CHAPTER 3

BINARY ISOMORPHOUS SYSTEMS

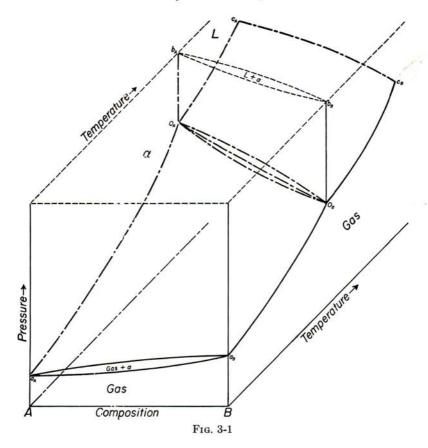
A binary isomorphous system is one in which two metals are mutually soluble in all proportions and in all states, the solid, liquid, and gas. The concept of liquid solution is familiar, and it is easy also to conceive of gaseous solution, because gases mix in all proportions. In solid solutions¹ the solute metal simply enters and becomes a part of the crystalline solvent, without altering its basic structure. There are two kinds of solid solutions: (1) substitutional solid solutions, in which the solute atom occupies, in the solvent crystal, a position belonging to one of the atoms of the solvent metal, and (2) interstitial solid solution, in which the solute atom enters one of the vacant spaces between atoms in the lattice of the solvent crystal without displacing a solvent atom. Isomorphous solid solutions are always of the substitutional kind. Both of the metals involved must have the same type of crystal structure, because it must be possible to replace, progressively, all the atoms of the initial solvent with atoms of the original solute without causing a change in crystal structure (i.e., a phase change).

In order to produce a complete phase diagram of a binary alloy system in which the three externally variable factors, pressure, temperature, and composition, are all represented, it is necessary to resort to the use of a three-dimensional space model as in Fig. 3-1. This is a *PTX diagram* (pressure-temperature-composition). Pressure is measured vertically, temperature horizontally to the rear, and composition horizontally across the front of the model. The composition is usually expressed in weight percentage as described in Chap. 1. The right side of the figure represents pure metal *B* and is the PT diagram of that metal; the left side, in like manner, is the PT diagram of pure metal *A* (compare with Fig. 2-1).

Within the space model there are three pairs of curved surfaces which serve to join the corresponding triple curves of the two pure metals. One of these pairs of surfaces, which joins the sublimation curves of A and B, intersects the front surface of the model in two curved lines $a_A a_B$, showing that the two surfaces enclose a space of lenticular cross section in which

¹ In some of the older literature the term "mixed crystals," a direct translation of the German *Mischkristalle*, is used in place of the term "solid solution."

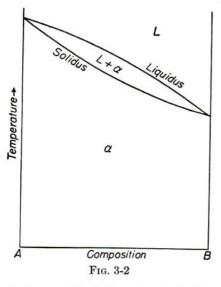
the solid (solution) and gas (solution) phases coexist. Another such pair b_Ab_B joining the melting curves encloses a similarly shaped space in which the liquid (solution) and solid (solution) phases coexist. The third pair joins the vaporization curves and encloses a space where liquid and gas coexist. Between the two-phase regions, three large spaces represent the conditions of individual stability of the three phases of the system. These



are the gas-solution region in the space along the bottom of the diagram, the solid-solution region in the upper front space, and the liquid-solution region in the upper rear portion of the model. Attention is directed to the condition that the one-phase regions are separated from each other by two-phase regions everywhere except at the sides of the diagram, where the one-phase regions contact one another along the triple curves of the pure metals.

Although the space diagram must extend upward indefinitely, the diagram in Fig. 3-1 has been arbitrarily cut off by a horizontal (isobaric)

plane. If the resulting cross section is considered to lie at 1 atmosphere of pressure, it will represent the phase relationships in all alloys composed of the metals A and B at normal pressure. This, then, is the usual TX diagram (temperature-composition diagram) of the AB alloy system (see Fig.



3-2 and compare with Fig. 1-1). Further discussion of the space diagram will be deferred to a later chapter. For the present it will be sufficient to appreciate that the TX diagrams, that are about to be discussed, are all (horizontal) sections taken arbitrarily through the PTX space diagram at a constant pressure of 1 atmosphere.

