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Grain boundary junction engineering

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Abstract

Under certain circumstances grain growth in polycrystals is controlled by the mobility of grain boundary junctions. The resulting microstructure is distinctly different from the granular assembly in the course of normal grain growth. Also, the structure established under junction control is rather stable even under the conditions characteristic for grain growth governed by grain boundary motion. This provides a means of controlling the grain microstructure evolution, in particular of ultrafine grained and nanocrystalline materials. It is demonstrated that such an effect can be expected not only for 2D arrangements but for 3D microstructures with quadruple junctions as well. The latter statement is supported by an assessment of the mobility of quadruple junctions. We propose to introduce a new branch of grain boundary engineering, namely grain boundary junction engineering.

Keywords: Grain boundary mobility; Triple junction; Quadruple point; Grain boundary kinetics; Junction kinetics

1. Introduction

It is known that the granular arrangement of polycrystals is liable to undergo grain growth, which in turn is determined by grain boundary motion. Several theoretical approaches have been proposed for 2D grain growth. The von Neumann–Mullins relation allows the definition of the rate of growth (shrinkage) of a grain of topological class n—equal to the number of sides of a grain—and the construction of the resulting grain microstructure. The rate of grain growth in a polycrystal, however, also depends on the mobility of grain boundary triple junctions and their spacing. Qualitatively this influence can be expressed by the dimensionless criterion

$$\Lambda = \frac{m_{tj} a}{m_b} \tag{1}$$

where m_b and m_{tj} are the mobility of grain boundary and triple junction, respectively, and a is the grain size. The dependency of the parameter Λ on the dihedral angle θ at the triple junction for grains with $n < 6$ (Fig. 1) and $n > 6$ makes it possible to measure the value of Λ experimentally and, as a result, the mobility of triple junctions for different grain boundary systems [3,4]

$$\Lambda = \frac{2\theta}{2\cos\theta - 1}, \quad n < 6 \tag{2}$$

$$\Lambda = -\frac{\ln\sin\theta}{1 - 2\cos\theta}, \quad n > 6 \tag{3}$$

It follows from Eqs. (1) to (3) that the strongest influence of triple junctions should be observed for small Λ, i.e. the influence of grain boundary junctions should be most pronounced for fine grained and nanocrystalline materials. It was found experimentally that the mobility of triple junctions can be very low [3,4].

2. Effect of boundary junctions on grain growth

The effect of triple junctions on grain growth was comprehensively considered in Ref. [2]. The most prominent features of grain growth in such systems are:

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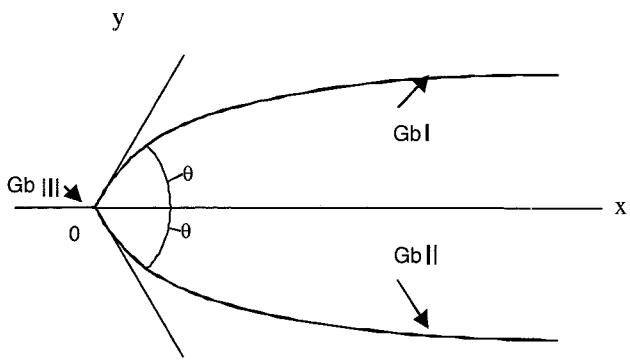

Fig. 1. Typical triple junction configuration for $n < 6$.

(i) The von Neumann–Mullins approach must be modified when the criterion Λ is rather small, i.e. when the triple junction mobility is not infinitely large or the grain size is small enough. In this case the contact angles at a triple junction deviate from the equilibrium value $\theta = \pi/3$ and the rate of grain area change $\dot{S}$ can be expressed as

$$\dot{S} = -A_b[2\pi - n(\pi - 2\theta)] \tag{4}$$

where $A_b = m_b\gamma_b$ is the reduced grain boundary mobility, γ_b is the grain boundary surface tension. Eqs. (2)–(4) describe the rate of grain area change $\dot{S}$ for grains of different topological classes for a given parameter Λ. Since a limited triple junction mobility reduces the steady state value of the angle θ as compared to the equilibrium angle, the shrinking rate of grains with $n < 6$ decreases. For grains with $n > 6$ triple junction drag increases the angle θ and also reduces the growth rate of such grains. In other words, microstructural evolution is slowed down due to triple junction drag for any n-sided grain.

