

CHAPTER 1

Introduction to Phase Diagrams

IN MATERIALS SCIENCE, the term *phase* refers to the distinct types of atomic bonding and arrangement of elements in a material of a given chemical composition. A phase is a physically homogeneous state of matter with a given chemical composition and structure. The simplest examples are the three states of matter (solid, liquid, or gas) of a pure metal. The three phases of a pure metal have the same chemical composition, but each phase is obviously distinct physically due to differences in the bonding and arrangement of atoms.

The solid phase of a pure element may also refer to physically distinct arrangements of atoms in the solid. *Polymorphism* is the general term for the ability of a solid to exist in more than one form. The bonding of atoms in solids often occurs in a repetitive arrangement—or crystal structure. Most solid metals and alloys have atoms arranged in a specific type of crystalline structure (see Appendix A, “Review of Metallic Structure,” in this book). Some pure metals also have different crystalline structure as a function of temperature. For example, solid iron has different crystal structures (and magnetic properties) as a function of temperature. The physical change in the arrangement of iron atoms represents a phase change. *Allotropy* is the general term to describe solid-phase polymorphism of an element. In this regard, iron (along with some other metals) is an allotropic element.

Alloying, or mixing of two or more elements, also affects the occurrence of phase changes. For example, the temperature for complete melting (100% liquid phase) of an alloy depends on the relative concentration of alloying elements. Another example is the effect of alloying on the crystalline phase of a solid. Depending on the mixture of two or more elements, the elements may form different crystalline phases and/or chemical compounds.

Phase diagrams are useful graphical representations of the phase changes in a material. Alloy phase diagrams are useful to metallurgists, materials

engineers, and materials scientists in four major areas: (1) development of new alloys for specific applications, (2) fabrication of these alloys into useful configurations, (3) design and control of heat treatment procedures for specific alloys that will produce the required mechanical, physical, and chemical properties, and (4) solving problems that arise with specific alloys in their performance in commercial applications.

1.1 Unary Systems

As noted, pure metals exist in three states of matter, solid, liquid, and vapor, depending on the specific combination of temperature and pressure. Each of these three states is referred to as a phase; that is, the solid, liquid, and vapor phases. Consider a solid block of metal in a container inside a furnace. Assuming atmospheric pressure, if the metal is heated to a high enough temperature, it will melt and form a liquid. On still further heating, it will start to boil and metal atoms will leave the container as a vapor or gas. Because matter can enter or leave the system, this condition is known as an open system. To create a closed system where no matter enters or leaves the system, an airtight cover can be placed on top of the container. If pressure is now applied inside the container, the vapor phase is compressed and the volume becomes smaller. Next, the pressure is released and the temperature is lowered so that the metal cools to the liquid state. On reapplication of pressure, the liquid metal volume remains fairly constant; that is, liquid metals are essentially incompressible. The same situation holds if the liquid metal is cooled so that only a solid remains. Because the metal atoms are almost as closely packed in a liquid as they are in a solid, there is almost no change in volume. Therefore, during the processing of metals, the effects of pressure and volume change can often be ignored. Because most metallic processes are conducted at atmospheric pressure, the pressure in phase diagrams is normally assigned a value of 1 atm and volume changes are ignored. Because the system considered so far contains only one pure metal, it is known as a unary system.

1.2 Binary Systems

Now consider the addition of a second metal, for example, an alloy of nickel and copper. The phase diagram for this system is shown in Fig. 1.1. This is known as an isomorphous phase diagram, because the alloys are completely miscible in each other in the solid state. Nickel and copper both have the face-centered cubic (fcc) crystalline structure and the atoms are of similar size. Alloys of metals containing metals with different crystalline structures will have somewhat more complex diagrams.

The diagram shows the phases present in all possible alloys of the two metals nickel (Ni) and copper (Cu), at all temperatures from 500 to 1500 °C (930 to 2730 °F). Alloy composition is plotted on the horizontal scale,