Applications of the Phase Rule

In applying the phase rule to the binary TX diagram it is important to remember that this is an isobaric section in which the pressure has been selected by free and arbitrary

choice and that the act of selecting a pressure constitutes the exercise of one degree of freedom. A one-phase region, such as the α or the L region, is tervariant; i.e., there are three degrees of freedom.

$$P + F = C + 2$$

1 + 3 = 2 + 2

Any point in a one-phase region is fixed by selecting first, a pressure of 1 atmosphere, which places the point somewhere upon the isobaric section under consideration; second, a temperature, which locates the vertical position of the point; and finally, a composition, which locates its lateral position. Three degrees of freedom have been utilized by the independent choice of pressure, temperature, and composition.

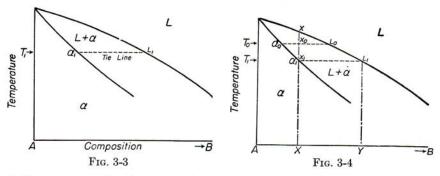
When two phases are coexistent, as in the $L+\alpha$ region of the diagram, it is evident that they must be at the same pressure and temperature, for physically they must lie side by side in the same environment, but it is not necessary that they have the same composition. The phase rule requires that there be two degrees of freedom in a two-phase two-component mixture.

$$P + F = C + 2$$

 $2 + 2 = 2 + 2$

The pressure has been selected in establishing the isobaric section, and only one degree of freedom remains. If this degree of freedom is employed in establishing the temperature, it follows that the compositions of the two phases must be fixed thereby.

This is illustrated in Fig. 3-3, where a horizontal line (dashed) has been drawn across the $L + \alpha$ region of the phase diagram at the arbitrarily selected temperature T_1 . Every point on the horizontal line except the ends lies within the $L + \alpha$ field and must represent the coexistence of liquid and solid solution. The left end, at α_1 , lies upon the solidus, where the alloy must be completely solid, and the right end lies upon the liquidus, at L_1 , where the alloy must be entirely molten. If, as was said above, the composition of the solid phase must be the same in all mixtures with liquid at this temperature, it is apparent that the composition so



designated must be that at α_1 , because this is the only composition that the solid could assume as the quantity of liquid approaches zero. Likewise, the composition of the liquid phase must be that at L_1 , where the quantity of solid reaches zero. Every mixture of L and α at this temperature T_1 must, then, be composed of various quantities of α_1 and α_2 .

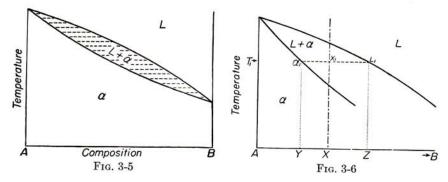
The horizontal line connecting α_1 and L_1 is known as a *tie-line*¹ because it joins the composition points of the *conjugate phases* that coexist at a designated temperature and pressure.

Exactly the same conclusions would have been reached if, instead of using the one remaining degree of freedom to designate a temperature, the choice of a composition had been elected. Suppose that it had been required that the α phase contain X% B. This should result in the simultaneous establishment of fixed values of the temperature and of the composition of the liquid phase. According to the stipulation that the solid phase must have the composition X, the point representing the solid must lie somewhere on the line Xx in Fig. 3-4. Let the conditions be tested at some randomly selected temperature T_0 . It will then appear, by

 1 In some of the literature the German word konode is used in place of the English equivalent tie-line.

repeating the argument cited in the previous example, the the only possible solid composition at this temperature is α_0 and not x_0 . Similar results will be obtained at any other temperature except T_1 ; here α_1 and x_1 are identical points, and all requirements are satisfied. By establishing the composition of the solid phase at X, the temperature of the equilibrium with liquid has been fixed at T_1 and the composition of the liquid phase has been fixed at Y. Two degrees of freedom, namely, pressure and composition, have been exercised, as predicted by the phase rule.

