COMPLEX BINARY PHASE DIAGRAMS

The structural units from which binary phase diagrams of metal systems are built have now been considered. It will be instructive to see how these are combined to create some of the well-known diagrams of complex configuration. Before proceeding with this, however, it will be helpful to review the structural units that will be used.

One-phase equilibrium, being tervariant, may be represented by an area of any shape which fills the space not occupied by the two-phase regions. There must be an area for each phase existing in the system, although sometimes the area may be of vanishingly narrow width.

Two-phase equilibrium is bivariant and must be represented by a pair of conjugate bounding lines, every point on one boundary being connected
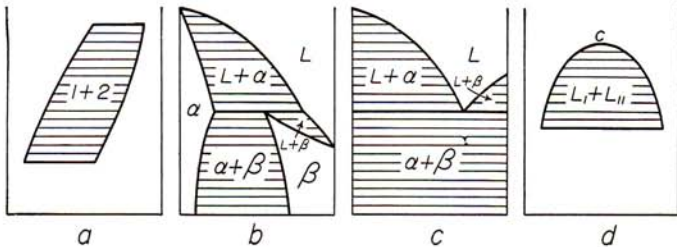

Fig. 11-1

by means of an (isothermal) tie-line with a conjugate point on the other boundary. Thus, it can be seen that the two-phase region must exist over a temperature range [except in the very rare limiting case where it exists as a horizontal line having no detectable area, (see Fig. 9-6)] and the two boundaries must, of course, span the same temperature range. Also, the boundaries must extend over ranges of composition. They are, therefore, never precisely straight and vertical, although they may very closely approach this condition. In its most general form the two-phase region appears as in Fig. 11-1a. Several of the ways in which the two-phase region may be drawn are illustrated in the other sketches of Fig. 11-1. Thus, in diagram b it is seen that the boundaries of the two-phase regions meet at points of congruent transformation (melting, in this example)

and that they terminate at separate points (without meeting) on a three-phase reaction isotherm. In the absence of information to the contrary, the $\alpha + \beta$ region of this diagram may be presumed to terminate at the absolute zero of temperature without closure of the boundary lines. Diagram c represents a case where the one-phase α and β regions are so narrow that the boundaries of the two-phase regions appear to be coincident with the composition lines of the pure components. The termination of a two-phase region in a critical point is illustrated in diagram d.

Three-phase equilibrium is univariant and is always represented by a horizontal line, the ends of which touch two one-phase regions and some intermediate point being in contact with a third one-phase region. Three two-phase regions terminate on every three-phase isotherm. Two classes of three-phase equilibrium have been distinguished: (1) the *eutectic type,* which may be represented thus:
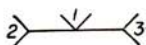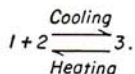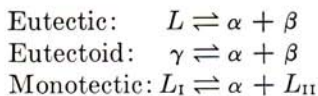

or thus:
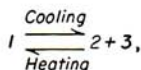
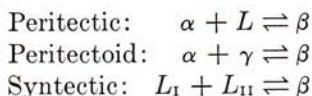and (2) the *peritectic type* which may be represented by:
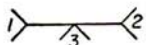
or:

In each of these classes three specific combinations have been named:

$$\text{Eutectic:} \quad L \rightleftharpoons \alpha + \beta$$
$$\text{Eutectoid:} \quad \gamma \rightleftharpoons \alpha + \beta$$
$$\text{Monotectic:} \, L_\mathrm{I} \rightleftharpoons \alpha + L_\mathrm{II}$$

and

$$\text{Peritectic:} \quad \alpha + L \rightleftharpoons \beta$$
$$\text{Peritectoid:} \quad \alpha + \gamma \rightleftharpoons \beta$$
$$\text{Syntectic:} \quad L_\mathrm{I} + L_\mathrm{II} \rightleftharpoons \beta$$

It will be evident that other reactions of both classes should be possible. In none of the above cases has the gas phase been considered, nor has reaction wholly within the liquid state been mentioned. Fundamentally, there is no reason why any combination of three phases could not be substituted for those discussed, although the occurrence in nature of some combinations appears very improbable. There can, of course, be only one gas phase in any combination, because all gases are completely miscible. Three conjugate liquid and three conjugate solid phases are possible.

