu of the atoms. Thus, a mole of carbon has a mass of 12 grams. The number of atoms in a mole is called the Avogadro number, $N_{av} = 6.023 \times 10^{23}$. Note that N_{av} = 1 gram/1 amu.

Calculating n, the number of atoms per cm^3 in a piece of material of density d (g/cm^3).

$n = N_{av} \times d / M$

where M is the atomic mass in amu (grams per mol). Thus, for graphite (carbon) with a density $d = 1.8\ g/cm^3$, M =12, we get 6×10^{23} atoms/mol × 1.8 g/cm^3 / 12 g/mol) = 9×10^{22} C/cm^3.

For a molecular solid like ice, one uses the molecular mass, $M(H_2O) = 18$. With a density of 1 g/cm^3, one obtains $n = 3.3 \times 10^{22}$ H_2O/cm^3. Note that since the water molecule contains 3 atoms, this is equivalent to 9.9×10^{22} atoms/cm^3.

Most solids have atomic densities around 6×10^{22} atoms/cm^3. The cube root of that number gives the number of atoms per centimeter, about 39 million. The mean distance between atoms is the inverse of that, or 0.25 nm. This is an important number that gives the scale of atomic structures in solids.

2.3 Electrons in Atoms

The forces in the atom are repulsions between electrons and attraction between electrons and protons. The neutrons play no significant role. Thus, Z is what characterizes the atom.

The electrons form a cloud around the neutron, of radius of 0.05 – 2 nanometers. Electrons do not move in circular orbits, as in popular drawings, but in 'fuzzy' orbits. We cannot tell how it moves, but only say what is the probability of finding it at some distance from the nucleus. According to quantum mechanics, only certain orbits are allowed (thus, the idea of a mini planetary system is not correct). The orbits are identified by a principal quantum number *n*, which can be related to the size, n = 0 is the smallest; n = 1, 2 .. are larger. (They are "quantized" or discrete, being specified by integers). The angular momentum *l* is quantized, and so is the projection in a specific direction *m*. The structure of the atom is determined by the *Pauli exclusion principle*, only two electrons can be placed in an orbit with a given *n, l, m* – one for each spin. Table 2.1 in the textbook gives the number of electrons in each *shell* (given by *n*) and subshells (given by *l*).

2.4 The Periodic Table

Elements are categorized by placing them in the periodic table. Elements in a column share similar properties. The noble gases have *closed shells*, and so they do not gain or lose electrons near another atom. Alkalis can easily lose an electron and become a closed shell; halogens can easily gain one to form a negative ion, again with a closed shell. The propensity to form closed shells occurs in molecules, when they share electrons to close a molecular shell. Examples are H_2, N_2, and NaCl.

The ability to gain or lose electrons is termed electronegativity or electropositivity, an important factor in ionic bonds.

2.5 Bonding Forces and Energies

The Coulomb forces are simple: attractive between electrons and nuclei, repulsive between electrons and between nuclei. The force between atoms is given by a sum of all the individual forces, and the fact that the electrons are located outside the atom and the nucleus in the center.

When two atoms come very close, the force between them is always repulsive, because the electrons stay outside and the nuclei repel each other. Unless both atoms are ions of the same charge (e.g., both negative) the forces between atoms is always attractive at large internuclear distances r. Since the force is repulsive at small r, and attractive at small r, there is a distance at which the force is zero. This is the equilibrium distance at which the atoms prefer to stay.

The interaction energy is the *potential* energy between the atoms. It is negative if the atoms are bound and positive if they can move away from each other. The interaction energy is the integral of the force over the separation distance, so these two quantities are directly related. The interaction energy is a *minimum* at the equilibrium position. This value of the energy is called the *bond energy*, and is the energy needed to separate completely to infinity (the work that needs to be done to overcome the attractive force.) The strongest the bond energy, the hardest is to move the atoms, for instance the hardest it is to melt the solid, or to evaporate its atoms.

2.6 Primary Interatomic Bonds

Ionic Bonding

This is the bond when one of the atoms is negative (has an extra electron) and another is positive (has lost an electron). Then there is a strong, direct Coulomb attraction. An example is NaCl. In the molecule, there are more electrons around Cl, forming Cl^- and less around Na, forming Na^+. Ionic bonds are the strongest bonds. In real solids, ionic bonding is usually combined with covalent bonding. In this case, the fractional ionic bonding is defined as $\%\text{ionic} = 100 \times [1 - \exp(-0.25\,(X_A - X_B)^2]$, where X_A and X_B are the electronegativities of the two atoms, A and B, forming the molecule.

Covalent Bonding

In covalent bonding, electrons are shared between the molecules, to saturate the valency. The simplest example is the H_2 molecule, where the electrons spend more time in between the nuclei than outside, thus producing bonding.

Metallic Bonding

In metals, the atoms are ionized, loosing some electrons from the valence band. Those electrons form a *electron sea*, which binds the charged nuclei in place, in a similar way that the electrons in between the H atoms in the H_2 molecule bind the protons.

2.7 Secondary Bonding (Van der Waals)

Fluctuating Induced Dipole Bonds

Since the electrons may be on one side of the atom or the other, a dipole is formed: the + nucleus at the center, and the electron outside. Since the electron moves, the dipole fluctuates. This fluctuation in atom A produces a fluctuating electric field that is felt by the electrons of an adjacent atom, B. Atom B then polarizes so that its outer electrons are on the side of the atom closest to the + side (or opposite to the – side) of the dipole in A. This bond is called van der Waals bonding.

Polar Molecule-Induced Dipole Bonds

A polar molecule like H_2O (Hs are partially +, O is partially –), will induce a dipole in a nearby atom, leading to bonding.

Permanent Dipole Bonds

This is the case of the hydrogen bond in ice. The H end of the molecule is positively charged and can bond to the negative side of another dipolar molecule, like the O side of the H_2O dipole.

2.8 Molecules

If molecules formed a closed shell due to covalent bonding (like H_2, N_2) then the interaction between molecules is weak, of the van der Waals type. Thus, molecular solids usually have very low melting points.

Chapter-3: STRUCTURE OF CRYSTALS

3.2 Fundamental Concepts

Atoms self-organize in *crystals*, most of the time. The crystalline lattice, is a periodic array of the atoms. When the solid is not crystalline, it is called amorphous. Examples of crystalline solids are metals, diamond and other precious stones, ice, graphite. Examples of amorphous solids are glass, amorphous carbon (a-C), amorphous Si, most plastics

To discuss crystalline structures it is useful to consider atoms as being hard spheres, with well-defined radii. In this scheme, the shortest distance between two like atoms is one diameter.

3.3 Unit Cells

The unit cell is the smallest structure that repeats itself by translation through the crystal. We construct these symmetrical units with the hard spheres. The most common types of unit cells are the faced-centered cubic (FCC), the body-centered cubic (FCC) and the hexagonal close-packed (HCP). Other types exist, particularly among minerals. The simple cube (SC) is often used for didactical purpose, no material has this structure.

3.4 Metallic Crystal Structures

Important properties of the unit cells are

- The type of atoms and their radii *R*.
- cell dimensions (side *a* in cubic cells, side of base *a* and height *c* in HCP) in terms of *R*.
- *n*, number of atoms per unit cell. For an atom that is shared with *m* adjacent unit cells, we only count a fraction of the atom, 1/*m*.
- *CN*, the coordination number, which is the number of closest neighbors to which an atom is bonded.
- *APF*, the atomic packing factor, which is the fraction of the volume of the cell actually occupied by the hard spheres. *APF* = Sum of atomic volumes/Volume of cell.

Unit Cell	*n*	*CN*	*a*/*R*	*APF*
SC	1	6	2	0.52
BCC	2	8	4Ö 3	0.68
FCC	4	12	2Ö 2	0.74
HCP	6	12		0.74

The closest packed direction in a BCC cell is along the diagonal of the cube; in a FCC cell is along the diagonal of a face of the cube.

3.5 Density Computations

The density of a solid is that of the unit cell, obtained by dividing the mass of the atoms (*n atoms* x M_{atom}) and dividing by V_c the volume of the cell (a^3 in the case of a cube). If the mass of the atom is given in amu (*A*), then we have to divide it by the Avogadro number to get M_{atom}. Thus, the formula for the density is:

3.6 Polymorphism and Allotropy

Some materials may exist in more than one crystal structure, this is called polymorphism. If the material is an elemental solid, it is called allotropy. An example of allotropy is carbon, which can exist as diamond, graphite, and amorphous carbon.

3.11 Close-Packed Crystal Structures

The FCC and HCP are related, and have the same *APF*. They are built by packing spheres on top of each other, in the hollow sites (Fig. 3.12 of book). The packing is alternate between two types of sites, *ABABAB*.. in the HCP structure, and alternates between three types of positions, *ABCABC…* in the FCC crystals.

Crystalline and Non-Crystalline Materials

3.12 Single Crystals

Crystals can be *single crystals* where the whole solid is one crystal. Then it has a regular geometric structure with flat faces.

3.13 Polycrystalline Materials

A solid can be composed of many crystalline grains, not aligned with each other. It is called *polycrystalline*. The grains can be more or less aligned with respect to each other. Where they meet is called a *grain boundary*.

3.14 Anisotropy

Different directions in the crystal have a different packing. For instance, atoms along the edge FCC crystals are more separated than along the face diagonal. This causes *anisotropy* in the properties of crystals; for instance, the deformation depends on the direction in which a stress is applied.

3.15 X-Ray Diffraction Determination of Crystalline Structure – not covered

3.16 Non-Crystalline Solids

In amorphous solids, there is no long-range order. But amorphous does not mean random, since the distance between atoms cannot be smaller than the size of the hard spheres. Also, in many cases there is some form of short-range order. For instance, the tetragonal order of crystalline SiO_2 (quartz) is still apparent in amorphous SiO_2 (silica glass.)

Chapter-4: IMPERFECTIONS

Imperfections in Solids

4.1 Introduction

Materials are often stronger when they have defects. The study of defects is divided according to their dimension:

0D (zero dimension) – point defects: vacancies and interstitials. Impurities.

1D – linear defects: dislocations (edge, screw, mixed)

2D – grain boundaries, surfaces.

3D – extended defects: pores, cracks.

Point Defects

4.2 Vacancies and Self-Interstitials

A vacancy is a lattice position that is vacant because the atom is missing. It is created when the solid is formed. There are other ways of making a vacancy, but they also occur naturally as a result of thermal vibrations.

An interstitial is an atom that occupies a place outside the normal lattice position. It may be the same type of atom as the others (self interstitial) or an impurity atom.

In the case of vacancies and interstitials, there is a change in the coordination of atoms around the defect. This means that the forces are not balanced in the same way as for other atoms in the solid, which results in lattice distortion around the defect.

The number of vacancies formed by thermal agitation follows the law:

$$N_V = N_A \times \exp(-Q_V/kT)$$

where N_A is the total number of atoms in the solid, Q_V is the energy required to form a vacancy, k is Boltzmann constant, and T the temperature in Kelvin (note, not in ^{o}C or ^{o}F).

When Q_V is given in joules, $k = 1.38 \times 10^{-23}$ J/atom-K. When using eV as the unit of energy, $k = 8.62 \times 10^{-5}$ eV/atom-K.

Note that kT(300 K) = 0.025 eV (room temperature) is much smaller than typical vacancy formation energies. For instance, Q_V(Cu) = 0.9 eV/atom. This means that N_V/N_A at room temperature is $\exp(-36) = 2.3 \times 10^{-16}$, an insignificant number. Thus, a high temperature is needed to have a high *thermal* concentration of vacancies. Even so, N_V/N_A is typically only about 0.0001 at the melting point.

