Studying the influence of triple junction energy and mobility on annealing processes

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Abstract. The kinetics of grain growth in nanocrystalline two-dimensional polycrystals and thin films can be controlled by the triple junctions of the microstructure. In the present work the influence of energy and mobility of grain boundaries and their junctions on annealing is investigated by analytic theories and modified Monte Carlo Potts model simulations. To that aim each structural feature of a polygonal grain is assigned its own specific energy and finite mobility, which results in four different limiting cases of self-similar growth kinetics each characterized by its own metrical and topological properties.

1. Introduction
Grain growth is based on the fact that polycrystalline materials (Figure 1a) are thermodynamically unstable and undergo continuous grain coarsening driven by a reduction of the total Gibbs free energy of the system. Conventionally, it is assumed that only the grain boundaries contribute to the reduction of the Gibbs free energy via the decrease of the total grain boundary area. In particular, for the simplest case of normal grain growth it follows that only two characteristic parameters enter the theory namely the specific energy and mobility of the grain boundaries [1-3]. However, in recent years it has been shown that at very small average grain sizes that are typical for nanocrystalline materials, triple junction controlled motion has been observed during recovery [4] and triple lines as well as quadruple points of polyhedral grain networks may have a likewise significant effect on grain growth kinetics. In particular, the effect of finite junction mobilities on grain growth has been studied by means of experimental, theoretical and simulation methods (compare [5-9] and the literature within).

This is, in particular, also true for coatings, thin films and layers, where the thermal stability is a subject of great technological importance [10, 11]. In such systems it is often observed that upon annealing grain growth almost stagnates when the average grain size and the film thickness are of nanocrystalline character [3, 5]. In an outstanding paper, Barmak et al. [12] observed that during annealing of nanocrystalline Al and Cu thin films a stage of very slow grain growth is reached that is characterized by grain size distributions showing a large population of very small grains. As a possible cause of grain growth stagnation they investigated amongst other forces triple junction drag, which is, according to Gottstein, Shvindlerman and co-workers [3, 6, 8, 9], an effective rate limiting process especially at very small grain sizes. For this purpose the real 3D film was approximated as an ideal two-dimensional polycrystal, which was subjected to triple junction controlled grain growth by means of a multi-vertex front tracking simulation method (compare [12] and the references within).

However, two-dimensional grain growth under the condition of triple-junction drag has already been studied by means of vertex dynamics simulation methods earlier by Weygand et al. [13] and
Novikov [7]. Other two-dimensional and also three-dimensional simulation methods of triple-junction controlled grain growth have been developed in recent years. While Barrales-Mora [14] investigated 2D triple junction limited grain growth by network models, Zöllner and Streitenberger [15, 16] extended the MC Potts model in order to simulate triple and quadruple junction mobility controlled grain growth. On the latter basis, two-dimensional simulations of triple-junction mobility limited coarsening have been performed by the present authors in [17-19].

Based on our work on three-dimensional nanocrystalline grain growth [15], in the present work we attribute to each type of grain boundary junction of a 2D polycrystal its own specific energy and mobility (Figure 1b). Looking for self-similar, quasi-stationary scaling states of two-dimensional grain growth we find four types of growth kinetics, which are characterized by average growth laws obeying power law behavior and associated self-similar grain size distributions. The theoretical considerations are substantiated by simulation results using a modified Monte Carlo Potts model [16, 17].

**Figure 1.** a – Detail of a grain microstructure obtained by grain growth under triple junction mobility and energy control; b – Sketch of two polyhedral grains highlighting the grain features and parameters of interest.

### 2. Theoretical background

In the following we assume that a two-dimensional polycrystalline grain ensemble can be represented by a polygonal network, where each grain may be approximated by an average $N$-gon as defined by Rios and Glicksman [20] (compare Figure 1b). Average $N$-gons, where $N$ is the number of sides or connecting neighbors of a grain, are two-dimensional proxies for the average metric, energetic and kinetic behavior of real network grains. They have only two types of grain junctions, the grain boundaries ($gb$) and the triple junctions ($tj$), where we assume that each of them is characterized by its own specific Gibbs free energy $\gamma_{gb}$ and $\gamma_{tj}$, respectively. Taking further into account that two grains share a grain boundary and three grains a triple point the total free energy of a polygonal network of $N_o$ grains can be written as

$$G = \sum_{i}^{N_o} \left( \frac{\gamma_{gb}}{2} L_i + \frac{\gamma_{tj}}{3} N_i \right) = \sum_{i}^{N_o} \left( \pi \gamma_{gb} R_i + \frac{1}{3} \gamma_{tj} N_i \right).$$

(1)

Here $\gamma_{gb}$ is the usual grain boundary energy, $\gamma_{tj}$ the triple point energy or line tension per unit length [3, 8], $L_i$ is the total boundary length, and $N_i$ the number of triple points of the $i$-th grain. In particular, $L_i$ is expressed by the grain area ($A_i$) equivalent radius using the relation $L_i = 2\pi\kappa \cdot R_i$. For sake of simplicity and without essential loss of general validity the form factor $\kappa$ will be mostly set equal to one.
An estimation on the basis of the average $N$-gon defined by Rios and Glicksman [20] yields $\kappa = 1.050$. In Eq. (1) each grain is now characterized by the grain size $R_i$ as a metrical property and the number of sides or neighbors $N_i$ as a topological property.