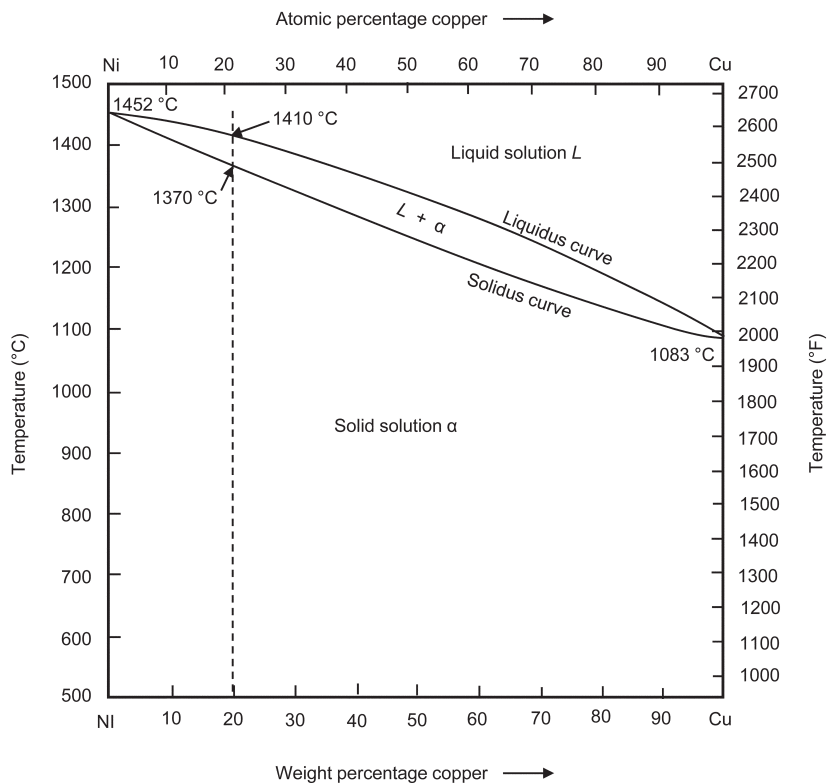


Fig. 1.1 The nickel-copper phase diagram. Adapted from Ref 1.1

along the base of the diagram, where the weight percentage 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 (2646 °F) to the melting point of copper at 1083 °C (1981 °F). 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 on heating. The lower curve, called the solidus, indicates the temperatures at which melting begins on heating or at which freezing is completed on cooling. Above the liquidus every alloy is molten, and this region of the diagram is, accordingly, labeled L for the 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 for the designation of a solid phase that 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 $L + \alpha$.

Therefore, the melting range of any desired alloy, for example, an alloy composed of 20% Cu (balance, 80% Ni), may be found by tracing the

vertical line originating at 20% Cu 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 (2498 °F) and is completely molten at 1410 °C (2570 °F).

1.3 Temperature and Composition Scales

The centigrade temperature scale is normally used for phase diagrams. However, the Fahrenheit scale may be used as convenience dictates. Alloy composition is normally expressed in weight percentage, but for certain types of scientific work the atomic percentage scale may be preferred. 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. %) may be accomplished by the use of the following formulas:

$$\text{wt}\% A = \frac{\text{at.}\% A \times \text{at. wt of } A}{(\text{at.}\% A \times \text{at. wt of } A) + (\text{at.}\% B \times \text{at. wt of } B)} \times 100 \quad (\text{Eq 1.1})$$

$$\text{at.}\% A = \frac{\text{wt}\% A / \text{at. wt of } A}{(\text{at.}\% A / \text{at. wt of } A) + (\text{wt}\% B / \text{at. wt of } B)} \times 100 \quad (\text{Eq 1.2})$$

The equation for converting from atomic percentages to weight percentages in higher-order systems is similar to that for binary systems, except that an additional term is added to the denominator for each additional component. For example, for ternary systems:

$$\text{at.}\% A = \frac{\text{wt}\% A / \text{at. wt of } A}{(\text{at.}\% A / \text{at. wt of } A) + (\text{wt}\% B / \text{at. wt of } B) + (\text{wt}\% C / \text{at. wt of } C)} \times 100 \quad (\text{Eq 1.3})$$

$$\text{wt}\% A = \frac{\text{at.}\% A \times \text{at. wt of } A}{(\text{at.}\% A \times \text{at. wt of } A) + (\text{at.}\% B \times \text{at. wt of } B) + (\text{at.}\% C \times \text{at. wt of } C)} \times 100 \quad (\text{Eq 1.4})$$

where *A*, *B*, and *C* represent the metals in the alloy.

1.4 Equilibrium

Phase diagrams record the phase relationships under equilibrium conditions. This is necessary because phase changes observed in practice tend to occur at different temperatures, depending on 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. Therefore, 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, where the two observations of temperature would coincide at the equilibrium transformation temperature.

