

6

PHASE DIAGRAMS

6-1 Introduction In the previous chapter it was indicated that there were many possibilities for the structure of an alloy. Since the properties of a material depend to a large extent on the type, number, amount, and form of the phases present, and can be changed by altering these quantities, it is essential to know (1) the conditions under which these phases exist and (2) the conditions under which a change in phase will occur.

A great deal of information concerning the phase changes in many alloy systems has been accumulated, and the best method of recording the data is in the form of *phase diagrams*, also known as *equilibrium diagrams* or *constitutional diagrams*.

In order to specify completely the state of a system in equilibrium, it is necessary to specify three independent variables. These variables, which are externally controllable, are temperature, pressure, and composition. With pressure assumed to be constant at atmospheric value, the equilibrium diagram indicates the structural changes due to variation of temperature and composition. The diagram is essentially a graphical representation of an alloy system.

Ideally, the phase diagram will show the phase relationships under equilibrium conditions, that is, under conditions in which there will be no change with time. Equilibrium conditions may be approached by extremely slow heating and cooling, so that if a phase change is to occur, sufficient time is allowed. In actual practice, phase changes tend to occur at slightly higher or lower temperatures, depending upon the rate at which the alloy is heated or cooled. Rapid variation in temperature, which may prevent phase changes that would normally occur under equilibrium conditions, will distort and sometimes limit the application of these diagrams.

It is beyond the scope of this text to cover all the possible conditions of equilibrium between phases in binary alloys. Only the most important ones

will be considered, and they may be classified as follows:

- 1 Components completely soluble in the liquid state
 - a Completely soluble in the solid state (Type I)
 - b Insoluble in the solid state: the eutectic reaction (Type II)
 - c Partly soluble in the solid state: the eutectic reaction (Type III)
 - d Formation of a congruent-melting intermediate phase (Type IV)
 - e The peritectic reaction (Type V)
- 2 Components partly soluble in the liquid state: the monotectic reaction (Type VI)
- 3 Components insoluble in the liquid state and insoluble in the solid state (Type VII)
- 4 Transformations in the solid state
 - a Allotropic change
 - b Order-disorder
 - c The eutectoid reaction
 - d The peritectoid reaction

A study of these diagrams will illustrate basic principles which may be applied to understand and interpret more complex alloy systems.

6-2 Coordinates of Phase Diagrams Phase diagrams are usually plotted with temperature, in degrees centigrade or Fahrenheit, as the ordinate and the alloy composition in weight percentage as the abscissa. It is sometimes more convenient for certain types of scientific work to express the alloy composition in atomic percent. The conversion from weight percentage to atomic percentage may be made by the following formulas:

$$\text{Atomic percent of A} = \frac{100X}{X + Y(M/N)} \quad (6-1)$$

$$\text{Atomic percent of B} = \frac{100Y(M/N)}{X + Y(M/N)} \quad (6-2)$$

where M = atomic weight of metal A
 N = atomic weight of metal B
 X = weight percentage of metal A
 Y = weight percentage of metal B

Regardless of the scale chosen for temperature or composition, there will be no difference in the form of the resulting phase diagram.

6-3 Experimental Methods The data for the construction of equilibrium diagrams are determined experimentally by a variety of methods, the most common being:

Thermal Analysis This is by far the most widely used experimental method. As was shown in Chap. 5, when a plot is made of temperature vs. time, at constant composition, the resulting cooling curve will show a change in slope when a phase change occurs because of the evolution of heat by the phase change. This method seems to be best for determining the initial and final temperature of solidification. Phase changes occurring solely in the solid state generally involve only small heat changes, and other methods give more accurate results.

Metallographic Methods This method consists in heating samples of an alloy to different temperatures, waiting for equilibrium to be established, and then quickly cooling to retain their high-temperature structure. The samples are then examined microscopically.

This method is difficult to apply to metals at high temperatures because the rapidly cooled samples do not always retain their high-temperature structure, and considerable skill is then required to interpret the observed microstructure correctly. This method is best suited for verification of a diagram.

X-ray diffraction Since this method measures lattice dimensions, it will indicate the appearance of a new phase either by the change in lattice dimension or by the appearance of a new crystal structure. This method is simple, precise, and very useful in determining the changes in solid solubility with temperature.

4 Type I—Two Metals Completely Soluble in the Liquid and Solid States

Since the two metals are completely soluble in the solid state, the only type of solid phase formed will be a substitutional solid solution. The two metals will generally have the same type of crystal structure and differ in atomic radii by less than 8 percent.

The result of running a series of cooling curves for various combinations or alloys between metals A and B, varying in composition from 100 percent A 0 percent B to 0 percent A 100 percent B, is shown in Fig. 6-1. In order to see the relationship between the cooling curves, they have been plotted on a single set of axes. However, the student should realize that each cooling curve has its own coordinates. In other words, each cooling curve is a separate experiment starting from zero time. The cooling curves for the pure metals A and B show only a horizontal line because the beginning and end of solidification take place at a constant temperature. However, since intermediate compositions form a solid solution, these cooling curves show two breaks or changes in slope. For an alloy containing 80A and 20B, the first break is at temperature T_1 , which indicates the beginning of solidification, and the lower break at T_2 indicates the end of solidification. All intermediate alloy compositions will show a similar type of cooling curve. The sense of the phase diagram, or some idea of its form, may be obtained by drawing a line connecting all the points that show the beginning of solidification, the upper dotted line in Fig. 6-1, and another line connecting all the points that show the end of solidification, which is the lower dotted line in Fig. 6-1.

It is now possible to determine the actual phase diagram by plotting temperature vs. composition. The appropriate points are taken from the series of cooling curves and plotted on the new diagram. For example, in Fig. 6-2, since the left axis represents the pure metal A, T_A is plotted along this line. Similarly, T_B is plotted. Since all intermediate compositions are percent-

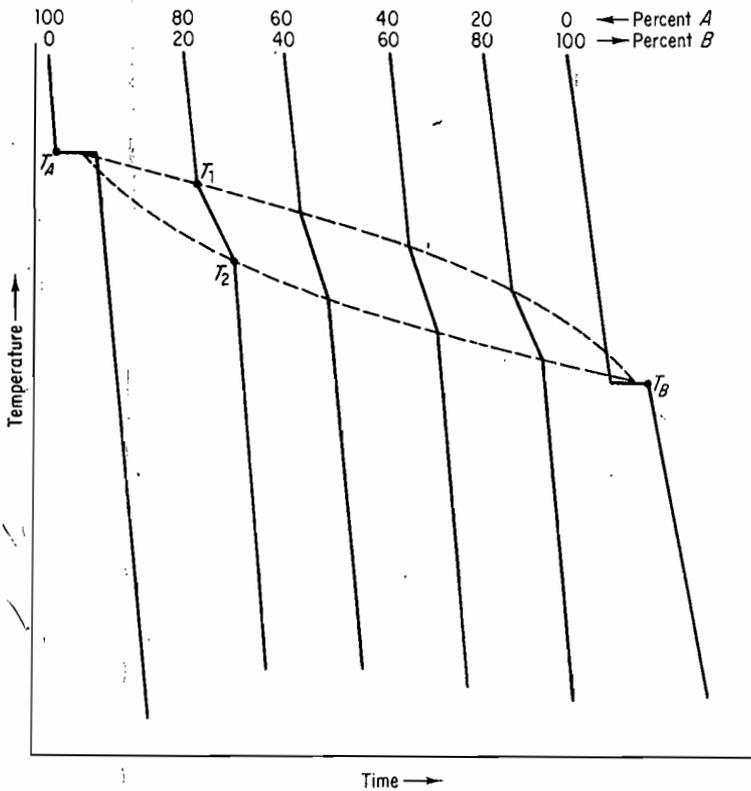


Fig. 6-1 Series of cooling curves for different alloys in a completely soluble system. The dotted lines indicate the form of the phase diagram.

ages of A and B , for simplicity the percent sign will be omitted. A vertical line representing the alloy $80A-20B$ is drawn, and T_1 and T_2 from Fig. 6-1 are plotted along this line. The same procedure is used for the other compositions.

The phase diagram consists of two points, two lines, and three areas. The two points T_A and T_B represent the freezing points of the two pure metals.

The upper line, obtained by connecting the points showing the beginning of solidification, is called the *liquidus* line; and the lower line, determined by connecting the points showing the end of solidification, is called the *solidus* line. The area above the liquidus line is a single-phase region, and any alloy in that region will consist of a homogeneous liquid solution. Similarly, the area below the solidus line is a single-phase region, and any alloy in this region will consist of a homogeneous solid solution. It is common practice, in the labeling of equilibrium diagrams, to represent solid solutions and sometimes intermediate alloys by Greek letters. In this case, let

us label the solid solution alpha (α). Uppercase letters such as *A* and *B* will be used to represent the pure metals. Between the liquidus and solidus lines there exists a two-phase region. Any alloy in this region will consist of a mixture of a liquid solution and a solid solution.

Specification of temperature and composition of an alloy in a two-phase region indicates that the alloy consists of a mixture of two phases but does not give any information regarding this mixture. It is sometimes desirable to know the actual chemical composition and the relative amounts of the two phases that are present. In order to determine this information, it is necessary to apply two rules.

6-5 Rule I—Chemical Composition of Phases To determine the actual chemical composition of the phases of an alloy, in equilibrium at any specified temperature in a two-phase region, draw a horizontal temperature line, called a *tie line*, to the boundaries of the field. These points of intersection are dropped to the *base line*, and the composition is read directly.

In Fig. 6-3, consider the alloy composed of 80A-20B at the temperature *T*. The alloy is in a two-phase region. Applying Rule I, draw the tie line *mo* to the boundaries of the field. Point *m*, the intersection of the tie line with the solidus line, when dropped to the base line, gives the composition of the phase that exists at that boundary. In this case, the phase is a solid solution α of composition 90A-10B. Similarly, point *o*, when dropped to the base line, will give the composition of the other phase constituting the mixture, in this case the liquid solution of composition 74A-26B.

6-6 Rule II—Relative Amounts of Each Phase To determine the relative amounts of the two phases in equilibrium at any specified temperature in a two-

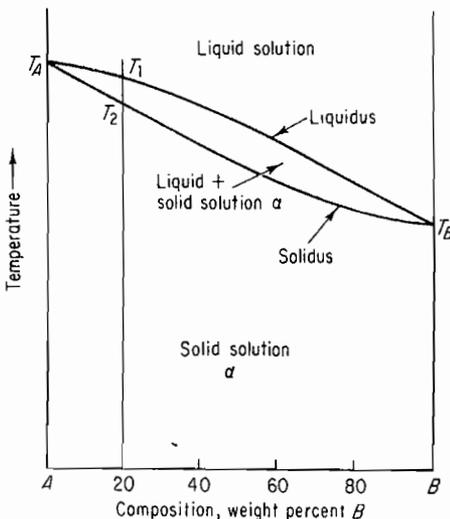


Fig. 6-2 Phase diagram of two metals completely soluble in the liquid and solid states.

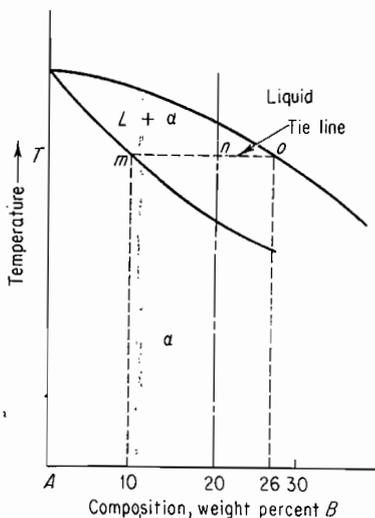


Fig. 6-3 Diagram showing the tie line mo drawn in the two-phase region at temperature T .

phase region, draw a vertical line representing the alloy and a horizontal temperature line to the boundaries of the field. The vertical line will divide the horizontal line into two parts whose lengths are inversely proportional to the amount of the phases present. This is also known as the lever rule. The point where the vertical line intersects the horizontal line may be considered as the fulcrum of a lever system. The relative lengths of the lever arms multiplied by the amounts of the phases present must balance.

In Fig. 6-3, the vertical line, representing the alloy 20B, divides the horizontal tie line into two parts, mn and no . If the entire length of the tie line mo is taken to represent 100 percent, or the total weight of the two phases present at temperature T , the lever rule may be expressed mathematically as

$$\text{Liquid (percent)} = \frac{mn}{mo} \times 100$$

$$\alpha \text{ (percent)} = \frac{no}{mo} \times 100$$

If the tie line is removed from the phase diagram and the numerical values are inserted, it will appear as shown in Fig. 6-4. Applying the above equations,

$$\text{Liquid (percent)} = \frac{10}{16} \times 100 = 62.5 \text{ percent}$$

$$\alpha \text{ (percent)} = \frac{6}{16} \times 100 = 37.5 \text{ percent}$$

$$\text{Liquid (percent)} = \frac{\alpha_2 T_2}{\alpha_2 L_2} \times 100 = \frac{20}{35} \times 100 = 57 \text{ percent}$$

$$\alpha_2 \text{ (percent)} = \frac{T_2 L_2}{\alpha_2 L_2} \times 100 = \frac{15}{35} \times 100 = 43 \text{ percent}$$

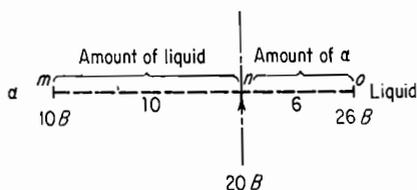


Fig. 6-4 The tie line mo removed from Fig. 6-3 to illustrate application of the lever rule.

To summarize both rules, the alloy of composition 80A-20B at the temperature T consists of a mixture of two phases. One is a liquid solution of composition 74A-26B constituting 62.5 percent of all the material present and the other a solid solution of composition 90A-10B making up 37.5 percent of all the material present.

6-7 Equilibrium Cooling of a Solid-Solution Alloy The very slow cooling, under equilibrium conditions, of a particular alloy 70A-30B will now be studied to observe the phase changes that occur (see Fig. 6.5). This alloy at temperature T_0 is a homogeneous single-phase liquid solution (Fig. 6.5a) and remains so until temperature T_1 is reached. Since T_1 is on the liquidus line, freezing or solidification now begins. The first nuclei of solid solution to form, α_1 , will be very rich in the higher-melting-point metal A and will be composed of 95A-5B (Rule I). Since the solid solution in forming takes material very rich in A from the liquid, the liquid must get richer in B. Just after the start of solidification, the composition of the liquid is approximated as 69A-31B (Fig. 6-5b).

When the lower temperature T_2 is reached, the liquid composition is at L_2 . The only solid solution in equilibrium with L_2 and therefore the only solid solution forming at T_2 is α_2 . Applying Rule I, α_2 is composed of 10B. Hence, as the temperature is decreased, not only does the liquid composition become richer in B but also the solid solution. At T_2 , crystals of α_2 are formed surrounding the α_1 composition cores and also separate dendrites of α_2 (Fig. 6-6). In order for equilibrium to be established at T_2 , the entire solid phase must be a composition α_2 . This requires diffusion of B atoms to the A-rich core not only from the solid just formed but also from the liquid. This is possible only if the cooling is extremely slow so that diffusion may keep pace with crystal growth (Fig. 6-5c).

At T_2 , the relative amounts of the liquid and solid solution may be determined by applying Rule II:

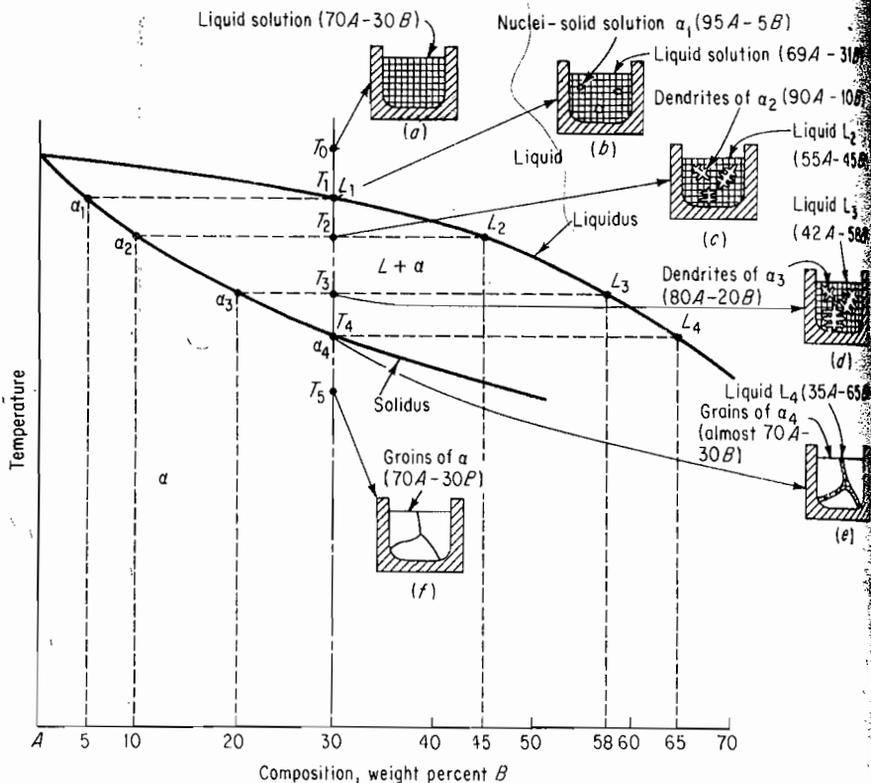


Fig. 6-5 The slow cooling of a 70A-30B alloy, showing the microstructure at various points during solidification.

As the temperature falls, the solid solution continues to grow at the expense of the liquid. The composition of the solid solution follows the solidus line while the composition of liquid follows the liquidus line, and both phases are becoming richer in B. At T_3 (Fig. 6-5d), the solid solution will make up approximately three-fourths of all the material present. The student should apply the lever rule at T_3 and determine the relative quantities of α_3 and L_3 . Finally, the solidus line is reached at T_4 and the last liquid L_4 , very rich in B, solidifies primarily at the grain boundaries (Fig. 6-5e). However, diffusion will take place and all the solid solution will be of uniform composition α (70A-30B), which is the overall composition of the alloy (Fig. 6-5f). Figure 6-7 shows the microstructure of a slow-cooled solid solution alloy. There are only grains and grain boundaries. There is no evidence of any difference in chemical composition inside the grains, indicating that diffusion has made the grain homogeneous.

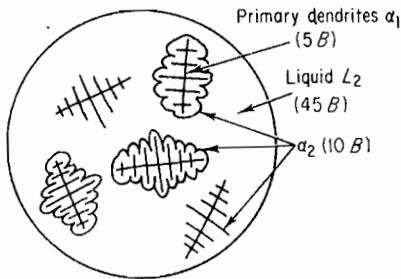


Fig. 6-6 Schematic picture of the alloy 30B at temperature T_2 before diffusion.

6-8 Diffusion It was pointed out in the previous section that diffusion, or the movement of atoms, in the solid state was an important phenomenon. Through the mechanism of diffusion under slow cooling the dendritic structure disappeared, and the grain became homogeneous. The purpose of this section is to explain briefly how diffusion in solids may occur.

Diffusion is essentially statistical in nature, resulting from many random movements of individual atoms. While the path of an individual atom may be zigzag and unpredictable, when large numbers of atoms make such

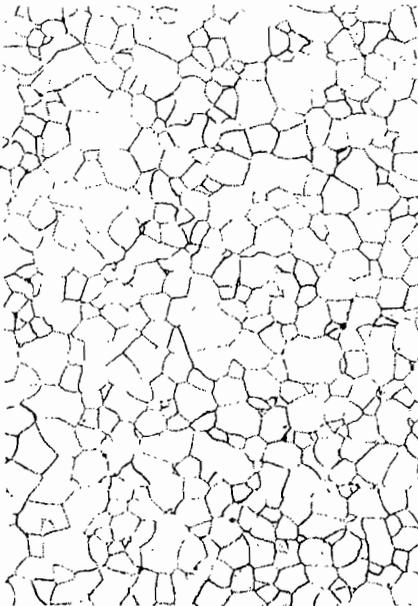


Fig. 6-7 Microstructure of a solid solution iron alloy; magnification 100X. (Courtesy of the Research Laboratory, U.S.Steel.)

movements they can produce a systematic flow.

There are three methods by which diffusion in substitutional solid solutions may take place; the vacancy mechanism, interstitial mechanism, and atom interchange mechanism. These are illustrated schematically in Fig. 6-8.

