CHAPTER 8

BINARY PERITECTIC SYSTEMS

Corresponding to the eutectic group of univariant reactions is a group of *peritectic*-type reactions, in which one phase decomposes with *rising* temperature into two new phases. It will be recalled that the eutectic-type reactions are all characterized by the decomposition with *falling* temperature of one phase into two new phases. The peritectic reaction itself consists, upon heating, in the decomposition of one solid phase into a liquid and a new solid phase:

$$L + \alpha \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \beta$$

In other words, the solid phase melts *incongruently*, i.e., with decomposition. This type of reaction is represented in Fig. 8-1, where the β phase of peritectic composition (point p) melts by decomposition into $L + \alpha$ of compositions l and a, at the peritectic reaction temperature. It is not necessary that the solid phase at the peritectic point be a terminal solid solution; indeed, it is more often an intermediate phase (Fig. 8-2) that melts incongruently.

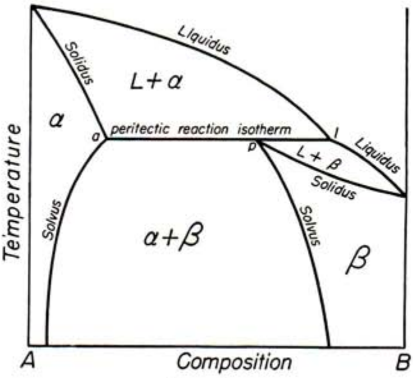

FIG. 8-1

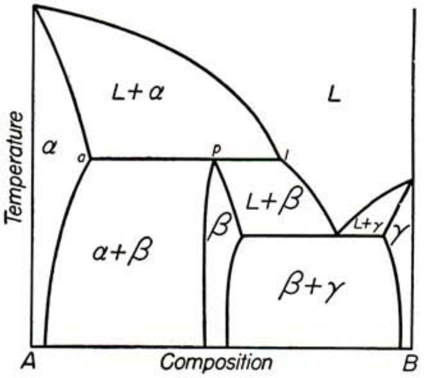

FIG. 8-2

All the arguments required to derive the method of representation of peritectic equilibrium from the phase rule have been cited in connection with the eutectic systems and need not be repeated here. The peritectic line must, of course, be horizontal (isothermal) because it represents univariant equilibrium among three phases. Where they intersect the peritectic reaction isotherm, all boundaries of two-phase regions must arrive at such angles that they project into other two-phase regions and not into one-phase regions of the diagram. Any one-phase region may touch the peritectic line at only one single composition point.

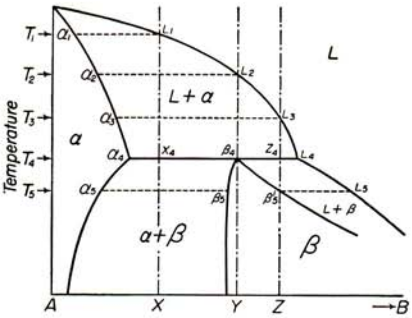

FIG. 8-3

Equilibrium Freezing of Peritectic Alloys

Consider the course of freezing of the *peritectic alloy*, composition Y in Fig. 8-3. Upon cooling from the fully molten condition, the liquidus is reached at temperature T_2, where crystals of the α phase (α_2) begin to form. The liquid composition is displaced to the right as the temperature falls, and more solid is deposited. The composition of the α phase changing along the solidus reaches the end of the *peritectic line* (α_4) when the liquid composition has reached the opposite end (L_4).

$$\%\alpha \text{ (alloy } Y \text{ above peritectic)} = \frac{\beta_4 L_4}{\alpha_4 L_4} \times 100 \approx 35\%$$

$$\%L \text{ (alloy } Y \text{ above peritectic)} = \frac{\alpha_4 \beta_4}{\alpha_4 L_4} \times 100 \approx 65\%$$

Peritectic reaction now occurs; the liquid and α react together to form β. Under "equilibrium" conditions freezing must be completed isothermally by this process, and all the previously formed α as well as the liquid must be consumed.

