CHAPTER 9

BINARY PERITECTOID SYSTEMS

The *peritectoid reaction* (also known as the metatectic reaction) is related to the peritectic in much the same way as the eutectoid to the eutectic. Only solid phases are involved in peritectoid reaction:

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

The solid phase β, upon heating, decomposes into two new solid phases (Fig. 9-1). This is one kind of incongruent transformation in the solid state.

Although peritectoid reaction is fairly common among the alloy systems at large, so few of the specific alloys of commerce occur within composition ranges involving peritectoid reaction that experience with this transformation has been very scanty. Upon the basis of its similarity to the peritectic it might be expected that the peritectoid transformation would be very slow. Reaction between the high-temperature phases (α and γ) during cooling is expected to proceed at the phase interface, where a layer of the low-temperature phase (β) should be formed. The continuation of the transformation would require diffusion through a growing septum of β and ordinarily at a relatively low temperature where diffusion rates are small. Thus, it should be common to find the transformation incomplete when the alloy has reached room temperature.

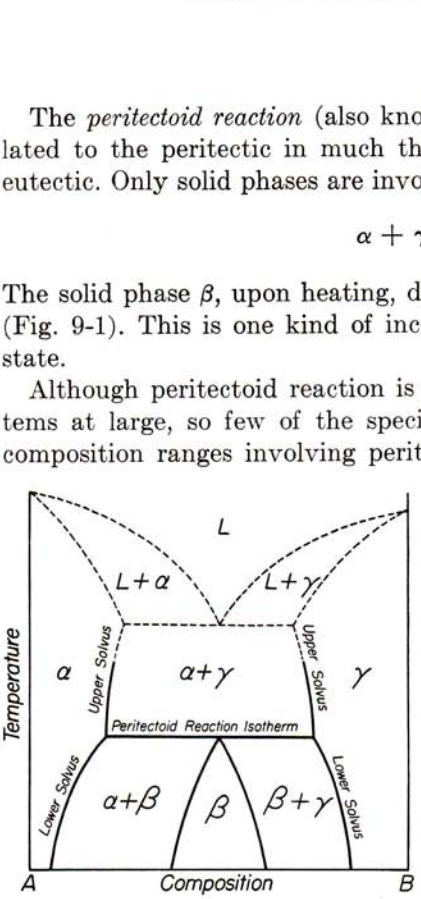

FIG. 9-1

Such experimental evidence as exists indicates the presence of several complicating factors. First, the transformation may proceed through a series of unstable transition states, which modify its mechanism and rate. Second, crystallographic factors, which influence the directions of diffusion and of phase growth, can affect the morphology of the reaction products. And finally, it frequently happens that the composition of the low-temperature phase (β) differs so little from the composition of one of the high-temperature phases that the impeding influence of diffusion upon the progress of transformation is minimized.

An example of the peritectoid is to be found in the silver-aluminum system (Fig. 9-2). Here the composition range of the β phase partially overlaps that of the high-temperature phase γ. Quenched from a temperature slightly above that of the reaction, the microstructure of a 7% aluminum alloy is composed of a matrix of γ with a few particles of α Fig. 9-3*A*). When this alloy has been cooled to a temperature slightly below that of the peritectoid and held there for some hours, the structure is found to be composed almost entirely of β, with a few particles of α remaining untransformed (Fig. 9-3*C*). Evidently the γ transforms to β with little or no composition change, and subsequently, the α is gradually dissolved by the β. The reaction to form β begins at the $\alpha\gamma$ phase interface and proceeds into the γ phase at a rapid rate. This can be seen in the microstructure of the alloy in its partly transformed condition (Fig. 9-3*B*). Three phases (α, β, and γ) are present in this microstructure. Since, according to the phase rule, there can be but two phases present at equilibrium in this type of situation, it is clear that the microstructure of Fig. 9-3*B* represents a nonequilibrium state.

