

## CHAPTER 4

### BINARY EUTECTIC SYSTEMS

In eutectic systems the first addition of either component metal to the other causes a lowering of the melting point, so that the liquidus curve passes through a temperature minimum known as the *eutectic point*. The liquid is miscible in all proportions, as in isomorphous systems, but miscibility in the solid state is limited (see Fig. 4-1).

Two solid phases,  $\alpha$  and  $\beta$ , are to be distinguished. These are solid-solution phases, which are referred to as *limited solid solutions* because the range of stability of each extends only partway across the diagram and as *terminal solid solutions* because each originates at a side of the diagram and extends inward, instead of being isolated somewhere in the mid-part of the diagram. The  $\alpha$  and  $\beta$  phases *may* have identical crystal structures but usually do not; each, of course, has the crystal structure of the component with which it is associated.

The phases are not restricted with regard to type of solid solution, i.e., whether substitutional or interstitial.

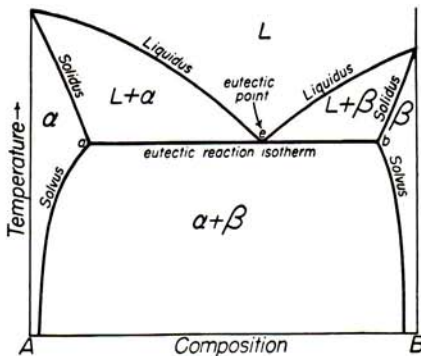


FIG. 4-1

Three two-phase regions are designated in Fig. 4-1, namely,  $L + \alpha$ ,  $L + \beta$ , and  $\alpha + \beta$ . It will be evident that the  $L + \alpha$  and  $L + \beta$  regions are in every way equivalent to the  $L + \alpha$  region in the isomorphous diagram. These areas are considered to be made up of tie-lines joining the

conjugate liquid and solid phases, represented on the liquidus and solidus, at each temperature within the range covered. In like manner, the  $\alpha + \beta$  region is regarded as being made up of tie-lines connecting, at each temperature, a composition of  $\alpha$ , represented on the  $\alpha$  solvus curve (or  $\alpha$  solid-solution boundary) with its conjugate  $\beta$  composition represented on the  $\beta$  solvus curve (or  $\beta$  solid-solution boundary).

The three two-phase regions meet at a special kind of tie-line that is common to all the regions and that joins the compositions of three con-

jugate phases that coexist at the eutectic temperature, namely,  $\alpha$  at  $a$ , liquid at  $e$ , and  $\beta$  at  $b$ . This tie-line is variously known as the *eutectic line*, the *eutectic horizontal*, and the *eutectic reaction isotherm*. Point  $e$ , representing the only liquid that can coexist simultaneously with both solid phases, is called the *eutectic point*, meaning the point, or composition, of lowest melting temperature.

### Application of the Phase Rule

The TX diagram of Fig. 4-1 is an isobaric section from a PTX space diagram, such as the one shown in Fig. 4-2, where the dashed section

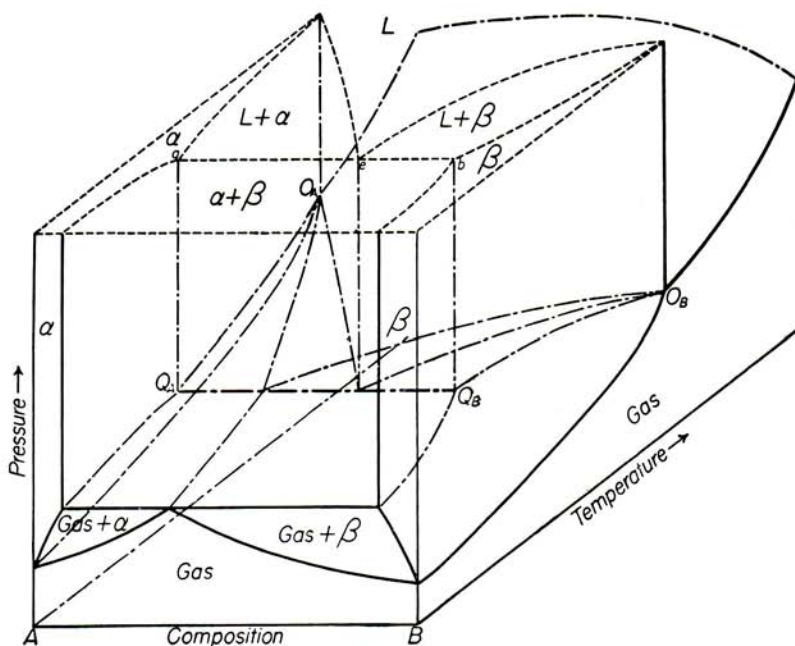


FIG. 4-2

across the top is the isobar represented in the previous figure. Again, one degree of freedom has been expended in establishing the pressure of the TX diagram. Hence, in the one-phase regions (liquid,  $\alpha$  and  $\beta$ ) which are ternariant, only the temperature and one composition remain to be selected in order to establish the equilibrium state. The two-phase regions are bivariant, so that a choice of temperature or of a composition, but not both, suffices to describe a fixed state of equilibrium. Both of these conditions have been discussed with reference to isomorphous equilibria and require no further comment here.

Three-phase equilibrium has been shown on the TX diagram at the eutectic reaction isotherm. Here univariant equilibrium obtains.

$$P + F = C + 2$$

$$3 + 1 = 2 + 2$$

Having used one degree of freedom in establishing the isobaric section, there should remain no further choice of conditions under which three phases may coexist. In other words, the three-phase equilibrium must be represented at a fixed temperature and the compositions of each of the three phases involved must also be fixed. The eutectic line satisfies these requirements; a horizontal line represents only one temperature on a TX diagram; the composition of the  $\alpha$  phase is fixed at  $a$ , that of the liquid phase at  $e$ , and that of the  $\beta$  phase at  $b$ . No one-phase region touches the eutectic line at more than a single point in composition.

There are four phases shown on the PTX diagram:  $\alpha$ ,  $\beta$ , liquid, and gas. The phase rule permits a four-phase invariant equilibrium.

$$P + F = C + 2$$

$$4 + 0 = 2 + 2$$

Therefore, at some *one fixed condition* of pressure and temperature it is possible to have a four-phase equilibrium among  $\alpha$ ,  $\beta$ , liquid, and gas, each of fixed composition. This occurs at the unique spatial tie-line  $Q_A Q_B$  in Fig. 4-2. In most alloy systems this equilibrium must occur at very low pressure, but in any case, the likelihood of an arbitrarily selected isobaric section coinciding with the pressure of the four-phase equilibrium is so slight that it is usually considered that a binary TX diagram

should not be expected to represent equilibrium among more than three phases.

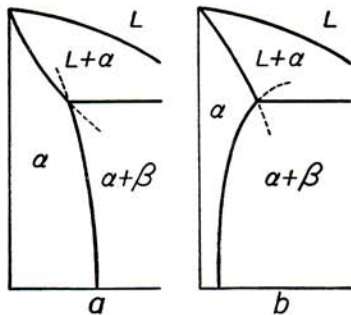


FIG. 4-3

fields (see Fig. 4-3). Thus, the solidus and solvus curves must meet at the eutectic horizontal at such angles that the solidus projects into the  $\alpha + \beta$  field and the solvus into the solid plus liquid field. This rule does not further restrict the direction of curvature of either line; i.e., the solidus may be either concave (Fig. 4-3a) or convex (Fig. 4-3b) with respect to the

### Some Other Rules of Construction

It can be shown through an application of the second law of thermo-dynamics (see Appendix V) that the boundaries of two-phase fields must meet at such angles that the extensions of the boundaries, beyond the point of intersection, project into two-phase fields, never into one-phase

base of the diagram, and the solvus may be either concave (Fig. 4-3a) or convex (Fig. 4-3b) with respect to the side of the diagram. However, concavity of the solvus (Fig. 4-3b) seems to be most common in eutectic systems.

