5

CONSTITUTION OF ALLOYS

5·1 Introduction An alloy is a substance that has metallic properties and is composed of two or more chemical elements, of which at least one is a metal.

An alloy system contains all the alloys that can be formed by several elements combined in all possible proportions. If the system is made up of two elements, it is called a *binary alloy system*; three elements, a *ternary alloy system*; etc. Taking only 45 of the most common metals, any combination of two gives 990 binary systems. Combinations of three give over 14,000 ternary systems. However, in each system, a large number of different alloys are possible. If the composition is varied by 1 percent, each binary system will yield 100 different alloys. Since commercial alloys often contain many elements, it is apparent that the number of possible alloys is almost infinite.

Alloys may be classified according to their structure, and complete alloy systems may be classified according to the type of their equilibrium or phase diagram. The basic types of phase diagrams will be studied in Chap. 6.

5·2 Classification of Alloys Alloys may be homogeneous (uniform) or mixtures. If the alloy is homogeneous it will consist of a single phase, and if it is a mixture it will be a combination of several phases. A phase is anything which is homogeneous and physically distinct. The uniformity of an alloy phase is not determined on an atomic scale, such as the composition of each unit lattice cell, but rather on a much larger scale. Any structure which is visible as physically distinct microscopically may be considered a phase. For most pure elements the term *phase* is synonymous with *state*. There is, therefore, for pure elements, a gaseous, liquid, and solid phase. Some metals are allotropic in the solid state and will have different solid phases. When the metal undergoes a change in crystal structure, it undergoes a phase change since each type of crystal structure is physically distinct.

In the solid state there are three possible phases: (1) pure metal, (2) i termediate alloy phase or compound, and (3) solid solution.

If an alloy is homogeneous (composed of a single phase) in the so state, it can be only a solid solution or a compound. If the alloy is a mi ture, it is then composed of any combination of the phases possible in th solid state. It may be a mixture of two pure metals, or two solid solutio or two compounds, or a pure metal and a solid solution, and so on. Th mixture may also vary in degree of fineness.

5·3 Pure Metal The characteristics of a pure metal have been discussed in deta in an earlier chapter. However, one property is worth repeating. Unde equilibrium conditions, all metals exhibit a definite melting or freezin point. The term *under equilibrium conditions* implies conditions of extremely slow heating and cooling. In other words, if any change is to occu sufficient time must be allowed for it to take place. If a cooling curve plotted for a pure metal, it will show a horizontal line at the melting or freezing point (Fig. 5·1).

5·4 Intermediate Alloy Phase or Compound Because the reason for referrin to this type of solid phase as an *intermediate alloy phase* will be more apparent during the study of phase diagrams, it will be simpler at this poin to call it a *compound*.

It is now necessary to obtain some understanding of compounds i general. Most ordinary chemical compounds are combinations of positiv and negative valence elements. The various kinds of atoms are combine in a definite proportion, which is expressed by a chemical formula. Som typical examples are water, H_2O (two atoms of hydrogen combined with one

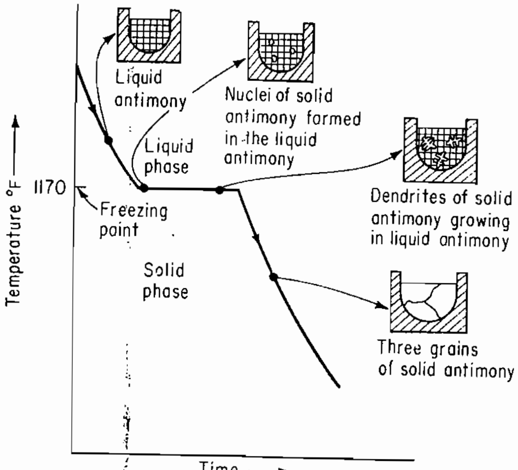

Fig. 5·1 Time-temperature cooling curve for the solidification of a small crucible of liquid antimony.

atom of oxygen), and table salt, NaCl (one atom of sodium combined with one atom of chlorine). The atoms that are combined to form the molecule, which is the smallest unit that has the properties of the compound, are held together in a definite bond. Various types of atomic bonding have been discussed in Chap. 2. The bond is generally strong, and the atoms are not easily separated. Most students are familiar with the classical high school chemistry demonstration of the electrolysis of water. By passing an electric current through water it is possible to separate the hydrogen and oxygen atoms.

