CHAPTER 7

CONGRUENT TRANSFORMATION OF ALLOYS

When one phase changes directly into another phase without any alteration in composition during the transformation, the phase change is said to be congruent. Conversely, an *incongruent phase change* is one which requires either a transient or a persistent composition change, as in the freezing of the solid solution or of the eutectic-type alloys, respectively. All pure components transform congruently. An example of the congruent melting of an alloy was presented at the end of Chap. 3, where it was pointed out that the minimum (or maximum) melting point in an iso-

morphous system lies at a point of congruent melting.

The intermediate phases, which are those that are not isomorphous with either of the components of the alloy system (i.e., they occur between the terminal phases), are often classified in two groups according to whether they are congruently melting or incongruently melting. The incongruently melting intermediate phases will be considered in succeeding chapters, where the peritectic, peritectoid (incongruently transforming). and syntectic reactions are discussed. For the moment, attention will be centered upon the congruently melting phases. These are sometimes re ferred to as intermetallic compounds. Although the use of this term is well justified in some instances upon the ground that a specific intermediate phase occurs at a composition corresponding to a simple ratio of the two kinds of atoms concerned, there are so many apparent exceptions that it seems better, on the whole, to regard all such phases simply as "intermediate phases" and to designate them by the use of Greek letters instead of molecular symbols. This practice has been adopted with increasing regularity in recent years by authors of phase diagrams.

An example of a congruently melting intermediate phase occurs in the magnesium-silicon system (Fig. 7-1). Here the β phase (which, incidentally, corresponds to the composition Mg₂Si) divides the phase diagram into two independent portions. A eutectic system is formed by the alloys of magnesium and β , and another eutectic system is formed by the alloys of β and silicon. Thus, it is seen that the congruently melting intermediate phase behaves as a *component*. Indeed, any intermediate phase which behaves congruently in all transformations to which it is subject may be

regarded as a component. This is the reason for defining the component (Chap. 1) in such manner as not to limit it to elemental substances. In the binary systems there is no particular advantage to be derived from splitting the phase diagrams into sections lying between terminal and intermediate "components." In ternary alloy systems, however, a degree of simplicity is gained by this procedure, as will be demonstrated in Chap. 17.

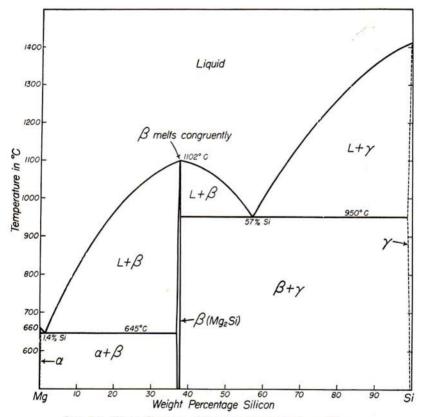


Fig. 7-1. Phase diagram of the system magnesium-silicon.

It will be evident that the example presented is only one of many possible combinations. The occurrence of two eutectics in this system is coincidental. Any type of equilibrium can occur among the several components. It should be noted also that the composition range of the intermediate phase may, in some instances, be very narrow, so that it can be represented only by a single line. As a matter of fact, the width of the β field has been exaggerated in Fig. 7-1 to permit it to be represented as an

area. Broad solid-solution ranges associated with intermediate phases are also found.

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Congruent Transformation in the Solid State

Congruent transformation may occur with solid-solid as well as solid-liquid phase changes. An interesting example is found in the iron-chromium system (Fig. 7-2). Here, three kinds of congruent transformation are represented, namely, (1) a minimum melting point at a, (2) congruent

transformation of the γ terminal solid solution to the α solid solution at a

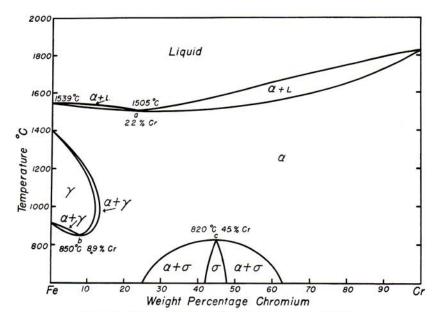


Fig. 7-2. Phase diagram of the system iron-chromium.

