
Phase-diagram Determination

12-1 INTRODUCTION

An alloy is a combination of two or more metals, or of metals and nonmetals. 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. As such it forms a sort of map of the alloy system involved. Phase diagrams are therefore of great importance in metallurgy, and much time and effort have been devoted to their determination. In this chapter we will consider how x-ray methods can be used in the study of phase diagrams of binary systems.

X-ray methods are, of course, not the only ones which can be used in investigations of this kind. The two classical methods are thermal analysis and microscopic examination, and many diagrams have been determined by these means alone. X-ray diffraction, however, supplements these older techniques in many useful ways and provides, in addition, the only means of determining the crystal structures of the various phases involved. Most phase diagrams today are therefore determined by a combination of all three methods. In addition, measurements of other physical properties may be used to advantage in some alloy systems: the most important of these subsidiary techniques are measurements of the change in length and of the change in electric resistance as a function of temperature.

In general, the various experimental techniques differ in sensitivity, and therefore in usefulness, from one portion of the phase diagram to another. Thus, thermal analysis is the best method for determining the liquidus and solidus, including eutectic and peritectic horizontals, but it may fail to reveal the existence of eutectoid and peritectoid horizontals because of the sluggishness of some solid-state reactions or the small heat effects involved. Such features of the diagram are best determined by microscopic examination or x-ray diffraction, and the same applies to the determination of solvus (solid solubility) curves.

The general principles of phase-diagram determination are described by Taylor [G.19], with special emphasis on x-ray methods.

* The pressure on the alloy is another effective variable, but it is usually held constant at that of the atmosphere and may be neglected.

12-2 GENERAL PRINCIPLES

The key to the interpretation of the powder patterns of alloys is the fact that each phase produces its own pattern independently of the presence or absence of any other phase. Thus a single-phase alloy produces a single pattern while the pattern of a two-phase alloy consists of two superimposed patterns, one due to each phase.

Assume, for example, that two metals A and B are *completely soluble* in the solid state, as illustrated by the phase diagram of Fig. 12-1. The solid phase α , called a *continuous solid solution*, is of the 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 α also varies continuously from that of pure A to that of pure B. Since all alloys in a system of this kind consist of the same single phase, their powder patterns appear quite similar, the only effect of a change in composition being to shift the diffraction-line positions in accordance with the change in lattice parameter.

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). Ultimately the solubility limit of B in A is reached, and 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 Fig. 12-2(a). Here the solid solutions α and β are called *primary solid solutions* or *terminal solid solutions*. Or the second phase which appears may have no connection with the B-rich solid solution, as in the system shown in Fig. 12-2(b). Here the effect of supersaturating α with metal B 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.

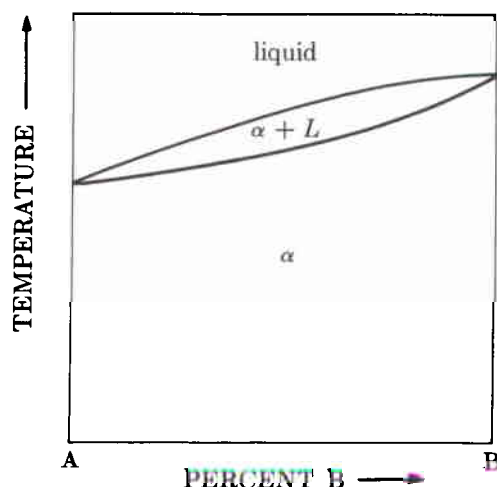


Fig. 12-1 Phase diagram of two metals, showing complete solid solubility.

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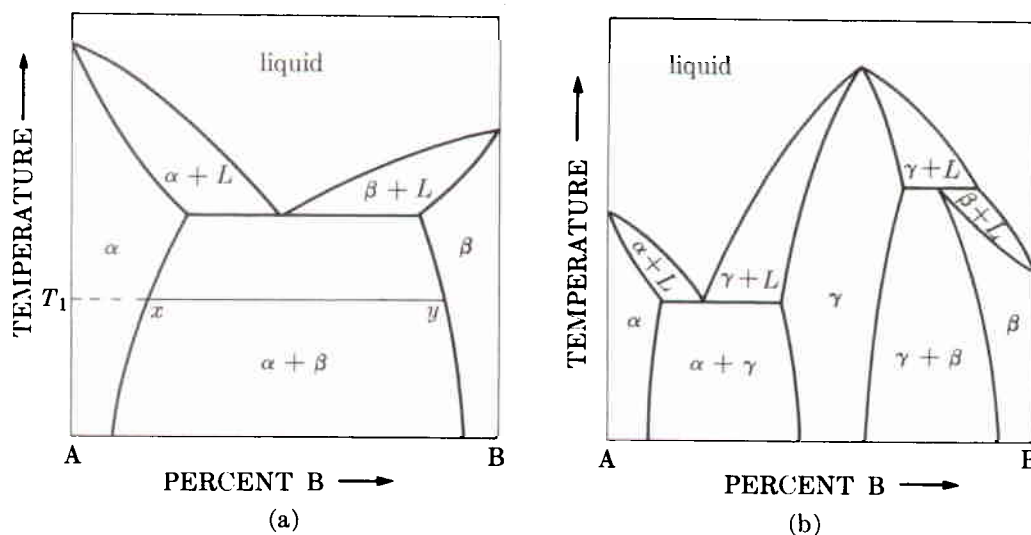