A further significance is now seen to reside in the liquidus and solidus curves. The solidus designates for each temperature the composition of the solid phase that may exist in equilibrium with liquid, and the liquidus designates for the same temperature the composition of the liquid phase



in equilibrium with solid. The $L + \alpha$ region may be thought of as being composed of an infinite number of tie-lines connecting the conjugate solid and liquid compositions (Fig. 3-5) at all temperatures within the limits of the field. It is customary to omit the tie-lines from binary diagrams, because their location is self-evident.

The Lever Principle

Further consideration of the nature of the tie-line reveals that it may be used to compute the relative quantities of two phases present at equilibrium in an alloy of stated gross composition at a given temperature. It has been pointed out that at temperature T_1 in Fig. 3-6, the alloy of composition Y is composed wholly of solid (α_1) while the alloy of composition Z is composed wholly of liquid (L_1) ; all intermediate compositions at this temperature must be composed of mixtures of various proportions of α_1 and L_1 . Since the compositions of the two phases are the same in all mixtures, there must be a linear relationship obtaining between the alloy composition and the proportions of the phases present at fixed temperature; i.e., the percentage of liquid must increase linearly from 0 at com-

position Y to 100 at composition Z. The tie-line can, therefore, be treated as a lever with its fulcrum at the gross composition of the alloy under consideration and the total weight of each of the two phases impinging upon the lever at the respective ends, where their compositions are represented.

In Fig. 3-6, the lever is the tie-line α_1L_1 , balanced upon its fulcrum at x_1 , the gross composition of the alloy under consideration. The length x_1L_1 will then be proportional to the total, or relative, weight of the solid phase of composition α_1 , while the length α_1x_1 will be proportional to the total, or relative, weight of the liquid phase L_1 . If the whole length of the tie-line α_1L_1 is taken to represent 100% (or the total of the two phases present in alloy X at temperature T_1), then the length x_1L_1 will be the percentage of solid and α_1x_1 the percentage of liquid. This is the *lever principle*, which may be conveniently expressed in mathematical form as follows:

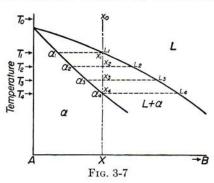
$$\%\alpha_1 = \frac{x_1 L_1}{\alpha_1 L_1} \times 100$$

$$\%L_1 = \frac{\alpha_1 x_1}{\alpha_1 L_1} \times 100$$

Equilibrium Freezing of a Solid-solution Alloy

The phase changes that accompany freezing under equilibrium conditions in a given alloy can be read from the phase diagram by observing

the phases that are present and their compositions at each successively lower temperature. Let X, Fig. 3-7, represent the gross composition of the alloy in which freezing behavior is to be considered. Observations will begin at temperature T_0 , where the alloy is entirely molten, point x_0 . No phase change occurs upon cooling until the temperature T_1 is reached, whereupon freezing begins with the initial deposition of crystals of com-



position α_1 , which is the only composition of solid that can be in equilibrium with liquid having the gross composition X, point L_1 . The separation of crystals of α_1 takes from the liquid a disproportionately large amount of the A component, causing the liquid to become richer in the B component. Thus, when a lower temperature T_2 is reached, the composition of the liquid has shifted to L_2 . The only solid that can remain in equilibrium with L_2 is α_2 . Hence, the composition of the solid must also

have moved toward higher B content. This can happen only by the preferential absorption of B from the liquid and the diffusion of the B metal into the solid formed previously at higher temperature. When equilibrium is established at temperature T_2 , the relative quantities of the solid and liquid phases may be computed by applying the lever principle:

$$\%\alpha_2 = \frac{x_2 L_2}{\alpha_2 L_2} \times 100 \approx 50\%^*$$

 $\%L_2 = \frac{\alpha_2 x_2}{\alpha_2 L_2} \times 100 \approx 50\%^*$

Growth of the solid at the expense of the liquid continues, with the compositions of both phases shifting toward greater B content as the temperature falls. At T_3 the solid phase will constitute about three-quarters of the material present and its composition will lie at α_3 . Finally, at T_4 , the liquid will disappear:

$$\%\alpha_4 = \frac{x_4L_4}{\alpha_4L_4} \times 100 = 100\%$$

The alloy is now completely frozen, and the composition of the solid phase has arrived at the gross composition of the alloy X.

