Phase Diagrams—Understanding the Basics F.C. Campbell, editor

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CHAPTER **2**

Solid Solutions and Phase Transformations

THE CRYSTALLINE STATE is an important mode of aggregation of metal atoms. However, assemblies of metal atoms can also exist in the two other states of matter; that is, the liquid and vapor states. Consider a metal specimen in the solid state that consists of 50% iron atoms and 50% copper atoms (Fig. 2.1a). These atoms do not form a homogeneous solid under equilibrium conditions; rather, they form two different solids, one rich in iron and the other rich in copper. Because it is convenient to distinguish between these two solids, it is conventional to label them with the first two letters of the Greek alphabet, α and β . Each of the distinguishable solid states is then called a phase, and one speaks of the α phase and the β phase.

Two or more different kinds of metal atoms will usually form a homogeneous solution in the liquid state. This behavior is shown for a 50% Fe-50% Cu liquid phase alloy in Fig. 2.1(b). Here also it is conventional to use the word *phase* rather than *state* and to speak of the liquid phase. In a few instances, such as that of the 50% Zn-50% Pb alloy shown in Fig. 2.1(c), two (or more) liquid phases exist at equilibrium. The usual nomenclature in this case is simply to use L_1 (liquid 1) and L_2 (liquid 2). All gases are completely miscible in one another and metal vapors are no exception to this rule. The vapor phase is shown in Fig. 2.1(d) in which the 50% Zn alloy can exist under suitable conditions of temperature and pressure.

2.1 One-Component (Unary) Systems

Before considering in some detail the phases that constitute metal systems, it is helpful to understand the nature of the equilibrium relations among these phases. The relations are relatively simple for a one-component system, that is, a system consisting of a single, pure metal.



Fig. 2.1 The distribution of atoms in solid, liquid, and vapor phases of alloys. (a) Two solid solutions formed in a 50% Fe-50% Cu alloy. (b) Liquid phase formed by 50% Fe-%50 Cu alloy. (c) Two liquid phases formed in a 50% Zn-50% Pb alloy. (d) Vapor phase formed by a 50% Zn-50% Pb alloy. Adapted from: Ref 2.1

How does one put a metal into the liquid condition for casting, or into the vapor phase for purification? Obviously, one or more external conditions must be altered, with the temperature and pressure being of the greatest importance. Although it is possible to change haphazardly the temperature and pressure of a metal until the desired effect is produced, it is much more satisfactory to choose the optimal conditions from data collected by previous workers. Fortunately, these data are not spread in long columns through many journals, but are concisely presented in a single diagram for each metal.

The one-component, or unary, diagram for magnesium is shown in Fig. 2.2. This diagram shows what phases are present as a function of the temperature and pressure. In this case the three phases that can exist correspond to the three states of matter: vapor, liquid, and solid. The interpretation of equilibrium diagrams is made easy by the following rule: Only points in the diagram have physical significance. Because the variables are temperature and pressure, evidently a point is determined by a temperature and a pressure. In Fig. 2.2 the point A is at a pressure P_A and at temperature *T*. Because A is in the field of the diagram labeled liquid, magnesium metal held long enough at pressure P_A and temperature *T* for equilibrium to be established will be entirely liquid. Similarly, magnesium metal at pressure P_B and temperature *T* will be a mixture of liquid and vapor. The temperature and pressure of the triple point will cause solid, liquid, and



Fig. 2.2 Unary diagram for magnesium. Adapted from: Ref 2.1

vapor to be in equilibrium. When two or more phases coexist, the relative amount of each phase cannot be determined from this diagram.

An elementary principle of chemistry states that every liquid or solid tends to be in equilibrium with a particular pressure of its vapor. How then, it may be asked, can there be a completely liquid region in the onecomponent diagram? Will not vapor exist in equilibrium with the liquid at point A in Fig. 2.2? The explanation lies in the manner in which the one-component system is determined (Fig. 2.3). Only the metal being investigated is contained in the cylinder that exerts pressure on the system; even air is excluded. If the external pressure is equal to the vapor pressure of the liquid metal at the given temperature, both liquid and vapor exist in equilibrium in the cylinder. This is the condition at point B in Fig. 2.2 and is shown schematically in Fig. 2.3(a). However, if the external pressure is greater than the vapor pressure of the liquid metal, the piston is forced down, the vapor condenses, and only the liquid phase remains. This is the condition at point A in Fig. 2.2 and is shown schematically in Fig. 2.3(b). An entirely different situation exists if magnesium metal is held at temperature T in contact with air at one atmosphere pressure (760 mm of mercury) as shown in Fig. 2.3(c). Of the total pressure of one atmosphere, only the partial pressure $P_{\rm B}$ is supplied by magnesium vapor. In this instance the significant pressure for most purposes is that of the vapor, not that of vapor and air combined.