The equilibrium states that are represented on phase diagrams are known as heterogeneous equilibria, because they refer to the coexistence of different states of matter. However, for two or more phases to attain mutual equilibrium, it is necessary that each be internally in a homogeneous state. In general, this means that each phase must be in the lowest free energy state possible 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 representation of so-called metastable equilibria. In carbon steels, for example, there is a solid phase, a carbide of iron (Fe_3C) called cementite, that decomposes into graphite and iron under conditions that are favorable to the attainment of true equilibrium. However, the rate of decomposition of the iron carbide is extremely slow 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.

1.5 The Phase Rule

The construction of phase diagrams is greatly facilitated by certain rules that come from thermodynamics. Foremost among these is Gibbs' phase rule. 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:

$$P + F = C + 2 \quad (\text{Eq 1.5})$$

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

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 completely define the equilibrium state of the system.

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 the mixture is carried to a degree of temperature and pressure where one or both of the compounds decompose, when it becomes necessary to consider four components (Na, Cl, H, and O). Through numerous examples in subsequent chapters the meaning of these definitions becomes clearer. However, for the present, it is 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. Then, there are three phases. Because only one metal is involved, the number of components is one. The phase rule is used to find the number of degrees of freedom:

$$F = C + 2 - P$$

$$F = 1 + 2 - 3 = 0$$

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

1.6 Theorem of Le Châtelier and the Clausius-Clapeyron Equation

Although the phase rule tells what lines and fields should be represented on a phase diagram, it does not usually define their shapes or the directions

of the lines. Further guidance in the latter respect may be explained by several additional thermodynamic rules.

The theorem of Le Châtelier says that if a system in equilibrium is subjected to a constraint by which the equilibrium is altered, a reaction takes place that opposes the constraint, that is, one by which its effect is partially annulled. Therefore, if an increase in the temperature of an alloy results in a phase change, that phase change will be one that proceeds with heat absorption, or if pressure applied to an alloy system brings about a phase change, this phase change must be one that 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 showing freezing, 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 on 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 on freezing, been selected as an example, the theorem of Le Châtelier would dictate that the solid-liquid line be drawn so 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.

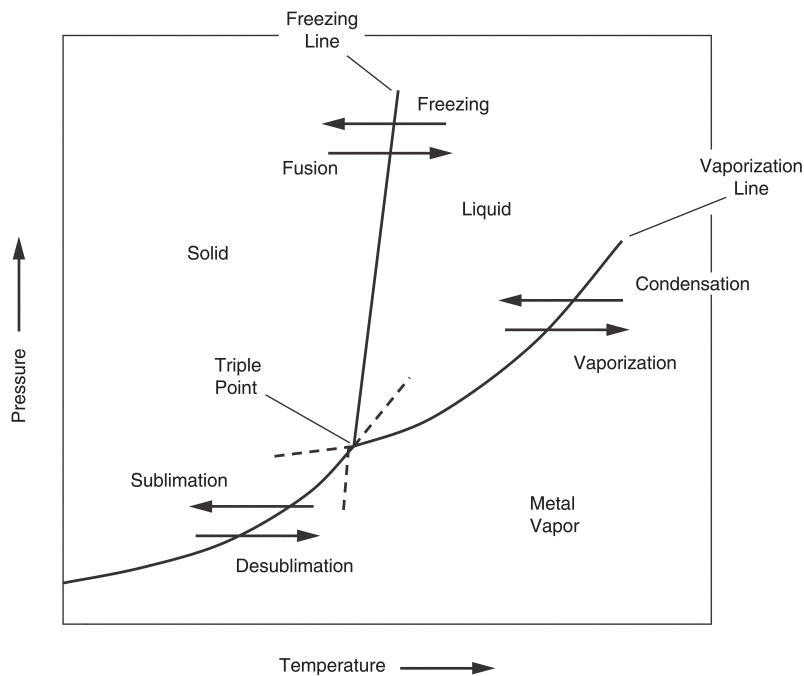


Fig. 1.2 Pressure-temperature diagram for a pure metal. Source: Ref 1.2

A quantitative statement of the theorem of Le Châtelier is found in the Clausius-Clapeyron equation. 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 on passing through the point of three-phase equilibrium, each would project into the region of the third phase. Thus, the sublimation-desublimation line must project into the liquid field, the vaporization curve into the solid field, and the solid-liquid curve into the vapor field.

