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3.205 Thermodynamics and Kinetics of Materials—Fall 2006

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Kinetics Lecture 2: Mass Diffusion and Heat Conduction

Lecture References

1. Porter and Easterling, *Phase Transformations in Metals and Alloys*, 1981, pp. 60–63, 69–71, 82–96.
2. Balluffi, Allen, and Carter, *Kinetics of Materials*, Chapter 3.
3. Poirier and Geiger, *Transport Phenomena in Materials Processing*, 1994, pp. 185–189 and 281–282 on heat conduction, and 417–434 on diffusion.

Key Concepts

- Fick's first law: $\vec{J} = -\mathbf{D}\nabla c$. This is an empirical law and it is consistent with the theory of linear irreversible thermodynamics.
- Fick's second law: $\frac{\partial c}{\partial t} = -\nabla \cdot \vec{J}$. This is a consequence of the conservation of matter. Note that if the diffusivity varies with c, the resulting differential equation is nonlinear.
- Self-diffusion in a chemically pure material can be measured by using a radioisotope that is easily tracked. The application of force-flux equations for the two isotopes yields a Fick's law-type expression for the radiotracer.
- Self-diffusion in a homogeneous alloy (uniform composition) can also be measured by using a radioisotope of one of the species. The application of force-flux equations for the various species present yields a Fick's law-type expression for the radiotracer.
- Self-diffusion in pure crystalline materials and in many alloy crystals occurs by the vacancy mechanism.
- Interdiffusion occurs in an alloy with composition gradients. The motion of each species in a laboratory frame fixed to the crystal follows Fick's first law, with a proportionality constant known as the *intrinsic diffusivity*. The intrinsic diffusivities and the self-diffusivities are related by P&E Eq. 2.64 with 2.69 (also *KoM* Eq. 3.13) and the relation involves a thermodynamic factor. Nonideality can either accelerate or retard interdiffusion kinetics, relative to kinetics measured in the absence of a chemical concentration gradient.
- Interdiffusion involves diffusion in a concentration gradient and the intrinsic diffusivities are not necessarily equal. This gives rise to a set of phenomena known as the *Kirkendall effect*. The interdiffusion can be described in a "volume-fixed" (laboratory) reference frame by a single diffusion coefficient known as the *interdiffusivity* which is related to the intrinsic diffusivities by the *Darken equation*, P&E Eq. 2.64 (also *KoM* Eq. 3.26).
- In addition to concentration gradients, other driving forces can lead to mass diffusion. These include thermal gradients, stress gradients, and capillary driving forces.
- The equations of heat *conduction* are of identical form to Fick's laws: $\vec{J_Q} = -k\nabla T$ and $\frac{\partial T}{\partial t} = -\nabla \cdot \vec{J_Q}$.