4.3 Impurities in Solids

All real solids are impure. A very high purity material, say 99.9999% pure (called 6N – six nines) contains ~ 6×10^{16} impurities per cm^3.

Impurities are often added to materials to improve the properties. For instance, carbon added in small amounts to iron makes steel, which is stronger than iron. Boron impurities added to silicon drastically change its electrical properties.

Solid solutions are made of a host, the solvent or matrix) which dissolves the solute (minor component). The ability to dissolve is called *solubility*. Solid solutions are:

- homogeneous
- maintain crystal structure
- contain randomly dispersed impurities (substitutional or interstitial)

Factors for high solubility

- Similar atomic size (to within 15%)
- Similar crystal structure
- Similar electronegativity (otherwise a compound is formed)
- Similar valence

Composition can be expressed in weight percent, useful when making the solution, and in atomic percent, useful when trying to understand the material at the atomic level.

Miscellaneous Imperfections

4.4 Dislocations—Linear Defects

Dislocations are abrupt changes in the regular ordering of atoms, along a line (dislocation line) in the solid. They occur in high density and are very important in mechanical properties of material. They are characterized by the Burgers vector, found by doing a loop around the dislocation line and noticing the extra interatomic spacing needed to close the loop. The Burgers vector in metals points in a close packed direction.

Edge dislocations occur when an extra plane is inserted. The dislocation line is at the end of the plane. In an edge dislocation, the Burgers vector is perpendicular to the dislocation line.

Screw dislocations result when displacing planes relative to each other through shear. In this case, the Burgers vector is parallel to the dislocation line.

4.5 Interfacial Defects

The environment of an atom at a surface differs from that of an atom in the bulk, in that the number of neighbors (coordination) decreases. This introduces unbalanced forces which result in *relaxation* (the lattice spacing is decreased) or *reconstruction* (the crystal structure changes).

The density of atoms in the region including the grain boundary is smaller than the bulk value, since void space occurs in the interface.

Surfaces and interfaces are very reactive and it is usual that impurities segregate there. Since energy is required to form a surface, grains tend to grow in size at the expense of smaller grains to minimize energy. This occurs by diffusion, which is accelerated at high temperatures.

Twin boundaries: *not covered*

4.6 Bulk or Volume Defects

A typical volume defect is porosity, often introduced in the solid during processing. A common example is snow, which is highly porous ice.

4.7 Atomic Vibrations

Atomic vibrations occur, even at zero temperature (a quantum mechanical effect) and increase in amplitude with temperature. Vibrations displace *transiently* atoms from their regular lattice site, which destroys the perfect periodicity we discussed in Chapter 3.

Chapter-5: DIFUSSION

5.1 Introduction

Many important reactions and processes in materials occur by the motion of atoms in the solid (transport), which happens by diffusion.

Inhomogeneous materials can become homogeneous by diffusion, if the temperature is high enough (temperature is needed to overcome energy barriers to atomic motion.

5.2 Diffusion Mechanisms

Atom diffusion can occur by the motion of vacancies (vacancy diffusion) or impurities (impurity diffusion). The energy barrier is that due to nearby atoms which need to move to let the atoms go by. This is more easily achieved when the atoms vibrate strongly, that is, at high temperatures.

There is a difference between diffusion and net diffusion. In a homogeneous material, atoms also diffuse but this motion is hard to detect. This is because atoms move randomly and there will be an equal number of atoms moving in one direction than in another. In inhomogeneous materials, the effect of diffusion is readily seen by a change in concentration with time. In this case there is a *net* diffusion. Net diffusion occurs because, although all atoms are moving randomly, there are more atoms moving in regions where their concentration is higher.

5.3 Steady-State Diffusion

The flux of diffusing atoms, J, is expressed either in number of atoms per unit area and per unit time (e.g., atoms/m^2-second) or in terms of mass flux (e.g., kg/m^2-second).

Steady state diffusion means that J does not depend on time. In this case, Fick's first law holds that the flux along direction x is:

$$J = -D\, dC/dx$$

Where dC/dx is the gradient of the concentration C, and D is the diffusion constant. The concentration gradient is often called the *driving force* in diffusion (but it is not a force in the mechanistic sense). The minus sign in the equation means that diffusion is down the concentration gradient.

5.4 Nonsteady-State Diffusion

This is the case when the diffusion flux depends on time, which means that a type of atoms accumulates in a region or that it is depleted from a region (which may cause them to accumulate in another region).

5.5 Factors That Influence Diffusion

As stated above, there is a barrier to diffusion created by neighboring atoms that need to move to let the diffusing atom pass. Thus, atomic vibrations created by temperature assist diffusion.

Also, smaller atoms diffuse more readily than big ones, and diffusion is faster in open lattices or in open directions. Similar to the case of vacancy formation, the effect of temperature in diffusion is given by a Boltzmann factor: $D = D_0 \times \exp(-Q_d/kT)$.

5.6 Other Diffusion Paths

Diffusion occurs more easily along surfaces, and voids in the material (short circuits like dislocations and grain boundaries) because less atoms need to move to let the diffusing atom pass. Short circuits are often unimportant because they constitute a negligible part of the total area of the material normal to the diffusion flux. .

Chapter-6: Mechanical Properties of Metals

1. Introduction

Often materials are subject to forces (loads) when they are used. Mechanical engineers calculate those forces and material scientists how materials deform (elongate, compress, twist) or break as a function of applied load, time, temperature, and other conditions.

Materials scientists learn about these mechanical properties by testing materials. Results from the tests depend on the size and shape of material to be tested (specimen), how it is held, and the way of performing the test. That is why we use common procedures, or *standards*, which are published by the ASTM.

2. Concepts of Stress and Strain

To compare specimens of different sizes, the load is calculated per unit area, also called normalization to the area. Force divided by area is called stress. In tension and compression tests, the relevant area is that perpendicular to the force. In shear or torsion tests, the area is perpendicular to the axis of rotation.

$\mathbf{s} = F/A_0$ tensile or compressive stress

$\mathbf{t} = F/A_0$ shear stress

The unit is the Megapascal = 10^6 Newtons/m^2.

There is a change in dimensions, or deformation elongation, DL as a result of a tensile or compressive stress. To enable comparison with specimens of different length, the elongation is also normalized, this time to the length L. This is called strain, e.

$\mathbf{e} = \mathbf{D}L/L$

The change in dimensions is the reason we use A_0 to indicate the initial area since it changes during deformation. One could divide force by the actual area, this is called true stress (see Sec. 6.7).

For torsional or shear stresses, the deformation is the angle of twist, q (Fig. 6.1) and the shear strain is given by:

$\mathbf{g} = \mathbf{tg}\ \mathbf{q}$

3. Stress—Strain Behavior

Elastic deformation. When the stress is removed, the material returns to the dimension it had before the load was applied. Valid for small strains (except the case of rubbers).

Deformation is *reversible, non permanent*

Plastic deformation. When the stress is removed, the material does not return to its previous dimension but there is a *permanent*, irreversible deformation.

In tensile tests, if the deformation is *elastic*, the stress-strain relationship is called Hooke's law:

$$\mathbf{s} = E\,\mathbf{e}$$

That is, *E* is the slope of the stress-strain curve. E is *Young's modulus* or *modulus of elasticity*. In some cases, the relationship is not linear so that E can be defined alternatively as the local slope:

$$E = \mathbf{ds/de}$$

Shear stresses produce strains according to:

$$\mathbf{t} = G\,\mathbf{g}$$

where *G* is the *shear modulus*.

Elastic moduli measure the *stiffness* of the material. They are related to the *second* derivative of the interatomic potential, or the first derivative of the force vs. internuclear distance (Fig. 6.6). By examining these curves we can tell which material has a higher modulus. Due to thermal vibrations the elastic modulus decreases with temperature. *E* is large for ceramics (stronger ionic bond) and small for polymers (weak covalent bond). Since the interatomic distances depend on direction in the crystal, *E* depends on direction (i.e., it is anisotropic) for single crystals. For *randomly* oriented policrystals, *E* is isotropic.

4. Anelasticity

Here the behavior is elastic but not the stress-strain curve is not immediately reversible. It takes a while for the strain to return to zero. The effect is normally small for metals but can be significant for polymers.

5. Elastic Properties of Materials

Materials subject to tension shrink laterally. Those subject to compression, bulge. The ratio of lateral and axial strains is called the *Poisson's ratio* n.

$$\mathbf{n} = \mathbf{e}_{\mathbf{lateral}}/\mathbf{e}_{\mathbf{axial}}$$

The elastic modulus, shear modulus and Poisson's ratio are related by $E = 2G(1+n)$

6. Tensile Properties

Yield point. If the stress is too large, the strain deviates from being proportional to the stress. The point at which this happens is the *yield point* because there the material yields, deforming permanently (plastically).

Yield stress. Hooke's law is not valid beyond the yield point. The stress at the yield point is called *yield stress*, and is an important measure of the mechanical properties of materials. In practice, the yield stress is chosen as that causing a permanent strain of 0.002 (strain offset, Fig. 6.9.)

The yield stress measures the resistance to plastic deformation.

The reason for plastic deformation, in normal materials, is not that the atomic bond is stretched beyond repair, but the motion of dislocations, which involves breaking and reforming bonds.

Plastic deformation is caused by the motion of dislocations.

Tensile strength. When stress continues in the plastic regime, the stress-strain passes through a maximum, called the *tensile strength* (s_{TS}) , and then falls as the material starts to develop a *neck* and it finally breaks at the *fracture point* (Fig. 6.10).

Note that it is called strength, not stress, but the units are the same, MPa.

For structural applications, the yield stress is usually a more important property than the tensile strength, since once the it is passed, the structure has deformed beyond acceptable limits.

Ductility. The ability to deform before braking. It is the opposite of **brittleness**. Ductility can be given either as percent maximum elongation e_{max} or maximum area reduction.

$$\%EL = e_{max} \times 100\ \%$$

$$\%AR = (A_0 - A_f)/A_0$$

These are measured after fracture (repositioning the two pieces back together).

Resilience. Capacity to absorb energy *elastically*. The energy per unit volume is the

area under the strain-stress curve in the elastic region.

Toughness. Ability to absorb energy up to fracture. The energy per unit volume is the *total area under the strain-stress curve*. It is measured by an impact test (Ch. 8).

7. True Stress and Strain

When one applies a constant tensile force the material will break after reaching the tensile strength. The material starts necking (the transverse area decreases) but the stress cannot increase beyond s_{TS}. The ratio of the force to the initial area, what we normally do, is called the engineering stress. If the ratio is to the actual area (that changes with stress) one obtains the *true stress.*

8. Elastic Recovery During Plastic Deformation

If a material is taken beyond the yield point (it is deformed plastically) and the stress is then released, the material ends up with a permanent strain. If the stress is reapplied, the material again responds elastically at the beginning up to a new yield point *that is higher than the original yield point* (strain hardening, Ch. 7.10). The amount of elastic strain that it will take before reaching the yield point is called *elastic strain recovery* (Fig. 6. 16).

9. Compressive, Shear, and Torsional Deformation

Compressive and shear stresses give similar behavior to tensile stresses, but in the case of compressive stresses there is no maximum in the s-e curve, since no necking occurs.

10. Hardness

Hardness is the resistance to plastic deformation (e.g., a local dent or scratch). Thus, it is a measure of *plastic* deformation, as is the tensile strength, so they are well correlated. Historically, it was measured on an empirically scale, determined by the ability of a material to scratch another, diamond being the hardest and talc the softer. Now we use standard tests, where a ball, or point is pressed into a material and the size of the dent is measured. There are a few different hardness tests: Rockwell, Brinell, Vickers, etc. They are popular because they are easy and non-destructive (except for the small dent).