Origin of Coring

The conditions of "equilibrium" freezing are not realizable in practice because of the very long time required at each decrement of temperature to readjust the compositions of the two phases. This adjustment can be accomplished only by the diffusion of A and B atoms in both phases, together with the exchange of atoms across the liquid-solid interface. Since diffusion proceeds slowly, especially in the solid state, true equilibrium cannot be maintained during cooling except at an infinitely slow rate.

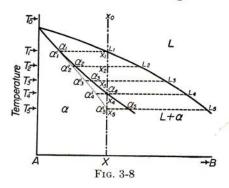
Certain departures from equilibrium freezing are, therefore, to be expected when ordinary cooling rates are used. In the example about to be described it will be assumed that homogeneous equilibrium is maintained in the liquid phase, but not in the solid phase, where the rate of diffusion is much lower. Referring again to the alloy of composition X, Fig. 3-8, freezing begins with the deposition of crystals of α_1 when the temperature T_1 is reached. At T_2 the liquid composition has shifted to L_2 , and the

*The inclusion of an approximate percentage here and elsewhere is intended to assist the reader in comparing the relative quantities of phases represented on the tie-lines.

¹ It is scarcely likely that equilibrium could be maintained in the liquid phase during freezing, but this assumption simplifies the argument without vitiating its conclusions.

solid forming at that temperature will have the composition α_2 . But the solid which had formed at temperatures above T_2 has not changed al-

together from its initial compositions, and the average composition of all the solid formed up to this point will be represented at α'_2 . As the temperature drops to T_3 , the average solid composition α'_3 is seen to depart more and more from the equilibrium composition α_3 . Under ideal conditions freezing should be completed at T_4 . Here, however, the average solid composition has not reached the gross composition



of the alloy X, and some liquid must remain. The relative quantities may be read from the tie line at T_4 :

% solid =
$$\frac{x_4L_4}{\alpha_4'L_4} \times 100 \approx 85\%$$

% liquid = $\frac{\alpha_4'x_4}{\alpha_4'L_4} \times 100 \approx 15\%$

Freezing continues, therefore, to lower temperature, and the solid now being deposited is richer in the B component than the original composition of the alloy X. Finally, at T_5 the average solid composition α'_5 coincides with the gross composition at x_5 and the alloy is completely solidified.

Nonequilibrium freezing is characterized by an increased temperature range over which liquid and solid are present and by a composition range remaining in the solidified alloy. If the rate of cooling is decreased, the displacement of the average solid compositions from the solidus will be less; likewise, if the diffusion rate in the solid state had been greater, the departures from equilibrium would have been less.

Undercooling normally precedes the initiation of freezing in alloys; i.e., the liquid cools below L_1 before freezing starts. When this happens, the first solid may have a composition nearer to the gross composition of the alloy than is α_1 . However, the release of latent heat of crystallization usually elevates the temperature again (recalescence) so that a modest

¹ For more detailed discussions of the theory of natural freezing, see G. H. Gulliver, The Quantitative Effect of Rapid Cooling upon the Constitution of Binary Alloys, J. Inst. Metals, 9:120–153 (1913), 11:252–272 (1914), 13:263–291 (1915); J. F. Russell, The Interpretation of Thermal Curves and Some Applications to Ferrous Alloys, J. Iron Steel Inst., 139:147-176 (1939); E. Scheuer, Zum Kornseigerungsproblem, Z. Metallkunde, 23:237–241 (1931).

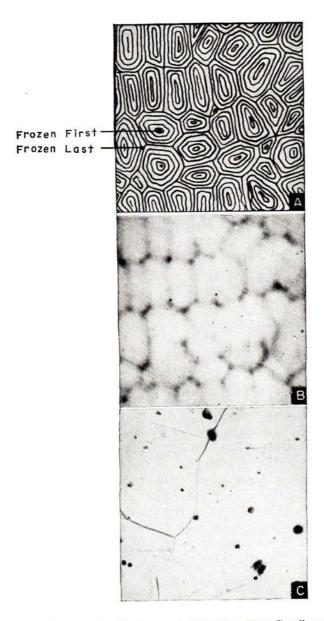


Fig. 3-9. Illustrates coring in a cast 70% Ni +30% Cu alloy. Nickel-rich areas are light gray, copper-rich areas are dark gray in B, magnification 100. The order of freezing of the cored structure is indicated upon the tracing A. Long heat treatment at a high temperature produces a uniform distribution of the copper and nickel as shown in photomicrograph C, magnification 100.

degree of initial undercooling may be expected to have but a minor influence upon the ultimate path of freezing.

