Coarsening in nanocrystalline thin films: A 4D problem

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Abstract. Materials properties of polycrystalline solids depend strongly on the microstructure. Hence, investigating grain microstructures as they change during grain growth, e.g., by thermal annealing, is of utmost importance. Historically, this has been done by optical microscopy yielding only a two-dimensional characterization. Consequential problems have long been recognized. In particular, a two-dimensional section through a three-dimensional polycrystal yields a rather poor idea about the true size and form of the individual grains, and therefore of the microstructure, and in addition, such a section represents only a snapshot in time and does not give any clues about structural changes during grain growth. In the present study, we investigate coarsening in nanocrystalline thin films using a modified three-dimensional Potts model. By taking the increased importance of higher order grain boundary junctions, i.e. triple lines, at smaller grain sizes into account, it is shown that the microstructure, as well as the associated growth kinetics, undergo distinct changes during coarsening.

1. Introduction

Computational investigations are an integral part of modern materials science and design [1]. They enable not only a very selective manipulation of a broad range of materials parameters that are experimentally inaccessible, e.g., due to technical limitations, but enable also predictions of material behaviour. This holds for processes such as deformation and recrystallization, as well as for the problem of microstructural coarsening during grain growth. In general, grain growth can be understood as a rather simple process: at elevated temperatures the grain boundaries—being two-dimensional defects in the three-dimensional samples—migrate such that the total grain boundary area, and thereby the total boundary energy, is reduced. However, in reality this process is very complex. The grain structure must satisfy a global constraint for volume conservation at all times, while the grain boundaries and their higher order junctions—namely triple lines and quadruple points—strive to preserve a local balance in the network. Understanding this process is of utmost importance as the grain microstructure of a material, characterized for examples by its average grain size and corresponding size distribution, influences strongly material properties. A temporal change in microstructure leads to changes in the properties and may result in materials failure in applications [2].

In contrast to grain growth in bulk materials, where surface effects are usually neglected, they are of great importance for thin films due to the increased material surface to volume ratio [3]. Nevertheless, thin films are still three-dimensional in nature, even though they are commonly treated...
as two-dimensional objects [4-6]. In such a simplified analysis it is assumed that the microstructure is bamboo-like, i.e. it is fully columnar throughout the film thickness. Although this is indeed the case for some materials, it is not true in general. Specifically, after deposition of a film or after deformation, e.g., by rolling and succeeding recrystallization, the average grain size may be noticeably smaller than the film thickness, and as such the microstructure contains grains of globular nature as in bulk materials. As a result, the associated growth kinetics describing microstructural changes during annealing are distinctively different from samples where the average grain size reaches the size of the film thickness [7].

In the present work, we study grain growth in nanocrystalline thin films, which are of nanocrystalline film thickness, using a modified three-dimensional Potts model. To that aim, the increased importance of the triple lines at smaller grain sizes is taken into account. It is shown that the microstructure as well as the associated growth kinetics undergo distinct changes.

2. Modified Potts model
The Potts model has been used for modelling grain growth for almost 40 years [8,9]. It is a lattice based model, where a given grain microstructure is mapped onto a either a square or hexagonal simulation lattice, such that grain boundaries are defined implicitly as locations between two neighbouring lattice points with different orientations. Triple lines and quadruple points are similarly resulting microstructural features. In typical simulations of bulk materials, periodic boundary conditions are implemented that treat a 3D sample as an infinite continuation in all three dimensions. Also, in the standard version of the Potts model only two materials parameters are taken into account: (i) the specific grain boundary mobility, \( m \), which depends on the crystallographic misorientation angle between two neighbouring grains and can be calculated by the Huang-Humphreys-equation, and (ii) the grain boundary energy per unit length, \( \gamma \), which can be calculated using the Read-Shockley-equation using also the crystallographic misorientation angle [10]. In addition, a purely technical parameter—namely the simulation temperature—has to be selected carefully [11]. This parameter does not reflect the actual temperature during thermal treatment, but is used to ensure the correct curvature of the grain boundaries as well as the associated correct dihedral angles at triple junctions.

The present implementation combines two previous approaches. On one hand, the thin films are treated as three-dimensional objects by introducing a finite film thickness, \( h \). This is different compared to many previous investigations [4-6], where grain growth in thin films was performed on two-dimensional lattices, but it has already been implemented successfully in Ref. [7]. On the other hand, it has been shown by Gottstein and Shvindlerman [12,13] that a limited triple junction mobility may exert a drag effect on grain boundaries in nanocrystalline materials that changes the grain growth kinetics as observed experimentally [14]. Hence, also in the present work, a limited triple junction mobility is taken into account as in, e.g., [15,16]. The modelling parameters have been selected as described in the following:

- The simulation lattice grid has a size of 500×500×\( h \) lattice points. The film thickness, \( h \), is selected large enough to allow initial three-dimensional growth, but it is also small enough compared to the other two dimensions (\( h \ll 500 \)) [7].
- The sizes of the grains follow a normal distribution, and the grains are equi-axed and randomly distributed in space. Here it should be mentioned that due to the limited film thickness \( h \), 3% of grains span the whole film thickness already at \( t = 0 \), i.e., are columnar.
- The simulation temperature has been set to \( k_B T = 0.8 J \) according to Ref. [11] preventing unphysical lattice effects such as, e.g., clinging of boundaries to the underlying grid.
- The mobilities and energies have been selected in such a way that a pure analysis of the effect of triple lines is possible without an overlaying effect of texture. Hence, all grain boundaries are assumed to have identical values for energy, \( \gamma_{gb} \), and mobility, \( m_{gb} \), whereas the triple lines have significantly lower values for the mobility, \( m_{tj} \), as introduced in [15,16].
3. Results

Already two decades ago, Gottstein and Shvindlerman [12] found that limited triple junction mobility may exert a drag effect on the adjoining grain boundaries that leads to deviations of the grain vertex angles at the junctions from their equilibrium. As a result, grain boundary controlled growth, i.e. normal grain growth follows

\[ \langle R \rangle^2 \propto t, \]  

whereas triple junction controlled grain growth results in

\[ \langle R \rangle \propto t. \]  

Here \( t \) is the annealing time and \( \langle R \rangle \) is the average grain radius, where the radius of each grain is calculated as the radius of a grain area equivalent circle. As a consequence of equation (1a) the average grain area, \( \langle A \rangle \), e.g., through a 3D section increases linearly with time. The two growth laws can alternatively also be derived by treating grain growth as a dissipative process [17,18].

In the following, at first the thickness of the sample, \( h \), is varied systematically such that \( h = \{10, 15, 20, 25\} \) lattice points assuming normal grain growth. As it can be seen in figure 1, the microstructure is characterized early on by a very large fraction of non-columnar grains, which decreases strongly, however, during annealing.

![Figure 1. Temporal development of the grain microstructure for normal grain growth with \( h = 15 \).](image)

This decrease in the number of globular grains is naturally coupled to an increase in the relative number of columnar grains, \( \eta = N_{\text{col}}: N \). In figure 2a, it is interesting to note how the slope of \( \eta(t) \) depends on the film thickness, but reaches in each case for long annealing times a steady state, where the relative number is close to 100%, hence forming two main growth regimes. The latter can also be observed with respect to the average growth law, as shown in figure 2b. In contrast to the theoretical description in the form of equation (1), here for reasons of measurements and comparability the average grain area, \( \langle A \rangle \), is analysed as the average area of all surface grains. All resulting curves show similar shapes. After an initial period of time (i), which depends on the initial microstructure [19] and is basically non-visible in the presented case, the first growth period (regime I) is coupled to a strong increase in \( \eta \). A short transition regime (t) follows during which the last 15 to 20% non-columnar grains are transformed. Finally, a period of slow growth follows for long annealing times (regime II).

As expected for normal grain growth, the average grain area increases as a linear function of time. The strong increase in average grain size in regime I is indicated by only one least-squares fit as the four curves yield very similar results. In contrast, the more or less constant number of columnar grains in regime II is associated with a much smaller slopes with similar values [7] of 0.0226 for \( h = 10 \), 0.0209 for \( h = 15 \), 0.0271 for \( h = 20 \), and 0.0267 for \( h = 25 \). These values are about 15 times smaller than the slope in regime I. It can be concluded that regime I has a larger slope—representing rather three-dimensional coarsening with higher grain curvatures—whereas regime II has a smaller slope—representing rather two-dimensional coarsening with reduced grain curvatures.
Figure 2. Temporal development of: a – relative number of columnar grains; b – average grain radius; both for different film thicknesses with 1: $h = 10$, 2: $h = 15$, 3: $h = 20$, and 4: $h = 25$. For more details see text.

In contrast, starting the simulations with constant film thickness, $h = 15$, and varying the triple line mobility, $m_{tj}$ with respect to the boundary mobility, $m_{gb}$, systematically with $m_{tj} < m_{gb}$ yields strong changes in the growth kinetics in agreement with previous 2D and 3D studies [15,16].

This finding is reflected in the average growth law (figure 3b) and with respect to the relative number of columnar grains (figure 3a), when analysing the effect of $m_{tj} = m_{gb}$ in comparison to $m_{tj} = 1/25m_{gb}$. The linear correlation $\langle A \rangle(t)$ holds only for normal, i.e. grain boundary controlled grain growth, where $m_{tj} = m_{gb}$, in both growth regimes I and II. In contrast, for $m_{tj} \ll m_{gb}$, equation (1b) predicts a linear relation between average radius and annealing time, which means that the average area increases as a quadratic function of time. This is observed to be indeed the case in figure 3b for growth regime I. Due to the much slower coarsening in this case, a longer time period has been considered up to $t = 9000$. This enables not only an observation of the initial coarsening regime (regime i), but also of the longer transition to the second growth regime (regime t).

