

CHAPTER 1

INTRODUCTION

When a metal melts it is said to undergo a *phase change*; the *solid phase* is transformed into the *liquid phase*. Other phase changes occur at the boiling point, where the *liquid phase* is transformed into the *gas phase*; at the sublimation point, where the *solid phase* is transformed into the *gas phase*; and at the temperature of allotropic transformation, where one kind of *solid phase* is changed into another kind of *solid phase*. The solid phases are always crystalline, and differences among solid phases are differences in composition, crystal structure, or crystal dimensions.

Under ordinary conditions, with the pressure constant, the phase changes in pure metals occur *isothermally*; that is, melting takes place at a single definite melting temperature, boiling at a fixed boiling point, and so on. Certain alloys likewise undergo *isothermal phase changes*, but it is more frequently found that the phase changes in alloys occur, instead, over ranges of temperature. Melting, for example, may begin at one temperature and not be completed until some higher temperature is reached, the alloy meanwhile existing in a mushy state composed of mixed liquid and solid. More complex phase changes, both isothermal and nonisothermal, are common. It is often found, for example, that more than two phases are involved in a single transformation. Thus, a molten alloy may freeze in such a way as to deposit a complex solid composed of several different solid phases.

Through the years an enormous body of information concerning the phase changes in alloys has been accumulated. Not only many thousands of commercial alloys but also a vastly greater number of alloys not in common use have been examined in this respect. Some systematic method of recording this information is required in order to condense it and to make available such individual items of data as may be needed in the daily handling of metals. The most successful method yet devised to accomplish this is the use of *phase diagrams*, also known as *constitutional diagrams* or *equilibrium diagrams*.

The Phase Diagram

A typical phase diagram, presented in Fig. 1-1, indicates the phases present in all possible alloys of the two metals nickel (Ni) and copper (Cu), at all temperatures from 500 to 1500°C. Alloy composition is given

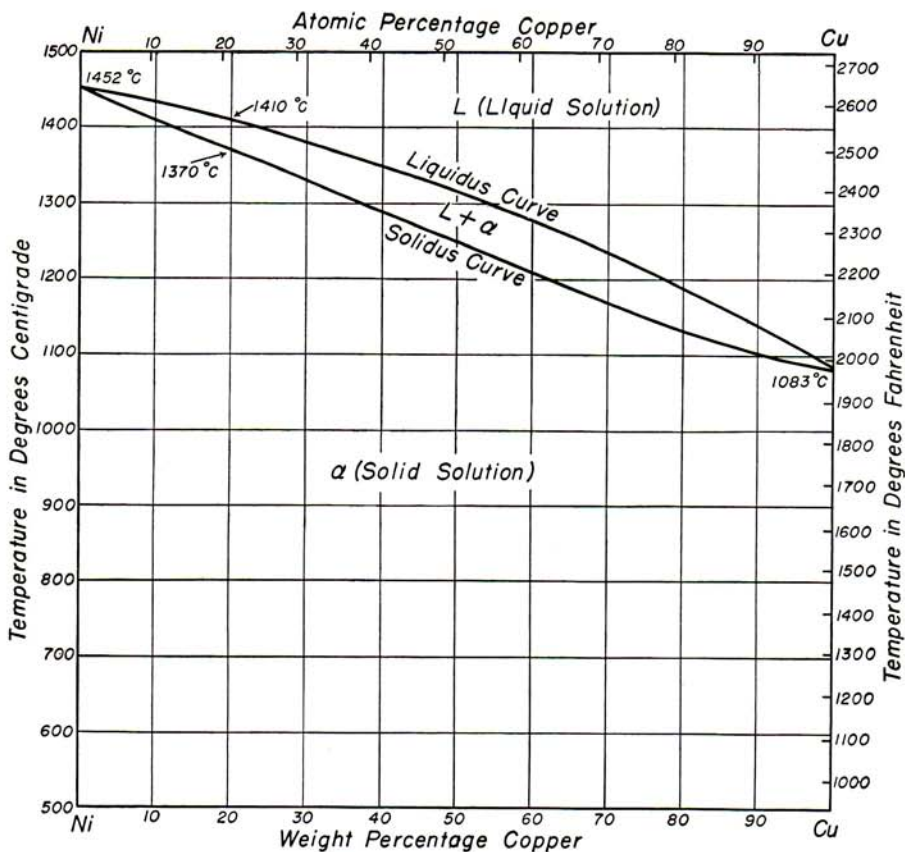


FIG. 1-1. The nickel-copper phase diagram.

