

Nature of Metals and Alloys

INTRODUCTION

Before beginning a study of heat treatment of metals and alloys, one should have a clear idea about nature of metals. One can prepare a list of many items made of metals and alloys of daily life. The list will probably include aluminium pots, rolled sheet of mild steel for making the body of refrigerator, scooter and car, steels for making parts, such as gears, pistons, crank shafts of locomotives, copper wire conductors, agricultural implements made of steel and cast irons, aeroplanes made of aluminium and magnesium alloys, and many others. In spite of knowing so much about metals, it is not an easy task to define a metal accurately. Chemists define metals in terms of acids and bases. The base is metal oxide or hydroxide. When metals react with acid, they liberate one or more atoms of hydrogen from acid. Physicists as well as chemists agree that metals have bright lustre (ability to reflect light), good electrical and thermal conductivity, malleability and ductility. In general all metals show all these properties. At the same time, there are non-metals which show one or more of the above mentioned properties. Besides this, metals among themselves show large variation with respect to these properties. For example, lead at room temperature is very soft while tungsten at room temperature is very hard and brittle.

The basic property associated with metals is high electrical and thermal conductivity. This distinguishes them from non-metallic substances. Amongst commonly used engineering metals the best conductor of electricity is copper. However, silver is the best electrical conducting metal. Lead, on the other hand, has poor conductivity. It has electrical conductivity which is one-twelfth of copper. When we compare the conductivity of non-metals such as diamond with copper, it is observed that conductivity of diamond is 10^{-9} times that of copper. Such a large difference in conductivity is due to electrons in metals which can move freely in conduction bands. In non-metals, free movement of electrons under the influence of external electrical field does not take place. Thus, it can be concluded that in metals electrons can move freely and permit flow of current under the action of a potential difference.

In general, the words metal and alloy are interchangeable. However, for engineering and scientific work, metals are metallic elements which are almost pure. Each metal has its own characteristics such as atomic weight, atomic volume, atomic number, melting point and density. By chance it may be possible that an alloy may have the same colour, melting point and density as a pure metal. However, X-ray diffraction techniques distinguish them clearly from parent metals. A very simple way of identification is chemical analysis as alloys contain more than one element.

An alloy may be defined as a combination of two or more elements. The element that is in major quantity should be a metal while the others may be metals, non-metals or combination of both. The resulting material should have metallic characteristics. Brass, bronze and steel are typical examples of alloys.

2.1 CRYSTAL STRUCTURE

A discussion of properties of metals and alloys has to start with consideration of the atom itself. However, the interrelations between individual atoms and heat treatment is far fetched. For a sound understanding of the principles of heat treatment, it is sufficient to go up to the level of crystals rather than atoms.

All metals are crystalline in nature, where atoms are arranged in a definite periodic order. When a solid is composed of only one crystal, it is called single crystal. When a solid is composed of several crystals, it is called a polycrystalline material. In fact, the individual crystals get aggregated to form the solid mass of a polycrystalline substance.

The term grain is used to denote a single crystal in polycrystalline aggregate. In general grains do not have perfect outward form.

On the basis of periodic arrangement of atoms, crystals are grouped into seven crystal structure systems. Cubic, tetragonal, orthorhombic, rhombohedral, hexagonal, monoclinic and triclinic are the seven crystal structure systems. Most of the metals and alloys belong to cubic and hexagonal crystal structure systems and hence are being discussed here.

In a crystal structure, the smallest unit is the unit cell which characterizes the specific arrangement and location of atoms. When the unit cell is repeated in three directions, complete arrangement of atoms in crystal becomes apparent.

2.1.1 Cubic Crystal Structure

Three types of unit cells with cubic crystal structure are possible: simple cubic (SC) structure, body centred cubic (BCC) structure, and face centred cubic (FCC) structure (Figure 2.1).

Simple Cubic In this case, atoms are located at all the corners of the unit cell.

Body Centred Cubic Structure In the BCC structure, 8 atoms are at corners of the unit cell and 1 atom is at the body centre position. Na, Cr, Mo and W are examples of the elements having BCC crystal structure [Figure 2.1(b)].

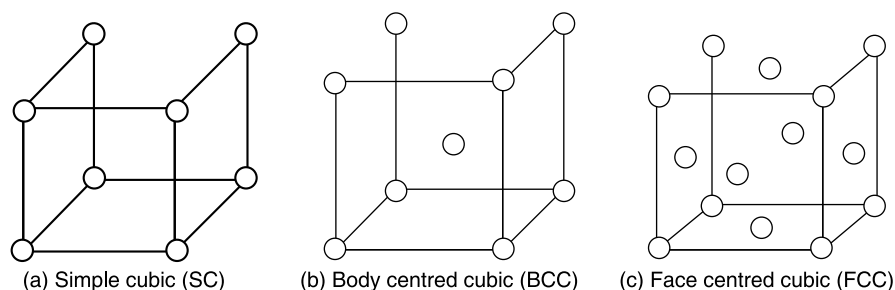


Figure 2.1 Unit cells.

Face Centred Cubic Structure In the FCC structure, 8 atoms are arranged at the 8 corners of the unit cell and 6 atoms at the 6 face centres. Cu, Ag, Au, Al, and Ni are the examples of the FCC elements.

2.1.2 Hexagonal Close Packed Crystal Structure

The arrangement of atoms in the hexagonal close packed (HCP) structure is illustrated in Figure 2.2. Be, Ti, Mg and Zn are some of the examples of metals that solidify into the HCP structure.

Generally, the FCC metals are soft, ductile and easily deformable, while the BCC and HCP metals are comparatively brittle and difficult to deform. Table 2.1 shows the crystal structures and lattice constant of some of the common metals.

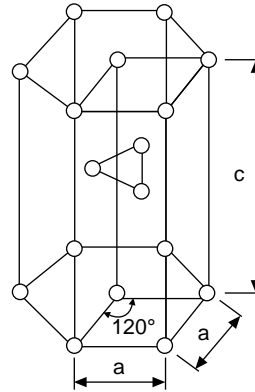


Figure 2.2 HCP (hexagonal close packed) structure.

Table 2.1 Crystal Structures and Lattice Constants of Some Common Metals

| Element | Crystal structure | Lattice constant (Å) | Temperature of measurement of lattice constant (°C) |
|-------------------------------|-------------------|----------------------|---|
| Aluminium | FCC | 4.0490 | 20 |
| Cobalt β | FCC | 3.552 | 20 |
| Copper | FCC | 3.6153 | 20 |
| Gold | FCC | 4.0783 | 20 |
| γ -iron (extrapolated) | FCC | 3.571 | 20 |
| γ -iron (908–1403°C) | FCC | 3.656 | 950 |
| Lead | FCC | 4.9495 | 20 |
| Nickel | FCC | 3.5238 | 20 |
| Silver | FCC | 4.0856 | 20 |
| α -iron | BCC | 2.8664 | 20 |
| Molybdenum | BCC | 3.1466 | 20 |
| Titanium β | BCC | 3.33 | 900 |
| Cadmium | HCP | 2.9787 | 20 |
| Cobalt α | HCP | 2.507 | 20 |
| Magnesium | HCP | 3.2092 | 20 |
| Zinc | HCP | 2.664 | — |

2.2 PROPERTIES OF METALS AND ALLOYS—ROLE OF HEAT TREATMENT

Metals occupy a significant position among engineering materials because of their chemical, physical and mechanical properties. Passivity and corrosion resistance are some of the chemical properties. The physical properties include density, electrical conductivity and

thermal conductivity. Tensile and compressive strength, hardness, ductility, resistance to fatigue, impact and abrasion resistance are some of the mechanical properties. In every engineering application, a suitable combination of these properties is required. Physical, mechanical and chemical properties are greatly affected by alloying additions and thermal treatment. For example, when about 4.5 percent copper is added to aluminium and heat treated, the alloy so formed and treated has very high hardness and strength. This is in contrast to pure aluminium which is soft. In many alloys, properties depend largely on their thermal and mechanical history in addition to their chemical composition. In other words, thermal treatment can change mechanical properties of alloys considerably as a result of the modifications that occur due to thermal treatment.