The shape of the solvus is frequently found to conform to the empirical relationship

$$\log \text{ at. } \% B = \frac{1}{T_k} + c$$

where  $B$  is the solute metal,  $T_k$  is the absolute temperature, and  $c$  is a constant. If the solvus appears as a straight line when plotted with the logarithm of the atomic percentage as the abscissa and the reciprocal of the absolute temperature as the ordinate, it is reasonable to conclude that the data represent equilibrium conditions (see Fig. 4-4). Failure of the solvus to become a straight line in this test does not necessarily mean that it is unreliable.<sup>1</sup> It is generally found that the eutectic point lies close to that component which has the lower melting point.

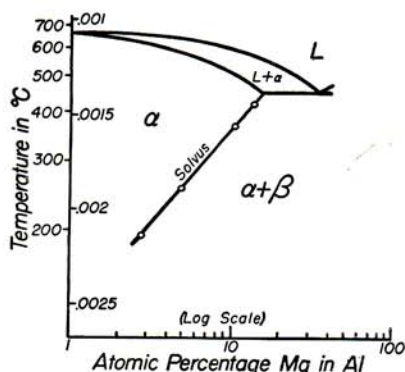
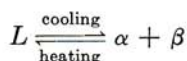


FIG. 4-4. Aluminum-rich portion of the aluminum-magnesium phase diagram; with log composition plotted versus reciprocal temperature (absolute), the solvus becomes straight.

### The Eutectic Alloy

When the eutectic alloy (composition  $e$  in Fig. 4-1) is heated through the eutectic temperature, the  $\alpha$  and  $\beta$  phases (compositions  $a$  and  $b$ ) react to form liquid (composition  $e$ ). Upon cooling through the eutectic temperature, the liquid decomposes into  $\alpha$  and  $\beta$ .



“Equilibrium” melting and freezing occur isothermally, as with a pure metal, but with the difference that the process is incongruent, which is to say that there is a difference in composition between the liquid and the individual solid phases.

During solidification the two solid phases are believed to deposit simultaneously. Barring the influence of undercooling, which is usually moder-

<sup>1</sup> For further details, see W. L. Fink and H. R. Freche, Correlation of Equilibrium Relations in Binary Aluminum Alloys of High Purity, *Trans. Am. Inst. Mining Met. Engrs.*, **111**:304-318 (1934).

ate in eutectic alloys, there is no coring effect, because freezing takes place at, or very close to, one temperature and the compositions of the phases are virtually constant. The relative proportions of the  $\alpha$  and  $\beta$  phases in the completely solidified alloy may be ascertained by treating the eutectic reaction isotherm (Fig. 4-1) as a tie-line.

$$\% \alpha = \frac{eb}{ab} \times 100 \approx 40\% \quad \% \beta = \frac{ae}{ab} \times 100 \approx 60\%$$

With further cooling below the eutectic temperature, successive tie-lines in the  $\alpha + \beta$  field call for changes in the compositions of the solid phases and also in their relative proportions. Such changes are rarely observed with normal rates of cooling, however, because of slow diffusion in

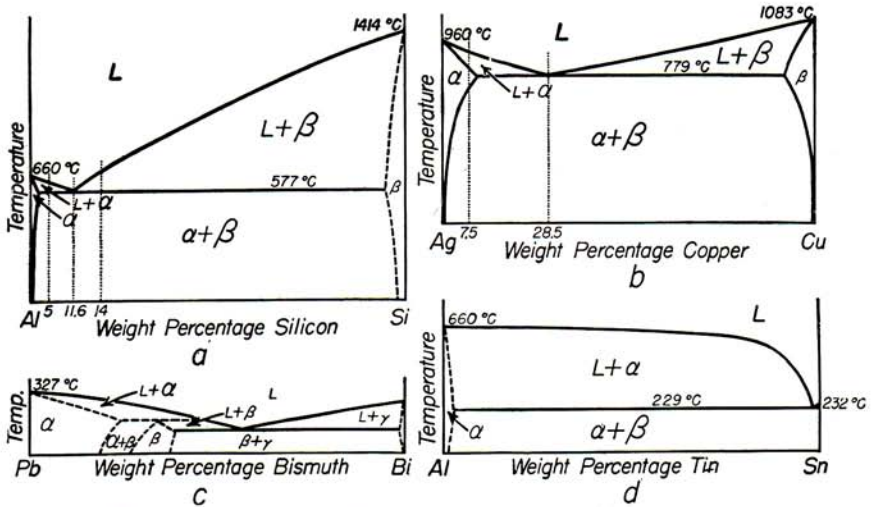


Fig. 4-5. Phase diagrams of some typical eutectic-type systems.

the solid state. The establishment of equilibrium at subeutectic temperature usually requires the use of heat treatments, which will be discussed presently.

The microstructure of eutectic alloys differs widely from system to system, depending, in part presumably, upon the relative proportions of the two solid phases and, in part, upon crystallographic relationships, which have yet to be elucidated. Among alloy systems having somewhere near equal proportions of the solid phases in the eutectic, Fig. 4-5b, for example, it often happens that the two phases are deposited in layers, or lamellae. Seen in cross section the lamellae appear as alternating bands of the  $\alpha$  and  $\beta$  phases (Fig. 4-6B). This is known as a pearlitic structure, be-

cause, as with a pearl, the structure may diffract light into an irregular pattern of iridescent colors.

When one of the phases predominates in the eutectic mixture (Fig. 4-5*a, c, and d*) this phase usually becomes a matrix in which particles of the lesser phase are embedded. Several types of eutectic structure are then distinguished upon the basis of the shapes assumed by the embedded

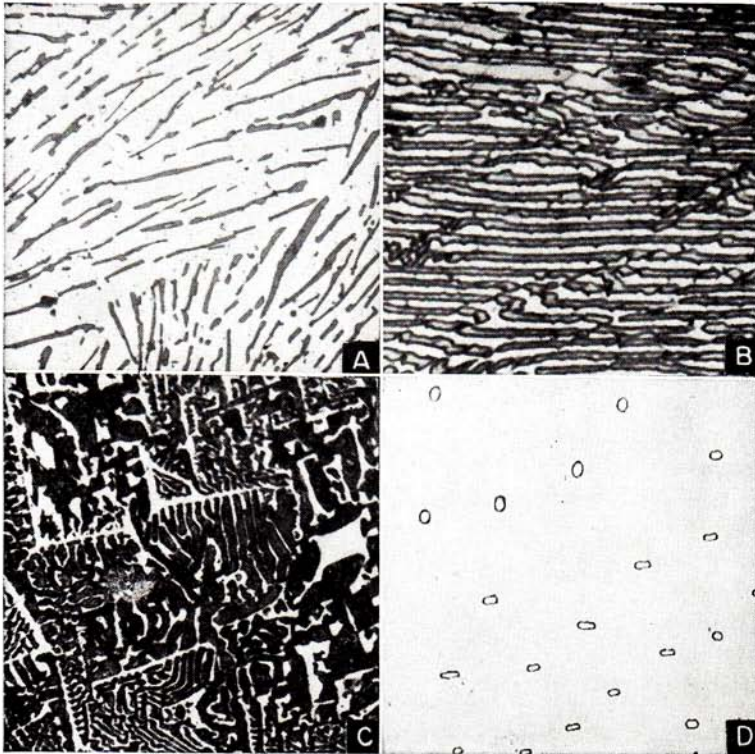


FIG. 4-6. Typical microstructures of some cast eutectic alloys: (A) Al-Si 11.6%, magnification 500; (B) Ag-Cu 28.5%, magnification 2,000; (C) Pb-Bi 56.5%, magnification 100; and (D) Al-Sn 99.5%, magnification 650. See also Fig. 4-5.

