

## 5

## Effects of Diffusion and Nucleation on Phase Transformations

A phase diagram is a construction for thermodynamic equilibrium, a static state, and therefore contains no information about how much time is needed before the phases appear with their equilibrium fractions and compositions. It might be assumed that the phases found after practical times of minutes or hours will be consistent with the phase diagram, since most phase diagrams were deduced from experimental measurements on such time scales.<sup>1</sup> However, a number of nonequilibrium phenomena such as those described in this chapter are well known, and were likely taken into account when a  $T$ - $c$  phase diagram was prepared.

For rapid heating or cooling, the kinetic processes of atom rearrangements often cause deviations from equilibrium, and some of these nonequilibrium effects are described in this Chapter 5. In general, first one seeks to understand the effects of the slowest processes. For faster heating or cooling, however, sometimes the slowest processes are inactive, so the next-slowest processes become important. Approximately, this Chapter 5 follows a course from slower to faster kinetic processes.

<sup>1</sup> On the other hand, this does not necessarily mean that all phases on phase diagrams are in fact equilibrium phases. Exceptions are found, especially at temperatures below about half the liquidus temperature.

**Box 5.1****Thermodynamics and Kinetics**

Two necessary conditions for a phase transformation to occur in a material are

- a driving force from a reduction of free energy, and
- a mechanism for atoms to move towards their equilibrium positions.

The phase diagram gives information about first condition, but most phase changes in materials occur by diffusional motions of atoms.

## 5.1 Non-Equilibrium Processing of Materials

### 5.1.1 Diffusion Lengths

The diffusional motion of atoms is thermally activated, and is more rapid at higher temperatures. An important consideration is the characteristic time  $\tau$  for diffusion over a characteristic length  $x$  (see Eq. 3.48)

$$\tau = \frac{x^2}{D(T)}, \quad (5.1)$$

where  $D(T)$  is the diffusion coefficient.

Minimizing the time when  $D(T)$  is large serves to minimize  $x$ , so one way to classify either kinetic phenomena or methods of materials processing is by effective cooling rate. Table 5.1 shows some kinetic phenomena that are suppressed by cooling at increasingly rapid rates. Insights into the phenomena listed in Table 5.1 are obtained with a rule of thumb that diffusion coefficients near the melting temperature of many (metallic) materials are  $D(T_m) \sim 10^{-8} \text{ cm}^2/\text{s}$ .<sup>2</sup> For an interatomic distance of typically  $2 \times 10^{-8} \text{ cm}$ , Eq. 5.1 gives a characteristic time of  $4 \times 10^{-8} \text{ s}$ . For ultrafast cooling, it seems possible to suppress all atom diffusion in solids below the melting temperature, suppressing crystal nucleation and growth. This allows the formation of amorphous metallic elements, but these are highly unstable and may persist only at cryogenic temperatures. At  $2/3$  of the melting temperature, the time scale for suppressing atom motion at the atomic scale is increased by a factor of  $10^4$  or so, owing to a decrease in  $D(T)$ .

### 5.1.2 Quenching Techniques

Some practical methods to achieve high cooling rates are also listed in Table 5.1. The cooling rates are approximate, since these depend on the sample thickness and thermal conductivity, which vary with the particular material and the equipment. Like the diffusion of atoms, the diffusion of heat has a quadratic relationship between the characteristic cooling time  $\tau$  and the sample thickness,  $x$ , as in Eq. 5.1, where  $D(T)$  is now a thermal diffusivity. Approximately, the techniques listed in Table 5.1 make thicknesses of materials that are proportional to the square root of the inverse cooling rate. Samples from melt spinning are tens of microns thick, and samples from laser surface melting are often less than  $0.1 \mu\text{m}$ , for example.

Iced brine quenching is an older technique, where a sample at elevated temperature is quickly immersed in a solution of rocksalt in water, cooled with ice. The salt serves to elevate the boiling temperature and improve the thermal conductivity. The rate of cooling depends on the thickness of the sample. The quench rate also depends on the formation of bubbles of water vapor on the sample surface, which

<sup>2</sup> Sometimes an estimate of  $D \sim 10^{-5} \text{ cm}^2/\text{s}$  for the liquid proves useful, too.

**Table 5.1** Cooling Rates, Methods, Typical Kinetic Phenomena

infinitesimal $10^{-6}$ K/s	geologic cooling	equilibrium (sometimes)
slow $10^0$ K/s		suppressed diffusion in solid
$10^1$ K/s	casting	dendrites
$10^3$ K/s	iced brine quench	suppressed precipitation
medium $10^4$ K/s		suppressed diffusion in liquid
$10^5$ K/s	melt spinning	extended solid solubility
fast $10^6$ K/s	piston-anvil quench	metallic glasses
$10^9$ K/s	laser surface melting	
ultrafast $10^{10}$ K/s		amorphous elements
$10^{11}$ K/s	physical vapor deposition	
–	shock wave	melting
–	high-energy ball milling	nanocrystallinity, glass formation
–	heavy ion irradiation	chemical mixing, glass formation

suppress thermal contact to the water bath. Stirring the mixture can improve the cooling rate.

In melt spinning, a steady stream of liquid metal is injected onto the outer surface of a spinning wheel of cold copper, for example. The liquid cools quickly when in contact with the wheel, making a solid ribbon that is thrown off the wheel and spooled. This method is suitable for high volume production. The liquid metal should have modest wetting of the spinning wheel, and optimizing the parameters of the system can be challenging.

Piston-anvil quenching, sometimes known as “splat quenching,” uses a pair of copper plates that impact a liquid droplet from two sides. The alloy is typically melted by levitation melting in an induction coil. When the radiofrequency heating current is stopped, the liquid droplet falls under gravity past an optical sensor that triggers the pistons. Like melt spinning, the sample is thin, perhaps 20 to 30 microns, but wetting properties are less of a concern.

Laser surface melting can be performed with either a pulsed or continuous laser. The sample may be moved in a raster pattern under laser illumination so a significant area can be treated. Once melted, the surface is cooled by the underlying solid material, and the thinner the melted region, the faster the cooling.

Physical vapor deposition may use a high temperature heater to evaporate a material under vacuum. The evaporated atoms move ballistically towards the cold surface of a substrate. When these atoms are deposited on the cold substrate, their thermal energy is removed quickly, in perhaps a hundred atom vibrations (approximately  $10^{-11}$  s), leading to very high cooling rates when the deposition rate is not too rapid and the substrate is isolated thermally from the hot evaporator.