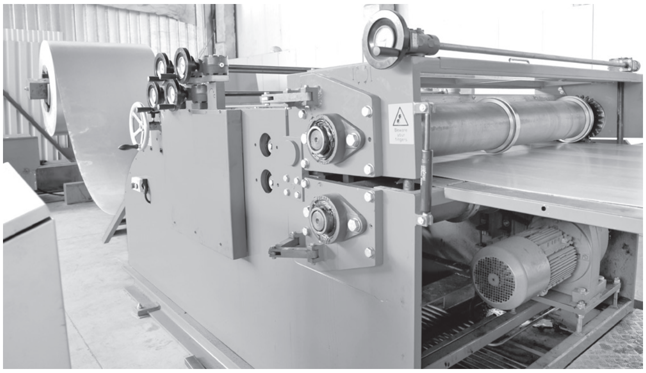
CHAPTER 10
Kinetics—Heat Treatment



Time is a factor! Passing steel sheet through this rolling mill will dramatically alter its mechanical properties that can then be altered further by subsequent heat treatments. (© Laurentiu Iordache / Alamy.)

10.1 Time—The Third Dimension

Time did not appear in any quantitative way in the discussion of phase diagrams in Chapter 9. Aside from requiring temperature changes to occur relatively slowly, we did not consider time as a factor at all. Phase diagrams summarized

Shackelford, James. Introduction to Materials Science for Engineers, Global Edition, Pearson Education Limited, 2015. ProQuest Ebook Central, http://ebookcentral.proquest.com/lib/ethz/detail.action?docID=5173617.
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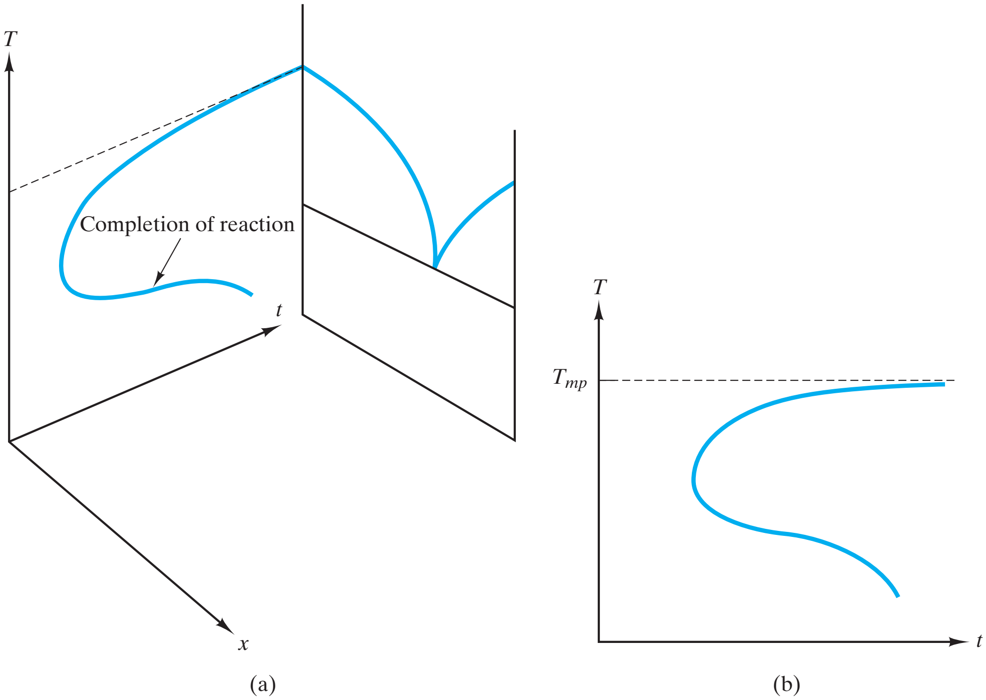

FIGURE 10.1 *Schematic illustration of the approach to equilibrium. (a) The time for solidification to go to completion is a strong function of temperature, with the minimum time occurring for a temperature considerably below the melting point. (b) The temperature–time plane with a transformation curve. We shall see later that the time axis is often plotted on a logarithmic scale.*

equilibrium states and, as such, those states (and associated microstructures) should be stable and unchanging with time. However, these equilibrium structures take time to develop, and the approach to equilibrium can be mapped on a time scale. A simple illustration of this concept is given in Figure 10.1, which shows a time axis perpendicular to the temperature–composition plane of a phase diagram. For component A, the phase diagram indicates that solid A should exist at any temperature below the melting point. However, Figure 10.1 indicates that the time required for the liquid phase to transform to the solid phase is a strong function of temperature.

Another way of stating this idea is that the time necessary for the solidification reaction to go to completion varies with temperature. In order to compare the reaction times in a consistent way, Figure 10.1 represents the rather ideal case of quenching the liquid from the melting point instantaneously to some lower temperature and then measuring the time for solidification to go to completion at that temperature. At first glance, the nature of the plot in Figure 10.1 may seem surprising. The reaction proceeds slowly near the melting point and at relatively low temperatures. The reaction is fastest at some intermediate temperature. To understand this "knee-shaped" transformation curve, we must explore some fundamental concepts of kinetics theory.

