

3.205 Thermodynamics and Kinetics of Materials—Fall 2006

November 21, 2006

Kinetics Lecture 8: Interface-Controlled and Diffusion-Controlled Growth

Lecture References

1. Porter and Easterling, *Phase Transformations in Metals and Alloys*, Van Nostrand Reinhold (International), Wokingham, 1988. Section 5.3, pp. 279–283, on diffusional growth; pp. 208–213 on alloy solidification.
2. Balluffi, Allen, and Carter, *Kinetics of Materials*, Section 20.1, “Growth of Planar Layers.”

Key Concepts

- The excess interfacial free energy per unit area  $\gamma$  is defined as a thermodynamic work term for creating a unit area of interface under specified conditions. Factors such as interfacial structure (e.g., degree of coherency), as well as local composition (e.g., “segregation”), can have a large influence on the magnitude of  $\gamma$ . The term *capillarity* refers to a large range of phenomena in which the interfacial free energy plays a central role, such as grain growth, particle coarsening, and sintering.
- A nucleated particle can grow spontaneously by adding atoms or molecules at its surface. For a single-component system like the freezing of water this involves water molecules moving across the liquid/solid interface and attaching in a certain orientation (ice is crystalline). Such movement requires thermal activation, but the molecular motion is short-range. In cases where the attachment kinetics are rate-controlling, such growth is called *interface controlled*. (Note that in the case of solidification of water, that heat flow kinetics will generally be rate-controlling.) During precipitation from supersaturated solution, the critical nucleus must gather material that is enriched in one of the components, relative to the average composition of the surrounding matrix. Thus, long-range diffusion is required for precipitate growth. The growth kinetics is said to be *diffusion-controlled*, and the kinetics can be modeled with the diffusion equation and suitable boundary conditions.
- Many interface-controlled growth processes proceed such that the particle size increases *linearly* in time, i.e.,  $r \propto t$ .
- Many diffusion-controlled growth processes proceed such that the particle size increases *parabolically* in time, i.e.,  $r \propto \sqrt{t}$ .
- Diffusional growth of a precipitate particle involves diffusion toward an interface that is moving, thus it is an example of what is called a *moving boundary problem*. Such problems are difficult to solve in closed, algebraic form, though some simple geometries are solvable. Typical boundary conditions assume “equilibrium at the interface,” as well as a mass- or energy-balance condition at the interface, known as a *Stefan condition*. Under straightforward circumstances, e.g. diffusional growth of a plate or spherical particle, the growth is parabolic: the particle radius advances proportional to  $\sqrt{t}$ .
- Solidification of a binary alloy can occur over a range of temperatures and the kinetics are governed by both heat flow and diffusion. Closed-form solutions to such problems are difficult to obtain. The advancing solid-liquid interface can build up a solute-rich boundary layer as solute is rejected into the retreating liquid. These phenomena allow for purification of materials by a process known as *zone refining* which is used extensively to control dopant levels in semiconductor crystals.