An engineer should have good knowledge about the basic properties of metal and alloys. The successful use of materials for various applications depend on a sound knowledge of these aspects. Properties of alloys can be improved by changing the chemical composition and by proper heat treatment. This understanding helps to reduce the cost of components and make their use economical. An important part of this information is the understanding of heat treatment processes and how they alter the properties. These aspects of heat treatment are discussed in detail in the chapters that follow.

2.3 NATURE OF ALLOYS

In physical metallurgy, the theory of alloys has been developed from fundamental principles. The nature of atoms that constitute an alloy decides the nature of the alloy. Thermodynamic principles are used extensively in arriving at the rules that govern formation of alloys. In the following sections, classification of alloys on conventional basis is carried out. Also, only binary alloys are taken up for discussion.

Pure metals have definite freezing point. When some element is added to a pure metal, the alloy so formed, in general, will solidify either at a higher or a lower temperature as compared to the pure metal. This may also give rise to such a condition that the alloy freezes over a range of temperature. In such cases, solidification proceeds progressively on cooling. Thus, most alloys do not freeze at a constant temperature.

Alloys are produced by melting techniques. Alloying additions of definite quantities are made to base metal. All the constituents are melted together in melting furnace. Solubility of metals constituting an alloy is of importance in this context.

Most of the metals form complete homogeneous solution in liquid state. (Lead-copper and lead-aluminium systems are exceptions to this. In liquid state, both these systems separate into two liquid layers.) When such alloys are cooled from liquid to solid state, there are three possibilities with regard to their solubility in each other: (i) Two metals may show complete solid solubility; (ii) two metals may have no solid solubility; and (iii) two metals may have limited solid solubility.

Solid solutions are formed under possibility (i) and possibility (iii) mentioned above. Solid solutions can be of two types: Substitutional solid solutions and interstitial solid solutions.

Substitutional Solid Solutions

There is direct substitution of the solvent atoms by those of the solute atoms. Crystal lattice of solvent is retained. The only change in the crystal lattice is that of the lattice parameters. Cu-Ni solid solution is a typical example of this type. In this case, Ni atoms substitute for the Cu atoms and form substitutional solid solution with copper. Figure 2.3 shows the arrangement of atoms in a substitutional solid solution. In this figure, hatched circles show solute atoms while empty circles show atoms of base element.

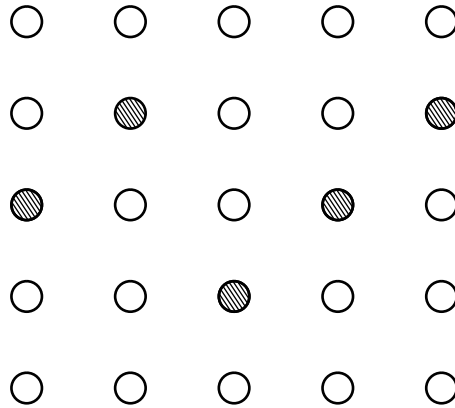


Figure 2.3 Arrangement of atoms in substitutional type of solid solution.

Interstitial Solid Solutions

These are formed when the size of the solute atom is very small as compared to the size of the solvent atoms. Hydrogen, boron, carbon and nitrogen form interstitial solid solution with a number of metals. Carbon in solution in α -iron and γ -iron form interstitial solid solutions which are popularly known as ferrite and austenite, respectively. In interstitial solid solutions, solute atoms occupy the interstitial sites in the crystal structure of the solvent metal. Figure 2.4 shows the arrangement of atoms in interstitial solid solutions. In this figure, the dark smaller circles represent solute atoms while empty circles represent atoms of base element.

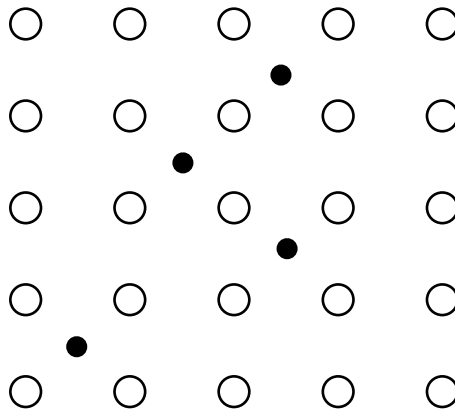


Figure 2.4 Arrangement of atoms in interstitial type of solid solution.

Hume-Rothery Rules

The rules governing the formation of substitutional solid solutions are called Hume-Rothery rules. According to these rules, the following factors affect solid solubility: (i) size, (ii) crystal structure, (iii) valency, and (iv) electrochemical nature of the species. We now discuss each of these factors.

Size Factor Formation of substitutional solid solution is favoured if the size difference between solute and solvent atoms does not exceed a value of 15 percent. When the solute atom is introduced in the crystal lattice of the solvent, lattice strains are introduced. The smaller the size difference between the solute and solvent atoms, the less will be the strains in the parent lattice. Accordingly, the chances of formation of substitutional solid solution are higher. A 15 percent limit has been arrived at empirically. This limit is based on the observations made in known solid solutions. If the size difference between the solute and solvent atoms exceeds 15 percent limit, then the lattice strains will be so high that the formation of substitutional solid solution will not be feasible. In such cases, the solute atoms will have separate identity and will be present as second phase particles in the matrix of the parent phase. For example, lead is insoluble in copper and is present as second phase particles in the form of globules.

Crystal Structure If two elements have the same crystal structure, then both of them will try to form a substitutional solid solution. This factor should not be viewed in isolation. For instance, considering the Cu-Ni binary system, the size factor effect is favourable. In addition, they also have the same crystal structure, namely, FCC. Due to these two favourable conditions, it is expected that Cu and Ni will form a continuous series of solid solution. This is what is observed in practice.

Valency (Relative valency effect) According to this rule, a metal of higher valency has tendency to dissolve to a large extent in a metal of lower valency than the extent to which the latter dissolves in the former. This rule is a general one and is applicable only for alloys of the univalent metals, such as Cu, Ag, and Au with those of higher valency. For example, in the Cu-Zn system, the solubility of Zn (valency + 2) in Cu (valency + 1) is about 40 percent. In contrast, the solubility of copper in zinc is negligible.

Electrochemical Factor Metals are arranged in electromotive series. Metals occupying higher position in the series are more electropositive. The metals occupying lower positions are electronegative with respect to those occupying higher positions. If two metals are positioned far apart in the electromotive series, the two can be considered relatively as electropositive and electronegative elements, and there is a strong chemical affinity between the two. Under such conditions, the two metals are likely to form a chemical compound rather than solid solution. Further, the larger the difference in the position of any two elements in the electromotive series, the greater the stability of the compound formed.

