

Chapter 2

Microstructure, Crystal Structure, Defects and Strengthening of Engineering Materials

2.1. Atomic Structure and Bonding

2.1.1 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 $N_{av} = 1 \text{ gram}/1 \text{ amu}$.

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

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

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

For a molecular solid like ice, one uses the molecular mass, $M(\text{H}_2\text{O}) = 18$. With a density of $1 \text{ g}/\text{cm}^3$, one obtains $n = 3.3 \times 10^{22} \text{ H}_2\text{O}/\text{cm}^3$. Note that since the water molecule contains 3 atoms, this is equivalent to $9.9 \times 10^{22} \text{ atoms}/\text{cm}^3$.

Most solids have atomic densities around 6×10^{22} atoms/cm³. 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.

2.1.2 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; $n = 1, 2 \dots$ 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).

2.1.3 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 H₂, N₂, and NaCl.

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

2.1.4 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.

2.1.5 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, losing 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 H₂ molecule bind the protons.

2.1.6 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 H₂O (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 H₂O dipole.

2.8 Molecules

If molecules formed a closed shell due to covalent bonding (like H₂, N₂) then the interaction between molecules is weak, of the van der Waals type. Thus, molecular solids usually have very low melting points.

2.2 Crystal Structures

2.2.1 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.

2.2.2 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 (BCC) 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.

2.2.3 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. $APF = \text{Sum of atomic volumes} / \text{Volume of cell}$.

Unit Cell	n	CN	a/R	APF
SC	1	6	2	0.52
BCC	2	8	$4\sqrt{3}$	0.68
FCC	4	12	$2\sqrt{2}$	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.

2.2.4 Density Computations

The density of a solid is that of the unit cell, obtained by dividing the mass of the atoms ($n \text{ atoms} \times M_{\text{atom}}$) 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:

$$\rho = \frac{nA}{V_c N_A}$$

2.2.5 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.

2.2.6 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.

2.3. Crystalline and Non-Crystalline Materials

2.3.1 Single Crystals

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

2.3.2 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*.

2.3.3 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.

2.3.4. 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 SiO₂ (quartz) is still apparent in amorphous SiO₂ (silica glass.)

2.4. Linear Defects - Dislocations

Dislocations are another type of defect in crystals. Dislocations are areas where the atoms are out of position in the crystal structure. Dislocations are generated and move when a stress is applied. The motion of dislocations allows slip – plastic deformation to occur.

Before the discovery of the dislocation by Taylor, Orowan and Polyani in 1934, no one could figure out how the plastic deformation properties of a metal could be greatly changed by solely by forming (without changing the chemical composition). This became even bigger mystery when in the early 1900's scientists estimated that metals undergo plastic deformation at forces much smaller than the theoretical strength of the forces that are holding the metal atoms together. Many metallurgists remained skeptical of the dislocation theory until the development of the transmission electron microscope in the late 1950's. The TEM allowed experimental evidence to be collected that showed that the strength and ductility of metals are controlled by dislocations.

There are two basic types of dislocations, the edge dislocation and the screw dislocation. Actually, edge and screw dislocations are just extreme forms of the possible dislocation structures that can occur. Most dislocations are probably a hybrid of the edge and screw forms but this discussion will be limited to Linear Defects - Dislocations