particles. If these particles are rounded, the eutectic is said to be of the nodular, globular, or spheroidal type (Fig. 4-6*D*). Elongated particles may appear nodular when seen in cross section and are sometimes included in this class. Flat platelets appear elongated, or needlelike, in cross section, and the eutectic structure formed by them is called acicular (Fig. 4-6*A*). An intricate pattern, known as *Chinese script* (Fig. 4-6*C*) results from the growth of the second phase in the form of obviously dendritic skeletons. Although differing in their structural appearance from system to system, the eutectics have the common characteristic that the composi-

tions and proportions of the phases are constant for any one alloy system and the two solid phases form concurrently.<sup>1</sup>

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### Hypoeutectic and Hypereutectic Alloys

Those alloys occurring upon one side of the eutectic composition are called hypoeutectic alloys, while those upon the other side are called hypereutectic alloys. There is no inflexible rule that can be used to determine, for any specific case, which side of the alloy system should be called hypoeutectic and which side hypereutectic. Custom favors the use of *hypoeutectic* for the designation of those alloys richer in the more common metal or the metal of more immediate importance in the application under consideration. Since most phase diagrams are drawn with the more common metal on the left, this means that the hypoeutectic alloys are usually those to the left of the eutectic composition while the hypereutectic alloys are those to the right.

Unlike the eutectic alloy itself, the hypo- and hypereutectic alloys undergo bivariant as well as univariant transformation during melting and freezing. The course of freezing passes through the zones of  $L + \alpha$  or  $L + \beta$  equilibrium, in addition to the eutectic  $L + \alpha + \beta$  equilibrium. Hence, it will be desirable once more to distinguish between "equilibrium" and "natural" melting and freezing.

The course of equilibrium freezing may be followed by reference to Fig.

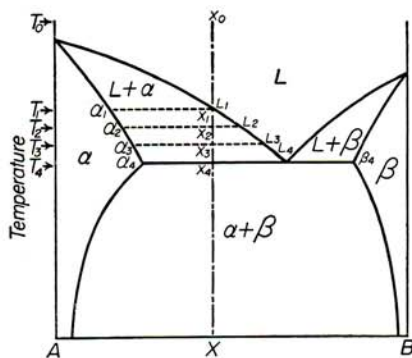


FIG. 4-7

4-7. At temperature  $T_0$  the hypoeutectic alloy of composition X is molten. Upon cooling the alloy to temperature  $T_1$ , freezing begins with the appearance of crystals having the composition  $\alpha_1$ . As freezing proceeds, with falling temperature, the composition of the liquid follows the liquidus to the right ( $L_1, L_2, L_3, L_4$ ) and the composition of the solid, likewise, follows the solidus to the right ( $\alpha_1, \alpha_2, \alpha_3, \alpha_4$ ), as in the equilibrium freezing of an isomorphous

alloy. At the eutectic temperature  $T_4$ , however, this process is interrupted with some liquid remaining:

$$\%L_4 = \frac{\alpha_4 X_4}{\alpha_4 L_4} \times 100 \approx 50\%$$

<sup>1</sup> The development of eutectic structures is discussed in detail by F. L. Brady, The Structure of Eutectics, *J. Inst. Metals*, **28**:369-419 (1922); A. M. Portevin, The Structure of Eutectics, *J. Inst. Metals*, **29**:239-278 (1923).

The microstructure of such an alloy, at this moment, is depicted in the drawing of Fig. 4-8A, where the white areas represent the solid  $\alpha$  and the black the remaining liquid. This liquid, which is of the eutectic composition,  $L_4$ , now freezes isothermally to a eutectic mixture of  $\alpha + \beta$ , Fig. 4-8B (actually the 5% silicon alloy of Fig. 4-5a). The proportions of  $\alpha$  and

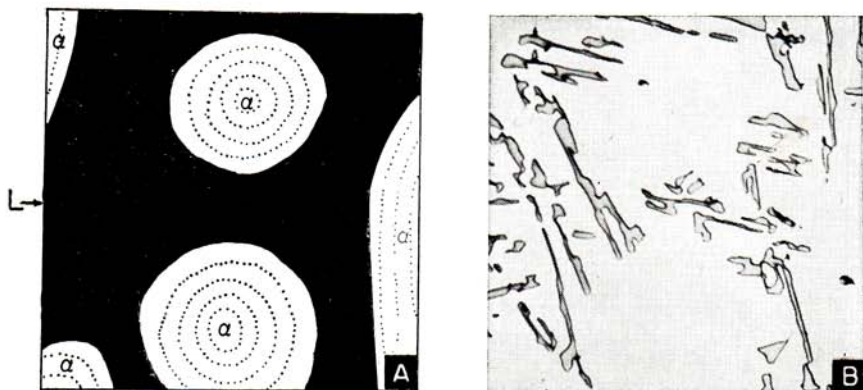


FIG. 4-8. Hypoeutectic Al-Si 5% alloy. Sketch *a* indicates the location of the primary  $\alpha$  and the eutectic liquid; the final microstructure at the end of freezing is shown in *b*. Magnification 500.

$\beta$  in this mixture are the same as in the eutectic alloy, (see, for example, Fig. 4-6A, the 11.6% silicon alloy of Fig. 4-5a), namely,

$$\% \alpha_4 \text{ (eutectic)} = \frac{L_4 \beta_4}{\alpha_4 \beta_4} \times 100 \approx 33\frac{1}{3}\%$$

$$\% \beta_4 \text{ (eutectic)} = \frac{\alpha_4 L_4}{\alpha_4 \beta_4} \times 100 \approx 66\frac{2}{3}\%$$

But some  $\alpha$  had formed during the initial stage of freezing, at temperatures above the eutectic. The *total* quantities of  $\alpha$  and  $\beta$  in the finally frozen alloy are, then,

$$\% \alpha_4 \text{ (total)} = \frac{x_4 \beta_4}{\alpha_4 \beta_4} \times 100 \approx 66\frac{2}{3}\%$$

$$\% \beta_4 \text{ (total)} = \frac{\alpha_4 x_4}{\alpha_4 \beta_4} \times 100 \approx 33\frac{1}{3}\%$$

The  $\alpha$  phase that appeared first is known as the *primary constituent* of the alloy; the  $\alpha + \beta$  eutectic mixture is the *secondary constituent*. In its metallographic usage, the word constituent denotes a unit of the microstructure. It may be composed of a single phase, or of several phases, as in the case of the eutectic constituent. The adjectives primary and secondary refer to the order in which the constituents appear during freezing.



Failure to maintain equilibrium conditions in the *natural* freezing of the hypo- and hypereutectic alloys results in coring of the primary constituent and in an excess over the equilibrium quantity of the secondary constituent.