In Chap. 2, under crystallization, it was pointed out that vacancies and interstitial sites were a normal feature of a crystal structure. These imperfections greatly facilitate diffusion, or the jumping of adjoining atoms. Figure 6-8a shows how a solute atom might move one atomic spacing to the left by jumping into a vacancy. It is equally probable, of course, that any one of the other atoms neighboring the vacancy could have made the jump. The vacancy has moved to the right to occupy the position of the previous atom and is now ready for another random interchange. The interstitial mechanism is illustrated in Fig. 6-8b, where an atom in normal position moves into an interstitial space, and the vacated spot is taken by the interstitial atom. As shown in the same figure, diffusion may occur by an interstitial atom wandering through the crystal, but this method is more likely in interstitial solid solutions.

It is possible for movement to take place by a direct interchange between two adjacent atoms, as shown in Fig. 6-8c, or by a four-atom ring interchange, as in Fig. 6-8d. However, these would probably occur only under special conditions, since the physical problem of squeezing between closely packed neighboring atoms would increase the barrier for diffusion. Experimental evidence has indicated that the use of vacancies is the primary method of diffusion in metals. The rate of diffusion is much greater in a rapidly cooled alloy than in the same alloy slow-cooled. The difference is due to the larger number of vacancies retained in the alloy by fast cooling. Vacancy migration also has a lower activation energy when compared with the other methods.

The rate of diffusion of one metal in another is specified by the diffusion coefficient, which is given in units of square centimeters per second. While

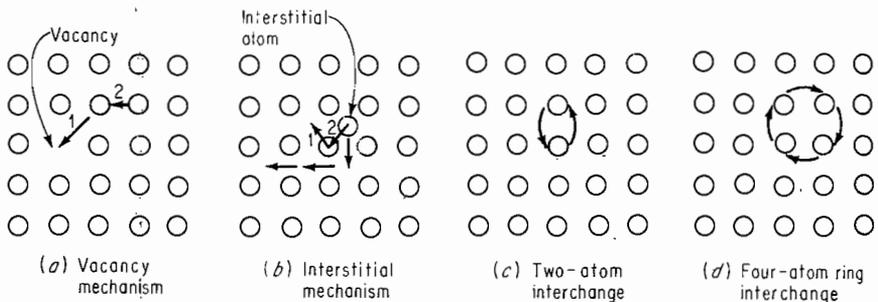


Fig. 6-8 Schematic diffusion mechanisms.

the diffusion coefficient is a function of many variables, the most important is temperature. As a general rule, it may be stated that the diffusion coefficient doubles for every 20-deg (centigrade) rise in temperature. This is not surprising, since all atoms are constantly vibrating about their equilibrium positions in the lattice, and since the amplitude of vibration increases with increasing temperature. The energy associated with these thermal vibrations, often referred to as the thermal energy, is sufficient to cause an atom to jump out of its lattice position under suitable conditions. Therefore, temperature is obviously an important factor in determining whether jumping or diffusion is likely to occur. An alloy has the lowest free energy when it is in a homogeneous condition, and this is the driving force for diffusion.

6.9 Nonequilibrium Cooling—Origin of Coring In actual practice it is extremely difficult to cool under equilibrium conditions. Since diffusion in the solid state takes place at a very slow rate, it is expected that with ordinary cooling rates there will be some difference in the conditions as indicated by the equilibrium diagram. Referring again to the alloy 30B (Fig. 6.9), solidification starts at T_1 , forming a solid solution of composition α_1 . At T_2 the liquid is at L_2 and the solid solution now forming is of composition α_2 (see Fig. 6.6). Since diffusion is too slow to keep pace with crystal growth, not enough time will be allowed to achieve uniformity in the solid, and the average composition will be between α_1 and α_2 , say α'_2 . As the temperature drops, the average composition of the solid solution will depart still further from equilibrium conditions. It seems that the composition of the solid solution is following a "nonequilibrium" solidus line α_1 to α'_5 , shown dotted in Fig. 6.9. The liquid, on the other hand, has essentially the composition given by the liquidus line, since diffusion is relatively rapid in liquid. At T_3 the average solid solution will be of composition α'_3 instead of α_3 . Under equilibrium cooling, solidification should be complete at T_4 ; however, since the average composition of the solid solution α'_4 has not reached the composition of the alloy, some liquid must still remain. Applying the lever rule at T_4 gives

$$\alpha'_4 \text{ (percent)} = \frac{T_4 L_4}{\alpha'_4 L_4} \times 100 \approx 75 \text{ percent}$$

$$L_4 \text{ (percent)} = \frac{\alpha'_4 T_4}{\alpha'_4 L_4} \times 100 \approx 25 \text{ percent}$$

Solidification will therefore continue until T_5 is reached. At this temperature the composition of the solid solution α'_5 coincides with the alloy composition, and solidification is complete. The last liquid to solidify, L_5 , is richer in B than the last liquid to solidify under equilibrium conditions. It is apparent from a study of Fig. 6.9 that the more rapidly the alloy is cooled

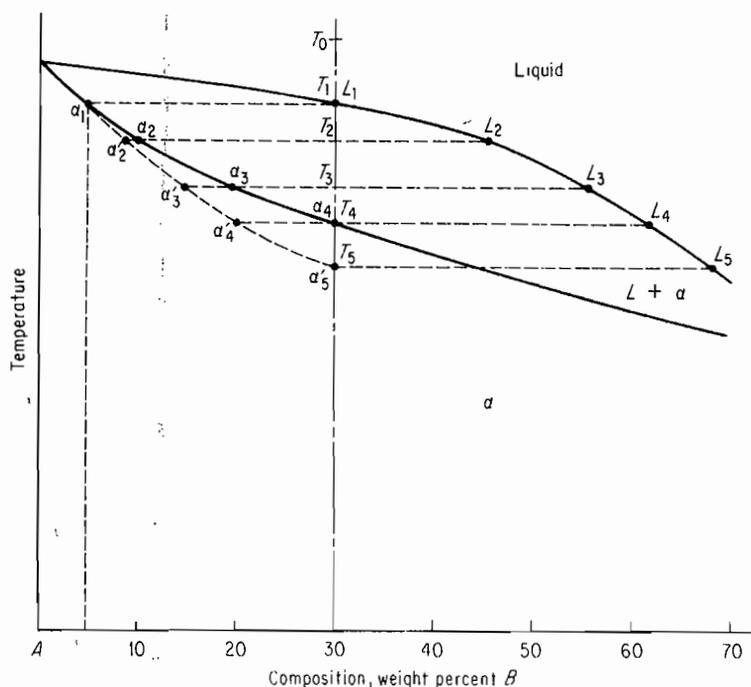


Fig. 6-9 Nonequilibrium cooling; the origin of coring.

the greater will be the composition range in the solidified alloy. Since the rate of chemical attack varies with composition, proper etching will reveal the dendritic structure microscopically (Fig. 6-10). The final solid consists of a "cored" structure with a higher-melting central portion surrounded by the lower-melting, last-to-solidify shell. The above condition is referred to as *coring* or *dendritic segregation*.

To summarize, nonequilibrium cooling results in an increased temperature range over which liquid and solid are present; final solidification occurs at a lower temperature than predicted by the phase diagram; the final liquid to solidify will be richer in the lower-melting-point metal; and since diffusion has not kept pace with crystal growth, there will be a difference in chemical composition from the center to the outside of the grains. The faster the rate of cooling, the greater will be the above effects.

6-10 Homogenization Cored structures are most common in as-cast metals. From the above discussion of the origin of a cored structure, it is apparent that the last solid formed along the grain boundaries and in the interdendritic spaces is very rich in the lower-melting-point metal. Depending upon the properties of this lower-melting-point metal, the grain boundaries may

act as a plane of weakness. It will also result in a serious lack of uniformity in mechanical and physical properties and, in some cases, increased susceptibility to intergranular corrosion because of preferential attack by a corrosive medium. Therefore, for some applications, a cored structure is objectionable.

There are two methods for solving the problem of coring. One is to prevent its formation by slow freezing from the liquid, but this results in large grain size and requires a very long time. The preferred method industrially is to achieve equalization of composition or homogenization of the cored structure by diffusion in the solid state.

At room temperature, for most metals, the diffusion rate is very slow; but if the alloy is reheated to a temperature below the solidus line, diffusion will be more rapid and homogenization will occur in a relatively short time.

Figure 6-11 shows the actual equilibrium diagram for the copper-nickel system, and the alloy 85Cu-15Ni is shown as a dotted line. The effect of homogenization on the cored structure of an 85Cu-15Ni alloy is illustrated by the series of photomicrographs in Fig. 6-12. The first picture of this sequence shows the microstructure of the alloy as chill-cast. As the equi-



Fig. 6-10 Fine-cored dendrites in a copper-lead alloy; magnification 100X. (Research Laboratories, National Lead Company.)

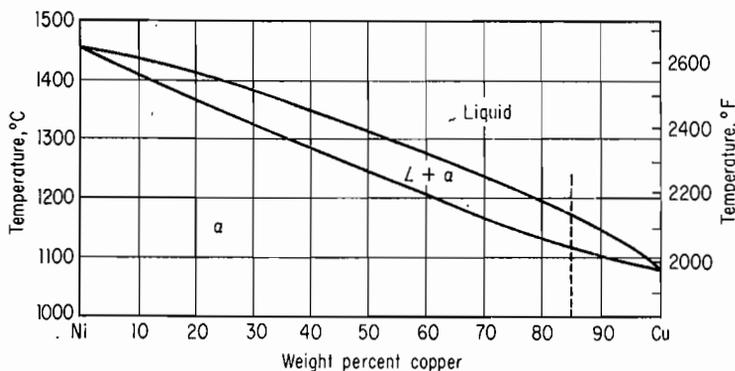


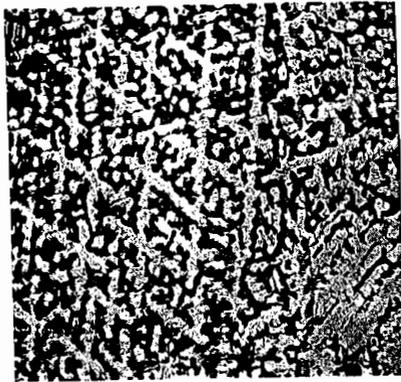
Fig. 6-11 , Copper-nickel equilibrium diagram. (From "Metals Handbook," 1948 ed., p. 1198, American Society for Metals, Metals Park, Ohio.)

librium diagram predicts, the first solid to be formed in the central axes of the dendrites is rich in nickel. Because of rapid cooling, there is a great difference in nickel content between the central axes of the dendrites and the interdendritic spaces. This difference is revealed by suitable etching. The next figure shows the same sample after heating at 1382°F for 3 h. Counterdiffusion of nickel and copper atoms between the nickel-rich cores and the copper-rich fillings has reduced the composition differences somewhat. The microstructure of the same sample heated to 1742°F for 9 h is shown in the third figure. The composition is completely equalized, and the dendrites have disappeared. The grain boundaries are clearly evident. Black particles are copper oxide or nickel oxide inclusions. The fourth figure illustrates the same alloy slowly cooled by casting in a hot mold. The dendritic structure is coarser than that of the chill-cast alloy. The last figure shows this same sample heated 15 h at 1742°F. The structure is now completely homogenized. Despite the smaller initial composition differences across the coarse dendrites as compared with the fine dendrites, it took a longer time for equalization because of the greater distance through which the copper and nickel atoms had to diffuse in the coarse structure. Extreme care must be exercised in this treatment not to cross the solidus line; otherwise liquation of the grain boundaries will occur, impairing the shape and physical properties of the casting (Fig. 6-13).

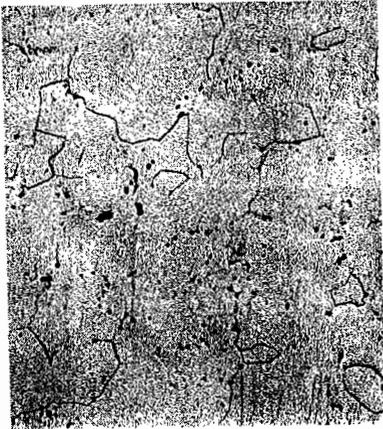
6-11 Properties of Solid-solution Alloys In general, in an alloy system forming a continuous series of solid solutions, most of the property changes are caused by distortion of the crystal lattice of the solvent metal by additions of the solute metal. The effect of composition on some physical and mechanical properties of annealed alloys in the copper-nickel system is given in Table 6-1. Electrical resistivity depends upon distortion of the lattice structure. Since the distortion increases with the amount of solute metal



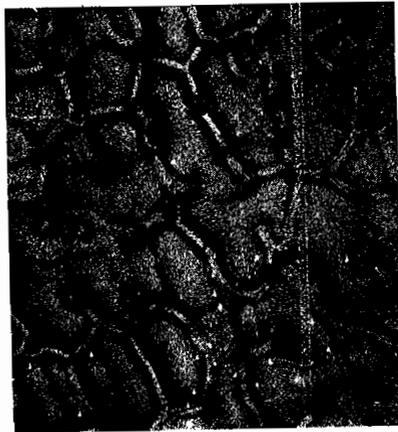
(a)



(b)



(c)



(d)



(e)

Fig. 6-12 Photomicrographs of an 85 Cu-15 Ni alloy. (a) chill-cast, 50x; (b) chill-cast, reheated 3 h at 1382°F, 50x; (c) chill-cast, reheated 9 h at 1742°F, 50x; (d) cast in a hot mold, 50x; (e) cast in a hot mold, reheated 15 h at 1742°F, 50x. (By permission from Brick, Gordon, and Phillips, "Structure and Properties of Alloys," 3d ed., McGraw-Hill Book Company, New York, 1965.)

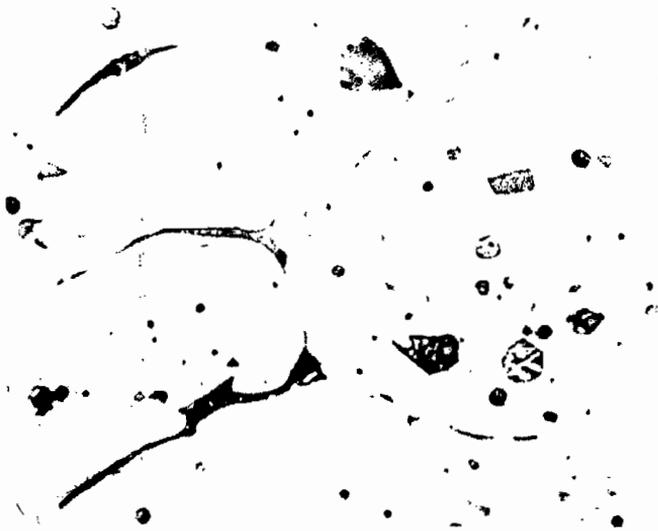


Fig. 6-13 Photomicrograph of an aluminum alloy in which some melting has occurred at the grain boundaries during heating. After cooling, these portions of the grain boundaries appear as dark, broad lines; magnification, 1,000X. (Alcoa Research Laboratories, Aluminum Company of America.)

added, and since either metal can be considered as the solvent, the maximum electrical resistivity should occur in the center of the composition range. This is verified by the values given in the table. As copper is added to nickel, the strength of the alloy increases, and as nickel is added to copper, the strength of that alloy also increases. Therefore, between pure copper and pure nickel there must be an alloy which shows the maximum strength. It turns out to be at approximately two-thirds nickel and one-third copper. This is a very useful commercial alloy known as *Monel*. It shows good strength and good ductility along with high corrosion resistance. The same behavior is also true of hardness in that there will be an alloy that shows the maximum hardness, although the maximum tensile strength and hardness do not necessarily come at the same composition.

6-12 Variations of Type I Every alloy in the Type I system covered has a melting point between the melting points of *A* and *B*. It is possible to have a system in which the liquidus and solidus lines go through a minimum or a maximum (Fig. 6-14a, b). The alloy composition *x* in Fig. 6-14a behaves just like a pure metal. There is no difference in the liquid and solid composition. It begins and ends solidification at a constant temperature with no change in composition, and its cooling curve will show a horizontal line. Such alloys are known as congruent-melting alloys. Because alloy *x* has the lowest melting point in the series, and the equilibrium diagram resembles

TABLE 6-1 P

COMPOSITION
NICKEL

permission f

6-13 T

Fig. 6-14
(b) Solid

TABLE 6-1 Properties of Annealed Copper-Nickel Alloys*

COMPOSITION PERCENT NICKEL	TENSILE STRENGTH, PSI	ELONGATION, % IN 2 IN.	BHN, 10 MM, 500 KG	LATTICE PARAMETER, 10^{-8} CM	ELECTRICAL RESISTIVITY, MICROHMS PER CU CM
0	30,000	53	36	3.6073	1.7
10	35,000	47	51	3.5975	14
20	39,000	43	58	3.5871	27
30	44,000	40	67	3.5770	38
40	48,000	39	70	3.5679	46
50	50,000	41	73	3.5593	51
60	53,000	41	74	3.5510	50
70	53,000	42	73	3.5432	40
80	50,000	43	68	3.5350	30
90	48,000	45	61	3.5265	19
100	43,000	48	54	3.5170	6.8

*By permission from R. M. Brick and A. Phillips, "Structure and Properties of Alloys," 2d ed., McGraw-Hill Book Company, New York, 1949.

the eutectic type to be discussed shortly, it is sometimes known as a *pseudoeutectic alloy*. Examples of alloy systems that show a minimum are Cu-Au and Ni-Pd. Those showing a maximum are rare, and there are no known metallic systems of this type.

6-13 Type II—Two Metals Completely Soluble in the Liquid State and Completely Insoluble in the Solid State Technically, no two metals are completely insoluble in each other. However, in some cases the solubility is so restricted that for practical purposes they may be considered insoluble.

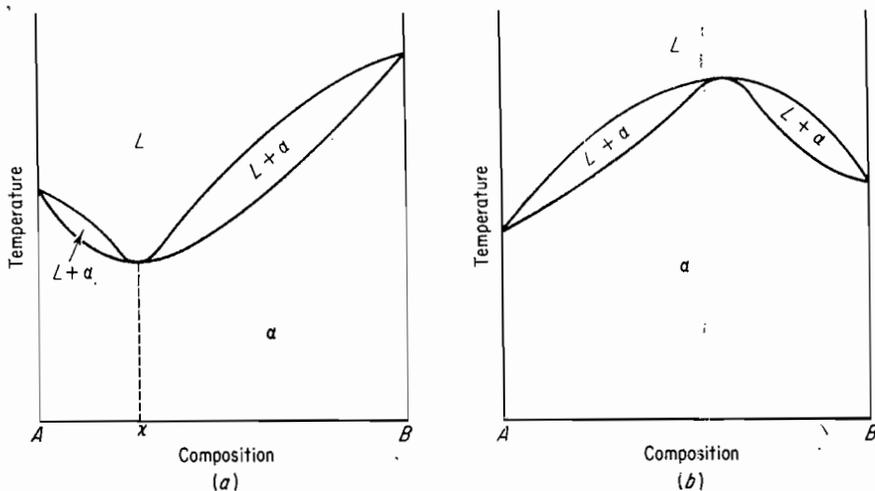


Fig. 6-14 (a) Solid-solution system showing a minimum.
 (b) Solid-solution system showing a maximum.

Raoult's law states that the freezing point of a pure substance will be lowered by the addition of a second substance provided the latter is soluble in the pure substance when liquid and insoluble when solidified. The amount of lowering of the freezing point is proportional to the molecular weight of the solute.

