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3.21 Kinetics of Materials—Spring 2006

April 26, 2006

Lecture 25: Heterogeneous Nucleation.

References

1. Balluffi, Allen, and Carter, *Kinetics of Materials*, Section 19.2.

Key Concepts

- In heterogeneous nucleation, special sites in a material can effectively catalyze the nucleation process by reducing the critical free energy of nucleation $\Delta\mathcal{G}_c$. Heterogeneous nucleation is always in kinetic competition with homogeneous nucleation, and the mechanism with the faster rate determines which will prevail.

- The steady-state nucleation rate is given by $J = Z\,\beta_c N \exp[-\Delta\mathcal{G}_c/(kT)]$. While the lower value of $\Delta\mathcal{G}_c$ favors heterogeneous nucleation, the value of N (the number of potential nucleation sites) is generally far larger for homogeneous nucleation. By using the expression for the steady-state nucleation rate, regimes of temperature, supersaturation, relative interfacial energies, and microstructure in which one nucleation mechanism or the the other dominates.

- In polycrystalline microstructures, possible heterogeneous nucleation sites include grain boundaries, edges and corners. When a small particle forms on one of these crystal imperfections, part of the imperfection is eliminated and the associated free-energy decrease lowers $\Delta\mathcal{G}_c$.

- The relative values of $\Delta\mathcal{G}_c$ for heterogeneous and homogeneous nucleation on grain boundaries are easily worked out for incoherent nuclei (no strain-energy term) with isotropic interfacial free energies. *Young's equation*, $\gamma^{\alpha\alpha} = 2\gamma^{\alpha\beta}\cos\psi$ determines the equilibrium dihedral angle at the junction of the α/α grain boundary and the α/β interfaces that enclose a lenticular particle. The resulting nucleation barrier for heterogeneous nucleation on the boundary is given by *KoM* Eq. 19.43, $\Delta\mathcal{G}_c^B = \left(\frac{2\pi R^3}{3}\Delta g_B + 2\pi R^2\gamma^{\alpha\beta}\right)(2 - 3\cos\psi + \cos^3\psi)$. The ratio of the barriers for heterogeneous boundary nucleation to homogenous nucleation in the bulk is thus $\Delta\mathcal{G}_c^B/\Delta\mathcal{G}_c^H = (2 - 3\cos\psi + \cos^3\psi)/2$ and thus simply dependent on the relative values of $\gamma^{\alpha\alpha}$ and $\gamma^{\alpha\beta}$.

- A simple geometrical model for an isotropic grain structure (e.g., cube-shaped grains) shows that the number of potential grain boundary nucleation sites per unit volume is $n^B = n(\delta/L)$, where n is the number of sites per unit volume in the polycrystal, δ is the grain boundary thickness, and L is the grain size. With this assumption, the ratio of steady-state nucleation rates is given by *KoM* Eq. 19.47 as $J^B/J^H = (\delta/L)\exp[-(\Delta\mathcal{G}_c^B - \Delta\mathcal{G}_c^H)/(kT)]$.

- This analysis of heterogeneous grain boundary nucleation shows that grain boundary nucleation is favored over homogeneous nucleation at small grain sizes, large values of $\cos\psi$, and small undercoolings (i.e., small values of $\Delta\mathcal{G}_c^H$). Similar analyses can be carried out to consider kinetics of heterogeneous nucleation on grain edges and corners.

Related Exercises in *Kinetics of Materials*

Review Exercises 19.7–9, pp. 491–495.