All conceivable combinations of the two types of three-phase equilibrium are listed in Tables 2 and 3.

Besides the six three-phase reactions that have been considered previously, there are three others that are definitely known to occur in systems involving metals; these reactions, which have no generally accepted names, are l, e, and v of the tables.

TABLE 2. EUTECTIC TYPES

a.	$L_I \rangle \overset{G}{\diagdown} \langle L_{II}$	
b.	$L_I \rangle \overset{G}{\diagdown} \langle \alpha$	Probably occur at low pressures or at high temperatures in metal systems
c.	$\alpha \rangle \overset{G}{\diagdown} \langle \beta$	
d.	$G \rangle \overset{L_I}{\diagdown} \langle L_{II}$	
e.	$G \rangle \overset{L_I}{\diagdown} \langle \alpha$	Commonly occurs in gas-metal systems
f.	$L_{II} \rangle \overset{L_I}{\diagdown} \langle L_{III}$	No case recorded among metal systems
g.	$\alpha \rangle \overset{L_I}{\diagdown} \langle L_{II}$	Monotectic
h.	$\alpha \rangle \overset{L_I}{\diagdown} \langle \beta$	Eutectic
i.	$G \rangle \overset{\alpha}{\diagdown} \langle L_I$	Probably does not occur
j.	$G \rangle \overset{\alpha}{\diagdown} \langle \beta$	Believed to occur in certain gas-metal systems
k.	$L_I \rangle \overset{\alpha}{\diagdown} \langle L_{II}$	Probably does not occur
l.	$L_I \rangle \overset{\alpha}{\diagdown} \langle \beta$	A rare case found in some metal systems
m.	$\beta \rangle \overset{\alpha}{\diagdown} \langle \gamma$	Eutectoid

Reaction l, which may be written

$$\alpha \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \beta + L$$
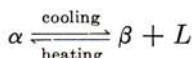
is thought to occur in copper-tin alloys between 38 and 58% tin (outside the range of commercial alloys). The melt freezes completely and then at a lower temperature (635°C) exhibits liquation.

Several gas-metal systems, of which the silver-oxygen system is the best known, undergo reaction e.

$$L \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha + \text{gas}$$
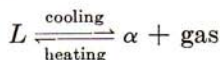
The liquid freezes with simultaneous evolution of gas, which may appear as bubbles rising to the top of the melt or as cavities in the solidified alloy. If the gas is evolved under some pressure late in the freezing

process, as happens with silver-oxygen, it may drive the last of the liquid out of the interstices between the solid dendrites with such force that liquid and gas are ejected from the surface of the nearly solid casting, causing behavior known as "spitting."

TABLE 3. PERITECTIC TYPES

n.	L_I ⟩—G—⟨ L_{II}	⎫
o.	L_I ⟩—G—⟨ α	⎬ Probably do not occur
p.	α ⟩—G—⟨ β	⎭
q.	G ⟩—L_I—⟨ L_{II}	Probably occurs at high temperature as in the Cu-O system
r	G ⟩—L_I—⟨ α	Known in nonmetallic systems (e.g., NaCl-H_2O)
s	L_{II} ⟩—L_I—⟨ L_{III}	No case recorded among metal systems
t.	L_{II} ⟩—L_I—⟨ α	Probably occurs, but no cases on record in metal systems
u.	α ⟩—L_I—⟨ β	Probably does not occur
v.	G ⟩—α—⟨ L_I	Occurs in the Pd-H system, possibly others
w.	G ⟩—α—⟨ β	Probably occurs in gas-metal systems at low pressure
x.	L_I ⟩—α—⟨ L_{II}	Syntectic
y.	L_I ⟩—α—⟨ β	Peritectic
z.	β ⟩—α—⟨ γ	Peritectoid

The reverse of this effect is observed with reaction v:

$$\text{Gas} + L \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha$$
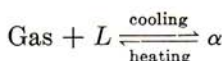
Solid palladium dissolves a considerable quantity of hydrogen, which, upon melting, "boils off" as gas bubbles.

Assembly of Structural Units into a Phase Diagram

In the assembly of the structural units into a complete phase diagram the following principles should be observed:

1. One-phase regions may touch each other only at single points (i.e., points of congruent transformation), never along a boundary line.