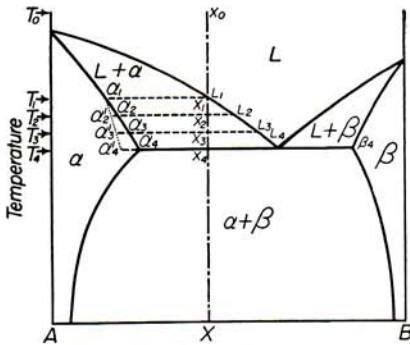


FIG. 4-9

The reasons for these differences are similar to those discussed in the case of the natural freezing of isomorphous alloys and are illustrated in Fig. 4-9. During the primary separation of the  $\alpha$  phase, the average composition of the solid follows a course of change such as  $\alpha_1, \alpha_2, \alpha_3, \alpha_4$ , because diffusion in the solid state is not sufficiently rapid to maintain equilibrium except with almost infinitely slow cooling. Thus, the primary  $\alpha$  phase is cored. At the eutectic temperature the quantity of liquid remaining is

$$\%L_4 \text{ (natural)} = \frac{\alpha'_4 x_4}{\alpha'_4 L_4} \times 100 \approx 66\%$$

instead of

$$\%L_4 \text{ (equilibrium)} = \frac{\alpha_4 x_4}{\alpha_4 L_4} \times 100 \approx 50\%$$

Hence, there is a larger quantity of eutectic liquid than would be present in "equilibrium" freezing, and this produces a correspondingly larger quantity of the eutectic constituent. The photomicrograph of Fig. 4-8b, of course, represents a structure produced by "natural" freezing. Coring of the  $\alpha$  phase, although really present and indicated by the dotted lines in Fig. 4-8a, is not evident in the photograph because there is no marked color change associated with composition difference in the aluminum-silicon solid solution. Neither is the line of demarcation between the primary and secondary constituents clearly defined in Fig. 4-8b. This is because the  $\alpha$  phase predominates in the eutectic and because the last layer of  $\alpha$  to form on the cored primary dendrites is of the same composition ( $\alpha_4$ ) as the  $\alpha$  phase of the eutectic constituent.

Hypereutectic freezing follows a similar course. Consider, for example, the aluminum-silicon alloy containing 14% silicon (Fig. 4-5a). Freezing begins with the primary separation of the  $\beta$  (silicon-rich) phase. As the  $\beta$  deposits, the liquid and solid compositions move toward the left until, at the eutectic temperature, the remaining liquid freezes isothermally to a secondary eutectic constituent. Two stages in this process are represented in Fig. 4-10. The primary  $\beta$  crystals, which in this case are idiomorphic

(exhibiting well-developed crystalline facets), are represented in black in the sketch, Fig. 4-10A, and appear gray in the photomicrograph, Fig. 4-10B. The eutectic liquid, white in the sketch, freezes to the now familiar eutectic mixture of  $\alpha + \beta$ . This time the line of demarcation between the

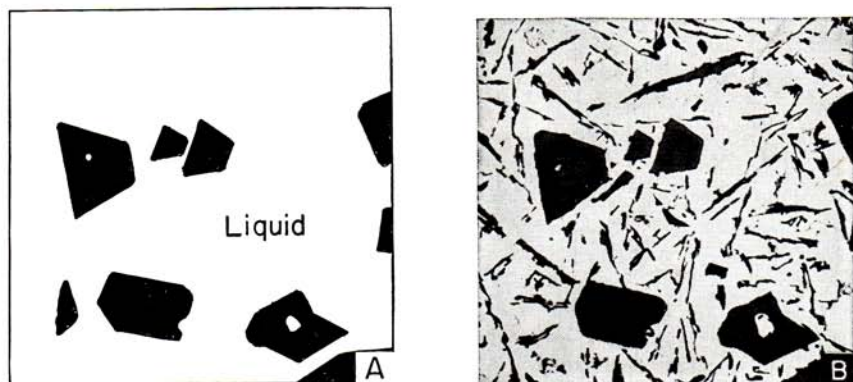


FIG. 4-10. Hypereutectic Al-Si 14% alloy. Sketch A shows the location of primary  $\beta$  and the eutectic liquid; photograph B shows the final cast microstructure. Magnification 100.

primary  $\beta$  constituent and the eutectic constituent is sharp, because the  $\beta$  phase is not physically continuous in this structure and the  $\alpha$  phase occurs only in the eutectic constituent.

### Terminal Solid Solutions

Under conditions of equilibrium freezing, alloys lying outside the composition range of the eutectic reaction isotherm, such as alloy X of Fig.

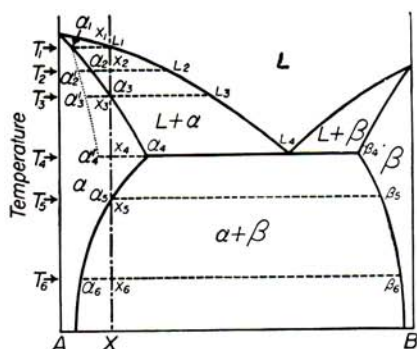


FIG. 4-11

4-11, should contain none of the eutectic constituent, because the process of freezing would be completed, at temperature  $T_3$ , before the composition of the liquid phase had reached that of the eutectic. Actually, however, such alloys, when solidified from the melt, do contain the eutectic constituent, except when the gross composition of the alloy lies *very close* to that of one of the pure metals. The explanation is, of course, to be found

in the coring effect, which causes the average composition of the solid phase to depart so widely from the solidus that freezing is not completed

before the eutectic temperature is reached. A small amount of liquid ( $L_4$ ) remains:

$$\%L_4 = \frac{\alpha'_4 x_4}{\alpha'_4 L_4} \times 100 \approx 8\%$$

and this freezes isothermally as a secondary eutectic constituent of  $\alpha + \beta$ .

A typical alloy of this kind is sterling silver (7.5% copper, balance silver; see Fig. 4-5b), the cast microstructure of which is presented in



FIG. 4-12. Sterling silver (7.5% Cu) as cast. Light areas, shading from white to light gray, are cored dendrite areas, silver-rich at their centers; dark areas are divorced eutectic. Magnification 100.

Fig. 4-12. Here the silver-rich  $\alpha$  phase is light colored and the copper-rich  $\beta$  is dark. Coring of the primary  $\alpha$  dendrites is faintly visible in the shading of the light-colored areas, which are lightest at their silver-rich centers and become grayer toward their perimeters, where the copper content is higher.

In this example (Fig. 4-12) the secondary (eutectic) constituent, composed of  $\alpha + \beta$ , differs in appearance from the silver-copper eutectic (28.5% copper) shown in Fig. 4-6b in that its structure appears not to be pearlitic. Instead, somewhat irregular masses of the  $\beta$  phase lie between the primary  $\alpha$  dendrite arms. The portion of the  $\alpha$  phase which belongs to the eutectic is physi-

cally continuous with the  $\alpha$  of the primary constituent, so that it is difficult to discern where the boundary between the primary and secondary constituents lies. The eutectic structure is, in effect, composed of but one layer of the  $\beta$  phase enclosed between two layers of the  $\alpha$  phase which have grown directly upon the surfaces of the primary  $\alpha$  masses. This is called a *divorced eutectic*. It is assumed that whereas the two solid phases of a normal eutectic are nucleated and grow together in a characteristic geometric pattern, one of the phases (the  $\alpha$ ) of the divorced eutectic is nucleated by primary crystals of its own kind before new nuclei can form for eutectic growth, thereby altering the geometric arrangement of the phases.