This phase diagram can be developed from a series of cooling curves in a manner analogous to that used for the solid solution diagram described previously, but in this case, the experimental curves show a different kind of behavior. The series of cooling curves for the pure metals and various alloys, and the room-temperature microstructures, are shown in Fig. 6-15. The cooling curves for the pure metals *A* and *B* show a single horizontal line at their freezing points, as expected. As *B* is added to *A*, the temperature for the beginning of solidification is lowered. As *A* is added to *B*, the temperature for the beginning of solidification for those alloys is also

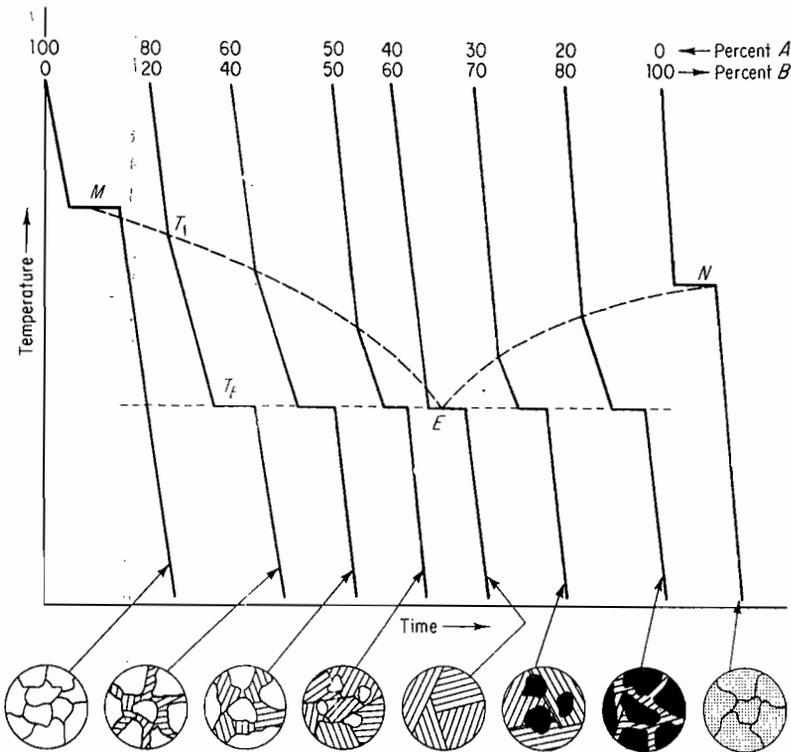


Fig. 6-15 Cooling curves and room-temperature microstructures for a series of alloys of two metals that are insoluble in the solid state. The upper dotted line indicates the form of the liquidus and the lower dotted line the form of the solidus line.

lowered. Therefore, since each metal lowers the freezing point of the other, the line connecting the points showing the beginning of solidification, the liquidus line, must show a minimum. This is illustrated by the upper dotted line in Fig. 6-15, showing a minimum at point E known as the eutectic point, for a composition of 40A-60B. Notice that over a wide range of compositions, a portion of the cooling curve that shows the end of solidification occurs at a fixed temperature. This lower horizontal line at T_E , shown dotted in Fig. 6-15, is known as the eutectic temperature. In one alloy, the eutectic composition 40A-60B, complete solidification occurs at a single temperature, the eutectic temperature. Although the freezing of the eutectic composition thus resembles that of a pure metal, it is not a congruent melting alloy since we will shortly see that the resulting solid is composed of two phases.

The actual phase diagram may now be constructed by transferring the breaks on the cooling curves to a plot of temperature vs. composition, as shown in Fig. 6-16. The melting points of the two pure metals, points M and N , are plotted on the vertical lines that represent the pure metals. For an alloy containing 80A-20B the beginning of solidification T_i and the end of solidification T_E are plotted as shown. The same procedure is followed for the remaining alloys. The upper line on the phase diagram connecting the two melting points, MEN , is the liquidus line and shows the beginning of solidification. The point at which the liquidus lines intersect, the minimum point E , is known as the eutectic point. T_E is called the eutectic temperature and 40A-60B the eutectic composition. The solidus line is always a continuous line connecting the melting points of the pure metals, so that the complete solidus line is $MFGN$.

This phase diagram consists of four areas. The area above the liquidus line is a single-phase homogeneous liquid solution, since the two metals are soluble in the liquid state. The remaining three areas are two-phase areas. Every two-phase area on a phase diagram must be bounded along a horizontal line by single phases. If the single-phase areas are labeled first, then the two-phase areas may be easily determined. For example, in Fig. 6-16, to determine the phases that exist in the two-phase area MFE , a horizontal tie line OL is drawn. This line intersects the liquidus at L , which means that the liquid is one of the phases existing in the two-phase area and intersects the left axis at point O . The left axis represents a single phase, the pure metal A , which below its melting point is solid. Therefore, the two phases existing in the area MFE are liquid and solid A . The same reasoning is applied to determine the two phases that exist in area NEG . These are liquid and solid B . The above ideas may be applied to any phase diagram and will be useful to the student for the labeling of more complex diagrams.

Since the two metals are assumed to be completely insoluble in the solid

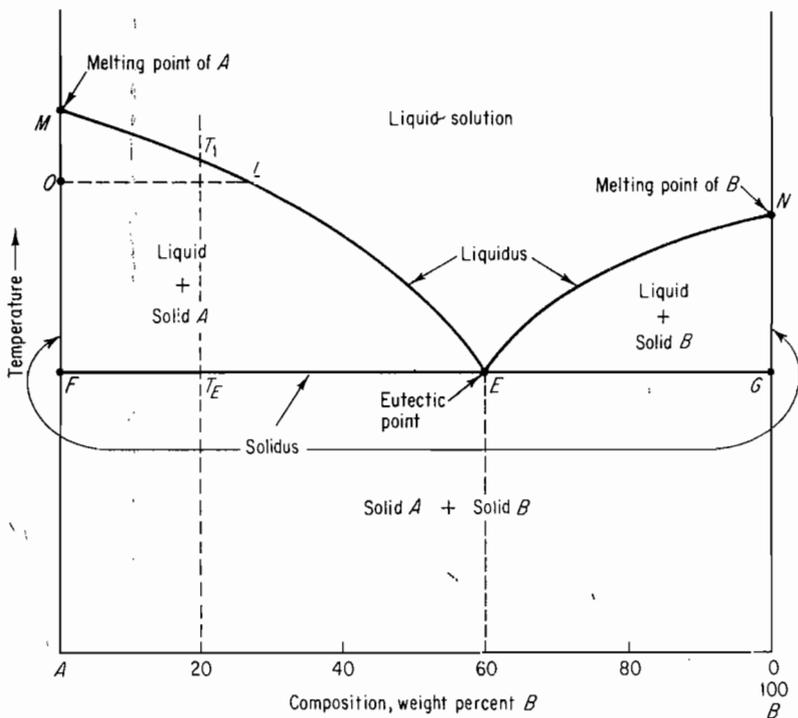
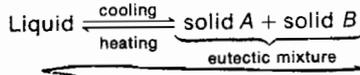


Fig. 6-16 Eutectic-type phase diagram.

state, it should be apparent that when freezing starts the only solid that can form is a pure metal. Also, every alloy when completely solidified must be a mixture of the two pure metals. It is common practice to consider alloys to the left of the eutectic composition as *hypoeutectic alloys* and those to the right as *hypereutectic alloys*. The way in which solidification takes place is of interest and will now be studied by following the slow cooling of several alloys.

Alloy 1 in Fig. 6-17 is the eutectic composition 40A-60B. As it is cooled from temperature T_0 , it remains a uniform liquid solution until point E, the eutectic-temperature line, is reached. Since this is the intersection of the liquidus and solidus lines, the liquid must now start to solidify, and the temperature cannot drop until the alloy is completely solid. The liquid will solidify into a mixture of two phases. These phases are always the ones that appear at either end of the horizontal eutectic-temperature line, in this case point F, which is the pure metal A, and point G, the pure metal B. Let us assume that a small amount of pure metal A is solidified. This leaves the remaining liquid richer in B; the liquid composition has shifted slightly to the right. To restore the liquid composition to its equilibrium value, B

will solidify. If slightly too much *B* is solidified, the liquid composition will have shifted to the left, requiring *A* to solidify to restore equilibrium. Therefore, at constant temperature, the liquid solidifies alternately pure *A* and pure *B*, resulting in an extremely fine mixture usually visible only under the microscope. This is known as the *eutectic mixture* (Fig. 6-18). The change of this liquid of composition *E* into two solids at constant temperature is known as the *eutectic reaction* and may be written as



Since solidification of the eutectic alloy occurs at constant temperature, its cooling curve would be the same as that for a pure metal or any congruent-melting alloy. The eutectic solidification, however, is incongruent since there is a difference in composition between the liquid and the individual solid phases.

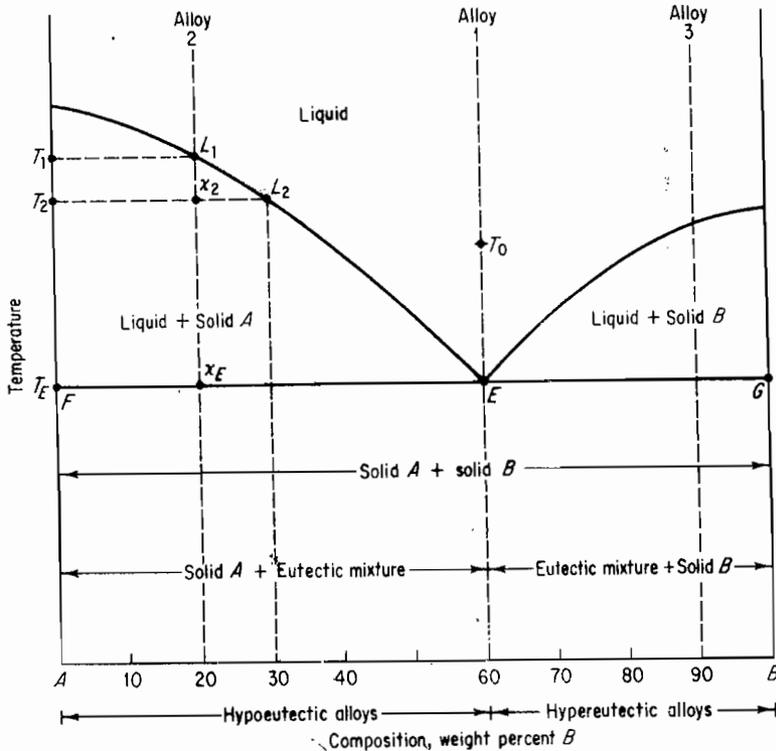


Fig. 6-17 Eutectic-type phase diagram.

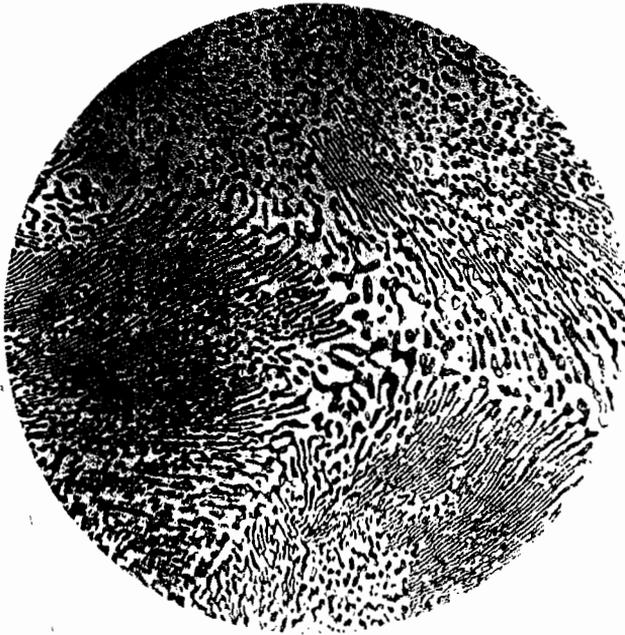


Fig. 6-18 Lead-bismuth eutectic mixture, 100X. (Research Laboratories, National Lead Company.)

Alloy 2, a hypoeutectic alloy composed of 80A-20B, remains a uniform liquid solution until the liquidus line, temperature T_1 , is reached. At this point the liquid L_1 is saturated in A, and as the temperature is dropped slightly, the excess A must solidify. The liquid, by depositing crystals of pure A, must become richer in B. Applying Rule I at temperature T_2 shows the solid phase to be pure A and the liquid composition L_2 as 70A-30B. The amount which has solidified up to this temperature would be found by applying Rule II:

$$A \text{ (percent)} = \frac{x_2 L_2}{T_2 L_2} \times 100 = \frac{10}{30} \times 100 = 33 \text{ percent}$$

$$L_2 \text{ (percent)} = \frac{T_2 x_2}{T_2 L_2} \times 100 = \frac{20}{30} \times 100 = 67 \text{ percent}$$

The microstructure would appear as in Fig. 6-19a. As solidification continues, the amount of pure solid A increases gradually by continued precipitation from the liquid. The liquid composition, becoming richer in B, is slowly traveling downward and to the right along the liquidus curve, while the amount of liquid is gradually decreasing. When the alloy reaches x_E , the eutectic line, the liquid is at point E. The conditions existing just

a fraction of a degree above T_E are:

Phases	Liquid	Solid A
Composition	40A-60B	100A
Relative amount	$\frac{T_E X_E}{T_E E} \times 100 = 33\%$	$\frac{x_E E}{T_E E} \times 100 = 67\%$

The microstructure would appear as in Fig. 6-19b. The remaining liquid (33 percent), having reached the eutectic point, now solidifies into the fine intimate mixture of A and B as described under alloy 1. When solidified, the alloy will consist of 67 percent of grains of primary A or proeutectic A (which formed between T_1 and T_E or before the eutectic reaction) and 33 percent eutectic (A + B) mixture (Fig. 6-19c). Every alloy to the left of the eutectic point E, when solidified, will consist of grains of proeutectic A and the eutectic mixture. The closer the alloy composition is to the eutectic composition, the more eutectic mixture will be present in the solidified alloy (see microstructures in Fig. 6-15).

Alloy 3, a hypereutectic alloy composed of 10A-90B, undergoes the same cooling process as alloy 2 except that when the liquidus line is reached the liquid deposits crystals of pure B instead of A. As the temperature is decreased, more and more B will solidify, leaving the liquid richer in A. The amount of liquid gradually decreases, and its composition gradually moves down and to the left along the liquidus line until point E is reached at the eutectic temperature. The remaining liquid now solidifies into the eutectic (A + B) mixture. After solidification, the alloy will consist of 75 percent grains of primary B or proeutectic B and 25 percent eutectic (A + B) mixture. The student should verify these figures and sketch the microstructure at room temperature. Every alloy to the right of the eutectic point, when solidified, will consist of grains of proeutectic B and the eutectic mixture. The only difference will be in the relative amounts (see microstructures in Fig. 6-15). The relationship between alloy composition and

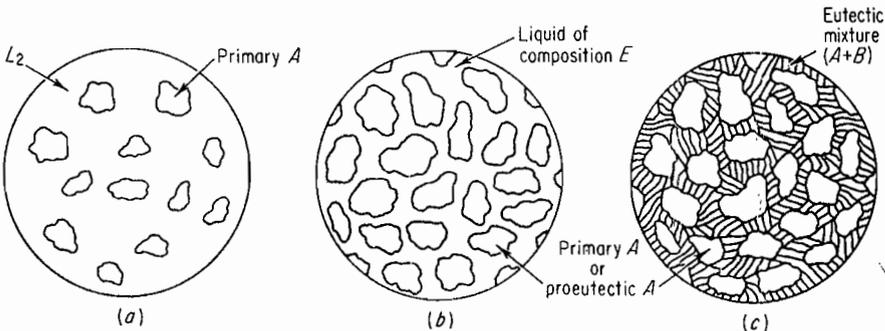
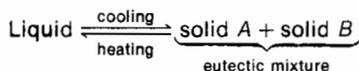


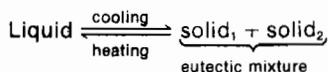
Fig. 6-19 Stages in the slow cooling of an 80A-20B alloy.

microstructure may be shown by using the eutectic composition as an imaginary boundary line. The area below the solidus line and to the left of the eutectic composition is labeled solid *A* + eutectic mixture, and that to the right, solid *B* + eutectic mixture (Fig. 6-17). Figure 6-20 shows the relation between alloy composition and relative amounts.

From the previous discussion it is apparent that, regardless of alloy composition, the same reaction takes place whenever the eutectic-temperature line is reached, namely;



The above reaction applies specifically to this diagram; however, the eutectic reaction may be written in general as



the only requirement being that the eutectic mixture consist of two different solid phases. This mixture may be two pure metals, two solid solutions, two intermediate phases, or any combination of the above.

The simplified aluminum-silicon phase diagram is shown in Fig. 6-21, neglecting the slight solubility of silicon in aluminum. The numbers at the bottom of this diagram refer to the photomicrographs in Fig. 6-22. Beginning with alloy 1 at the left of Fig. 6-21, the microstructure of pure aluminum is shown in Fig. 6-22a. Alloy 2 (Fig. 6-22b), containing 8 percent silicon, consists of dendrites of primary or proeutectic aluminum surrounded by the eutectic mixture of aluminum and silicon. Notice the fine alternate light and dark structure of the eutectic. Since the eutectic is formed from

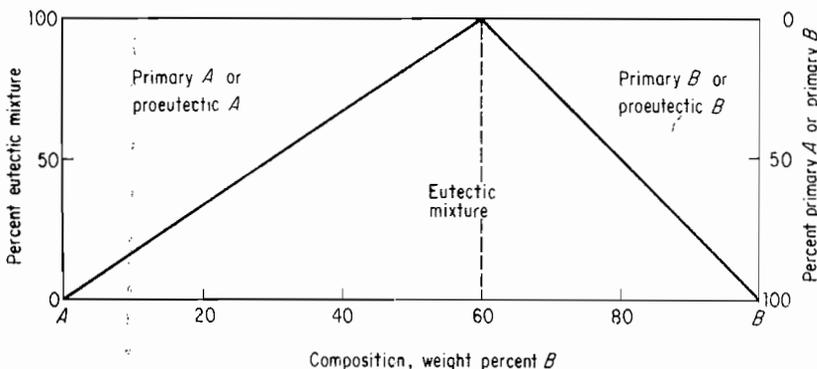


Fig. 6-20 Diagram showing the linear relationship between the parts of the microstructure and alloy composition for the eutectic system of Fig. 6-17.

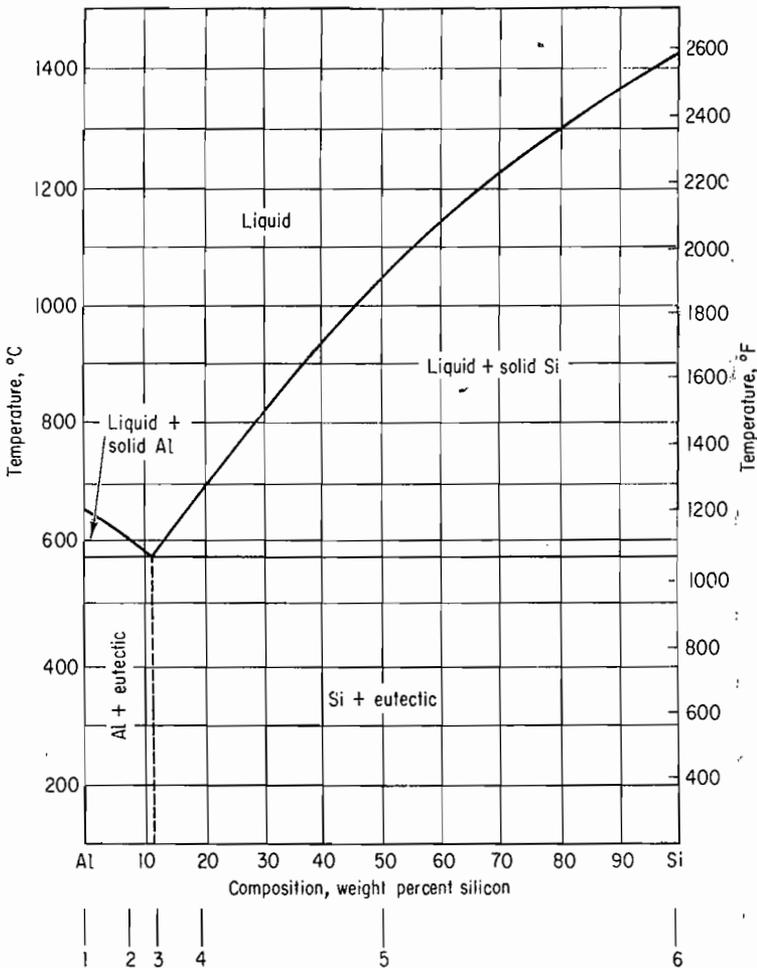


Fig. 6-21 Simplified aluminum-silicon phase diagram. The numbers on the bottom correspond to the photomicrographs in Fig. 6-22.

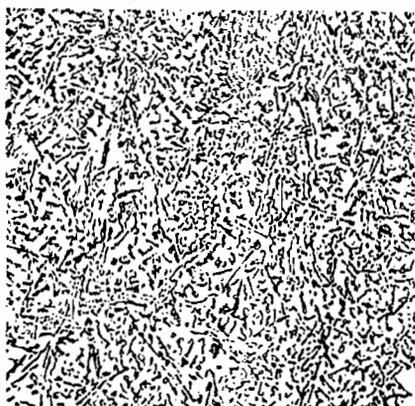
the last liquid to solidify, it fills the spaces between the arms of the dendrites. Alloy 3 (Fig. 6-22c) is the eutectic composition of 12 percent silicon and consists entirely of the eutectic mixture. As we move to the right, the microstructure will consist of primary silicon (black) and the eutectic mixture, the amount of primary silicon increasing with increasing silicon content as shown in Fig. 6-22d and e. Finally, Fig. 6-22f shows the microstructure of pure silicon. It is therefore possible to predict from an equilibrium diagram, with reasonable accuracy, the proportions of each phase which will exist in an alloy after slow cooling to room temperature.