The solidification of an alloy begins with the appearance of small solid particles (nuclei) which, barring undercooling, contain more of the higher melting component metal than any subsequently formed solid. Upon the nuclear crystallites successive layers of the solid phase are deposited, each layer being a little richer than its predecessor in the low-melting component. The final solid is composed, then, of a "cored" structure, in which each unit has a high-melting central portion surrounded by lower melting material (see Fig. 3-9A). The majority of metals freeze by the formation of treelike growths, called dendrites, whose branches become thicker as freezing proceeds until all the space is filled with solid and a continuous crystal has been developed. Hence, the cored structure in most metals has the geometry of the dendrite. This condition is sometimes referred to as dendritic segregation.

Seen in cross section under the microscope, the sectioned branches of the dendrite appear in the more or less regular pattern of the rounded figures depicted in Fig. 3-9A. A photomicrograph of a cored copper-nickel (30-70) alloy (see Fig. 1-1) is presented in Fig. 3-9B. This picture was obtained by oxidizing the polished surface of the sample in the air; the more easily oxidized, lower-melting, copper-rich regions of the alloy were darkened by this procedure, while the higher-melting, tarnish-resistant, nickel-rich cores were left bright.

Homogenization

For some uses the cored cast structure is objectionable and must be eliminated by a suitable heat treatment. The equalization, or homogenization, of the composition of the cast alloy, by eliminating coring, occurs spontaneously through the action of diffusion under favorable conditions. Diffusion in the solid state is most rapid at a temperature just below that of melting, and in most alloys its rate is approximately halved with each 50°C lowering of the temperature. Except with metals of very low melting point, diffusion is scarcely detectable at room temperature.

The choice of a suitable heat-treating temperature for homogenization is limited on the high side by the onset of melting if the solidus curve is crossed and on the low side by the marked deceleration of the process as the temperature is decreased. Allowance must be made also for the fact that some of the solid, which is richer in the low-melting component than the average composition of the alloy (α_5 in Fig. 3-8), may begin to melt below the equilibrium solidus temperature of the alloy. The equilibrium solidus may be approached more closely without inducing melting if the cast alloy is heated slowly than if it is quickly heated to a high tempera-

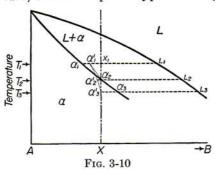
ture, because time is thereby furnished for the lowest melting solid to be eliminated.

After homogenization, the dendritic cored structure is no longer visible in the microstructure (Fig. 3-9C). It should be noted that homogenization is an adjustment toward a state of homogeneous equilibrium not involving a heterogeneous phase change. Therefore, the phase diagram does not predict the change and is useful, in this case, only in the selection of a suitable heat-treating temperature.

Liquation

Where an alloy has been heated only slightly above the solidus temperature, so that melting has just begun, it is said to have been liquated, or burned. Melting usually begins at the grain boundaries and interdendritic regions of the alloy, forming a thin film of liquid that separates each crystal of the solid from its neighbor (Fig. 3-11A). The strength of the alloy is destroyed almost immediately with the onset of melting. Large or complex castings will sag out of shape, and if disturbed while liquated, the material may crack and fall to pieces. Alloys with a long temperature interval between liquidus and solidus are often characterized as being "hot short" because their strength and ductility may be destroyed by liquation at a temperature far below that at which the onset of melting is otherwise evident. As has been pointed out above, melting (liquation) may be encountered below the solidus temperature if the alloy is cored.