Fig. 12-2 Phase diagrams showing (a) partial solid solubility, and (b) partial solid solubility together with the formation of an intermediate phase.

Phase diagrams much more complex than those just mentioned are often encountered in practice, but they are always reducible to a combination of fairly simple types. When an unknown phase diagram is being investigated, it is best to make a preliminary survey of the whole system by preparing a series of alloys at definite composition intervals, say 5 or 10 atomic percent, from pure A to pure B. The powder pattern of each alloy and each pure metal is then prepared. These patterns may appear quite complex but, no matter what the complexities, the patterns may be unraveled and the proper sequence of phases across the diagram may be established, if proper attention is paid to the following principles:

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. These compositions are fixed at the intersections of a horizontal "tie line" with the boundaries of the two-phase field. Thus, in the system illustrated in Fig. 12-2(a), the tie line drawn at temperature T_1 shows that the compositions of α and β at equilibrium at this temperature are x and y respectively. The powder pattern of a two-phase alloy brought to equilibrium at temperature T_1 will therefore consist of the superimposed patterns of α of composition x and β of composition y . The patterns of a series of alloys in the xy range will all contain the same diffraction lines at the same positions, but the

intensity of the lines of the α phase relative to the intensity of the lines of the β phase will decrease in a regular manner as the concentration of B in the alloy changes from x to y , since this change in total composition decreases the amount of α relative to the amount of β .

These principles are illustrated with reference to the hypothetical alloy system shown in Fig. 12-3. This system contains two substitutional terminal solid solutions α and β , both assumed to be face-centered cubic, and an intermediate phase γ , which is body-centered cubic. The solubility of either A or B in γ is assumed to be negligibly small: the lattice parameter of γ is therefore constant in all alloys in which this phase appears. On the other hand, the parameters of α and β vary with composition in the manner shown by the lower part of Fig. 12-3. Since 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 from a_1 for pure A to a_3 for a solution of composition x , which represents the limit of solubility of B in A at room temperature. In two-phase ($\alpha + \gamma$) alloys containing more than x percent B, the parameter of α remains constant at its saturated value a_3 . Similarly, the addition of A to B causes the parameter of β to decrease from a_2 to a_4 at the solubility limit, and then remain constant in the two-phase ($\gamma + \beta$) field.

Calculated powder patterns are shown in Fig. 12-4 for the eight alloys designated by number in the phase diagram of Fig. 12-3. It is assumed that the alloys have been brought to equilibrium at room temperature by slow cooling. Examination of these patterns reveals the following:

1. Pattern of pure A (face-centered cubic).
2. Pattern of α almost saturated with B. The expansion of the lattice causes the lines to shift to smaller angles 2θ .

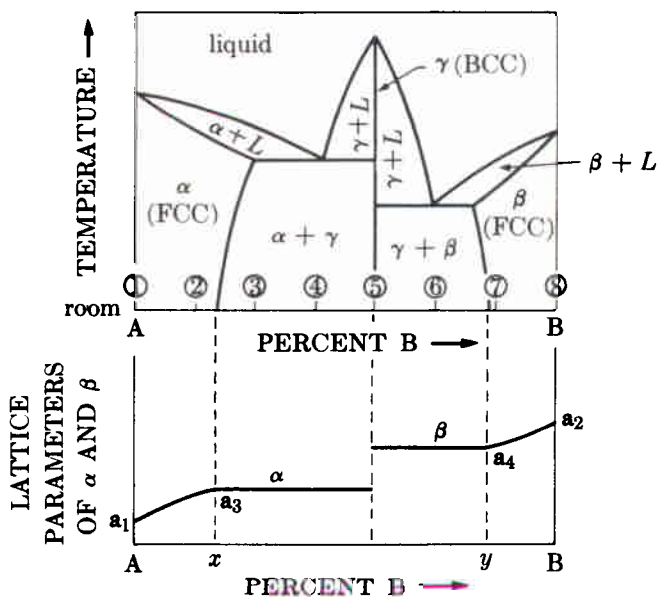


Fig. 12-3 Phase diagram and lattice constants of a hypothetical alloy system.