(a) Alloy 1. 99.95% Al



(b) Alloy 2. 8% Si



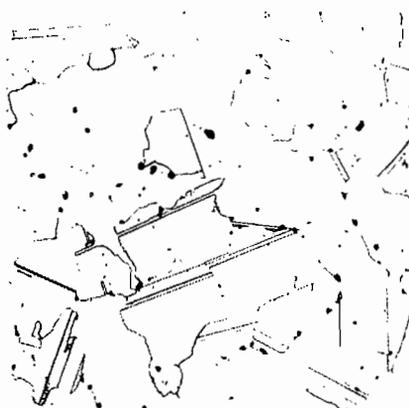
(c) Alloy 3. 12% Si



(d) Alloy 4. 20% Si



(e) Alloy 5. 50% Si



(f) Alloy 6. Pure Si

Fig. 6-22 Photomicrographs of aluminum-silicon alloys as numbered at the bottom of Fig. 6-21. (Research Laboratories, Aluminum Company of America.)

6-14 Type III—Two Metals Completely Soluble in the Liquid State but Only Partly Soluble in the Solid State Since most metals show some solubility for each other in the solid state, this type is the most common and, therefore, the most important alloy system.

From the discussion of the previous two types, it is assumed that the student is familiar with the method of determining a phase diagram from a series of cooling curves. The remaining types will be drawn and studied directly.

The phase diagram of this type is shown in Fig. 6-23. The melting points of the two pure metals are indicated at points T_A and T_B , respectively. The liquidus line is T_AET_B , and the solidus line is T_AFEGT_B . The single-phase areas should be labeled first. Above the liquidus line, there is only a single-phase liquid solution. At the melting points, where the liquidus and solidus lines meet, the diagram resembles the cigar-shaped diagram of Type I (complete solid solubility), and since these metals are partly soluble in the solid state, a solid solution must be formed. Alloys in this system never solidify crystals of pure A or pure B but always a solid solution or mixture of solid solutions. The single-phase α (alpha) and β (beta) solid-solution

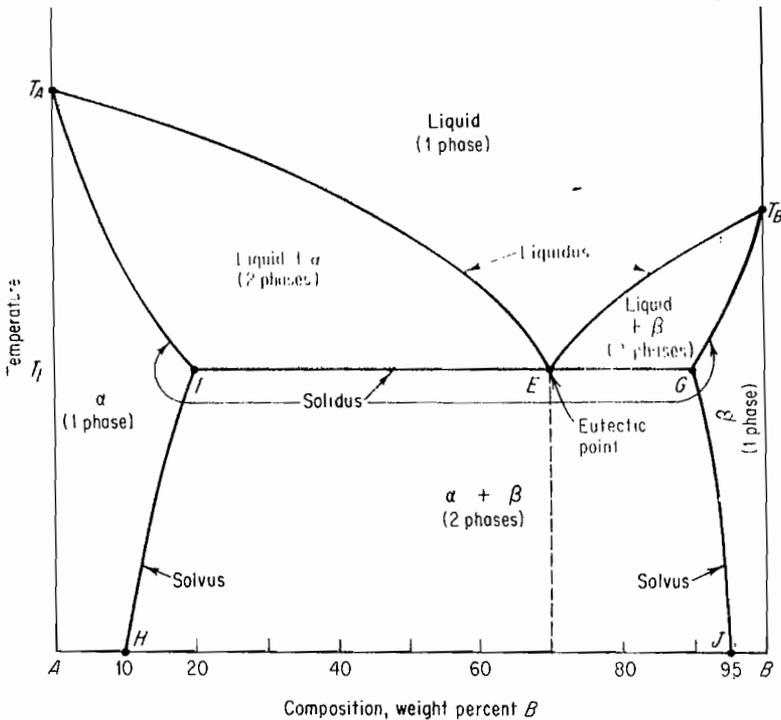


Fig. 6-23 Phase diagram illustrating partial solid solubility.

areas are now labeled. Since these solid solutions are next to the axes, they are known as *terminal solid solutions*. The remaining three two-phase areas may now be labeled as liquid + α , liquid + β , and $\alpha + \beta$. At T_E , the α solid solution dissolves a maximum of 20 percent B as shown by point F and the β solid solution a maximum of 10 percent A as shown by point G. With decreasing temperature, the maximum amount of solute that can be dissolved decreases, as indicated by lines FH and GJ. These lines are called *solvus* lines and indicate the maximum solubility (saturated solution) of B in A (α solution) or A in B (β solution) as a function of temperature. Point E, where the liquidus lines meet at a minimum, as in Type II, is known as the *eutectic point*. The slow cooling of several alloys will now be studied.

Alloy 1 (Fig. 6.24), composed of 95A-5B, when slow-cooled will follow a process exactly the same as any alloy in Type I: When the liquidus line is crossed at T_1 , it will begin to solidify by forming crystals of α solid solution extremely rich in A. This process continues, with the liquid getting richer in B and gradually moving down along the liquidus line. The α

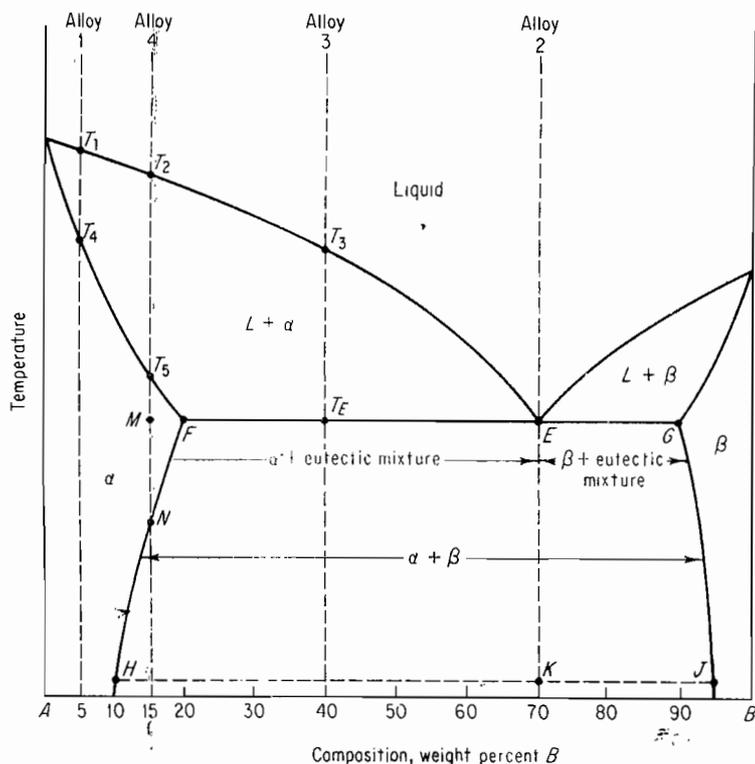


Fig. 6.24 Phase diagram illustrating partial solid solubility.

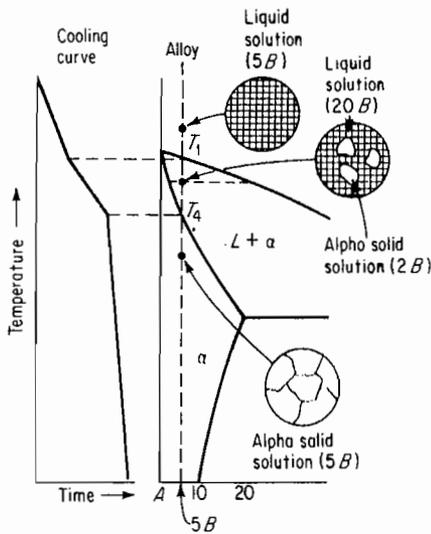
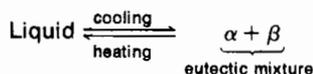


Fig. 6-25 The cooling curve and microstructure at various temperatures during solidification of a 95A-5B alloy.

solid solution, also getting richer in B, is moving down along the solidus line. When the solidus line is finally crossed at T_4 and with diffusion keeping pace with crystal growth, the entire solid will be a homogeneous α solid solution and will remain that way down to room temperature. The process of solidification and the cooling curve for this alloy are shown in Fig. 6-25.

Alloy 2, 30A-70B, is the eutectic composition and remains liquid until the eutectic temperature is reached at point E. Since this is also the solidus line, the liquid now undergoes the eutectic reaction, at constant temperature, forming a very fine mixture of two solids. The two solids that make up the eutectic mixture are given by the extremities of the eutectic-temperature line, α of composition F and β of composition G. The eutectic reaction can be written as



This reaction is the same as the one which occurred in the Type II diagram, except for the substitution of solid solutions for pure metals. The relative amounts of α and β in the eutectic mixture may be determined by applying Rule II (lever rule):

$$\alpha \text{ (percent)} = \frac{EG}{FG} \times 100 = \frac{20}{70} \times 100 = 28.6 \text{ percent}$$

$$\beta \text{ (percent)} = \frac{EF}{FG} \times 100 = \frac{50}{70} \times 100 = 71.4 \text{ percent}$$

Because of the change in solubility of B in A , line FH , and of A in B , line GJ , there will be a slight change in the relative amounts of α and β as the alloy is cooled to room temperature. The relative amounts of α and β at room temperature are

$$\alpha \text{ (percent)} = \frac{KJ}{HJ} \times 100 = \frac{25}{85} \times 100 = 29.4 \text{ percent}$$

$$\beta \text{ (percent)} = \frac{HK}{HJ} \times 100 = \frac{60}{85} \times 100 = 70.6 \text{ percent}$$

The eutectic mixture is shown in Fig. 6-29c. Notice the similarity between this picture and the eutectic mixture formed in Type II (Fig. 6-18). It is not possible to tell microscopically whether the eutectic mixture is made up of two solid solutions or two pure metals.

Alloy 3, 60A-40B, remains liquid until the liquidus line is reached at T_3 . The liquid starts to solidify crystals of primary or proeutectic α solid solution very rich in A . As the temperature decreases the liquid becomes richer and richer in B , gradually moving down and to the right along the liquidus line until it reaches point E . Examining the conditions which exist just above the eutectic temperature T_E , there are two phases present:

Phases	Liquid	Primary α
Chemical composition	30A-70B	80A-20B
Relative amounts	40%	60%

The student should verify the above numbers by applying Rules I and II at the eutectic temperature. Since the remaining liquid (40 percent) is at point E , the right temperature and composition to form the eutectic mixture, it now solidifies by forming alternately crystals of α and β of the composition appearing at the ends of the eutectic temperature line (points F and G). The temperature does not drop until solidification is complete, and when complete, the microstructure appears as shown in Fig. 6-26.

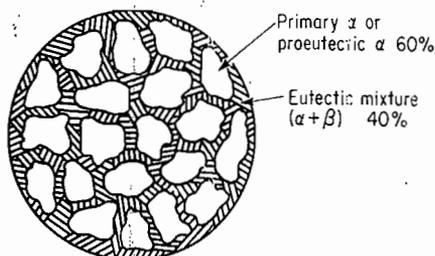


Fig. 6-26 Schematic picture of the microstructure, after solidification, of alloy 3 in Fig. 6-24.

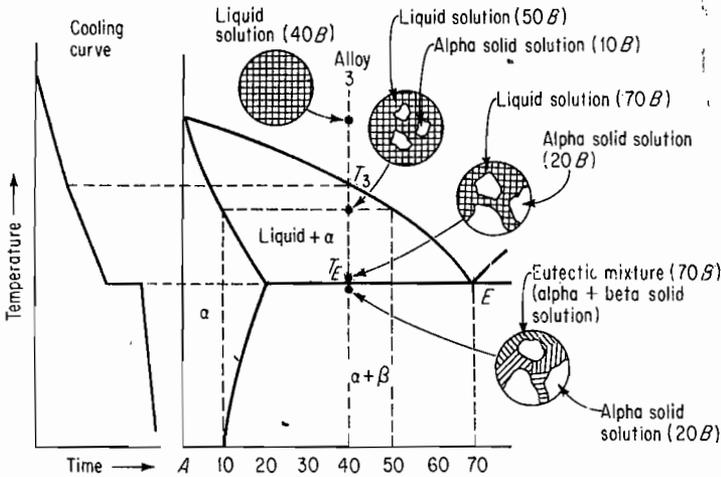


Fig. 6-27 The cooling curve and microstructure at various temperatures during solidification of a 60A-40B alloy.

Notice the similarity in microstructure between this alloy and Fig. 6-19c. As the alloy cools to room temperature because of the change in solubility indicated by the solvus line FH , some excess β is precipitated from the solution. The process of solidification and the cooling curve for this alloy are shown in Fig. 6-27.

Alloy 4, 85A-15B, follows the same process as described for alloy 1. The microstructure at various temperatures and the cooling curve for this alloy are shown in Fig. 6-28. Solidification starts at T_2 and is complete at T_3 , the resultant solid being a homogeneous single phase, the α solid solution. At point M the solution is unsaturated. The solvus line FH , as explained previously, shows the decrease in solubility of B in A with decreasing temperature. As the alloy cools, the solvus line is reached at point N . The α solution is now saturated in B . Below this temperature, under conditions of slow cooling, the excess B must come out of solution. Since A is soluble in B , the precipitate does not come out as the pure metal B , but rather the β solid solution. At room temperature, the alloy will consist largely of α with a small amount of excess β , primarily along the grain boundaries (Fig. 6-28). The student should determine the amount of excess β by applying the lever rule at the line HJ (Fig. 6-24).

If the β phase is relatively brittle, the alloy will not be very strong or ductile. The strength of an alloy to a large extent is determined by the phase that is continuous through the alloy. In this case, although the β solution constitutes only about 5 percent of the alloy, it exists as a continuous network along the grain boundaries. Therefore, the alloy will tend to rupture along these boundaries. This alloy, however, may be made to undergo a

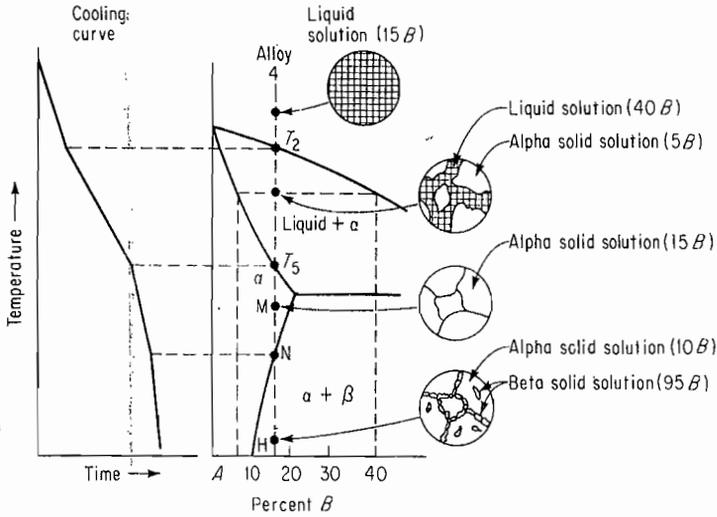
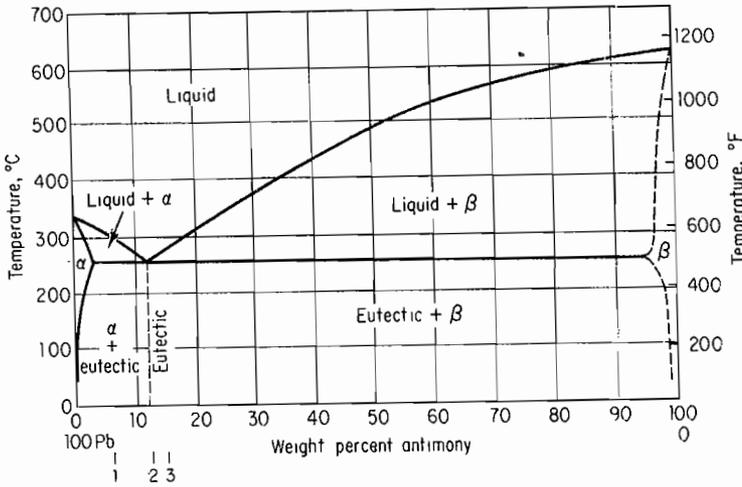


Fig. 6-28 The cooling curve and microstructure at various temperatures for an 85A-15B alloy.

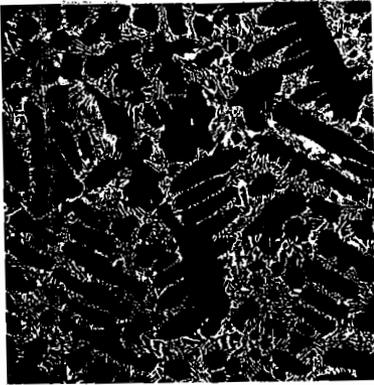
significant change in strength and hardness after being properly heat-treated.

The lead-antimony equilibrium diagram and photomicrographs of various alloys in this system are shown in Fig. 6-29. Alloy 1 (Fig. 6-29b), containing 6.5 percent antimony, illustrates a typical hypoeutectic structure of primary α dendrites (black) and the eutectic mixture filling the spaces between the dendrites. Alloy 2 (Fig. 6-29c), containing 11.5 percent antimony, consists entirely of the eutectic mixture of α and β solid solutions. To the right of the eutectic composition, the alloys consist of primary β (white) surrounded by the eutectic mixture (Fig. 6-29d) and differ only in the relative amounts of the phases present. The amount of the eutectic mixture decreases as the alloy composition moves away from the eutectic composition.

The lead-tin equilibrium diagram and photomicrographs of various alloys in this system are shown in Fig. 6-30. Alloy 1 (Fig. 6-30b), containing 70 percent tin, is to the right of the eutectic composition. The microstructure consists of primary β dendrites (white) surrounded by the eutectic mixture. Alloy 2 (Fig. 6-30c) is the eutectic composition and consists entirely of a very fine mixture of α and β solid solutions. Alloys 3 and 4 (Fig. 6-30d and e), containing 60 and 50 percent tin, respectively, consist of dendrites of the lead-rich primary α solid solution (black) surrounded by the eutectic mixture, the amount of α increasing as the alloy composition moves to the left. Notice the similarity of the photomicrographs shown in Figs. 6-22, 6-29, and 6-30.



(a)



(b) Alloy 1

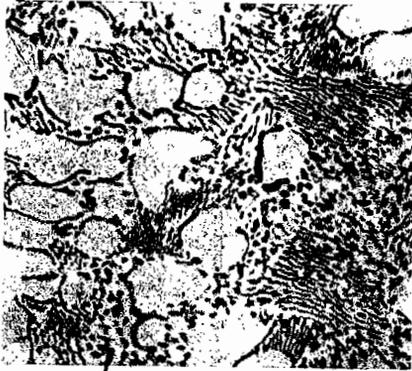
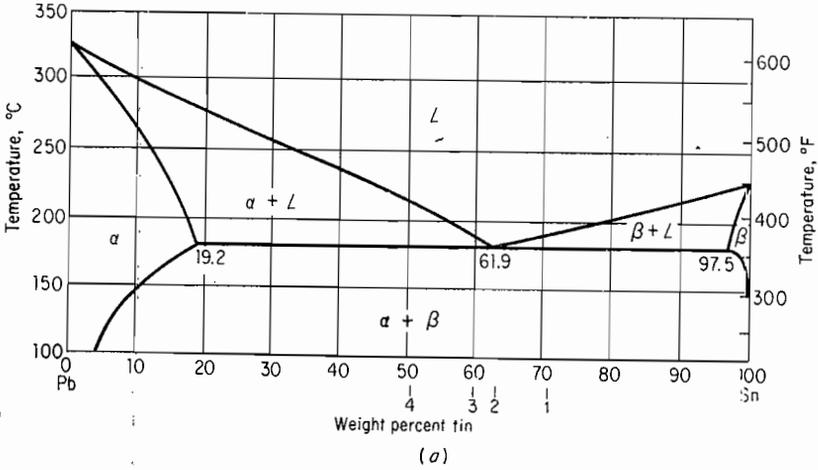


(c) Alloy 2

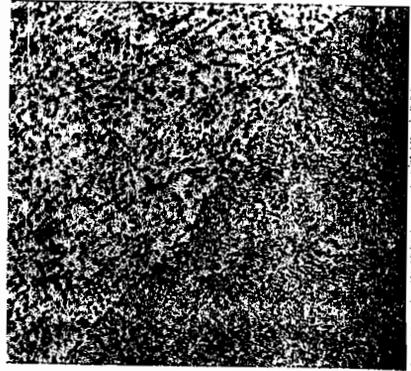


(d) Alloy 3

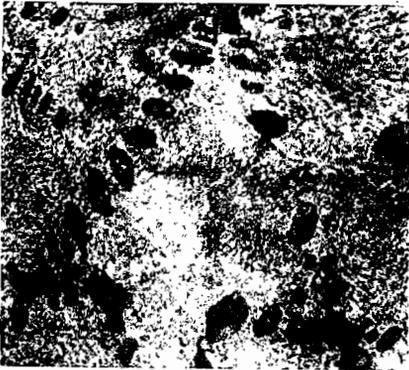
Fig. 6-29 (a) The lead-antimony equilibrium diagram. (b) 6.5 percent antimony alloy, 75X. (c) Eutectic alloy, 11.5 percent antimony, 250X. (d) 12.25 percent antimony alloy, 250X. (American Smelting and Refining Company.)