1.7 The Lever Rule

The lever rule is one of the cornerstones of understanding and interpreting phase diagrams. A portion of a binary phase diagram is shown in Fig. 1.3. In this diagram, all phases present are solid phases. There are two single-phase fields labeled α and β , separated by a two-phase field labeled $\alpha + \beta$. It indicates that, at a temperature such as b , pure metal A can dissolve metal B in any proportion up to the limit of the single-phase α field at composition a . At the same temperature, metal B can dissolve metal A in any proportion up to composition c , which, at this temperature, is the boundary of the single-phase β field. Therefore, at temperature b , any alloy that contains less than $a\%$ of metal B will exist at equilibrium as the homogeneous α solid solution; and any alloy containing more than $c\%$ of metal B will exist as the β solid solution. However, any alloy whose overall composition is between a and c (for example, at d) will, at the same temperature, contain more metal B than can be dissolved by the α and more metal A than can be dissolved by the β . It will therefore exist as a mixture of α and β solid solutions. At equilibrium, both solid solutions

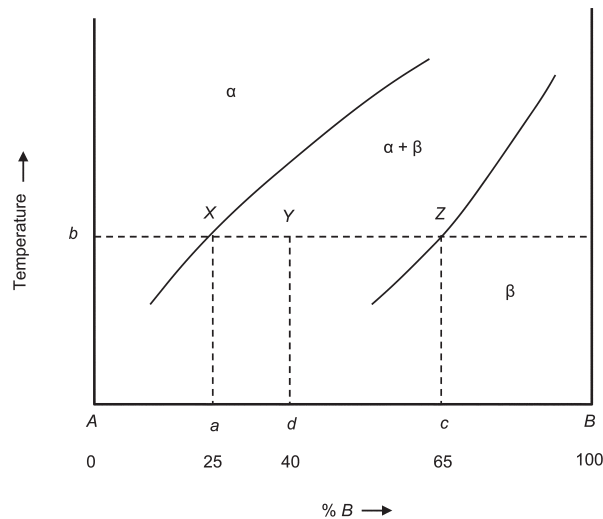


Fig. 1.3 Portion of hypothetical phase diagram

will be saturated. The composition of the α phase is therefore $a\%$ of metal B and that of the β phase is $c\%$ of metal B .

When two phases are present, as at composition Y in Fig. 1.3, their relative amounts are determined by the relation of their chemical compositions to the composition of the alloy. This is true because the total weight of one of the metals, for example metal A , present in the alloy must be divided between the two phases. This division can be represented by:

$$W_0 \left(\frac{\%A_0}{100} \right) = W_\alpha \left(\frac{\%A_\alpha}{100} \right) + W_\beta \left(\frac{\%A_\beta}{100} \right) \quad (\text{Eq 1.6})$$

$$\left(\begin{array}{c} \text{weight of metal} \\ A \text{ in alloy} \end{array} \right) = \left(\begin{array}{c} \text{weight of metal} \\ A \text{ in } \alpha \text{ phase} \end{array} \right) + \left(\begin{array}{c} \text{weight of metal} \\ A \text{ in } \beta \text{ phase} \end{array} \right)$$

where W_0 , W_α , and W_β are the weights of the alloy, the α phase, and the β phase, respectively, and $\%A_0$, $\%A_\alpha$, and $\%A_\beta$ are the respective chemical compositions in terms of metal A . Because the weight of the alloy is the sum of the weight of the α phase and the weight of the β phase, the following relationship exists:

$$W_0 = W_\alpha + W_\beta \quad (\text{Eq 1.7})$$

This equation can be used to eliminate W_α from Eq 1.6, and the resulting equation can be solved for W_β to give the expression:

$$W_\beta = W_0 \left(\frac{\%A_0 - \%A_\alpha}{\%A_\beta - \%A_\alpha} \right) \quad (\text{Eq 1.8})$$

Although a similar expression can be obtained for the weight of the α phase W_α , the weight of the α phase is more easily obtained by means of Eq 1.7.

Because the weight of each phase is determined by chemical composition values according to Eq 1.8, the tie-line ac shown in Fig. 1.3 can be used to obtain the weights of the phases. In terms of the lengths in the tie-line, Eq 1.8 can be written as:

$$W_\beta = W_0 \left(\frac{\text{length of line } d - a}{\text{length of line } c - a} \right) \quad (\text{Eq 1.9})$$

where the lengths are expressed in terms of the numbers used for the concentration axis of the diagram. *The lever rule, or inverse lever rule can be*

stated: *The relative amount of a given phase is proportional to the length of the tie-line on the opposite side of the alloy point of the tie-line.* Thus, the weights of the two phases are such that they would balance, as shown in Fig. 1.4.