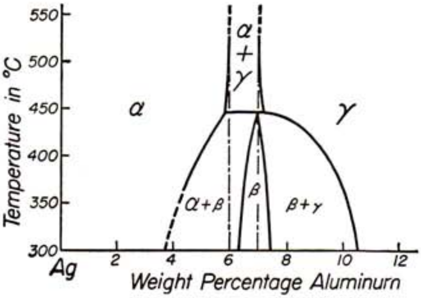

FIG. 9-2. Portion of the phase diagram of the system silver-aluminum.

A hypoperitectoid alloy, 6% aluminum, quenched from above the peritectoid temperature, is found to be composed of a matrix of α with embedded particles of γ (Fig. 9-4*A*). Again, with long heat treatment below the reaction temperature, the γ is converted to β and much of the α is consumed by solution in the β (Fig. 9-4*B*).

Limiting Cases of the Peritectoid

Rather common among phase diagrams of the alloy systems is the occurrence of a limiting case of the peritectoid in association with a limiting

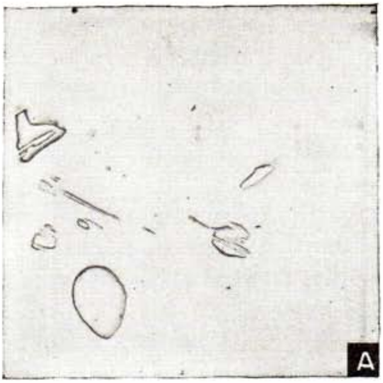

FIG. 9-3 (*A*). A near-peritectoid alloy, Ag + 7% Al, stabilized by long heat treatment above the peritectoid temperature and then quenched. "Islands" are the α phase embedded in a matrix of γ. Magnification 150.

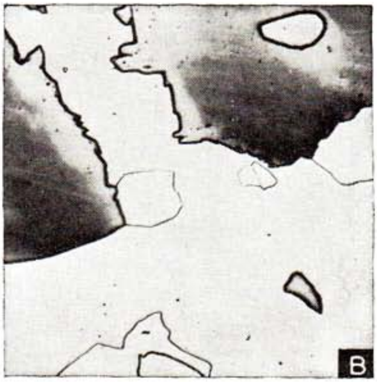

FIG. 9-3 (*B*). Same as *A*, partially transformed by cooling to a temperature slightly below that of the peritectoid and holding 20 min before quenching. Much of the light-colored γ has been transformed to dark-colored β without greatly affecting the "islands" of α, which are also light colored. Magnification 150.

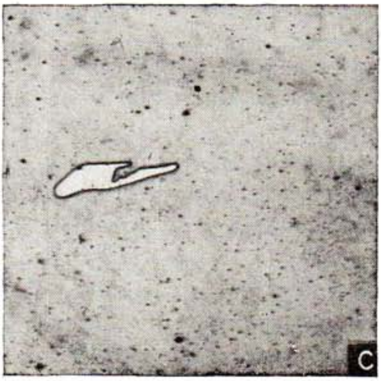

FIG. 9-3 (*C*). Same as *A*, fully transformed by cooling to and holding 2 hr at a temperature slightly below the peritectoid. Dark matrix is β; light area is residual α that has not yet been dissolved by the β. Magnification 150.