The electronegativity of the elements in the periodic table increases from left to right in any period and from bottom to top in any group. Therefore, if magnesium of group II is alloyed with elements of group IV, such as silicon, tin or lead, the formation of compound of the type Mg_2 (Si, Sn or Pb) will take place. The order of stability will be Mg_2Pb , Mg_2Sn and Mg_2Si in ascending order as it is obvious by their melting points: 550, 778 and 1085°C, respectively. The extent of solid solubility is very small in all these cases.

2.3.1 When Two Metals Show Complete Solid Solubility

When two metals show complete solid solubility, an isomorphous system is formed (see Section 2.4.1). Since solid solution is a homogeneous phase, its microstructure would resemble that of a pure metal.

2.3.2 When Two Metals have No Solid Solubility in Each Other

When a solid solution is not formed, the formation of compounds may take place. The phases which form in the intermediate regions of the phase diagram may give rise to the formation of compounds. The compounds may be (i) electrochemical compounds, (ii) size factor compound, or (iii) electron compounds. These are now discussed.

Electrochemical Compounds

The important characteristics of electrochemical compounds are: (i) They follow the valency laws; (ii) the range of solid solubility is small; (iii) they have high melting points; and (iv) their crystal structures correspond to specific chemical compounds such as NaCl or CaF₂.

The range of solid solubility decides whether the intermediate phase is a solid solution or compound. If the phase exists over a narrow range, then it is called a compound; if the phase exists over a wide range, it is referred to as a solid solution. Magnesium-based compounds, such as Mg₂Pb, Mg₂Sn or Mg₂Si, are common examples of electrochemical compounds and satisfy these conditions.

Size Factor Compounds

These compounds are formed when there is appreciable difference in the atomic diameters of the participating elements. There are two types of size factor compounds, namely, interstitial and substitutional. If

$$\frac{\text{radius of interstitial atom}}{\text{radius of metal atom}} = 0.41$$

then interstitial solid solutions are formed. Again, if

$$0.59 > \frac{\text{radius of interstitial atom}}{\text{radius of metal atom}} > 0.41$$

interstitial compounds are formed. Borides, carbides and nitrides of transition metals are examples of this category. These phases occur over a small range of composition having a mean formula of type of M₂X or MX (M denotes symbol of solvent metal and X of solute element). Carbides and nitrides of titanium, zirconium, vanadium, niobium and tantalum are the examples of the ones which crystallize into NaCl type of structure. If

$$\frac{\text{radius of interstitial atom}}{\text{radius of metal atom}} > 0.59$$

then the distortion in the parent lattice is too large and, consequently, more complex crystal structure results. For example, in Fe₃C (iron carbide), the ratio is 0.63, and it has a complex structure.

When the difference in the sizes of atoms of two elements is about 20 to 30%, it is possible to achieve efficient packing of the atoms provided the crystal structure common to the Laves phase is adopted. In this phase, each 'A' atom has 12 'B' atoms and 4 'A' atoms as neighbours. They have the common formula AB_2 . Further, each B atom is surrounded by 6 like and 6 unlike atoms.

Electron Compounds

These compounds are formed at specific electron to atom (e/a) ratio. W. Hume-Rothery and coworkers pointed out that the (e/a) ratio controls formation of certain intermediate phases which are termed as electron compounds. Besides this (e/a) ratio is important in governing the limit of primary solid solutions. The three (e/a) ratios corresponding to specific crystal structures in an alloy system are $3/2$, $21/13$ and $7/4$.

The β -brass phase ($CuZn$) having the BCC structure has an (e/a) ratio of $3/2$. Other examples of this category are Cu_3Al (BCC), Cu_5Si (β -manganese, complex cubic), and Ag_3Al (CPH). In the case of Ag-Al system, the Ag_3Al structure gets 3 valency electrons from the aluminium, and one each from silver atoms which give rise to an (e/a) ratio of 6 electrons to 4 atoms. This is the same as $e/a = 3/2$.

The γ -brass phase (Cu_5Zn_8), which has a complex cubic structure, is an example of electron compound having (e/a) ratio of $21/13$. Other examples are Cu_9Al_4 and $Cu_{31}Sn_8$.

$CuZn_3$ which is ϵ -brass phase, has an HCP structure corresponding to (e/a) ratio of $7/4$. Other examples of this category are Cu_3Sn and Cu_3Si .

2.3.3 When Two Metals are Soluble to Limited Extent in Solid State

In addition to the possibilities of formation of solid solution over a complete range of composition and of compounds, the third possibility is that of partial solid solubility of two elements in each other. Copper and nickel have complete solid solubility in all proportions and both of them have the FCC structure. However, with an increase in the difference of size factor, the solid solubility limits are changed. For example, the Cu-Ag system (eutectic system) exhibits only partial solid solubility. Such a system can be understood with the help of the relevant phase diagram.

2.4 PHASE DIAGRAMS

Depending on the number of components (metals) that constitute an alloy, binary, ternary, quaternary and complex multicomponent phase diagrams are required for studying the corresponding system. Only binary phase diagrams are discussed in this section.

Freezing of binary alloys from molten state generally occurs as a continuous process over a range of temperature and, even after completion of solidification, some constitutional changes occur in an alloy. These changes which take place during and after solidification of the alloy can be represented graphically by taking temperature on the Y-axis and composition on the X-axis. These graphs are known as phase diagrams, equilibrium diagrams or constitutional diagrams. Knowledge of these diagrams is very helpful in controlling and understanding heat treatment processes. With the help of phase diagrams it is possible to estimate the temperatures at which melting commences and is completed. Also, the possible phase changes that take

place by varying the composition or temperature of the alloy can be studied with the help of these diagrams. However, the rate of reactions and structural arrangement of phases are not revealed by phase diagrams.

The word *equilibrium* has been used to denote the fact that during investigations the rate of change of temperature or of composition is extremely slow. This ensures that the alloy comes to a state of rest before a variable such as temperature is changed. But this situation is rarely met with in practice. Nevertheless, these diagrams are very helpful in revealing the path through which changes are likely to take place. Phase changes in commercial alloys of industrial importance can be studied with the help of phase diagrams which incorporate isomorphous, eutectic, eutectoid and peritectic reactions.

2.4.1 Isomorphous System

In this binary system, both elements are soluble in all proportions, both in liquid and in solid states. All alloys belonging to such a system will give rise to a single liquid phase on melting and a single solid phase on freezing. The single phase solid solution so formed is normally denoted by alpha (α). At any point in the α -range, the two metals dissolve in each other at crystal lattice level, they cannot be distinguished from each other under microscope, and their microstructure resembles that of a pure metal. Figure 2.5 is a typical example of an isomorphous system, namely, the nickel-copper phase diagram.