Just as the line separating the liquid and vapor areas of the diagram in Fig. 2.2 gives the vapor pressure of the liquid metal as a function of temperature, so the corresponding line for the solid gives the vapor pressure of the solid. It is significant that a solid metal need not melt on being heated.

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Fig. 2.3 (a) and (b) Difference between the conditions under which onecomponent diagrams are valid. (c) Usual conditions of heating a metal. Adapted from: Ref 2.1

For example, if magnesium is held in a vacuum of 1 mm of mercury and is heated to slightly over 600 °C (1110 °F), the metal will completely vaporize without the formation of any liquid. Moderate pressures above that of the triple point have little effect on the melting point of a metal, and the line separating the solid and liquid regions is almost vertical.

The application of the phase rule to the one-component diagram for magnesium (Fig. 2.4) will show the significance of its terms. In this case there is only one component, magnesium, and in general the number of components is equal to the number of metals present in the system being considered. At point 1 in Fig. 2.4 there is only one phase present, gaseous magnesium; therefore at this point the phase rule becomes:

$$F = C + 2 - P$$

 $F = 1 + 2 - 1 = 2$

That is, there are two degrees of freedom. If both the pressure and temperature in a unary system are freely and arbitrarily selected, the situation corresponds to having two degrees of freedom and is called bivariant equilibrium.

The situation at point 2 is significantly different. Because the liquid and vapor phases exist in equilibrium at this point, there are two phases present and the phase rule yields:

$$F = C + 2 - P$$

 $F = 1 + 2 - 2 = 1$

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Fig. 2.4 Unary diagram for magnesium with points in one-, two-, and three-phase regions of the diagram. Adapted from: Ref 2.1

This condition is called univariant equilibrium or monovariant equilibrium. Either pressure or temperature may be freely selected, but not both. Once a pressure is selected, there is only one temperature that will satisfy equilibrium conditions, and conversely, once a temperature is selected, there is only one pressure that will satisfy equilibrium conditions.

How can there be only one degree of freedom when it is evident that both temperature and pressure must change in order to proceed from point 2 to point 2', where the two phases continue to exist? The answer is that only one of the variables can be changed independently. To increase the pressure without losing either of the phases originally present, the temperature must also be raised exactly the proper amount. Similarly, the temperature can be changed arbitrarily but the two phases will continue to exist only if the pressure is also varied by a specific, not an independent, amount. Only one of the variables, therefore, can be independently changed at point 2 if two phases are to remain. A similar analysis shows that there are zero degrees of freedom at point 3, the triple point, in Fig. 2.4. The triple point is also called an invariant point because, at that location on the diagram, all externally controllable factors are fixed (no degrees of freedom). At this point, all three states (phases) are in equilibrium, but any changes in pressure and/or temperature will cause one or two of the states (phases) to disappear.

2.2 Solid Solutions

Pure metals are rarely used for industrial applications unless high conductivity, high ductility, or good corrosion resistance are required. Because pure metals tend to be much weaker than alloys, alloying elements are added to improve strength and hardness. In addition, alloying element additions can often be accomplished without major reductions in the attributes associated with pure metals, that is, conductivity, ductility, and corrosion resistance. When two metals are mixed in the liquid state to produce a solution, the resulting alloy is called a binary alloy. While a great number of alloys are binary, many more alloys contain a number of alloying elements. In the case of high-temperature superalloys, as many as ten alloying elements may used to obtain the desired performance.

The metals nickel and copper completely dissolve in each other in the liquid state and then retain their complete solubility in each other on freezing to form a series of alloys. The improvement in strength properties in these alloys is shown in Fig. 2.5. Note that the yield strength, the tensile strength, and the hardness all are improved as a result of alloying. While the ductility is reduced somewhat with alloying, the reduction is very moderate and these alloys all still have very good ductility.

When a metal is alloyed with another metal, either substitutional or interstitial solid solutions (Fig. 2.6) are usually formed. Substitutional solid solutions are those in which the solute and solvent atoms are nearly the same size, and the solute atoms simply substitute for solvent atoms on the crystalline lattice. Interstitial solid solutions are those in which the solute atoms are much smaller and fit within the spaces between the existing



Fig. 2.5 Solid-solution strengthening for copper-nickel alloys. Source: Ref 2.2

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Fig. 2.6 Solid solutions. Source: Ref 2.2

solvent atoms on the crystalline structure. However, the only solute atoms small enough to fit into the interstices of metal crystals are hydrogen, nitrogen, carbon, and boron. The other small-diameter atoms, such as oxygen, tend to form compounds with metals rather than dissolve in them. When both small and large solute atoms are present, the solid solution can be both interstitial and substitutional.