by the horizontal scale, along the base of the diagram, where the percentage, by weight, of copper is read directly, the remainder being nickel. Temperature is read vertically, either from the centigrade scale on the left or from the Fahrenheit scale on the right. Two curves cross the diagram from the melting point of nickel at 1452°C to the melting point of copper at 1083°C. Of these, the upper curve, called the *liquidus*, denotes for each possible alloy composition the temperature at which freezing

begins during cooling or, equivalently, at which melting is completed upon heating. The lower curve, called the *solidus*, indicates the temperatures at which melting begins upon heating or at which freezing is completed upon cooling. Above the liquidus every alloy is molten, and this region of the diagram is, accordingly, labeled "L" for liquid phase or liquid solution. Below the solidus all alloys are solid, and this region is labeled " α " because it is customary to use a Greek letter (see Appendix I) for the designation of a solid phase which is also a solid solution. At temperatures between the two curves the liquid and solid phases are present together, as is indicated by the designation " $L + \alpha$."

Thus, the melting range of any desired alloy, say an alloy composed of 20% copper (balance, 80% nickel), may be found by tracing the vertical line originating at 20% copper on the base of the diagram to its intersections with the solidus and liquidus. In this way, it will be found that the alloy in question begins to melt at 1370°C and is completely molten at 1410°C.

Temperature and Composition Scales

Custom favors the use of the centigrade scale of temperature in the construction of phase diagrams. The Fahrenheit scale may be used alternatively, however, as convenience dictates (see temperature-conversion table, Appendix IV). It is likewise most common to express alloy composition in "weight percentage," but for certain types of scientific work the "atomic percentage" scale (top edge of Fig. 1) may be preferred. The scale upon which the composition is expressed makes no fundamental difference in the form of the resulting phase diagram. If desired, composition may also be given in terms of the percentage by volume, but this usage is rare in the representation of metal systems.

The conversion from weight percentage (wt. %) to atomic percentage (at. %) or the reverse may be accomplished by the use of the following formulas:

$$\text{At. \% } X = \frac{(\text{wt. \% } X)/(\text{at. wt. } X)}{(\text{wt. \% } X)/(\text{at. wt. } X) + (\text{wt. \% } Y)/(\text{at. wt. } Y)} \times 100$$

$$\text{Wt. \% } X = \frac{(\text{at. \% } X)(\text{at. wt. } X)}{(\text{at. \% } X)(\text{at. wt. } X) + (\text{at. \% } Y)(\text{at. wt. } Y)} \times 100$$

where X and Y represent the two metals in the alloy. Tables for making these conversions (useful when a large number of such computations is to be made) and also formulas for ternary and higher order systems are given in Appendix III. A table of atomic weights (at. wt.) appears in Appendix II.

Equilibrium

All properly constructed phase diagrams record the phase relationships only as they occur under conditions of *equilibrium*. This is necessary because phase changes as observed in practice tend to occur at different temperatures, depending upon the rate at which the metal is being heated or cooled. With rapid heating, any phase change, such as melting, occurs at a slightly higher temperature than with slow heating. Conversely, with rapid cooling the phase change occurs at a lower temperature than with slow cooling. Thus, transformations observed during heating are at higher temperature than the reverse transformations observed during cooling, except in the hypothetical case wherein the rates of heating and cooling are infinitely slow, whereupon the two observations of temperature would coincide at the *equilibrium transformation temperature*.

The equilibrium states that are represented upon phase diagrams are known as *heterogeneous equilibria*, because they refer to the coexistence of different states of matter. For two or more phases to attain mutual equilibrium, however, it is necessary that each be internally in a homogeneous state. In general, this means that each phase must be in the lowest energy state of which it is capable under the restrictions imposed by its environment. Thus, the chemical composition must be identical everywhere within the phase, the molecular and atomic species of which the phase is composed (if more than one) must be present in equilibrium proportions, and crystalline phases must be free of internal stresses.