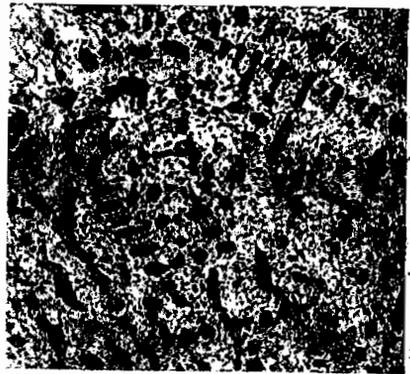
(b) Alloy 1



(c) Alloy 2



(d) Alloy 3



(e) Alloy 4

Fig. 6-30 (a) The lead-tin equilibrium diagram. (b) 70 percent tin alloy. (c) Eutectic alloy. (d) 60 percent tin alloy. (e) 50 percent tin alloy. All photomicrographs at 200X. (From H. Manko, "Solders and Soldering," McGraw-Hill Book Company, New York, 1964.)

6-15 Properties in Eutectic Alloy Systems It was shown in Fig. 6-20 that there is a linear relationship between the constituents appearing in the microstructure and the alloy composition for a eutectic system. This would seem to indicate that the physical and mechanical properties of a eutectic system should also show a linear variation. In actual practice, however, this ideal behavior is rarely found. The properties of any multiphase alloy depend upon the individual characteristics of the phases and how these phases are distributed in the microstructure. This is particularly true for eutectic alloy systems. Strength, hardness, and ductility are related to the size, number, distribution, and properties of the crystals of both phases. In many commercially important eutectic alloy systems, one phase is relatively weak and plastic while the other phase is relatively hard and brittle. As the eutectic composition is approached from the plastic-phase side, there will be an increase in the strength of the alloy. There will be a decrease in strength beyond the eutectic composition due to the decrease in the amount of the small eutectic particles and the increase in size and amount of the proeutectic brittle phase. Therefore, in this kind of system the eutectic composition will generally show maximum strength. This is illustrated in Fig. 6-31, which shows the variation in tensile strength and elongation for cast aluminum-silicon alloys containing up to 14 percent silicon. The tensile strength shows a maximum at very near the eutectic composition. The aluminum-silicon phase diagram is given in Fig. 6-21.

Another important point is that the resulting properties of a mixture most nearly resemble those of the phase which is continuous—that is, the phase that forms the background or matrix in which particles of the other phase are imbedded. The eutectic mixture is always the microconstituent which is continuous, since it is the last liquid to solidify and surrounds the primary grains. It is generally true that the phase which makes up the greater proportion in the eutectic mixture will be the continuous phase. If this phase

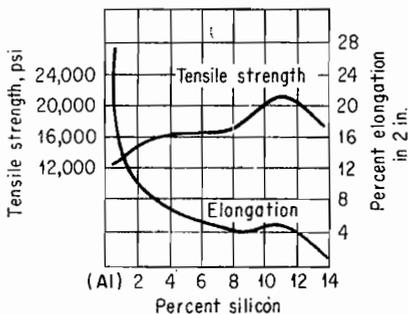


Fig. 6-31 Variation of typical properties of cast aluminum-silicon alloys up to 14 percent silicon. (From Guy, "Elements of Physical Metallurgy," Addison-Wesley Publishing Co., Reading, Mass., 1959.)

is plastic, the entire series of alloys will show some plasticity. If this phase is brittle, the entire series of alloys will be relatively brittle.

In addition to the above factors, an increase in cooling rate during freezing may result in a finer eutectic mixture, a greater amount of eutectic mixture, and smaller primary grains, which in turn will influence the mechanical properties considerably.

6-16 Age Hardening There are only two principal methods for increasing the strength and hardness of a given alloy: cold working or heat treatment. The most important heat-treating process for nonferrous alloys is age hardening, or precipitation hardening. In order to apply this heat treatment, the equilibrium diagram must show partial solid solubility, and the slope of the solvus line must be such that there is greater solubility at a higher temperature than at a lower temperature. These conditions are satisfied by Fig. 6-24. Let us consider the left side of the diagram involving the α solid solution. Alloy compositions that can be age-hardened are usually chosen between point *F* containing 20 percent *B* and point *H* containing 10 percent *B*. Commercially, most age-hardenable alloys are chosen of compositions slightly to the left of point *F*, although the maximum hardening effect would be obtained by an alloy containing 20 percent *B*. The phase which is dissolved may be a terminal solid solution, as in this case, or an intermediate alloy phase.

Two stages are generally required in heat treatment to produce age hardening: solution treatment and aging.

Solution Treatment If alloy 4 (Fig. 6-24, microstructure shown in Fig. 6-32a) is reheated to point *M*, all the excess β will be dissolved and the structure will be a homogeneous α solid solution. The alloy is then cooled rapidly (quenched) to room temperature. A supersaturated solution results, with the excess β trapped in solution. The quench is usually carried out in a cold-water bath or by a water spray. Drastic quenching tends to set

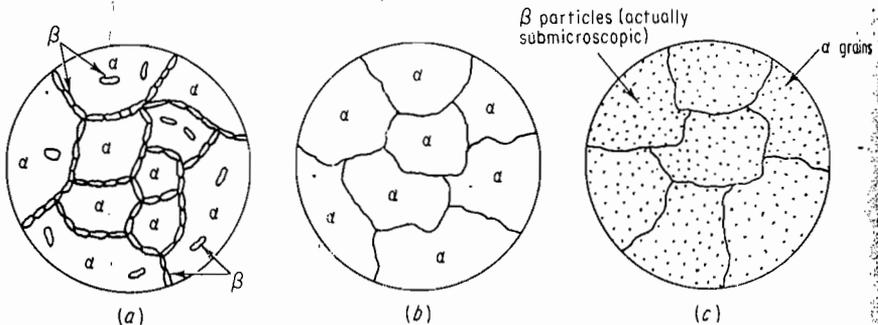


Fig. 6-32 Microstructure of an 85A-15B alloy. (a) After slow cooling; (b) after reheating and rapid cooling to room temperature; (c) after aging.

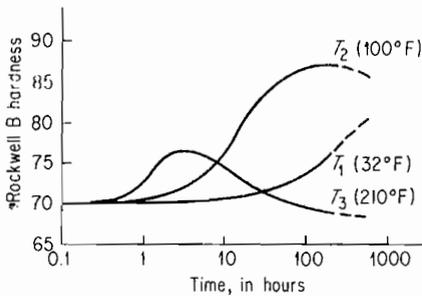


Fig. 6-33 Effect of temperature on the aging curves during precipitation hardening. Curves are for a 0.06 percent carbon steel. (After Davenport and Bain.)

up stresses which often result in distortion, especially if the parts are intricately designed. In such instances, boiling water may be used as a quench medium to minimize distortion. If α is a ductile phase, the alloy will be ductile immediately after quenching. This allows warped or distorted parts to be straightened easily. The straightening operations should be carried out as soon as possible after quenching. The microstructure is shown schematically in Fig. 6-32b.

Aging Process The alloy, as quenched, is a supersaturated solid solution and is in an unstable state. The excess solute will tend to come out of solution. The speed at which precipitation occurs varies with temperature. Figure 6-33 shows the effect of three temperatures on the aging curves of an iron alloy. At the low temperature the diffusion rate is so slow that no appreciable precipitation occurs. At T_3 , hardening occurs quickly, due to rapid diffusion, but softening effects are also accelerated, resulting in a lower maximum hardness. The optimum temperature seems to be T_2 , at which maximum hardening occurs within a reasonable length of time. Those alloys in which precipitation takes place at room temperature—so that they obtain their full strength after 4 or 5 days at room temperature—are known as *natural-aging* alloys. Those alloys which require reheating to elevated temperatures to develop their full strength are *artificial-aging* alloys. However, these alloys also age a limited amount at room temperature, the rate and extent of the strengthening depending upon the alloys (see Table 6-2). Refrigeration retards the rate of natural aging. At 32°F, the beginning of the aging process is delayed for several hours, while dry ice (−50 to −100°F) retards aging for an extended period. Use is made of this fact in the aircraft industry when aluminum-alloy rivets, which normally age at room temperature, are kept in deep-freeze refrigerators until they are driven. The rivets have previously been solution-treated, and as a single phase they are very ductile. After being driven, aging will take place at room temperature, with a resulting increase in strength and hardness. In the early

TABLE 6-2 Effect of Aging on Properties of Aluminum Alloy 2014 (3.5 to 4.5 Percent Copper)

ALLOY AND CONDITION	ULTIMATE STRENGTH, PSI	YIELD STRENGTH, PSI	ELONGATION, % IN 2 IN.	BHN, 500 KG, 10 MM	SHEAR STRENGTH, PSI
Annealed	27,000	14,000	18	45	18,000
Solution-treated, naturally aged	62,000	42,000	20	105	38,000
Solution-treated, artificially aged	70,000	60,000	13	135	42,000

theory of the aging process, it was thought that the excess phase comes out of solution as fine submicroscopic particles, many of which fall on the slip planes (Fig. 6-32c). These particles were considered to have a keying action, thereby interfering with movement along planes of ready slip, thus increasing strength and hardness.

Subsequent studies have led to a more complete understanding of the age-hardening process. The strengthening of a heat-treatable alloy by aging is not due merely to the presence of a precipitate. It is due to both the uniform distribution of a finely dispersed submicroscopic precipitate and the distortion of the lattice structure by those particles before they reach a visible size.

It is not possible to state definitely in what manner precipitate particles harden the matrix or solvent lattice. While there are several theories of precipitation hardening, the most useful is the *coherent lattice theory*. After solution treatment and quenching, the alloy is in a supersaturated condition, with the solute atoms distributed at random in the lattice structure, Fig. 6-34a. During an incubation period, the excess solute atoms tend to migrate to certain crystallographic planes, forming *clusters* or embryos of the precipitate. During aging, these clusters form an intermediate crystal structure, or *transitional lattice*, maintaining registry (coherency) with the lattice structure of the matrix. The excess phase will have different lattice parameters from those of the solvent, and as a result of the atom matching (coherency), there will be considerable distortion of the matrix, Fig. 6-34b. The distortion of the matrix extends over a larger volume than would be the case if the excess phase were a discrete particle. It is this distortion that interferes with the movement of dislocations and accounts for the rapid increase in hardness and strength during aging (see Fig. 6-35). Eventually, the equilibrium excess phase is formed with its own lattice structure (Fig. 6-34c). This causes a loss of coherency with the matrix and less distortion. Hardness and strength will decrease, and the alloy is "over-aged." There will now be a boundary between the excess phase and the matrix so that the precipitated particle will be visible under the microscope. Electrical conductivity decreases during aging because of lattice distortion;

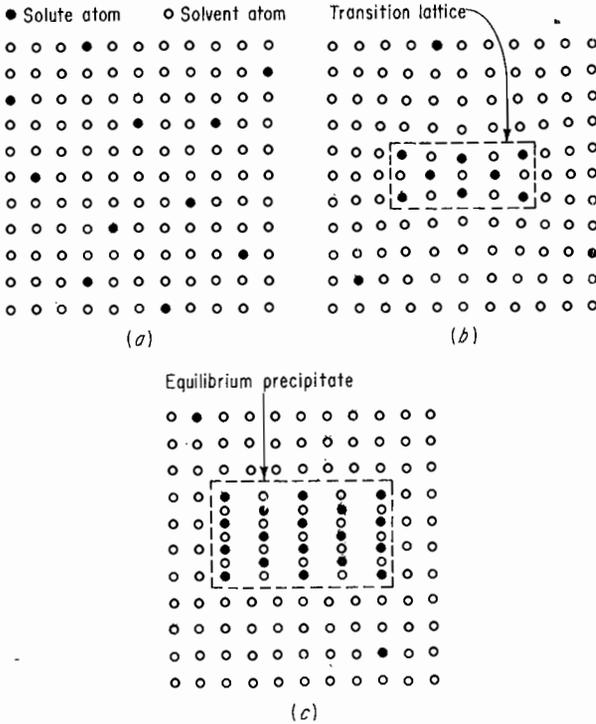


Fig. 6-34 The stages in the formation of an equilibrium precipitate. (a) Supersaturated solid solution. (b) Transition lattice coherent with the solid solution. (c) Equilibrium precipitate essentially independent of the solid solution. From Guy, "Elements of Physical Metallurgy," Addison-Wesley Publishing Company, Inc., Reading, Mass., 1959.)

then it increases when precipitation takes place. The effect of aging time on some properties is shown in Fig. 6-35.

Aging does not have the same effect on the properties of all alloys. In some alloys the change in hardness and strength may be small; in others the changes may be large. This is not due to the amount dissolved in excess of the saturation limit, but to the effect of the precipitate on lattice distortion. For example, magnesium can dissolve 46 percent lead at the eutectic temperature but only 2 percent lead at room temperature. With proper heat treatment, precipitation takes place but no age hardening occurs. This is due to the absence of a transition lattice and very little localized distortion during precipitation. On the other hand, if the precipitation involves extensive changes in the lattice, a large amount of distortion occurs with wide changes in properties. In this case, the greater the amount of metal dissolved in excess of the saturation limit, the greater the distortion produced and the greater will be the effect on hardness and

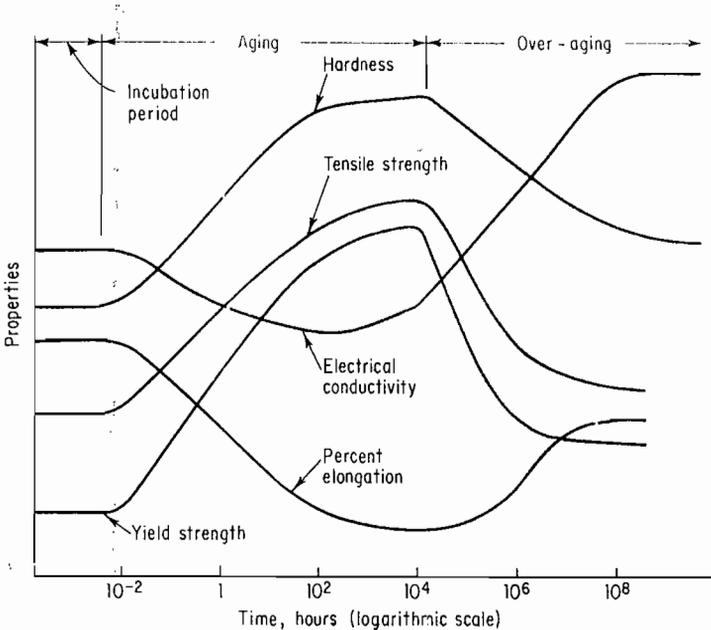


Fig. 6-35 Effect of aging time on properties. (By permission from L. F. Mondolfo and O. Zmeskal, "Engineering Metallurgy," McGraw-Hill Book Company, New York, 1955.)

strength. This is illustrated for some copper-beryllium alloys in Table 6-3. Figure 12-16 shows the copper-rich portion of the copper-beryllium alloy system. Notice that copper dissolves up to a maximum of 2.2 percent beryllium at 1600°F. At room temperature the solubility of beryllium in copper is approximately 0.2 percent. Referring to Table 6-3, while there is no difference in strength and hardness of both alloys after solution annealing (solution treatment), there is a difference after aging. The alloy containing 1.90–2.15 percent beryllium is closer to the maximum solubility of beryllium in copper, and upon aging more of the γ (gamma) phase will be precipitated, resulting in a greater hardness and strength as shown.

TABLE 6-3 Effect of Aging and Composition on the Mechanical Properties of Some Copper-Beryllium Alloys

ALLOY AND CONDITION	TENSILE STRENGTH, PSI	ELONGATION, % IN 2 IN.	ROCKWELL HARDNESS
1.90–2.15% Be:			
Solution-annealed	60,000–80,000	35–50	B 45–65
After aging	165,000–180,000	5–8	C 36–40
1.60–1.80% Be:			
Solution-annealed	60,000–80,000	35–50	B 45–65
After aging	150,000–165,000	5–8	C 33–37

6-17 Type IV—The Congruent-melting Intermediate Phase When one phase changes into another phase isothermally (at constant temperature) and without any change in chemical composition, it is said to be *congruent phase change* or *congruent transformation*. All pure metals solidify congruently. We have previously seen an example of a congruent-melting alloy as a variation of a Type I phase diagram. The alloy x in Fig. 6-14a goes from a liquid phase to a single solid phase at constant temperature without a change in composition, and it is therefore a congruent-melting alloy. Intermediate phases are so named because they are single phases that occur between the terminal phases on a phase diagram. Type IV will consider the formation of an intermediate phase by congruent melting, while Type V will cover the incongruent melting intermediate phase. Any intermediate phase may be treated as another component on a phase diagram. If the intermediate phase has a narrow range of composition, as do intermetallic compounds and interstitial compounds, it is then represented on the diagram as a vertical line and labeled with the chemical formula of the compound. If the intermediate phase exists over a range of composition, it is usually an electron compound and is labeled with a Greek letter. In recent years some authors tend to use Greek letters for all intermediate phases.

In Fig. 6-36, the intermediate alloy phase is shown as a vertical line. Since it is a compound, it is indicated as A_mB_n , where m and n are subscripts which indicate the number of atoms combined in the compound. For example, magnesium and tin form an intermediate phase which has the chemical formula Mg_2Sn . In this case, Mg is equivalent to A; 2 is equivalent to m ; tin, Sn, is equivalent to B; and n is equal to 1.

It is apparent from Fig. 6-36 that the A-B system may be separated into two independent parts, one to show all the alloys between A and the com-

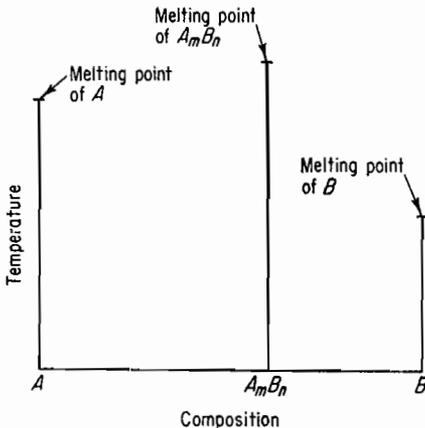
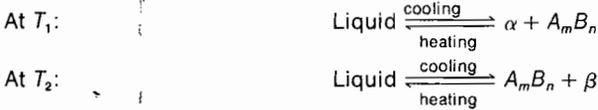


Fig. 6-36 Composition and melting point of pure A, pure B, and a compound A_mB_n .

pound A_mB_n , and the other to show those between A_mB_n and B . The portion of the diagram between A and A_mB_n may be any of the types studied in this chapter; similarly for the portion between A_mB_n and B . If the compound shows no solubility for either pure metal and the pure metals show some solubility for each other, the equilibrium diagram will be as shown in Fig. 6-37. This diagram shows two different eutectic mixtures. The eutectic equations may be written as follows:



The study of many actual systems that show the formation of several congruent-melting intermediate phases may be simplified by the above approach.

