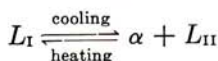


CHAPTER 6

BINARY MONOTECTIC SYSTEMS

Another important three-phase reaction of the eutectic class is the *monotectic* (Fig. 6-1), in which one liquid phase decomposes with decreasing temperature into a solid phase and a new liquid phase.



Over a certain composition range, the two liquids are mutually immiscible, as are oil and water, and so constitute individual phases. Conformity of this type of system with the phase rule and other thermodynamic principles can be argued along lines parallel to those adopted in constructing

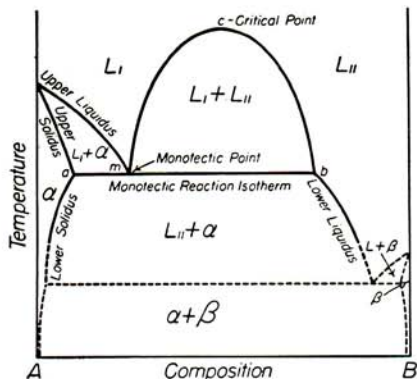


FIG. 6-1

the eutectic diagram. Accepted nomenclature follows the familiar pattern by which the meaning of such terms as *monotectic point*, *monotectic reaction isotherm*, *hypomonotectic*, and *hypermonotectic* will be understood. It should be noted, however, that the liquidus and solidus curves are differently located (Fig. 6-1) and that these have been designated as "upper" and "lower" to distinguish them. There is no special name for the boundary of the $L_I + L_{II}$ field; it will be called simply the

limit of liquid immiscibility. The eutectic reaction, depicted by dashed lines in this example, is included merely to carry the diagram into the temperature range where all phases are solid. There are several other constructions that could as well have been used for this purpose.

Monotectic Decomposition

Above the *monotectic temperature*, the *monotectic alloy*, Y in Fig. 6-2, is composed solely of a single liquid phase L_I . At (or slightly below) the *monotectic temperature*, this liquid decomposes in a manner entirely

analogous to the decomposition of the eutectic liquid, the only difference being that one of the products is a liquid instead of a solid phase. Thus, the resulting monotectic constituent resembles the eutectic constituent in all respects except that one of the phases is fluid. As it happens, all known

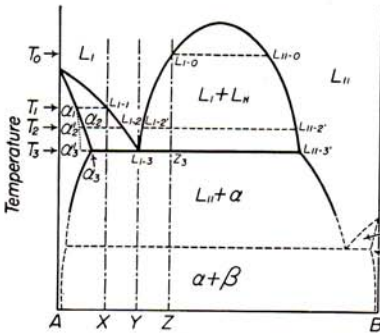


FIG. 6-2

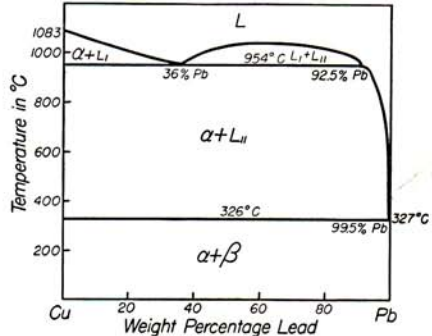


FIG. 6-3. Phase diagram of the system copper-lead.

binary monotectic points in metal systems are located nearer to the composition of the solid phase than to that of the second liquid so that the solid phase predominates in the monotectic constituent.

$\% \alpha$ (monotectic)

$$= \frac{L_{1-3}L_{II-3}'}{\alpha_3L_{II-3}'} \times 100 \approx 75\%$$

$\% L_{II}$ (monotectic)

$$= \frac{\alpha_3L_{1-3}}{\alpha_3L_{II-3}} \times 100 \approx 25\%$$

Accordingly, the liquid L_{II} appears in pockets apparently surrounded by the solid α phase (Fig. 6-4). This is a picture of a copper-lead monotectic alloy (Fig. 6-3) and was, of course, taken after the alloy had cooled to room temperature. The liquid L_{II} had meanwhile frozen as a eutectic constituent composed of 99.5% lead and 0.5% copper and appears as gray areas in the picture.