The insertion of substitutional and/or interstitial alloying elements strains the crystalline lattice of the host solvent structure (Fig. 2.7). This increase in distortion, or strain, creates barriers to dislocation movement. The distortion energy causes some hardening and strengthening of the alloy, and is called solid-solution hardening. The solute atoms have a different size than the host atoms, which alters the crystal lattice. As a result, a moving dislocation is either attracted to, or repelled by, the solute; however, both situations result in a strength increase. When the dislocation is attracted to a solute, the additional force required to pull the dislocation away from it is the cause of the added strength. If the dislocation is repelled by the solute, an additional force is required to push the dislocation past the solute atom.

Studies of solid-solution hardening indicate that the hardening depends on the differences in elastic stiffness and atomic size between the solvent and solute. In general, larger differences result in greater strengthening, but at the same time, the greater the difference in sizes between the solute and solvent atoms, the more restricted is their mutual solubilities. The solvent phase becomes saturated with the solute atoms and reaches its limit of homogeneity when the distortion energy reaches a critical value determined by the thermodynamics of the system. The effects of several alloying elements on the yield strength of copper are shown in Fig. 2.8. Nickel and zinc atoms are approximately the same size as copper



Fig. 2.7 Lattice distortions caused by solute additions. Source: Ref 2.2



Fig. 2.8 The effects of several alloying elements on the yield strength of copper. Source: Ref 2.3 as published in Ref 2.2

atoms, but beryllium and tin atoms are much different from copper atoms. Increases in the atomic size difference and the amount of alloying both result in increases in solid-solution strengthening.

2.3 Interstitial Solid Solutions

The four elements carbon, nitrogen, hydrogen, and boron have such small diameters that they can form interstitial solid solutions. In general, these interstitial solid solutions have somewhat limited composition ranges. Only the transition metals (e.g., iron, nickel, titanium, and zirconium) have appreciable solubilities for carbon, nitrogen, and boron. Very small atoms, such as carbon, nitrogen, and hydrogen can fit in the spaces between the larger atoms. These sites are called interstitial sites and can be of either the tetrahedral or octahedral variety (Fig. 2.9). Interstitial atoms generally



Fig. 2.9 Representative interstitial sites in unit cells. Source: Ref 2.3 as published in Ref 2.2

strengthen a metal more than substitutional atoms do, because the interstitials cause more distortion. Carbon atoms in the body-centered cubic (bcc) form of iron are particularly potent hardeners in this respect.

Carbon, nitrogen, and boron are all important alloying elements in steels. Interstitial carbon in iron forms the basis of steel hardening. Indeed, steels are alloys of iron and small amounts of carbon. Although not as important as carbon, nitrogen and boron are also useful alloying elements in certain steels. In addition, carbon and nitrogen are diffused into the surfaces to provide hardness and wear resistance in processes called carburizing and nitriding. On the other hand, hydrogen is almost never a welcome addition to any metal. It usually results in sharp decreases in ductility and produces brittle fracture modes, a mechanism called hydrogen embrittlement.

2.4 Substitutional Solid Solutions

These four rules giving a qualitative estimate of the ability of two metals to form substitutional solid solutions were developed by Hume-Rothery and are summarized as:

- *Rule 1-Relative Size Factor.* If the sizes of the solute and solvent atoms differ by less than 15%, the metals are said to have a favorable size factor for solid-solution formation. Each of the metals will be able to dissolve an appreciable amount of the other metal, on the order of 10% or more. If the size factor differs by more than 15%, then solid-solution formation tends to be severely restricted.
- *Rule 2–Chemical Affinity Factor.* The greater the chemical affinity of two metals, the more restricted is their solid solubility. When their chemical affinity is great, they tend to form compounds rather than a solid solution.
- *Rule 3—Relative Valency Factor.* If a solute atom has a different valence from that of the solvent metal, the number of electrons per atom, called the electron ratio (*e/a*), will be changed by alloying. Crystal structures are more sensitive to a decrease in the electron ratio than to an increase. Therefore, a metal of high valence can dissolve only a small amount of a lower-valence metal, while a lower-valence metal may have good solubility with a higher-valence metal.
- *Rule 4—Lattice Type Factor*. Only metals that have the same type of lattice structure (e.g., face-centered cubic) can form a complete series of solid solutions. Also, for complete solid solubility, the size factor must usually be less than 8%.

There are numerous exceptions to these rules. In general, an unfavorable size factor alone is sufficient to severely limit solid solubility to a minimal level. If the size factor is favorable, then the other three rules should be evaluated to determine the probable degree of solid solubility. Metallic systems that display complete solid solubility are quite rare, with the copper-nickel system being the most important.

