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3.205 Thermodynamics and Kinetics of Materials—Fall 2006

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Kinetics Lecture 6: Short-Circuit Diffusion in Crystals.

Lecture References

1. Porter and Easterling, *Phase Transformations in Metals and Alloys*, 1981, pp. 98–103.
2. Balluffi, Allen, and Carter, *Kinetic Processes in Materials*, Chapter 9. There is also a brief overview of the structure of interfaces in Appendix B.
3. Allen and Thomas, *The Structure of Materials*, John Wiley & Sons, New York, 1999. Sections 5.2 and 5.3 provide a good introduction the line and planar imperfections that can significantly influence diffusion.

Key Concepts

- Real crystals contain imperfections that provide paths for rapid diffusion; these include dislocations, grain boundaries, and free surfaces.
- The *diffusivities* for bulk, dislocations, grain boundaries, and free surfaces generally follow the trends

$$D^{XL} < D^D < D^B < D^S \tag{1}$$

  and the respective *activation energies* follow

$$E^{XL} > E^D > E^B > E^S \tag{2}$$

- The open "core" structure of edge dislocations provides a fast diffusion channel. The dislocation diffusivity in low stacking-fault energy, which have widely dissociated dislocations, is smaller than that for undissociated dislocations.
- Grain-boundary geometry is specified by at least *five* variables (degrees of freedom): two for the rotation axis, $\hat{r}$, one for the rotation angle, θ, and two for the grain boundary orientation, $\hat{n}$. Grain boundaries can be classified into three categories: tilt, twist, and mixed. In tilt boundaries the rotation axis lies in the boundary plane, and in twist boundaries it lies perpendicular to the boundary plane. Mixed boundaries have both tilt and twist character. Tilt boundaries can be described as an array of parallel edge dislocations. Twist boundaries consist of crossing arrays of screw dislocations.
- Grain-boundary diffusion likely occurs through rapid motion of vacancies and self-interstitials in the plane of the grain boundary. Diffusion kinetics on individual boundaries are highly dependent on boundary structure.
- Imperfections enhance the total diffusivity over that produced by bulk diffusion alone. The extent of enhancement depends on the defect density (e.g., grain size and dislocation density), as well as on temperature. Detailed models for the relative contributions have been developed and are reviewed in the lecture notes and the text.