2. Adjacent one-phase regions are separated from each other by two-phase regions involving the same two phases.

3. Three two-phase regions must originate upon every three-phase

isotherm; i.e., six boundary lines must radiate from each three-phase reaction horizontal.

4. Two three-phase isotherms may be connected by a two-phase region provided that there are two phases which are common to both of the three-phase equilibria.
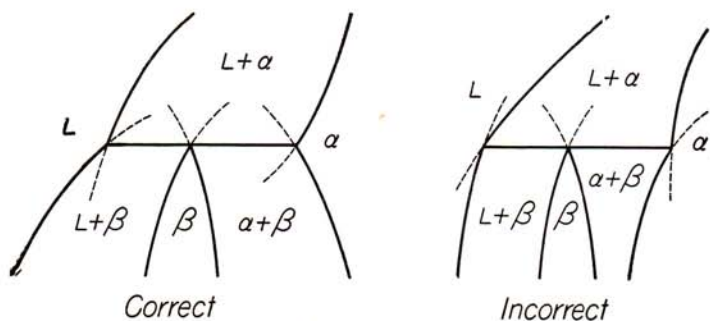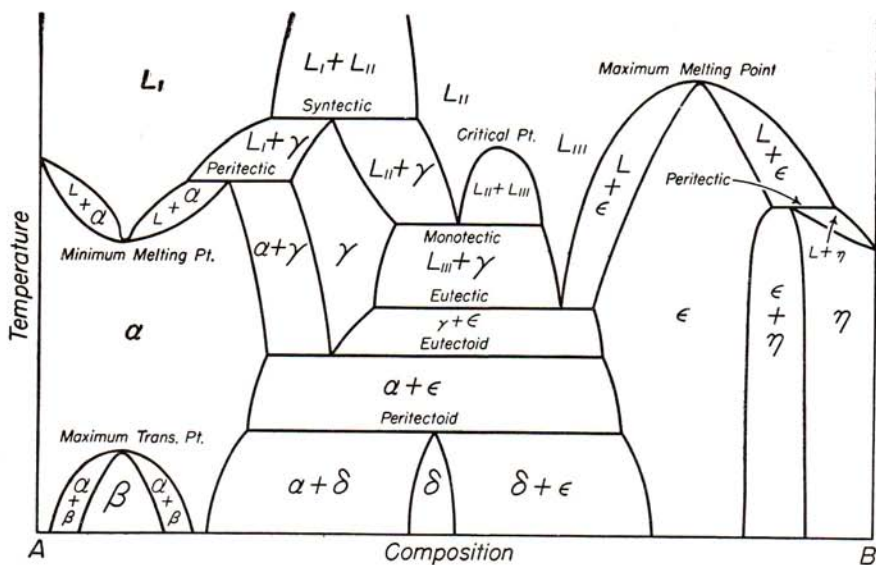

Fig. 11-2

Fig. 11-3

5. All boundaries of two-phase fields must project into two-phase fields where they join a three-phase isotherm, never into one-phase fields (see Fig. 11-2 and Appendix V).

The application of these rules in the construction of a complex diagram is illustrated by the imaginary phase diagram of Fig. 11-3, wherein all the structural units that have been discussed in previous chapters are in-

cluded. One way of viewing complex diagrams is to consider that any binary diagram is made up of a characteristic group of univariant equilibria whose establishment fixes the identity and approximate location of all the bivariant equilibria. The univariant equilibria are, of course, the melting, boiling, and allotropic transformation points of the components of the system, including those of congruent intermediate phases, and the three-phase equilibria represented by isothermal reaction lines. To these may be added the critical points where two-phase equilibria terminate. Having located all the univariant equilibria on the phase diagram, there is usually only one possible arrangement of the two-phase regions, although the exact positions of the two-phase boundaries must be established from additional experimental data.
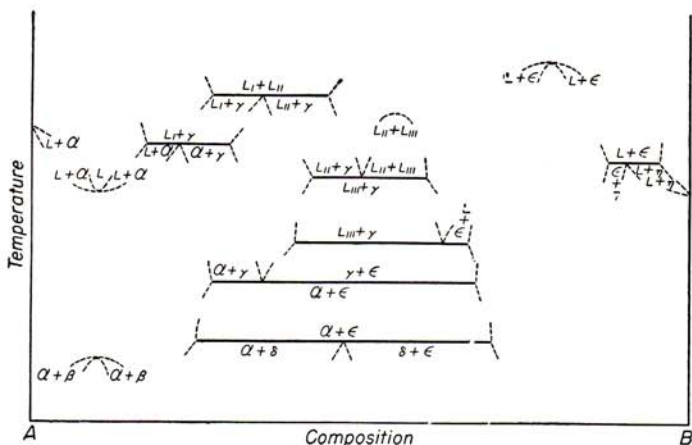