2.5 Intermediate Phases

When the electrochemical properties of the alloying element metals are similar, normal substitutional solid solutions will form during solidification. However, when the metals have widely divergent electrochemical properties, they are more likely to form a chemical compound, often with some degree of covalent or ionic bonding present. For example, strongly electropositive magnesium will combine with weakly electropositive tin to form Mg_2Sn , which is often described as being an intermetallic compound.

Between these two extremes of substitutional solid solution on the one hand and intermetallic compound on the other, phases are formed that exhibit a gradation of properties. These phases are collectively termed *intermediate phases*. At one extreme there are true intermetallic compounds while at the other are ordered structures that can be classified more accurately as secondary solid solutions. These intermediate phases are often grouped into categories determined by their structures.

Intermetallic Compounds. Two chemically dissimilar metals tend to form compounds with ordinary chemical valence. These compounds have stoichiometric compositions with limited solubility. These compounds are generally formed when one metal has chemical properties that are strongly metallic, such as magnesium, and the other metal has chemical properties that are only weakly metallic, such as tin. Frequently, such a compound has a melting point that is higher than that of either of the parent metals. For example, the intermetallic compound Mg₂Sn melts at 780 °C (1436 °F), whereas pure magnesium and tin melt at 650 and 230 °C (1202 and 450 °F), respectively. This is an indication of the high strength of the bond in Mg₂Sn. Because they exhibit either covalent or ionic bonding, they exhibit nonmetallic properties such as brittleness and poor electrical conductivity. Examples include the covalent compounds Mn₂Sn, Fe₃Sn, and Cu₆Sn₅, and the ionic compounds Mg₂Si and Mg₂Sn.

Electron Phases. These compounds appear at definite compositions and depend on the ratio of electrons to atoms (e/a) at those compositions. The most important of these are the intermediate phases of the copperzinc system. The valence of a metal is defined by the number of electrons in the outer shell of the atom. In electron compounds, the normal valence laws are not obeyed, but in many instances there is a fixed ratio between the total number of valence bonds of all the atoms involved and the total number of atoms in the empirical formula of the compound in question.

There are three such ratios, commonly referred to as Hume-Rothery ratios:

- Ratio 3/2 (21/14): β structures, such as CuZn, Cu₃Al, Cu₅Sn, Ag₃Al
- Ratio 21/13: γ structures, such as Cu₅Zn₈, Cu₉Al₄, Cu₃₁Sn₈, Ag₅Zn₈, Na₃₁Pb₈
- Ratio 7/4 (21/12): ε structures, such as CuZn₃, Cu₃Sn, AgCd₃, Ag₅Al₃

For example, in the β structure compound CuZn, copper has a valence of 1 and zinc a valence of 2, giving a total of 3 valences and a ratio of 3 valences to 2 atoms. In the compound Cu₃₁Sn₈, copper has a valence of 1 and tin a valence of 4. Therefore 31 valences are donated by the copper atom and 32 (4 × 8) by the tin atoms, making a total of 63 valences. In all, 39 atoms are present and the ratio is:

$$\frac{\text{Total number of valences}}{\text{Total number of atoms}} = \frac{63}{39} = \frac{21}{13}$$

These phases exist over a range of compositions and are metallic in nature. These Hume-Rothery ratios have been valuable in relating structures that appeared unrelated. However, there are many electron compounds that do not fall into any of the three groups.

Interstitial Compounds. These are compounds of transition metals with carbon, nitrogen, hydrogen, or boron; the interstitial atomic radius must be less than 2/3 that of the transition metal atom. These compounds are hard and have very high melting points due to the covalent nature of their bonding. When the solid solubility of an interstitially dissolved element is exceeded, a compound is precipitated from the solid solution. The small nonmetal atoms still occupy interstitial positions but the overall crystal structure of the compound is different from that of the original interstitial solid solution. Compounds of this type have some metallic and some nonmetallic properties and comprise carbides, nitrides, hydrides, and borides. Examples include TiH₂, TiN, TaC, WC, and Fe₃C. All of these compounds are extremely hard and the carbides find application in tool steels and cemented carbide cutting materials. The compound Fe₃C (cementite) is important in steels.

Laves Phases. These compounds have a composition of AB_2 that forms because of the dense packing that can be achieved if the ratio of the *B* atoms to *A* atoms (*B*/*A*) is approximately 1.2. In these phases, the *A* atoms have 12 nearest *B* neighbors and 4 nearest *A* neighbors. Each *B* atom has 6 *A* and 6 *B* nearest neighbors. This arrangement produces an average coordination number of $(2 \times 12 + 16)/3 = 13.33$. These hard and brittle

phases, such as NbFe₂, TiFe₂, and TiCo₂, cause deterioration in ductility and stress-rupture properties. Undesirable Laves phase formation can be a problem in nickel, iron-nickel, and cobalt-base superalloys exposed to elevated temperatures for long times.