6-18 Type V—The Peritectic Reaction In the peritectic reaction a liquid and a solid react isothermally to form a new solid on cooling. The reaction is expressed in general as

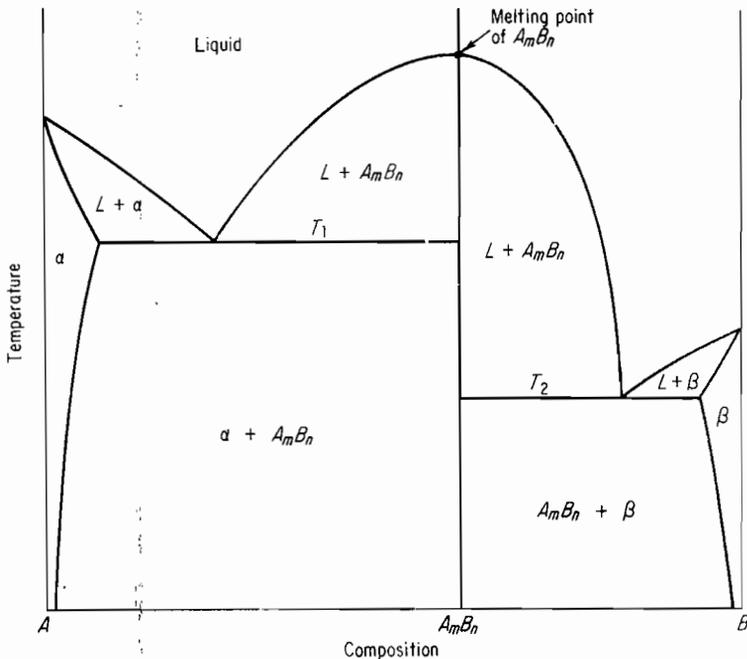
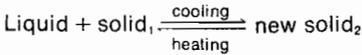


Fig. 6-37 Equilibrium diagram illustrating an intermediate alloy which is an intermetallic compound.

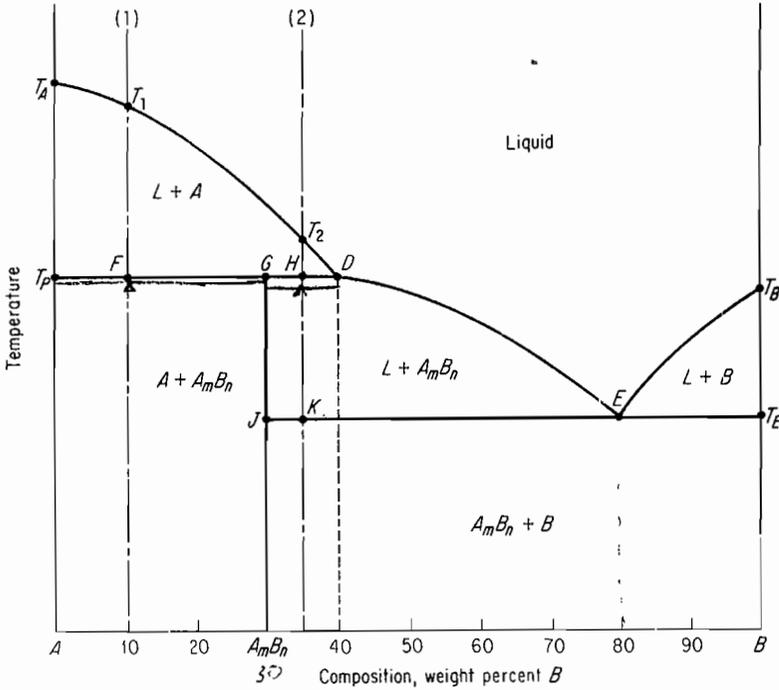


Fig. 6-38 Phase diagram showing the formation of an incongruent melting intermediate phase by a peritectic reaction.

The new solid formed is usually an intermediate phase (Fig. 6-38), but in some cases it may be a terminal solid solution (Fig. 6-39).

Consideration of Fig. 6-38 shows that the compound A_mB_n , 70A-30B, when heated to the peritectic temperature, point G, decomposes into two phases, liquid and solid A. Therefore, this is an example of an incon-

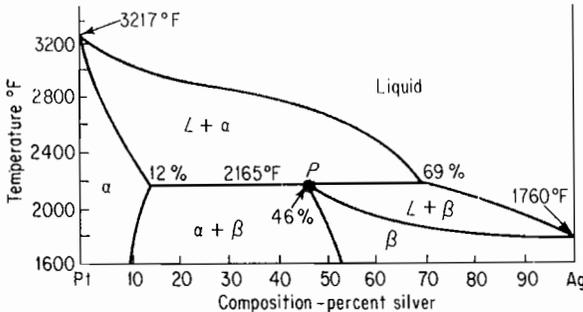


Fig. 6-39 Silver-platinum alloy system showing the formation of a terminal solid solution by a peritectic reaction.

gruents-melting intermediate alloy. The student should realize that the peritectic reaction is just the reverse of the eutectic reaction, where a single phase formed two new phases on cooling. The liquidus line is $T_A D E T_B$ and the solidus line is $T_A T_P G J T_B$. The peritectic-reaction line is $T_P D$. Notice that only part of this line, the length $T_P G$, coincides with the solidus line. The slow cooling of several alloys will now be studied.

Alloy 1, 90A-10B, remains liquid until the liquidus line is reached at T_1 . Solidification now takes place by forming crystals of the pure metal A. As the temperature falls, the liquid is decreasing in amount, and its composition is moving down along the liquidus line. Let us examine the conditions that exist just above the peritectic temperature T_p :

Phases	Liquid	Solid A
Composition	60A-40B	100 A
Relative amount	$\frac{T_p F}{T_p D} \times 100 = 25\%$	$\frac{F D}{T_p D} \times 100 = 75\%$

The conditions that exist just below the peritectic temperature are:

Phases	$A_m B_n$	Solid A
Composition	70A-30B	100 A
Relative amount	$\frac{T_p F}{T_p G} \times 100 = 33\%$	$\frac{F G}{T_p G} \times 100 = 67\%$

A first glance at these two areas seems to indicate that the liquid has disappeared at the horizontal line and in its place is the compound $A_m B_n$. Consideration of the chemical compositions shows that this is not possible. The liquid contains 60A, while $A_m B_n$ contains 70A. The liquid is not rich enough in A to form the compound by itself. The liquid must therefore react with just the right amount of solid A, in this case 8 percent, to bring its composition to that of the compound $A_m B_n$. The following reaction must have taken place at the peritectic temperature:

Composition:	60A	100A	70A
Equation:	Liquid + solid A		solid $A_m B_n$
Relative amount:	25%	8%	33%

The reaction takes place all around the surface of each grain of solid A where the liquid touches it. When the correct composition is reached, the layer solidifies into $A_m B_n$ material surrounding every grain of A. Further reaction is slow since it must wait for the diffusion of atoms through the peritectic wall of $A_m B_n$ in order to continue (see Fig. 6-40). When diffusion is completed, all the liquid will have been consumed, and since only 8 percent of pure A was required for the reaction, there will be 67 percent of A left. The final microstructure will show grains of primary A surrounded by

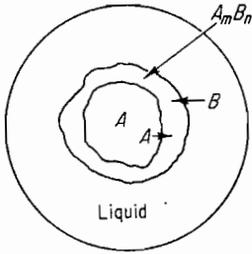


Fig. 6-40 Schematic picture of the peritectic reaction. Envelope of $A_m B_n$ increases in thickness by diffusion of A atoms outward and B atoms inward.

the compound $A_m B_n$. Figure 6-41 shows the microstructure at various temperatures in the slow cooling of this alloy. The story will be the same for any alloy to the left of point G. The only difference will be in the amount of excess A remaining after the peritectic reaction is complete. The closer the alloy composition is to the composition of the compound, the less primary A will remain.

Alloy 2, 65A-35B, solidifies pure A when the liquidus line is crossed at T_2 , and as solidification continues, the liquid becomes richer in B. When point H is reached, the liquid composition is 60A-40B. Applying the lever rule for this alloy, there is $\frac{35}{40} \times 100$ or 87.5 percent liquid and 12.5 percent solid A. Since the line GD is not part of the solidus line, some liquid must remain after the reaction takes place. It is therefore the solid A which must disappear in reacting with some of the liquid to form the compound $A_m B_n$.

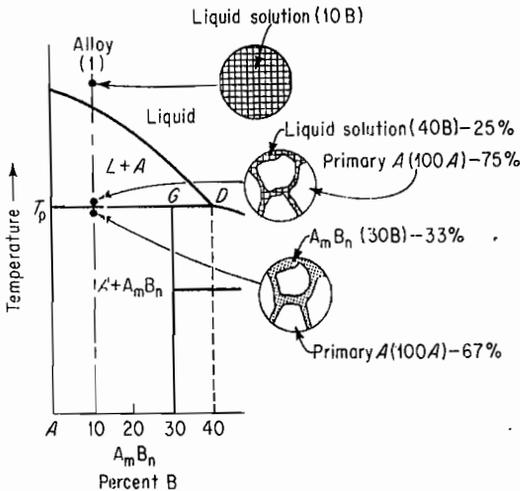
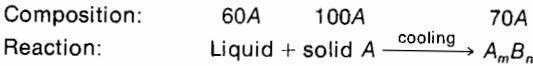


Fig. 6-41 Slow cooling of a 90A-10B alloy showing the microstructure at various temperatures.

The same reaction takes place again:



✓ The amount of liquid entering into the above reaction may be determined by applying the lever rule below the reaction temperature.

$$\text{Liquid (percent)} = \frac{GH}{DG} \times 100 = \frac{10}{20} \times 100 = 50 \text{ percent}$$

✓ Since there was 87.5 percent liquid before the reaction and 50 percent liquid after the reaction, it is apparent that 37.5 percent of the liquid reacted with 12.5 percent of solid A to give 50 percent of the compound A_mB_n at the peritectic temperature. As cooling continues, the liquid now separates crystals of A_mB_n . The liquid becomes richer in B, and its composition gradually moves down and to the right along the liquidus line until it reaches point E, the eutectic temperature. At this temperature, there is only $\frac{5}{50} \times 100$ or 10 percent liquid left. Since the liquid has reached the eutectic point, it now solidifies into the eutectic mixture of $A_mB_n + B$. This alloy, at room temperature, will consist of 90 percent primary or proeutectic A_mB_n surrounded by 10 percent of the eutectic ($A_mB_n + B$) mixture. Figure 6-42 shows the cooling curve and the changes in microstructure at various points in the slow cooling of this alloy.

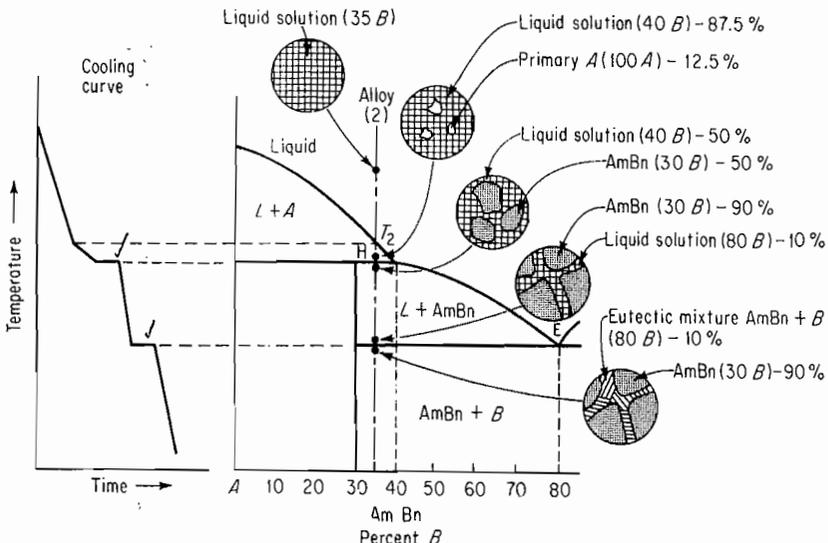


Fig. 6-42 The cooling curve and the microstructure at various temperatures during the slow cooling of a 65A-35B alloy.

Fig. 6
 alloy.
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The student should study the slow cooling of alloys on either side of the peritectic point P in the equilibrium diagram that illustrates the formation of a terminal solid solution by a peritectic reaction (Fig. 6-39).

The peritectic reaction was described under equilibrium conditions. In actual practice, however, this condition is rarely attained. Since the new phase forms an envelope around the primary phase, it will act as a hindrance to the diffusion which is essential to continue the reaction (see Fig. 6-40). As the layer of the new phase becomes thicker, the diffusion distance increases, so that the reaction is frequently incomplete. For example, according to the phase diagram of the silver-platinum alloy system, Fig. 6-39, a 60 percent Ag alloy should be a single phase β at room temperature. The actual cast structure, Fig. 6-43, however, is not a single phase. The light areas are primary α grains surrounded by the dark two-

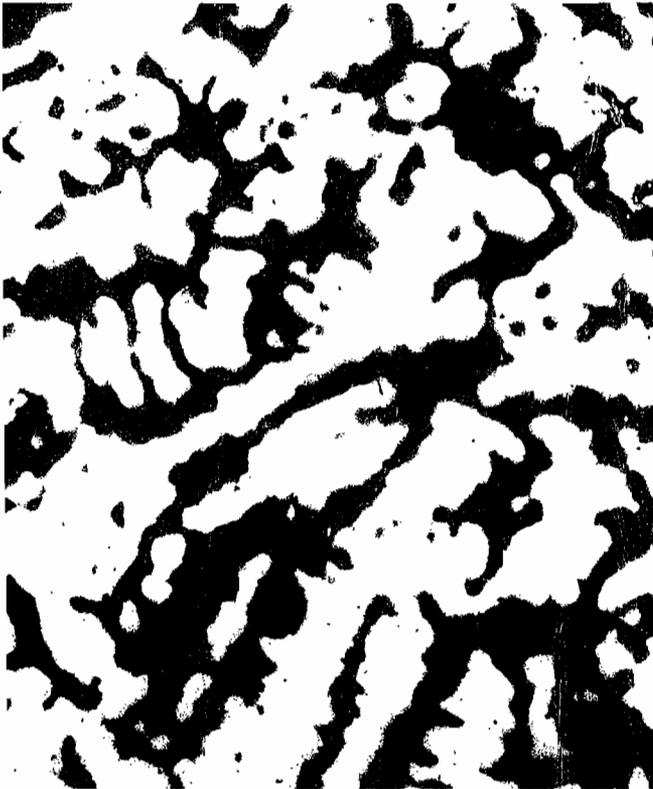


Fig. 6-43 40 percent Platinum + 60 percent silver cast alloy. Light areas are primary α ; dark two-toned areas are β . Magnification 100X. (By permission from F. N. Rhines, "Phase Diagrams in Metallurgy," McGraw-Hill Book Company, New York, 1956.)

toned areas of β , indicating that the peritectic reaction was not complete.

Since peritectic alloys are usually two-phase mixtures, their mechanical properties follow the same principles stated for eutectic alloys with two differences: (1) the individual phases are more likely to be different than predicted for equilibrium conditions, and (2) cast grain size is usually coarse.

6-19 Type VI—Two Liquids Partly Soluble in the Liquid State: The Monotectic Reaction In all the types discussed previously, it was assumed that there was complete solubility in the liquid state. It is quite possible, however, that over a certain composition range two liquid solutions are formed that are not soluble in each other. Another term for solubility is miscibility. Substances that are not soluble in each other, such as oil and water, are said to be immiscible. Substances that are partly soluble in each other are said to show a miscibility gap, and this is Type VI.

The equilibrium diagram for this type is shown in Fig. 6-44. The liquidus line is $T_A C F E T_B$, and the solidus line is $T_A T_E J T_B$. Alloys having compositions between point C and point F at a temperature just above T_M will consist of two liquid solutions, L_1 and L_2 . The lines CD and FG show the composition of the liquid phases in equilibrium with each other at higher temperatures. In most cases, these lines are shown dotted because experimental difficulties at high temperatures usually prevent an accurate determination of their position. Since these lines tend to approach each other, it is possible that at higher temperatures the area will be closed and a single homogeneous liquid solution will exist. This area should be treated like any other two-phase area, and the same rules may be applied to determine the chemical composition of L_1 and L_2 and their relative amounts at any temperature. L_1 is a liquid solution of B dissolved in A , whereas L_2 is a liquid solution of A dissolved in B .

Let us study the slow cooling of several alloys. Alloy x containing 10 percent B is a single-phase liquid solution L_1 , and it remains that way until the liquidus line is crossed at x_1 . Solidification starts by forming crystals of the pure metal A . The liquid becomes richer in B , gradually moving down and to the right along the liquidus line. When the alloy has reached the monotectic temperature line T_M at point x_2 , the liquid composition is given by point C , which is 80A and 20B. The horizontal line on any phase diagram indicates that a reaction must take place. What is the reaction in this case? Below the line, the two phases present are solid A and L_2 . Offhand, it seems that L_1 has disappeared and that in its place we have L_2 , but a more careful study of the diagram indicates that this could not have happened. The composition of L_2 is given by point F , which is 40A and 60B, whereas L_1 has a composition of 80A and 20B; so although L_1 has disappeared, by itself it could not have formed L_2 . Remember that L_1 is a liquid solution rich in A , whereas L_2 is a liquid solution rich in B . The problem is that L_1 has too

much A. Therefore, what must occur at the horizontal line is that enough solid A is precipitated from L_1 to bring its composition to the right one to form L_2 .

To prove this, we can apply Rule II both above and below the horizontal line T_M . Above the line we have 50 percent solid A ($10/20 \times 100$) and 50 percent L_1 . Below the line, we have 17 percent L_2 ($10/60 \times 100$) and 83 percent solid A. Therefore, at the horizontal line, the 50 percent of L_1 must have formed 17 percent L_2 and 33 percent solid A. The 33 percent, plus the 50 percent already existing, gives a total of 83 percent solid A as determined by the calculations. The reaction is summarized as follows:

Composition:	80A	40A	100A
Equation:	$L_1 \xrightarrow{\text{cooling}}$	$L_2 + \text{solid A}$	
Relative amount:	50%	17%	33%

When one liquid forms another liquid, plus a solid, on cooling, it is known as a monotectic reaction; the general equation for the monotectic reaction

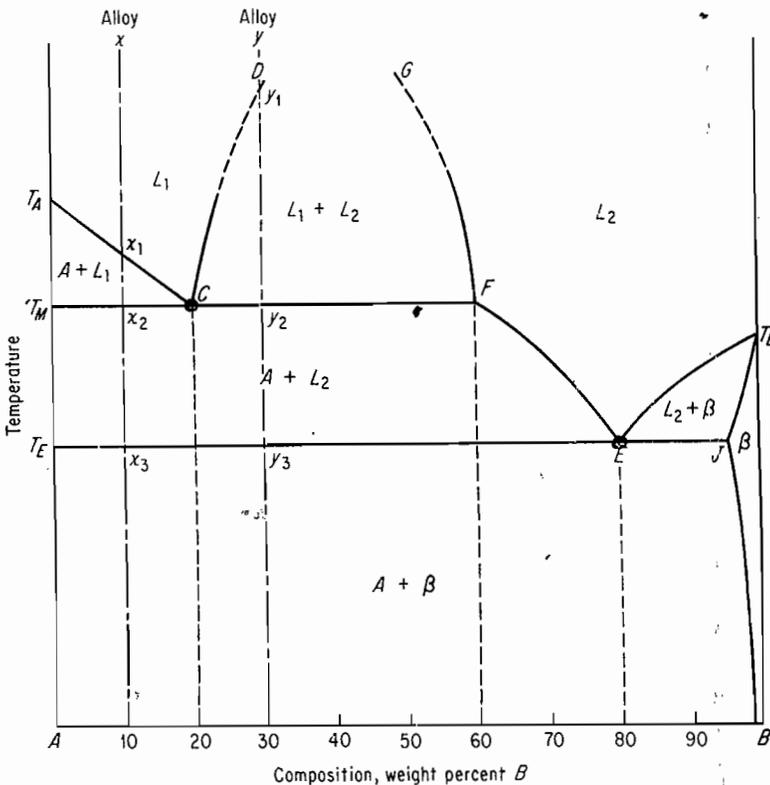
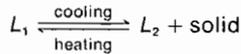


Fig. 6-44 Hypothetical equilibrium diagram of two metals partly soluble in the liquid state: the monotectic reaction.

may be written as.



Point *C* is known as the monotectic point. It should be apparent that the monotectic reaction resembles the eutectic reaction, the only difference being that one of the products is a liquid phase instead of a solid phase. It turns out that all known binary monotectic points in metal systems are located nearer the composition of the solid phase, so that the solid phase predominates in the reaction. In this case, 33 percent solid *A* was formed compared with 17 percent L_2 . As in the case of the eutectic, alloys to the left of point *C*, such as alloy *x*, are known as hypomonotectic alloys, whereas alloys to the right of point *C* up to point *F* are known as hypermonotectic alloys.

We now continue with the discussion of the slow cooling of alloy *x*. After the monotectic reaction is complete and as the temperature is dropped, more solid *A* will be formed from L_2 . When the eutectic temperature is reached at T_E , the alloy is at x_3 and L_2 will be at point *E*. This is the right temperature and right composition to form the eutectic mixture. The eutectic reaction now takes place, with L_2 forming a very fine mixture of solid *A*, plus solid β . The final microstructure will consist of 87.5 percent grains of primary *A* surrounded by 12.5 percent of the eutectic (*A* + β) mixture. The student should verify these percentages.