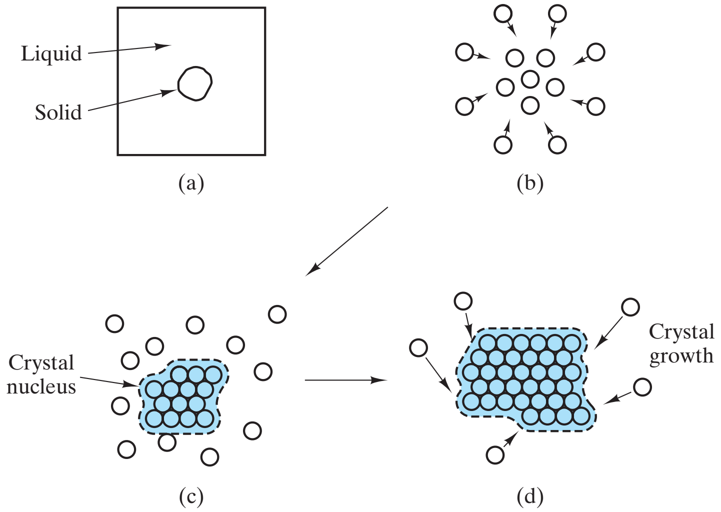

FIGURE 10.2 *(a) On a microscopic scale, a solid precipitate in a liquid matrix. The precipitation process is seen on the atomic scale as (b) a clustering of adjacent atoms to form (c) a crystalline nucleus followed by (d) the growth of the crystalline phase.*

For this discussion, we focus more closely on the precipitation of a single-phase solid within a liquid matrix (Figure 10.2). This process is an example of **homogeneous nucleation**, meaning that the precipitation occurs within a completely homogeneous medium. The more common case is **heterogeneous nucleation**, in which the precipitation occurs at some structural imperfection such as a foreign surface. The imperfection reduces the surface energy associated with forming the new phase.

Even homogeneous nucleation is rather involved. The precipitation process actually occurs in two stages. The first stage is **nucleation**. The new phase, which forms because it is more stable, first appears as small nuclei. These nuclei result from local atomic fluctuations and are, typically, only a few hundred atoms in size. This initial stage involves the random production of many nuclei. Only those larger than a given size are stable and can continue to grow. These critical-size nuclei must be large enough to offset the energy of formation for the solid–liquid interface. The rate of nucleation (i.e., the rate at which nuclei of critical size or larger appear) is the result of two competing factors. At the precise transformation temperature (in this case, the melting point), the solid and liquid phases are in equilibrium, and there is no net driving force for the transformation to occur. As the liquid is cooled below the transformation temperature, it becomes increasingly unstable. The classical theory of nucleation is based on an energy balance between the nucleus and its surrounding liquid. The key principle is that a small cluster of atoms (the nucleus) will be stable only if further growth reduces the net energy of the system. Taking the nucleus in Figure 10.2a as spherical, the energy balance can be illustrated as shown in Figure 10.3, demonstrating that the nucleus will be stable if its radius, r, is greater than a critical value, r_c.

The driving force for solidification increases with decreasing temperature, and the rate of nucleation increases sharply. This increase cannot continue indefinitely. The clustering of atoms to form a nucleus is a local-scale diffusion process. As such, this step will decrease in rate with decreasing temperature. This rate

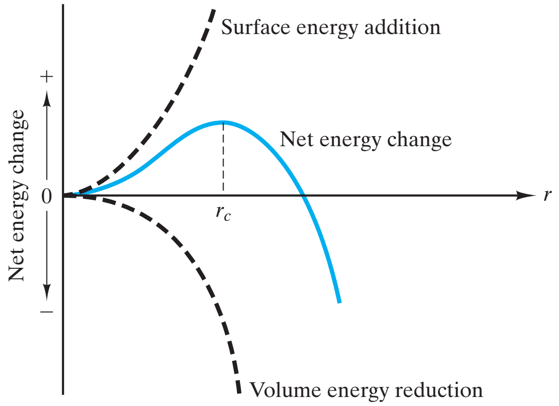

FIGURE 10.3 *Classical nucleation theory involves an energy balance between the nucleus and its surrounding liquid. A nucleus (cluster of atoms) as shown in Figure 10.2(c) will be stable only if further growth reduces the net energy of the system. An ideally spherical nucleus will be stable if its radius, r, is greater than a critical value, r_c.*

