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Grain Boundary Migration in Thin Films: The Effects of Grain Grooves in Nano Films

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Abstract

We simulate the shrinking of a circular cylinder grain immersed in a thin single crystal film, with circular "surface triple junctions" at both external surfaces. A numerical code is used to describe the coupled motion by mean curvature of the grain boundary and the motion by surface diffusion of the external surfaces.

Our results indicate stagnation of the grain shrinkage in comparison to the shrinkage rate of a freely moving grain boundary. We present a geometric explanation for the known phenomenon that when the grain size in polycrystalline films is of the order of magnitude of the film's thickness, grain growth is seen to stop.

The simulations also show that there exists a critical value, R, for the initial radius, such that when R<R*, grains shrink and annihilate, and when R>R*, groove depth growth during grain shrinkage leads to break up of the film.*

Keywords

Thin films, grain boundaries, surface diffusion, grain growth stagnation, capillary instabilities.

1 Introduction

Stagnation of grain growth in polycrystalline films during annealing when the average grain radius becomes greater than the film's thickness has been often reported. It has been observed and discussed for various polycrystalline films [1-4]. The recent work [4] contains experimental observation of grain growth and

stagnation in Al foils, as well as a detailed review. Proposed explanations for this phenomenon include solute drag, pinning of grain boundary by defects, and stagnation due to grain grooving resulting from surface diffusion. Frost [1] undertook simulations of 2D grain growth using a stagnation criteria based on Mullins' conjecture [5], that the grain boundary gets pinned at the grain groove, and therefore the grain boundary takes on a catenoidal shape, which is stationary, since its mean curvature is zero. One of the aims of our work is to check this conjecture within the framework of a very simple model system.

It is well known that often in polycrystalline nano-films, the grain grooves traverse the entire thickness of the film in a reasonable amount of time, and this leads to void formation, which can then lead to the onset of capillary instability and to agglomeration of the film. The possibility of void formation due to surface grooving and the theory of groove growth for flat stationary grain boundaries were proposed by Mullins [6]. Modern experimental techniques now allow such phenomena to be observed. See for example the recent paper [7] for experimental data on the kinetics of void formation and agglomeration of the thin copper film, which also contains many references.

We report here on the results of a numerical investigation of circular grain shrinkage. A single cylindrical grain is initially immersed in a single crystal film, and the grain boundary is attached to external crystal surfaces via circular "surface triple junctions" on both surfaces, see Figure *1*. We describe below the kinetics of grain boundary motion coupled to surface diffusion in such a bicrystal. The results indicate a rate of stagnation of the grain boundary migration which differs from the model proposed in [1], and a rate of void formation which does not conform with predictions of [6]. These differences are not surprising, because we consider here for the first time dynamics which are truly 3D and couple the time evolution of the grain boundary and of the external surfaces.

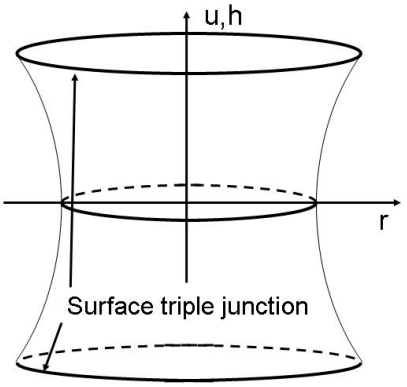

Figure 1. The shape of the shrinking grain.

2 Model Problem

A detailed description and derivation of the mathematical model and the numerical method are given in [8]. The model gives equations for coupled surface and grain boundary motion in an axisymmetric geometry. Its formulation follows from the physics described in Mullins' pioneering papers [5], [9]. We consider a geometry in which the external surface, *h(r,t),* and the grain boundary, *r(u,t),* both depend on one spatial variable, u or r, and on time, *t;* see Figure *1*. Taking the motion of the exterior surface to be governed by surface diffusion, and taking the motion of the grain boundary to be governed by motion by mean curvature, we arrive at the following problem for $t > 0$:

$$h_t = -B(\frac{k_r}{\sqrt{1+h_r^2}})_r,\ 0<r<\infty,\ r\neq R(t),$$
$$k = r^{-1}(rh_r(1+h_r^2)^{-1/2}), \tag{1}$$

$$r_t = A(\frac{r_{uu}}{1+r_u^2}-\frac{1}{r}),\ 0<u<u^*,$$
$$u^* = L + h(R(t),t). \tag{2}$$