2.6 Free Energy and Phase Transformations

Free energy is important because it determines whether or not a phase transformation is thermodynamically possible. Essentially, the change in free energy, either ΔF or ΔG , must be negative for a reaction to occur. If the free-energy change is zero, the system is in a state of equilibrium and no reaction will occur. Likewise, if the free-energy change is positive, the reaction will not occur. To summarize:

- If ΔF or $\Delta G > 0$ or positive, the reaction will not occur.
- If ΔF or $\Delta G = 0$, the system is in equilibrium, and the reaction will not occur.
- If ΔF or $\Delta G < 0$ or negative, the reaction will occur.

The more negative the free-energy change (larger negative number), the greater the driving force for a transformation. In other words, if the free-energy change is a small negative number, the driving force is low, and as it becomes more negative, the driving force increases. The following develops these concepts in a little more detail.

The internal energy, E, of a system (e.g., an alloy) is made up of two parts: the kinetic energy that is due to atomic vibrations of the metallic lattice, and the potential energy that is a function of the bond strengths. The internal energy can also be thought of as the sum of the free energy, F, and the bound energy (TS):

$$E = F + TS \tag{Eq 2.1}$$

where E is the internal energy, F is the Hemholtz free energy, T is the absolute temperature in degrees Kelvin (K), and S is entropy, a measure of the randomness of the system.

The Gibbs free energy is defined as:

 $G = H - TS \tag{Eq 2.2}$

Because the enthalpy, H, at constant pressure is the heat content:

$$H = E + PV \tag{Eq 2.3}$$

When dealing with liquids and solids, the *PV* term is usually very small in comparison to *E*; therefore the enthalpy, *H*, can be considered as being

equal to the internal energy, $E(H \sim E)$. Therefore, this allows the Gibbs free energy to be expressed as:

$$G = E - TS \tag{Eq 2.4}$$

which is the same as the Hemholtz free energy, F:

$$F = E - TS \tag{Eq 2.5}$$

What is really important in metallurgical processes is not the free energy, G, itself, but the change in free ΔG . It can be shown that, at constant temperature and pressure:

$$\Delta G = \Delta H - T \Delta S \tag{Eq 2.6}$$

A system is said to be in equilibrium when it attains the state of lowest Gibbs free energy and the change in ΔG is then 0:

$\Delta G = 0 \text{ at constant } T \text{ and } P \tag{Eq 2.7}$

All phase transformations occur to lower the total energy of the system. Any transformation that results in a reduction in free energy, G, is possible; that is:

$$\Delta G = G_f - G_i < 0 \tag{Eq 2.8}$$

where G_f is the free energy of the final state and G_i is the free energy of the initial state.

At low temperatures, the solid phase is the most stable state because there is strong bonding between atoms and the system has the lowest free energy and entropy. As the temperature increases, the *TS* term begins to dominate and the solid phase has more freedom of atomic movement due to increasing temperature, until it melts and becomes a liquid phase.

A more detailed review of basic thermodynamics and Gibbs free energy is given in Chapter 3, "Thermodynamics and Phase Diagrams," in this book, and Chapter 13, "Computer Simulation of Phase Diagrams," covers thermodynamic modeling and computer simulation of phase diagrams.

2.7 Kinetics

Thermodynamics allows the calculation of the driving force for a phase transformation; however, it tells nothing about how fast the transformation will occur. Kinetics must be used to calculate the speed at which the transformation will occur. In a large number of metallurgical processes, the reaction rate increases exponentially with increases in temperature and can be described by the Arrhenius equation:

rate =
$$Ce^{-Q/RT}$$

(Eq 2.9)

where C is a pre-exponential constant that is independent of temperature, R is the universal gas constant, Q is the activation energy, and T is the absolute temperature.

Taking the logarithm of each side of Eq 2.9 allows the equation to be rewritten as:

$$\ln(\text{rate}) = \ln C - \frac{Q}{RT}$$
(Eq 2.10)

A semilogarithmic plot of ln (rate) versus the reciprocal of absolute temperature (1/T) gives a straight line, as shown in Fig. 2.10. The slope of this plot is -Q/R and ln C is obtained by extrapolating the plot to 1/T = 0 ($T = \infty$). Thus, if the rate at two different temperatures is known, the rate at a third temperature can be determined. Likewise, if the rate and activation energy, Q, is known at one temperature, then the rate at any other temperature can be determined.

The form of the Arrhenius given in Eq 2.10 can also be written as:

 $rate = Ce^{-q/kT}$ (Eq 2.11)

where q is the activation energy per atomic scale unit ($q = Q/N_{AV}$), and k is Boltzmann's constant ($k = R/N_{AV} = 13.8 \times 10^{-24} \text{ J/K}$).