When a compound is formed, the elements lose their individual identity and characteristic properties to a large extent. A good example is table salt (NaCl). Sodium (Na) is a very active metal that oxidizes rapidly and is usually stored under kerosene. Chlorine (Cl) is a poisonous gas. Yet one atom of each combines to give the harmless and important compound, table salt. Water (H_2O) is composed of elements that are normally gases at room temperature, yet the compound is a liquid at room temperature. What exists then is not the individual elements but rather the combination or compound. The compound will have its own characteristic physical, mechanical, and chemical properties.

Most compounds, like pure metals, also exhibit a definite melting point within narrow limits of temperature. Therefore, the cooling curve for a compound is similar to that for a pure metal (see Fig. 5·1). It is then referred to as a *congruent melting phase*. In reference to equilibrium diagrams, the intermediate alloy phases are phases whose chemical compositions are intermediate between the two pure metals and generally have crystal structures different from those of the pure metals.

The three most common intermediate alloy phases are:

Intermetallic Compounds or Valency Compounds These are generally formed between chemically dissimilar metals and are combined by following the rules of chemical valence. Since they generally have strong bonding (ionic or covalent), their properties are essentially nonmetallic. They usually show poor ductility and poor electrical conductivity and may have a complex crystal structure. Examples of valency compounds are CaSe, Mg_2Pb, Mg_2Sn, and Cu_2Se.

Interstitial Compounds These compounds formed between the transition metals such as scandium (Sc), titanium (Ti), tantalum (Ta), tungsten (W), and iron (Fe), with hydrogen, oxygen, carbon, boron, and nitrogen. The word *interstitial* means between the spaces, and the latter five elements have relatively small atoms that fit into the spaces of the lattice structure of the metal. These same five elements also form interstitial solid solutions, which will be described shortly. The interstitial compounds are metallic, may have a narrow range of composition, high melting points, and are extremely hard. Examples are TiC, TaC, Fe_4N, Fe_3C, W_2C, CrN, and TiH.

Many of these compounds are useful in hardening steel and in cemented carbide tools.

Electron Compounds A study of the equilibrium diagrams of the alloy of copper, gold, silver, iron, and nickel with the metals cadmium, mag nesium, tin, zinc, and aluminum shows striking similarities. A number o

TABLE 5·1 Examples of Electron Compounds

ELECTRON-ATOM RATIO 3:2 (B.C.C. STRUCTURE)	ELECTRON-ATOM RATIO 21:13 (COMPLEX CUBIC)	ELECTRON-ATOM RATIO 7:4 (C.P.H. STRUCTURE)
AgCd	Ag_5Cd_8	$AgCd_3$
AgZn	Cu_9Al_4	Ag_5Al_3
Cu_3Al	$Cu_{31}SN_8$	$AuZn_3$
AuMg	Au_5Zn_8	Cu_3Si
FeAl	Fe_5Zn_{21}	$FeZn_7$
Cu_5Sn	Ni_5Zn_{21}	Ag_3Sn

Intermediate phases are formed in these systems with similar lattice struc tures. Hume-Rothery first pointed out that these intermediate phases ar found to exist at or near compositions in each system that have a defini ratio of valence electrons to atoms and are therefore called *electron com pounds*. Some examples are given in Table 5·1. For example, in the com pound AgZn, the atom of silver has one valence electron, while that of zin has two valence electrons so that the two atoms of the compound wi have three valence electrons, or an electron-to-atom ratio of 3:2. In th compound Cu_9Al_4, each atom of copper has one valence electron and eac atom of aluminum three valence electrons, so that the 13 atoms that mak up the compound have 21 valence electrons, or an electron-to-atom rati of 21:13. For the purpose of calculation, the atoms of iron and nickel ar assumed to have zero valence.

Many electron compounds have properties resembling those of soli solutions, including a wide range of composition, high ductility, and lo hardness.

5·5 Solid Solutions Any solution is composed of two parts: a solute and a so vent. The solute is the minor part of the solution or the material which i dissolved, while the solvent constitutes the major portion of the solutio It is possible to have solutions involving gases, liquids, or solids as eithe the solute or the solvent. The most common solutions involve water as th solvent, such as sugar or salt dissolved in water.

The amount of solute that may be dissolved by the solvent is generall a function of temperature (with pressure constant) and usually increase with increasing temperature.

There are three possible conditions for a solution: unsaturated, satu rated, and supersaturated. If the solvent is dissolving less of the solut than it could dissolve at a given temperature and pressure, it is said to be *unsaturated.* If it is dissolving the limiting amount of solute, it is *saturated.* If it is dissolving more of the solute than it should, under equilibrium conditions, the solution is *supersaturated.* The latter condition may be accomplished by doing work on the solution, such as stirring, or preventing equilibrium conditions by rapidly cooling the solution. The supersaturated condition is an unstable one, and given enough time or a little energy, the solution tends to become stable or saturated by rejecting or precipitating the excess solute.