Liquation may also have an effect upon the physical properties and microstructure of the alloy after it has been returned to room temperature, because a special type of coring is developed at the grain boundaries

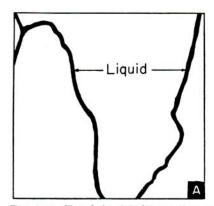


and at other localities where liquid has appeared. The reason for this can be seen by reference to Fig. 3-10. Assume that the alloy X has been homogenized, melting will begin when the temperature T_2 is reached, the liquid having the composition L_2 . When temperature T_1 is reached, the liquid composition will be L_1 , but the composition of the solid phase will not have had time to

reach its equilibrium value at α_1 ; instead the average solid composition will lie at some intermediate point α'_1 . For this reason the quantity of liquid formed will be less than that to be expected at equilibrium:

$$\%L_1 = \frac{\alpha_1' x_1}{\alpha_1 L_1} \times 100 \approx 5\%$$

If the material is now rapidly cooled, freezing will occur in the normal manner, with a layer of α_1 being deposited first on existing solid grains, followed by layers of increasing B content up to α_3 , at T_3 , where the supply of liquid is exhausted. Thus, coring occurs in the melted zone, coincident with the grain boundaries (Fig. 3-11). A photomicrograph of this effect in the copper-nickel alloy used for previous demonstrations is presented in Fig. 3-11B; compare the breadth of the grain boundary zone in the liquated sample with the narrow grain boundary in the homogenized



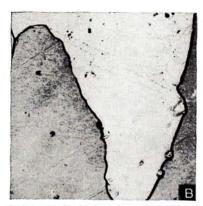


Fig. 3-11. Sketch in A indicates that portion of the metal which was melted. Upon subsequent freezing, the center of the melted zone became copper-rich, and this has caused the grain boundaries in B to appear as broad dark lines, magnification 100. Compare with the grain boundaries in Fig. 3-9C.

sample (Fig. 3-9C). The effects of liquation can usually be eliminated by the same kind of heat treatment as that employed for the homogenization of cast alloys.

Annealing

Solid-solution alloys are commonly subjected to annealing heat treatments to eliminate or to modify the effects of plastic forming at room temperature and to control grain size. The alterations in the metal that are affected thereby involve no phase changes, so that the phase diagram cannot, in general, be used to predict what will occur. It can sometimes be of assistance, nevertheless, in selecting suitable annealing temperatures. As a very rough approximation it can be said that a temperature (centigrade or Fahrenheit) of approximately one-half of the melting point of the alloy will usually produce a full anneal and a temperature of about one-quarter of the melting point will usually serve to relieve internal stresses. There are important exceptions to this statement, particularly among the metals of low melting point.

Isothermal Diffusion

If pieces of the two component metals of an isomorphous system are brought into intimate contact and are maintained for some time at a temperature where diffusion is appreciable, alloying will take place in the solid state. During the early stages the composition will vary from pure metal A at one side of the composite sample to pure metal B at the other side. Much later, the composition will become uniform throughout and will be the same as though the two metals were alloyed by melting them together.

No phase change is involved in the above examples. If, however, the temperature of diffusion lies above the melting point of one of the metals, a phase change does occur. Suppose that temperature T_1 (Fig. 3-6) is chosen for the experiment and the pieces of metals A and B are of such relative size that together they would have the composition X. Metal B is melted, and the piece of metal A is immersed in the melt. Soon the composition of the solid will vary from pure A at the center to Y at the surface, while the liquid composition will vary from Z at the surface of contact with the solid to pure B at remote locations. After a time the solid will all reach the composition Y and the liquid will reach the composition Z. The two phases will then be in stable equilibrium. If, on the other hand, the quantity of A had been relatively larger, so that the gross composition had lain to the left of Y, the liquid phase would have disappeared entirely as equilibrium was approached, all of the B component being used to form the solid solution. Or if the gross composition had lain to the right of Z, the solid phase would have dissolved completely in the melt.

Physical Properties of Isomorphous Alloys

The physical properties of alloys can be divided into two groups, namely, those which are structure sensitive and those which are structure insensitive. Structure-insensitive properties, such as density, change only with the externally controllable variables, temperature, pressure, and composition. In the ideal case the change is linear (see, for example, the density vs. composition curve in Fig. 3-12), but both positive and negative deviations are encountered in nonideal isomorphous alloys. The structure-sensitive properties, such as hardness, tensile strength, and electrical conductivity, vary with the grain size, degree of coring, and other structural conditions. If these conditions are held constant and the composition is varied (Fig. 3-12), it is found that the change in properties is not linear but passes through a maximum or minimum. The change in properties is most rapid with the first addition of alloying element to

either of the component metals and continues at a decelerating pace until reversal occurs at the maximum or minimum. Although the absolute values of the several properties differ widely from system to system, the iorms of the curves are generally the same in all binary isomorphous alloy systems.