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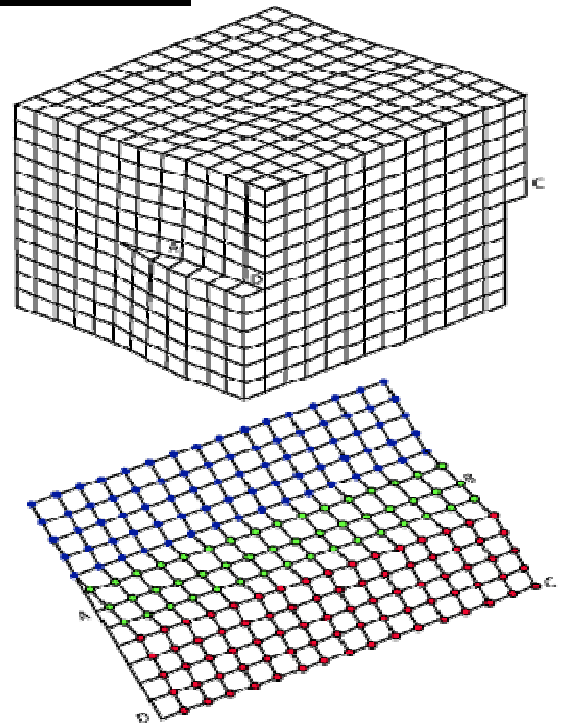
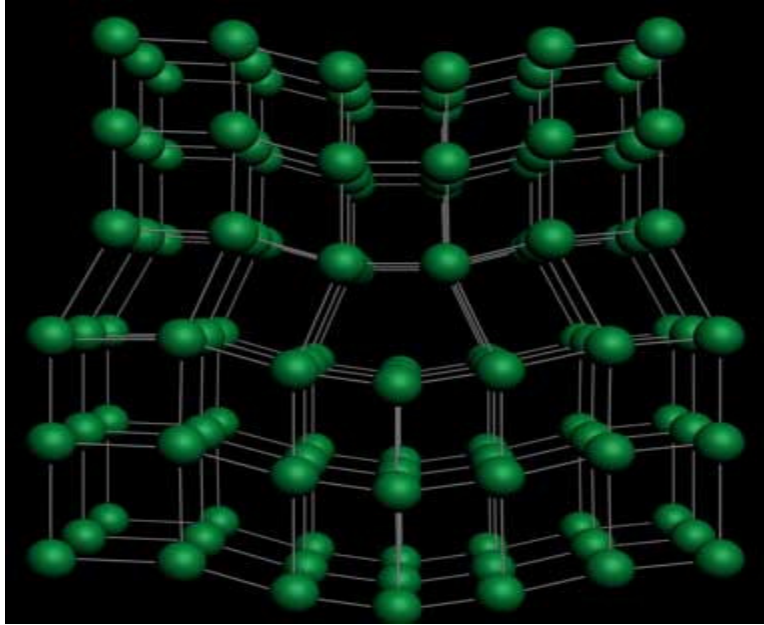
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Edge Dislocations

The edge defect can be easily visualized as an extra half-plane of atoms in a lattice. The dislocation is called a line defect because the locus of defective points produced in the lattice by the dislocation lie along a line. This line runs along the top of the extra half-plane. The inter-atomic bonds are significantly distorted only in the immediate vicinity of the dislocation line. Understanding the movement of a dislocation is key to understanding why dislocations allow deformation to occur at much lower stress than in a perfect crystal. Dislocation motion is analogous to movement of a caterpillar. The caterpillar would have to exert a large force to move its entire body at once. Instead it moves the rear portion of its body forward a small amount and creates a hump. The hump then moves forward and eventually moves all of the body forward by a small amount. As shown in the set of images above, the dislocation moves similarly moves a small amount at a time. The dislocation in the top half of the crystal is slipping one plane at a time as it moves to the right from its position in image (a) to its position in image (b) and finally image (c). In the process of slipping one plane at a time the dislocation propagates across the crystal. The movement of the dislocation across the plane eventually causes the top half of the crystal to move with respect to the bottom half. However, only a small fraction of the bonds are broken at any given time. Movement in this

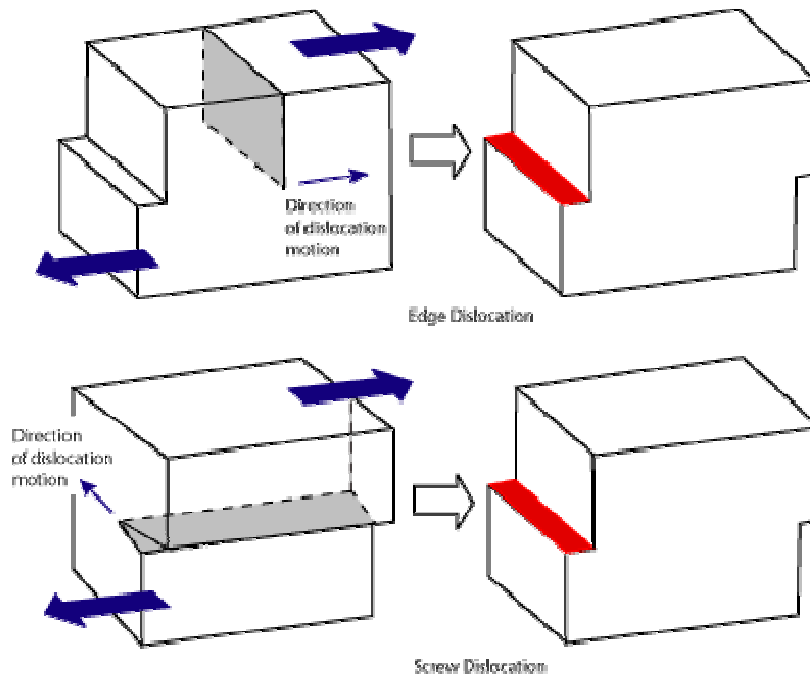
manner requires a much smaller force than breaking all the bonds across the middle plane simultaneously.