In (1), B is the coefficient of surface diffusion, k is the mean curvature, and $r = R(t)$ denotes the location of the grain groove. In (2), A is a reduced mobility, and L is equal to half the film's thickness. Note that h is zero when $u = L$. Equations (1) and (2) are to be solved for $t > 0$ in conjunction with the boundary conditions:

$$h(R(t)-0,t) = h(R(t)+0,t), \tag{3}$$

$$k(R(t)-0,t) = k(R(t)+0,t), \tag{4}$$

$$\frac{k_r}{\sqrt{1+h_r^2}}|_{r=R(t)-0} = \frac{k_r}{\sqrt{1+h_r^2}}|_{r=R(t)+0}, \tag{5}$$

$$h_r(0,t) = 0, \tag{6}$$

$$k_r(0,t) = 0, \tag{7}$$

$$h(\infty,t) = h_r(\infty,t) = 0, \tag{8}$$

$$r_u(0,t) = 0, \tag{9}$$

$$r(L+h(R(t),t),t) = R(t), \tag{10}$$

$$\arctan h_r(R(t)+0,t) - \arctan h_r(R(t)-0,t) = 2\arcsin(m/2), \tag{11}$$

$$\arctan h_r(R+0,t) + \arctan h_r(R-0,t) = \pi + 2\arctan r_u^{-1}(L+h(R,t),t), \tag{12}$$

where in (11), m denotes the ratio of the grain boundary to external surface energies, and the initial conditions:

$$r(u,0) = R_0 \quad 0<u<L,\ t=0, \tag{13}$$

$$h(r,0) = 0 \quad 0<r<\infty,\ t=0. \tag{14}$$

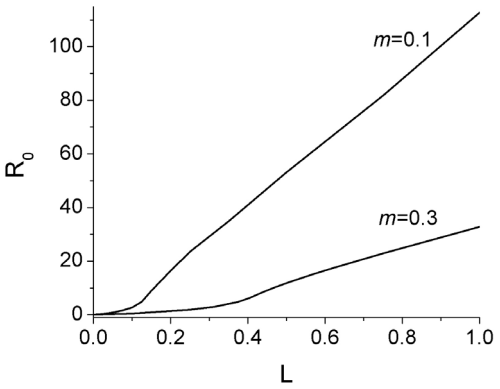

Figure 2. A diagram of the grain annihilation-break up transition for m=0.1 and m=0.3. The area above the curve corresponds to voiding, and the area below the curve corresponds to grain annihilation.

Equations (1) and (2) describe, respectively, the motion by surface diffusion of the upper exterior surface and the motion by mean curvature of the grain boundary in the axially symmetric geometry described in Figure 1. Equations (3), (10) describe the attachment of the grain boundary and the exterior surface at the groove root. Equations (6), (7) are conditions at the origin reflecting the assumed axial symmetry and boundedness of the solution. Equation (9) follows from symmetry with respect to the mid-plane of the film. Conditions (4)-(5), (11)-(12) reflect physical conditions which are assumed to hold at the groove root. The first two of these conditions express continuity of the chemical potential (the mean curvature) and balance of mass flux. The latter two express Young's law at the triple junction line which states that forces at the

groove root are in local mechanical equilibrium, or in other words, that the mobility of the triple junction has been assumed to be infinite. Equation (8) reflects the assumption that the exterior surface is asymptotically flat far away from the embedded grain. The last two condition (13)-(14) describe the initial geometry in which a cylindrical grain of radius R_0 is embedded in a flat external thin film.

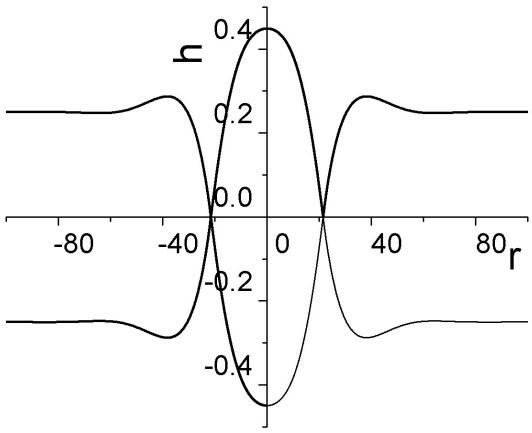

Figure 3. Snap shot of the film's central cross-section at break up. Here m = 0.1, L = 0.25, R_0 = 30, and t = 1761.

2.1 Parameters

Problem (1)-(14) contains three physical parameters and two geometric parameters which reflect the initial conditions. The physical parameters are A, the reduced mobility of the grain boundary, B, the surface diffusion coefficient, and m, the ratio of the grain boundary energy to the external surface energy, which appears in Young's law. Note that $[A]$ = cm^2/s, $[B]$ = cm^4/s, and $[m]$ = 1. The geometric parameters are L, half the film thickness, and R_0, the initial radius of the grain.