### Homogenization, or Solution Heat Treatment

If the terminal solid-solution alloy  $X$  of Fig. 4-11 is brought to equilibrium by subjecting it to long heat treatment at a temperature between  $T_3$  and  $T_5$ , it should, according to the phase diagram, be composed of the

$\alpha$  phase alone (see Fig. 4-13). During this heat treatment the homogeneous condition is being approached in two ways simultaneously: (1) Coring of the  $\alpha$  phase is being eliminated by a redistribution of the components, as in the homogenization of an isomorphous alloy, and (2) the  $\beta$  phase is dissolving in the  $\alpha$  phase.<sup>1</sup> The rate at which these changes proceed will depend, of course, upon the temperature of heat treatment, because both changes are effected by diffusion and the diffusion velocity doubles, approximately, in most alloys for each temperature rise of 50°C. By quickly cooling the homogenized alloy to room temperature it is usually possible to retain the homogeneous condition, at least temporarily. The phase diagram indicates that the  $\beta$  phase should again be stable in this alloy at room temperature, but except in metals of low melting point, the rate of diffusion at room temperature is ordinarily so slow that the second solid phase does not reappear for a very long time.

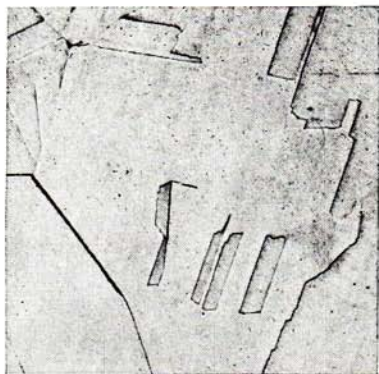


FIG. 4-13. Same as Fig. 4-12, homogenized by heat treatment just below the eutectic temperature and quenched to room temperature; only the silver-rich solid solution is present in this structure. Magnification 100.

The same heat treatment applied to an alloy within the span of the eutectic reaction isotherm, such as alloy *X* in Fig. 4-9, will not cause the  $\beta$  phase to disappear, but coring of the  $\alpha$  phase can be eliminated, and any excess over the equilibrium quantity of the  $\beta$  phase will dissolve in the  $\alpha$ . In addition, the remaining particles of the  $\beta$  phase may become *spheroidized*, i.e., assume rounded shapes of minimum surface.

### Precipitation in the Solid State

As has been remarked above, the homogenized terminal solid solution when cooled below  $T_5$  (Fig. 4-11) becomes unstable and tends to reject the  $\beta$  phase. Actual precipitation of the  $\beta$  phase takes place if the temperature is high enough so that the rate of diffusion is appreciable. This condition may be realized either by slow cooling from high temperature or by re-heat-treating at a temperature only a little below  $T_5$ . The  $\beta$  precipitate usually takes the form of small idiomorphic particles situated along the grain boundaries and within the grains of the  $\alpha$  phase (Fig. 4-14). In the majority of cases it is evident, also, that the  $\beta$  particles,

<sup>1</sup> If the temperature is above  $T_4$ , the  $\beta$  phase will, of course, be replaced by liquid and homogenization will proceed by the solution of liquid in the  $\alpha$  phase.

having a more or less regular form and size, are arranged in a systematic fashion with respect to orientation. Many of the particles within a single



FIG. 4-14. Same as Fig. 4-13, but slowly cooled from the homogenizing temperature. Parallel platelets of copper-rich solid solution have formed upon certain crystallographic planes of the parent silver-rich solid solution, producing a Widmanstätten structure. Magnification 1,000.

$\alpha$  grain lie parallel to one another, and if the precipitate particles be assigned to groups according to the direction assumed, it is found that there is a limited number of such groups (1, 3, 4, 6, 12, 24). This is called a *Widmanstätten structure*. The newly formed crystals of the  $\beta$  phase take their orientations from the parent  $\alpha$  crystal within which they grow.<sup>1</sup> In the sketch of Fig. 4-15a the particles are drawn as though they were square platelets placed parallel to the cube planes of the parent crystal, in the manner indicated by Fig. 4-15b. Since the parent  $\alpha$  crystals occur in various orientations in the microstructure, the traces of the  $\beta$  platelets likewise assume different orientations from one  $\alpha$  grain to the next, but the number of directions in any one  $\alpha$  grain is

always the same (three in this example).

Precipitation in the solid state occurs by the formation of oriented nuclei which grow at a rate depending upon the speed with which the appropriate variety of atoms is delivered by diffusion. Therefore, the rate of precipitation tends to be very slow at room temperature and to increase as the temperature is raised. The compositions of the participating phases also change somewhat with temperature as can be seen by reference to Fig. 4-11, where the solvus curves slope inward as the eutectic temperature is approached. At any stated temperature, such as  $T_6$ , the compositions and relative proportions of the  $\alpha$  and  $\beta$  phases can be computed from the tie-line connecting the two solvus curves.

The precipitation of a second phase from a solid solution is sometimes accompanied by a marked change in mechanical properties. In general, the hardness and strength decrease during precipitation because the solid solution is becoming more dilute. But in the *age-hardening alloys*, there is a substantial increase in hardness and allied properties. This increase is associated with the formation of a transition state that forms first. Subsequently this may change into the stable precipitate, with a reversal in the direction of the property change. The transition state, being unstable

<sup>1</sup> For further details of the Widmanstätten structure, see C. S. Barrett, "Structure of Metals," chap. 22, pp. 538-580, McGraw-Hill Book Company, Inc., New York, 1952.

at all temperatures and compositions, is not distinguished upon the phase diagram, and there is no known thermodynamic criterion by which

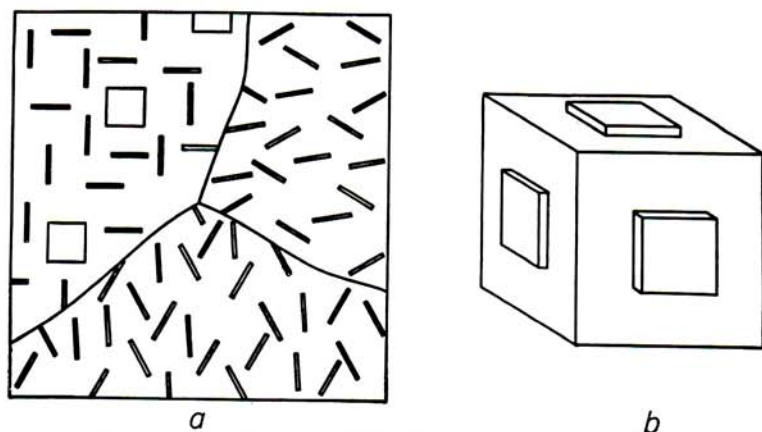


Fig. 4-15. Schematic representation of precipitate particle arrangement in a Widmanstätten structure. A matrix crystal with platelets parallel to three cube faces is represented in *b*; the appearance of these platelets in a microstructure including three differently oriented matrix crystals is shown in *a*.

its existence could be predicted. From the viewpoint of alloy constitution it can be said only that age hardening becomes possible when the solid solubility decreases with falling temperature, but among the many alloys having this characteristic only a limited number exhibit appreciable age hardening.