If the alloy composition had lain to the left of the peritectic point, as at X in Fig. 8-3, the α phase would not have been totally consumed in forming β. In this alloy, freezing begins at T_1, where α_1 first appears. Just above the peritectic temperature the quantities of α and liquid will be

$$\%\alpha \text{ (alloy } X \text{ above peritectic)} = \frac{x_4 L_4}{\alpha_4 L_4} \times 100 \approx 80\%$$

$$\%L \text{ (alloy } X \text{ above peritectic)} = \frac{\alpha_4 x_4}{\alpha_4 L_4} \times 100 \approx 20\%$$

Just below the peritectic temperature the liquid will have disappeared and there will be only the solid phases α and β.

$$\%\alpha \text{ (alloy } X \text{ below peritectic)} = \frac{x_4\beta_4}{\alpha_4\beta_4} \times 100 \approx 70\%$$

$$\%\beta \text{ (alloy } X \text{ below peritectic)} = \frac{\alpha_4x_4}{\alpha_4\beta_4} \times 100 \approx 30\%$$

Notice that the quantity of the α phase has decreased during peritectic reaction from about 80 to about 70%.

Had the composition of the alloy lain to the right of the peritectic point, alloy Z in Fig. 8-3, for example, then an excess of liquid would have survived the peritectic reaction. Freezing in this case begins at T_3, where α_3 is first rejected. There is a small quantity of the α phase present by the time the peritectic temperature is reached:

$$\%\alpha \text{ (alloy } Z \text{ above peritectic)} = \frac{z_4L_4}{\alpha_4L_4} \times 100 \approx 10\%$$

$$\%L \text{ (alloy } Z \text{ above peritectic)} = \frac{\alpha_4z_4}{\alpha_4L_4} \times 100 \approx 90\%$$

But this is entirely consumed in forming the β phase:

$$\%\beta \text{ (alloy } Z \text{ below peritectic)} = \frac{z_4L_4}{\beta_4L_4} \times 100 \approx 30\%$$

$$\%L \text{ (alloy } Z \text{ below peritectic)} = \frac{\beta_4z_4}{\beta_4L_4} \times 100 \approx 70\%$$

Observe that the quantity of liquid has been reduced to about 70% and that the quantity of β formed is much greater than that of the α originally present.

Natural Freezing of Peritectic Alloys

The departure from equilibrium in the natural freezing of peritectic alloys is usually very large. This is because the reaction product, the β phase, necessarily forms at the interface between α and liquid, establishing a hindrance to the diffusion which is necessary for the continuation of the reaction (see Fig. 8-4). In order to change α into β, some A atoms must diffuse out of the α phase and are replaced by B atoms, which must come, ultimately, from the liquid phase, both having been transported through the zone of β. As the β layer grows thicker, the distance

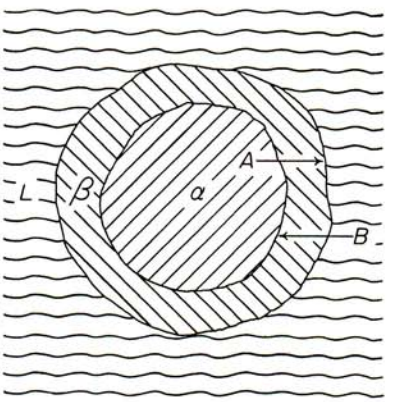

FIG. 8-4. Schematic representation of primary α undergoing peritectic reaction with liquid L to form an envelope of β. The reaction progresses by the diffusion of A atoms outward and B atoms inward through the shell of β.

over which the two kinds of atoms must be transported increases. Thus, the first layer of β forms quickly, but its growth proceeds at a decelerating pace, so that the reaction is frequently incomplete when the temperature has fallen well below that of the peritectic and, indeed, has become so low that further diffusion is negligible.