Screw Dislocations

There is a second basic type of dislocation, called screw dislocation. The screw dislocation is slightly more difficult to visualize. The motion of a screw dislocation is also a result of shear stress, but the defect line movement is perpendicular to direction of the stress and the atom displacement, rather than parallel. To visualize a screw dislocation, imagine a block of metal with a shear stress applied across one end so that the metal begins to rip. This is shown in the upper right image. The lower right image shows the plane of atoms just above the rip. The atoms represented by the blue circles have not yet moved from their original position. The atoms represented by the red circles have moved to their new position in the lattice and have reestablished metallic bonds. The atoms represented by the green circles are in the process of moving. It can be seen that only a portion of the bonds are broke at any given time. As was the case with the edge dislocation, movement in this manner requires a much smaller force than breaking all the bonds across the middle plane simultaneously.

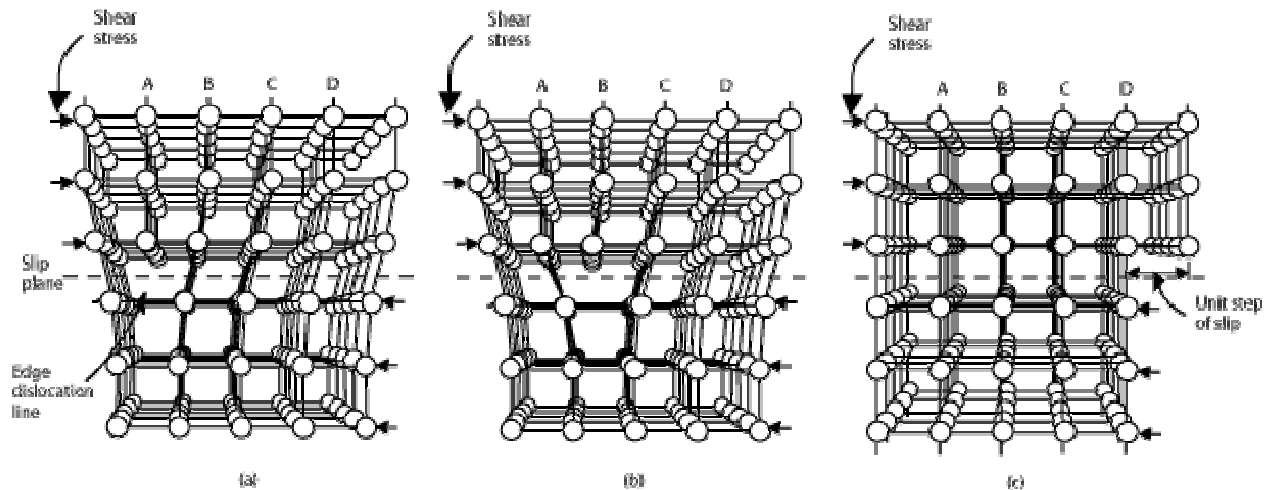
If the shear force is increased, the atoms will continue to slip to the right. A row of the green atoms will find there way back into a proper spot in the lattice (and become red) and a row of the blue atoms will slip out of position (and become green). In this way, the screw dislocation will move upward in the image, which is perpendicular to direction of the stress. Recall that the edge dislocation moves parallel to the direction of stress. As shown in the image below, the net plastic deformation of both edge and screw dislocations is the same, however.



The dislocations move along the densest planes of atoms in a material, because the stress needed to move the dislocation increases with the spacing between the planes. FCC and BCC metals have many dense planes, so dislocations move relatively easy and these materials have high ductility. Metals are strengthened by making it more difficult for dislocations to move. This may involve the introduction of obstacles, such as interstitial atoms or grain boundaries, to “pin” the dislocations. Also, as a material plastically deforms, more dislocations are produced and they will get into each others way and impede movement. This is why strain or work hardening occurs.