Fig. 11-4

Imagine, for example, that the melting points of the pure metals A and B (Fig. 11-3) and the points of congruent melting and transformation of the α and ϵ phases are known and that the horizontal reaction lines have all been inserted (Fig. 11-4). A two-phase region issues from each point of congruent transformation, and it can be named, because the two phases involved are the two phases that partake in the congruent transformation itself. Three two-phase regions issue from each horizontal reaction line, and these also can be named, because they constitute all possible pairs of the three phases involved in the three-phase reaction, i.e., in the reaction $\gamma \rightleftarrows \alpha + \epsilon$ the two-phase pairs will be $\alpha + \gamma$, $\gamma + \epsilon$, and $\alpha + \epsilon$. If all the two-phase regions are thus correctly designated at their termini, it will be found that the two-phase boundaries can be drawn without ambiguity. Where the same pair of phases has been named twice, connecting boundary lines are drawn to close the two-phase region. If the same pair is

named four times, as, for example, $L_I + \alpha$ or $L_3 + \epsilon$ in Fig. 11-4, it will be evident that two systems are involved and that the two-phase regions should be closed in such a way that no two-phase region crosses the composition of congruency. This applies also to the $\alpha + \beta$ equilibria in Fig. 11-4. If a two-phase pair is found to have no matching pair elsewhere on the diagram, it may be associated with a two-phase equilibrium that extends beyond the limits of the diagram. Thus, in Fig. 11-4, the regions $\alpha + \beta$, $\alpha + \delta$, $\delta + \epsilon$, and $\epsilon + \eta$ are terminated at the base line of the diagram and may be presumed to extend to the absolute zero of temperature without closure; region $L_I + L_{II}$ having no critical point may be presumed to terminate upon some three-phase reaction line at a higher temperature beyond the limits of the diagram. Care must, of course, be taken to ensure that the boundaries are so drawn that all projections extend into two-phase regions.

Although this manner of thinking about the synthesis of phase diagrams may seem artificial and, perhaps, too remote from questions of interpretation, it is commonly observed that a little practice in the construction of imaginary diagrams is very helpful in developing a "feel for phase diagrams." This feel is almost indispensable in the interpretation of diagrams taken at random from the literature, because instances of the misinterpretation of experimental data, resulting in an impossible construction of the diagram, are encountered from time to time and must be recognized if the user of the diagram is to make a sound judgment of the conclusions that may be derived therefrom. For practice purposes a set of problems of this kind is included at the end of this chapter. It is intended that the data given should be inserted on the coordinate frame of a diagram and that the diagram should then be completed with all regions properly labeled. A diagram having been completed, the list of rules given in the previous section should be checked to see that no errors have been made.

