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3.205 Thermodynamics and Kinetics of Materials—Fall 2006

November 7, 2006

Kinetics Lecture 4: Mechanisms of Diffusion in Materials

Lecture References

1. Porter and Easterling, *Phase Transformations in Metals and Alloys*, 1981, pp. 60–69.
2. Balluffi, Allen, and Carter, *Kinetic Processes in Materials*, Chapters 7–8.

Key Concepts

- Diffusion kinetics generally obey *scaling relationships* — the most important is that the diffusion distance x scales with $\sqrt{t}$. Thus, if a given process takes 100 s in a material of thickness 1 mm, in a material 3 mm thick it will take 900 s.
- A very useful "rule of thumb" in diffusion problems is that for *many* processes, $x^2 = 4Dt$ is a good approximation. Thus, if one knows D and wants to know how long it will take a species to diffuse 100 μm, one can estimate the time by calculating $t = x^2/(4D)$.
- Phase diagrams are often essential in understanding diffusional processes that can be expected to occur in processes like the application of coatings where one material might be joined to something quite different. The phase diagram will indicate what, if any, intermediate phases might form, and also provide a very good guide to the compositions of phases that form. Knowledge of the phase diagram allows boundary conditions to the diffusion equation to be specified, and thus enables quantitative modeling of kinetic processes involving multiple phases.
- A material's structure has a great influence on diffusion kinetics and the various atomistic mechanisms are quite well understood for most materials. The most important mechanisms in crystalline materials are the *interstitial* and *vacancy* mechanisms.
- Diffusive processes involve *thermally activated jumps* of atoms or molecules, and these jumps occur at a rate $\Gamma' = \nu \exp\left[-G^m/(kT)\right]$.
- If jumps can occur to any of z neighboring sites, the total jump frequency is $\Gamma = z\Gamma'$.
- *Random walk* models are very useful in modeling atomistic diffusion processes. Most diffusive processes in crystals can be described by a *lattice random walk* with jumps of fixed length in specific directions. The mean square displacement for a random walk of n jumps of length r is $\langle R^2 \rangle = nr^2$.
- Random walk of a vacancy in a diffusion couple results in intermixing of the two components.
- The relation between the diffusivity and the mean square displacement in three dimensions is $D = \frac{\Gamma r^2}{6} f$, where f is called the *correlation factor*.
- More detailed models that relate the diffusivity to atomistic processes are presented in the lecture notes, for diffusion of interstitials, vacancies, and of solute atoms that diffuse via the vacancy mechanism.