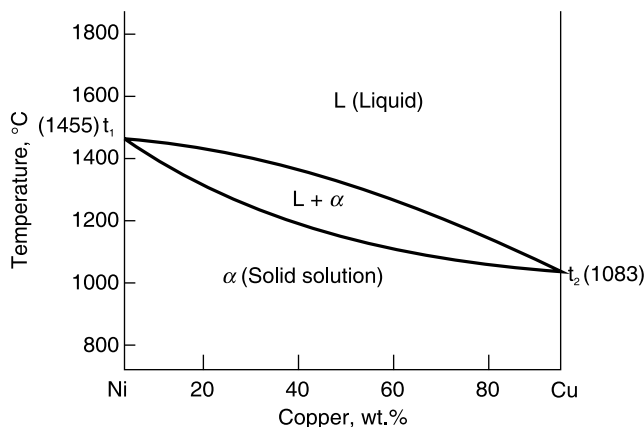
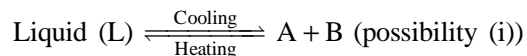


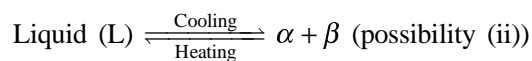
Figure 2.5 Nickel-copper phase diagram.

2.4.2 Eutectic System

In this system, the two elements are completely soluble in all proportions in the liquid state. On cooling, two possibilities may arise: (i) the two elements are completely insoluble in the solid state; (ii) the two elements are partly soluble in the solid state. These reactions can be shown as



where A and B are metals, and



where α is A rich solid solution and β is B rich solid solution.

These reactions take place at a fixed temperature, called eutectic temperature, and the composition of participating phases is also fixed. Gibb's phase rule can be applied to this equilibrium system. This rule states that for a system consisting of a number of phases in equilibrium, $P + F = C + 2$, where P is the number of phases in equilibrium with each other, F is the degree of freedom, and C is the number of components. For the metallurgical system, pressure is normally maintained constant at one atmosphere. Hence, one degree of freedom is excluded, and the modified phase rule for condensed system is $P + F = C + 1$. This rule is very helpful in studying phase diagrams. On applying the modified phase rule to eutectic equilibrium, the degree of freedom (F) becomes zero. In this case, $P = 3$, $C = 2$. On substituting these values in the equation $P + F = C + 1$, F comes out to be zero. This clearly indicates that the three phases coexist at a single temperature. This temperature is the melting point of the eutectic alloy. Since the three phases also have a fixed composition, the system is invariant. The term eutectic refers to the lowest melting alloy in the entire alloy system. The characteristic feature of eutectic alloy is that it melts at fixed temperature just like a pure metal. Cooling curves for the eutectic alloy and pure metal are identical. Eutectic alloys have very good casting characteristics such as excellent fluidity and minimum porosity. Figures 2.6 and 2.7 show the phase diagram of Bi-Cd and Pb-Sn system, respectively. Both are of the eutectic type.

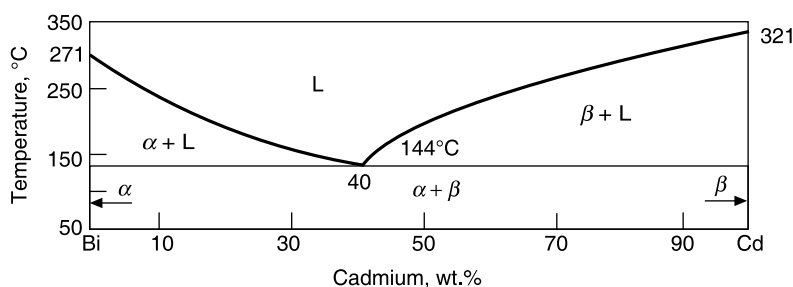


Figure 2.6 Bismuth-cadmium phase diagram.

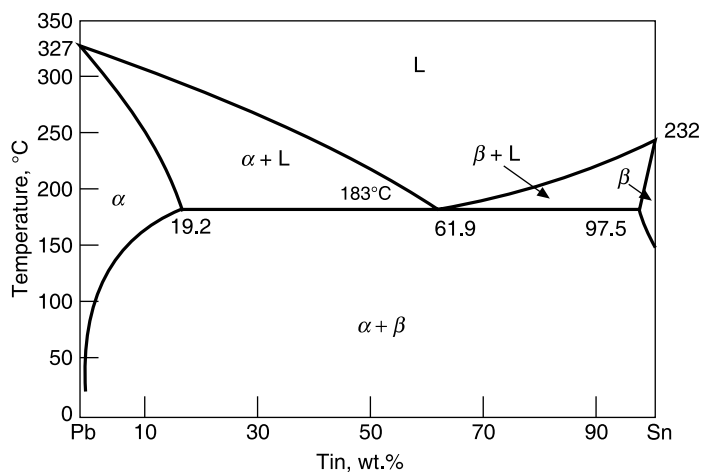


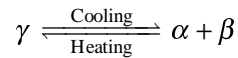
Figure 2.7 Lead-tin phase diagram.

It may be observed that the Bi-Cd system comes under category 1 of the eutectic system since both the metals are completely insoluble in each other. The two metals appear as mechanical mixture in the eutectic.

It is seen that Sn and Pb are partially soluble in each other in solid state. The Pb rich and Sn rich solid solutions are designated as α and β , respectively. In the solid condition, in the two-phase field region, the alloy consists of mechanical mixture of α and β .

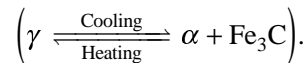
2.4.3 Eutectoid System

This is a solid state transformation, i.e. solid-to-solid transformation. In this case, one solid solution on cooling changes to two solids:



which is the generalized representation of the eutectoid reaction. The temperature at which this reaction takes place is called eutectoid temperature, and the particular composition is known as eutectoid composition of the alloy. The microstructure of the alloy having eutectoid composition shows alternate layers of α and β . Comparing this structure with that of the eutectic alloy, it can be seen that both of them have similar appearance. Hence, at times eutectic and eutectoid microconstituents are microstructurally indistinguishable.

Eutectoid reaction occurs in the Fe-Fe₃C phase diagram at a temperature of 723°C. In this case, austenite changes to pearlite:

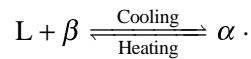


The microstructure of pearlite shows completely lamellar structure which consists of alternate layers of ferrite and cementite. This is discussed in detail in Chapter 3.

2.4.4 Peritectic System

Ag-Pt is a typical example of the peritectic system. Figure 2.8 depicts the Ag-Pt phase diagram. Peritectic reaction is a common feature of some of the more complex phase diagrams, e.g. the one at the Cu-Zn system.

Peritectic reaction is represented as



In general, peritectic reactions are rarely completed during normal solidification. This is due to the fact that primary β crystals are covered by the layers of α , which prevent the diffusion process. Therefore, on cooling, unreacted β -phase may be seen in peritectic alloys.

2.4.5 Phase Diagram Showing the Presence of Intermetallic Compounds

Figure 2.9 shows the presence of the intermetallic compound Mg₂Sn which contains 29.08 percent magnesium. The melting point of this compound is 778°C which can be lowered by the addition of either magnesium or tin. The equilibrium diagram consists of two eutectic phase diagrams which are joined together.

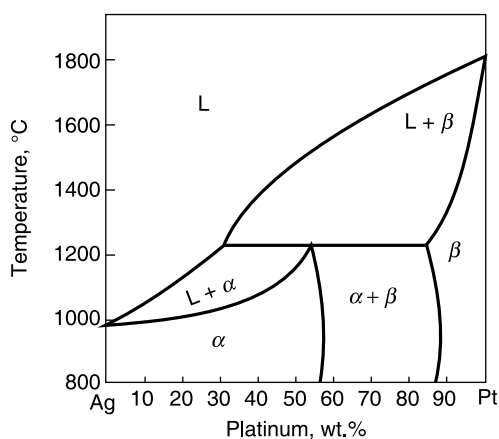


Figure 2.8 Silver-platinum phase diagram.