The parameters A and B may be used to define a length scale, $\sigma = (B/A)^{1/2}$, and a time scale, $\tau = B/A^2$. Since typically $B \approx 10^{-20}$-10^{-19}cm^4/s and $A \approx 10^{-12}$-10^{-7}cm^2/s, it follows that typically $\sigma \approx 10^{-6}$-10^{-4}cm and $\tau \approx 10^{-8}$-10^{4}s. Setting $t \to t/\tau$, $r \to r/\sigma$, and $u \to u/\sigma$, $h \to h/\sigma$, $L \to L/\sigma$, $R_0 \to R_0/\sigma$, a dimensionless formulation of problem (1)-(14) is obtained. The dimensionless formulation, which for simplicity we shall not write out explicitly, can be written out in terms of the three dimensionless parameters: L, R_0, and m.

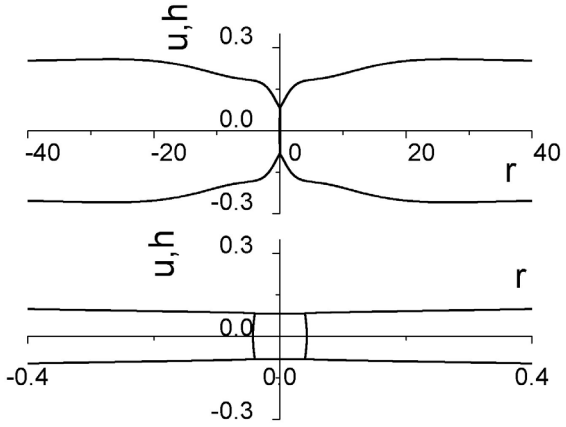

Figure 4. A snap shot of the film's central cross-section at a time close to grain annihilation. The same plot is presented in two scales. Here m=0.1, L=0.25, R_0 =20, and t=773.6.

3 Numerical Procedure

Suppose that the solution is known up to time t for some $t > 0$, and suppose that we use the past values of $R(t)$ to approximate $R(t + \Delta t)$, for some fixed $\Delta t > 0$. Taking $R(t + \Delta t)$ to be now known, we can use the equations in problem (1)-(14) to approximate $h(r, t + \Delta t)$ and then $r(u, t + \Delta t)$. This can be accomplished by first solving a "surface problem" for $h(r, t + \Delta t)$ using finite differences based on the equations for surface diffusion and the boundary conditions which depend on h and k only: (1), (3)-(8) and (11). Having

approximated $h(r,t+\Delta t)$, an approximation for $u^*(t+\Delta t)=L+h(R(t+\Delta t),t+\Delta t)$ which appears in (2), (10) is implied. The value of $u^*(t+\Delta t)$, the boundary conditions (9)-(10), and the equation for grain boundary motion, (2), together constitute a "grain boundary problem" whose solution by a finite difference scheme gives an estimate of $r(u,t+\Delta t),\ 0<u<u^*(t+\Delta t)$. By now, all of the equations and boundary conditions in problem (1)-(14) have been used, except for the Young's law, (12), which connects $h_r(R(t+\Delta t),t+\Delta t)$ and $r_u(u^*,t+\Delta t)$. This last condition can be used to correct our approximation for $R(t+\Delta t)$. The process can be iterated until sufficient accuracy is achieved. Implicit finite difference schemes are used at each step to solve the "surface" and "grain boundary" problems.

We remark that while the initial conditions have been taken in accordance with equations (13)-(14), Young's law has been imposed at the groove root on the finest finite difference scale for the sake of compatibility.

4 Numerical Results

Solutions were calculated for two values of *m*, *m*=0.1 and *m*=0.3. These values of *m* are typical for metals. Various values of $10^{-4}<L<1$ and R_0 were taken for each value of *m*. Note that dimensionless units were used, and *L*=1 corresponds to a film thickness in range 10^{-6}-10^{4}cm (10-1000nm), depending on values of A and *B*.

4.1 The annihilation-break up transition

Grains can either annihilate or form a void when the grain groove traverses the entire thickness of the film, depending on the initial grain radius and on the values of *m* and *L*. The dependence of the critical value, *R*,* on *L* is presented in Figure *2*. In fact, voiding can occur above the curve in diagram, since small voids can form then disappear [10]. The central cross-section of the film is presented at break up in Figure *3* and just prior to the grain annihilation in Figure *4*.