When the entire process of natural freezing is considered, it is found that further deviation from equilibrium is caused by the familiar coring effect. Alloy X of Fig. 8-5 begins freezing by the deposition of a cored primary α constituent. Hence, at the peritectic temperature, the quantity of the α is less and that of the liquid larger than should be the case under conditions of equilibrium:

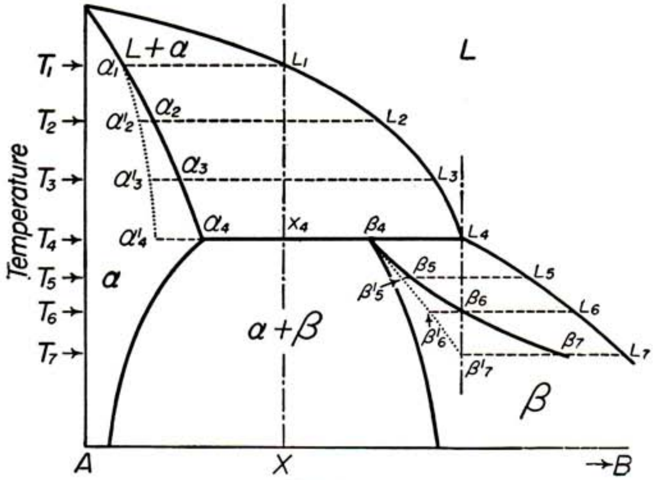

FIG. 8-5

$$\%\alpha'_4 \text{ (alloy } X \text{ above peritectic)} = \frac{x_4L_4}{\alpha'_4L_4} \times 100 \approx 60\%$$

$$\%L_4 \text{ (alloy } X \text{ above peritectic)} = \frac{\alpha'_4x_4}{\alpha'_4L_4} \times 100 \approx 40\%$$

Also, the primary α constituent is richer in the A component than it would otherwise be. Partial reaction of liquid with the α phase now occurs. A layer of β, of peritectic composition, is formed at the expense of some of the α and a larger share of the liquid. When, as usually happens, the temperature falls below T_4 before peritectic reaction is complete, the remaining liquid, of composition L_4, will freeze directly to cored β; that is, L_4 deposits β_4 first, then successive β compositions along the lower solidus, yielding average β compositions of β'_5, β'_6, and β'_7. At T_7 the liquid is finally consumed and the alloy is entirely solid. The microstructure now consists of a primary cored α constituent surrounded by zones of

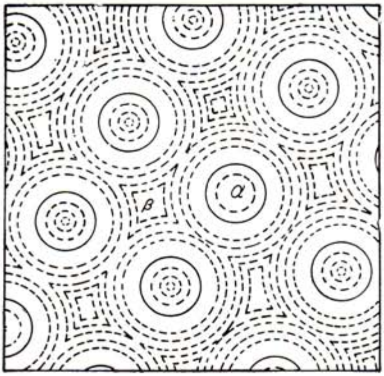

FIG. 8-6. Schematic representation of "envelopment" in a cast peritectic-type alloy. A residue of cored primary α is represented by the solid circles concentric about smaller dashed circles; surrounding the cored α is a layer of β of peritectic composition, the remaining space being filled with cored β, represented by dashed curved lines.

secondary peritectic β of constant composition, with tertiary cored β filling the remaining space (Fig. 8-6).

Envelopment

Frequently, the layer of peritectic β is so thin that it is not perceptible in the microstructure. When it is sufficiently thick to be seen, however, it appears in the form of "envelopes" surrounding each of the particles of

FIG. 8-7. Cast Pt + 25% Ag hypoperitectic alloy. White and light gray matrix is primary cored α (Pt-rich); dark spots are β. Magnification 500.

FIG. 8-8. Cast Pt + 60% Ag hyperperitectic alloy. White and light gray areas are residual cored α; dark two-toned areas are β, the outer portions being of peritectic composition and the darkest central areas being the cored β that formed at temperatures below that of the peritectic reaction. Magnification 1,000.

the primary constituent. This structural feature bears the name *envelopment*. Examples of envelopment appear in Figs. 8-7 and 8-8, which depict the microstructures of two alloys of the peritectic system silver-platinum (Fig. 8-9). Coring of the light-colored α phase is shown by a change from white to light gray; β envelopment is seen as a medium-gray layer between the light and dark areas; the darkest areas are the cored β.

Freezing of Some Other Alloys

An alloy, such as Z in Fig. 8-10, which, under equilibrium conditions, would freeze to a structure composed of β alone, may develop a two-phase structure through the process of natural freezing. Primary cored α crystals separate in the temperature range T_1 to T_4. If peritectic reaction is incomplete at T_4, some of this primary α constituent may remain enveloped by secondary peritectic β as is seen to have occurred in the 60% silver alloy of Fig. 8-8. The remaining liquid freezes to cored β. Further changes in the solid state will be discussed presently.

