

Lecture 10 Grain Growth

The phenomenon. A polycrystal, held at temperature T for time t , the average grain diameter grows to D . Empirically it is found that

$$D^n = B \exp\left(-\frac{q}{kT}\right)t.$$

The parameters B , q and n are fitted to the experimental data. Typically the exponent $n \approx 2$, so that the growth slows down when the average diameter is large. A grain grows at the expense of its neighbors: small grains disappear and big ones get bigger. Total number of atoms is conserved.

The cause for grain growth is readily understood. Atoms at a grain boundary are poorly packed, and have higher energy than atoms in the lattice. As the grains grow in size and their numbers decrease, the net amount of grain boundary reduces, and thereby the free energy of the system reduces. But how does each atom know about this global agenda of reducing the energy of the system? If you cannot wait for an answer, jump to the last paragraph of this lecture.

Kinematics (or how things move). A grain is a piece of a single crystal. In a polycrystal, two neighboring grains of different crystalline orientations meet at a *grain boundary*. Atoms at the grain boundary are poorly packed, and do not belong to the lattice of either grain. The grain boundary moves as atoms detach from the lattice of one grain, and attach to the lattice of the other grain. The structure of the grain boundary itself is preserved. Grain boundary motion is facilitated by local adjustment of atomic position, not long-range atomic diffusion.

This poorly packed region, which we call the grain boundary, is thin. It is of atomic dimension. The grain size is typically much larger than the atomic dimension. Consequently,

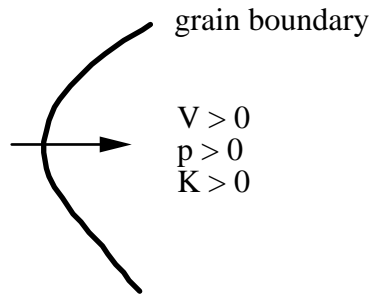
we can model the grain boundary as a mathematical surface, with no thickness. Two neighboring grains meet at a surface (i.e., the grain boundary). Three neighboring grains meet at a line (i.e., the triple junction). Four neighboring grains meet at a point (i.e., the vertex). As the grain boundaries move, the triple junctions and the vertices also move.

Energetics: driving force on the grain boundary. A bicrystal consists of two crystals of different orientations bonded by the grain boundary. The reference state is a single crystal of the same number of atoms. The excess free energy of the bicrystal relative to the single crystal defines the grain boundary energy. Denote the grain-boundary energy per unit area by γ . The grain boundary energy density depends on the relative orientations of the two grains, as well as the orientation of the grain boundary.

The free energy of the polycrystal is a sum over all grain boundaries:

$$G = \sum \gamma A.$$

We neglect the line energy of the triple junction, and the point energy of the vertex.



Consider an element of a grain boundary, of area dA , with the sum of the principal curvatures K . Assume that the grain boundary energy density γ is isotropic. We now remove some atoms from one grain, and append them to the other grain, so that the element of the grain boundary moves by a distance δr_n . The sign convention is shown in the figure. We have shown before that, associated with the motion of the grain boundary, the area of the surface element

changes by $-K\delta r_n dA$. Consequently, the free energy change associated with the motion of the element is $-\gamma K\delta r_n dA$.

Define the driving force for grain boundary migration, p , as the free energy reduction per unit area moving per unit distance. Equivalently, the driving force is the free energy reduction associated with a unit volume of atoms detaches from one grain and attach to the other). Thus,

$$p = \gamma K.$$

The driving force is the product of the grain boundary energy density and the curvature.

This driving force has the unit of pressure. Indeed, it has the same form as the Laplace formula for the difference in the pressures on the two sides of a liquid surface. However, there is no reason to think this quantity as pressures in the interior of the solid grains. The two kinds of surfaces have different kinematics: the liquid surface moves because the liquid flows, and the grain boundary moves because atoms switch the allegiance from one grain to the other. Inside the liquid, the matter deforms, allowing the pressure to do work. Inside the grains, however, atoms need do nothing for the grain boundary to move; for all we know, the interior of the grains can be rigid. If we treat the grains as elastic bodies, then we can investigate the stress field inside the grains. In that case, it is the boundary stress, rather than the boundary energy, that causes the stress field inside the grains. We will pick up this topic at a later point.