11. Variability of Material Properties

Tests do not produce exactly the same result because of variations in the test equipment, procedures, operator bias, specimen fabrication, etc. But, even if all those parameters are controlled within strict limits, a variation remains in the materials, due to uncontrolled variations during fabrication, non homogenous composition and structure, etc. The measured mechanical properties will show scatter, which is often distributed in a Gaussian curve (bell-shaped), that is characterized by the mean value and the standard deviation (width).

12. Design/Safety Factors

To take into account variability of properties, designers use, instead of an average value of, say, the tensile strength, the probability that the yield strength is above the minimum value tolerable. This leads to the use of a *safety factor* $N > 1$ (typ. 1.2 - 4). Thus, a working value for the tensile strength would be $s_W = s_{TS} / N$.

Not tested: *true stress-true stain relationships, details of the different types of hardness tests, but should know that hardness for a given material correlates with tensile strength. Variability of material properties*

Chapter 7. DISLOCATIONS AND STRENGTHENING MECHANISM

1. Introduction

The key idea of the chapter is that plastic deformation is due to the motion of a large number of dislocations. The motion is called slip. Thus, the strength (resistance to deformation) can be improved by putting obstacles to slip.

2. Basic Concepts

Dislocations can be *edge dislocations*, *screw dislocations* and exist in combination of the two (Ch. 4.4). Their motion (slip) occurs by sequential bond breaking and bond reforming (Fig. 7.1). The number of dislocations per unit volume is the *dislocation density*, in a plane they are measured per unit area.

3. Characteristics of Dislocations

There is strain around a dislocation which influences how they interact with other dislocations, impurities, etc. There is *compression* near the extra plane (higher atomic density) and *tension* following the dislocation line (Fig. 7.4)

Dislocations interact among themselves (Fig. 7.5). When they are in the same plane, they repel if they have the same sign and annihilate if they have opposite signs (leaving behind a perfect crystal). In general, when dislocations are close and their strain fields add to a larger value, they repel, because being close increases the potential energy (it takes energy to strain a region of the material).

The number of dislocations increases dramatically during plastic deformation. Dislocations spawn from existing dislocations, and from defects, grain boundaries and surface irregularities.

4. Slip Systems

In single crystals there are preferred planes where dislocations move (slip planes). There they do not move in any direction, but in preferred crystallographic directions (slip direction). The set of slip planes and directions constitute slip systems.

The slip planes are those of highest packing density. How do we explain this? Since the distance between atoms is shorter than the average, the distance perpendicular to the plane has to be longer than average. Being relatively far apart, the atoms can move more easily with respect to the atoms of the adjacent plane. (We did not discuss direction and plane nomenclature for slip systems.)

BCC and FCC crystals have more slip systems, that is more ways for dislocation to propagate. Thus, those crystals are more ductile than HCP crystals (HCP crystals are more brittle).

5. Slip in Single Crystals

A tensile stress s will have components in any plane that is not perpendicular to the stress. These components are *resolved shear stresses*. Their magnitude depends on orientation (see Fig. 7.7).

$$t_{\mathbf{R}} = s \cos f \cos l$$

If the shear stress reaches the *critical resolved shear stress* t_{CRSS}, slip (plastic deformation) can start. The stress needed is:

$$s_{\mathbf{y}} = t_{\mathbf{CRSS}} / (\cos f \cos l)_{\mathbf{max}}$$

at the angles at which t_{CRSS} is a maximum. The minimum stress needed for yielding is when $f = l = 45$ degrees: $s_{\mathbf{y}} = 2t_{\mathbf{CRSS}}$. Thus, dislocations will occur first at slip planes oriented close to this angle with respect to the applied stress (Figs. 7.8 and 7.9).

6. Plastic Deformation of Polycrystalline Materials

Slip directions vary from crystal to crystal. When plastic deformation occurs in a grain, it will be constrained by its neighbors which may be less favorably oriented. As a result, *polycrystalline metals are stronger than single crystals* (the exception is the perfect single crystal, as in whiskers.)

7. Deformation by Twinning

This topic is not included.

Mechanisms of Strengthening in Metals

General principles. Ability to deform plastically depends on ability of dislocations to move. Strengthening consists in hindering dislocation motion. We discuss the methods of grain-size reduction, solid-solution alloying and strain hardening. These are for single-phase metals. We discuss others when treating alloys. Ordinarily, strengthening reduces ductility.

8. Strengthening by Grain Size Reduction

This is based on the fact that it is difficult for a dislocation to pass into another grain, especially if it is very misaligned. Atomic disorder at the boundary causes discontinuity in slip planes. For high-angle grain boundaries, stress at end of slip plane may trigger new dislocations in adjacent grains. Small angle grain boundaries are not effective in blocking dislocations.

The finer the grains, the larger the area of grain boundaries that impedes dislocation motion. Grain-size reduction usually improves toughness as well. Usually, the yield strength varies with grain size d according to:

$$s_{\mathbf{y}} = s_{\mathbf{0}} + k_{\mathbf{y}} / d^{\mathbf{1/2}}$$

Grain size can be controlled by the rate of solidification and by plastic deformation.

9. Solid-Solution Strengthening

Adding another element that goes into interstitial or substitutional positions in a solution increases strength. The impurity atoms cause lattice strain (Figs. 7.17 and 7.18) which can "anchor" dislocations. This occurs when the strain caused by the alloying element compensates that of the dislocation, thus achieving a state of low potential energy. It costs strain energy for the dislocation to move away from this state (which is like a potential well). The scarcity of energy at low temperatures is why slip is hindered.

Pure metals are almost always softer than their alloys.

10. Strain Hardening

Ductile metals become stronger when they are deformed plastically at temperatures well below the melting point (**cold working**). (This is different from hot working is the shaping of materials at high temperatures where large deformation is possible.) Strain hardening (work hardening) is the reason for the elastic recovery discussed in Ch. 6.8.

The reason for strain hardening is that the dislocation density increases with plastic deformation (cold work) due to multiplication. The average distance between dislocations then decreases and dislocations start blocking the motion of each one.

The measure of strain hardening is the percent cold work (%CW), given by the relative reduction of the original area, A_0 to the final value A_d :

$$\mathbf{\%CW = 100\ (A_0 - A_d)/A_0}$$

Recovery, recrystallization and Grain Growth

Plastic deformation causes 1) change in grain size, 2) strain hardening, 3) increase in the dislocation density. Restoration to the state before cold-work is done by heating through two processes: recovery and recrystallization. These may be followed by grain growth.

11. Recovery

Heating à increased diffusion à enhanced dislocation motion à relieves internal strain energy and reduces the number of dislocation. The electrical and thermal conductivity are restored to the values existing before cold working.

12. Recrystallization

Strained grains of cold-worked metal are replaced, upon heating, by more regularly-spaced grains. This occurs through short-range diffusion enabled by the high temperature. Since recrystallization occurs by diffusion, the important parameters are both temperature and time.

The material becomes softer, weaker, but more ductile (Fig. 7.22).

Recrystallization temperature: is that at which the process is complete in one hour. It is typically 1/3 to 1/2 of the melting temperature. It falls as the %CW is increased. Below a "critical deformation", recrystallization does not occur.

13. **Grain Growth**

The growth of grain size with temperature can occur in all polycrystalline materials. It occurs by migration of atoms at grain boundaries by diffusion, thus grain growth is faster at higher temperatures. The "driving force" is the reduction of energy, which is proportional to the total area. Big grains grow at the expense of the small ones.

Chapter 8. FAILURE

1. Introduction

Failure of materials may have huge costs. Causes included improper materials selection or processing, the improper design of components, and improper use.

2. Fundamentals of Fracture

Fracture is a form of failure where the material separates in pieces due to stress, at temperatures below the melting point. The fracture is termed ductile or brittle depending on whether the elongation is large or small.

Steps in fracture (response to stress):

- track formation
- track propagation

Ductile vs. brittle fracture

	Ductile	**Brittle**
deformation	extensive	little
track propagation	slow, needs stress	fast
type of materials	most metals (not too cold)	ceramics, ice, cold metals
warning	permanent elongation	none
strain energy	higher	lower
fractured surface	rough	smoother
necking	yes	no

- **Ductile Fracture**

Stages of ductile fracture

- Initial necking
- small cavity formation (microvoids)
- void growth (elipsoid) by coalescence into a crack
- fast crack propagation around neck. Shear strain at 45^{o}
- final shear fracture (cup and cone)

The interior surface is fibrous, irregular, which signify plastic deformation.

- **Brittle Fracture**

There is no appreciable deformation, and crack propagation is very fast. In most brittle materials, crack propagation (by bond breaking) is along specific crystallographic planes (*cleavage* planes). This type of fracture is transgranular (through grains) producing grainy texture (or faceted texture) when cleavage direction changes from grain to grain. In some materials, fracture is intergranular.

5. Principles of Fracture Mechanics

Fracture occurs due to *stress concentration* at flaws, like surface scratches, voids, etc. If *a* is the length of the void and r the radius of curvature, the enhanced stress near the flaw is:

s_m » 2 s_0 $(a/r)^{1/2}$

where s_0 is the applied macroscopic stress. Note that *a* is 1/2 the length of the flaw, not the full length for an internal flaw, but the full length for a surface flaw. The stress concentration factor is:

$K_t = s_m/s_0$ » 2 $(a/r)^{1/2}$

Because of this enhancement, flaws with small radius of curvature are called *stress raisers.*

6. Impact Fracture Testing

Normalized tests, like the Charpy and Izod tests measure the *impact energy* required to fracture a notched specimen with a hammer mounted on a pendulum. The energy is measured by the change in potential energy (height) of the pendulum. This energy is called *notch toughness.*

Ductile to brittle transition occurs in materials when the temperature is dropped below a *transition temperature.* Alloying usually increases the ductile-brittle transition temperature (Fig. 8.19.) For ceramics, this type of transition occurs at much higher temperatures than for metals.

Fatigue

Fatigue is the catastrophic failure due to dynamic (fluctuating) stresses. It can happen in bridges, airplanes, machine components, etc. The characteristics are:

- long period of cyclic strain
- the most usual (90%) of metallic failures (happens also in ceramics and polymers)
- is brittle-like even in ductile metals, with little plastic deformation
- it occurs in stages involving the initiation and propagation of cracks.

- **Cyclic Stresses**

These are characterized by *maximum*, *minimum* and *mean stress, the stress amplitude*, and the *stress ratio* (Fig. 8.20).

- **The *S—N* Curve**

S—N curves (stress-number of cycles to failure) are obtained using apparatus like the one shown in Fig. 8.21. Different types of *S—N* curves are shown in Fig. 8.22.

Fatigue limit (endurance limit) occurs for *some* materials (like some ferrous and Ti allows). In this case, the *S—N* curve becomes horizontal at large *N* . This means that there is a maximum stress amplitude (the fatigue limit) below which the material never fails, no matter how large the number of cycles is.

For other materials (e.g., non-ferrous) the *S—N* curve continues to fall with *N*.

Failure by fatigue shows substantial *variability* (Fig. 8.23).

Failure at low loads is in the elastic strain regime, requires a large number of cycles (typ. 10^4 to 10^5). At high loads (plastic regime), one has low-cycle fatigue ($N < 10^4 - 10^5$ cycles).

- **Crack Initiation and Propagation**

Stages is fatigue failure:

I. crack initiation at high stress points (stress raisers)

II. propagation (incremental in each cycle)

III. final failure by fracture

$N_{\text{final}} = N_{\text{initiation}} + N_{\text{propagation}}$

Stage I - propagation

- slow
- along crystallographic planes of high shear stress
- flat and featureless fatigue surface

Stage II - propagation

crack propagates by repetive plastic blunting and sharpening of the crack tip. (Fig. 8.25.)