An exception to the rule that only true equilibrium states are recorded on phase diagrams is found in the occasional representation of so-called *metastable equilibria*. In ordinary carbon steels, for example, there is found a solid phase, a carbide of iron (Fe_3C), that decomposes into graphite and iron under conditions that are favorable to the attainment of true equilibrium. The rate of decomposition of the iron carbide is very slow, however, under the most favorable conditions and is usually imperceptible under ordinary conditions. Because of its reluctance to decompose, this phase is said to be metastable, and it is represented on the usual (metastable) iron-carbon phase diagram. Evidently, metastability is a concept incapable of definition except by fiat, because there is no fundamental basis for saying that those substances that revert to the stable form at less than a certain rate are *metastable* while those that decompose more rapidly are *unstable*. The recognition of "metastable phase diagrams" is simply a practical artifice that has been found useful in certain instances, even though in violation of the basic assumptions of the phase rule,

The Phase Rule

The construction of phase diagrams is greatly facilitated by certain rules which come from the science of thermodynamics. Foremost among these is Gibbs' phase rule.¹ This rule says that the maximum *number of phases* P which can coexist in a chemical system, or alloy, plus the *number of degrees of freedom* F is equal to the *sum of the components* C of the system plus 2.

$$P + F = C + 2$$

The *phases* P are the homogeneous parts of a system which, having definite bounding surfaces, are conceivably separable by mechanical means alone, for example, gas, liquid, and solid.²

The *degrees of freedom* F are those externally controllable conditions of temperature, pressure, and composition which are independently variable and which must be specified in order to define completely the state of the system at equilibrium.³

The *components* C are the smallest number of substances of independently variable composition making up the system. In alloy systems, it is usually sufficient to count the number of elements present; in the case of a mixture of stable compounds, such as salt and water, the number of components may be taken as two ($\text{NaCl} + \text{H}_2\text{O}$), unless carried to a degree of temperature and pressure where one or both of the compounds

¹ Formal derivations of the phase rule will be found in a large number of available texts, including J. S. Marsh, "Principles of Phase Diagrams," p. 24, McGraw-Hill Book Company, Inc., New York, 1935; A. C. D. Rivett, "The Phase Rule," chap. I, Oxford University Press, New York, 1923; A. Findlay, "The Phase Rule," p. 13, Longmans, Green & Co., Ltd., London, 1931, and pp. 17-19, Longmans, Green & Co., Inc., New York, 1951; L. Page, "Introduction to Theoretical Physics," p. 277, D. Van Nostrand Company, Inc., New York, 1928; John E. Ricci, "The Phase Rule and Heterogeneous Equilibrium," pp. 14-18, D. Van Nostrand Company, Inc., New York, 1951.

² In succeeding chapters the term *phase* will often be found used in a looser sense to designate the several states of matter in an alloy system, whether these are individually "homogeneous" or not. It should be understood that within its precise meaning the term *phase* can be applied only to states of matter at equilibrium and, hence, necessarily homogeneous.

³ The assumption is here made that temperature, pressure, and concentration are the only externally controllable variables capable of influencing the phase relationships. Such variables as the electrostatic field, the magnetic field, the gravitational field, and surface-tension forces are considered to have no appreciable influence. If one of these variables should become important, in a specific instance, it would be necessary to include it among the externally controllable variables and to increase the constant in the phase rule from 2 to 3, that is, $P + F = C + 3$.

decomposes, when it becomes necessary to consider four components (Na, Cl, H, and O).

Through numerous examples in subsequent chapters the meaning of these somewhat formidable definitions will become clear. For the present, however, it will be sufficient to illustrate the application of the phase rule with a simple example. Suppose that it is desired to ascertain under what conditions a pure metal can exist with the gas, liquid, and solid phases all present in a state of equilibrium. There are, then, three phases. Since only one metal is involved the number of components is one. The phase rule is equated to find the number of degrees of freedom, thus:

$$P + F = C + 2$$

$$3 + 0 = 1 + 2$$

There are seen to be no degrees of freedom, which means that the coexistence of these three phases can occur only at one specific temperature and one specific pressure (the composition is, of course, fixed, only one metal being present).