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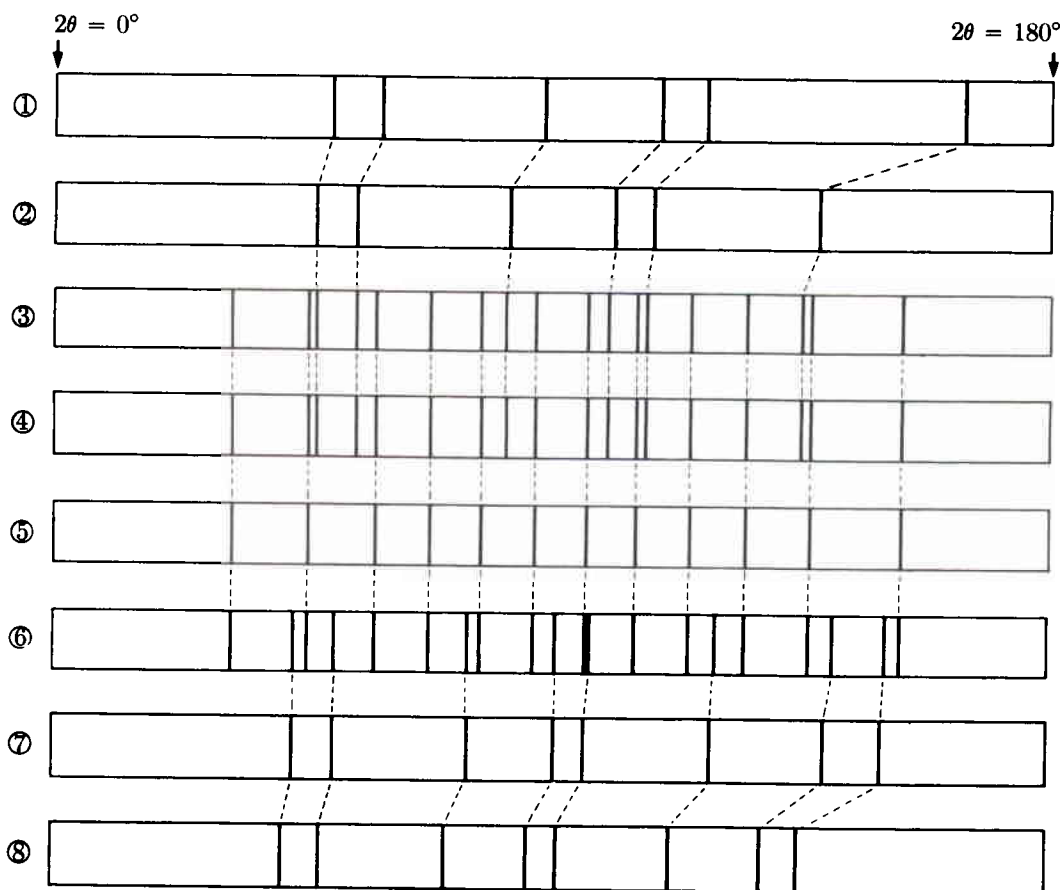


Fig. 12-4 Calculated powder patterns of alloys 1 to 8 in the alloy system shown in Fig. 12-3.

3. Superimposed patterns of α and γ . The α phase is now saturated and has its maximum parameter a_3 .
4. Same as pattern 3, except for a change in the relative intensities of the two patterns which is not indicated on the drawing.
5. Pattern of pure γ (body-centered cubic).
6. Superimposed patterns of γ and of saturated β with a parameter of a_4 .
7. Pattern of pure β with a parameter somewhat greater than a_4 .
8. Pattern of pure B (face-centered cubic).

When an *unknown* phase diagram is being determined, the investigator must, of course, work in the reverse direction and deduce the sequence of phases across the diagram from the observed powder patterns. This is done by visual comparison of patterns prepared from alloys ranging in composition from pure A to pure B, and the previous example illustrates the nature of the changes which can be expected from one pattern to another. Corresponding lines in different patterns are identified by placing the films side by side as in Fig. 12-4 and noting which

lines are common to the two patterns.* This may be difficult in some alloy systems where the phases involved have complex diffraction patterns, or where it is suspected that lines due to $K\beta$ radiation may be present in some patterns and not in others. It is important to remember that a diffraction pattern of a given phase is characterized not only by line positions but also by line intensities. This means that the presence of phase X in a mixture of phases cannot be proved merely by coincidence of the lines of phase X with a set of lines in the pattern of the mixture; the lines in the pattern of the mixture which coincide with the lines of phase X must also have the *same relative intensities* as the lines of phase X. The addition of one or more phases to a particular phase weakens the diffraction lines of that phase, simply by dilution, but it cannot change the intensities of those lines relative to one another. Finally, it should be noted that the crystal structure of a phase need not be known for the presence of that phase to be detected in a mixture: it is enough to know the positions and intensities of the diffraction lines of that phase.