Energetics: local equilibrium at the triple junction. Next consider a junction at which several grain boundaries meet. In the three-dimension, the length of the junction is L . Now allow the junction to move by a virtual displacement $\delta \mathbf{u}$. Let \mathbf{t} be the unit vector in the direction of a grain-boundary. Associated with the junction motion, the length of the grain-boundary decreases by $\mathbf{t} \cdot \delta \mathbf{u}$. Thus, the free energy varies by

$$\delta G = -L \sum \gamma \mathbf{t} \cdot \delta \mathbf{u}$$

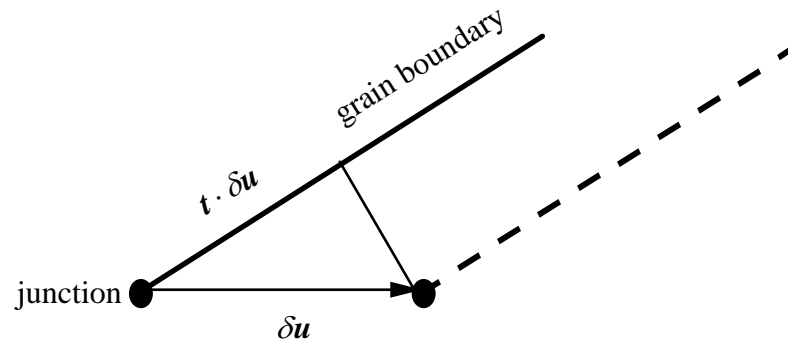
It sums over all the grain-boundaries meeting at the junction. The force on the triple junction is

$$f = L \sum \gamma \mathbf{t}.$$

If the triple junction is in local equilibrium, the free energy variation vanishes for arbitrary virtual motion. Consequently, the grain boundary tensions balance:

$$\sum \gamma \mathbf{t} = 0.$$

This is a familiar result. We can regard the grain boundary energy as a force in the tangent direction of the grain boundary. The local equilibrium of the triple junction is equivalent to a force balance. For example, when three grain-boundaries of identical surface tensions meet at a line, they form 120° angle from one another.



Kinetics (or the relation between the force and rate). We adopt a simple kinetic law.

The velocity of the grain boundary, v_n , is proportional to the driving pressure, p :

$$v_n = mp,$$

which defines the interface mobility m . In practice, m is determined experimentally.

The algorithm for grain growth. In summary, we have obtained two rules:

- (1) The velocity of an element of a grain boundary is proportional to the mean curvature of the element: $v_n = m\gamma K$.
- (2) Each triple junction is in local equilibrium: $\gamma_1 \mathbf{t}_1 + \gamma_2 \mathbf{t}_2 + \gamma_3 \mathbf{t}_3 = 0$.

At a given time, the grain structure is known. Calculate the curvature of each element of all grain boundaries. Update the grain boundary positions according to rule (1) for a small time step. Maintain the angles at the triple junctions according to rule (2). This algorithm has been implemented numerically (see Thompson, 1990). The main difficulty is to calculate the curvature, and to maintain the angles. We'll talk about a more effective algorithm at a later point.

The parabolic growth law. Now we can understand the parabolic growth law readily. A dimensional consideration indicates that $m\gamma$ has the dimension of $(\text{length})^2/\text{time}$, the same as the coefficient of diffusion. If we assume that the final grain size is much larger than the initial grain size, the problem has only one length scale: the grain size. The grain structure grows in a self-similar way. A dimensional consideration requires that the grain size increase with the time as $D^2 \sim m\gamma t$.

We can also make a slightly different argument. Let the average grain diameter be D . Its growth rate is proportional to the mobility m , the surface tension γ , and the curvature. The latter is inversely proportional to the grain diameter, $1/D$. Thus

$$\frac{dD}{dt} \approx m \frac{\gamma}{D}.$$

The solution to this differential equation is

$$D^2 - D_0^2 \approx 2m\gamma t.$$

This gives us a parabolic growth law.