Using Eq 1.9, the *weight* of the β phase at composition Y in Fig. 1.3 is:

$$W_{\beta} = W_{\alpha} \left(\frac{40 - 25}{65 - 25} \right) = W_{\alpha} (0.375)$$

The *percentage* of β phase can be determined by use of the equation:

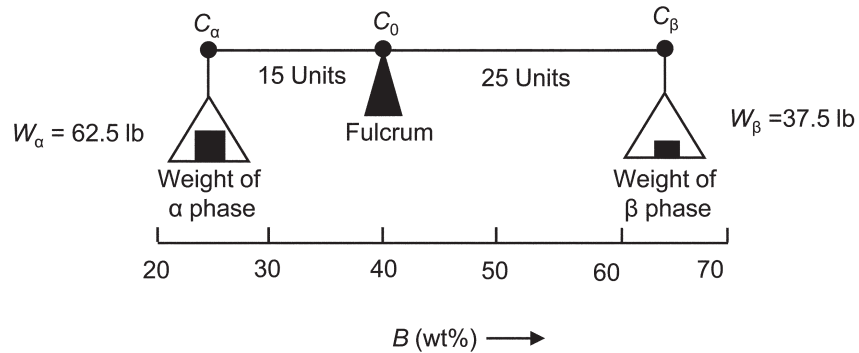
$$\text{Percentage of } \beta \text{ phase} = \left(\frac{W_{\beta}}{W_0} \right) 100 = \left(\frac{\%A_0 - \%A_{\alpha}}{\%A_{\beta} - \%A_{\alpha}} \right) 100 \quad (\text{Eq 1.10})$$

At composition Y the percentage of β phase is:

$$\% \beta \text{ phase} = \left(\frac{40 - 25}{65 - 25} \right) 100 = 37.5\%$$

The percentage of α phase is the difference between 100% and 37.5%, or 62.5%.

Other rules and aids of this type are 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 con-



$$\text{Wt\% } \alpha = \frac{C_{\beta} - C_0}{C_{\beta} - C_{\alpha}} = \frac{65 - 40}{65 - 25} = 0.625 \text{ or } 62.5\%$$

$$\text{Wt\% } \beta = \frac{C_0 - C_{\alpha}}{C_{\beta} - C_{\alpha}} = \frac{40 - 25}{65 - 25} = 0.375 \text{ or } 37.5\%$$

Fig. 1.4 Visual representation of lever rule

struction of more complex phase diagrams, such as are encountered in binary and ternary systems.

1.8 Relationships between Alloy Constitution and Physical Properties

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. However, any change that does occur must constitute 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.

1.9 Phase Diagram Resources

Starting in 1978, ASM International established a cooperative agreement with the National Institute of Standards and Technology (then National Bureau of Standards) to publish and continue to update phase diagrams so that engineers and scientists would have the best thermodynamic tools on which to base new discoveries, explain failures, and so forth. The program that resulted has spanned more than 20 years and involved hundreds of scientific workers, comprehensive scans of the literature, and substantial publications. The binary and ternary books and CDs that have been developed are well-known internationally and are commonly cited as authoritative.

In 1987, the Alloy Phase Diagram International Commission (APDIC) was formed in partnership with other programs operating in Europe and Asia. This group continues to thrive after 20 years and meets once per year to share information regarding projects and alloy systems that are under study. This meeting forms the basis for international collaborations.

Some current phase diagram compilations are given in the Selected References. Another resource is the Alloy Phase Diagram Center published by ASM International (Ref 1.3). This database contains over 30,000 binary and ternary alloy phase diagrams, each with their associated crystal and reaction data.