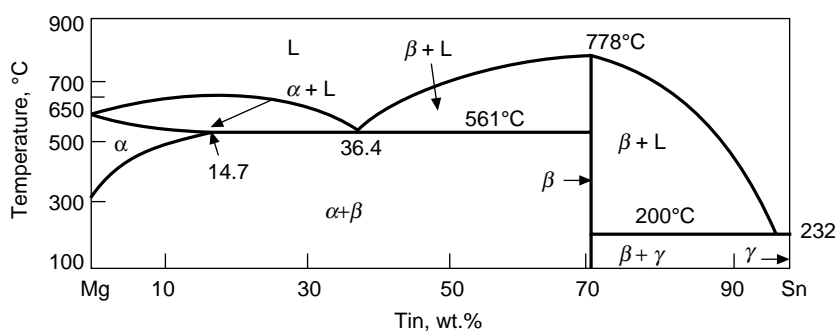


Figure 2.9 Magnesium-tin phase diagram.

2.5 METALLOGRAPHY

Metallography is the study of the internal structure of metals and alloys under microscope at different magnifications. Useful information on grain size, shape and distribution and on percentage of various constituents in the structure can be obtained by metallographic techniques.

Preparation of the sample is necessary for revealing the microstructure of a given specimen. There are two types of metallographic examinations. They are: (i) Macroexamination where the structure is observed with naked eye or under low magnification ($\times 5$); and (ii) microexamination where small areas at high magnification (50 to 2000 \times) are observed for this purpose.

2.5.1 Macroexamination

Macroexamination reveals the following:

- (i) Segregation of impurities (for instance, antimony in bearing metals and sulphur and phosphorus in steel)

- (ii) Presence of non-metallic inclusions, e.g. sulphides and oxides
- (iii) Grain size
- (iv) Fabrication techniques (for instance, casting, rolling, forging and welding).
- (v) Casting defects (e.g. blow holes, pipe formation seams and laps).

Sulphur Print

An indication of the distribution and segregation of sulphur in steels and cast irons can be detected with the help of a silver bromide paper. In this process, first of all the specimen is ground plain and polished with emery papers of successively finer grades. The surface so obtained should be free from dirt and grease. A piece of bromide paper is soaked for 2 minutes in 3% sulphuric acid. The bromide paper is taken out of acid solution and excess acid is wiped off with the help of blotting paper. Now bromide paper with sensitized side is placed in intimate contact with polished surface of the specimen for one or two minutes. During this period, the sulphides react with sulphuric acid and evolve H_2S gas, which stains bromide paper. After this, the bromide paper is removed and washed in water for about 3 minutes and fixed in 20 percent hypo for about 5 minutes. It is finally washed in water for 15 to 20 minutes and dried. The intensity of brown stains on bromide paper indicates the degree of segregation of sulphur. This technique has a limitation. It is not applicable to non-ferrous metals and high alloy steels.

Phosphorus Print

Segregation of phosphorus in steels is detected by phosphorus printing. In this case, a piece of photographic paper is soaked in an aqueous solution of ammonium molybdate (containing 5 gm of ammonium molybdate per 100 cc of water) plus 35 cc of nitric acid (having a density of 1.2). The photographic paper is then taken out and the excess solution is wiped off and the paper is placed with sensitized surface in intimate contact with the polished surface of the specimen. The paper is removed after 5 minutes and developed in an aqueous solution containing 35 percent HCl plus 5 cc saturated stannous chloride solution plus a small quantity of alum. The complex phospho-molybdate, occurring over certain areas as a result of the process associated with the first stage is partly reduced during development. As a result, there is a change in the colour of the molybdates from yellow brown to blue. The blue areas so formed on the paper correspond to phosphorus rich areas on the surface of steel. The intensity of the staining indicates the amount of phosphorus present as segregation.

Macroetching

Macroetching of metals involves deep etching with a suitable reagent that reacts selectively with metal structure. The structure so revealed can be examined by naked eye or at a low magnification. The surface of metal to be examined is ground and polished with the help of emery paper. After this, the metal is immersed in the reagent until the structure is clear. Alternatively, the metal surface may be swabbed with the reagent. The metal surface is then washed in water and methylated spirit and finally dried.

Following are the macroetching reagents used for different types of alloys to reveal different kinds of structures.

(i) *Fry's reagent* This reagent is used to reveal overstrain (strains beyond elastic limit) regions in mild steels. It is necessary to heat the specimen to about 230°C for 30 minutes before etching. Etching time varies from 2 to 22 hours. The composition of Fry's reagent is as follows:

| | |
|-------------------|--------|
| Cupric chloride | 90 gm |
| Hydrochloric acid | 120 cc |
| Water | 100 cc |

(ii) *Humphrey's reagent* This reagent is used to reveal dendritic and fibrous structure in steel. In this case, the prepared steel sample is first immersed in Heyn's reagent (10 gm copper ammonium chloride plus 100 cc water) for about 2 minutes. Then the sample is transferred to Humphrey's reagent. The sample is kept immersed in this reagent for 1/2 hour to 4 hours, while the bath is kept under agitation. The copper coating deposited on the sample is removed with cotton wool. The surface is then washed with spirit and dried. The Humphrey reagent contains the following:

| | |
|--------------------------------|--------|
| Copper ammonium chloride | 10 gm |
| Concentrated hydrochloric acid | 5 cc |
| Water | 100 cc |

(iii) To study segregation in steel, the reagent used has the following analysis:

| | |
|------------------|--------|
| Iodine | 10 gm |
| Potassium iodide | 20 gm |
| Water | 100 cc |

(iv) The reagent recommended for macroetching of aluminium and its alloys contains the following:

| | |
|-------------------|--------|
| Hydrofluoric acid | 10 cc |
| Nitric acid | 1 cc |
| Water | 200 cc |

(v) For copper, brass and bronze, the reagent contains the following:

| | |
|----------------------|--------|
| Nitric acid | 45 cc |
| Water | 50 cc |
| Potassium dichromate | 0.2 gm |

2.5.2 Microexamination

Preparation of metal samples for microexamination involves a number of steps, such as sampling, flattening, grinding, polishing and etching. The sample for microexamination of metals and alloys is cut with the help of hacksaw to a suitable size, say measuring 10 mm dia. ×10 mm to 20 mm dia. ×20 mm. (If samples are too small to be handled with ease, they are mounted on a bakelite or lucite base for preparation.) The sample so cut is filed and ground. Grinding may be carried out either manually or on a grinding wheel. Further polishing is carried out on various grades of emery papers (silicon carbide). Subsequently, grades of emery papers with increasing fineness are used. The next stage is the final polishing which is carried out on a rotating disc covered with a sylvet or billiards cloth, which is soaked in water,

sprinkled with a slurry of alumina or calcined magnesia. The disc rotates at a speed of 100–400 rpm. When the polished surface of the sample becomes scratch-free and mirror like, it is taken for etching. Only after etching, does the internal structure of metal become apparent under microscope. This is due to the fact that chemical attack by etchant varies from phase to phase. For example, in steel, the etchant (3% nital, i.e. solution 3% of concentrated nitric acid in absolute methyl alcohol) reacts differently with ferrite and cementite. So these phases are distinguished separately under microscope. Grain boundaries are attacked more easily and at a faster rate by etchant. Therefore, they look as thin dark lines under microscope. Similarly, chemical attack of non-metallic inclusions by etchants varies widely with different types of inclusions. After etching, the sample is washed in running water and alcohol, and then dried in hot air.