(ii) The topological class n^* of stable grains, i.e. $\dot{S}(n^*) = 0$, for finite Λ is not constant any more and depends on Λ.

For $n < 6$

$$n_L^* = \frac{2 + \sqrt{3}\Lambda}{1 + \frac{\sqrt{3}}{6}\Lambda} \tag{5}$$

and for $n > 6$:

$$n_H^* = \frac{6}{1 - \frac{6}{\pi\Lambda B}} \tag{6}$$

In summary, grains with a number of sides $n_L^* < n < n_H^*$ become locked and can neither grow nor shrink [1,2]. Since $n_{L,H}^*$ is distinctly different from the von Neumann–Mullins limit $n^* = 6$ for small Λ, the influence of these locked grains might be very important for the stability of ultrafine grained and nanocrystalline materials.

(iii) At an intermediate situation, when the triple junction influence is tangibly large, but nevertheless, the evolution of the system can be still considered as governed by grain boundary motion, the time dependence of the average grain area $\langle S \rangle$ is practically linear; however, the rate of grain area change $\dot{S}$, contrary to the von Neumann–Mullins relation, is defined not only by the topological class n but by the criterion Λ as well: $\dot{S} = \dot{S}(n, \Lambda)$ (Figs. 2 and 3). We would like

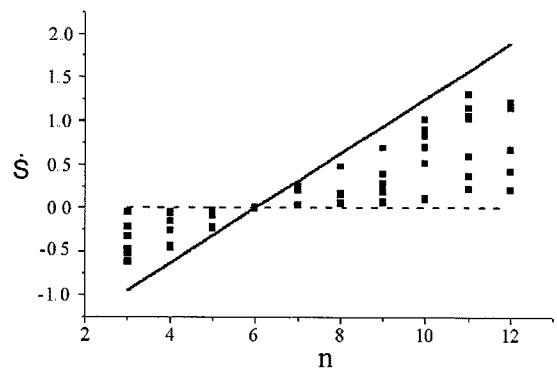

Fig. 2. Simulation result for $0.1 < \Lambda < 1.0$ [2]: $\dot{S}$ as function of n for $0.1 < \Lambda < 10$. Solid squares are the results of computer experiment, the line is the von Neumann–Mullins relation.

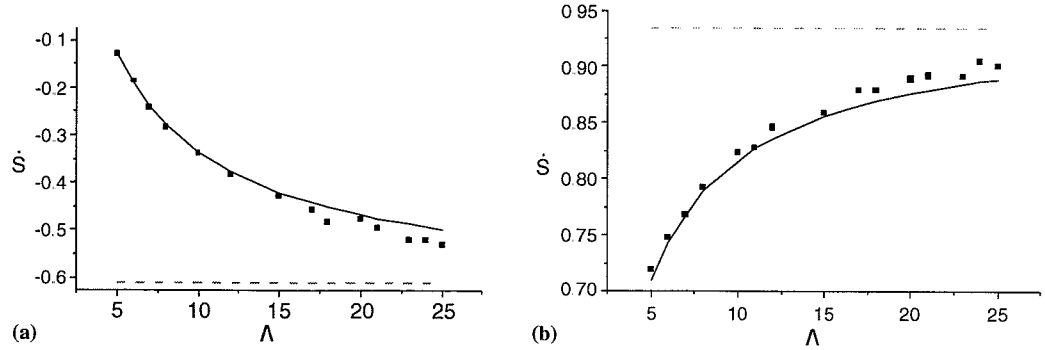

Fig. 3. The rate of grain area change $\dot{S}$ as a function of Λ: (a) for grains with $n = 4$. (■) are the results of computer simulations. The solid line represents the theoretical prediction for intermediate kinetics ($5 < \Lambda < 25$), the dotted line corresponds to the von Neumann–Mullins relation and (b) for grains with $n = 9$. The solid line represents the theoretical prediction for intermediate kinetics. The dotted line corresponds to the von Neumann–Mullins relation [2].