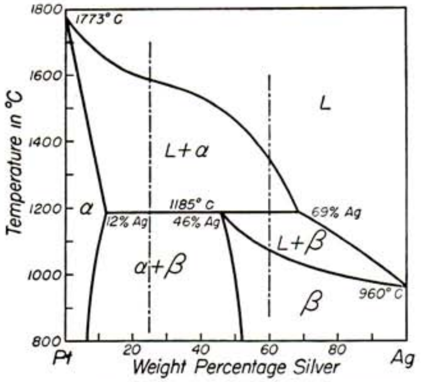

FIG. 8-9. Phase diagram of the system platinum-silver.

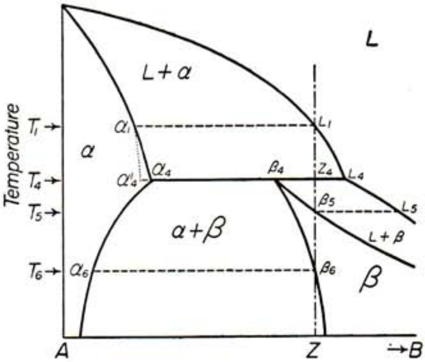

FIG. 8-10

The reverse of this effect is found in alloys beyond the end of the peritectic isotherm, on the side toward the solid (α) phase, alloy W in Fig. 8-11. Here, equilibrium freezing would produce a structure composed wholly of the α phase, but natural freezing develops some of the β phase in the cast structure. Coring of the primary α constituent being sufficient, some liquid will remain at T_4:

$$\%\alpha \text{ (alloy } W \text{ above peritectic)} = \frac{W_4L_4}{\alpha_4'L_4} \times 100 \approx 90\%$$

$$\%L \text{ (alloy } W \text{ above peritectic)} = \frac{\alpha_4'W_4}{\alpha_4'L_4} \times 100 \approx 10\%$$

This liquid will react with α to form peritectic β, and if it is not thus consumed, it will freeze directly to cored β.

Evidently, nonequilibrium freezing can result in an excess of either the α or the β phase in the microstructure. Alloys rich in A tend to have an excess of the β phase, while those rich in B tend to have an excess of the α phase. Differing relative diffusion rates in the several phases and differing constitutional relationships, with regard to the compositions of the phases on the peritectic line, from alloy system to alloy system can have a pronounced influence upon the character of the cast microstructure.

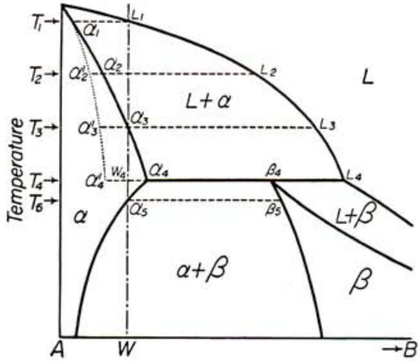

FIG. 8-11

It should be noted that although the eutectic and peritectic structures both involve two phases, the two types of microstructure may be distinguished readily by the facts that (1) the peritectic has no *two-phase constituent* and (2) both phases of the peritectic alloy may be cored.

Heat Treatment of Peritectic Alloys

Where there exists coring inhomogeneity, or nonequilibrium proportions of the phases present, a homogenizing heat treatment, at a temperature such as to ensure an appreciable rate of diffusion without causing a phase change, may be expected to cause the structure of the alloy to change in the direction of equilibrium. Thus, alloy W of Fig. 8-11 can be converted to homogeneous α by heating for some time at a temperature between T_3 and T_5; rapid cooling (quenching) to room temperature should, in general, cause the homogeneous α structure to be retained as a supersaturated solid solution. At any temperature where the diffusion rate becomes appreciable, up to T_5, however, the β phase may reappear as a Widmanstätten precipitate. Age hardening is possible in this type of alloy just as in those alloy systems of the eutectic group where the solvus inclines toward lower solubility at low temperature.

In like manner, alloy Z of Fig. 8-10 could be homogenized to uniform β if it were heated for a long time at some temperature between T_5 and T_6. Slow cooling or quenching followed by reheating to a temperature below T_6 might be expected to cause the appearance of a Widmanstätten precipitate of the α phase. This alloy, too, might be subject to age hardening if the essential crystallographic relationships are present.