The occurrence of two liquids in the hypermonotectic alloys, that is, alloys of compositions between *C* and *F*, above the monotectic temperature, introduces structural considerations which have not been discussed up to this point. Given enough time, the two liquids will separate into two layers according to density, with the lighter layer on top. It is quite possible, however, to have two liquids existing as an emulsion wherein tiny droplets of one liquid remain suspended in the other liquid. Unfortunately, knowledge of this behavior with respect to metals is very limited at the present time.

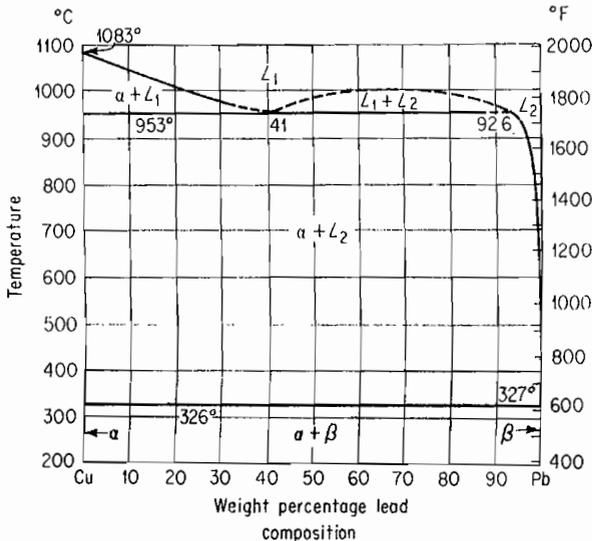
Consider the slow cooling of a hypermonotectic alloy *y* containing 70*A*-30*B*. At the elevated temperature, this alloy will be composed of a single homogeneous liquid phase L_1 . Upon cooling, the limit of liquid immiscibility is crossed at y_1 , and the second liquid L_2 will make its appearance, probably at the surface of the confining vessel, and possibly also at various points through the liquid bath. The composition of L_2 may be obtained by drawing a tie line in the two-phase region and applying Rule I. As the temperature decreases, the quantity of L_2 increases, so that just above the monotectic temperature, at point y_2 , the amount of L_2 present would be equal to $10/40 \times 100$, or 25 percent. Conditions being favorable, this liquid will exist as a separate layer in the crucible or mold. That portion of the

mixture which is composed of L_1 now reacts according to the monotectic equation to form more of $L_2 + \text{solid } A$. With continued cooling, more solid A is formed from L_2 , its composition becoming richer in B , until the eutectic temperature is approached at point y_3 . At that temperature, the remaining L_2 (37.5 percent) undergoes the eutectic reaction and solidifies into a very fine mixture of $A + \beta$.

An example of an alloy system showing a monotectic reaction is that between copper and lead given in Fig. 6-45. Notice that in this case the $L_1 + L_2$ region is closed. Also, although the terminal solids are indicated as α and β , the solubility is actually so small that they are practically the pure metals, copper and lead.

Type VII—Two Metals Insoluble in the Liquid and Solid States This will complete the study of basic phase or equilibrium diagrams that involve the liquid and solid states. If points C and F in Fig. 6-44 are moved in opposite directions, they will eventually hit the axes to give the diagram shown in Fig. 6-46. There are many combinations of metals which are practically insoluble in each other. When cooled, the two metals appear to solidify at their individual freezing points into two distinct layers with a sharp line of contact and almost no diffusion.

An alloy system which comes very close to this type is that between aluminum and lead shown in Fig. 6-47. Notice that the two-phase liquid region extends almost entirely across the diagram. This condition corresponds



6-45 The copper-lead equilibrium diagram. (From Metals Handbook, 1948 ed., p. 1200, American Society for Metals, Metals Park, Ohio.)

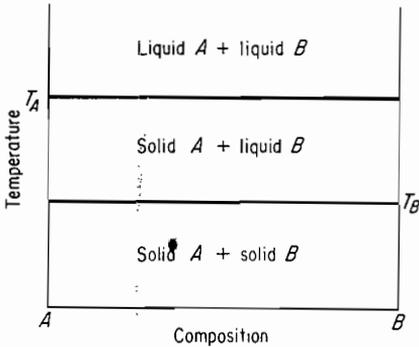


Fig. 6-46 Hypothetical equilibrium diagram for two metals insoluble in the liquid and solid states.

to a limiting case of the monotectic reaction and the eutectic reaction. The upper of the two horizontal lines represents a monotectic reaction in which the monotectic point is very close to the composition and melting point of pure aluminum. The lower horizontal line represents a eutectic reaction in which the eutectic point is practically coincident with the composition and melting point of pure lead.

6-21 Interrelation of Basic Types The various types of equilibrium diagrams that have been discussed may be combined in many ways to make up actual diagrams. It is important for the student to understand the interrelation

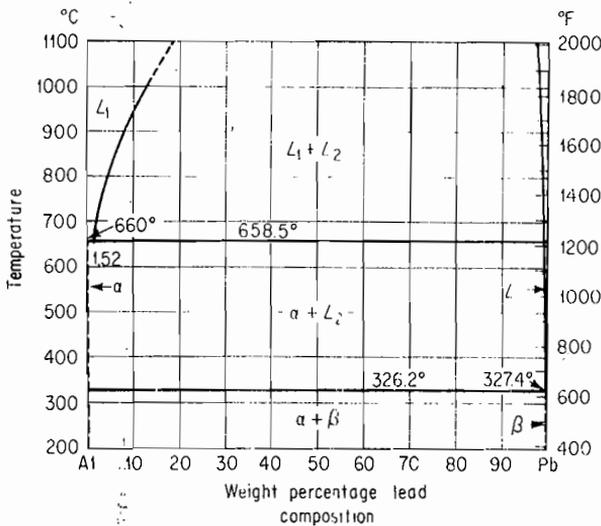
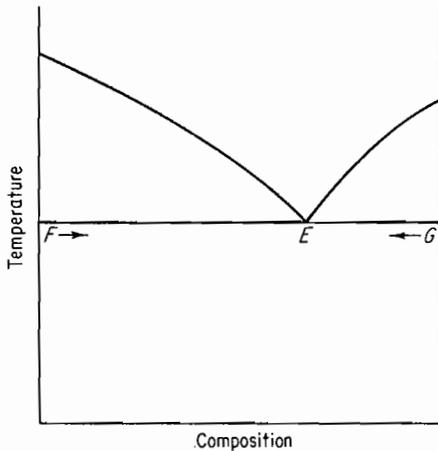


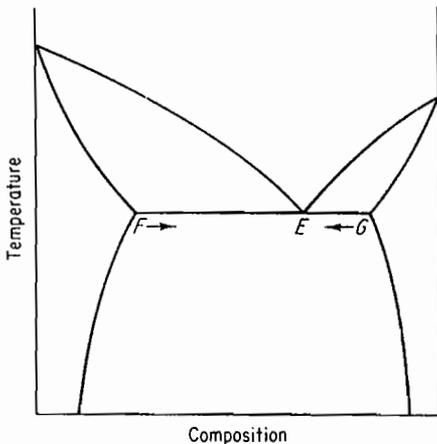
Fig. 6-47 The aluminum-lead alloy system. (From Metals Handbook, 1948 ed., p. 1165, American Society for Metals, Metals Park, Ohio.)

Fig. 6-4
solubili

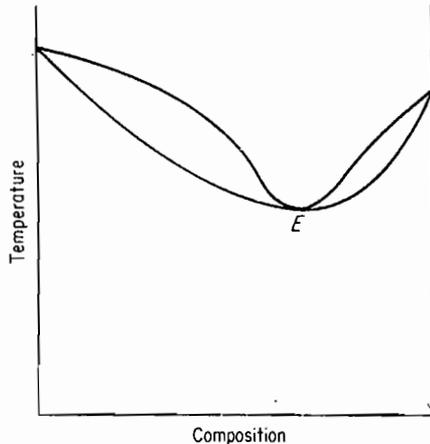
between the basic types to make the study of complex diagrams much simpler. The first three types differ only by the solubility in the solid state. Starting with a completely insoluble system of Type II (Fig. 6-48a), if the points at either end of the eutectic line (*F* and *G*) are moved toward each other, that is, toward greater solubility in the solid state, this will result in a diagram of Type III, partly soluble in the solid state (Fig. 6-48b). If they are moved until they coincide with the eutectic composition at *E*, a completely soluble system results (Fig. 6-48c). Types IV and V are determined by the intermediate phase. If this phase decomposes on heating (incongruent melting), the diagram will show a peritectic reaction. If the intermediate



(a) Insoluble in the solid state



(b) Partly soluble in the solid state



(c) Completely soluble in the solid state

Fig. 6-48 Interrelation of equilibrium diagrams as the solubility in the solid state is varied.

phase shows a true melting point (congruent melting), the diagram may show a eutectic reaction.

TRANSFORMATIONS IN THE SOLID STATE

There are several equilibrium changes and reactions which take place entirely in the solid state.

6-22 Allotropy During the discussion of metals and crystal structure in Chap. 2, it was pointed out that several metals may exist in more than one type of crystal structure depending upon temperature. Iron, tin, manganese, and cobalt are examples of metals which exhibit this property, known as *allotropy*. On an equilibrium diagram, this allotropic change is indicated by a point or points on the vertical line which represents the pure metal. This is illustrated in Fig. 6-49. In this diagram, the gamma solid-solution field is "looped." The pure metal A and alloys rich in A undergo two transformations. Many of the equilibrium diagrams involving iron such as Fe-Si, Fe-Mo, and Fe-Cr show this looped solid-solution field. Since the type of iron that exists in this temperature range is gamma iron, the field is usually called the *gamma loop*.

In some alloy systems involving iron, the gamma loop is not closed. This is illustrated by the iron-nickel equilibrium diagram shown in Fig. 6-50. This diagram shows the freezing point of pure iron at 1539°C (2795°F), forming the δ solid solution, which is body-centered cubic. The γ solid solution is formed by a peritectic reaction at 1512°C (2757°F). Notice that for pure iron the allotropic change from δ (b.c.c.) crystal structure to the γ (f.c.c.) form occurs at 1400°C (2554°F), but for the alloy this change begins at a higher

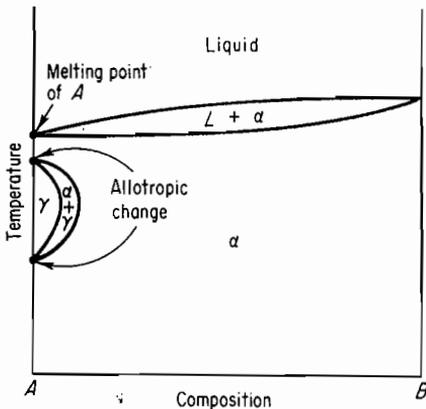


Fig. 6-49 Hypothetical equilibrium diagram showing metal A undergoing two allotropic changes.

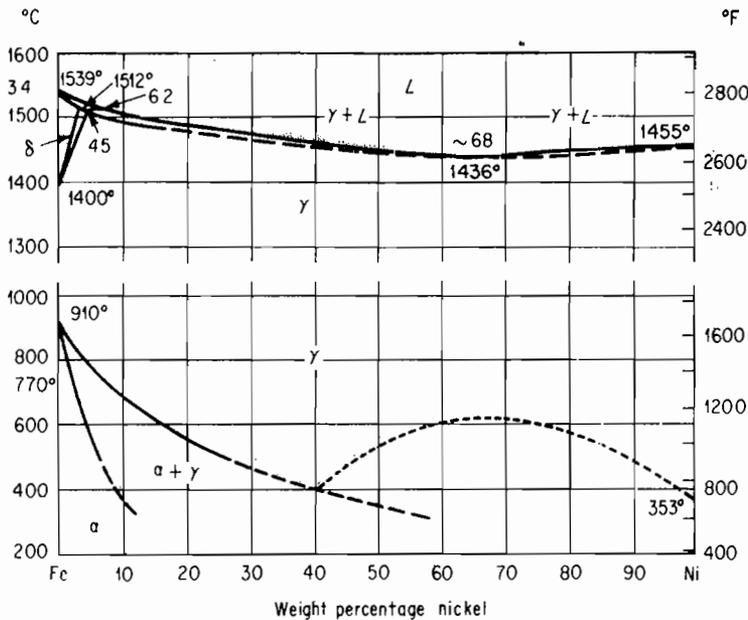


Fig. 6-50 The iron-nickel equilibrium diagram. (From Metals Handbook, 1948 ed., p. 1211, American Society for Metals, Metals Park, Ohio.)

temperature. The last allotropic change takes place at 910°C(1666°F), forming the α (b.c.c.) crystal structure.

6:23 Order-disorder Transformation Ordinarily in the formation of a substitutional type of solid solution the solute atoms do not occupy any specific position but are distributed at random in the lattice structure of the solvent. The alloy is said to be in a "disordered" condition. Some of these random solid solutions, if cooled slowly, undergo a rearrangement of the atoms where the solute atoms move into definite positions in the lattice. This structure is now known as an *ordered solid solution* or *superlattice* (Fig. 6-51). Ordering is most common in metals that are completely soluble in the solid state, and usually the maximum amount of ordering occurs at a simple atomic ratio of the two elements. For this reason, the ordered phase is sometimes given a chemical formula, such as AuCu and AuCu₃ in the gold-copper alloy system. On the equilibrium diagram, the ordered solutions are frequently designated as α' , β' , etc. or α' , α'' , etc., and the area in which they are found is usually bounded by a dot-dash line. The actual equilibrium diagram for the Au-Cu system is shown in Fig. 6-52.

When the ordered phase has the same lattice structure as the disordered phase, the effect of ordering on mechanical properties is negligible. Hard-

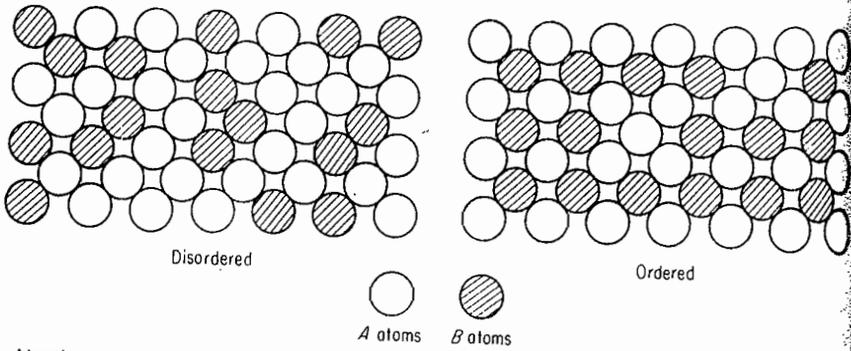


Fig. 6-51 Atomic arrangements in a disordered and ordered solid solution.

ening associated with the ordering process is most pronounced in those systems where the shape of the unit cell is changed by ordering. Regardless of the structure formed as a result of ordering, an important property change produced, even in the absence of hardening, is a significant reduction in electrical resistance (Fig. 6-53). Notice the sharp decrease in

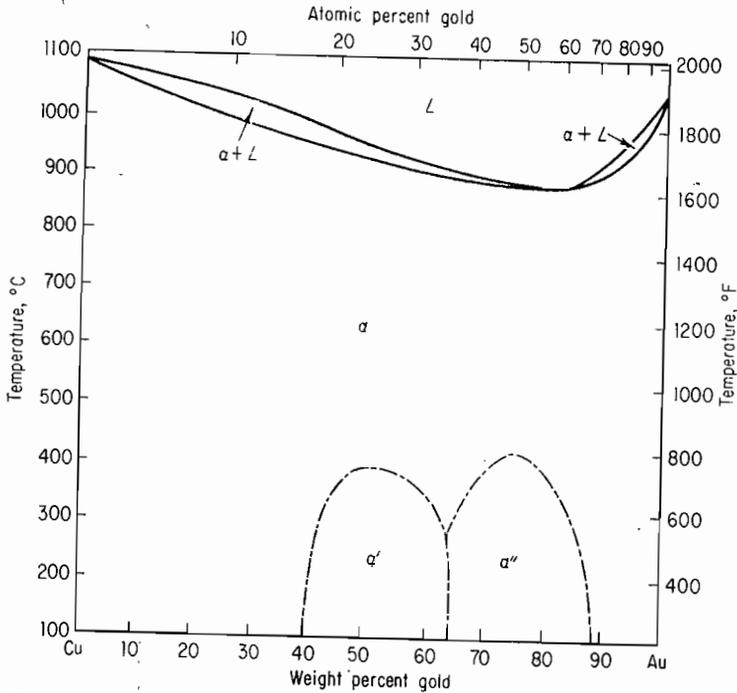


Fig. 6-52 The gold-copper equilibrium diagram. (From Metals Handbook, 1948., p. 1171, American Society for Metals, Metals Park, Ohio.)

Fig. 6-53 gold-copper Structure New York

Fig. 6-54 Handbook Metals Pa

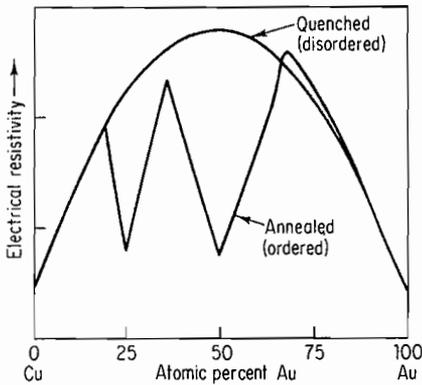


Fig. 6-53 Electrical resistivity vs. composition for the gold-copper system. (By permission from C. S. Barrett, "Structure of Metals," 2d. ed., McGraw-Hill Book Company, New York, 1952.)

electrical resistivity at the compositions which correspond to the ordered phases $AuCu_3$ and $AuCu$. In the gold-copper equilibrium diagram there was no two-phase region between the disordered and ordered solid solutions. In some cases there will be a two-phase region between the ordered and disordered solid solutions. Most frequently this is associated with the formation of a crystal structure which is different from that of the disordered phase from which it forms. This is illustrated by the copper-palladium alloy system shown in Fig. 6-54. This diagram shows three ordered phases: α' , α'' , and β . Copper and palladium are both face-cen-

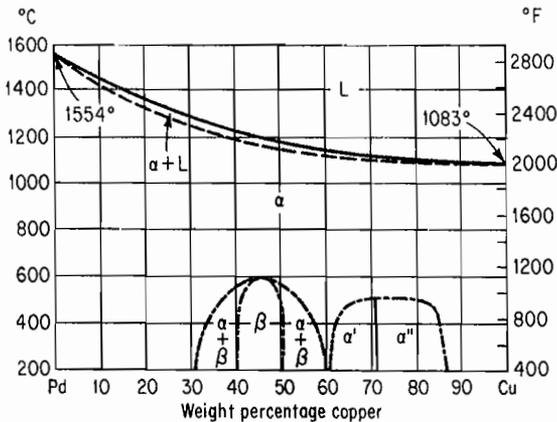
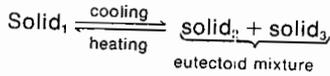


Fig. 6-54 The copper-palladium alloy system. (From Metals Handbook, 1948 ed., p. 1201, American Society for Metals, Metals Park, Ohio.)

tered cubic, and the ordered solutions α' and α'' are face-centered cubic; however, β is body-centered cubic and shows a two-phase region on each side.

6-24 The Eutectoid Reaction This is a common reaction in the solid state. It is very similar to the eutectic reaction but does not involve the liquid. In this case, a solid phase transforms on cooling into two new solid phases. The general equation may be written as



The resultant eutectoid mixture is extremely fine, just like the eutectic mixture. Under the microscope both mixtures generally appear the same, and it is not possible to determine microscopically whether the mixture resulted from a eutectic reaction or a eutectoid reaction. An equilibrium diagram illustrating the eutectoid reaction is shown in Fig. 6-55.