Some Errors of Construction

Some fundamental errors of construction which should be recognized easily are presented in Fig. 11-5. Diagram a is impossible because the three-phase equilibrium $L \rightleftharpoons \alpha + \beta$ is not isothermal (is not univariant) and therefore defies the phase rule. Similarly, the range of composition over which β is represented in the $L + \alpha \rightleftharpoons \beta$ reaction of diagram b is incompatible with univariant equilibrium. Four phases cannot partake in equilibrium (diagram c) except at a point of invariant equilibrium, the occurrence of which is highly improbable. The projection of two-phase boundaries must not extend into one-phase regions, as in diagram d, because this construction represents thermodynamic instability.
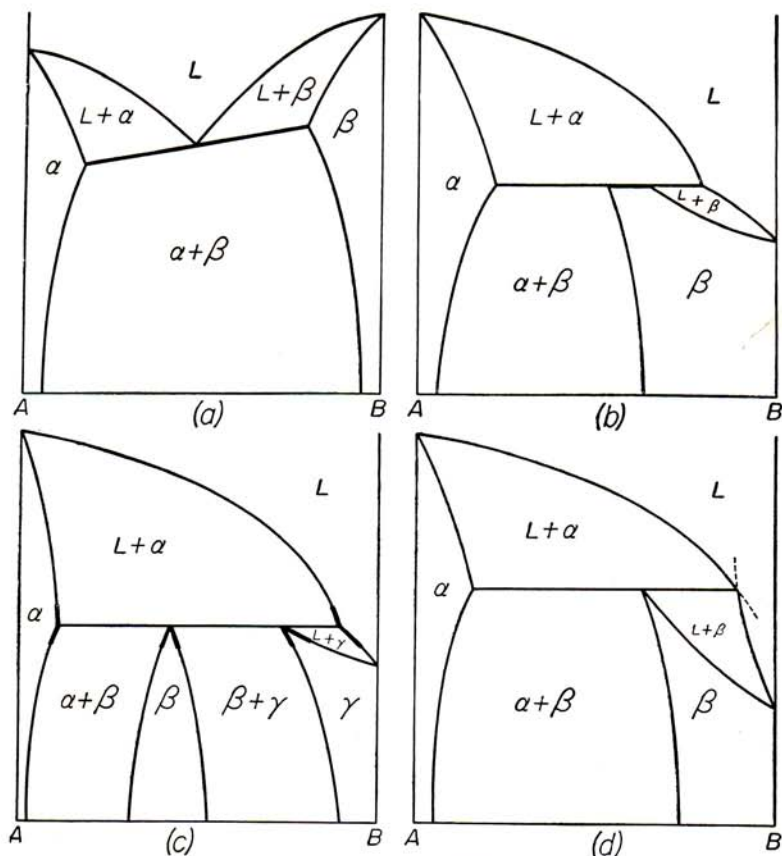
Fig. 11-5. Errors in phase-diagram construction.

Interpretation of Complex Phase Diagrams

The prediction of the course of transformation and of the resulting alloy structure in systems of complex constitutional type differs from that in simple systems only in that a sequence of wholly or partially completed transformations may have to be considered. This matter has received some incidental attention in earlier chapters. It will be recalled, for example, that upon the completion of monotectic decomposition (Chap. 6), a liquid phase L_{II} remains distributed in pockets throughout the solid α phase; upon subsequent cooling this liquid undergoes eutectic reaction while the α phase remains unchanged.

The principle of interpretation illustrated here may be stated as follows: With each successive phase change, as the temperature is altered, the alloy is broken up into constituent particles of different

kinds, each kind having its own composition (or the reverse process in which two phases combine to form one may occur). Thenceforward each particle behaves in accordance with its composition, undergoing such changes as the phase diagram reports for that composition. Where the composition difference is continuous, as in a cored solid solution, then each tiny layer of substantially uniform composition should be regarded as capable of unique behavior in accordance with the constitutional demands to which it is subject.

Superimposed upon changes that accompany temperature rise or fall is a constant tendency to establish heterogeneous equilibrium among the
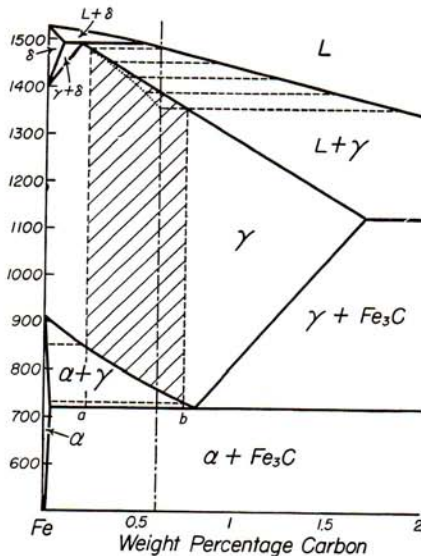

Fig. 11-6. Phase diagram of the metastable system Fe-C. Shaded zone represents the composition span in the cored 0.6% C alloy immediately after the completion of solidification and before eutectoid transformation.

different particles by the operation of diffusion. The higher the temperature and the slower the temperature change, the more important does this factor become.