Considering grain growth as a non-equilibrium dissipative process the reduction of the Gibbs free energy per unit time, that is $\dot{G} = \frac{dG}{dt}$, must be related to the generated dissipated heat per unit time $Q$. Following the approach developed by the present authors in [15] the total dissipated heat per unit time of all grains is given by the expression

$$Q = \sum \frac{N_i L_{gb} v_{gb}^2}{2m_{gb}} + \frac{N_i v_{ji}^2}{3m_{ji}} = \sum \frac{\pi}{m_{gb}} R_i + \frac{1}{3m_{ji}} N_i \dot{R}_i^2,$$

(2)

where $m_{gb}$ and $m_{ji}$ are the finite mobilities, $v_{gb}$ and $v_{ji}$ the corresponding velocities, and the simplifying assumption $v_{gb} = v_{ji} = \dot{R}_i$ has been used.

In order to derive the evolution equation $\dot{R}_i = \frac{dR_i}{dt}$ of grain $i$ we apply a thermodynamic approach on the basis of Onsager’s principle of constrained maximum dissipation and as we have applied it to three-dimensional nanocrystalline grain growth in [15] according to which the total dissipated energy per unit time $Q$ acquires an extremum with respect to the growth velocities $\dot{R}_i$, subject to the conditions of energy conservation, $\dot{G} + Q = 0$, and total area conservation, $\dot{A} = 0$. For the variation with respect to $\dot{R}_i$ in Eq. (3) it has to be taken into consideration that the number of faces $N_i$ and the grain size $R_i$ are not independent of each other. Similar as in our statistical theory of normal [22] and 3D nanocrystalline grain growth [15] this grain topology-grain size-correlation is taken into account by considering $N_i$ as a continuous function of the reduced grain size $x_i = R_i / \langle R \rangle$ such that $dN_i / dR_i = \left( dN_i / dx_i \right) \langle R \rangle$, where $\langle R \rangle$ is the average grain size of the ensemble. With this assumption we obtain from Eqs. (1) to (3) the following evolution equation of an effective polygonal grain in a two-dimensional polycrystal (suppressing from now on the index $i$),

$$\frac{\partial}{\partial \dot{R}} (Q + \eta(\dot{G} + Q) + \mu \dot{A}) = 0,$$

(3)

where we have used $R = \langle R \rangle x$ and $N' = dN / dx$.

In general, power law behavior of the average growth law, $\langle R \rangle \propto t^n$, and self-similar scaling of the grain size distribution function, $F(R, t) = g(t) \cdot f(x)$, are observed only in the case that the evolution equation is separable (cf. [1, 15] and the literature within), that is $\dot{R} = \langle \dot{R} \rangle \cdot \tilde{G}(x)$, where $\langle \dot{R} \rangle$ is the average and $\tilde{G}(x)$ the dimensionless size-dependent part of the growth law. In particular, for Eq. (4) this is only true if the time evolution is controlled only by one particular specific energy and mobility (see illustration in Fig. 1b), where the evolution equation $\dot{R}$ as given by Eq. (4) reduces to the following separated growth laws
It can be noted that in Eq. (5) only the relevant parameters are remaining compared to Eq. (4). The top row of the matrix form Eq. (5) represents two types of growth laws that are controlled by the grain boundary energy $\gamma_{gb}$ in conjunction with the finite mobilities $m_{gb}$ and $m_{gb}$. The lower row represents two further types of possible growth laws, this time controlled by the specific energy of triple junctions $\gamma_{tj}$ in conjunction with one of the finite mobilities $m_{gb}$ and $m_{tj}$. All these growth laws are separable and represent, therefore, different quasi-stationary self-similar growth regimes. Applying the requirement of total area conservation [19], we obtain four different types of average growth laws, from which after integration the following power law behavior for the average grain size follows,

$$\frac{\langle R \rangle^2}{\langle R \rangle} \propto t.$$  

In particular, the top row represents here also the two types of growth kinetics that are controlled by the grain boundary energy $\gamma_{gb}$ in conjunction with the finite mobility of grain boundaries and triple junctions, respectively, as they have been derived in [3, 6]. In addition, the second row represents two further types of possible growth kinetics controlled by the specific energy of the triple junctions $\gamma_{tj}$ in conjunction with one of the finite mobilities of grain boundaries and triple junctions $m_{gb}$ and $m_{tj}$, respectively. The time exponents $n$ in the power laws of Eq. (6) vary in the range of 1/3 to 1 (respectively $1/n$ varies between 1 and 3). This agrees with the corresponding kinetics controlled by triple lines in the case of three-dimensional nanocrystalline grain growth considered in Ref. [15], which has partly been observed experimentally [3-6].

