Chapter four: Phase–diagram determination

4.1 Introduction

An alloy is a combination of two or more metals. It may consist of a single phase or of a mixture of phases, and these phases may be of different types, depending only on the composition of the alloy and the temperature, provided the alloy is at equilibrium. The changes in the constitution of the alloy produced by given changes in composition or temperature may be conveniently shown by means of a *phase diagram*, also called an *equilibrium diagram* or *constitution diagram*. It is a plot of temperature vs. composition, divided into areas wherein a particular phase or mixture of phases is stable. Phase diagrams are great importance in metallurgy.

4.2 General principles

Assume that two metals A and B are *completely soluble in the solid state*, as illustrated by the phase diagram of the following Figure. The solid phase α, called a continuous solid solution (substitutional type), it varies in composition, but not in crystal structure, from pure A to pure B, which must necessarily have the same structure. The lattice parameter of a also varies continuously from that of pure A to that of pure B.
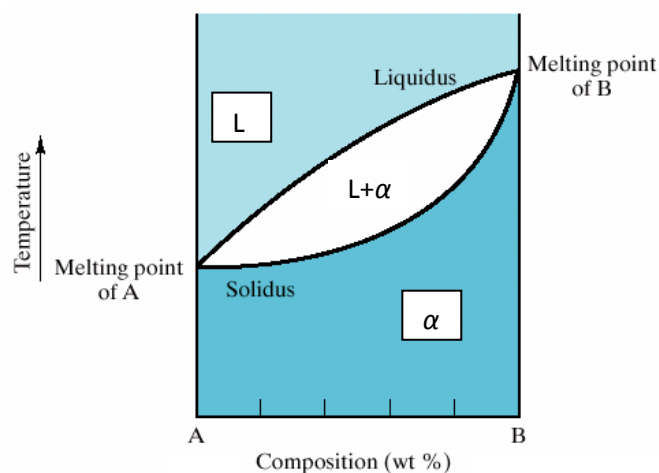

Fig.1.

More commonly, the two metals A and B are only *partially soluble in the solid state*. The first additions of B to A go into solid solution in the A lattice, which may expand or contract as a result, depending on the relative sizes of the A and B atoms and the type of solid solution formed (substitutional or interstitial). Further additions of B cause the precipitation of a second phase. This second phase may be a B-rich solid solution with the same structure as B, as in the alloy system illustrated by Figure 2. Here the solid solutions α and β are called terminal solid solutions
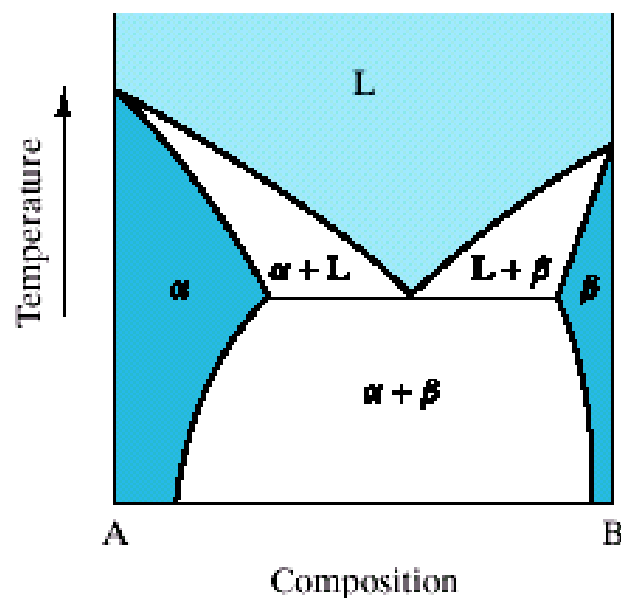

Fig.2.

The second phase may have no connection with the B-rich solid solution, as in the system shown in Figure 3. Here the effect of super saturating α with metal β is to precipitate the phase designated γ. This phase is called *an intermediate solid solution* or *intermediate phase*. It usually has a crystal structure entirely different from that of either α or β, and it is separated from each of these terminal solid solutions, on the phase diagram, by at least one two-phase region.

Fig.3.

This system contains two substitutional solid solutions α and β, and an intermediate phase γ. The lattice parameter of γ is constant in all alloys in which this phase appears. On the other hand, the parameters of α and β vary with composition. If the B atom is assumed to be larger than the A atom, the addition of B expands the A lattice, and the parameter of α increases. In two-phase (α + γ) alloys containing more than percent B, the parameter of α remains constant. Similarly, the addition of A to B causes the parameter of β to decrease and then remain constant in the two-phase (γ + β) field.

The following are the general principles for the phase diagram:

(1) **Equilibrium:** Each alloy must be at equilibrium at the temperature where the phase relations are being studied.

(2) **Phase sequence:** A horizontal (constant temperature) line drawn across the diagram must pass through single-phase and two-phase regions alternately.