Table 2.2 lists some etching reagents in common use.

2.6 METALLURGICAL MICROSCOPE

Microscope is an important tool for a metallurgical engineer. Metallurgical microscope is very helpful in determining the size, shape and distribution of various phases, including inclusions in metals. Grain size determination is also made with the help of metallurgical microscope. All these studies have a great bearing on the mechanical properties of metals. No structure property correlation can be made without the help of metallography.

Construction of a metallurgical microscope is similar to that of a biological microscope, except the manner by which the specimen is illuminated. Metallic specimens are opaque to light. These specimens are polished and etched. Reflected light from the surface of the specimen reveals microscopic details. In contrast, in the case of biological microscope, transmitted light reveals the structural details of biological specimens.

Different types of metallurgical microscopes are available. All of them work on the principle of reflection of light from the specimen surface. Figure 2.10 shows typical metallurgical microscope and its working principle. Such a microscope essentially consists of two parts: the compound microscope, and the electrical illuminating system. A beam of light from illuminating source enters into the tube of microscope from the side. The light falls on the surface of right prism and is reflected downwards. The reflected light passes through the objective lens of microscope and falls on the surface of metallic specimen, the surface reflects back the light. The reflected light again passes through the objective lens and reaches the eye piece. Magnified virtual image is formed during the process. The objective lens resolves the structure of metal, whereas the eye piece magnifies the image formed by the objective.

The whole body of microscope is mounted on a base or foot. A draw tube carrying the eye piece at its top slides in the upper end of the body tube of the microscope. Body tube is connected to the upper end of the limb with the help of rack and pinion device. By sliding the draw tube, the distance between the eye piece and objective lens changes. This helps in proper focusing of the specimen.

During coarse adjustment, the body tube is lowered or raised to get the correct focus. The final stage of coarse focusing is always carried out by lowering the head to the level of stage. The stage then approaches the cover glass. Fine adjustment helps in final focusing of the specimen.

Table 2.2 Etching Reagents for Microscopic Examination

| Etching reagents | Composition | Metals and alloys which can be etched | Etching time (seconds) |
|---|---|---|--|
| Nitric acid (nital) | Conc. nitric acid Absolute methyl or ethyl alcohol | Carbon steels and cast irons | 10-30 |
| Picric acid (picral) | Picric acid Absolute methyl or ethyl alcohol | Carbon steels and low alloy steels (etch pearlite, do not reveal ferrite grains) | 15-60 |
| Hydrochloric acid + nitric acid + water | Hydrochloric acid Nitric acid Water Pickling restrainer (flour trace) (used at about 70-80°C) | 18/8 stainless steel | 15-60 |
| Ferric chloride | Ferric chloride Conc. hydrochloric acid Water | Copper and its alloys such as bronzes, high zinc brasses and aluminium bronze | |
| Ammonium hydroxide + hydrogen peroxide | Ammonium hydroxide Water Hydrogen peroxide | Copper and its alloys | |
| Hydrofluoric acid + nitric acid | Hydrofluoric acid Nitric acid Water | Aluminium and its alloys | 15-60 (use freshly prepared solution) |
| Ethylene glycol + nitric acid | Ethylene glycol Distilled water Conc. nitric acid | Magnesium and its alloys | |

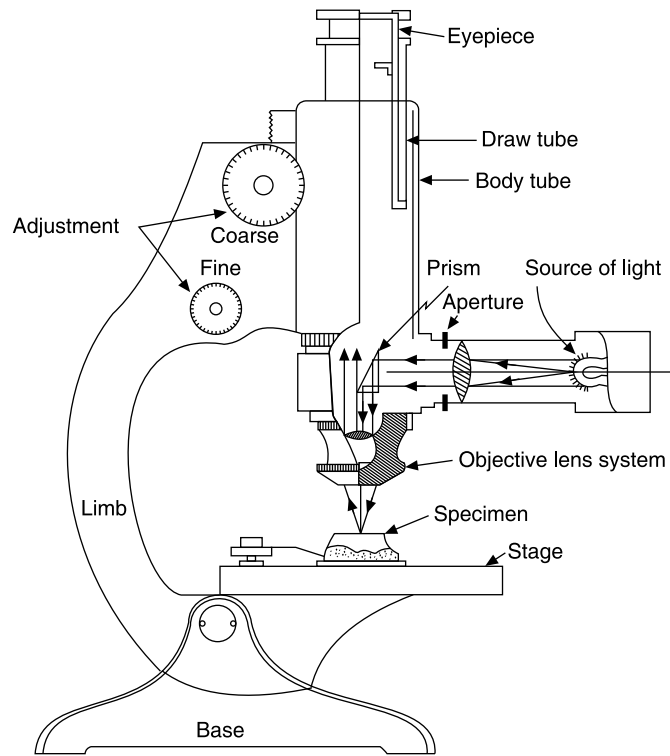


Figure 2.10 A typical metallurgical microscope.

The eye piece is easily detachable and is available with varying powers such as $\times 5$, $\times 8$, $\times 10$, $\times 12$, etc. These numbers are marked on the holder of the eye piece. If the objective lens enlarges the microstructure by 50, the eye piece further magnifies the image formed by objective by 5, 8, 10 times, and so on. The total magnification is the power of objective multiplied by the power of eye piece. Thus the microstructure is magnified by $50 \times 5 = 250$ times, when the objective lens with a magnification of 50 is used in combination with an eye piece having a power of $\times 5$.

A permanent record of microstructures can be obtained with the help of a photographic camera, which may be mounted above the eye piece.

Magnification depends on the focal length. The shorter the focal length of the lens, the greater will be the magnification of structure. The resolving power of an objective lens is its ability which makes it possible to see distinctly two separate lines in a structure. It is expressed as the number of lines per centimetre, which can be separately resolved. Human eye cannot resolve distances less than 0.1 mm. Therefore, magnification by microscope is increased to see distinctly the details of an object.

The resolution δ is related to wavelength λ of illumination, refractive index μ of medium between the lens and specimen and the numerical aperture by the equation

$$\delta = \frac{0.5 \lambda}{\text{numerical aperture}} = \frac{0.5 \lambda}{\mu \sin \alpha}$$

where α is half the angle subtended by the maximum cone of light rays coming to the objective lens. The numerical aperture is the quantitative measurement of light gathering power of an objective lens.

The ability of a lens to give clarity and sharpness to images of object a little out of focus is measured in terms of depths of focus which is of great significance when the surface of the object is not perfectly plain. It is inversely proportional to numerical aperture. It may, at times be observed that, when the image of the flat surface of the specimen is projected on to a screen, the centre may be sharply focused whereas the edges appear blurred. This situation is due to the curvature of field produced by the objective. To overcome this problem, a special eye piece may be used. Compensation is thus obtained to give a sharp definition over the whole field of view. This is called the flatness of field, which can also be increased by reducing the aperture. This results in increased depth of focus. Correspondingly, there is a decrease in resolving power.