A solid solution is simply a solution in the solid state and consists of two kinds of atoms combined in one type of space lattice. There is usually a considerable difference in the solubility of the solute in the liquid and solid states of the solution. The solute is generally more soluble in the liquid state than in the solid state. Moreover, when solidification of the solution starts, the temperature may be higher or lower than the freezing point of the pure solvent. Most solid solutions solidify over a range in temperature. Figure 5·2 shows the cooling curve for a solid solution alloy containing 50 percent Sb (antimony) and 50 percent Bi (bismuth). Compare this cooling curve with the one shown in Fig. 5·1. Notice that this alloy begins to solidify at a temperature lower than the freezing point of pure antimony (1170°F) and higher than the freezing point of pure bismuth (520°F). The process of solidification and the composition of the solid solution alloy and the liquid solution during freezing will be explained

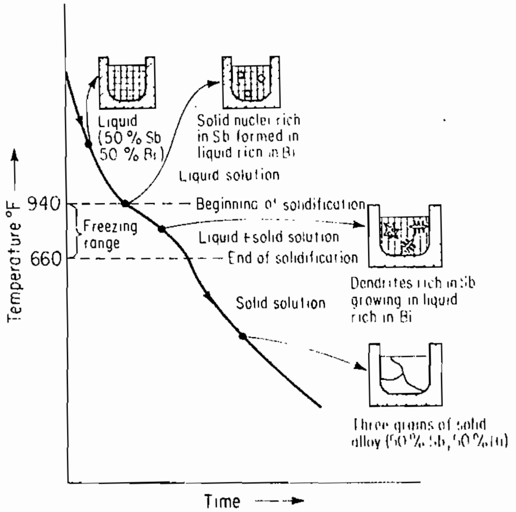

Fig. 5·2 Time-temperature cooling curve for the solidification of a small crucible of 50 percent antimony, 50 percent bismuth alloy.

in the next chapter. There are two types of solid solutions, substitution and interstitial.

5·6 Substitutional Solid Solution In this type of solution, the atoms of the solu substitute for atoms of the solvent in the lattice structure of the solven For example, silver atoms may substitute for gold atoms without losing th f.c.c. (face-centered cubic) structure of gold, and gold atoms may substitute for silver atoms in the f.c.c. lattice structure of silver. All alloys in th silver-gold system consist of an f.c.c. lattice with silver and gold atom distributed at random through the lattice structure. This entire system consists of a continuous series of solid solutions.

Several factors are now known, largely through the work of Hume-Rothery, that control the range of solubility in alloy systems.

Crystal-structure Factor Complete solid solubility of two elements is never attained unless the elements have the same type of crystal lattic structure.

Relative-size Factor The size factor is favorable for solid-solution formation when the difference in atomic radii is less than about 15 percent. If the relative size factor is greater than 8 percent but less than 15 percent the alloy system usually shows a minimum. If the relative-size factor is greater than 15 percent, solid-solution formation is very limited. For example, silver and lead are both f.c.c., and the relative-size factor is about 20 percent. The solubility of lead in solid silver is about 1.5 percent, and the solubility of silver in solid lead is about 0.1 percent. Antimony and bismuth are completely soluble in each other in all proportions. They have the same type of crystal structure (rhombohedral) and differ in atomic radii by about 7 percent. However, the solubility of antimony in f.c.c. aluminum is less than 0.1 percent, although the relative-size factor is only about 2 percent.

Chemical-affinity Factor The greater the chemical affinity of two metals the more restricted is their solid solubility and the greater is the tendency toward compound formation. Generally, the farther apart the elements are in the periodic table, the greater is their chemical affinity.

Relative-valence Factor If the solute metal has a different valence from that of the solvent metal, the number of valence electrons per atom, called the electron ratio, will be changed. Crystal structures are more sensitive to a decrease in the electron ratio than to an increase. In other words, a metal of lower valence tends to dissolve more of a metal of higher valence than vice versa. For example, in the aluminum-nickel alloy system, both metals are face-centered cubic. The relative-size factor is approximately 14 percent. However, nickel is lower in valence than aluminum, and in accord with the relative-valence factor solid nickel dissolves 5 percent aluminum, but the higher valence aluminum dissolves only 0.04 percent nickel.