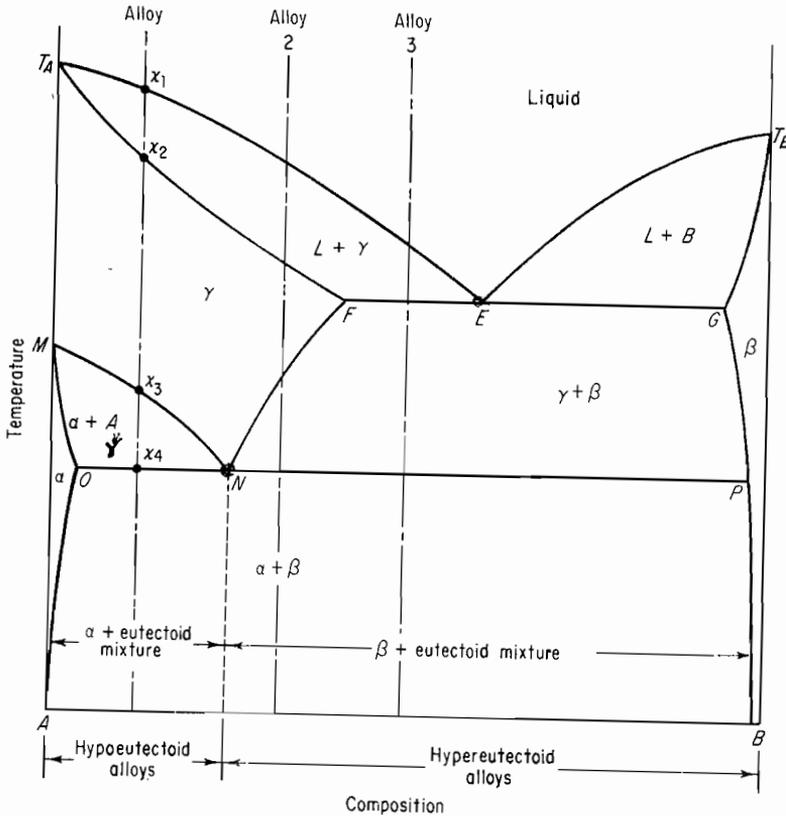
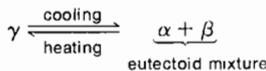


Fig. 6-55 Phase diagram illustrating the eutectoid reaction.

The liquidus line is T_AET_B and the solidus line is T_AFGT_B . The eutectic mixture is composed of the phases that occur at both ends of the eutectic temperature line, namely, γ solid solution (point F) and β solid solution (point G). Point M indicates an allotropic change for the pure metal A .

The significance of the solvus line MN is that, as the alloy composition is increased in B , the temperature at which the allotropic change takes place is decreased, reaching a minimum at point N . The solvus line FN shows the decrease in solubility of B in γ as the temperature is decreased. Point N is known as the *eutectoid point*. Its composition is the eutectoid composition, and the line OP is the eutectoid temperature line. Like the eutectic diagram, it is common practice to call all alloys to the left of the eutectoid composition *hypoeutectoid alloys* and those to the right of point N *hypereutectoid alloys*.

When the hypoeutectoid alloy 1 is slow-cooled, γ solid solution is formed when the liquidus line is crossed at x_1 . More and more γ is formed until the solidus line is crossed at x_2 . It remains a uniform solid solution until the solvus line is crossed at x_3 . The pure metal A must now start to undergo an allotropic change, forming the α solid solution. Notice that the α solid solution dissolves much less of B than does the γ solid solution. Some of the B atoms that are dissolved in the area that will undergo the allotropic change must now diffuse out of that area. When sufficient diffusion of B atoms has taken place, the remaining A atoms rearrange themselves into the new crystal structure, forming the α solid solution. The excess B atoms dissolve in the remaining γ solution, which becomes richer in B as the temperature falls. The composition of the remaining γ is gradually moving down and to the right along the solvus line MN . When the alloy reaches the eutectoid temperature x_4 , the remaining γ has now reached the eutectoid point N . The significance of the eutectoid line is that this temperature is the end of the crystal structure change that started at x_3 , and the remaining γ must now transform by the eutectoid reaction, forming alternate layers of α and β in an extremely fine mixture. The reaction may be written as



The microstructure at room temperature consists of primary α or proeutectoid α which was formed between x_3 and x_4 , surrounded by the eutectoid mixture of $\alpha + \beta$. This is shown in Fig. 6-56. In drawing the cooling curve for a given alloy from the phase diagram, it is important to remember that whenever a line is crossed on the phase diagram, there must be a corresponding break in the cooling curve. Also, when a horizontal line is crossed on the phase diagram, indicating a reaction, this will show on the cooling curve as a horizontal line. The cooling curve for alloy 1 is shown in Fig.

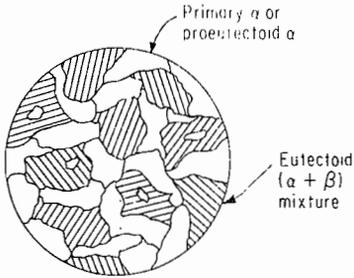
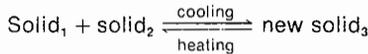


Fig. 6-56 Microstructure of a slow-cooled hypoeutectoid alloy, alloy 1 of Fig. 6-55.

6-57. The description of the slow cooling of the hypereutectoid alloys 2 and 3 is left as an exercise for the student.

6-25 The Peritectoid Reaction This is a fairly common reaction in the solid state and appears in many alloy systems. The peritectoid reaction may be written in general as



The new solid phase is usually an intermediate alloy, but it may also be a solid solution. The peritectoid reaction has the same relationship to the peritectic reaction as the eutectoid has to the eutectic. Essentially, it is the replacement of a liquid by a solid. Two hypothetical phase diagrams to illustrate the peritectoid reaction are shown in Figs. 6-58 and 6-59.

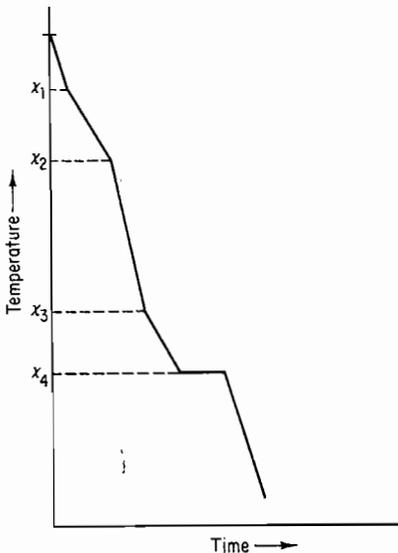


Fig. 6-57 Cooling curve for alloy 1 of Fig. 6-55.

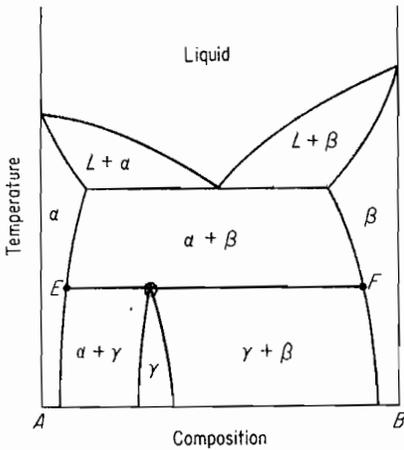
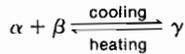


Fig. 6-58 Phase diagram showing the formation of an intermediate phase γ by a peritectoid reaction.

In Fig. 6-58, two solid phases α and β react at the peritectoid-temperature line EF to form an intermediate phase γ . The equation may be written as



In Fig. 6-59, two solid phases, the pure metal A and β solid solution, react at the peritectoid-temperature line CD to form a new solid phase, the terminal solid solution γ . The equation may be written as

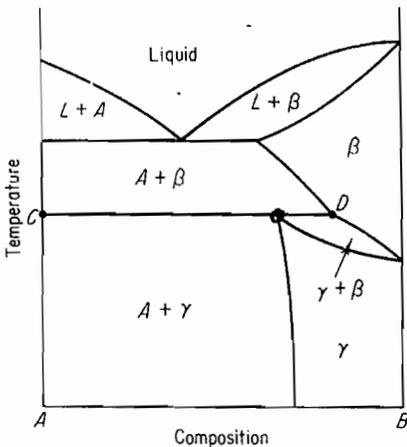
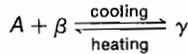


Fig. 6-59 Phase diagram showing the formation of the terminal solid solution γ by a peritectoid reaction.

It was pointed out in the discussion of the peritectic reaction that the microstructure of a peritectic alloy rarely shows complete transformation (Fig. 6-43). This is because diffusion through the new phase is required in order to reach equilibrium. Since the peritectoid reaction occurs entirely in the solid state and usually at lower temperatures than the peritectic reaction, the diffusion rate will be slower and there is less likelihood that equilibrium structures will be reached. Figure 6-60 shows a portion of the silver-aluminum phase diagram containing a peritectoid reaction. If a 7 percent aluminum alloy is rapidly cooled from the two-phase area just above the peritectoid temperature, the two phases will be retained, and the microstructure will show a matrix of γ with just a few particles of α (Fig. 6-61a). If the same alloy is slow-cooled to just below the peritectoid temperature and held there for 20 min before rapid cooling, some transformation will take place. The microstructure, Fig. 6-61b, shows that some γ has transformed to the new phase β , while much of the original α remains. The phase diagram indicates that there should be only a single-phase β , so obviously equilibrium has not been achieved. Even after holding for 2 hr at just below the peritectoid temperature, a single-phase structure is still not produced (Fig. 6-61c).

The similarity, in both the general equation and the appearance on an equilibrium diagram, for the monotectic, eutectic, and eutectoid reactions and the peritectic and peritectoid reactions is apparent from a study of Table 6-4. These reactions are by no means the only ones that may occur on equilibrium diagrams. However, they are by far the most common ones, and the student should become familiar with them.

6-26 Complex Diagrams Some of the equilibrium diagrams discussed under the simple types are the same as actual ones. Many alloy systems have diagrams which show more than one type of reaction and are generally more complex than the simple types. However, even the most complex diagrams show mainly the reactions that have been covered. The student

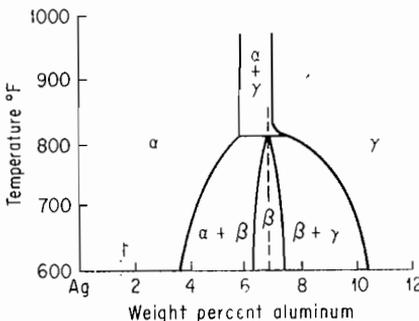


Fig. 6-60 A portion of the silver-aluminum phase diagram.

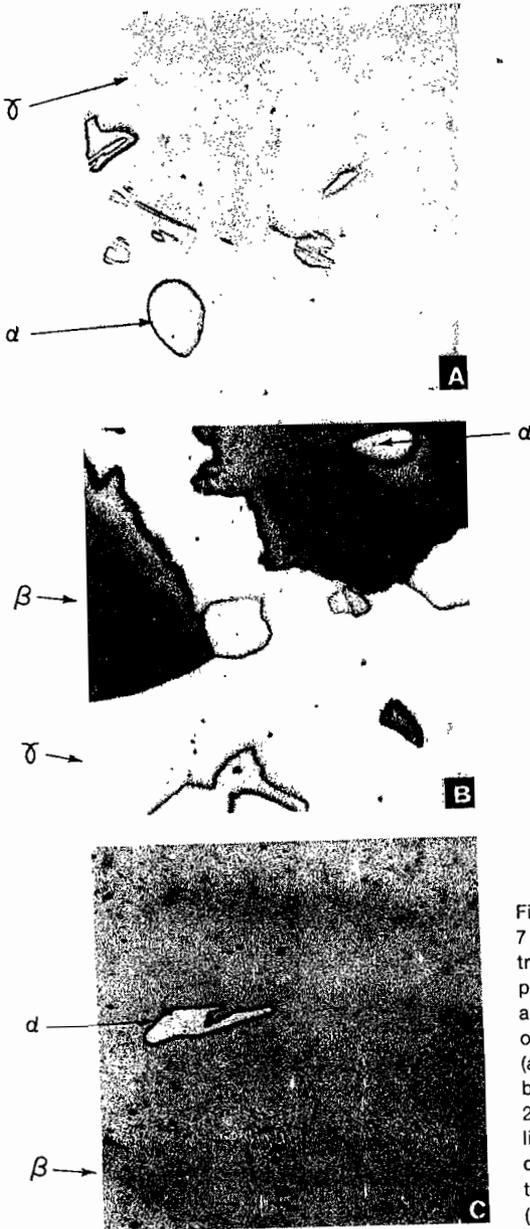


Fig. 6-6: (a) A peritectoid alloy, Ag + 7 percent Al, stabilized by long heat treatment above the peritectoid temperature and then quenched. "Islands" are the γ phase embedded in a matrix of γ . Magnification 150X. (b) Same as (a), cooled to a temperature slightly below that of the peritectoid and held 20 min before quenching. Much of the light-colored γ has transformed to the dark-colored β without greatly affecting the islands of γ . Magnification 150X. (c) Same as (a), cooled to a temperature slightly below the peritectoid and held for 2 hr before quenching. Dark matrix is β ; light area is residual α that has not yet been dissolved by the β . Magnification 150X. (By permission from F. N. Rhines, "Phase Diagrams in Metallurgy," McGraw-Hill Book Company, New York, 1956.)

TABLE 6-4 Equilibrium-diagram Reactions

NAME OF REACTION	GENERAL EQUATION	APPEARANCE ON DIAGRAM
peritectic	$L_1 \xrightleftharpoons[\text{heating}]{\text{cooling}} L_2 + \text{solid}$	
eutectic	$\text{Liquid} \xrightleftharpoons[\text{heating}]{\text{cooling}} \text{solid}_1 + \text{solid}_2$	
eutectoid	$\text{Solid}_1 \xrightleftharpoons[\text{heating}]{\text{cooling}} \text{solid}_2 + \text{solid}_3$	
peritectoid	$\text{Liquid} + \text{solid}_1 \xrightleftharpoons[\text{heating}]{\text{cooling}} \text{new solid}_2$	
eutectoid	$\text{Solid}_1 + \text{solid}_2 \xrightleftharpoons[\text{heating}]{\text{cooling}} \text{new solid}_3$	

should be able to label a phase diagram completely; understand the significance of every point, line, and area; determine the various reactions that occur at the horizontal lines; and describe the slow cooling and microstructure of any alloy on a binary equilibrium diagram. The application of some of the principles in this chapter will now be illustrated for a complex equilibrium diagram such as the cobalt-tungsten alloy system shown in Fig. 6-62.

The freezing point of cobalt is shown on the left axis as 1495°C. The freezing point of tungsten, 3410°C, is where the two dotted lines on the right would meet and is above the range of temperatures shown. Since two-phase areas must be bounded by single phases on either side of a horizontal line, it is necessary to first label the single-phase areas. The upper line on the diagram is the liquidus line, so above the liquidus line there is a single homogeneous liquid solution indicated by L . On the left, from the freezing point of cobalt, there is a very thin, cigar-shaped area which resembles Type I. Therefore, there must be a solid solution formed below this area. The solid solution is labeled β . Once the β area has been labeled, the portion between the very thin lines is labeled as $\beta + L$. Next to this area is a portion of the diagram which looks like a variation of Type I and shows a maximum at 1500°C. The area between the points 35, 45, and 1500°C would also be $\beta + L$. Along the right axis, the dotted line indicates a small solid solution area which is labeled as epsilon, ϵ . Now the area above 1690°C may be labeled as $L + \epsilon$. The first horizontal line is at 1690°C. Above the line there is $L + \epsilon$. Below the line a new solid solution δ appears. The stu-

Fig. 6-62
Handbook,
Metals Park

dent should recognize that this is a peritectic reaction. After the δ region has been labeled, the area to the right may be labeled as $\delta + \epsilon$. The area to the left of the δ region above 1465°C may now be labeled as $L + \delta$. The area between 1100° and 1465° may also be labeled as $\beta + \delta$. The students should recognize the eutectic point at 45 percent W and 1465°C . Above the line is a liquid solution and below the line two solids β and δ . At 1100°C is another horizontal line and therefore, another reaction. Above the line are two solids δ and β . Below the line a new phase appears, an intermediate alloy phase, which is labeled γ . This is a peritectoid reaction. Once the γ region has been labeled, the area to the right becomes $\gamma + \delta$ and the area to the left $\beta + \gamma$. The point A on the vertical line representing cobalt must be an allotropic change. Below point A there is a very tiny amount of solubility of tungsten in cobalt. The solid solution area is too small to be shown on the diagram, but it is labeled α as indicated. The triangle $AB3$ may now be labeled as $\alpha + \beta$, although it is not labeled in the diagram. The dotted horizontal line at 350°C indicates another reaction. This is the eutectoid reaction, with the eutectoid point at 3 percent W and 350°C . Above the line is β solid solution, while below the line are two solid solutions $\alpha + \gamma$. The diagram is now completely labeled. Two intermediate alloy phases are shown on the diagram, γ and δ . Since their range of composition is not very great, they are most likely intermetallic compounds. The γ phase appears to correspond to the formula Co_7W_2 and the δ phase to the formula CoW . Another significant fact that may be determined from the diagram is the very large difference in solubility of tungsten in cobalt depending upon the type of

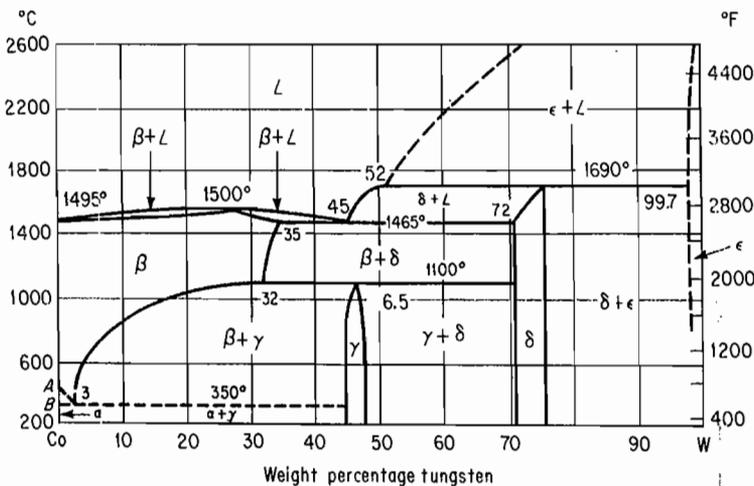


Fig. 6-62 The cobalt-tungsten alloy system. (From Metals Handbook, 1948 ed., p. 1193, American Society for Metals, Metals Park, Ohio.)

crystal structure. In the β solid solution, where cobalt is face-centered cubic, the maximum solubility of tungsten in cobalt is given as 35 percent at 1465°C. However, once the allotropic change has occurred and cobalt becomes close-packed hexagonal below point A, the solubility of tungsten in cobalt is almost negligible. The reactions and specific equations that occur at each horizontal line on this diagram are given below.

TEMPERATURE	REACTION	EQUATION
1690°C	Peritectic	$L + \epsilon \xrightarrow{\text{cooling}} \delta$
1465°C	Eutectic	$L \xrightarrow{\text{cooling}} \beta + \delta$
1100°C	Peritectoid	$\beta + \delta \xrightarrow{\text{cooling}} \gamma$
350°C	Eutectoid	$\beta \xrightarrow{\text{cooling}} \alpha + \gamma$

QUESTIONS

- 6-1 What information may be obtained from an equilibrium diagram?
- 6-2 Explain the importance of equilibrium diagrams in the development of new alloys.
- 6-3 Platinum and gold are completely soluble in both the liquid and solid states. The melting point of platinum is 3225°F and that of gold is 1945°F. An alloy containing 40 percent gold starts to solidify at 2910°F by separating crystals of 15 percent gold. An alloy containing 70 percent gold starts to solidify at 2550°F by separating crystals of 37 percent gold.
- Draw the equilibrium diagram to scale on a piece of graph paper and label all points, lines, and areas.
 - For an alloy containing 70 percent gold (1) give the temperature of initial solidification; (2) give the temperature of final solidification; (3) give the chemical composition and relative amounts of the phases present at 2440°F; (4) draw the cooling curve.
- 6-4 Bismuth and antimony are completely soluble in both the liquid and solid states.
- Check the crystal-structure factor and calculate the relative-size factor for these metals.
 - Bismuth melts at 520°F and antimony melts at 1170°F. An alloy containing 50 percent bismuth starts to solidify at 940°F by separating crystals of 90 percent antimony. An alloy containing 80 percent bismuth starts to solidify at 750°F by separating crystals of 75 percent antimony.
- Draw the equilibrium diagram to scale on a piece of graph paper labeling all lines, points, and areas.
 - For an alloy containing 40 percent antimony, (a) give the temperature of initial solidification; (b) give the temperature of final solidification; (c) give the chemical composition and relative amounts of the phases present at 800°F; (d) draw the cooling curve.
- 6-5 Bismuth (melting point 520°F) and cadmium (melting point 610°F) are assumed to be completely soluble in the liquid state and completely insoluble in the solid state. They form a eutectic at 290°F containing 40 percent cadmium.
- Draw the equilibrium diagram to scale on a piece of graph paper labeling all points, lines, and areas.