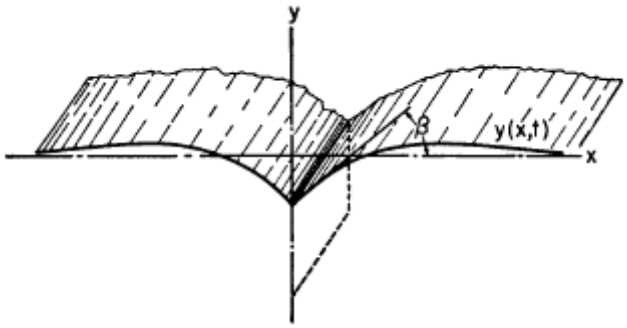
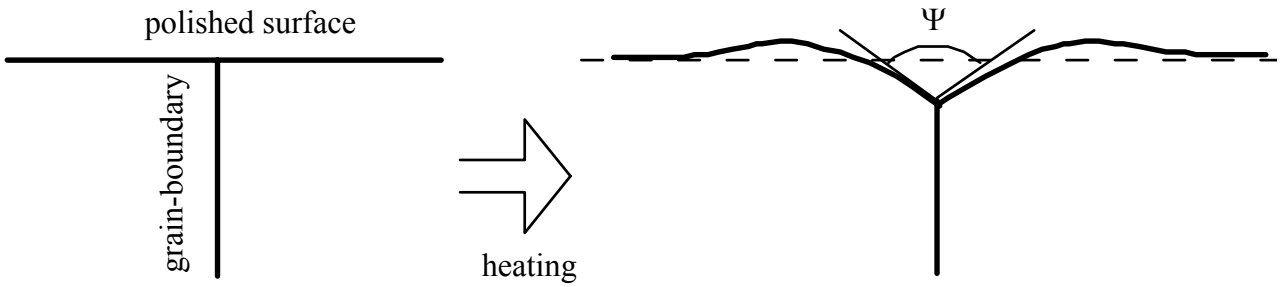
Lecture 7 Grain boundary grooving

The phenomenon. A polished polycrystal has a flat surface. At room temperature, the surface remains flat for a long time. At an elevated temperature atoms move. The surface grows grooves along triple junctions, where the surface meet grain boundaries. The grooves reveal the grain boundaries in the microscope. Atoms may move in many ways. They may diffuse in the lattice, diffuse on the surface, or evaporate into the vapor phase. Here we will only consider surface diffusion. Atoms diffuse on the surface away from the triple junction, making a dent along the junction, and piling two bumps nearby. The process conserves the total mass. The process of grooving was modeled by Mullins (1957).





The driver and the passenger. Let γ_s be the surface energy per unit area, and γ_b be the grain boundary energy per unit area. The free energy of the system is the sum of the surface energy and the grain boundary energy:

$$G = \gamma_s A_s + \gamma_b A_b .$$

As the groove grows, the grain boundary area decreases, but the surface area increases. The net free energy must decrease. We may say that the grain boundary is the driver, and the surface the passenger.

Local equilibrium and the dihedral angle. Atoms at the triple junction adjust their positions rapidly compared to diffusion on the surface. During the motion of the surface, the triple junction maintains local equilibrium. Local equilibrium at the triple junction implies that the surface tensions balance one another, giving the dihedral angle, Ψ :

$$\cos\frac{\Psi}{2}=\frac{\gamma_b}{2\gamma_s}.$$

If you like, you may think the grain boundary tension as a force, pulling the surface down.