No quantitative treatment of the relative influences of these factors is possible in any complex system at the present time. The best that can be done is to obtain a qualitative view of the process of successive transformation. An example will be used to illustrate. If an iron-carbon alloy, 0.6% carbon, is cast from the molten state and is allowed to cool slowly to room temperature, a series of changes will occur (see Fig. 11-6). Beginning at the liquidus temperature, a cored γ phase will appear, which when fully solidified will possess a composition range of 0.3 to 0.75% carbon. Each layer of differing composition will reach the γ boundary of

the $\alpha + \gamma$ field at a different point (in composition and temperature) and will transform accordingly. The layer of composition a will reject a large quantity of proeutectoid α and a little eutectoid pearlite, while the layer of composition b will reject a little proeutectoid α and much eutectoid pearlite, intermediate layers behaving in intermediate fashion. Thus, the cored structure of the original γ solid solution results in a segregation of the constituents of subsequent transformation.

This effect is most pronounced in the example of Fig. 11-7, which shows a banded structure resulting from dendritic segregation (coring) in a 0.3% carbon steel. Light-colored areas are those predominating in the α phase; darker areas are those composed of the pearlite constituent.

Obviously each combination of phase changes will produce a different result, making available a large variety of structures among the alloy

FIG. 11-7. Binary steel, 0.3% C, showing banding of the eutectoid constituent result. ing from dendritic segregation. Magnification 100.

systems. None of these presents any particular difficulty in interpretation provided that the phase changes are considered one at a time and the influence of each change upon each of the constituents of the alloy is noted and carried forward to the next transformation.

Isothermal diffusion behavior in complex systems presents no new factors. An example is given in Fig. 11-8, where the structure produced by permitting blocks of copper and zinc to lie in contact for several days at 400°C is shown. It will be observed that there is a layer in the "alloy" corresponding to each *one-phase* region crossed by the horizontal line drawn across the phase diagram at 400°C. No layers corresponding to two-phase regions are formed, the two-phase regions being represented in the sample by the interfaces between the one-phase layers. It should be noted, however, that if diffusion had been permitted to continue until equilibrium was approximated, no more than two layers would persist in the sample. These could correspond to any two adjacent phases of the

system, depending upon the gross composition of the sample. Indeed, at equilibrium, the structure of the diffusion sample would be given by applying the lever principle to the tie-line which crosses the gross composition at the temperature of diffusion. If the gross composition falls within a one-phase region, the "alloy" at equilibrium will, of course, be composed of but one phase.
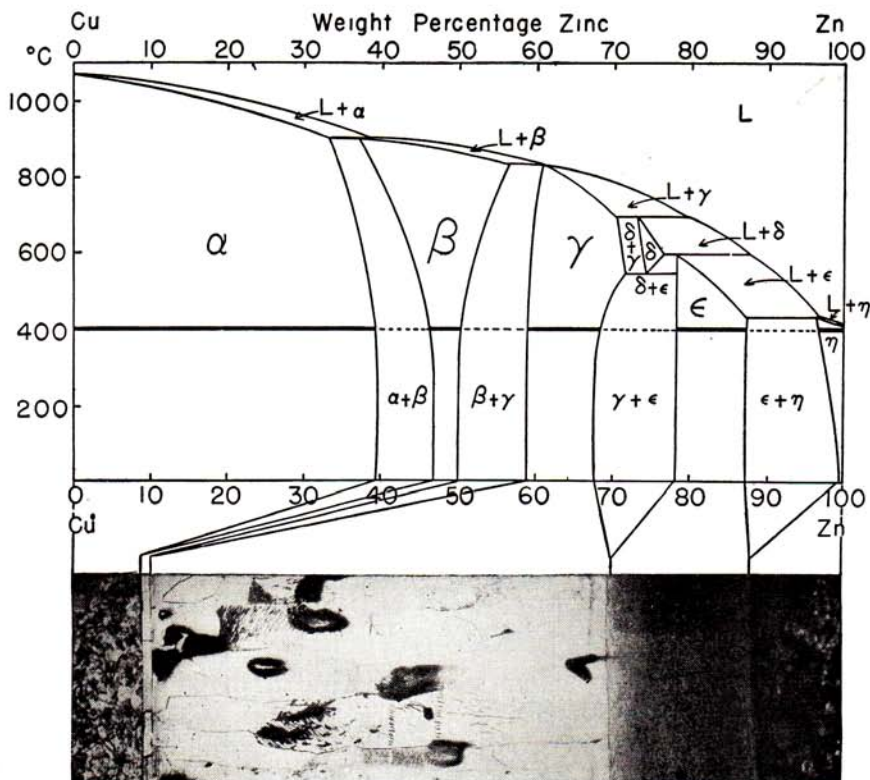