The activation energy, q, for an atom to move from one stable position to another is shown in Fig. 2.11. In other words, the activation energy is that energy provided by temperature that must be supplied to overcome



Fig. 2.10 Typical Arrhenius plot. Source: Ref 2.2

the energy barrier. For an Arrhenius type reaction, an increase in temperature of approximately 10 °C (18 °F) nearly doubles the reaction rate of the process.

2.8 Liquid-Solid Phase Transformations

At any temperature, the thermodynamically stable state is the one with the lowest free energy. The equilibrium temperature for transition between two states is the temperature at which both have the same free energy. For the liquid-to-solid transition, this is the melting temperature. Compared to a solid metal, a liquid metal has a higher internal energy (equal to the latent heat of fusion) and a higher entropy due to its more random structure. The result is that as the temperature decreases toward the melting point, T_m , the liquid phase starts to develop more order, the entropy term decreases, and the free energy for the liquid rises at a faster rate than that of the solid, as illustrated in Fig. 2.12. At T_m , the equilibrium melting point, the free energies of both phases are equal. However, solidification does not occur



Fig. 2.11 Activation energy, metastable to stable state. Source: Ref 2.2



Fig. 2.12 Gibbs free-energy curves during solidification. Source: Ref 2.2

because the free-energy change is zero ($\Delta G = 0$) and it must be negative. Below $T_{\rm m}$, the free energy does become negative ($\Delta G < 0$) and the metal solidifies. The free-energy change is thus:

$$\Delta G = \Delta G_S - \Delta G_L < 0 \tag{Eq 2.12}$$

Immediately below $T_{\rm m}$, the free-energy change is very small, so solidification occurs slowly, but at larger undercooling or supercooling $(T_{\rm m} - T)$, the free-energy change becomes greater and the solidification rate is much more rapid.

As a metal freezes, solidification starts on a small scale with groups of atoms joining together in clusters (Fig. 2.13). As the temperature falls during the solidification process, the thermal agitation of the atoms in the liquid decreases, allowing small random aggregations of atoms to form into small crystalline regions called embryos. An embryo is a small cluster of atoms that has not yet reached a large enough size to become stable and grow. Therefore, embryos are constantly forming and then remelting. Eventually, as the temperature becomes lower, some of the embryos will reach a critical size and become nuclei that are then stable and capable of further growth into crystals. These crystals then continue to grow until they impinge on other growing crystals. Each of these crystals becomes grains in the final solidified structure. The crystalline structure within each grain is uniform but changes abruptly at the interfaces (grain boundaries) with adjacent crystals. This process of forming nuclei in the freezing melt and their subsequent growth is characterized as a nucleation and growth process.

Nucleation can occur by either homogeneous or heterogeneous nucleation. Homogenous nucleation occurs when nucleation takes place throughout the bulk of the liquid without preference for any point; that is, the probability of nucleation is the same everywhere within the volume of the liquid. When a solid nucleates preferentially at certain points in the liquid and the probability of nucleation occurring at certain preferred sites is much more than at other sites, it is called heterogeneous nucleation. Heterogeneous nucleation can occur at small solid inclusions within the melt and at sur-



Fig. 2.13 Nucleation and growth during solidification. Source: Ref 2.2

face irregularities on mold walls. While homogeneous nucleation can be made to occur in carefully controlled laboratory conditions, heterogeneous nucleation is the nucleation mechanism that is observed in all commercial casting operations.

Consider homogeneous nucleation in which a spherical nuclei of radius r forms within the bulk of the liquid. Because the formation of a nucleus requires the creation of an interface between the solid and liquid, it creates an increase in the free energy of the system. The surface energy required for a sphere of surface area $4\pi r^2$ is $4\pi r^2\sigma$, where σ is the surface energy per unit area and is shown as increasing the free energy of the system in Fig. 2.14. As was previously illustrated in Fig. 2.12, there is a free-energy reduction when the metal transforms from a liquid to a solid. This free energy is known as the volume free energy G_v , which, for a spherical nuclei, is $4/3\pi r^3 G_v$, and contributes to a decrease in free energy in Fig. 2.14. Thus, the total change in free energy, ΔG , is the sum of the decrease in volume free energy and the increase in surface free energy.

$$\Delta G = \frac{4}{3} \pi r^3 \Delta G_v + 4\pi r^2 \sigma$$
 (Eq 2.13)

where $\frac{4}{3}\pi r^3$ is the volume of a spherical embryo of radius r, ΔG_v is the volume free energy, $4 \pi r^2$ is the surface area of a spherical embryo, and σ is the surface free energy.