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2.5. Planar Defects

A disruption of the long-range stacking sequence can produce two other common types of crystal defects: 1) a stacking fault and 2) a twin region. A change in the stacking sequence over a few atomic spacings produces a stacking fault whereas a change over many atomic spacings produces a twin region.

A stacking fault is a one or two layer interruption in the stacking sequence of atom planes. Stacking faults occur in a number of crystal structures, but it is easiest to see how they occur in close packed structures. For example, it is known from a previous discussion that face centered cubic (fcc) structures differ from hexagonal close packed (hcp) structures only in their stacking order. For hcp and fcc structures, the first two layers arrange themselves identically, and are said to have an AB arrangement. If the third layer is placed so that its atoms are directly above those of the first (A) layer, the stacking will be ABA. This is the hcp structure, and it continues ABABABAB. However it is possible for the third layer atoms to arrange themselves so that they are in line with the first layer to produce an ABC arrangement which is that of the fcc structure. So, if the hcp structure is going along as ABABAB and suddenly switches to ABABABCABAB, there is a stacking fault present.

Alternately, in the fcc arrangement the pattern is ABCABCABC. A stacking fault in an fcc structure would appear as one of the C planes missing. In other words the pattern would become ABCABCAB_ABCABC.

If a stacking fault does not correct itself immediately but continues over some number of atomic spacings, it will produce a second stacking fault that is the twin of the first one. For example if the stacking pattern is ABABABAB but switches to

ABCABCABC for a period of time before switching back to ABABABAB, a pair of twin stacking faults is produced. The red region in the stacking sequence that goes ABCABCACBACBABCABC is the twin plane and the twin boundaries are the A planes on each end of the highlighted region.

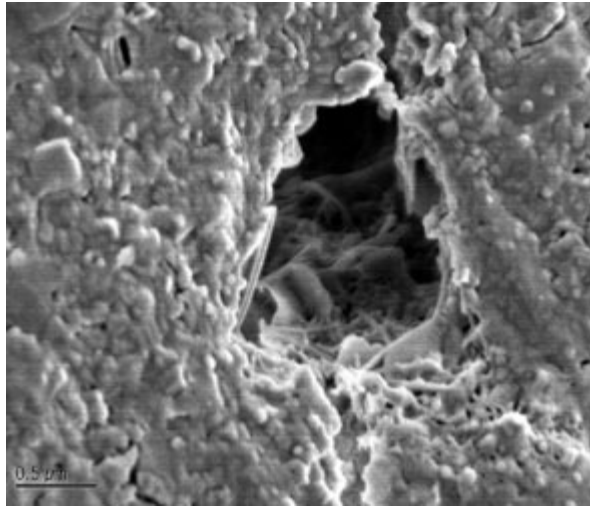
2.6. Grain Boundaries in Polycrystals

Another type of planar defect is the grain boundary. Up to this point, the discussion has focused on defects of single crystals. However, solids generally consist of a number of crystallites or grains. Grains can range in size from nanometers to millimeters across and their orientations are usually rotated with respect to neighboring grains. Where one grain stops and another begins is known as a grain boundary. Grain boundaries limit the lengths and motions of dislocations. Therefore, having smaller grains (more grain boundary surface area) strengthens a material. The size of the grains can be controlled by the cooling rate when the material is cast or heat treated. Generally, rapid cooling produces smaller grains whereas slow cooling results in larger grains. For more information, refer to the discussion on solidification.

2.7. Bulk Defects

Bulk defects occur on a much bigger scale than the rest of the crystal defects discussed in this section. However, for the sake of completeness and since they do affect the movement of dislocations, a few of the more common bulk defects will be mentioned. Voids are regions where there are a large number of atoms missing from the lattice. The image to the right is a void in a piece of metal. The image was acquired using a Scanning Electron Microscope (SEM). Voids can occur for a number of reasons. When voids occur due to air bubbles becoming trapped when a material solidifies, it is commonly called porosity. When a void occurs due to the shrinkage of a material as it solidifies, it is called cavitation.

Another type of bulk defect occurs when impurity atoms cluster together to form small regions of a different phase. The term 'phase' refers to that region of space occupied by a physically homogeneous material. These regions are often called precipitates. Phases and precipitates will be discussed in more detail later.