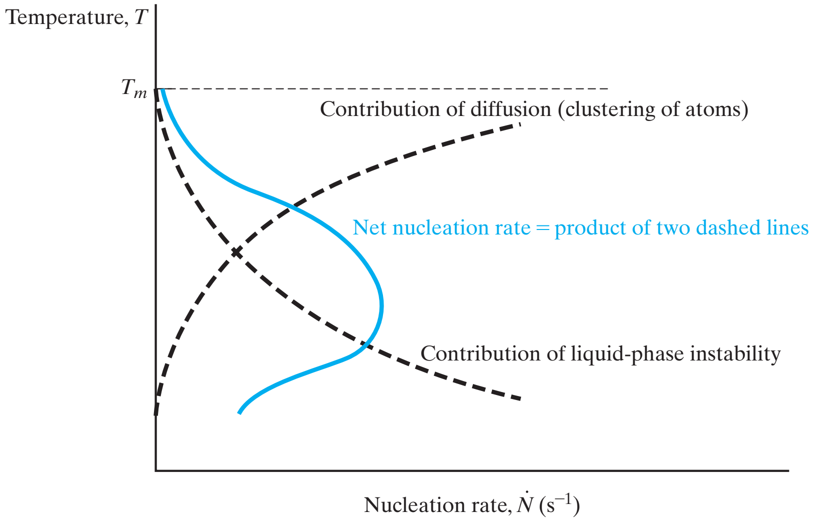

FIGURE 10.4 *The rate of nucleation is a product of two curves that represent two opposing factors (instability and diffusivity).*

decrease is exponential in nature and is another example of Arrhenius behavior (see Section 5.1). The overall nucleation rate reflects these two factors by increasing from zero at the transformation temperature (T_m) to a maximum value somewhere below T_m and then decreasing with further decreases in temperature (Figure 10.4). In a preliminary way, we now have an explanation for the shape of the curve in Figure 10.1. The time for reaction is long just below the transformation temperature because the driving force for reaction is small and the reaction rate is therefore small. The time for reaction is again long at low temperatures because the diffusion rate is small. In general, the time axis in Figure 10.1 is the inverse of the rate axis in Figure 10.4.

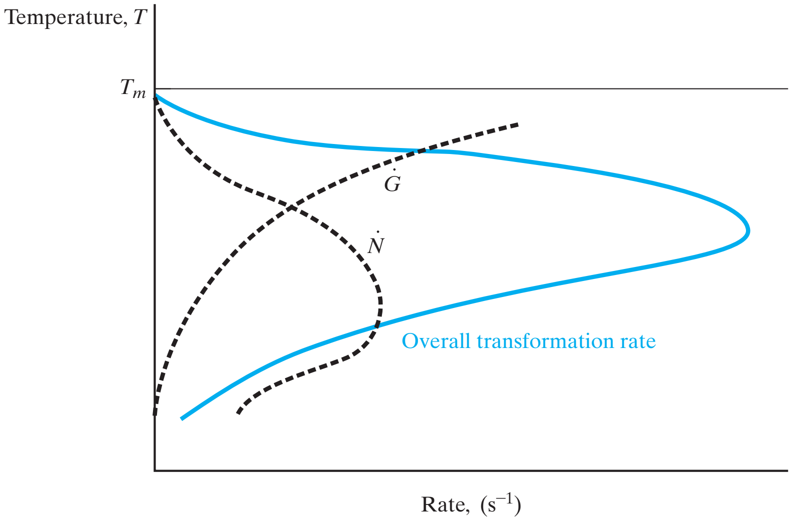

FIGURE 10.5 *The overall transformation rate is the product of the nucleation rate, $\dot{N}$, (from Figure 10.4) and the growth rate, $\dot{G}$ (given in Equation 10.1).*

Our explanation of Figure 10.1 using Figure 10.4 is preliminary because we have not yet included the growth step (see Figure 10.2). This process, like the initial clustering of atoms in nucleation, is diffusional in nature. As such, the growth rate, $\dot{G}$, is an Arrhenius expression,

$$\dot{G} = Ce^{-Q/RT}, \qquad (10.1)$$

where C is a preexponential constant, Q is the activation energy for self-diffusion in this system, R is the universal gas constant, and T is the absolute temperature. This expression is discussed in some detail in Section 5.1. Figure 10.5 shows the nucleation rate, $\dot{N}$, and the growth rate, $\dot{G}$, together. The overall transformation rate is shown as a product of $\dot{N}$ and $\dot{G}$. This more complete picture of phase transformation shows the same general behavior as nucleation rate. The temperature corresponding to the maximum rate has shifted, but the general argument has remained the same. The maximum rate occurs in a temperature range where the driving forces for solidification and diffusion rates are both significant. Although this principle explains these knee-shaped curves in a qualitative way, we must acknowledge that transformation curves for many practical engineering materials frequently include additional factors, such as multiple diffusion mechanisms and mechanical strains associated with solid-state transformations.

EXAMPLE 10.1

At 900°C, growth rate, $\dot{G}$, is a dominant term in the crystallization of a copper alloy. By dropping the system temperature to 400°C, the growth rate drops six orders of magnitude and effectively reduces the crystallization rate to zero. Calculate the activation energy for self-diffusion in this alloy system.