- . Crack Propagation Rate (not covered)

- **. Factors That Affect Fatigue Life**

- Mean stress (lower fatigue life with increasing s_{mean}).
- Surface defects (scratches, sharp transitions and edges). Solution:

- polish to remove machining flaws
- add *residual compressive stress* (e.g., by shot peening.)
- case harden, by carburizing, nitriding (exposing to appropriate gas at high temperature)

- **. Environmental Effects**

- Thermal cycling causes expansion and contraction, hence thermal stress, if component is restrained. Solution:

  - eliminate restraint by design
  - use materials with low thermal expansion coefficients.

- Corrosion fatigue. Chemical reactions induced pits which act as stress raisers. Corrosion also enhances crack propagation. Solutions:

  - decrease corrosiveness of medium, if possible.
  - add protective surface coating.
  - add residual compressive stresses.

Creep

Creep is the time-varying plastic deformation of a material stressed at high temperatures. Examples: turbine blades, steam generators. Keys are the time dependence of the strain and the high temperature.

- **. Generalized Creep Behavior**

At a constant stress, the strain increases initially fast with time (primary or transient deformation), then increases more slowly in the secondary region at a steady rate (creep rate). Finally the strain increases fast and leads to failure in the tertiary region. Characteristics:

- *Creep rate*: de/dt
- *Time to failure.*

- **. Stress and Temperature Effects**

Creep becomes more pronounced at higher temperatures (Fig. 8.37). There is essentially no creep at temperatures below 40% of the melting point.

Creep increases at higher applied stresses.

The behavior can be characterized by the following expression, where K, n and Q_c are constants for a given material:

$$de/dt = K s^n \exp(-Q_c/RT)$$

- . Data Extrapolation Methods (not covered.)
- . **Alloys for High-Temperature Use**

These are needed for turbines in jet engines, hypersonic airplanes, nuclear reactors, etc. The important factors are a high melting temperature, a high elastic modulus and large grain size (the latter is opposite to what is desirable in low-temperature materials).

Some creep resistant materials are stainless steels, refractory metal alloys (containing elements of high melting point, like Nb, Mo, W, Ta), and superalloys (based on Co, Ni, Fe.)

Chapter-9: PHASE DIAGRAMS

9.1 Introduction

Definitions

Component: pure metal or compound (e.g., Cu, Zn in Cu-Zn alloy, sugar, water, in a syrup.)

Solvent: host or major component in solution.

Solute: dissolved, minor component in solution.

System: set of possible alloys from same component (e.g., iron-carbon system.)

Solubility Limit: Maximum solute concentration that can be dissolved at a given temperature.

Phase: part with homogeneous physical and chemical characteristics

9.2 Solubility Limit

Effect of temperature on solubility limit. Maximum content: saturation. Exceeding maximum content (like when cooling) leads to precipitation.

9.3 Phases

One-phase systems are homogeneous. Systems with two or more phases are heterogeneous, or mixtures. This is the case of most metallic alloys, but also happens in ceramics and polymers.

A two-component alloy is called binary. One with three components, ternary.

9.4 Microstructure

The properties of an alloy do not depend only on concentration of the phases but how they are arranged structurally at the microscopy level. Thus, the microstructure is specified by the number of phases, their proportions, and their arrangement in space.

A binary alloy may be

a. a single solid solution
b. two separated, essentially pure components.
c. two separated solid solutions.
d. a chemical compound, together with a solid solution.

The way to tell is to cut the material, polish it to a mirror finish, etch it a weak acid (components etch at a different rate) and observe the surface under a microscope.

9.5 Phase Equilibria

Equilibrium is the state of minimum energy. It is achieved given sufficient time. But the time to achieve equilibrium may be so long (the *kinetics* is so slow) that a state that is not at an energy minimum may have a long life and appear to be stable. This is called a *metastable state.*

A less strict, operational, definition of equilibrium is that of a system that does not change with time during observation.

Equilibrium Phase Diagrams

Give the relationship of composition of a solution as a function of temperatures and the quantities of phases in equilibrium. These diagrams do not indicate the dynamics when one phase transforms into another. Sometimes diagrams are given with pressure as one of the variables. In the phase diagrams we will discuss, pressure is assumed to be constant at one atmosphere.

9.6 Binary Isomorphous Systems

This very simple case is one complete liquid and solid solubility, an *isomorphous* system. The example is the Cu-Ni alloy of Fig. 9.2a. The complete solubility occurs because both Cu and Ni have the same crystal structure (FCC), near the same radii, electronegativity and valence.

The *liquidus line* separates the liquid phase from solid or solid + liquid phases. That is, the solution is liquid above the liquidus line.

The *solidus line* is that below which the solution is completely solid (does not contain a liquid phase.)

Interpretation of phase diagrams

Concentrations: Tie-line method

a. locate composition and temperature in diagram
b. In two phase region draw tie line or isotherm
c. note intersection with phase boundaries. Read compositions.

Fractions: lever rule

a. construct tie line (isotherm)
b. obtain ratios of line segments lengths.

Note: the fractions are inversely proportional to the length to the boundary for the particular phase. If the point in the diagram is close to the phase line, the fraction of that phase is large.

Development of microstructure in isomorphous alloys

a) Equilibrium cooling

Solidification in the solid + liquid phase occurs gradually upon cooling from the liquidus line. The composition of the solid and the liquid change gradually during cooling (as can be determined by the tie-line method.) Nuclei of the solid phase form and they grow to consume all the liquid at the solidus line.

b) Non-equilibrium cooling

Solidification in the solid + liquid phase also occurs gradually. The composition of the liquid phase evolves by diffusion, following the equilibrium values that can be derived from the tie-line method. However, diffusion in the solid state is very slow. Hence, the new layers that solidify on top of the grains have the equilibrium composition at that temperature but once they are solid their composition does not change. This lead to the formation of layered (cored) grains (Fig. 9.14) and to the invalidity of the tie-line method to determine the composition of the solid phase (it still works for the liquid phase, where diffusion is fast.)

9.7 Binary Eutectic Systems

Interpretation: Obtain phases present, concentration of phases and their fraction (%).

Solvus line: limit of solubility

Eutectic or invariant point: Liquid and two solid phases exist in equilibrium at the *eutectic composition* and the *eutectic temperature.*

Note:

- the melting point of the eutectic alloy is lower than that of the components (eutectic = easy to melt in Greek).
- At most two phases can be in equilibrium within a phase field.
- Single-phase regions are separated by 2-phase regions.

Development of microstructure in eutectic alloys

Case of lead-tin alloys, figures 9.9–9.14. A layered, eutectic structure develops when cooling below the eutectic temperature. Alloys which are to the left of the eutectic concentration (*hipoeutectic*) or to the right (*hypereutectic*) form a *proeutectic* phase before reaching the eutectic temperature, while in the solid + liquid region. The eutectic structure then adds when the remaining liquid is solidified when cooling further. The eutectic microstructure is lamellar (layered) due to the reduced diffusion distances in the solid state.

To obtain the concentration of the eutectic microstructure in the final solid solution, one draws a vertical line at the eutectic concentration and applies the lever rule treating the eutectic as a separate phase (Fig. 9.16).

9.8 Equilibrium Diagrams Having Intermediate Phases or Compounds

A *terminal phase* or *terminal solution* is one that exists in the extremes of concentration (0 and 100%) of the phase diagram. One that exists in the middle, separated from the extremes, is called an *intermediate phase* or solid solution.

An important phase is the *intermetallic compound*, that has a precise chemical compositions. When using the lever rules, intermetallic compounds are treated like any other phase, except they appear not as a wide region but as a vertical line.

9.9 Eutectoid and Peritectic Reactions

The *eutectoid* (eutectic-like) reaction is similar to the eutectic reaction but occurs from one solid phase to two *new* solid phases. It also shows as V on top of a horizontal line in the phase diagram. There are associated eutectoid temperature (or temperature), eutectoid phase, eutectoid and proeutectoid microstructures.

Solid Phase 1 à Solid Phase 2 + Solid Phase 3

The *peritectic* reaction also involves three solid in equilibrium, the transition is from a solid + liquid phase to a *different* solid phase when cooling. The inverse reaction occurs when heating.

Solid Phase 1 + liquid à Solid Phase 2

9.10 Congruent Phase Transformations

Another classification scheme. *Congruent* transformation is one where there is no change in composition, like allotropic transformations (e.g., a-Fe to g-Fe) or melting transitions in pure solids.

9.13 The Iron–Iron Carbide (Fe–Fe_3C) Phase Diagram

This is one of the most important alloys for structural applications. The diagram Fe—C is simplified at low carbon concentrations by assuming it is the Fe—Fe_3C diagram. Concentrations are usually given in weight percent. The possible phases are:

- a-ferrite (BCC) Fe-C solution
- g-austenite (FCC) Fe-C solution
- d-ferrite (BCC) Fe-C solution
- liquid Fe-C solution
- Fe_3C (iron carbide) or cementite. An intermetallic compound.

The maximum solubility of C in a- ferrite is 0.022 wt%. d-ferrite is only stable at high temperatures. It is not important in practice. Austenite has a maximum C concentration of 2.14 wt %. It is not stable below the eutectic temperature (727 C) unless cooled rapidly (Chapter 10). Cementite is in reality metastable, decomposing into a-Fe and C when heated for several years between 650 and 770 C.

For their role in mechanical properties of the alloy, it is important to note that:

Ferrite is soft and ductile

Cementite is hard and brittle

Thus, combining these two phases in solution an alloy can be obtained with intermediate properties. (Mechanical properties also depend on the microstructure, that is, how ferrite and cementite are mixed.)

9.14 Development of Microstructures in Iron—Carbon Alloys

The eutectoid composition of austenite is 0.76 wt %. When it cools *slowly* it forms *perlite*, a lamellar or layered structure of two phases: a-ferrite and cementite (Fe_3C).

Hypoeutectoid alloys contain *proeutectoid ferrite* plus the eutectoid perlite. Hypereutectoid alloys contain *proeutectoid cementite* plus perlite.

Since reactions below the eutectoid temperature are in the solid phase, the equilibrium is not achieved by usual cooling from austenite. The new microstructures that form are discussed in Ch. 10.

9.15 The Influence of Other Alloying Elements

As mentioned in section 7.9, alloying strengthens metals by hindering the motion of dislocations. Thus, the strength of Fe-C alloys increase with C content and also with the addition of other elements.

Chapter-10: Phase Transformations in Metals

10.1 Introduction

The goal is to obtain specific *microstructures* that will improve the mechanical properties of a metal, in addition to grain-size refinement, solid-solution strengthening, and strain-hardening.

10.2 Basic Concepts

Phase transformations that involve a change in the microstructure can occur through:

- Diffusion

- Maintaining the type and number of phases (e.g., solidification of a pure metal, allotropic transformation, recrystallization, grain growth.
- Alteration of phase composition (e.g., eutectoid reactions, see 10.5)

- Diffusionless

- Production of metastable phases (e.g., martensitic transformation, see 10.5)

10.3 The Kinetics of Solid-State Reactions

Change in composition implies atomic rearrangement, which requires diffusion. Atoms are displaced by *random walk*. The displacement of a given atom, d, is not linear in time t (as would be for a straight trajectory) but is proportional to the square root of time, due to the tortuous path: $d = c(Dt)^{1/2}$ where c is a constant and D the diffusion constant. This time-dependence of the rate at which the reaction (phase transformation) occurs is what is meant by the term reaction *kinetics*.