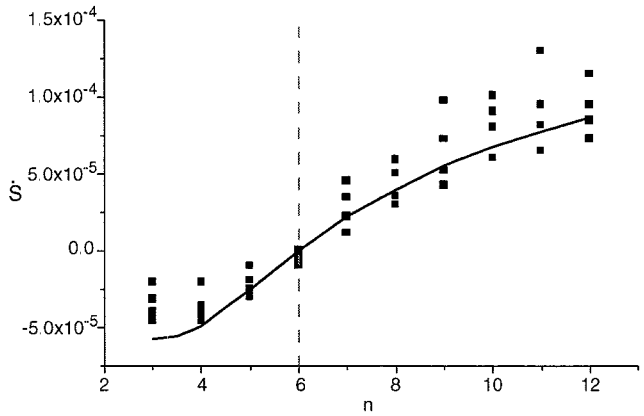

Fig. 4. $\dot{S}$ versus topological class n. Simulation results (■) for $\Lambda \sim 10^{-4}$: the solid line represents the dependency predicted by Eq. (9) [2], the dotted line corresponds to the von Neumann–Mullins relation.

to note that triple junction drag does not only slow down the grain microstructure evolution, it changes the final distribution of the grains of different topological classes as well as shown in Ref. [5]

$$\frac{d\Lambda}{dt} = -\tilde{\beta} \cdot \frac{2\pi - n(\pi - 2\theta)}{\Lambda} \tag{7}$$

where $\tilde{\beta}$ is a kinetic coefficient.

Eq. (7) demonstrates that the way triple junction drag affects the growth of grains of different topological classes n is markedly different.

(iv) Under triple junction kinetics grains should be bordered by straight lines, i.e. the grain boundaries in a 2D polycrystal represent a system of polygons. Moreover, the system of polygons tends to approach a system of equilateral polygons. The only exception is the triangle which will collapse without transforming into a regular polygon.

(v) The rate of grain area change of a regular n-sided polygon with an interior and exterior circle of radius $\tilde{r}$ and $\tilde{R}$, respectively, under triple junction kinetics can be described by

$$T_0\Omega = -(5.4 \pm 0.5) \times 10^{-11}\ m^3/m^2 \tag{8}$$

$$\dot{S} = -m_{tj}\gamma n\tilde{R} \sin\left(\frac{2\pi}{n}\right)\left[2\sin\left(\frac{\pi}{n}\right) - 1\right]$$

$$= -2m_{tj}\gamma n\tilde{r} \sin\left(\frac{\pi}{n}\right)\left[2\sin\left(\frac{\pi}{n}\right) - 1\right] \tag{9}$$

The rate of grain area change $\dot{S}$ for triple junction kinetics is represented in Fig. 4.

3. Grain boundary junction engineering

Evidently, the grain microstructure obtained during grain growth governed by junction mobility differs markedly from the microstructure obtained under grain boundary kinetics. This behavior can be utilized to influence microstructural evolution during recovery, recrystallization and especially grain growth, which will be referred to as grain boundary junction engineering.

All processes which affect the properties of a material due to a change in grain boundary properties and distribution, can be considered as a part of grain boundary engineering (GBE). We will confine ourselves here to grain growth. In recent years the thermal stability of grain microstructures has attracted special attention in particular for nanocrystalline materials. To maintain the beneficial properties of a fine grained material the microstructure should be rather stable. The traditional way to stabilize grain microstructures utilizes impurity drag or Zener drag. However, both methods change the chemistry of the material and, as a consequence, its physical and mechanical properties. Besides, the efficiency of microstructure stabilization by impurities and particles is often overrated [6]. We propose another approach, which is based on the essential difference between grain microstructures formed by junction kinetics and by boundary kinetics.

One possible method of junction kinetics treatment (JKT) is schematically depicted in Fig. 5, which shows a sequence of annealings. As detailed in Ref. [5], annealing at a relatively low temperature initiates grain growth at triple junction kinetics, and the obtained grain microstructure resulting from this treatment is a typical "junction" microstructure, a system of polygonal grains which tends to assume an equilateral shape, etc. Fig. 6 presents the results of grain growth studied by computer simulations. Evidently, a subsequent annealing at boundary kinetics conditions (after junction kinetics) requires a much larger time to reach the same grain size. An increase of the effect of JKT as expressed by the grain area ratio after junction controlled growth, S_i/S_0, conspicuously delays regular grain growth under boundary kinetics (bk).