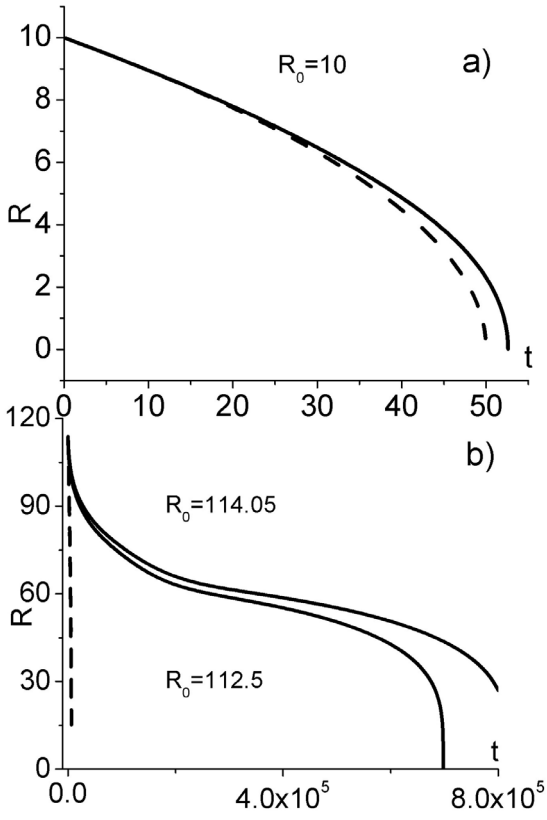

Figure 5. The grain radius *R(t)* as a function of time. Here *m*=0.1, *L*=1, and R_0 = a) 10, and b) R_0 =112.5, R_0 =114.05. The dashed lines describe a freely moving grain boundary. The critical radius for the annihilation-break up transition here is 112.75

4.2 The dynamics of grain shrinkage

Suppose that *m*=0. In this case the grain boundary does not interact with the external surface, hence *r* is independent of *u*, and the

mean curvature is given simply by $1/r$. The kinetics of grain shrinkage is given by

$$r(u,t) = \sqrt{R_0^2 - 2t}. \qquad (15)$$

This dependence can easily be seen to correspond to that of a freely moving grain boundary, and we shall use the kinetics of (15) as a basis for comparison in evaluating stagnation. The data presented in Figure *5* show that for L=10, the grain groove hardly affects the motion of the grain boundary, while in vicinity of critical radius, R*, the rate of motion is significantly slower. Note that we have not observed pinning of the grain boundary. Figure 6 shows the inclination, r_u, of the grain boundary at the groove root, and that the order of magnitude of the inclination is $O(m^2)$, which contradicts assumptions made in [5].

The time dependence of the groove depth is presented in Figure *7*. The behavior is quite complicated due to transients caused by the

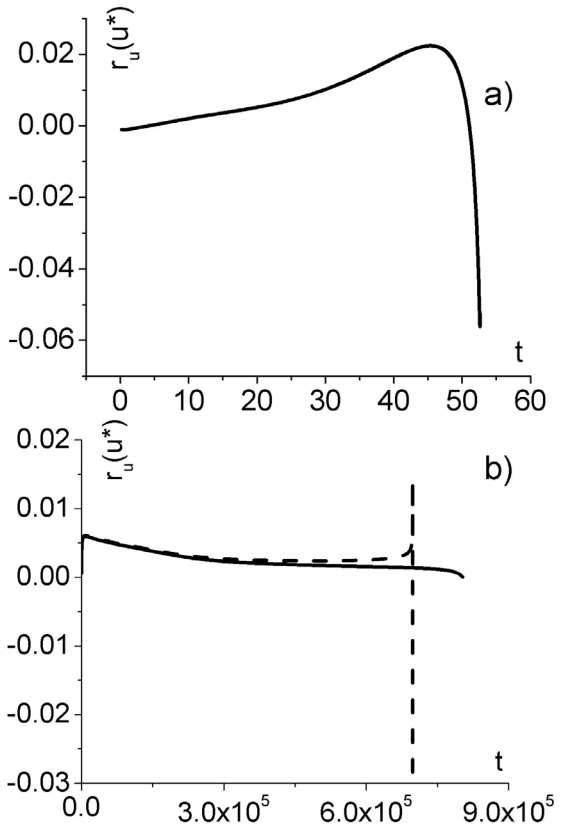

Figure 6. Inclination of the grain boundary at the groove root as a function of time. m=0.1, L=1. a) R_0 =10; b) R_0 =112.5 (dashed line), R_0 =114.05 (solid line). The annihilation-break up transition occurs for given m, and L at R_0= 112.75.