D is called a constant because it does not depend on time, but it depends on temperature as we have seen in Ch. 5. Diffusion occurs *faster at high temperatures.*

Phase transformation requires two processes: *nucleation* and *growth*. **Nucleation** involves the formation of very small particles, or *nuclei* (e.g., grain boundaries, defects). This is similar to rain happening when water molecules condensed around dust particles. During **growth**, the nuclei grow in size at the expense of the surrounding material.

The kinetic behavior often has the S-shape form of Fig. 10.1, when plotting percent of material transformed vs. the logarithm of time. The nucleation phase is seen as an incubation period, where nothing seems to happen. Usually the transformation rate has the form $r = A\ e^{-Q/RT}$ (similar to the temperature dependence of the diffusion constant), in which case it is said to be *thermally activated.*

10.4 Multiphase Transformations

To describe phase transformations that occur during cooling, *equilibrium* phase diagrams are inadequate if the transformation rate is slow compared to the cooling rate. This is usually the case in practice, so that equilibrium microstructures are seldom obtained. This means that the transformations are delayed (e.g., case of supercooling), and *metastable* states are formed. We then need to know the effect of **time** on phase transformations.

Microstructural and Property Changes in Fe-C Alloys

10.5 Isothermal Transformation Diagrams

We use as an example the cooling of an eutectoid alloy (0.76 wt% C) from the austenite (g-phase) to pearlite, that contains ferrite (a) plus cementite (Fe_3C or iron carbide). When cooling proceeds below the eutectoid temperature (727 ^oC) nucleation of pearlite starts. The S-shaped curves (fraction of pearlite vs. log. time, fig. 10.3) are displaced to longer times at higher temperatures showing that the transformation is dominated by nucleation (the nucleation period is longer at higher temperatures) and not by diffusion (which occurs faster at higher temperatures).

The family of S-shaped curves at different temperatures can be used to construct the TTT (Time-Temperature-Transformation) diagrams (e.g., fig. 10.4.) For these diagrams to apply, one needs to cool the material quickly to a given temperature T_o before the transformation occurs, and keep it at that temperature over time. The horizontal line that indicates constant temperature T_o intercepts the TTT curves on the left (beginning of the transformation) and the right (end of the transformation); thus one can read from the diagrams when the transformation occurs. The formation of pearlite shown in fig. 10.4 also indicates that the transformation occurs sooner at low temperatures, which is an indication that it is controlled by the rate of nucleation. At low temperatures, nucleation occurs fast and grain growth is reduced (since it occurs by diffusion, which is hindered at low temperatures). This reduced grain growth leads to fine-grained microstructure (*fine pearlite*). At higher temperatures, diffusion allows for larger grain growth, thus leading to *coarse pearlite*.

At lower temperatures nucleation starts to become slower, and a new phase is formed, *bainite.* Since diffusion is low at low temperatures, this phase has a very fine (microscopic) microstructure.

Spheroidite is a coarse phase that forms at temperatures close to the eutectoid temperature. The relatively high temperatures caused a slow nucleation but enhances the growth of the nuclei leading to large grains.

A very important structure is *martensite*, which forms when cooling austenite very fast (*quenching*) to below a maximum temperature that is required for the transformation. It forms nearly instantaneously when the required low temperature is reached; since no thermal activation is needed, this is called an *athermal transformation.* Martensite is a different phase, a body-centered tetragonal (BCT) structure with interstitial C atoms. Martensite is *metastable* and decomposes into ferrite and pearlite but this is extremely slow (and not noticeable) at room temperature.

In the examples, we used an eutectoid composition. For hypo- and hypereutectoid alloys, the analysis is the same, but the proeutectoid phase that forms before cooling through the eutectoid temperature is also part of the final microstructure.

10.6 Continuous Cooling Transformation Diagrams - not covered

10.7 Mechanical Behavior of Fe-C Alloys

The strength and hardness of the different microstructures is inversely related to the size of the microstructures. Thus, spheroidite is softest, fine pearlite is stronger than coarse pearlite, bainite is stronger than pearlite and martensite is the strongest of all. The stronger and harder the phase the more brittle it becomes.

10.8 Tempered Martensite

Martensite is so brittle that it needs to be modified in many practical cases. This is done by heating it to 250-650 ^{o}C for some time (tempering) which produces *tempered martensite*, an extremely fine-grained and well dispersed cementite grains in a ferrite matrix.

Chapter 11. Thermal Processing of Metal Alloys

Annealing Processes

11.1 Introduction

Annealing is a heat treatment where the material is taken to a high temperature, kept there for some time and then cooled. High temperatures allow diffusion processes to occur fast. The time at the high temperature (soaking time) is long enough to allow the desired transformation to occur. Cooling is done slowly to avoid the distortion (warping) of the metal piece, or even cracking, caused by stresses induced by differential contraction due to thermal inhomogeneities. Benefits of annealing are:

- relieve stresses
- increase softness, ductility and toughness
- produce a specific microstructure

11.2 Process Annealing

Deforming a piece that has been strengthened by cold working requires a lot of energy. Reverting the effect of cold work by process annealing eases further deformation. Heating allows recovery and recrystallization but is usually limited to avoid excessive grain growth and oxidation.

11.3 Stress Relief

Stresses resulting from machining operations of non-uniform cooling can be eliminated by stress relief annealing at moderately low temperatures, such that the effect of cold working and other heat treatments is maintained.

11.4 Annealing of Ferrous Alloys

Normalizing (or austenitizing) consists in taking the Fe-C alloy to the austenitic phase which makes the grain size more uniform, followed by cooling in air.

Full anneal involves taking hypoeutectoid alloys to the austenite phase and hypereutectoid alloys over the eutectoid temperature (Fig. 11.1) to soften pieces which have been hardened by plastic deformation, and which need to be machined.

Spheroidizing consists in prolongued heating just below the eutectoid temperature, which results in the soft spheroidite structure discussed in Sect. 10.5. This achieves maximum softness that minimizes the energy needed in subsequent forming operations.

Heat Treatment of Steels

1.5 Hardenability

To achieve a full conversion of austenite into hard martensite, cooling needs to be fast enough to avoid partial conversion into perlite or bainite. If the piece is thick, the interior may cool too slowly so that full martensitic conversion is not achieved. Thus, the martensitic content, and the hardness, will drop from a high value at the surface to a lower value in the interior of the piece. Hardenability is the ability of the material to be hardened by forming martensite.

Hardenability is measured by the Jominy end-quench test (Fig. 11.2). Hardenability is then given as the dependence of hardness on distance from the quenched end. High hardenability means that the hardness curve is relatively flat.

11.6 Influence of Quenching Medium, Specimen Size, and Geometry

The cooling rate depends on the cooling medium. Cooling is fastest using water, then oil, and then air. Fast cooling brings the danger of warping and formation of cracks, since it is usually accompanied by large thermal gradients.

The shape and size of the piece, together with the heat capacity and heat conductivity are important in determining the cooling rate for different parts of the metal piece. Heat capacity is the energy content of a heated mass, which needs to be removed for cooling. Heat conductivity measures how fast this energy is transported to the colder regions of the piece.

Precipitation Hardening

Hardening can be enhanced by extremely small precipitates that hinder dislocation motion. The precipitates form when the solubility limit is exceeded. Precipitation hardening is also called age hardening because it involves the hardening of the material over a prolonged time.

11.7 Heat Treatments

Precipitation hardening is achieved by:

a) solution heat treatment where all the solute atoms are dissolved to form a single-phase solution.

b) rapid cooling across the solvus line to exceed the solubility limit. This leads to a supersaturated solid solution that remains stable (metastable) due to the low temperatures, which prevent diffusion.

c) precipitation heat treatment where the supersaturated solution is heated to an intermediate temperature to induce precipitation and kept there for some time (aging).

If the process is continued for a very long time, eventually the hardness decreases. This is called overaging.

The requirements for precipitation hardening are:

- appreciable maximum solubility
- solubility curve that falls fast with temperature composition of the alloy that is less than the maximum solubility

11.8 Mechanism of Hardening

Strengthening involves the formation of a large number of microscopic nuclei, called zones. It is accelerated at high temperatures. Hardening occurs because the deformation of the lattice around the precipitates hinder slip. Aging that occurs at room temperature is called natural aging, to distinguish from the artificial aging caused by premeditated heating.

11.9 Miscellaneous Considerations

Since forming, machining, etc. uses more energy when the material is hard, the steps in the processing of alloys are usually:

- solution heat treat and quench
- do needed cold working before hardening
- do precipitation hardening

Exposure of precipitation-hardened alloys to high temperatures may lead to loss of strength by overaging.

Chapter 12. Ceramics - Structures and Properties

12.1 Introduction

Ceramics are inorganic and non-metallic materials that are commonly electrical and thermal insulators, brittle and composed of more than one element (e.g., two in Al_2O_3)

Ceramic Structures

12.2 Crystal Structures

Ceramic bonds are mixed, ionic and covalent, with a proportion that depends on the particular ceramics. The ionic character is given by the difference of electronegativity between the cations (+) and anions (-). Covalent bonds involve sharing of valence electrons. Very ionic crystals usually involve cations which are alkalis or alkaline-earths (first two columns of the periodic table) and oxygen or halogens as anions.

The building criteria for the crystal structure are two:

- maintain neutrality
- charge balance dictates chemical formula
- achieve closest packing

the condition for minimum energy implies maximum attraction and minimum repulsion. This leads to contact, configurations where anions have the highest number of cation neighbors and viceversa.

The parameter that is important in determining contact is the ratio of cation to anion radii, rC/rA. Table 13.2 gives the coordination number and geometry as a function of r_C/r_A. For example, in the NaCl structure (Fig. 13.2), $r_C = r_{Na} = 0.102$ nm, $r_A = r_{Cl-} = 0.181$ nm, so $r_C/r_A = 0.56$. From table 13.2 this implies coordination number = 6, as observed for this rock-salt structure.

Other structures were shown in class, but will not be included in the test.

12.3 Silicate Ceramics

Oxygen and Silicon are the most abundant elements in Earth’s crust. Their combination (silicates) occur in rocks, soils, clays and sand. The bond is weekly ionic, with Si^{4+} as the cation and O^{2-} as the anion. $r_{Si} = 0.04$ nm, $r_{O-} = 0.14$ nm, so $r_C/r_A = 0.286$. From table 13.2 this implies coordination number = 4, that is tetrahedral coordination (Fig. 13.9).

The tetrahedron is charged: $Si^{4+} + 4\ O^{2-}$ Þ $(Si\ O_4)^{4-}$. Silicates differ on how the tetrahedra are arranged. In silica, (SiO_2), every oxygen atom is shared by adjacent tetrahedra. Silica can be crystalline (e.g., quartz) or amorphous, as in glass.

Soda glasses melt at lower temperature than amorphous SiO_2 because the addition of Na_2O (soda) breaks the tetrahedral network. A lower melting point makes it easy to form glass to make, for instance, bottles.

12.4 Carbon

Carbon is not really a ceramic, but an allotropic form, diamond, may be thought as a type of ceramic. Diamond has very interesting and even unusual properties:

- diamond-cubic structure (like Si, Ge)
- covalent C-C bonds
- highest hardness of any material known
- very high thermal conductivity (unlike ceramics)
- transparent in the visible and infrared, with high index of refraction
- semiconductor (can be doped to make electronic devices)
- metastable (transforms to carbon when heated)

Synthetic diamonds are made by application of high temperatures and pressures or by chemical vapor deposition. Future applications of this latter, cheaper production method include hard coatings for metal tools, ultra-low friction coatings for space applications, and microelectronics.