Intermediate alloys, such as X in Fig. 8-5, cannot be homogenized to a single phase, but the relative proportions of the two phases may be adjusted toward the equilibrium ratio by heat treatment. Coring within the individual constituents may be eliminated, and spheroidization of the minor constituent may occur.

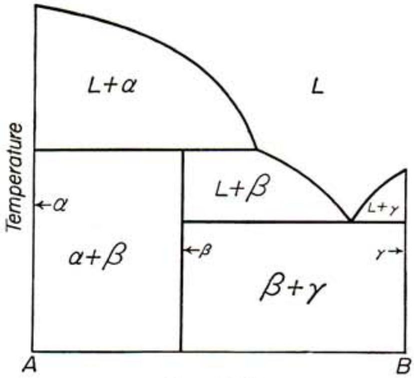

FIG. 8-12

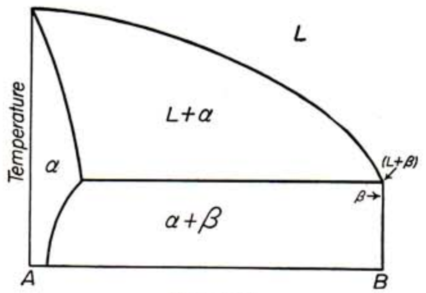

FIG. 8-13

Liquation occurs as in eutectic alloys, but with the difference that melting may be encountered at temperatures below that of the peritectic. If any of the cored β constituent is present, and it may be present even in alloys to the left of the peritectic line, then liquation can be encountered at the fusion temperature of the lowest melting zone in the β constituent. For this reason, a slow approach to the desired homogenizing temperature is especially important when dealing with peritectic alloys.

Limiting Cases of the Peritectic

Where the solid-solution range of the β intermediate phase becomes very narrow (Fig. 8-12), it may appear upon the phase diagram as a single line. Likewise the terminal solid-solution ranges become very narrow in some systems, so that no areas corresponding to the solid phases can be shown. These conditions influence the interpretation of the phase diagram only to the extent that the coring effect becomes negligible; incomplete peritectic reaction persists in such systems.

If the peritectic point falls very close to one end of the peritectic reaction isotherm, it may become difficult to distinguish between a eutectic and a peritectic system; compare Fig. 8-13 with Fig. 4-22. The only means of distinguishing between the two cases, in some instances, has been to make a very careful comparison of the reaction temperature with the melting point of the B component (see Chap. 21). If the reaction temperature is higher, the system is peritectic; if lower, it is eutectic. In either case the $L + \beta$ field becomes so small that it cannot be shown.

Mechanical Properties of Peritectic Alloys

Peritectic alloys, being usually two-phase aggregates, have mechanical properties that may be associated with microstructure in accordance with the principles stated for eutectic alloys. Two special characteristics of peritectic alloys should, however, be noted in this connection, namely: (1) the individual phases are ordinarily far removed from their respective states of homogeneous equilibrium and (2) the particle size of the cast peritectic alloy is rarely fine. The first of these characteristics means that a regular (linear) change in properties across the range of two-phase alloys is not to be expected unless special steps, such as working and heat treatment, have been taken to establish a state of near equilibrium. The coarseness of the peritectic structure is reflected in the physical properties only in a negative sense; that is, hardening by the deliberate refinement of the reaction products is very limited.

PRACTICE PROBLEMS

1. The system AB forms a congruently melting compound $AxBy$; alloys between A and $AxBy$ are of the eutectic type; those between $AxBy$ and B are of the peritectic type. Draw a phase diagram for this system.

2. Considering an alloy such as X, Fig. 8-5, how would the cast microstructure be altered by moving the peritectic point β_4 a little to the left? to the right?

3. Consider that alloy W, Fig. 8-11, was made homogeneous by long heat treatment at T_4. Then, just before cooling to room temperature, the heat-treating temperature was increased briefly to T_2. Deduce the resulting microstructure of alloy W.

4. Deduce the cast microstructure of a hyperperitectic alloy (that is, having its composition midway between p and l) in the system illustrated in Fig. 8-2.