2.7 ELECTRON MICROSCOPE

In the ordinary metallurgical microscope, the maximum magnification that can be achieved is in the range of $\times 2000$. When microstructural details beyond $\times 2000$ are required (say, between $\times 2000$ and $\times 200,000$), we go for an electron microscope in which light rays are replaced by a beam of electrons. A beam of electron is obtained by accelerating thermal electrons from a filament by applying a high voltage. According to De Broglie's principle, wavelength of beam of electrons is related to applied voltage by the formula

$$\lambda \approx \sqrt{\frac{150}{\text{Applied voltage}}} \text{ \AA}$$

The optimum resolution of an electron microscope is of the order of 10 \AA . The depth of focus in this case is almost infinite.

The electron microscope essentially consists of an electron gun and condenser and projector lens (see Figure 2.11). For passage of electron beam, vacuum is necessary. Electrons are emitted by a hot tungsten filament cathode and are accelerated to form a high velocity beam. The electron beam can be focused by electric or magnetic fields which act as lenses.

Current-carrying coils act as the source of electric field. The coils are completely enclosed in a soft-iron shroud. There is a narrow gap in the bore. The focal lengths are fixed physically as required. The arc is actually controlled by altering the current through the coils.

An objective lens enlarges the image about 40 times, and this is further magnified 40 times with the help of

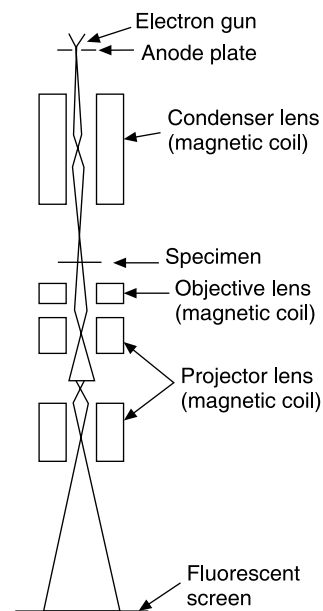


Figure 2.11 Schematic diagram of electron microscope.

the first projector lens. The second projector lens magnifies the image by about 50 times. The image is projected on a fluorescent screen or a photographic plate or film.

The following points should be kept in mind to ensure defect-free image by electron microscope:

- (i) Velocity of electrons should be uniform.
- (ii) Concentration of electrons at all points should be small to avoid mutual repulsion.
- (iii) Image-forming rays should have a small divergence.
- (iv) Object and image must be small.
- (v) Lens pole pieces should be free of constructional defects.
- (vi) Optical and magnetic alignment should be accurate.

For transmission electron microscope, thin foils of the metal are used as specimen. The thickness of thin foils varies from 1000 to 2000 Å. The specimen is prepared either by ion bombardment or by electropolishing technique.

2.8 IMPERFECTIONS IN METAL CRYSTALS

A crystal is made up of atoms, ions or molecules, which are arranged in a repetitive pattern in three dimensions. In an ideal crystal, this arrangement is regular and perfect throughout the crystal, while in a real crystal this situation does not exist. During crystallization from molten metal and processing of solid metals and alloys, lattice distortions and other imperfections creep in, which make crystals irregular. Because of the presence of these imperfections, physical and mechanical properties of engineering metals are greatly affected. Hence, there is always some discrepancy between theoretically computed and the real strength of metals. The extent and degree of imperfections can be changed by heat treatment process. Therefore, it is necessary to have some idea about imperfections in metals. Different types of imperfections in metals can be grouped as (i) point defects, (ii) line defects, (iii) surface defects, and (iv) volume defects. These are now discussed.

2.8.1 Point Defects

In crystal lattice, point defect is completely local in its effect. A vacant lattice site is a typical example of point defect. When point defect gets introduced in crystal lattice, internal energy of the crystal increases. The number of vacancies at equilibrium present in a crystal at a given temperature can be determined by the equation

$$n_0 = Ne^{-\Delta E/kT}$$

where

- n_0 = number of vacancies per mole
- N = total number of atomic sites per mole
- ΔE = activation energy for formation of vacancy
- k = Boltzmann constant
- T = temperature in absolute scale.

Vacancies, interstitialcies and impurities are examples for point defects in a crystal, which will be now discussed.

Vacancies When there is a vacant site or unoccupied atomic position within a crystal lattice, a vacancy is said to exist in the crystal lattice. Vacancies are atomic sites from which the atoms are missing, and exist in metal at all temperatures above absolute zero. Vacancies play a great role in diffusion of atoms in the crystal lattice. They help in transport of atoms. For example, many industrial processes such as annealing, homogenization, precipitation of second phase particles, and case carburizing require large scale migration of atoms in the crystal lattice.

Vacancies arise from thermal vibrations. They are also introduced during solidification. There is slight distortion in lattice planes due to vacancy because atoms surrounding a vacancy have tendency to come closer.

When vacancies are generated by displacement of atoms from crystal lattice site to the surface, a Schottky defect is formed. Figures 2.12(a) and 2.12(b) show vacancy and Schottky imperfection in a crystal, respectively.

Interstitialcies When an atom is displaced from a regular site and occupies an interstitial site, an interstitialcy is formed. The atom may be a parent atom or a foreign atom. Interstitialcy also gives rise to lattice distortion because interstitial atom tends to push the surrounding atoms apart. The smaller the size of the interstitial atom relative to the parent atom, the smaller is the lattice distortion in the crystal. Figure 2.12(c) shows interstitialcy point defect.

When an ion is displaced from the crystal lattice into an interstitial site, a Frankel defect is formed as in Figure 2.12(d).

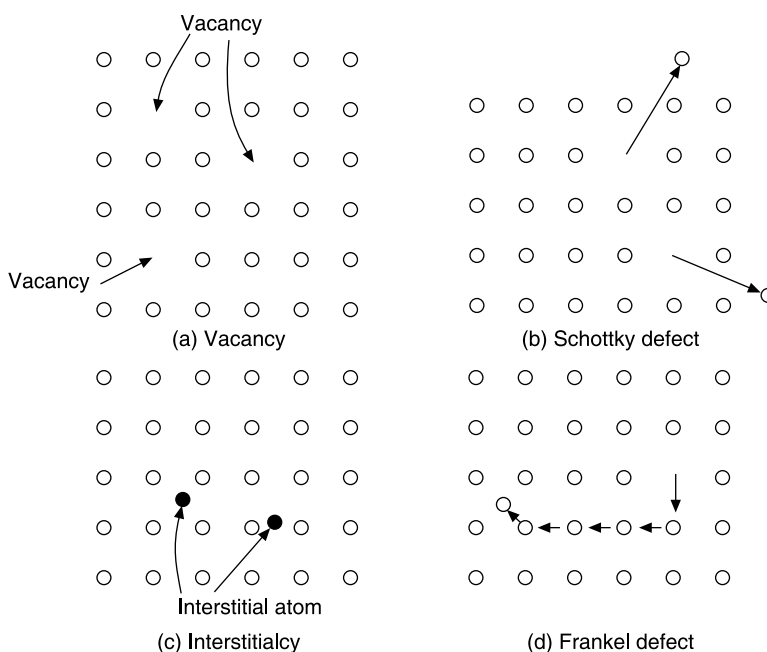


Figure 2.12 Various types of point defects.

Impurities Impurities are foreign atoms which are present in the crystal lattice. Impurity atoms may occupy either interstitial or substitutional position. An interstitial impurity is a small atom which occupies an interstitial void space between atoms at lattice points of the crystal. When a foreign atom substitutes a parent atom in the crystal lattice, a substitutional type of defect is generated. Both interstitial and substitutional impurities create distortions in the lattice.