The total free-energy, ΔG , curve in Fig. 2.14 shows that there is a critical radius, r^* , that the particle must reach before it becomes a stable nuclei and continued growth is assured. If the embryo is very small, further growth of the embryo would cause the total free energy to increase. Therefore, the



Fig. 2.14 Free-energy curves for homogeneous nucleation. Source: Ref 2.2

embryo remelts and causes a decrease in the free energy. When the particle becomes a nuclei at the critical radius, r^* , growth is assured because the total free-energy curve then decreases continuously as it becomes larger.

Very large undercoolings and highly polished molds are required to cause homogenous nucleation, and it is rarely, if ever, observed in practice. In reality, the degree of undecooling is usually very small, often only a degree or two. Whereas homogeneous nucleation assumes nucleation occurs randomly throughout the liquid, heterogeneous nucleation occurs at preexisting particles in the liquid or at rough areas on the mold. Thus, heterogeneous nucleation does not incur the free-energy penalty of having to form a new surface; rather, it uses a preexisting surface. In actual castings, heterogeneous nucleation usually occurs at defects on the cold mold wall, such as cracks and crevices. However, for an inclusion or a defect on the mold wall to serve as a nucleation site, the liquid metal must be able to wet the surface. In addition, in many castings, a fine grain size is desirable, and nucleation agents are added to the melt to form as many nuclei as possible. Because each of these nuclei eventually grows and forms a grain, a larger number of nuclei results in a finer or smaller grain size. For example, a combination of 0.02 to 0.05% Ti and 0.01 to 0.03% B is added to many aluminum alloys. Solid titanium boride particles form and serve as effective sites for heterogeneous nucleation. Ultrasonic agitation of the mold during casting also promotes finer grain size by breaking up growing particles and helping to distribute them through the melt. Once a melt has been populated with nuclei, the growth of the solid is controlled almost exclusively by the rate of heat removal. Important liquid-solid transformations include the eutectic, peritectic, and monotectic reactions that are covered in Chapters 5, 6, and 7 in this book, respectively.

2.9 Solid-State Phase Transformations

Solid-state phase transformations occur when one or more parent phases, usually on cooling, produces a new phase or phases. The most important mechanisms are nucleation, growth, and diffusion. However, not all transformations rely on diffusion. For example, the important martensitic transformation in steels occurs quite suddenly by a combination of shear mechanisms.

Solid-state transformations differ from liquid-to-solid transformations (solidification) in several important ways. In solids, the atoms are bound much tighter than in liquids and diffuse much more slowly, by a factor of approximately 10^{-5} slower, even at temperatures approaching the melting point. Instead of transforming directly to the equilibrium phase, metastable transition phases can form prior to forming the final equilibrium phase. Like solidification, nucleation in solid-state reactions is almost always heterogeneous. Heterogeneous nucleation occurs at structural defects such as grain boundaries, dislocations, and interstitial atoms.

During a solid-state phase transformation, at least one new phase is normally formed that has different physical/chemical characteristics and/or a different structure than the parent phase. During nucleation, very small particles or nuclei of the new phase, often consisting of only a few hundred atoms, reach a critical size that is capable of further growth. During the growth stage, the nuclei grow in size, resulting in the disappearance of some, or all, of the parent phase. The transformation is complete when the growth of the new phase particles proceeds until the equilibrium fraction is attained.

Particle growth in a solid is controlled by diffusion, in which atoms diffuse from the parent phase across the phase boundary and into the growing second-phase particles. Because this is a diffusion-controlled process, the grow rate, \dot{G} , is determined by temperature:

$$\dot{G} = C e^{-Q/RT} \tag{Eq 2.14}$$

where Q is the activation energy and C is the pre-exponential constant.

Both Q and C are independent of temperature. The temperature dependence of the growth rate, \dot{G} , and the nucleation rate, \dot{N} , is shown in the Fig. 2.15 curves. At a given temperature, the overall transformation rate is given as the product of \dot{G} and \dot{N} . For transformations that occur at high temperatures, the nucleation rate will be low and the growth rate will be high. This will result in fewer particles that will grow to large sizes and the resulting transformation product will be coarse. On the other hand, if the transformation occurs at lower temperatures, where there is a much higher driving force for nucleation, many particles will form where the growth rate is lower, and the resulting transformation product will be much finer.



Fig. 2.15 Transformation rate as a function of temperature. Source: Ref 2.4 as published in Ref 2.2

The rate of transformation and the time required for the transformation to proceed to some degree of completion are inversely proportional to one another. The time to reach a 50% degree of completion in the reaction is frequently used. Therefore, the rate of a transformation is taken as the reciprocal of time required for the transformation to proceed halfway to completion, $t_{0.5}$, or:

rate =
$$\frac{1}{t_{0.5}}$$
 (Eq 2.15)

If the logarithm of this transformation time is plotted versus temperature, the result is a C-shaped curve, like the one shown in Fig. 2.16, which is a mirror image of the transformation rate curve previously shown in Fig. 2.15.

