5.5 Alternate Diffusion Paths

A final word of caution is in order about using specific diffusivity data to analyze a particular material process. Figure 5.17 shows that the self-diffusion coefficients for silver vary by several orders of magnitude, depending on the route for diffusional transport. To this point, we have considered **volume diffusion**, or **bulk diffusion**, through a material's crystal structure by means of some defect mechanism. However, there can be "short circuits" associated with easier diffusion paths. As seen in Figure 5.17, diffusion is much faster (with a lower Q) along a grain boundary. As we saw in Section 4.4, this region of mismatch between adjacent crystal grains in the material's microstructure is a more open structure, allowing enhanced grain-boundary diffusion. The crystal surface is an even more open region, and **surface diffusion** allows easier atom transport along the free surface less hindered by adjacent atoms. The overall result is that

$$Q_{\text{volume}} > Q_{\text{grain boundary}} > Q_{\text{surface}} \text{ and } D_{\text{volume}} < D_{\text{grain boundary}} < D_{\text{surface}}.$$

This result does not mean that surface diffusion is always the important process just because D_{surface} is greatest. More important is the amount of diffusing region available. In most cases, volume diffusion dominates. For a material with a small average grain size (see Section 4.4) and therefore a large grain-boundary area, **grain-boundary diffusion** can dominate. Similarly, in a fine-grained powder with a large surface area, surface diffusion can dominate.

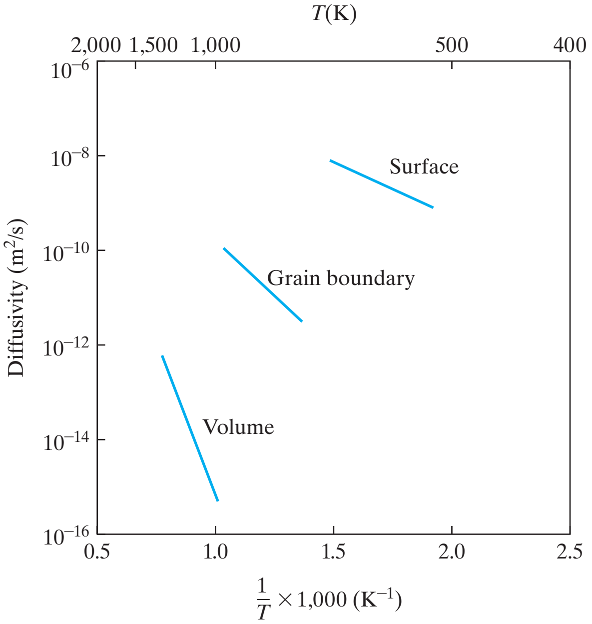

FIGURE 5.17 *Self-diffusion coefficients for silver depend on the diffusion path. In general, diffusivity is greater through less-restrictive structural regions.*

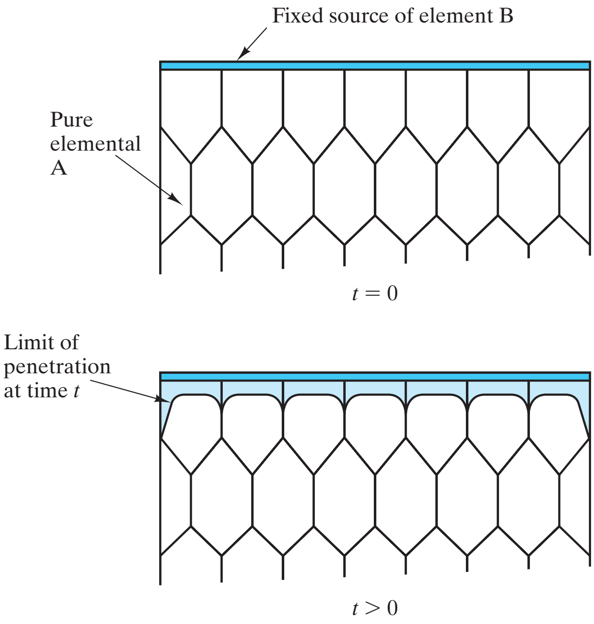

FIGURE 5.18 *Schematic illustration of how a coating of impurity* B *can penetrate more deeply into grain boundaries and even further along a free surface of polycrystalline* A*, consistent with the relative values of diffusion coefficients* ($D_{\text{volume}} < D_{\text{grain boundary}} < D_{\text{surface}}$).

For a given polycrystalline microstructure, the penetration of a diffusing species will tend to be greater along grain boundaries and even greater along the free surface of the sample (Figure 5.18).