REFERENCES

- 1.1 F.N. Rhines, *Phase Diagrams in Metallurgy*, McGraw-Hill, 1956, p 2

- 1.2 F.C. Campbell, *Elements of Metallurgy and Engineering Alloys*, ASM International, 2008
- 1.3 *Alloy Phase Diagram Center*, 2011, <http://www.asminternational.org/portal/site/www/info/apdc/> (07 November 2011)

SELECTED REFERENCES

- A.T. Dinsdale, SGTE Data for Pure Elements, *CALPHAD*, Vol 15 (No. 4), 1991, p 317–425
- G. Effenberg and S. Ilyenko, Ed., *Landolt-Börnstein Series*, O. Madelung (Editor-in-Chief), Vol IV/11: *Ternary Alloy Systems. Phase Diagrams, Crystallographic and Thermodynamic Data*, Subvolumes A to C, Springer, 2004–2006
- S.P. Garg, M. Venkatraman, N. Krishnamurthy, and R. Krishnan, Ed., *Phase Diagrams of Binary Tantalum Alloys*, Indian Institute of Metals, 1996
- K.P. Gupta, Ed., *Phase Diagrams of Ternary Nickel Alloys*, Parts 1 and 2, Indian Institute of Metals, 1990
- M.E. Kassner and D.E. Peterson, Ed., *Phase Diagrams of Binary Actinide Alloys*, ASM International, 1995
- Yu.V. Levinsky and G. Effenberg, Ed., *Pressure Dependent Phase Diagrams of Binary Alloys*, ASM International, 1997
- F.D. Manchester, Ed., *Phase Diagrams of Binary Hydrogen Alloys*, ASM International, 2000
- T.B. Massalski and H. Okamoto, Ed., *Binary Alloy Phase Diagrams*, 2nd ed., ASM International, 1990
- J.L. Murray, Ed., *Phase Diagrams of Binary Titanium Alloys*, ASM International, 1987
- S.V.N. Naidu and P.R. Rao, Ed., *Phase Diagrams of Binary Tungsten Alloys*, Indian Institute of Metals, 1991
- P. Nash, Ed., *Phase Diagrams of Binary Nickel Alloys*, ASM International, 1991
- H. Okamoto and T.B. Massalski, Ed., *Phase Diagrams of Binary Gold Alloys*, ASM International, 1987
- H. Okamoto, Ed., *Phase Diagrams of Binary Iron Alloys*, ASM International, 1993
- H. Okamoto, *Desk Handbook: Phase Diagrams for Binary Alloys*, ASM International, 2000
- H. Okamoto, *Phase Diagrams of Dilute Binary Alloys*, ASM International, 2002
- G. Petzow and G. Effenberg, Ed., *Ternary Alloys: A Comprehensive Compendium of Evaluated Constitutional Data and Phase Diagrams*, 15 volumes, Wiley-VCH, 1989–1996
- B. Predel, Ed., *Landolt-Börnstein Series*, O. Madelung (Editor-in-Chief), Vol IV/5: *Phase Equilibria, Crystallographic and*

Thermodynamic Data of Binary Alloys, Subvolumes A to J, Springer, 1991–1998, Vol IV/12, 2006

- A.A. Prince, G.V. Raynor, and D.S. Evans, Ed., *Phase Diagrams of Ternary Gold Alloys*, The Institute of Metals, 1990
- V. Raghavan, *Phase Diagrams of Ternary Iron Alloys*, Parts 1–6, ASM International and The Indian Institute of Metals, 1987–1993
- V. Raghavan, S.P. Garg, M. Venkatraman, N. Krishnamurthy, and R. Krishnan, Ed., *Phase Diagrams of Quaternary Iron Alloys*, Indian Institute of Metals, 1996
- P. Rogl and G. Effenberg, Ed., *Phase Diagrams of Ternary Metal-Boron-Carbon Systems*, ASM International, 1998
- J.F. Smith, Ed., *Phase Diagrams of Binary Vanadium Alloys*, ASM International, 1989
- P.R. Subramanian, D.J. Chakrabarti, and D.E. Laughlin, Ed., *Phase Diagrams of Binary Copper Alloys*, ASM International, 1994
- L. Tanner and H. Okamoto, Ed., *Phase Diagrams of Binary Beryllium Alloys*, ASM International, 1987
- E.Yu. Tonkov and E.G. Ponyatovsky, *Phase Transformations of Elements under High Pressure*, CRC Press, 2004
- P. Villars, A. Prince, and H. Okamoto, Ed., *Handbook of Ternary Alloy Phase Diagrams*, 10 volumes, ASM International, 1995
- J.H. Westbrook, Ed., *Moffatt's Handbook of Binary Phase Diagrams*, 5 loose-leaf volumes, Genium Publ., 2006
- C.E.T. White and H. Okamoto, *Phase Diagrams of Indium Alloys and their Engineering Applications*, ASM International, 1991
- D.A. Young, *Phase Diagrams of the Elements*, University of California Press, 1991