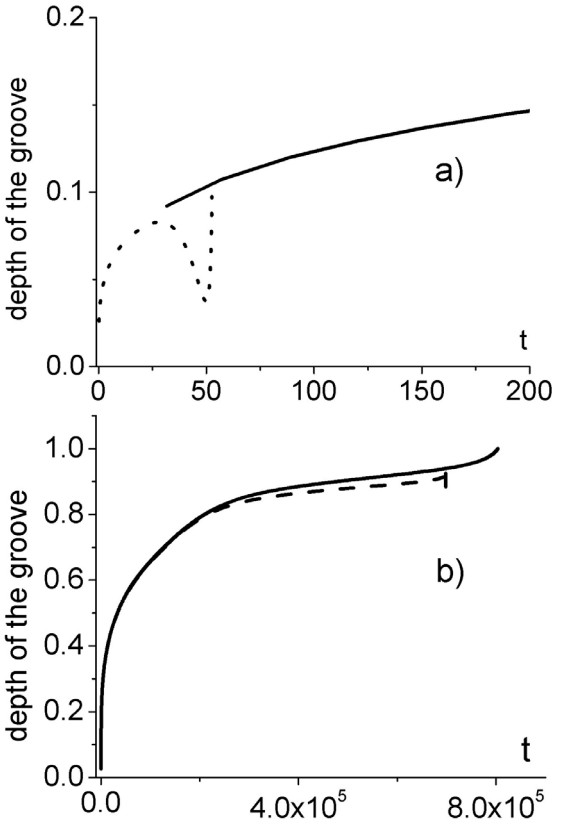

Figure 7. Depth of the groove as a function of time on two different time scales. Here m=0.1, L=1, a) R_0 =10 (dotted line), R_0 =112.5 and R_0 =114.05 (two coincide solid lines), and b) R_0 =112.5 (dashed line), R_0 =114.05 (solid line). The critical radius of annihilation-break up transition here is 112.75

initially flat surface and due to grain annihilation or voiding. Note that groove depth of stationary flat grain boundary according to [6] should be about 3.8 at t = 200 and about 30 at t=800000, and in Figures 7a, 7b the groove depth can be seen to be much smaller than this. Thus we see that the grain boundary motion strongly affects the kinetics of groove growth.

Conclusions

Our results show that in a three-dimensional polycrystalline film with a columnar structure, the grain growth is strongly affected by interaction with the free surfaces. This differs significantly from the results of the analysis for a single shrinking grain attached to one external surface in a 3D geometry [8], where the kinetics has been seen to be almost unaffected by the surface. The influence of the surface does not lead to the formation of a stationary catenoidally shaped grain boundary which stops the grain boundary migration, as has been suggested by Mullins [5] and which was used as a basis for interpretation of the simulations in [1]. Nevertheless, it is possible to qualitatively understand our observations by generalizing Mullins' suggestion [5].

In our geometry there are two important limiting shapes for the grain boundary. One of the limiting shapes is a catenoid; this shape is stationary and does not move since the principle curvatures are in two different directions and their net effect balances out. The second shape is a cylindrically shaped grain boundary, where one component of the mean curvature vanishes and the other component drives the grain boundary migration; this corresponds to a freely moving grain boundary whose velocity is apparently maximal. All other shapes appear to lead to velocities with intermediary values.

The catch is that neither of the limiting shapes can be precisely achieved when $0 < m < 2$, since realization of the former requires that $m = 2$ and realization of the latter requires that $m = 0$. Indeed the present analysis is based on the assumption $0 < m << 1$. This implies that the inclination, r_u, at the grain boundary is small and thus that the grain shape must be close in some sense to that of the "freely moving" case. However, if radius of the grain boundary becomes much larger than the film thickness, then the "catenoidal" in plane component of the curvature becomes dominant and the effect of the *1/r* component decreases. But our results show that grain boundary does not become stationary and the grain groove remains mobile. Delay in the grain boundary migration can allow the groove root depth to grow and can lead to voiding.

It is rather a happy coincidence that on one hand the dimensions of the nano film system are on the order of about 10 nm or in other words, about 100 inter-atomic distances, continuum models can be realistically implemented in describing to nano-films systems, and on the other hand voiding in thin films takes place on a laboratory time scale. This allows the annihilation-break up transition both to be successfully modeled with continuum models and to be realized experimentally on a laboratory time scale. Note that for thicker films, a continuum model would be justified, but the transition would be become difficult to explore experimentally.

We will amplify the analytical aspects of this qualitative explanation of the behavior which has been demonstrated here in a forthcoming publication.

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