minimum transformation point b, and (3) congruent transformation of the σ intermediate solid-solution phase to α at a maximum transformation point c. In this case the only fully congruent alloy is that corresponding to the composition of the minimum melting point; the " σ alloy" and the " γ alloy" melt incongruently. Hence, the division of this diagram into two individually complete parts is possible only at the minimum melting composition. It is worth noting also that the so-called " γ loop" does not pass through a minimum or maximum in all alloy systems in which it is found. The $\alpha + \gamma$ region may, alternately, be formed as a crescent with its maximum and minimum points occurring at the pure metal composition.

Ordered Crystal Structure

Many of the intermediate phases have ordered crystal structures. This means that the two kinds of atoms, instead of being located at random on the crystal lattice as in ordinary terminal solid solutions of the substitutional type, have specific positions on the crystal lattice. In a simple case, for example, the two kinds of atoms might alternate along any principal direction in the crystal lattice, so that in space each A atom would have only B atoms as nearest neighbors and each B atom would have only A atoms as nearest neighbors.

This detail of crystal structure would not require special comment were it not for the fact that there are a few cases where an ordered crystalline variety transforms (congruently) into a disordered crystalline variety that is crystallographically identical except for the absence of ordering. For this reason, the question has been raised whether or not such transformation should be regarded as a true phase change.

The subject of heterogeneous equilibrium, however, does not deal with the structure of the phases per se; it is concerned only with the conditions of coexistence of distinguishable states of matter. To prove a difference in phase, it is sufficient to show that at equilibrium, the two states can coexist in physical contact with a sharp boundary between them. Criteria for distinguishing two states so situated may be any externally measurable property. Recent studies have demonstrated, for the contested cases of Cu₃Au and some others, that the ordered and disordered states can coexist at equilibrium. Thus, it is correct to represent the order-disorder transformation upon the phase diagram as a normal phase change.

Physical Properties of Intermediate Phases

Ductility and softness are usually associated with simple crystal types, such as those of most of the common metals and their associated terminal solid solutions. Crystals of complex structure usually exhibit great hardness but are relatively brittle and often fragile. Since the majority of intermediate phases have complex crystal structures, it is to be expected that they will tend to be hard and brittle. There are, of course, noteworthy exceptions. Eutectic, eutectoid, and other two-phase constituents involving an intermediate phase naturally partake of the properties of that phase in accordance with its proportion and distribution. Hence, multiphased alloys that include intermediate phases are, as a class,

¹ For a detailed review of this subject, see F. C. Nix and W. Shockley, Order-Disorder Transformations in Alloys, *Revs. Mod. Phys.* **10**:1 (1938).

² F. N. Rhines and J. B. Newkirk, The Order-Disorder Transformation Viewed as a Classical Phase Change, *Trans. Am. Soc. Metals*, **45**:1029-1055 (1952).

harder and more brittle than those composed of terminal solid solutions alone.

PRACTICE PROBLEMS

1. Draw a phase diagram for the system AB, which has an intermediate phase γ at 50% B; the partial system $A\gamma$ is of the eutectic type; the partial system γB is of the monotectic type at high temperature with a eutectic reaction at lower temperature.

2. Deduce the structural changes that will occur in cooling an (8.9%) iron-chromium alloy from 1600°C to room temperature. What difference would be found if the composition were changed to 8.0% chromium? (Note: use Fig. 7-2 in answering this

problem.)

3. Iron-chromium alloys (Fig. 7-2) composed of 44 and 45% chromium, respectively, will both transform from α to σ upon cooling from 1000°C to room temperature. What differences should be observed in the paths of transformation of these two alloys?