

3.21 Kinetics of Materials—Spring 2006

March 20, 2006

Lecture 15: Short-Circuit Diffusion in Crystals.

References

1. Balluffi, Allen, and Carter, *Kinetics of Materials*, Chapter 9.

Key Concepts

- Line and planar defects in crystals are often regions in which some atoms are not fully coordinated and thus not as closely packed as in a perfect crystal. If such “open” regions are connected over significant distances, then the regions form “channels” or “conduits” through which species can diffuse rapidly compared to a crystal that is free of line and planar defects. These high-diffusivity paths are said to be diffusion “short circuits.”
- *Grain boundaries* are interfaces along which two misoriented crystals abut. *Low-angle grain boundaries* have small misorientations (less than about  $10^\circ$ ), and their structure can be modeled using periodic arrays of dislocations. *Tilt boundaries* have the crystal misorientation axis in the plane of the boundary, and consist of arrays of edge dislocations. *Twist boundaries* have the crystal misorientation axis perpendicular to the plane of the grain boundary, and consist of arrays of screw dislocations. Most grain boundaries are “mixed”—that is, they have some tilt and some twist character.
- In a crystal with imperfections, “bulk crystal” diffusion will occur in parallel with “short-circuit” diffusion and in some regimes of behavior more than one mechanism may contribute to significant transport. The total amount of material transported by diffusion for a given diffusion path depends on both the magnitude of the diffusivity and the effective “cross section” of the particular path. In metal and ceramic surfaces and along solid-solid interfaces diffusion occurs in a thin slab of thickness  $\delta \approx 1 \text{ nm}$ ]; along dislocations in metal and ionic crystals diffusion occurs in a cylindrical “pipe” of diameter  $\delta \approx 1 \text{ nm}$ ].
- In f.c.c. metals the self-diffusivities generally follow  $D^S > D^B \approx D^D(\text{undissoc}) > D^D(\text{dissoc}) > D^{XL}$  and the activation energies vary as  $E^S < E^B \approx E^D(\text{undissoc}) < E^D(\text{dissoc}) < E^{XL}$  (see *KoM* Fig. 9.1).
- Factors influencing the contribution of grain boundary diffusion to total diffusivity include grain boundary structure (see *KoM* Fig. 9.2), grain size and temperature (see *KoM* Figs. 9.4–9.5), and whether or not the grain boundaries are stationary or moving (see *KoM* Fig. 9.6).
- A solution to a two-dimensional diffusion problem due to Fisher gives insight to the A, B, and C regimes of behavior for a solute source placed initially on the surface of a polycrystal (see *KoM* Section 9.2.2).
- Computer simulations indicate that the mechanisms of grain boundary diffusion involve point imperfections (vacancies and interstitials), much like diffusion in bulk crystals (see *KoM* Fig. 9.9).

Related Exercises in *Kinetics of Materials*

Review Exercises 9.1–9.5, pp. 225–227.