This relation can be derived as follows. Let the triple junction move up by a distance δa. The grain boundary area increases by δa, and the surface area decreases by $2\cos(\Psi/2)\delta a$. Consequently, the free energy change associated with the motion of the triple junction is

$$\delta G=+\gamma_b\delta a-2\gamma_s\cos\left(\frac{\Psi}{2}\right)\delta a$$

In equilibrium, $\delta G=0$ for any δa. This leads to $\gamma_b-2\gamma_s\cos\left(\frac{\Psi}{2}\right)=0.$

Differential geometry of a curve in a plane. The model is for a small groove, its depth and width being much smaller than the grain size, so that the two grains are taken to be infinitely large. The problem becomes two-dimensional. In the cross-section normal to the triple junction, the surface is a curve, the grain boundary a straight line, and the triple junction a point. A curve in a plane can be described in many ways. For example, we can prescribe the coordinates of a point on the curve, *x* and *y*, as functions of the curve length *s*. The functions $x(s)$ and $y(s)$ describe a set of points that trace the curve.

Consider a tangent line at a point on the surface. Let θ be the angle between the *x*-axis to the tangent line. Thus,

$$\frac{\partial x}{\partial s}=\cos\theta,\quad \frac{\partial y}{\partial s}=\sin\theta.$$

We can locally fit the curve to a circle. Let the radius of the circle be *R*. Consider two nearby points on the curve, separated by an arc length ds. The tangent line rotates by $d\theta$, so that $ds = Rd\theta$. The curvature *K* is defined as the inverse of the radius. We write

$$K=-\frac{\partial\theta}{\partial s}.$$

We have adopted a sign convention. The solid is beneath the surface. The curvature is positive when the solid is convex. $K=+1/R$ for a cylindrical solid of radius *R*, and $K=-1/R$ for a cylindrical hole of radius *R*.

When the surface evolves with time, we represent the family of curves by a function of two variables: $y(x,t)$ is the height of the surface at location *x* and time *t*. At a given time, the curve has the length, the tangent angle, and the curvature. In the above expressions, the differential dy/dx becomes the partial differential $\partial y/\partial x$, with time fixed.

Atomic flux. The atomic flux is proportional to the gradient of the curvature:

$$\Omega J=-B\frac{\partial K}{\partial s}.$$

The constant coefficient *B* is given by $B=\Omega\gamma_s D_s\delta_s/kT$. For a given surface shape, this expression calculates the atomic flux. To close the problem, we need an expression of the change in the surface height due to atoms relocation on the surface.

Mass conservation. Consider the motion of a surface element dx. When the time goes from t to $t+\Delta t$, $J(x,t)\Delta t$ number of atoms flow into the element, $J(x+dx,t)\Delta t$ number of

atoms flow out of the element, and the surface height changes from $y(x,t)$ to $y(x,t+\Delta t)$. Mass conservation requires that

$$\frac{\partial y}{\partial t} = -\Omega \frac{\partial J}{\partial x}.$$

Partial differential equation. Collecting the above equations, we obtain a set of partial differential equations to evolve the four unknown functions $y(x,t)$, $\theta(x,t)$, $K(x,t)$, $J(x,t)$:

$$\frac{\partial y}{\partial x} = \tan\theta, \quad \frac{\partial \theta}{\partial x} = -\frac{K}{\cos\theta}, \quad B\frac{\partial K}{\partial x} = -\frac{\Omega J}{\cos\theta}, \quad \frac{\partial y}{\partial t} = \frac{\Omega \partial J}{\partial x}.$$

The initial and the boundary conditions. The surface is initially flat:

$$y(x,0) = 0.$$

The dihedral angle fixes the slope of the surface at the triple junction:

$$\sin\theta(0,t) = \frac{\gamma_b}{2\gamma_s}.$$

At the triple junction, we assume that no mass diffuse into or out of the grain boundary. Consequently, at the triple junction the atomic flux on the surface vanishes:

$$J(0,t) = 0.$$

The surface remote from the groove remains flat at all time

Self-similar profile. The initial geometry has no length scale. Inspecting the partial differential equations, we note that the time and the mobility set a length scale, $(Bt)^{1/4}$. Consequently, the groove grows with a self-similar profile. Define the dimensionless coordinates:

$$X = (Bt)^{-1/4} x, \quad Y = (Bt)^{-1/4} y.$$

Describe the groove profile by a function $Y(X)$. Note that

$$\frac{\partial y(x,t)}{\partial t} = \frac{\partial}{\partial t}\left[(Bt)^{1/4} Y(X)\right] = \frac{1}{4} B^{1/4} t^{-3/4}\left(Y - X\frac{dY}{dX}\right)$$