This phenomenon can be seen more clearly in Fig. 7, where the ratio of the growth rates with and without JKT is presented for different $W = \frac{d(S_t/S_0)/dt_{afterJKT}}{d(S_t/S_0)/dt_{bk}}$. The numerator of W is the slope of the time dependency of the mean grain area change after JKT, while the denominator is the rate of mean grain area change at boundary kinetics. The value

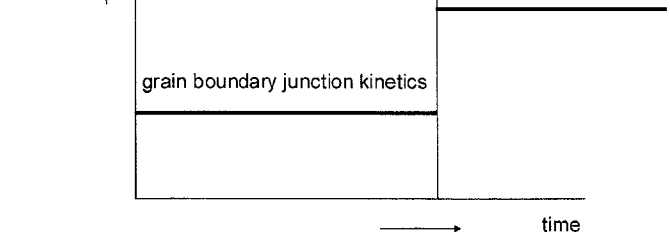

Fig. 5. Procedure of junction kinetics heat treatment (JKT): two consecutive annealings, at junction and grain boundary kinetics, respectively.

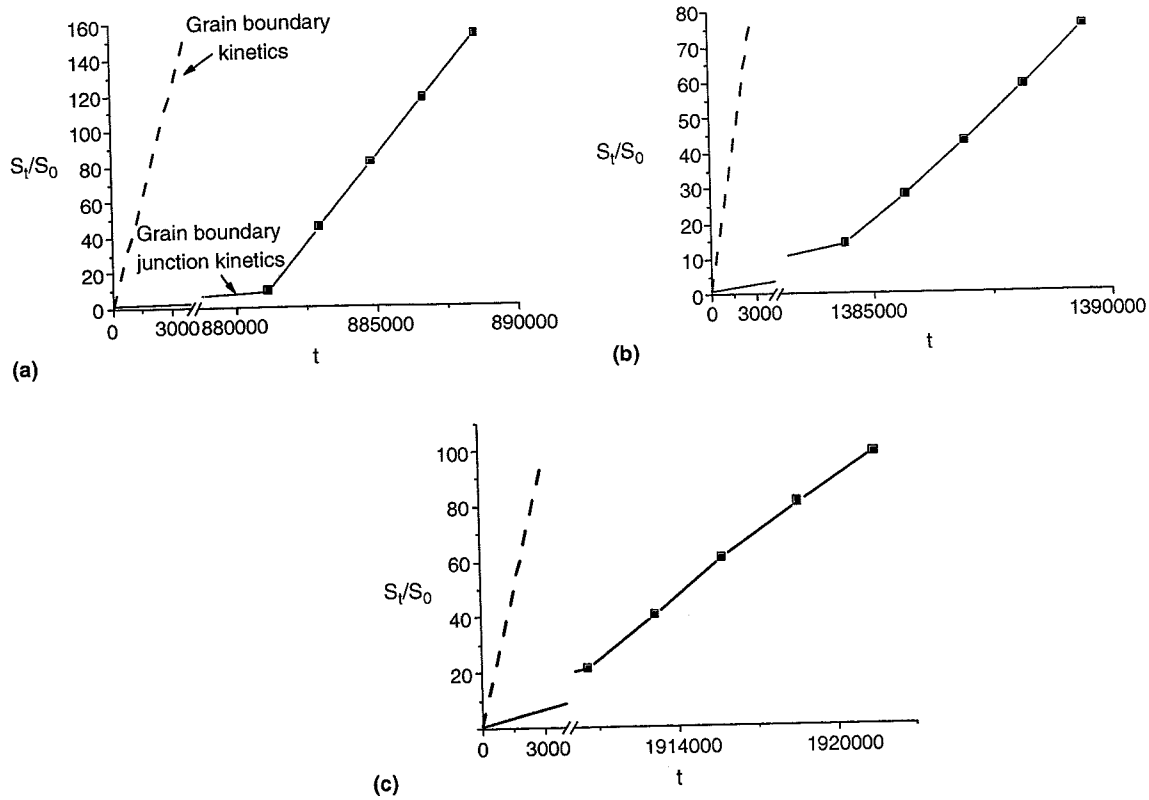

Fig. 6. The kinetics of mean grain area change for JKT: boundary kinetics (----) and junction kinetics (—), (■)—annealing at boundary kinetics after heat treatment at junction kinetics ($A = 10^{-4}$) for different starting ratios $\frac{S_t}{S_0}$: 10 (a); 15 (b); 20 (c) correspondingly [5]; the time of annealing is given in the arbitrary units.