### Liquation

Partial melting, which may occur inadvertently in the course of heat treatment and which is known as liquation, or burning, of the alloy, commonly proceeds with the formation of a continuous film<sup>1</sup> of liquid along the grain boundaries of the  $\alpha$  phase and sometimes also in pockets between the dendrite arms. If the terminal solid-solution alloy *X* in Fig. 4-16 has previously been homogenized, the first liquid to form upon liquation will have the composition  $L_2$ . As the temperature rises above the solidus, the liquid becomes richer in the *A* component; the  $\alpha$  phase also becomes enriched in the *A* component, but its average composition lags

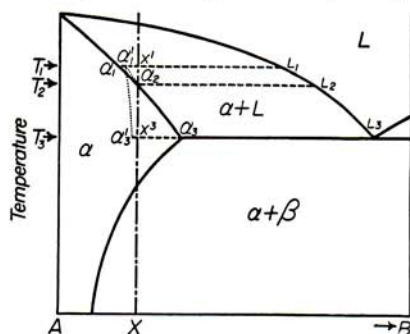


FIG. 4-16

<sup>1</sup> Continuous film formation occurs when the liquid phase "wets" the solid phase. This condition appears to be very common among metal systems.

behind the increase demanded by the solidus. Thus the percentage of the liquid phase is less than the equilibrium quantity at any given temperature such as  $T_1$ :

$$\%L_1 = \frac{\alpha'_1 x_1}{\alpha'_1 L_1} \times 100 \approx 10\%$$

If the alloy is now cooled, the liquid composition proceeds in the reverse direction down the liquidus. Cored  $\alpha$  phase is deposited until the eutectic temperature is reached, where any remaining liquid is converted to the eutectic constituent  $\alpha + \beta$ . In this way liquation may cause the reappearance of the eutectic constituent, and the work of the solution heat treatment is thereby undone.

Because the liquid existed as a continuous grain boundary film during liquation and because the film was relatively thin, the resulting eutectic constituent is usually highly divorced. Consequently, liquation may result in the formation of an almost *continuous grain boundary network* of the  $\beta$  phase, Fig. 4-17. Any liquid existing in interdendritic pockets freezes in place as eutectic *rosettes*.



FIG. 4-17. Same as Fig. 4-13 reheated to slightly above the solidus temperature of the alloy and quickly cooled. Liquation at grain boundaries and at many isolated points within the grains has resulted in the development of a continuous film of eutectic copper solid solution at the grain boundaries and eutectic rosettes within the grains. Magnification 100.

When overheating occurs, before homogenization has progressed to the disappearance of the  $\beta$  phase (or when dealing with an alloy within the composition span of the eutectic isotherm), melting begins at the eutectic temperature and the first liquid is of the eutectic composition. For this reason, the temperature of the homogenizing heat treatment is usually established below the eutectic temperature. After the  $\beta$  phase is dissolved, the temperature may be raised gradually to just below the solidus without the advent of liquation. By rehomogenizing, the segregation caused by liquation can usually be eliminated.

The time required is often much longer, however, than is needed for the homogenization of the original cast structure. This is because the bulk of the diffusion required to redistribute the  $B$  component must operate over the relatively long path from the grain boundary to the interior of the grain whereas in the "as-cast" structure the major part of the  $\beta$  phase resides in interdendritic spaces and the diffusion path is accordingly shorter.

### “Modification” of the Eutectic

There are several eutectic alloys that are subject to a marked lowering of the apparent eutectic temperature either when cooled very quickly from the molten condition or when cooled at a normal rate after the addition of some special reagent. Not only is the eutectic temperature lowered, but the composition of the eutectic point is shifted and the particle size of the eutectic constituent is refined. This effect is known as the “modification” of the eutectic.

Aluminum-silicon alloys are among the best known of those that are subject to modification. If a small quantity of sodium is added to the

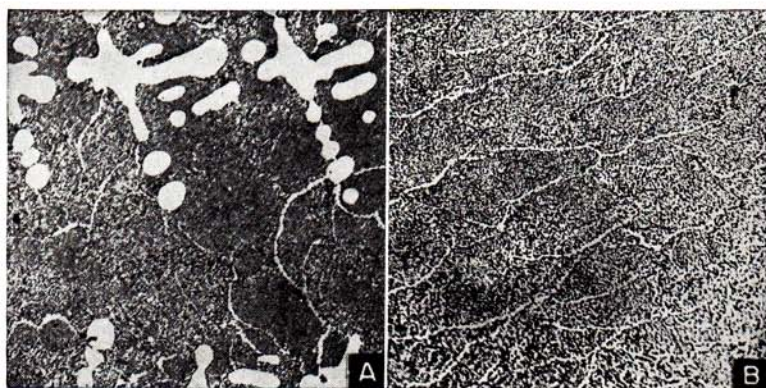


Fig. 4-18. (A) Aluminum-silicon eutectic alloy (11.6% silicon, see Fig. 4-6A) modified with sodium. The structure is now hypoeutectic; light areas are primary aluminum-rich solid solution, dark areas the modified eutectic constituent. Magnification 100. (B) Aluminum-silicon hypereutectic alloy (14% silicon, see Fig. 4-10B) modified with sodium. The structure is now composed altogether of the modified eutectic constituent. Magnification 100. (Courtesy of The Aluminum Company of America.)

aluminum-silicon eutectic alloy (11.6% silicon, see Fig. 4-5a), or if the eutectic alloy is rapidly chilled from the melt, the cast microstructure will appear somewhat as in Fig. 4-18A, which should be compared with the photograph of the normal cast structure of this alloy as shown in Fig. 4-6A. It is apparent from the microstructure that this alloy has become hypoeutectic; there are large primary dendrites of the  $\alpha$  phase, which were not present in the unmodified material. The alloy containing 14% silicon was seen to be hypereutectic in its normal cast state, Fig. 4-10B, but when modified, it appears as though of eutectic composition, Fig. 4-18B. Modification has shifted the eutectic point from 11.6 to 14% silicon (Fig. 4-19). At the same time the eutectic temperature has been reduced. The extent of its reduction depends upon the conditions of modification, the lowest value regularly observed being about 555°C.



If the aluminum-rich liquidus is projected, it is found that it passes very close to 14% silicon at 555°C. From this it has been concluded by some that modification results from the undercooling of the  $\beta$  phase, so that bivariant crystallization of the  $\alpha$  phase can continue below the normal eutectic temperature and until the  $\beta$  phase begins to appear at some

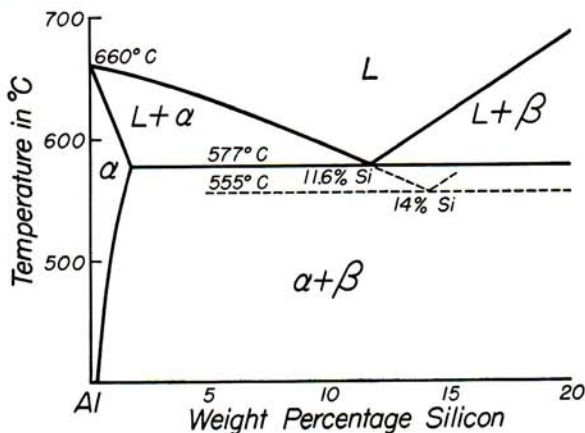


FIG. 4-19

lower temperature. The rate of nucleation being greater at lower temperature, a finer eutectic structure is produced.<sup>1</sup>

### Isothermal Diffusion Structures

Progress from nonequilibrium toward equilibrium at constant temperature is well illustrated by diffusion couples. Consider, for example, a piece of pure copper held at some elevated temperature until a stable state is established. If now a piece of silver is laid upon the copper (with good contact), equilibrium will have been destroyed, because pure copper and pure silver cannot coexist at equilibrium. Silver will begin to dissolve in the copper, and the copper will begin to dissolve in the silver. Dissolution will progress until one of the metals has wholly dissolved in the other or until both become saturated at the temperature concerned. Similar processes are met in welding and soldering or when a structure composed of two or more metals is heated or when metal powders are mixed and heated to sinter them together.