3. Grain growth under boundary and junction control

According to the above Eq. (6) the average grain size of the ensemble shows power law behavior for all four kinetics of grain growth controlled by the grain boundary or triple junction energy in conjunction with one of the finite mobilities of grain boundaries or triple junctions. These four cases have been simulated using the modified Potts model according to Refs. [16-19], where details regarding the implementation and particularly regarding the parameters can be found, yielding:

- $\langle R \rangle^2 \propto t$ for grain growth controlled by the energy and mobility of the grain boundaries (subsequently named grain boundary-grain boundary-control; Figure 2a),
- $\langle R \rangle \propto t$ for grain growth controlled by the energy of grain boundaries and mobility of triple points (grain boundary-triple junction-control; Figure 2b),
- $\langle R \rangle^3 \propto t$ for grain growth controlled by the energy of triple points and mobility of grain boundaries (triple junction-grain boundary-control; Figure 2c) and also
- $\langle R \rangle^2 \propto t$ for grain growth controlled by the energy and mobility of triple points (triple junction-triple junction-control; Figure 2d)

just as expected according to Eq. (6). While these four kinetics hold mostly for longer annealing times (sections II), we can clearly take notice of the early transient growth regime showing deviations (sec-
tions I), of which the duration seems to depend on the growth kinetics itself and on the initial grain microstructure.

Figure 2. Average growth laws for grain growth under grain boundary and/or triple junction control for: a – grain boundary-grain boundary-control; b – grain boundary-triple junction-control; c – triple junction-grain boundary-control; d – triple junction-triple junction-control. Black: simulation results. Grey: late time behavior according to the analytical fit, Eq. (6).

However, such temporal developments of the average grain size characterize microstructures only partly. The corresponding counterpart is the grain size distribution, in which also the width of the distribution and the standard deviation, respectively, are of importance. The latter is shown for all four kinetics in Figure 3 as the standard deviation $sd$ of the scaled grain size $x$. Again different growth regimes (I, II and III) can be found in the temporal development of $sd[x]$. We find it particularly true that the growth kinetics in Eq. (6) as seen in Figure 2 are apparently associated with a quasi-stationary, self-similar state, where the standard deviation and therewith also the scaled grain size distribution is time-independent, although $sd[x]$ shows clearly visible fluctuations. Nevertheless, each quasi-stationary state is characterized by its own value of $sd[x](t)$, which indicates that each growth kinetics is characterized by a different scaled size distribution.

One may notice that the durations of the quasi-stationary states for the different kinetics in Figure 3, where particularly Fig. 3c and d show the transition (III) from the temporarily limited self-similar...
growth regime to the true self-similar regime of normal grain growth for large grains and long annealing times, are of different lengths compared to those in Figure 2, of which the origin is a subject of future interest.

Figure 3. Temporal development of the standard deviation of the scaled grain size for: a – grain boundary-grain boundary-control; b – grain boundary-triple junction-control; c – triple junction-grain boundary-control; d – triple junction-triple junction-control.

Self-similarity can alternatively also be determined through an analysis of the topology of the microstructures, e.g., by finding a time-independent relation between the scaled grain size $x$ and the number of sides or neighboring grains $N$, where $N$ characterizes also the number of triple junctions in a two-dimensional grain network. This relation is shown in Figure 4 for each kinetics at three different annealing times, which have been taken from the self-similar regimes (II) according to Fig. 3. In particular, the data have been plotted by categorizing them in size resp. neighbor classes because of the variation of this relation for individual grains (compare Ref. [18]). It can be seen that the results are indeed time-independent in all four cases.

These topological relations, which are also needed in the evolution equations of Eq. (5), show the following characteristic features. In the cases of grain boundary mobility controlled grain growth of Figs. 4a and 4c, that is for $m_{gb} \ll m_{tj}$ in both cases, the course of $N(x)$ exhibits a pronounced curvature, which can be described by the quadratic function
\[ N(x) = c_2 x^2 + c_1 x + c_0. \] (7)

This non-linear behavior of \( N(x) \) has already been proven as a characteristic property of 2-D normal grain growth (where \( \gamma_t = 0 \)), which is important for a consistent mean-field theoretical description of normal grain growth in agreement with the simulation results [21, 22]. The results in Fig. 4c show that also for triple-junction energy driven grain growth (where \( \gamma_{gb} = 0 \)) with finite grain boundary mobility gives a similar non-linear behavior of the topological function, which is also well described by Eq. (7).