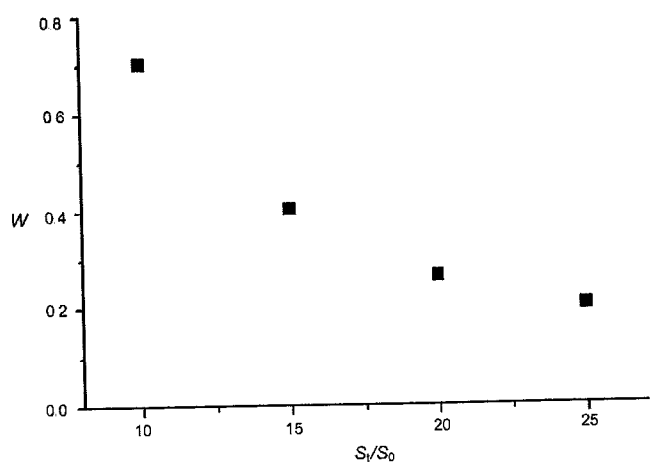

Fig. 7. The dependence of $W = \frac{d(S_t/S_0)/dt_{\text{after JKT}}}{d(S_t/S_0)/dt_{bk}}$ on $\frac{S_t}{S_0}$ [5].

W^{-1} is a measure for the stabilization of the grain microstructure in the course of such a treatment.

3D polycrystals incorporate, besides grain boundaries and triple junctions, grain boundary quadruple points. Unfortunately, our knowledge of the thermodynamic and kinetic properties of quadruple points, first of all their mobility, is close to zero. Recently a new concept was put forward which opens up a way to study in a quantitative experiment the kinetic properties of a quadruple junction [7]. In the framework of a uniform triple junction model

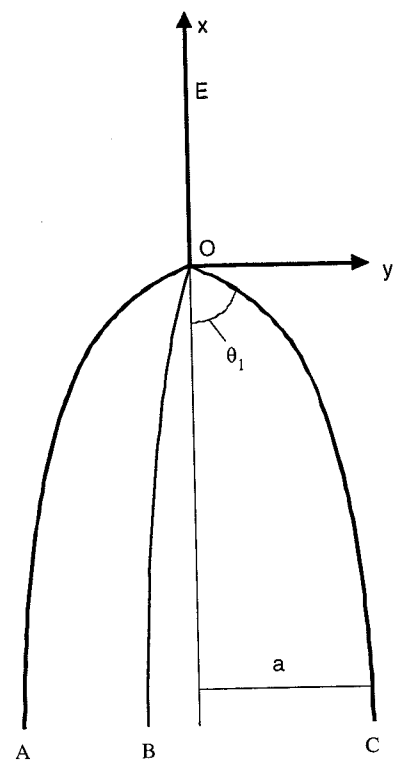

Fig. 8. Four grain boundary triple junctions meet at a grain boundary quadruple point. A, B, C and E, are the triple lines which form the quadruple point.

the motion of a special configuration of a quadruple point was considered (Fig. 8). The derived relation relates a dimensionless criterion Λ_{qp} to the steady-state value of the angle θ_1 (Fig. 8):

$$\Lambda_{qp} = \frac{m_{qp}a}{m_{tj}} = \frac{2\theta_1}{2\cos\theta_1 - 1} \tag{10}$$

If the product $m_{qp}a$ is large, the quadruple point does not affect the motion of the four adjoining boundaries.[1] then $\Lambda_{qp} \to \infty$ and the equilibrium angle at the tip of the quadruple point $\theta_1 \to \pi/3$. In the case that $m_{qp}a$ is small, the quadruple junction drags the triple junctions and, consequently, grain boundary motion. Despite essentially zero knowledge of quadruple point kinetics we contend that quadruple junctions will drag grain boundary motion. This contention is based on the understanding that any physical and especially geometrical restriction hinders grain boundary motion. In other words, grain growth at quadruple junctions kinetics can be used as well to slow down grain growth during subsequent annealing at grain boundary kinetics.

4. How to evaluate the mobility of grain boundary junctions?

To predict the kinetics and topology of grain microstructure evolution the mobility of grain boundary junctions needs to be known. This chapter describes how the quantity can be obtained.

Undoubtedly, the most correct way to determine the mobility of grain boundary junctions is the study of motion of a grain boundary system with a single junction [1,3,4] or to examine the evolution of a certain grain of defined topological class in the course of grain growth [2]. However, in general this a cumbersome procedure which requires sophisticated techniques of grain microstructure analysis.