When the fraction of material transformed is plotted versus the logarithm of time at a constant temperature, an S-shaped curve similar to that in Fig. 2.17 is obtained, which is typical of the kinetic behavior for most solid-state reactions. For solid-state transformations displaying the kinetic behavior in Fig. 2.17, the fraction of transformation, y, is a function of time, t, and follows the Avrami equation:

 $y = 1 - e^{-kt^n}$ (Eq 2.16)

where k and n are time-independent constants for the particular reaction. The value for k depends on the temperature and the properties of the initial phase, while the coefficient n has the values listed in Table 2.1.



Fig. 2.16 Transformation rate versus temperature. Source: Ref 2.4 as published in Ref 2.2

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Fig. 2.17 Fraction reacted as a function of time. Source: Ref 2.4 as published in Ref 2.2

Table 2.1 Values of *n* in Avrami equation

Type of transformation		Value of <i>n</i>
Cellular	Constant rate of nucleation Zero rate of nucleation Nucleation at grain edges Nucleation at grain boundaries	4 3 2 1
Precipitation	 Particle growing from small dimensions Constant rate of nucleation Zero rate of nucleation Thickening of needles Thickening of plates 	2.5 1.5 1 0.5
Source: Ref 2.5 as published	in Ref 2.2	

The values of *n* in the Avrami equation distinguish between cellular transformations and precipitation transformations. A cellular transformation is one in which an entirely new phase is formed during the transformation, such as a solid-state transformation in which a higher-temperature γ phase transforms in two lower-temperature phases, α and β . In this reaction, γ disappears and is replaced by a mixture of α and β . It is called a cellular reaction because α and β grow as cells or nodules into the γ phase.

2.10 Polymorphism (Allotropy)

The structure of solid elements and compounds under stable equilibrium conditions is crystalline, and the crystal structure of each is unique. Some elements and compounds, however, are polymorphic (multishaped); that is, their structure transforms from one crystal structure to another with changes in temperature and pressure, each unique structure constituting a distinctively separate phase. The term *allotropy* (existing in another form) is usually used to describe polymorphic changes in chemical elements.

The important metal iron undergoes a series of allotropic transformations during heating and cooling, as shown in Fig. 2.18. Note that an allotropic transformation is a solid-state phase transformation, and as such, occurs at a constant temperature during either heating or cooling. Under equilibrium cooling conditions, the solidification of pure iron from the liquid occurs at 1540 °C (2800 °F) and forms what is called delta iron (δ_{Fe}), which has a bcc structure. Delta iron is then stable on further cooling until it reaches 1390 °C (2541 °F), where it undergoes a transformation to a face-centered cubic (fcc) structure called gamma iron (γ_{Fe}). On still further cooling to 900 °C (1648 °F), it undergoes yet another phase transformation, transforming from the fcc structure back to the bcc structure, called ferrite iron (α_{Fe}) to distinguish it from the higher-temperature delta iron. This last transformation, $\gamma_{Fe} \rightarrow \alpha_{Fe}$, is extremely important because it forms the basis for the hardening of steel. Note that the $\gamma_{Fe} \rightarrow \alpha_{Fe}$ transformation occurs at 900



Fig. 2.18 Polymorphic transformations in pure iron. Source: Ref 2.6

°C (1648 °F) on cooling, somewhat lower than the 910 °C (1673 °F) temperature transformation on heating. This temperature differential is known as the temperature hysteresis of allotropic phase transformation and its magnitude increases with increases in the cooling rate. The temperatures (designated *A*) associated with heating contain the subscript "c," which is French for *chauffage*, meaning heating, while the ones for cooling have the subscript "r" for the French *refroidissement*, meaning cooling.

Many other metals, as well as some nonmetals, also exhibit allotropic transformations. For example, titanium, zirconium, and hafnium all exhibit a transition from a hexagonal close-packed (hcp) structure to bcc on heating. Note that in each case, a close-packed structure is stable at room temperature, while a looser packing is stable at elevated temperatures. While this is not always the case, it is a trend experienced with many metals. Allotropic transformations are a type of massive transformation. Massive transformations occur by a transition in crystal structure and are characterized by the chemical invariance between parent and product phases. These transformations can occur both on heating and cooling, although the mechanism requires rapid heating and cooling rates, because the ability of atoms to diffuse the long distances typical of diffusion-controlled transformations is impaired.

Important solid-state transformation structures include eutectoid and peritectoid structures, martensitic and bainitic structures, and precipitation structures (see Chapters 8, "Solid-State Transformations;" 15, "Nonequilibrium Reactions—Martensitic and Bainitic Structures;" and 16 "Nonequilibrium Reactions—Precipitation Hardening;" in this book, respectively).

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