(3) **Single-phase regions:** In a single-phase region, a change in composition generally produces a change in lattice parameter and therefore a shift in the positions of the diffraction lines of that phase.

(4) **Two-phase regions:** In a two-phase region, a change in composition of the alloy produces a change in the relative amounts of the two phases but no change in their compositions.

4.3 Solid solution

Any solid solution may be classified as one of the following types:

   (1) Interstitial

   (2) Substitutional: (a) Random (b) Ordered (c) Defect

 4.3.1 An interstitial solid solution

An interstitial solid solution of B in A is to be expected only when the B atom is so small compared to the A atom that it can enter the interstices of the A lattice without causing much distortion. As a consequence, about the only interstitial solid solutions are those formed between a metal and one of the elements, carbon, nitrogen, hydrogen, and boron, all of which have atoms less than 2Å in diameter. The interstitial addition of B to A is always accompanied by an increase in the volume of the unit cell.

The density of an interstitial solid solution is given by the basic density equation

$$\rho = \frac{1.66020 \sum A}{V}$$

Where $\sum A = n_s A_s + n_i A_i$; n_s and n_i are numbers of solvent and interstitial atoms, respectively, per unit cell; and A_s and A_i are atomic weights of solvent and interstitial atoms,

respectively. Note that the value of n_s is constant and that n_i is normally a small fraction of unity.

4.3.2 Substitutional solid solution

The formation of a *random substitutional solid solution* of B and A may be accompanied either by an increase or decrease in cell volume, depending on whether the B atom is larger or smaller than the A atom. In continuous solid solutions of ionic salts, the lattice parameter of the solution is directly proportional to the atomic percent solute present, this relationship known as Vegard's law. In terminal and intermediate solid solutions, the lattice parameter may or may not vary linearly with the atomic percent solute.

The density of a random substitutional solid solution is found with the $\sum A$ factor being given by:

$$\sum n_{solvent} A_{solvent} + n_{solute} A_{solute}$$

where *n* again refers to the number of atoms per cell and A to the atomic weight.

There are some solutions which have this random structure only at elevated temperatures. When these solutions are cooled below a certain critical temperature Tc, the A atoms arrange themselves in an orderly, periodic manner on one set of atomic sites, and the B atoms do likewise on another set. The solution is then said to be *ordered solid solution*. If the ordered solution is heated above Tc, the atomic arrangement becomes random again and the solution is said to be disordered.

4.3.3 Defect Substitutional solid solution

Defect substitutional solid solution is an empty space where atoms are missing, which mostly happens at high temperatures because at elevated temperatures, the atoms are excited or move randomly, depart from their location, and leave behind an empty lattice location.

4.4 Determination of solvus curves

There are two methods of using diffraction patterns to locate a solvus curve on a phase diagram: (1) disappearing-phase method, and (2) parametric method.

4.4.1 Disappearing-phase method

This method depends on the fact that in a two-phase region amount of each phase is proportional to the intensity of the diffraction lines from that phase. From diffraction patterns made at room temperature, the ratio of the intensity I_β of a prominent line of the β phase to the intensity I_α of a prominent line of the α phase is plotted as a function of composition (weight percent B). This ratio also varies nonlinearly with weight composition.

4.4.2 Parametric method

The parametric method is based on observations of the α solid solution itself. This method depends on the fact that the lattice parameter of a solid solution generally changes with composition up to the saturation limit, and then remains constant beyond that point.

4.5 Ternary system

Phase diagram in a ternary system can only be represented completely in three dimensions, since there are three independent variables (two compositions and the temperature). The composition is plotted in an equilateral triangle whose corners represent the three pure components, A, B, and C.

The study of a ternary system of components A, B, and C begins with a determination of the three binary phase diagrams AB, BC, and CA. We then make up a number of ternary alloys, choosing their compositions. The diffraction patterns of these exploratory alloys will disclose the number and kind of phases at equilibrium in each alloy at the temperature selected.

From Figure 4, the phase boundaries have been drawn to conform to the diffraction results represented by the small circles. This section shows three terminal ternary solid solutions, α, β, and γ, joined in pairs by three two-phase regions, $(\alpha + \beta)$, $(\beta + \gamma)$, and $(\alpha + \gamma)$, and in the center a single region where the three phases, α, β, and γ, are in equilibrium. In a single-phase region the composition of the phase involved, say a, is continuously variable. In the $(\alpha + \gamma)$ field, tie lines have been drawn to connect the single-phase compositions which are in equilibrium in the two-phase field. Along the line *de*, for example, α of composition *d* is in equilibrium with γ of composition *e.* In a three-phase field, the compositions of the phases are fixed and are given by the corners of the three-phase triangle. Thus the compositions of α, β, and γ which are at equilibrium in any alloy within the three-phase field are given by *a, b,* and *c*, respectively

Fig.4.