Graphite has a layered structure with very strong hexagonal bonding within the planar layers (using 3 of the 3 bonding electrons) and weak, van der Waals bonding between layers using the fourth electron. This leads to easy interplanar cleavage and applications as a lubricant and for writing (pencils). Graphite is a good electrical conductor and chemically stable even at high temperatures. Applications include furnaces, rocket nozzles, electrodes in batteries.

A recently (1985) discovered formed of carbon is the C_{60} molecule, also known as fullerene or bucky-ball (after the architect Buckminster Fuller who designed the geodesic structure that C_{60} resembles.) Fullerenes and related structures like bucky-onions amd nanotubes are exceptionally strong. Future applications are as a structural material and possibly in microelectronics, due to the unusual properties that result when fullerenes are doped with other atoms.

12.5 Imperfections in Ceramics

Imperfections include point defects and impurities. Their formation is strongly affected by the condition of charge neutrality (creation of unbalanced charges requires the expenditure of a large amount of energy.

Non-stoichiometry refers to a change in composition so that the elements in the ceramic are not in the proportion appropriate for the compound (condition known as stoichiometry). To minimize energy, the effect of non-stoichiometry is a redistribution of the atomic charges (Fig. 13.1).

Charge neutral defects include the Frenkel and Schottky defects. A *Frenkel-defect* is a vacancy- interstitial pair of cations (placing large anions in an interstitial position requires a lot of energy in lattice distortion). A *Schottky-defect* is the a pair of nearby cation and anion vacancies.

Introduction of impurity atoms in the lattice is likely in conditions where the charge is maintained. This is the case of electronegative impurities that substitute a lattice anions or electropositive substitutional impurities. This is more likely for similar ionic radii since this minimizes the energy required for lattice distortion. Defects will appear if the charge of the impurities is not balanced.

12.6 Ceramic Phase Diagrams (not covered)

12.7 Brittle Fracture of Ceramics

The brittle fracture of ceramics limits applications. It occurs due to the unavoidable presence of microscopic flaws (micro-cracks, internal pores, and atmospheric contaminants) that result during cooling from the melt. The flaws need to crack formation, and crack propagation (perpendicular to the applied stress) is usually transgranular, along cleavage planes. The flaws cannot be closely controlled in manufacturing; this leads to a large variability (scatter) in the fracture strength of ceramic materials.

The compressive strength is typically ten times the tensile strength. This makes ceramics good structural materials under compression (e.g., bricks in houses, stone blocks in the pyramids), but not in conditions of tensile stress, such as under flexure.

Plastic deformation in crystalline ceramics is by slip, which is difficult due to the structure and the strong local (electrostatic) potentials. There is very little plastic deformation before fracture.

Non-crystalline ceramics, like common glass deform by viscous flow (like very high-density liquids). Viscosity decreases strongly with increases temperature.

Chapter 13. Ceramics - Applications and Processing

13.1 Introduction

Ceramics properties that are different from those of metals lead to different uses. In structures, designs must be done for compressive loads. The transparency to light of many ceramics leads to optical uses, like in windows, photographic cameras, telescopes and microscopes. Good thermal insulation leads to use in ovens, the exterior tiles of the Shuttle orbiter, etc. Good electrical isolation are used to support conductors in electrical and electronic applications. The good chemical inertness shows in the stability of the structures thousands of years old.

13.2 Glass Properties

A special characteristic of glasses is that solidification is gradual, through a viscous stage, without a clear melting temperature. The specific volume does not have an abrupt transition at a temperature but rather shows a change in slope at the *glass-transition temperature* (Fig. 14.3).

The melting point, working point, softening point and annealing point are defined in terms of viscosity, rather than temperature (Fig. 14.4), and depend on glass composition..

13.4 Heat Treating Glasses

Similar to the case of metals, annealing is used at elevated temperatures is used to remove stresses, like those caused by inhomogeneous temperatures during cooling.

Strengthening by glass tempering is done by heating the glass above the glass transition temperature but below the softening point and then quenched in an air jet or oil bath. The interior, which cools later than the outside, tries to contract while in a plastic state after the exterior has become rigid. This causes residual compressive stresses on the surface and tensile stresses inside. To fracture, a crack has first to overcome the residual compressive stress, making tempered glass less susceptible to fracture. This improvement leads to use in automobile windshields, glass doors, eyeglass lenses, etc.

Chapter 15. Polymer Structures

14.1 Introduction

Polymers are common in nature, in the form of wood, rubber, cotton, leather, wood, silk, proteins, enzymes, starches, cellulose. Artificial polymers are made mostly from oil. Their use has grown exponentially, especially after WW2. The key factor is the very low production cost and useful properties (e.g., combination of transparency and flexibility, long elongation).

14.2 Hydrocarbon Molecules

Most polymers are organic, and formed from hydrocarbon molecules. These molecules can have single, double, or triple carbon bonds. A *saturated hydrocarbon* is one where all bonds are single, that is, the number of atoms is maximum (or saturated). Among this type are the paraffin compounds, C_nH_{2n+2} (Table 15.1). In contrast, non-saturated hydrocarbons contain some double and triple bonds.

Isomers are molecules that contain the same molecules but in a different arrangement. An example is butane and isobutane.

14.3 Polymer Molecules

Polymer molecules are huge, macromolecules that have internal covalent bonds. For most polymers, these molecules form very long chains. The backbone is a string of carbon atoms, often single bonded.

Polymers are composed of basic structures called *mer* units. A molecule with just one mer is a monomer.

14.4 The Chemistry of Polymer Molecules

Examples of polymers are polyvinyl chloride (PVC), poly-tetra-chloro-ethylene (PTFE or Teflon), polypropylene, nylon and polystyrene. Chains are represented straight but in practice they have a three-dimensional, zig-zag structure (Fig. 15.1b).

When all the mers are the same, the molecule is called a homopolymer. When there is more than one type of mer present, the molecule is a *copolymer*.

14.5 Molecular Weight

The mass of a polymer is not fixed, but is distributed around a mean value, since polymer molecules have different lengths. The average molecular weight can be obtained by averaging the masses with the fraction of times they appear (number-average) or with the mass fraction of the molecules (called, improperly, a weight fraction).

The *degree of polymerization* is the average number of mer units, and is obtained by dividing the average mass of the polymer by the mass of a mer unit.

Polymers of low mass are liquid or gases, those of very high mass (called high-polymers, are solid). Waxes, paraffins and resins have intermediate masses.

14.6 Molecular Shape

Polymers are usually not linear; bending and rotations can occur around single C-C bonds (double and triple bonds are very rigid) (Fig. 15.5). Random kings and coils lead to entanglement, like in the spaghetti structure shown in Fig. 15.6.

14.7 Molecular Structure

Typical structures are (Fig. 15.7):

- linear (end-to-end, flexible, like PVC, nylon)
- branched
- cross-linked (due to radiation, vulcanization, etc.)
- network (similar to highly cross-linked structures).

14.8 Molecular Configurations

The regularity and symmetry of the side-groups can affect strongly the properties of polymers. Side groups are atoms or molecules with free bonds, called free-radicals, like H, O, methyl, etc.

If the radicals are linked in the same order, the configuration is called *isostatic*

In a stereoisomer in a *syndiotactic* configuration, the radical groups alternative sides in the chain.

In the *atactic* configuration, the radical groups are positioned at random.

14.9 Copolymers

Copolymers, polymers with at least two different types of mers can differ in the way the mers are arranged. Fig. 15.9 shows different arrangements: random, alternating, block, and graft.

14.10 Polymer Crystallinity

Crystallinity in polymers is more complex than in metals (fig. 15.10). Polymer molecules are often partially crystalline (*semicrystalline*), with crystalline regions dispersed within amorphous material. .

Chain disorder or misalignment, which is common, leads to amorphous material since twisting, kinking and coiling prevent strict ordering required in the crystalline state. Thus, linear polymers with small side groups, which are not too long form crystalline regions easier than branched, network, atactic polymers, random copolymers, or polymers with bulky side groups.

Crystalline polymers are denser than amorphous polymers, so the degree of crystallinity can be obtained from the measurement of density.

14.11 Polymer Crystals

Different models have been proposed to describe the arrangement of molecules in semicrytalline polymers. In the fringed-micelle model, the crystallites (micelles) are embedded in an amorphous matrix (Fig.15.11). Polymer single crystals grown are shaped in regular platelets (lamellae) (Fig. 15.12). Spherulites (Fig. 15.4) are chain-folded crystallites in an amorphous matrix that grow radially in spherical shape “grains”.

Chapter 15. Polymers. Characteristics, Applications and Processing

15.1 Introduction

15.2 Stress-Strain Behavior

The description of stress-strain behavior is similar to that of metals, but a very important consideration for polymers is that the mechanical properties depend on the strain *rate*, temperature, and environmental conditions.

The stress-strain behavior can be brittle, plastic and highly elastic (elastomeric or rubber-like), see Fig. 16. 1. Tensile modulus (modulus) and tensile strengths are orders of magnitude smaller than those of metals, but elongation can be up to 1000 % in some cases. The tensile strength is defined at the fracture point (Fig. 16.2) and can be lower than the yield strength.

Mechanical properties change dramatically with temperature, going from glass-like brittle behavior at low temperatures (like in the liquid-nitrogen demonstration) to a rubber-like behavior at high temperatures (Fig. 16.3).

In general, decreasing the strain rate has the same influence on the strain-strength characteristics as increasing the temperature: the material becomes softer and more ductile.

15.3 Deformation of Semicrystalline Polymers

Many semicrystalline polymers have the spherulitic structure and deform in the following steps (Fig. 16.4):

- elongation of amorphous tie chains
- tilting of lamellar chain folds towards the tensile direction
- separation of crystalline block segments
- orientation of segments and tie chains in the tensile direction

The macroscopic deformation involves an upper and lower yield point and necking. Unlike the case of metals, the neck gets stronger since the deformation aligns the chains so increasing the tensile stress leads to the growth of the neck. (Fig. 16.5).

15.4 Factors that Influence the Mechanical Properties of Polymers

The tensile modulus decreases with increasing temperature or diminishing strain rate.

Obstacles to the steps mentioned in **16.4** strengthen the polymer. Examples are cross-linking (aligned chains have more van der Waals inter-chain bonds) and a large mass (longer molecules have more inter-chain bonds). Crystallinity increases strength as the secondary bonding is enhanced when the molecular chains are closely packed and parallel. Pre-deformation by drawing, analogous to strain hardening in metals, increases strength by orienting the molecular chains. For undrawn polymers, heating increases the tensile modulus and yield strength, and reduces the ductility - opposite of what happens in metals.

15.5 Crystallization, Melting, and Glass Transition Phenomena

Crystallization rates are governed by the same type of S-curves we saw in the case of metals (Fig. 16.7). Nucleation becomes slower at higher temperatures.

The melting behavior of semicrystalline polymers is intermediate between that of crystalline materials (sharp density change at a melting temperature) and that of a pure amorphous material (slight change in slope of density at the glass-transition temperature). The glass transition temperature is between 0.5 and 0.8 of the melting temperature.

The melting temperature increases with the rate of heating, thickness of the lamellae, and depends on the temperature at which the polymer was crystallized.

Melting involves breaking of the inter-chain bonds, so the glass and melting temperatures depend on:

- chain stiffness (e.g., single vs. double bonds)
- size, shape of side groups
- size of molecule
- side branches, defects
- cross-linking

Rigid chains have higher melting temperatures.

15.6 Thermoplastic and Thermosetting Polymers

Thermoplastic polymers (thermoplasts) soften reversibly when heated (harden when cooled back)

Thermosetting polymers (thermosets) harden permanently when heated, as cross-linking hinder bending and rotations. Thermosets are harder, more dimensionally stable, and more brittle than thermoplasts.