Texture of a thin film. In the above, we have assumed that the grain boundary energy is the only cause for grain growth. In reality, other forms of free energy can also drive grain growth. For a thin film deposited on a substrate, the grain-boundaries are often perpendicular to the surface of the substrate. It is often found that the grains have some crystallographic

relationships with respect to the substrate. For example, for two copper crystals deposited on a single crystal silicon substrate, both surface tension and elastic energy differ for the two grains. (Include the surface tension of the film-vacuum interface and of the film-substrate interface.) Such difference in the free energy makes one grain grow at the expense of the other.

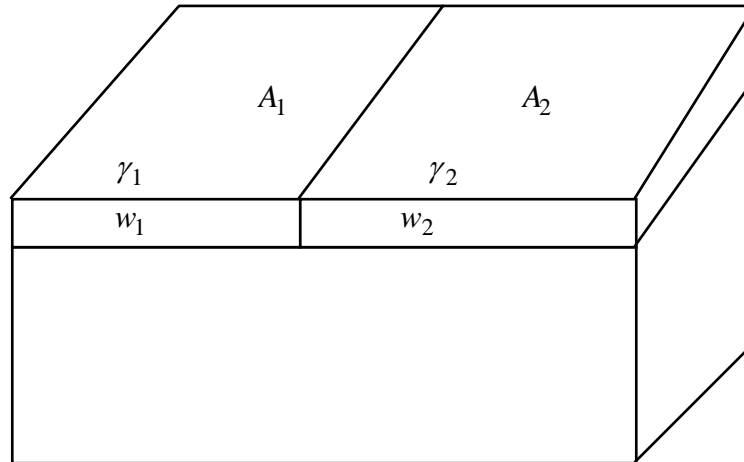
Let the film thickness be h , and area for the two types of grains be A_1 and A_2 . We'll assume that grains are large compared to the film thickness. The free energy is

$$G = (w_1 h + \gamma_1) A_1 + (w_2 h + \gamma_2) A_2.$$

The driving pressure is the free energy change per volume of grain growth. Thus,

$$p = -\frac{1}{h} \frac{\partial G}{\partial A_2} = (w_2 + \gamma_2 / h) - (w_1 + \gamma_1 / h).$$

The grain boundary velocity is $v = mp$. The survival grains should have the lowest combination $w + \gamma / h$.



An atomistic picture of the grain boundary migration. The mobility can be understood from the atomic point of view. Assume a cubic crystal lattice, with the atomic spacing a , and the volume per atom $\Omega = a^3$. When an atom relocates from one grain to the other, it has to jump over an energy barrier, ε_m . Of all jiggles made by the atom, the fraction

$\exp(-\varepsilon_m / kT)$ exceeds the energy barrier. Let ν be the atomic vibration frequency. Consequently, per unit time, the atom jumps $\nu \exp(-\varepsilon_m / kT)$ times over the energy barrier. The free energies (per atom) on the two grains differ by $p\Omega$. Consequently, the grain boundary velocity is

$$v_n = \frac{\Omega}{a^2} \left[\nu \exp\left(-\frac{\varepsilon_m}{kT}\right) - \nu \exp\left(-\frac{\varepsilon_m + p\Omega}{kT}\right) \right].$$

When the driving pressure is small, namely, $p\Omega \ll kT$, the above becomes

$$v_n = \frac{\nu a^4}{kT} \exp\left(-\frac{\varepsilon_m}{kT}\right) p,$$

giving the grain boundary mobility

$$m = \frac{\nu a^4}{kT} \exp\left(-\frac{\varepsilon_m}{kT}\right).$$

Once again, how does each atom know about the global agenda of reducing the energy of the system? At the grain boundary, an atom performs mindless thermal motion. Most of the time, this atom vibrates with a tiny magnitude. Occasionally, the atom jumps so violently that it detaches from the lattice of one grain, and attaches to the lattice of the other grain. If the two states have the identical energy, the jump forward and backward have the same probability. However, if the two states have different energies, the probability will be biased. This bias causes the macroscopic migration of the grain boundary, in the direction that reduces the energy of the system.

Readings

Thompson, C.V. (1990) Grain growth in thin films. *Annu. Rev. Mater. Sci.* **20**, 245-268.