<sup>1</sup> For details, see R. S. Archer and L. W. Kempf, Modification and Properties of Sand Cast Aluminum-Silicon Alloys, *Trans. Am. Inst. Mining Met. Engrs.*, **73**:587 (1926); B. Otani, Silumin and Its Structure, *J. Inst. Metals*, **36**:243 (1926); A. G. C. Gwyer and W. H. L. Phillips, The Constitution and Structure of the Commercial Aluminum Alloys, *J. Inst. Metals*, **36**:283 (1926); L. Guillet, Aluminum-Silicon Alloys and Their Industrial Uses, *Rev. mét.*, **19**:303 (1922).

The application of the phase diagram to predict alloy behavior in such cases is demonstrated in Fig. 4-20. Two examples are shown. At a temperature of  $700^{\circ}\text{C}$  (below the eutectic) copper and silver are brought together. The two metals become mutually saturated at their interface, and if the time for diffusion is short, the composition in each metal will vary from saturation at the interface to pure metal at locations remote from the interface. These are the composition ranges shown by the heavy lines  $gh$  and  $ij$ . No two-phase structure corresponding to the  $\alpha + \beta$  field is produced; instead, the interface where the  $\alpha$  and  $\beta$  phases meet represents the

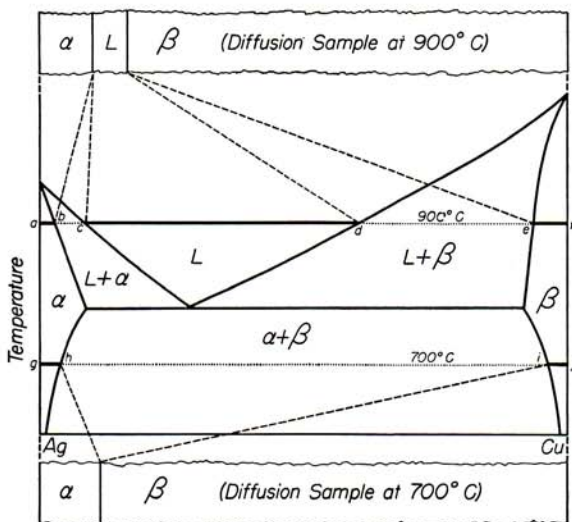


FIG. 4-20. Schematic representation of diffusion structures produced by isothermal diffusion between silver and copper at two temperatures. The top bar represents the layers produced at  $900^{\circ}\text{C}$ , the dashed lines associating these layers with the corresponding composition ranges upon the phase diagram. The bottom bar gives the same information for a diffusion temperature of  $700^{\circ}\text{C}$ .

entire two-phase region. This must be so because the only compositions of  $\alpha$  and  $\beta$  which may coexist at this temperature are those at  $h$  and  $i$ , and these compositions exist in the metal only at the interface. From this observation a general principle emerges, namely, that *isothermal diffusion between two metals results in the formation of one-phase layers corresponding to all one-phase fields crossed by drawing a line across the phase diagram at the temperature of diffusion, and the layers occur in the same sequence as the fields on the phase diagram.*

At  $900^{\circ}\text{C}$  (above the eutectic) three one-phase fields are crossed:  $\alpha$ , liquid, and  $\beta$ . The corresponding structure will be composed of a layer of the silver solid solution separated from the  $\beta$  by a layer of liquid. In each layer the composition varies across the one-phase field, as represented on

the phase diagram, namely,  $\alpha$  from  $a$  to  $b$ , liquid from  $c$  to  $d$ , and  $\beta$  from  $e$  to  $f$ . Thus, if a piece of silver-plated copper is heated above the eutectic temperature, melting will occur at the junction between the two metals; this is far below the melting point of either pure metal.

If diffusion is allowed to proceed for a longer time at either temperature considered above, copper will eventually diffuse to the far side of the silver and silver to the far side of the copper. The range of compositions appearing in the sample will then extend from somewhere inside the  $\alpha$  field to somewhere inside the  $\beta$  field. If the quantity of silver is small compared with that of the copper, at the lower temperature, the silver will be consumed entirely in saturating the copper and only one phase, the  $\beta$ , will remain. At the higher temperature, if the gross composition of the composite sample lay between  $e$  and  $f$ , the sample would, in time, be converted wholly to  $\beta$ ; if it lay between  $c$  and  $d$ , the entire sample would eventually melt; or if between  $d$  and  $e$ , equilibrium would be reached when saturated copper of composition  $e$  was in contact with liquid of composition  $d$ .

In practice it sometimes happens that diffusion structures are produced while the temperature is changing. Under such conditions the structure that is developed may be understood by combining the principles of isothermal phase change with those of phase change accompanying temperature variation. For example, if the material represented in Fig. 4-20 at  $900^{\circ}\text{C}$  is cooled to room temperature, the liquid layer must freeze to a series of alloys having compositions ranging from  $c$  to  $d$ , thereby forming a two-phase layer of  $\alpha + \beta$  between the one-phase zones of  $\alpha$  and  $\beta$ . This is, obviously, *not an exception* to the rule that two-phase layers are never formed by isothermal diffusion in a binary system.

### Physical Properties of Eutectic Alloys

The properties of alloys of the eutectiferous systems depend both upon the individual characteristics of the phases and upon the mode of distribution of these phases in the microstructure. This is true, of course, of any multiphase alloy. Individually the phases behave as solid solutions whose properties vary within the composition range covered in the same manner as do those of the isomorphous solid solutions. That is, the property change is most rapid with the first addition of the solute to the solvent component, each successive addition augmenting the change to a diminishing degree. Hardness and tensile strength increase with alloying; elongation and electrical conductivity decrease.

With two phases coexisting, the composition, and hence the physical properties of the individual phases, "ideally" should remain constant across the entire range of two-phase equilibrium. The properties of the

alloy should be simply those of a mixture of two substances of fixed characteristics. Departure from equilibrium interferes with the realization of this condition in many cases, but there are also many cases where the condition is realized or very nearly so. Obviously, there may be, and usually are, great differences between the properties of the two solid phases. If a phase is an intermediate solid solution (to be discussed in a later chapter), it is often very hard or brittle or both. Terminal solid solutions of the more common metals are usually relatively soft and ductile.

When two phases occur together in the structure, the resulting properties of the mixture most nearly resemble those of the physically continuous phase, i.e., that phase which forms the matrix in which particles of the other phase are embedded. As the quantity of the embedded phase increases with composition change, it tends toward a state of physical continuity and its properties are gradually approached. Thus the properties change more or less regularly with composition in the two-phase alloy from those of one of the saturated phases to those of the other. The change is almost linear in some systems (Fig. 4-21), but in others it deviates widely from this course.

Such deviations may be assignable to one or more of several causes, including (1) inhomogeneity of the individual phases, causing their properties to continue to change within the composition range of two-phase equilibrium; (2) peculiarities of particle shape that cause one of the phases to remain physically continuous over a disproportionately large range of composition; and (3) variations in particle size across the two-phase zone. The latter effect has two aspects, the size of the individual particles of the phases and the grain size within each particle. In cast alloys the individual particles are most commonly single crystals, but mechanical and thermal treatments, subsequently applied, may cause them to recrystallize to polycrystalline particles. A fine particle size is to be associated with greater hardness and decreased ductility but has little influence upon other than the mechanical properties. It is frequently observed that a maximum or minimum occurs in a property at the eutectic composition. This is presumed to be the result of a minimum particle size that is often found in eutectic and near-eutectic alloys.