Because of the continuity of the copper-rich α phase in the monotectic structure, the physical properties of this alloy more nearly resemble those of copper than those of lead. Lead is often added to alloys in which it introduces monotectic reaction because it makes the machining of the metal easier, by reducing the ductility just enough to cause chips to



FIG. 6-4. Microstructure of cast monotectic alloy Cu + 36% Pb. Light areas are the Cu-rich matrix of the monotectic constituent; dark areas are the Pb-rich portion, which existed as L_{II} at the monotectic temperature. Magnification 100.

break away, without seriously decreasing hardness and strength. Leaded alloys are used also for bearings, where the continuous phase of the high-melting metal gives strength to the member, while the lead, occurring in pockets at the running surface, serves to reduce the friction between bearing and axle.

Hypomonotectic Alloys

Alloys on the " α side" of the monotectic point, the *hypomonotectic alloys*, composition X in Fig. 6-2, for example, pass through a state of bivariant equilibrium before the univariant monotectic reaction occurs. Freezing begins with a primary separation of the α phase, which may be cored because of failure to maintain equilibrium in the α phase: $\alpha_1, \alpha_2', \alpha_3'$. At the monotectic temperature T_3 there will be some excess of L_{I-3} over the equilibrium quantity, and this will react to yield the secondary monotectic constituent. Thus, the hypomonotectic copper-lead alloy of Fig. 6-5 is composed of cored copper-rich primary dendrites interlaid with a divorced monotectic composed of α_3 continuous with the primary α dendrites and L_{II-3}' in the interdendritic spaces. According to the copper-lead diagram (Fig. 6-3) the L_{II} in the pockets between the α dendrites should, with further cooling below the monotectic temperature, deposit a tertiary α phase, which will be physically continuous with and indistinguishable in the picture from the primary and secondary α . Finally, at the eutectic temperature the L_{II} will decompose into a fourth-order constituent, the eutectic of copper-rich α and lead-rich β . This eutectic, being of very fine particle size, is not resolved in the photomicrograph and appears as dark spots where the L_{II} had been located.

Hypermonotectic Alloys

The occurrence of two-liquid immiscibility in the hypermonotectic alloys at temperatures above the monotectic introduces structural considerations which have no parallel in the examples discussed up to this point. Given time enough, the two liquids will separate into two layers placed according to density, with the lighter layer on top, as oil floats on water. It is quite possible, however, to have the two liquids existing as an emulsion, wherein tiny droplets of one liquid remain suspended in the other liquid. Which of these conditions will be the more nearly approached in a given heating and cooling cycle must depend upon the physical characteristics of the alloy system concerned, upon the conditions of formation of the second liquid, and upon the opportunity afforded for the segregation of the two liquids. Knowledge of these matters with respect to metals is fragmentary and unsatisfactory at the present time.

Suppose that a hypermonotectic alloy, such as Z in Fig. 6-2, is heated to a high temperature above T_0 ; the alloy will be composed of one liquid phase. When, upon cooling, the limit of liquid immiscibility is crossed at L_{I-0} , the second liquid L_{II-0} should make its appearance, probably at the surface of the confining vessel and possibly, also, at various points



FIG. 6-5. Hypomonotectic Cu + 5% Pb alloy, as cast. Light areas are primary and monotectic Cu; dark areas are Pb which existed as L_{II} at the monotectic temperature. Magnification 100.



FIG. 6-6. Microstructure at the interface between the two layers in a Cu + 50% Pb hypermonotectic alloy. Upper layer is the product of the monotectic decomposition of L_I (36% Pb); lower layer contains light particles of Cu, precipitated during the cooling of L_{II} from the monotectic temperature down to that of the eutectic, embedded in the dark Pb-rich Pb-Cu eutectic constituent. Magnification 100.

throughout the liquid bath. As the temperature falls, the quantity of L_{II} increases, so that just above the monotectic temperature its amount will be

$$\%L_{II} = \frac{L_{I-3}z_3}{L_{I-3}L_{II-3}} \times 100 \approx 20\%$$

Conditions being favorable, this liquid will exist as a separate layer in the crucible or mold. That portion of the mixture which is composed of L_{I-3} will now react to form the monotectic constituent. In the case of the copper-lead (50-50) alloy in Fig. 6-6, this is the upper of the two layers; the lower layer of L_{II-3} remains unchanged during this reaction. Now the alloy is composed of an upper layer in which pockets of L_{II} are surrounded by the α phase and a lower layer of L_{II} , which is still fully molten. With continued cooling the L_{II} in both layers rejects a small quantity of the α phase in descending to the eutectic temperature and then freezes as a

eutectic constituent of $\alpha + \beta$. The two layers and their respective structures are apparent in Fig. 6-6.