2.8.2 Line Defects

Line defects are also known as dislocations. Dislocation is the region of localized lattice disturbance between slipped and unslipped regions of a crystal. Due to lattice disturbances, elastic strain fields and stresses are associated with dislocations. Metals deform plastically by the mechanism of slip. Slipping is facilitated in the presence of dislocations. Strain hardening, creep, fatigue and fracture are the mechanical phenomena, in which dislocations play a major role. Dislocations are of two types: edge dislocation and screw dislocation. Figure 2.13(a) shows an edge dislocation in which the burger's vector lies perpendicular to the dislocation line. A burger circuit is drawn around the dislocation line and the vector required to close the circuit, RS , is known as the burger vector of the dislocation. An edge dislocation moves in the direction of the burger vector (slip direction). It has an extra row of atoms either above or below the slip plane in crystal. When the extra row of atoms is above the slip plane, it is called positive and is denoted by sign \perp . When the extra row of atoms is below the slip plane, it is called negative edge dislocation and is represented by sign \top . In edge dislocation, the atoms above the edges are in compression and those below are in tension as shown in Figure 2.13(a). An edge dislocation undergoes gliding in crystal and produces a slip step of one atom width at the edge of the crystal.

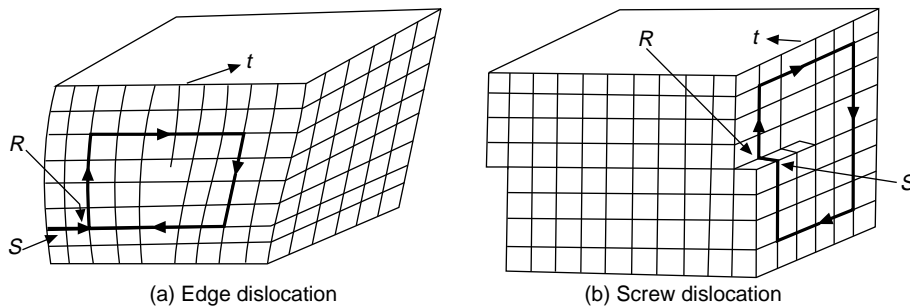


Figure 2.13 Line defects.

Figure 2.13(b) shows a screw dislocation. Here, the burger vector is parallel to the dislocation line and distortion is of shear type. The distortion follows a helical path, and it may follow right-hand (positive) or left-hand (negative) screw rule. Positive and negative dislocations are shown by clockwise and anticlockwise signs, respectively. Screw dislocation shows cross slip, where it moves from one slip plane to another.

Two dislocations (either edge or screw) of opposite signs, if present on the same plane, attract each other and can annihilate each other.

Dislocations are introduced in a crystal due to growth accidents, thermal stresses, phase transformations and segregation of solute atoms. The dislocation density in annealed crystal

is about 10^6 to 10^{10} mm^{-3} . Perfect crystals, which are totally free from dislocations, are called whiskers and have very high strength.

2.8.3 Surface Defects

Grain boundaries, tilt boundaries, twist boundaries, coherent and incoherent precipitate interfaces are categorized under surface defects.

During solidification of metal, nucleation and growth process starts. During this process, crystals nucleate and grow at different points. When the growing surfaces of these two crystals meet, some atoms are caught in the boundary region of two crystals and do not belong to any one of the two crystals. This region of atoms is called grain boundary (see Figure 2.14). At grain boundaries, atomic packing is imperfect. Thickness of the grain boundary can be estimated by field ion microscopy. When the orientation difference between two adjacent crystals is more than 10 to 15° , the boundary is termed as high-angle grain boundary.

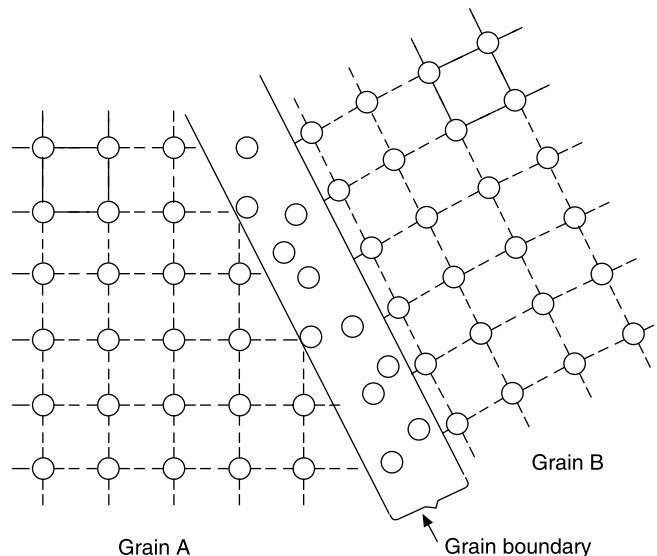


Figure 2.14 Grain boundary.

Tilt boundaries are low-angle grain boundaries, and the orientation difference between two adjacent crystals is less than 10° . This may be regarded as an array of parallel edge dislocations of same sign arranged one below the other.

Twist boundaries are also low-angle grain boundaries but in this case an array of screw dislocations are present instead of edge dislocations.

When the arrangement of atoms on one side of a boundary is a mirror image of that of the other side, twin boundary is formed.

In some instances, crystal structures of the two phases may be similar and the lattice parameters may be nearly equal. In such cases the boundary between the two grains (called an interface) is coherent. There is one-to-one correspondence of atoms at the interface. When such matching does not exist at the interface, the interface is said to be incoherent.

2.8.4 Volume Defects

Inclusions and stacking faults constitute volume defects. When there is a discrepancy in the packing sequence of the rows of atoms, stacking fault results. For example, for an FCC metal the stacking sequence is of *ABC ABC ABC ...*. If the sequence changes to *ABC AB ABC* in practice, then stacking faults (which are usually introduced by deformation of annealed metals and alloys) occur.

A stacking fault occurs when a metal crystal has two adjacent crystallo-graphic planes which do not fit in the normal geometric pattern within the system. Stacking faults may be caused either by slip or some other mechanism.

2.9 SIGNIFICANCE OF IMPERFECTIONS IN HEAT TREATMENT

The role of imperfections in heat treatment is very important. Imperfections account for crystal growth, diffusion mechanism, annealing and precipitation. Besides this, other metallurgical phenomena, such as oxidation, corrosion, yield strength, creep, fatigue and fracture, are governed by imperfections. Imperfections are not always harmful to metals. Sometimes they are generated to obtain the desired properties. For example, carbon is added in steel as interstitial impurity to improve the mechanical properties, and these properties are further improved by different heat treatment processes.

QUESTIONS

- 2.1 Differentiate between metals and non-metals.
- 2.2 Define an alloy.
- 2.3 What is a solid solution? Give examples of solid solutions.
- 2.4 Copper can dissolve any amount of nickel in solid state and vice versa. Justify the above statement with the help of Hume Rothery Rules for the formation of solid solutions.
- 2.5 Find out electron-to-atom ratio for the following compositions: Ag_3Al , Cu_5Zn_8 , Cu_9Al_4 , CuZn_3 , Cu_3Sn .
- 2.6 What information do we get from the study of phase diagrams?
- 2.7 What is metallography? Discuss the importance of metallography with special reference to heat treatment.
- 2.8 What is the role of imperfections in heat treatment?