Figure 3. Temporal development of: a – relative number of columnar grains; b – average grain area; for normal grain growth with $m_{tj} = m_{gb}$ and triple junction control with $m_{tj} = 1/25m_{gb}$. The least-squares fits in figure 3b yield for normal grain growth $\langle A \rangle = 0.8082 t + 134.4$ for growth regime I and $\langle A \rangle = 0.0592 t + 613.8$ in regime II in contrast to triple junction control with $\langle A \rangle = 5.5 \times 10^{-6} t^2 + 0.0277 t + 153.5$ in regime I.
Overall, a reduced triple junction mobility follows the theoretical prediction in terms of equation (1b), whereas grain boundary controlled growth follows equation (1a). In addition, the results agree well with the experimental measurements of Barmak et al. [6], who investigated grain growth in 100 nm-thin Al films and observed very fast initial coarsening followed by very slow coarsening, cf. figure 9a in [6].

![Figure 4. a – Scaled size distribution for normal grain growth showing time-independence for three random annealing times, i.e., self-similarity in growth regime I together with analytic theory (dashed line) from [17,18]; b – Temporal evolution of standard deviations; c – Scaled size distribution for triple junction controlled grain growth showing self-similarity in growth regime I in comparison with analytic theory (dashed line) from [17,18].](image)

On the other hand, the average growth laws according to equation (1) have furthermore been shown analytically and numerically to be associated with distinct self-similar growth regimes [15-18], where statistical self-similarity is a feature of grain growth in polycrystalline materials [20] that can be confirmed, e.g., with respect to the time-independent scaled size distribution $f(x)$, where the scaled grain size is defined as $x = R/R$ and the condition $\int f(x)dx = 1$ holds.

A direct result of the time-independence of $f(x)$ is the fact that the associated standard deviation of the scaled grain size $\sigma_x$ is constant. In order to check this fact, in figure 4b the standard deviation is plotted as a function of annealing time for both coarsening kinetics. The differences can be spotted easily. In general, triple junction control is associated with larger values describing a broader distribution, where the three growth regimes (initial i, regime I, and transient t) can be detected. In contrast, for normal grain growth the strong changes in the microstructure in the transient and initial regime can be observed, where the latter changes its value from approx. 0.535 to 0.43 within just about 50 time steps. This explains why the initial regime could not be detected in the previous figures. In addition, normal grain growth shows a slow but steady increase of the value within growth regime II, which means that the microstructure is not fully self-similar.

However, when comparing the first growth regimes (I), where the major structural changes happen it can be seen in figure 4a and figure 4c that both show time-independence in $f(x)$, but exhibit clearly different distributions, taking shapes (dashed lines) that have been predicted analytically in [17,18].

4. Summary and conclusions
In the present work, grain growth in nanocrystalline thin films has been studied. To achieve this aim, two approaches have been combined, taking the three-dimensional nature of such films into account, as well as considering the increased importance of triple lines at small grain sizes.

Firstly, the introduction of a finite film thickness yields a temporal evolution of the grain microstructures that can be divided clearly into two main growth regimes. The first growth regime (I) is characterized by a strong increase in average grain size and in the relative number of columnar grains, and represents three-dimensional coarsening with higher grain curvatures. In contrast, the late coarsening regime (II) has a strongly reduced slope regarding the average growth law, and represents quasi-two-dimensional coarsening with reduced grain curvatures. This is true for a range of film
thicknesses and in stark contrast to two-dimensional grain growth simulations, which never yield such behaviour.

Secondly, the additional introduction of reduced triple junction mobilities slows the overall coarsening process down visibly and leads to a number of changes:

1. In contrast to normal grain growth, triple junction controlled growth is characterized by a quadratic relation between average grain area and annealing time clearly visible in regime I. This is in agreement with predictions according to Eq. (1b), even though the basic assumption behind this equation, namely purely two-dimensional grain growth, is not fulfilled. Due to the reduction of coarsening speed, growth regime I is ten times longer than for normal grain growth and the initial coarsening regime (i) becomes visible.

2. The two different average growth laws are associated with different grain microstructures:

   a. In regime I, the scaled grain size distribution is narrower for normal grain growth and shifted to a larger number of relatively small grains for triple junction control. This is in agreement with findings on two-dimensional junction controlled grain growth.

   b. The scaled size distributions shown in the present work from growth regime I, where the major changes in the microstructures take place, are self-similar.

   c. Nevertheless, there is an overall temporal change from the initial grain size distribution to long annealing times. The standard deviations—characterizing the width of the distributions—show strong reductions during initial and transient growth regimes. In addition, for long annealing times normal grain growth shows a slow but steady increase in the standard deviation indicating a slight non-self-similarity.

Overall, grain growth in thin films is a four-dimensional problem, for which the introduction of a finite film thickness yields substantial differences in the development of the microstructure compared to purely two-dimensional considerations, even though some analytic theories of 2D grain growth can be applied. In particular, for triple junction controlled grain growth, as may happen in nanocrystalline materials, substantial changes in microstructure and microstructural evolution can be observed.

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