Phase diagram determination by x-ray methods usually begins with a determination of the room-temperature equilibria. The first step is to prepare a series of alloys by melting and casting, or by melting and solidification in the melting crucible. The resulting ingots are homogenized at a temperature just below the solidus to remove segregation, and very slowly cooled to room temperature.† Powder specimens are then prepared by grinding or filing, depending on whether the alloy is brittle or not. If the alloy is brittle enough to be ground into powder, the resulting powder is usually sufficiently stress-free to give sharp diffraction lines. Filed powders, however, must be re-annealed to remove the stresses produced by plastic deformation during filing before they are ready for x-ray examination. Only relatively low temperatures are needed to relieve stresses, but the filings should again be slowly cooled, after the stress-relief anneal, to ensure equilibrium at room temperature. Screening is usually necessary to obtain fine enough particles for x-ray examination, and when two-phase alloys are being screened, the precautions mentioned in Sec. 6-3 should be observed.

After the room-temperature equilibria are known, a determination of the phases present at high temperatures can be undertaken. Powder specimens are sealed in small evacuated silica tubes, heated to the desired temperature long enough for equilibrium to be attained, and rapidly quenched. Diffraction patterns of the quenched powders are then made at room temperature. This method works very well in many alloy systems, in that the quenched powder retains the structure it had at the elevated temperature. In some alloys, however, phases stable at high temperature will decompose on cooling to room temperature, no matter how rapid

* Superposition of the two films is generally confusing and may make some of the weaker lines almost invisible. A better method of comparison consists of slitting each Debye-Scherrer film lengthwise down its center and placing the center of one film adjacent to the center of another. The curvature of the diffraction lines then does not interfere with the comparison of line positions.

† Slow cooling alone may not suffice to produce room-temperature equilibrium, which is often very difficult to achieve. It may be promoted by cold working and recrystallizing the cast alloy, in order to decrease its grain size and thus accelerate diffusion, prior to homogenizing and slow cooling.

the quench, and such phases can be studied only by means of a high-temperature camera or diffractometer.

The latter instrument is of particular value in work of this kind because it allows continuous observation of a diffraction line. For example, the temperature below which a high-temperature phase is unstable, such as a eutectoid temperature, can be determined by setting the diffractometer counter to receive a prominent diffracted beam of the high-temperature phase, and then measuring the intensity of this beam as a function of temperature as the specimen is slowly cooled. The temperature at which the intensity falls to that of the general background is the temperature required, and any hysteresis in the transformation can be detected by a similar measurement on heating.

12-3 SOLID SOLUTIONS

Inasmuch as solid solubility, to a greater or lesser extent, is so common between metals, we might digress a little at this point to consider how the various kinds of solid solutions may be distinguished experimentally. Irrespective of its extent or its position on the phase diagram, any solid solution may be classified as one of the following types, solely on the basis of its crystallography:

1. Interstitial.
2. Substitutional.
 - a) Random.
 - b) Ordered. (Because of its special interest, this type is described separately in Chap. 13.)
 - c) Defect. (A very rare type.)

Information on specific solid solutions, particularly on the variation of lattice parameter with composition, is given by Pearson [G.16].

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 of any importance in metallurgy are those formed between a metal and one of the elements, carbon, nitrogen, hydrogen, and boron, all of which have atoms less than 2 Å in diameter. The interstitial addition of B to A is always accompanied by an increase in the volume of the unit cell. If A is cubic, then the single lattice parameter a must increase. If A is not cubic, then one parameter may increase and the other decrease, as long as these changes result in an increase in cell volume. Thus, in austenite, which is an interstitial solid solution of carbon in face-centered cubic γ -iron, the addition of carbon increases the cell edge a . But in martensite, a metastable interstitial solid solution of carbon in α -iron, the c parameter of the body-centered tetragonal cell increases while the a parameter decreases, when carbon is added. These effects are illustrated in Fig. 12-5.

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

$$\rho = \frac{1.66042 \sum A}{V'}, \quad (3-7)$$