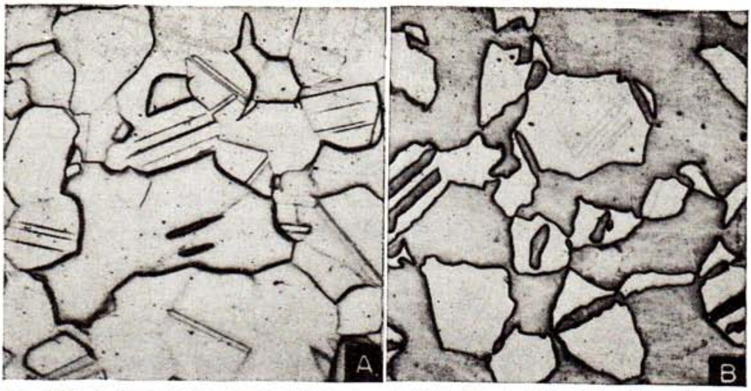

FIG. 9-4. (*A*) A hypoperitectoid alloy, Ag + 6% Al, stabilized by long heating at a temperature somewhat above that of the peritectoid, followed by quenching. The heavily outlined areas are γ; the α matrix is distinguished by exhibiting occasional twin bands across the grains. Magnification 150. (*B*) Same as *A*, fully transformed by holding 2 hr at a temperature slightly below the peritectoid, followed by quenching. The gray matrix is β; the lighter areas are residual α. Magnification 150.

case of the eutectoid (see Fig. 9-5). Here the peritectoid and eutectoid compositions each coincide very nearly with one of the ends of their respective reaction isotherms. It is possible to tell that one of these reactions is a peritectoid and the other a eutectoid by observing the relative positions of the two-phase fields. With peritectoid reaction two two-phase fields ($\beta + \beta'$ and $\beta' + \gamma$) lie below the reaction isotherm and one ($\beta + \gamma$) above, while the reverse is true of the eutectoid. Occasionally, there is no perceptible temperature difference between the two reactions, and the connecting two-phase field ($\beta + \beta'$) reduces to a horizontal line (see Fig. 9-6). This is a limiting condition which probably is never actually attained but which is so closely approached that the diagram cannot be drawn otherwise. Equilibria of this variety are sometimes associated with a change from an ordered to a disordered crystal; β', for example, may be "ordered," while β is "disordered."

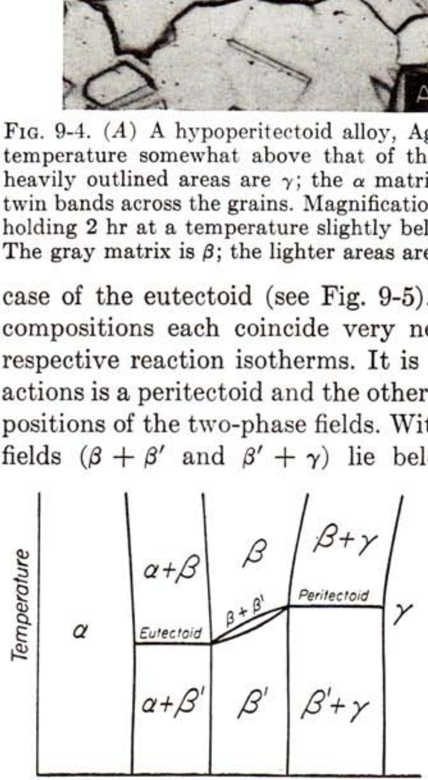

FIG. 9-5

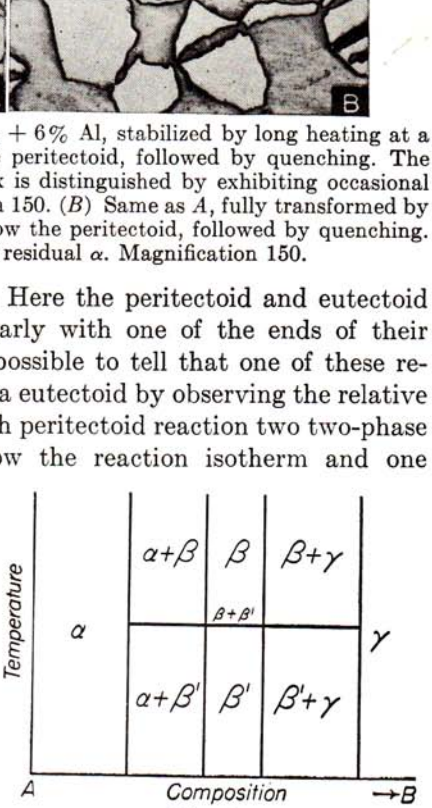

FIG. 9-6