CHAPTER 16

TERNARY FOUR-PHASE EQUILIBRIUM—CLASS III

The inverse of class I four-phase equilibrium is class III four-phase equilibrium, the ternary equivalent of peritectic equilibrium:

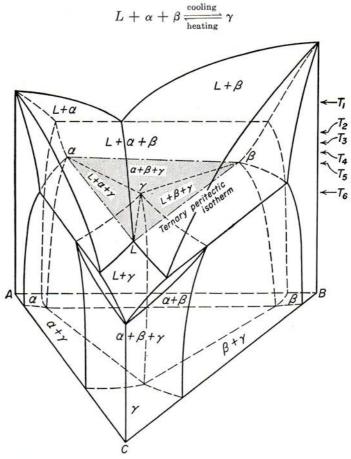


Fig. 16-1. Temperature-composition diagram of an ideal ternary peritectic system, class III.

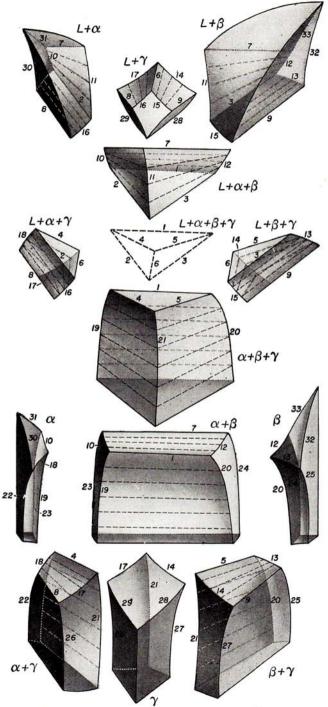


Fig. 16-2. Exploded model of the phase diagram shown in Fig. 16-1. 187

Three phases interact isothermally upon cooling to form one new phase, or conversely, upon heating, one phase decomposes isothermally into three new phases.

Class III four-phase equilibrium is illustrated in the diagram of Fig. 16-1. Three phases α , β , and L, located at the corners of a horizontal triangular reaction plane, combine to form the γ phase, whose composition

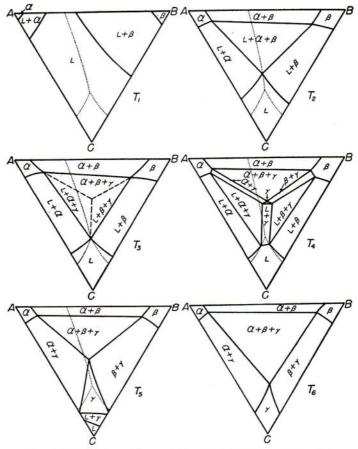


Fig. 16-3. Isotherms through the space diagram of Fig. 16-1.

lies within the triangle. One three-phase field $L+\alpha+\beta$ descends from higher temperature to the ternary peritectic temperature, and three three-phase regions $\alpha+\beta+\gamma$, $L+\alpha+\gamma$, and $L+\beta+\gamma$ issue beneath and proceed to lower temperature (see Fig. 16-3). The obvious equivalence of this construction to that of the ternary eutectic disposes of any necessity of further demonstrating its conformity with the phase rule.

Once again, the regions of this diagram, other than the four-phase re-

action plane itself, are similar in designation and general form to those found in the two preceding chapters (see Fig. 16-2). Edges along which the various regions meet in the assembled diagram have been identically numbered in order to facilitate the visualization of the diagram.

Freezing of Alloys

Although class III reaction is probably fairly common among ternary alloy systems, no example has yet been studied in detail, and it is therefore not feasible to support an analysis of ternary peritectic behavior with experimental observation. The perfection of the correlation between constitution and reaction behavior in all the examples discussed up to this point is such, however, as to lend confidence in the reliability of the deductive approach. The analysis that follows is wholly deductive.