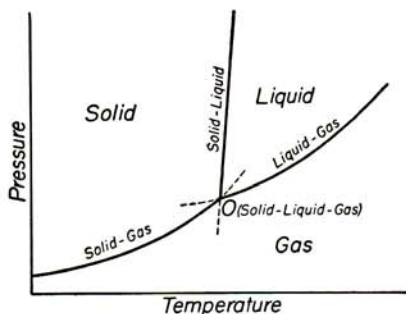


FIG. 1-2

If one such set of specific conditions of temperature and pressure is now found by experiment, it will be unnecessary to look for another set, because the phase rule shows that only one can exist. Moreover, if it is desired to construct a phase diagram in which the coexistence of the three phases is represented, it becomes apparent at once that the coordinates of the diagram should be temperature and

pressure and that the coexistence of the three phases must be indicated by a single point on this diagram (see point O in Fig. 1-2).

Other Rules

Although the phase rule tells what lines and fields should be represented upon a phase diagram, it does not usually define their shapes or the directions of the lines. Further guidance in the latter respect may be had from several additional rules of thermodynamic derivation.

The *theorem of Le Châtelier*, for example, says that *if a system in equilibrium is subjected to a constraint by which the equilibrium is altered, a reaction takes place which opposes the constraint, i.e., one by which its effect is partially annulled* (Ostwald). Thus, if an increase in the temperature of an alloy results in a phase change, that phase change will be one which proceeds with heat absorption, or if pressure applied to an alloy system

brings about a phase change, this phase change must be one which is accompanied by a contraction in volume.

The usefulness of this rule can again be shown by reference to Fig. 1-2. Consider the line labeled "solid-liquid," which represents for a typical pure metal the temperature at which melting occurs at various pressures. This line slopes upward away from the pressure axis. The typical metal contracts upon freezing. Hence, applying an increased pressure to the liquid can cause the metal to become solid, experiencing at the same time, an abrupt contraction in volume. Had the metal bismuth, which expands upon freezing, been selected as an example, the theorem of Le Châtelier would demand that the solid-liquid line be so drawn that the conversion of liquid to solid with pressure change would occur only with a reduction in pressure; that is, the line should slope upward *toward* the pressure axis.

A quantitative statement of the theorem of Le Châtelier is found in the Clausius-Clapeyron equation (see Appendix V). Referring again to Fig. 1-2, this equation leads to the further conclusion that each of the curves representing two-phase equilibrium must lie at such an angle that upon passing through the point of three-phase equilibrium, each would project into the region of the third phase. Thus, the solid-gas line must project into the liquid field, the liquid-gas curve into the solid field, and the solid-liquid curve into the gas field.

Other rules and aids of this type will be mentioned in subsequent chapters as opportunities for their application arise. Foremost among these is the second law of thermodynamics, which leads to rules governing the construction also of more complex phase diagrams such as are encountered in binary and ternary systems.

Relationships between Alloy Constitution and Physical Properties

At the present stage of the development of the science of physical metallurgy no fundamental relationships have been established associating states of phase equilibrium with the physical and mechanical properties of alloys. Nevertheless, experience has shown that there are striking similarities in the structure and properties among alloy systems having similar phase diagrams.

One of the more successful correlations is that with the structural alterations that an alloy undergoes during temperature change, as in manufacturing operations. True equilibrium is, of course, rarely attained by metals and alloys in the course of ordinary manufacture and application. Rates of heating and cooling are usually too fast, times of heat treatment too short, and phase changes too sluggish for the ultimate equilibrium state to be reached. Any change that does occur must, however, consti-

tute an *adjustment toward equilibrium*. Hence, the direction of change can be ascertained from the phase diagram, and a wealth of experience is available to indicate the probable degree of attainment of equilibrium under various circumstances.

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Advantages of Phase Diagrams

From what has been said in this introductory chapter it will be seen that the use of phase diagrams for recording phase changes in alloys offers three important advantages:

1. The conditions under which phase changes occur can be recorded simply and clearly for a large number of alloy compositions in relatively small space.
2. The existence of certain rules of construction greatly reduces the number of experimental observations necessary to determine the phase relationships that exist in a whole series of alloys.
3. The recognition of quasi relationships between the constitution of alloys and their structure and properties makes the phase diagram an invaluable guide in the control of metallurgical processes.