Fig. 11-8. Illustrates the correlation between the one-phase layers formed in a Cu-Zn diffusion couple and the Cu-Zn phase diagram. The horizontal line across the phase diagram at 400°C represents the sequence of states occurring in the diffusion couple. Oval spots in the γ layer of the diffusion couple are holes, resulting from the fact that Zn has diffused to the left more rapidly than Cu has diffused toward the right. Magnification 500.

The reason for the absence of two-phase layers in isothermal diffusion structures is to be found in the requirement that a composition gradient must exist for diffusion to occur. In a two-phase alloy, each phase tends toward a fixed equilibrium composition (as dictated by the appropriate tie-line) and no composition gradient can be maintained across a layer of the aggregate. The only composition difference that can be maintained

is that between the two phases. Thus, diffusion can proceed only across the two-phase interface and not through the two-phase structure.

The γ layer in the microstructure of the diffusion couple shown in Fig. 11-8 exhibits several dark oval spots; these are cavities.[1] They formed because there is a large difference between the diffusion velocities of zinc and of copper. The zinc diffuses faster, and the space vacated agglomerates into cavities.

PRACTICE PROBLEMS

1. A melts at 1000°, B melts at 500°. There is a peritectic reaction: α (5% B) + L (75% B) $\rightleftharpoons \beta$ (50% B) at 800° and another peritectic reaction: β (55% B) + L (90% B) $\rightleftharpoons \gamma$ (80% B) at 600°. Complete the diagram.

2. A melts at 1000°; B melts at 700°. There is a peritectic reaction: α (5% B) + L (50% B) $\rightleftharpoons \beta$ (30% B) at 800°; a eutectic reaction: L (80% B) $\rightleftharpoons \beta$ (60% B) + γ (95% B) at 600°; and a eutectoid reaction: β (50% B) $\rightleftharpoons \alpha$ (2% B) + γ (97% B) at 400°. Complete the diagram.

3. A melts at 800°; B melts at 700°; the β phase melts congruently at 1000°, its composition being 50% B. The following isothermal reactions occur:

Monotectic: L_I (60% B) $\rightleftharpoons \beta$ (55% B) + L_{II} (80% B), at 950°
Peritectic: β (85% B) + L_{II} (95% B) $\rightleftharpoons \sigma$ (52% B), at 800°
Eutectic: L_I (20% B) $\rightleftharpoons \alpha$ (5% B) + β (40% B), at 650°
Eutectoid: β (45% B) $\rightleftharpoons \alpha$ (3% B) + σ (90% B), at 500°
Peritectoid: α (2% B) + σ (95% B) $\rightleftharpoons \gamma$ (50% B), at 300°

Complete the diagram.

4. Construct a phase diagram involving three peritectic reactions only.

5. Construct a phase diagram involving two monotectic and one eutectic reaction.

6. Construct a phase diagram involving two monotectic and one peritectic reaction.

7. Construct a phase diagram involving two peritectic, one eutectoid, and one peritectoid reaction.

8. Ascertain the order in which the several univariant temperatures would occur if one component having an allotropic transformation and another component having none are associated in a system involving (a) a peritectic and a peritectoid reaction or (b) a eutectic and a peritectoid reaction.

[1] For further details, see F. N. Rhines and B. J. Nelson, Structure of Copper-Zinc Alloys Oxidized at Elevated Temperatures, *Trans. Am. Inst. Mining Met. Engrs.*, **156**:171–194 (1944).