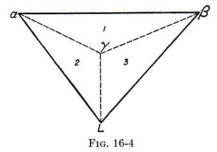
Three essentially distinct types of class III four-phase reaction should occur during cooling:

1.
$$L + \alpha + \beta \rightarrow \alpha + \beta + \gamma$$

2.
$$L + \alpha + \beta \rightarrow L + \alpha + \gamma$$

3.
$$L + \alpha + \beta \rightarrow L + \beta + \gamma$$

corresponding to alloys falling within the zones numbered 1, 2, and 3 in Fig. 16-4. In each case, the phases present above the ternary peritectic temperature all either diminish in quantity or disappear altogether. This



can be demonstrated by analyzing the tie-triangles by the use of the lever principle. Consider alloy X, Fig. 16-5, an alloy of the first type. Above the peritectic temperature the relative proportions of the three phases should be

$$\%\beta = \frac{WX}{W\beta} \times 100 \approx 42\%$$

$$\%\alpha = \frac{WL}{\alpha L} \frac{X\beta}{W\beta} \times 100 \approx 42\%$$

$$\%L = \frac{\alpha W}{\alpha L} \frac{X\beta}{W\beta} \times 100 \approx 16\%$$

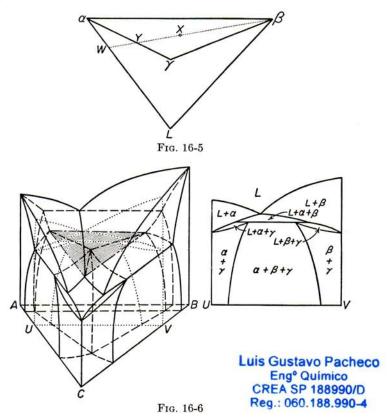
and just below this temperature

$$\%\beta = \frac{YX}{Y\beta} \times 100 \approx 34\%$$

$$\%\alpha = \frac{Y\gamma}{\alpha\gamma} \frac{X\beta}{Y\beta} \times 100 \approx 33\%$$

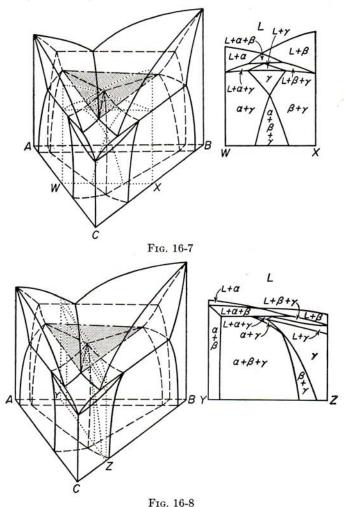
$$\%\gamma = \frac{\alpha Y}{\alpha\gamma} \frac{X\beta}{Y\beta} \times 100 \approx 33\%$$

The liquid phase has vanished and the quantities of α and β are sharply reduced. A similar condition obtains with alloys of the second and third types.



Such reaction requires that the γ phase be formed preferentially at three-way junctions of L, α , and β in the structure of the alloy, because the composition of the γ phase requires the borrowing of A component from the α , B component from the β , and C component from the liquid. As with binary peritectic reaction, it is to be expected that the formation of the

 γ phase should retard its own further growth by lengthening the path over which solid-phase diffusion must act to supply the necessary components. Thus, incomplete reaction should be common; any remaining liquid would, of course, freeze to cored γ .



Occurrence of Class III Four-phase Equilibrium

No example of class III equilibrium corresponding to the diagram discussed above, in which the low-temperature phase is one of the terminal solid solutions, has been reported in the research literature. There are, however, examples of the interaction of liquid and three solid phases in which the low-temperature solid is an intermediate phase ("ternary compound"). A tabulation of all conceivable combinations of phases in class III four-phase equilibrium is given in Table 4, Chap. 18. Future constitutional studies will probably reveal the existence of a number of these.

Vertical Sections

Three typical vertical sections through the space diagram are presented in Figs. 16-6, 16-7, and 16-8. As should be expected, the four-phase reaction plane is intersected in a horizontal line in all sections. Here again the complexity of the vertical sections, as well as their other limitations, make the use of isothermal sections preferable.

PRACTICE PROBLEM

1. Deduce the cast microstructures of alloys 1, 2, and 3 in Fig. 16-4, assuming, first, that equilibrium is maintained during cooling and, second, that natural freezing conditions prevail.