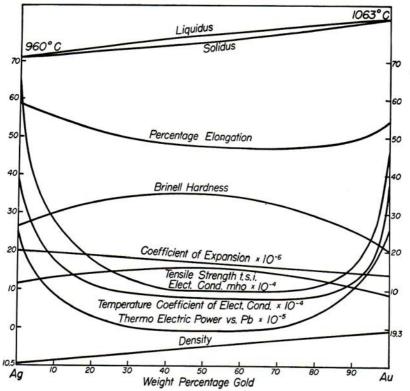


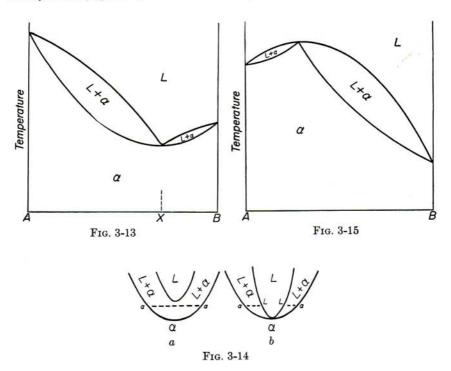
Fig. 3-12. Properties of annealed silver-gold alloys at room temperature. (From Broniewski and Wesolowski.)

Minima and Maxima

There are some binary isomorphous systems in which the liquidus and solidus do not descend continuously from the melting temperature of one metal to that of the other but, instead, pass through a minimum temperature, which lies below the melting points of both components (Fig. 3-13). When this occurs, the *liquidus and solidus meet tangentially* at the minimum point*. That these lines must meet will become evident if tie-lines are

^{*} C. Wagner, Thermodynamics of the Liquidus and the Solidus of Binary Alloys, Acta Metallurgica 2 (2): 242-249 (1954).

drawn in the $L+\alpha$ region in the vicinity of the minimum point. Should the liquidus and solidus fail to meet, as in the impossible case depicted in Fig. 3-14a, some tie-lines in the $\alpha+L$ region would indicate equilibrium between solid and solid $(\alpha-\alpha)$ instead of between liquid and solid. But if the liquidus and solidus meet at the minimum point (Fig. 3-14b), all the lines join conjugate liquid and solid compositions.



The alloy which has the composition of the minimum melting point behaves much like a pure metal. It melts and freezes isothermally and exhibits no coring in its cast structure. Alloys such as this, which melt and freeze with the liquid and solid phases undergoing no changes in composition, are called *congruently melting alloys*. A congruently melting alloy may be treated as a component of an alloy system. Thus the system AB in Fig. 3-13 may be divided into two systems at composition X. One will be the simple isomorphous binary system AX; the other the simple isomorphous binary system XB.

Maxima are also possible in isomorphous systems (see Fig. 3-15.) As in the case of the minimum, the liquidus and solidus meet tangentially at the maximum and the alloy of this composition is congruent in its melting and freezing behavior.

PRACTICE PROBLEMS

- 1. Compare qualitatively the range of composition difference (coring) that would develop in the course of the natural freezing of a 90% Ni + 10% Cu alloy (Fig. 1-1) with that which would develop in a 50% Ni + 50% Cu alloy. What generalization can be deduced from this result?
- 2. Upon one set of coordinates, draw isomorphous diagrams for the two alloy systems AB and AC, where A melts at 1000°C, B melts at 800°C, and C melts at 200°C. Compare qualitatively the ranges of composition difference (coring) that would develop in the course of the natural freezing of an alloy from each system, where both alloys have the same content of component A. What generalization can be deduced from this result relating to the effect of the difference in the melting points of the component metals upon the extent of coring?
- **3.** An isomorphous alloy system (AB) has a minimum at 70% B, as in Fig. 3-13 Predict the course of natural freezing of an alloy (a) at 70% B, (b) at 10% B, (c) at 95% B, (d) at 65% B.