In contrast, the two cases of triple-junction mobility controlled grain growth of Figs. 4b and 4d, that is for \( m_{gb} \gg m_t \) in both cases, show clearly a linear dependence of the topological function on the relative grain size described by

\[ N(x) = c_1 x + c_0. \] (8)

or alternatively by \( x(N) = a_t N + a_0 \) as for triple junction energy-triple junction mobility control in Fig. 4d. A linear behavior of \( N(x) \) resp. \( x(N) \) is in agreement with theoretical results based on \( N \)-sided polygonal grain models with straight grain boundaries (cf. [20, 23]), an assumption which is in agreement with the observed grain microstructure under triple junction mobility control in Fig. 1a.

Figure 5 shows the corresponding grain size distributions, where the symbols represent the simulation results and the solid lines our analytical expression [19]:

\[ f(x) = \frac{2x_c \bar{f}(x + x_1)}{(x^2 + (x_1 - \bar{f})x + x_c \bar{f})^2} \exp[-2 \frac{x_1 + \bar{f}}{\Delta} \left( \arctan\left( \frac{2x + x_1 - \bar{f}}{\Delta} \right) - \arctan\left( \frac{x_1 - \bar{f}}{\Delta} \right) \right)] \] (9)

with

\[ \Delta = 4x_c \bar{f} - (x_1 - \bar{f})^2 \geq 0. \]

Eq. (9) is derived from the solution of the continuity equation for the grain size distribution function \( F(R,t) = g(t) \cdot f(x) \), where \( R \) is given by one of the expressions in Eq. (5) (for the procedure see Ref. [19]). \( f(x) \) is normalized to one. For given values of \( x_1 \) and \( \bar{f} \), the scaled critical grain size \( x_c \) is determined from the scaling condition \( \langle x \rangle = \int xf(x)dx = 1 \).

For purely triple junction drag—the two cases in the right column in Eq. (5)—the parameter \( x_1 \) is given by \( x_1 = c_0 / c_1 = -a_t \) following from the linear topological function Eq. (8) represented in Figs. 4b and 4d. For the two cases of grain boundary mobility dominated grain growth—the left hand column in Eq. (5)—\( N(x) \) is given by the quadratic polynomial Eq. (7) represented in Figs. 4a and 4c. One can show [24] that under this condition Eq. (9) is also a solution for these two cases, when the parameter \( x_1 \) is formally set equal to zero, that is \( x_1 = 0 \).
The comparison of the analytical grain size distributions $f(x)$, where $\Gamma^*$ is used as a free fit parameter, with the numerical data resulting from the MC Potts model simulations shows in Figure 5 that the scaled analytical grain size distribution function Eq. (9) reflects the essential features of the grain size distributions of all the four considered cases of self-similar grain growth controlled by the respective pair of grain boundary and triple point energy and mobility, where self-similarity is shown again for the same three different annealing times as in Fig. 4.

A prominent feature of the two grain size distributions for triple junction mobility controlled grain growth in Figs. 5b and 5d is the non-zero value of the size distribution at $x = 0$. This property reflects the influence of the finite triple junction mobility on the grain growth kinetics leading to an accumulation of grains having very small sizes, as is typical for nanocrystalline materials [15, 19].

**Figure 4.** Topological correlation showing $N(x)$ for: a – grain boundary-grain boundary-control; b – grain boundary-triple junction-control; c – triple junction-grain boundary-control; d – triple junction-triple junction-control.
4. Conclusions

In the present paper we have investigated the influence of the energy and mobility of grain boundaries and their triple junctions in nanocrystalline two-dimensional polycrystals and thin films on annealing by analytic theories and modified Monte Carlo Potts model simulations. To that aim each structural feature of a polygonal grain has been assigned its own specific energy and finite mobility.

As a result we have derived four different limiting cases of self-similar growth kinetics each characterized by its own:

- average growth law following Eq. (6) as shown in Figure 2, where also the influence of the initial microstructure on annealing can be seen,
- standard deviation of the scaled grain size (Figure 3), which indicates that each kinetics is characterized by
- scaled grain size distribution, which we find to be in good agreement with our analytical solution, Eq. (9), as presented in Figure 5, and
topological relation between number of neighboring grains and scaled grain size as can be seen in Figure 4.

It is particularly noteworthy that while grain growth under triple junction mobility control has been in the focus of investigations in recent years [6-9, 15-19], the present paper is to our knowledge the first record of grain growth kinetics under triple junction energy control in two-dimensional polycrystalline grain microstructures.

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