Large effects of heat treatment upon the physical properties can, as a rule, be associated with corresponding changes in microstructure. During the homogenization of a terminal solid-solution alloy the quantity of dissolved solute is increased and the solid solution is thereby hardened. The reverse process takes place during precipitation unless age hardening intervenes. Spheroidization increases the physical continuity of the matrix phase and increases its influence upon the mechanical properties. Changes in the grain or particle size tend to harden or soften the alloy accordingly as the change is toward finer or coarser size. If liquation

during heat treatment causes the lesser phase to be distributed in a film at the grain boundaries of the major phase, then the properties of the alloy will become predominantly those of the lesser phase, even though it be present in very small proportion. And if, in addition, the lesser phase is brittle, the alloy will be brittle—hence the expression “spoiled by burning.”

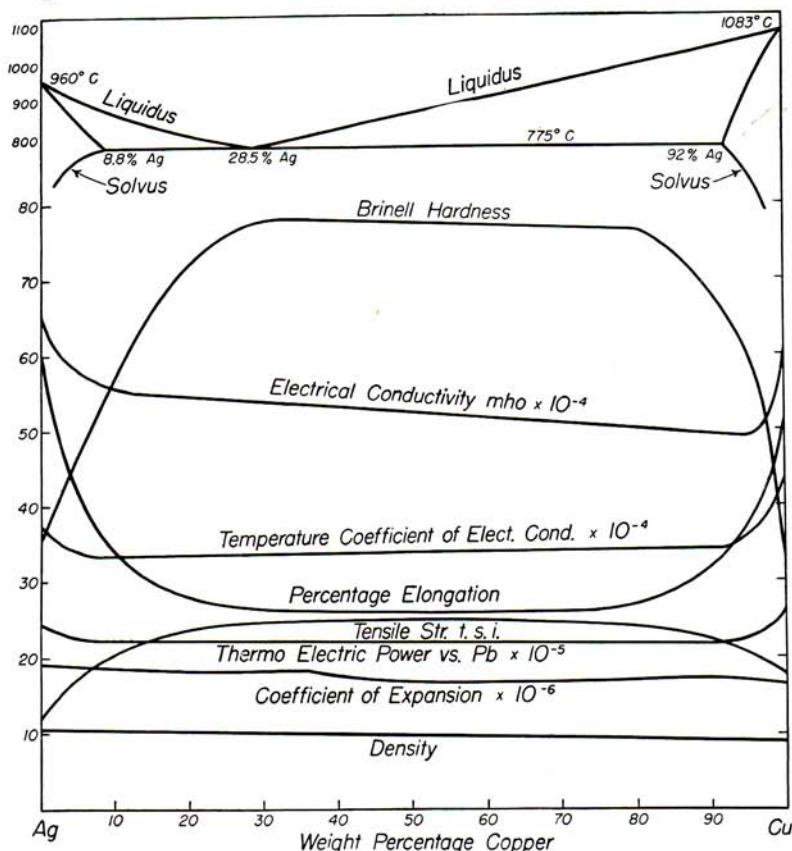


FIG. 4-21. Properties of annealed silver-copper alloys at room temperature. (From Broniewski and Weslowski.)

These principles of correlation between microstructure and physical properties apply alike to all multiphased alloys. Differences that are observed among typical alloys of the several constitutional types discussed in this and succeeding chapters are generally to be associated with differences in the relative importance of the several structural factors that have been mentioned. Eutectic alloys only occasionally exhibit large property effects that can be associated with the particle size as a major influence, while the eutectoid alloys about to be considered exhibit very

important particle-size effects. The subject having been discussed in some detail in this and the preceding chapter, consideration of the correlation of the physical properties with constitution and microstructure will be minimized in succeeding chapters.

### Limiting Cases of the Eutectic

There are many alloy systems in which the eutectic composition occurs very close to one of the components (Fig. 4-22, see also Fig. 4-5*d*). The eutectic constituent is then composed predominantly of one phase in which a few widely separated particles of the second phase are embedded. Such a eutectic alloy closely resembles the dominant pure metal in its properties.

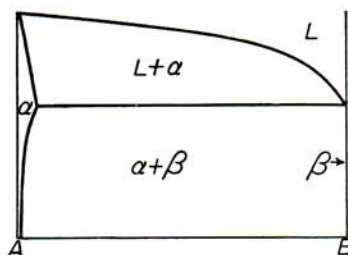


FIG. 4-22

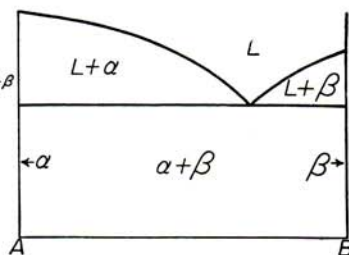


FIG. 4-23

The range of terminal solid solution is sometimes very narrow, so narrow, in fact, that it cannot be represented on the phase diagram because its width is less than that of the boundary line used to enclose it. In such cases, the eutectic reaction isotherm is extended to the composition of the pure component (Fig. 4-23). It should not be assumed, however, that this means that there is no range of solid solubility, for it is inconceivable that any two elements should be totally insoluble in one another at temperatures above absolute zero. Where the solid-solubility range is very small, coring in the primary constituent becomes minute because no substantial range of solid solutions can exist, but the likelihood of a eutectic constituent appearing in the microstructure is increased by low solid solubility.

### PRACTICE PROBLEMS

1. In the eutectic alloy system  $AB$  the compositions of the three conjugate phases of the eutectic are  $\alpha = 15\% B$ ,  $L = 75\% B$ ,  $\beta = 95\% B$ . Assuming equilibrium freezing of an alloy composed of equal parts of  $A$  and  $B$  to a temperature infinitesimally below that of the eutectic, compute (a) the percentages of primary  $\alpha$  and eutectic  $\alpha + \beta$ , (b) the percentages of total  $\alpha$  and total  $\beta$ . How would each of the above answers be affected if equilibrium were not maintained during freezing?

2. Draw a eutectic diagram for the following case:  $A$  melts at  $1000^{\circ}\text{C}$ ,  $B$  melts at  $700^{\circ}\text{C}$ , an alloy composed of 25%  $B$  is just completely frozen at  $500^{\circ}\text{C}$  and at equilibrium is made up structurally of  $73\frac{1}{3}\%$  of primary  $\alpha$  and  $26\frac{2}{3}\%$  of eutectic  $\alpha + \beta$ , whereas an alloy composed of 50%  $B$  at the same temperature is made up structurally of 40% of primary  $\alpha$  and 60% of eutectic  $\alpha + \beta$ , the total of  $\alpha$  in this alloy being 50%.

3. A certain eutectic alloy system has a completely symmetrical phase diagram (that is,  $A$  and  $B$  have the same melting temperature, the eutectic point is at 50%  $B$ , and the solubility limits of the terminal solid solutions are identical). By means of long heat treatment, an alloy may be brought to equilibrium at a series of temperatures below the eutectic. When this is done with the eutectic alloy (50%  $B$ ), no change is observed in the relative quantities of  $\alpha$  and  $\beta$  in going from one temperature to another, but an alloy composed of 25%  $B$  exhibits a progressive change in the proportion of the two phases. Why should this be so? What change, if any, is occurring in the eutectic alloy?