Similarly, make the curvature and the flux dimensionless by multiplying K by $(Bt)^{1/4}$, and J by $\Omega(t/B)^{1/2}$. We will still use K and J to denote the dimensionless quantities. The governing equations become

$$\frac{dY}{dX} = \tan\theta, \quad \frac{d\theta}{dX} = -\frac{K}{\cos\theta}, \quad \frac{dK}{dX} = -\frac{J}{\cos\theta}, \quad \frac{dJ}{dX} = \frac{1}{4}(Y - X\tan\theta)$$

This is a set of four ordinary differential equations for the functions $Y(X)$, $\theta(X)$, $K(X)$, $J(X)$. The boundary conditions at the triple junction are

$$\sin\theta(0) = \gamma_b / 2\gamma_s, \quad J(0) = 0.$$

Physically it is evident that θ, K, J should all vanish at $X = \infty$. The normalized problem has only one parameter, γ_b / γ_s.

The boundary value problem is solved numerically by a shooting method. We use the triple junction, $X = 0$, as the initial point. Prescribed at this point are the slope $\theta(0)$ and the flux $J(0)$. We guess values for $Y(0)$ and $K(0)$, and then integrate the ordinary differential equations using the Runge-Kutta method to a large value of X. The goal is to guess such values of $Y(0)$ and $K(0)$ that everything vanishes at $X = \infty$. This is a nonlinear algebraic problem for $Y(0)$ and $K(0)$.

Small slope approximation. The above PDE is nonlinear, and was difficult to solve in Mullins's time. He decided to linearize the problem on the basis of the following physical considerations. Typically the surface tension is larger than the grain boundary tension, so that the grooving surface has small slopes. The partial differential equation becomes

$$\frac{\partial y}{\partial t} = -B\frac{\partial^4 y}{\partial x^4}$$

This equation governs the surface profile $y(x,t)$.

As stated before, the size of the groove scales with the time as $(Bt)^{1/4}$. The force that drives the groove enters the problem through the slope at the triple junction, γ_b / γ_s. Because the governing equation is linear, the groove depth *d* (i.e., the distance from the groove root to the plane of the initial flat surface) must be linear in γ_b / γ_s. Mullins's analysis gives

$$d = 0.39(\gamma_b / \gamma_s)(Bt)^{1/4}.$$

The spacing between the peaks of the two bumps, *w*, has the same time scaling, but is independent of γ_b / γ_s under the small slope simplification. Mullins's analysis gives

$$w = 4.6(Bt)^{1/4}.$$

A full nonlinear solution by Sun and Suo confirms that Mullins results are accurate for practical range of the value of γ_b / γ_s.

Experiments and extensions. The dihedral angle, the groove width, and the groove depth can be measured experimentally. From such measurements one can deduce the combinations γ_b / γ_s and $M_s\gamma_s$. The absolute values of γ_s and γ_b have to be determined by some other experiments. See Tsoga and Nikolopoulos (1994) for a thermal grooving experiment.

At an intersection between the free surface and a three-grain junction. The surface form a pit at the point of emergence of the three-grain junction. The surface profile is still self-similar, all lengths following the same time scaling as above. Genin *et al.* (1992) analyzed the problem, and found that the pit depth is greater than the groove depth, but within a factor of 3 for all the configurations considered by them.

Grain-boundary grooving and pitting may break a polycrystalline thin film on a substrate. If the grain size is much larger than the film thickness, the above analysis estimates the time needed for a three-grain junction to pit through the film thickness. However, if the grain size is

comparable to the film thickness, mass transported from the grooves piles up on the grains, stopping the grooving process. Srolovitz and Safran (1986) and Miller *et al.* (1990) demonstrated that a critical ratio of grain size and film thickness exists, below which the grains reach an equilibrium configuration without breaking the film.

References

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