The Field of Two-liquid Immiscibility

As with all two-phase equilibria, the field of $L_I + L_{II}$ should be regarded as being made up of an infinite number of tie-lines connecting, at each temperature, the composition of L_I that can exist at equilibrium with the conjugate composition of L_{II} . This region has been closed at the top by the meeting of the two lateral boundaries, as it is drawn in Figs. 6-1 and 6-2 and as shown in detail in Fig. 6-7. With increasing temperature the tie-lines become progressively shorter until the ultimate tie-line, at the top of the area, has zero length. This is a critical point c where the two

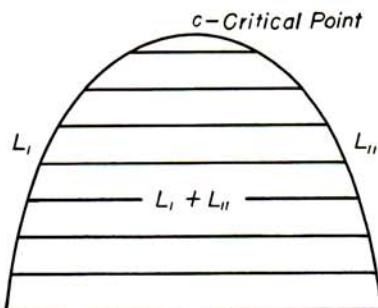


FIG. 6-7

liquid phases, having identical composition, become indistinguishable; i.e., the meniscus between them vanishes. At higher temperature, only one liquid solution exists over the entire composition range of the alloy system.

Two-liquid equilibria terminating in critical points have been shown to exist, but it is worth mentioning that this construction has been included in a number of the published phase diagrams where the experimental observations needed to justify the inclusion of a critical point are lacking. The two-liquid region can terminate, also, at high temperature on another three-phase isotherm, such, for example, as one involving the two liquids and the gas phase (Chap. 11).

Limiting Cases of the Monotectic

Very limited ranges of terminal solid solubility are found in most alloy systems of the monotectic type. This seems reasonable, because any tendency to segregate into separate phases in the liquid state might be expected to be even more pronounced in the solid state. As a result of the

narrow ranges of solid solubility, coring and accompanying effects tend to be less pronounced in monotectic than in eutectic systems.

There are many combinations of metals which are thought to be virtually insoluble in both the liquid and solid states. This condition corresponds to a limiting case of the monotectic, combined with the eutectic (or peritectic) reaction (see Fig. 6-8). The upper of the two horizontal lines represents a monotectic reaction in which the monotectic point L_I is

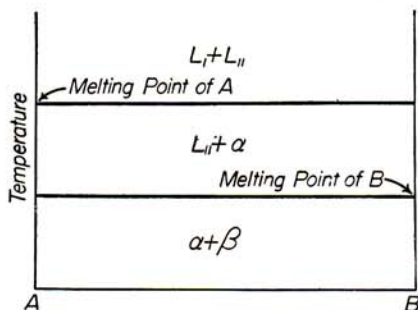


FIG. 6-8

almost coincident with the melting point and composition of pure A , and L_{II} is nearly coincident with the composition of pure B . The eutectic point, on the lower of the two horizontal lines, is, similarly, nearly coincident with the melting point and composition of pure B . Thus, the two metals when melted in the same container appear to melt at their individual melting points and to remain as separate layers throughout melting and freezing.

PRACTICE PROBLEMS

1. Draw a phase diagram of a monotectic type system (similar to that shown in Fig. 6-1) where A is the higher melting metal but the monotectic point m occurs at 75% B (instead of at 25% B). How will this change affect the relative proportions of the products of monotectic transformation? How might this affect the freezing behavior of the monotectic alloy?

2. In Fig. 6-2, consider an alloy of composition midway between pure A and composition X . Deduce the cast microstructure of this alloy. How will the cast microstructure be altered by heating for a long time at temperature T_3 ? If then this alloy is slowly cooled, what sequence of further changes will occur?

3. With reference to Fig. 6-7, consider three alloys having compositions, respectively, (a) slightly to the left of point c , (b) coincident with point c , and (c) slightly to the right of point c . Trace the course of transformation of each of these alloys upon cooling, and compare them.