15.7 Viscoelasticity

At low temperatures, amorphous polymers deform elastically, like glass, at small elongation. At high temperatures the behavior is viscous, like liquids. At intermediate temperatures, the behavior, like a rubbery solid, is termed *viscoelastic*.

Viscoelasticity is characterized by the viscoelastic relaxation modulus

$$E_r = \mathbf{s(t)/e_0}.$$

If the material is strained to a value e_0.it is found that the stress needs to be reduced with time to maintain this constant value of strain (see figs. 16.11 and 16.12).

In viscoelastic creep, the stress is kept constant at s_0 and the change of deformation with time e(t) is measured. The time-dependent *creep modulus* is given by

$E_c = s_0/e(t)$.

15.8 Deformation and Elastomers

Elastomers can be deformed to very large strains and the spring back elastically to the original length, a behavior first observed in natural rubber. Elastic elongation is due to uncoiling, untwisting and straightening of chains in the stress direction.

To be elastomeric, the polymer needs to meet several criteria:

- must not crystallize easily
- have relatively free chain rotations
- delayed plastic deformation by cross-linking (achieved by vulcanization).
- be above the glass transition temperature

15.9 Fracture of Polymers

As other mechanical properties, the fracture strength of polymers is much lower than that of metals. Fracture also starts with cracks at flaws, scratches, etc. Fracture involves breaking of covalent bonds in the chains. Thermoplasts can have both brittle and ductile fracture behaviors. Glassy thermosets have brittle fracture at low temperatures and ductile fracture at high temperatures.

Glassy thremoplasts often suffer *grazing* before brittle fracture. Crazes are associated with regions of highly localized yielding which leads to the formation of interconnected microvoids (Fig. 16.15). Crazing absorbs energy thus increasing the fracture strength of the polymer.

15.10 Miscellaneous Characteristics

Polymers are brittle at low temperatures and have low impact strengths (Izod or Charpy tests), and a brittle to ductile transition over a narrow temperature range.

Fatigue is similar to the case of metals but at reduced loads and is more sensitive to frequency due to heating which leads to softening.

15.11 Polymerization

Polymerization is the synthesis of high polymers from raw materials like oil or coal. It may occur by:

- addition (chain-reaction) polymerization, where monomer units are attached one at a time
- condensation polymerization, by stepwise intermolecular chemical reactions that produce the mer units.

15.12 Elastomers

In *vulcanization*, crosslinking of the elastomeric polymer is achieved by an irreversible chemical reaction usually at high temperatures (hence ‘vulcan’), and usually involving the addition of sulfur compounds. The S atoms are the ones that form the bridge cross-links. Elastomers are thermosetting due to the cross-linking.

Rubbers become harder and extend less with increasing sulfur content. For automobile applications, synthetic rubbers are strengthened by adding carbon black.

In silicone rubbers, the backbone C atoms are replaced by a chain of alternating silicon and oxygen atoms. These elastomers are also cross-linked and are stable to higher temperatures than C-based elastomers.

Chapter 16. Composites

16.1 Introduction

The idea is that by combining two or more distinct materials one can engineer a new material with the desired combination of properties (e.g., light, strong, corrosion resistant). The idea that a better combination of properties can be achieved is called the principle of combined action.

New - High-tech materials, engineered to specific applications

Old - brick-straw composites, paper, known for > 5000 years.

A type of composite that has been discussed is perlitic steel, which combines hard, brittle cementite with soft, ductile ferrite to get a superior material.

Natural composites: wood (polymer-polymer), bones (polymer-ceramics).

Usual composites have just two phases:

- matrix (continuous)
- dispersed phase (particulates, fibers)

Properties of composites depend on

- properties of phases
- geometry of dispersed phase (particle size, distribution, orientation)
- amount of phase

Classification of composites: three main categories:

- particle-reinforced (large-particle and dispersion-strengthened)
- fiber-reinforced (continuous (aligned) and short fibers (aligned or random)
- structural (laminates and sandwich panels)

Particle-reinforced composites

These are the cheapest and most widely used. They fall in two categories depending on the size of the particles:

- large-particle composites, which act by restraining the movement of the matrix, if well bonded.
- dispersion-strengthened composites, containing 10-100 nm particles, similar to what was discussed under precipitation hardening. The matrix bears the major portion of the applied load and the small particles hinder dislocation motion, limiting plastic deformation.

16.2 Large-Particle Composites

Properties are a combination of those of the components. The *rule of mixtures* predicts that an upper limit of the elastic modulus of the composite is given in terms of the elastic moduli of the matrix (E_m) and the particulate (E_p) phases by:

$$\mathbf{E_c = E_m V_m + E_p V_p}$$

where V_m and V_p are the volume fraction of the two phases. A lower bound is given by:

$$\mathbf{E_c = E_m E_p / (E_p V_m + E_m V_p)}$$

Fig. 17.3 - modulus of composite of WC particles in Cu matrix vs. WC concentration.

Concrete

The most common large-particle composite is concrete, made of a cement matrix that bonds particles of different size (gravel and sand.) Cement was already known to the Egyptians and the Greek. Romans made cement by mixing lime (CaO) with volcanic ice.

In its general from, cement is a fine mixture of lime, alumina, silica, and water. Portland cement is a fine powder of chalk, clay and lime-bearing minerals fired to 1500^o C (calcinated). It forms a paste when dissolved in water. It sets into a solid in minutes and hardens slowly (takes 4 months for full strength). Properties depend on how well it is mixed, and the amount of water: too little - incomplete bonding, too much - excessive porosity.

The advantage of cement is that it can be poured in place, it hardens at room temperature and even under water, and it is very cheap. The disadvantages are that it is weak and brittle, and that water in the pores can produce crack when it freezes in cold weather.

Concrete is cement strengthened by adding particulates. The use of different size (stone and sand) allows better packing factor than when using particles of similar size.

Concrete is improved by making the pores smaller (using finer powder, adding polymeric lubricants, and applying pressure during hardening.

Reinforced concrete is obtained by adding steel rods, wires, mesh. Steel has the advantage of a similar thermal expansion coefficient, so there is reduced danger of cracking due to thermal stresses. *Pre-stressed concrete* is obtained by applying tensile stress to the steel rods while the cement is setting and hardening. When the tensile stress is removed, the concrete is left under compressive stress, enabling it to sustain tensile loads without fracturing. Pre-stressed concrete shapes are usually prefabricated. A common use is in railroad or highway bridges.

Cermets

are composites of ceramic particles (strong, brittle) in a metal matrix (soft, ductile) that enhances toughness. For instance, tungsten carbide or titanium carbide ceramics in Co or Ni. They are used for cutting tools for hardened steels.

Reinforced rubber

is obtained by strengthening with 20-50 nm carbon-black particles. Used in auto tires.

16.3 Dispersion-Strengthened Composites

Use of very hard, small particles to strengthen metals and metal alloys. The effect is like precipitation hardening but not so strong. Particles like oxides do not react so the strengthening action is retained at high temperatures.

Fiber-reinforced composites

In many applications, like in aircraft parts, there is a need for high strength per unit weight (specific strength). This can be achieved by composites consisting of a low-density (and soft) matrix reinforced with stiff fibers.

The strength depends on the fiber length and its orientation with respect to the stress direction.

The efficiency of load transfer between matrix and fiber depends on the interfacial bond.

16.4 Influence of Fiber Length

Normally the matrix has a much lower modulus than the fiber so it strains more. This occurs at a distance from the fiber. Right next to the fiber, the strain is limited by the fiber. Thus, for a composite under tension, a shear stress appears in the matrix that pulls from the fiber. The pull is uniform over the area of the fiber. This makes the force on the fiber be minimum at the ends and maximum in the middle, like in the tug-of-war game.

To achieve effective strengthening and stiffening, the fibers must be larger than a *critical length* l_c, defined as the minimum length at which the center of the fiber reaches the ultimate (tensile) strength s_f, when the matrix achieves the maximum shear strength t_m:

$$l_c = s_f d / 2 t_m$$

Since it is proportional to the diameter of the fiber d, a more unified condition for effective strengthening is that the aspect ratio of the fiber is $l/d > s_f / 2 t_m$.

16.5 Influence of Fiber Orientation

The composite is stronger along the direction of orientation of the fibers and weakest in a direction perpendicular to the fiber. For discontinuous, random fibers, the properties are isotropic.

16.6 Polymer Matrix Composites

Largest and most diverse use of composites due to ease of fabrication, low cost and good properties.

Glass-fiber reinforced composites (GFRC) are strong, corrosion resistant and lightweight, but not very stiff and cannot be used at high temperatures. Applications include auto and boat bodies, aircraft components.

Carbon-fiber reinforced composites (CFRC) use carbon fibers, which have the highest specific module (module divided by weight). CFRC are strong, inert, allow high temperature use. Applications include fishing rods, golf clubs, aircraft components.

Kevlar, and aremid-fiber composite (Fig. 17.9) can be used as textile fibers. Applications include bullet-proof vests, tires, brake and clutch linings.

Wood:

This is one of the oldest and the most widely used structural material. It is a composite of strong and flexible cellulose fibers (linear polymer) surrounded and held together by a matrix of lignin and other polymers. The properties are anisotropic and vary widely among types of wood. Wood is ten times stronger in the axial direction than in the radial or tangential directions.

Chapter 17. Electrical Properties

Electrical Conduction

17.2 Ohm's Law

When an electric potential V is applied across a material, a current of magnitude I flows. In most metals, at low values of V, the current is proportional to V, according to Ohm's law:

$$I = V/R$$

where R is the electrical resistance. R depends on the intrinsic *resistivity* r of the material and on the geometry (length l and area A through which the current passes).

$$R = rl/A$$

17.3 Electrical Conductivity

The *electrical conductivity* is the inverse of the resistivity: $s = 1/r$.

The electric field in the material is $E=V/l$, Ohm's law can then be expressed in terms of the current density $j = I/A$ as:

$$j = sE$$

The conductivity is one of the properties of materials that varies most widely, from 10^7 (W-m) typical of metals to 10^{-20} (W-m) for good electrical insulators. Semiconductors have conductivities in the range 10^{-6} to 10^4 (W-m).

17.4 Electronic and Ionic Conduction

In metals, the current is carried by electrons, and hence the name *electronic conduction*. In ionic crystals, the charge carriers are ions, thus the name *ionic conduction* (see Sect. 19.15).

17.5 Energy Band Structures in Solids

When atoms come together to form a solid, their valence electrons interact due to Coulomb forces, and they also feel the electric field produced by their own nucleus and that of the other atoms. In addition, two specific quantum mechanical effects happen. First, by Heisenberg's uncertainty principle, constraining the electrons to a small volume raises their energy, this is called *promotion*. The second effect, due to the Pauli exclusion principle, limits the number of electrons that can have the same property (which include the energy). As a result of all these effects, the valence electrons of atoms form wide valence bands when they form a solid. The bands are separated by gaps, where electrons cannot exist. The precise location of the bands and band gaps depends on the type of atom (e.g., Si vs. Al), the distance between atoms in the solid, and the atomic arrangement (e.g., carbon vs. diamond).

In semiconductors and insulators, the valence band is filled, and no more electrons can be added, following Pauli's principle. Electrical conduction requires that electrons be able to gain energy in an electric field; this is not possible in these materials because that would imply that the electrons are promoted into the forbidden band gap.

In metals, the electrons occupy states up to the *Fermi level*. Conduction occurs by promoting electrons into the *conduction band*, that starts at the Fermi level, separated by the valence band by an infinitesimal amount.