By considering the above four factors, some estimate of the solid solubility of one metal in another can be determined. It is important to note that an unfavorable relative-size factor alone is sufficient to limit solubility to a low value. If the relative-size factor is favorable, then the other three factors should be considered in deciding on the probable degree of solid solubility. While the Hume-Rothery rules are a very good guide to solid solubility, there are exceptions to these rules.

The lattice structure of a solid solution is basically that of the solvent with slight changes in lattice parameter. An expansion results if the solute atom is larger than the solvent atom and a contraction if the solute atom is smaller.

5·7 Interstitial Solid Solutions These are formed when atoms of small atomic radii fit into the spaces or interstices of the lattice structure of the larger solvent atoms. Since the spaces of the lattice structure are restricted in size, only atoms with atomic radii less than 1 angstrom are likely to form interstitial solid solutions. These are hydrogen (0.46), boron (0.97), carbon (0.77), nitrogen (0.71), and oxygen (0.60).

This type of solution differs from interstitial compounds in that the amount of smaller atoms required to form the compound is always greater than the amount that may be dissolved interstitially. When a small amount of solute is added to the solvent and the difference in atomic radii is great enough, an interstitial solid solution is formed. In this condition, the solute atoms have considerable mobility and may move in the interstitial spaces of the lattice structure. More solute atoms may be dissolved interstitially until the solution becomes saturated at that temperature. Increasing the amount of solute atoms beyond this limit severely restricts the mobility of these atoms in a particular area and the interstitial compound of fixed composition starts to form. The interstitial compound, showing a narrow range of composition, is expressed by a chemical formula, but the interstitial solution, being of variable composition, cannot be represented by a chemical formula. The lattice structure always shows an expansion when this type of solution is formed.

Interstitial solid solutions normally have very limited solubility and generally are of little importance. Carbon in iron is a notable exception and forms the basis for hardening steel, which will be discussed in Chap. 8. Carbon dissolves in iron interstitially. The maximum solubility of carbon in γ iron (f.c.c.) is 2 percent at 2065°F, while the maximum solubility of carbon in α iron (b.c.c.) is only 0.025 percent at 1333°F.

Both types of solid solutions are illustrated in Fig. 5·3. Distortion of the lattice structure will exist in the region of the solute atom. This distortion will interfere with the movement of dislocations on slip planes and will therefore increase the strength of the alloy. This is the primary basis for the strengthening of a metal by alloying.

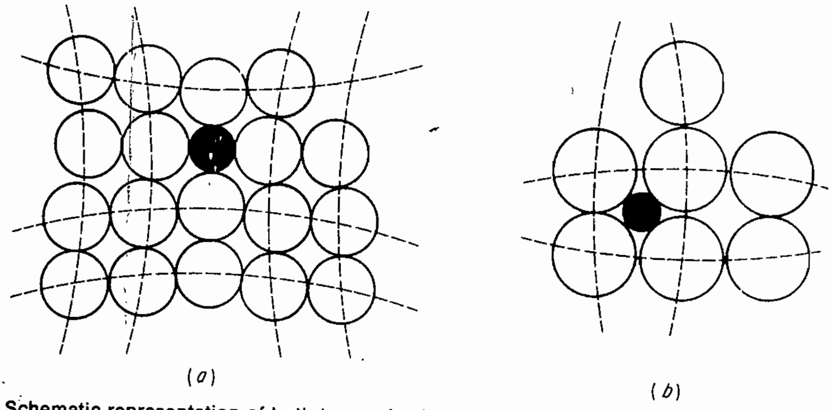

Fig. 5·3 Schematic representation of both types of solid solutions. (a) Substitutional; (b) interstitial.

In contrast to intermetallic and interstitial compounds, solid solution in general are easier to separate, melt over a range in temperature, hav properties that are influenced by those of the solvent and solute, an usually show a wide range of composition so that they are not expresse by a chemical formula.

A summary of the possible alloy structures is shown in Fig. 5·4.

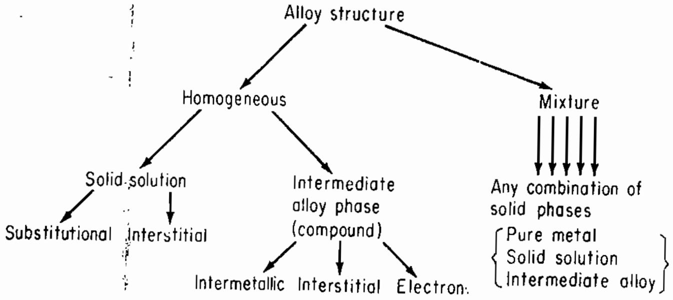

Fig. 5·4 Possible alloy structures.