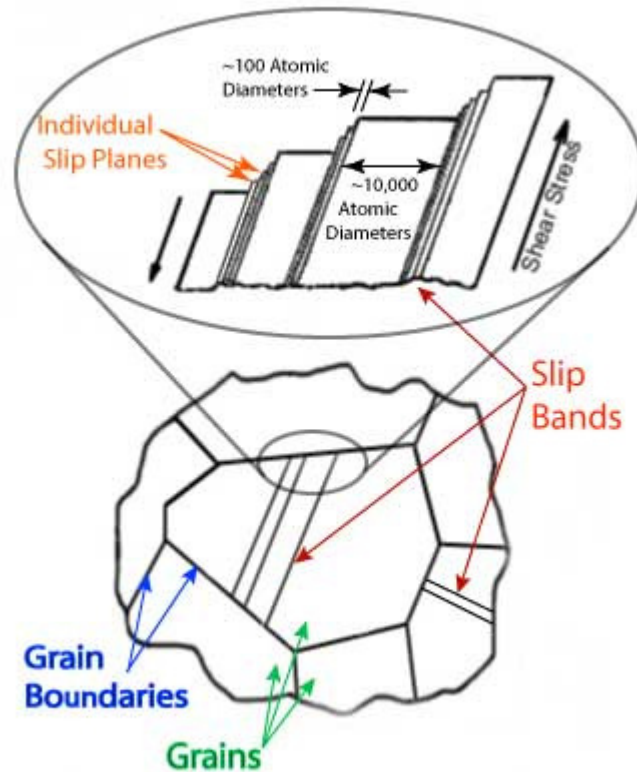


2.8. Elastic/Plastic Deformation

When a sufficient load is applied to a metal or other structural material, it will cause the material to change shape. This change in shape is called deformation. A temporary shape change that is self-reversing after the force is removed, so that the object returns to its original shape, is called elastic deformation. In other words, elastic deformation is a change in shape of a material at low stress that is recoverable after the stress is removed. This type of deformation involves stretching of the bonds, but the atoms do not slip past each other.

When the stress is sufficient to permanently deform the metal, it is called plastic deformation. As discussed in the section on crystal defects, plastic deformation involves the breaking of a limited number of atomic bonds by the movement of dislocations. Recall that the force needed to break the bonds of all the atoms in a crystal plane all at once is very great. However, the movement of dislocations allows atoms in crystal planes to slip past one another at a much lower stress levels. Since the energy required to move is lowest along the densest planes of atoms, dislocations have a preferred direction of travel within a grain of the material. This results in slip that occurs along parallel planes within the grain.

These parallel slip planes group together to form slip bands, which can be seen with an optical microscope. A slip band appears as a single line under the microscope, but it is in fact made up of closely spaced parallel slip planes as shown in the image.



2.9. Imperfections in Metals

2.9.1 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.

2.9.2 Point Defects

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 °C or °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 $kT(300 \text{ K}) = 0.025 \text{ eV}$ (room temperature) is much smaller than typical vacancy formation energies. For instance, $Q_V(\text{Cu}) = 0.9 \text{ eV/atom}$. 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.

2.10 Impurities in Solids

All real solids are impure. A very high purity material, say 99.9999% pure (called 6N – six nines) contains $\sim 6 \times 10^{16}$ 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.

2.11 Miscellaneous Imperfections

2.11.1 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.

2.11.2 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.

2.11.3 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.

2.12 Diffusion

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).

2.12.1 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.

2.12.2 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/m²-second) or in terms of mass flux (e.g., kg/m²-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:

$$J = -D \frac{dC}{dx}$$

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.

2.12.3 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).

2.12.4 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: $D = D_0 \times \exp(-Q_d/kT)$.

2.12.5 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.

2.13 Dislocations and Strengthening Mechanisms

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.

Dislocations can be *edge dislocations*, *screw dislocations* and exist in combination of the two. 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.

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.

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).

2.13.1 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.

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

2.13.2 Solid-Solution Strengthening

Adding another element that goes into interstitial or substitutional positions in a solution increases strength. The impurity atoms cause lattice strain 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.

2.13.3 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 :

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

2.13.4 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.

Recovery

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

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.

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.

2.14 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.