17.6 Conduction in Terms of Band and Atomic Bonding Models

Conduction in metals is by electrons in the conduction band. Conduction in insulators is by electrons in the conduction band and by holes in the valence band. *Holes* are vacant states in the valence band that are created when an electron is removed.

In metals there are empty states just above the Fermi levels, where electrons can be promoted. The promotion energy is negligibly small so that at any temperature electrons can be found in the conduction band. The number of electrons participating in electrical conduction is extremely small.

In insulators, there is an energy gap between the valence and conduction bands, so energy is needed to promote an electron to the conduction band. This energy may come from heat, or from energetic radiation, like light of sufficiently small wavelength.

A working definition for the difference between semiconductors and insulators is that in semiconductors, electrons can reach the conduction band at ordinary temperatures, where in insulators they cannot. The probability that an electron reaches the conduction band is about $\exp(-E_g/2kT)$ where E_g is the band gap and kT has the usual meaning. If this probability is, say, $< 10^{-24}$ one would not find a single electron in the conduction band in a solid of 1 cubic centimeter. This requires $E_g/2kT > 55$. At room temperature, $2kT = 0.05$ eV; thus $E_g > 2.8$ eV can be used as the condition for an insulator.

Besides having relatively small E_g, semiconductors have covalent bond, whereas insulators usually are partially ionic bonded.

17.7 Electron Mobility

Electrons are accelerated in an electric field E, in the opposite direction to the field because of their negative charge. The force acting on the electron is $-eE$, where e is the electric charge. This force produces a constant acceleration so that, in the absence of obstacles (in vacuum, like inside a TV tube) the electron speeds up continuously in an electric field. In a solid, the situation is different. The electrons scatter by collisions with atoms and vacancies that change drastically their direction of motion. Thus electrons move randomly but with a net drift in the direction opposite to the electric field. The drift velocity is *constant*, equal to the electric field times a constant called the *mobility m*,

$$v_{\mathbf{d}} = -m_{\mathbf{e}} E$$

which means that there is a friction force proportional to velocity. This friction translates into energy that goes into the lattice as heat. This is the way that electric heaters work.

The electrical conductivity is:

$s = n\,|e|\,m_{\mathbf{e}}$

where n is the concentration of electrons (n is used to indicate that the carriers of electricity are negative particles).

17.8 Electrical Resistivity of Metals

The resistivity then depends on collisions. Quantum mechanics tells us that electrons behave like waves. One of the effects of this is that electrons do not scatter from a perfect lattice. They scatter by defects, which can be:

- atoms displaced by lattice vibrations
- vacancies and interstitials
- dislocations, grain boundaries
- impurities

One can express the total resistivity r_{tot} by the Matthiessen rule, as a sum of resistivities due to thermal vibrations, impurities and dislocations. Fig. 19.8 illustrates how the resistivity increases with temperature, with deformation, and with alloying.

17.9 Electrical Characteristics of Commercial Alloys

The best material for electrical conduction (lower resistivity) is silver. Since it is very expensive, copper is preferred, at an only modest increase in r. To achieve low r it is necessary to remove gases occluded in the metal during fabrication. Copper is soft so, for applications where mechanical strength is important, the alloy CuBe is used, which has a nearly as good r. When weight is important one uses Al, which is half as good as Cu. Al is also more resistant to corrosion.

When high resistivity materials are needed, like in electrical heaters, especially those that operate at high temperature, nichrome (NiCr) or graphite are used.

17.10 Intrinsic Semiconduction

Semiconductors can be *intrinsic* or *extrinsic*. Intrinsic means that electrical conductivity does not depend on impurities, thus intrinsic means pure. In extrinsic semiconductors the conductivity depends on the concentration of impurities.

Conduction is by electrons and holes. In an electric field, electrons and holes move in opposite direction because they have opposite charges. The conductivity of an intrinsic semiconductor is:

$s = n\,|e|\,m_{\mathbf{e}} + p\,|e|\,m_{\mathbf{h}}$

where p is the hole concentration and m_h the hole mobility. One finds that electrons move much faster than holes:

$$m_e > m_h$$

In an intrinsic semiconductor, a hole is produced by the promotion of each electron to the conduction band. Thus:

$$n = p$$

Thus, $s = 2 n |e| (m_e + m_h)$ (only for intrinsic semiconductors).

17.11 Extrinsic Semiconduction

Unlike intrinsic semiconductors, an extrinsic semiconductor may have different concentrations of holes and electrons. It is called *p-type* if $p>n$ and *n-type* if $n>p$. They are made by *doping*, the addition of a very small concentration of impurity atoms. Two common methods of doping are diffusion and ion implantation.

Excess electron carriers are produced by substitutional impurities that have more valence electron per atom than the semiconductor matrix. For instance phosphorous, with 5 valence electrons, is an electron *donor* in Si since only 4 electrons are used to bond to the Si lattice when it substitutes for a Si atom. Thus, elements in columns V and VI of the periodic table are donors for semiconductors in the IV column, Si and Ge. The energy level of the donor state is close to the conduction band, so that the electron is promoted (ionized) easily at room temperature, leaving a hole (the ionized donor) behind. Since this hole is unlike a hole in the matrix, it does not move easily by capturing electrons from adjacent atoms. This means that the conduction occurs mainly by the donated electrons (thus *n-type*).

Excess holes are produced by substitutional impurities that have fewer valence electrons per atom than the matrix. This is the case of elements of group II and III in column IV semiconductors, like B in Si. The bond with the neighbors is incomplete and so they can capture or accept electrons from adjacent silicon atoms. They are called *acceptors*. The energy level of the acceptor is close to the valence band, so that an electron may easily hop from the valence band to complete the bond leaving a hole behind. This means that conduction occurs mainly by the holes (thus *p-type*).

17.12 The Temperature Variation of Conductivity and Carrier Concentration

Temperature causes electrons to be promoted to the conduction band and from donor levels, or holes to acceptor levels. The dependence of conductivity on temperature is like other thermally activated processes:

$$s = A \exp(-E_g/2kT)$$

where A is a constant (the mobility varies much more slowly with temperature). Plotting $\ln s$ vs. $1/T$ produces a straight line of slope $E_g/2k$ from which the band gap energy can be determined. Extrinsic semiconductors have, in addition to this dependence, one due to the thermal promotion of electrons from donor levels or holes from acceptor levels. The dependence on temperature is also exponential but it eventually saturates at high temperatures where all the donors are emptied or all the acceptors are filled.

This means that at low temperatures, extrinsic semiconductors have larger conductivity than intrinsic semiconductors. At high temperatures, both the impurity levels and valence electrons are ionized, but since the impurities are very low in number and they are exhausted, eventually the behavior is dominated by the intrinsic type of conductivity.

17.14 Semiconductor Devices

A semiconductor *diode* is made by the intimate junction of a *p*-type and an *n*-type semiconductor (an *n-p junction).* Unlike a metal, the intensity of the electrical current that passes through the material depends on the polarity of the applied voltage. If the positive side of a battery is connected to the *p*-side, a situation called *forward bias*, a large amount of current can flow since holes and electrons are pushed into the junction region, where they recombine (annihilate). If the polarity of the voltage is flipped, the diode operates under *reverse bias*. Holes and electrons are removed from the region of the junction, which therefore becomes depleted of carriers and behaves like an insulator. For this reason, the current is very small under reverse bias. The asymmetric current-voltage characteristics of diodes (Fig. 19.20) is used to convert alternating current into direct current. This is called rectification.

A *p-n-p junction transistor* contains two diodes back-to-back. The central region is very thin and is called the *base*. A small voltage applied to the base has a large effect on the current passing through the transistor, and this can be used to amplify electrical signals (Fig. 19.22). Another common device is the MOSFET transistor where a *gate* serves the function of the base in a junction transistor. Control of the current through the transistor is by means of the electric field induced by the gate, which is isolated electrically by an oxide layer.

17.15 Conduction in Ionic Materials

In ionic materials, the band gap is too large for thermal electron promotion. Cation vacancies allow ionic motion in the direction of an applied electric field, this is referred to as *ionic conduction.* High temperatures produce more vacancies and higher ionic conductivity.

At low temperatures, electrical conduction in insulators is usually along the surface, due to the deposition of moisture that contains impurity ions.

17.16 Electrical Properties of Polymers

Polymers are usually good insulators but can be made to conduct by doping. Teflon is an exceptionally good insulator.

Dielectric Behavior

A *dielectric* is an electrical insulator that can be made to exhibit an electric dipole structure (displace the negative and positive charge so that their center of gravity is different).

17.17 Capacitance

When two parallel plates of area A, separated by a small distance l, are charged by $+Q$, $-Q$, an electric field develops between the plates

$$E = D/\mathbf{ee_0}$$

where $D = Q/A$. e_0 is called the vacuum permittivity and e the relative permittivity, or *dielectric constant* ($e = 1$ for vacuum). In terms of the voltage between the plates, $V = E\,l$,

$$V = Dl/ee_0 = Q\,l/Aee_0 = Q\,/\,C$$

The constant $C = Aee_0/l$ is called the capacitance of the plates.

17.18 Field Vectors and Polarization

The dipole moment of a pair of positive and negative charges ($+q$ and $-q$) separated at a distance d is $p = qd$. If an electric field is applied, the dipole tends to align so that the positive charge points in the field direction. Dipoles between the plates of a capacitor will produce an electric field that opposes the applied field. For a given applied voltage V, there will be an increase in the charge in the plates by an amount Q' so that the total charge becomes $Q = Q' + Q_0$, where Q_0 is the charge of a vacuum capacitor with the same V. With $Q' = PA$, the charge density becomes $D = D_0\,E + P$, where the *polarization* $P = e_0\,(e-1)\,E$.

19.19 Types of Polarization

Three types of polarization can be caused by an electric field:

- *Electronic polarization*: the electrons in atoms are displaced relative to the nucleus.
- *Ionic polarization*: cations and anions in an ionic crystal are displaced with respect to each other.
- *Orientation polarization*: permanent dipoles (like H_2O) are aligned.

17.20 Frequency Dependence of the Dielectric Constant

Electrons have much smaller mass than ions, so they respond more rapidly to a changing electric field. For electric field that oscillates at very high frequencies (such as light) only electronic polarization can occur. At smaller frequencies, the relative displacement of positive and negative ions can occur. Orientation of permanent dipoles, which require the rotation of a molecule can occur only if the oscillation is relatively slow (MHz range or slower). The time needed by the specific polarization to occur is called the *relaxation time*.

17.21 Dielectric Strength

Very high electric fields ($>10^8$ V/m) can free electrons from atoms, and accelerate them to such high energies that they can, in turn, free other electrons, in an avalanche process (or electrical discharge). This is called *dielectric breakdown*, and the field necessary to start the is called the *dielectric strength* or breakdown strength.

17.22 Dielectric Materials

Capacitors require dielectrics of high *e* that can function at high frequencies (small relaxation times). Many of the ceramics have these properties, like mica, glass, and porcelain). Polymers usually have lower e.

17.23 Ferroelectricity

Ferroelectric materials are ceramics that exhibit permanent polarization in the absence of an electric field. This is due to the asymmetric location of positive and negative charges within the unit cell. Two possible arrangements of this asymmetry results in two distinct polarizations, which can be used to code "0" and "1" in ferroelectric memories. A typical ferroelectric is barium titanate, $BaTiO_3$, where the Ti^{4+} is in the center of the unit cell and four O^{2-} in the central plane can be displaced to one side or the other of this central ion (Fig. 19.33).

17.24 Piezoelectricity

In a *piezolectric* material, like quartz, an applied mechanical stress causes electric polarization by the relative displacement of anions and cations.