We propose a rather simple approach for evaluation of the mobility of grain boundary junctions, namely from the temporal evolution of the grain size. Let us consider the motion of a grain boundary driven by grain boundary curvature κ with triple and quadruple junctions. Due to the fact that triple and quadruple junctions have their own mobility the motion of such a boundary can be considered as the motion of a boundary with mobile defects [8,9]. The velocity of such a boundary is given by

$$V = P_{eff} m_b \tag{11}$$

where P_{eff} is the effective driving force

$$P_{eff} = \gamma_b \kappa - \frac{f_1}{a_1} - \frac{f_2}{a_2^2} \tag{12}$$

and a_1 and a_2 are the spacings of the respective junctions; since a_1 and a_2 are of the same order of magnitude, we will assume for simplicity $a_1 = a_2 = a$ in the following. f_1 and f_2 are the dragging forces of triple and quadruple junctions, respectively; in accordance with the Einstein relation

$$f_1 = \frac{V}{m_{tj}}$$
$$f_2 = \frac{V}{m_{qp}} \tag{13}$$

we arrive at

$$V\left[1 + \frac{m_b}{a m_{tj}} + \frac{m_b}{a^2 m_{qp}}\right] = m_b \gamma_b \kappa \tag{14}$$

Eqs. (1), (10) and (14) yield

$$V = \frac{m_b \gamma_b \kappa}{1 + \frac{1}{\Lambda} + \frac{1}{\Lambda_{qp}}} \tag{15}$$

where $\Lambda_{qp} = \frac{m_{qp}a^2}{m_b}$.

Eqs. (14) or (15) define the different types of grain growth kinetics in polycrystals. The first one is the well-known grain boundary kinetics: $\frac{1}{\Lambda}, \frac{1}{\Lambda_{qp}} \ll 1$, the velocity V is proportional to the grain boundary curvature, and the mean grain size increases in proportion to the square root of the annealing time: $V = \frac{d\langle R\rangle}{dt} \sim \frac{1}{\langle R\rangle} \Rightarrow \langle R\rangle \sim \sqrt{t}$. If grain boundary motion is controlled by the mobility of triple junctions ($\frac{1}{\Lambda} \gg 1$ and $\frac{1}{\Lambda} \gg \frac{1}{\Lambda_{qp}}$), the velocity V is constant: $V = \frac{d\langle R\rangle}{dt} = \text{const.} \Rightarrow \langle R\rangle \sim t$. Finally, if the mobility of the quadruple junctions (points) determines the motion of the grain boundary system ($\frac{1}{\Lambda_{qp}} \gg 1$ and $\frac{1}{\Lambda_{qp}} \gg \frac{1}{\Lambda}$) the velocity V is proportional to the radius of curvature: $V = \frac{d\langle R\rangle}{dt} \sim \langle R\rangle \Rightarrow \langle R\rangle \sim e^t$. Under grain boundary kinetics we observe the classical grain growth kinetics, which is to hold for rather large grains. The time dependency of the mean grain size determined by triple junction kinetics ($\langle R\rangle \sim t$) was observed for grain growth in ultrafine grained and nanocrystalline materials [10–13].

There are indications that in the course of grain growth in nanocrystalline systems quadruple junction kinetics were also observed [13]. To estimate the mobility of a quadruple point we used the experimental data of Ref. [12], where the authors studied grain growth in nanocrystalline Al, because this effect is expected to become significant for very small grain sizes. As discussed above in the case when the mobility of quadruple junctions controls grain growth an exponential dependency of the mean grain size on the annealing time must be observed. In fact the experimental data [12] for grain growth in Al at 600 °C demonstrate such a dependency (Fig. 9) and yield the mobility of a quadruple junction (point)

$$\frac{d\ln R}{dt} = m_{qp}\gamma_b = 1.9 \times 10^{-4}\ \text{s}^{-1} \tag{16}$$

This approach is most reliable if the extracted kinetic parameters do not depend on the kinetic properties of other structural elements of the polycrystal. However,

[1] It should be taken into account that the motion of the configuration of triple junctions discussed is not completely steady-state [7]. To be able to observe a steady-state motion of the quadruple junction the shrinkage of the triangle in the cross section perpendicular to the main axis has to be slow compared to the motion of the quadruple junction.

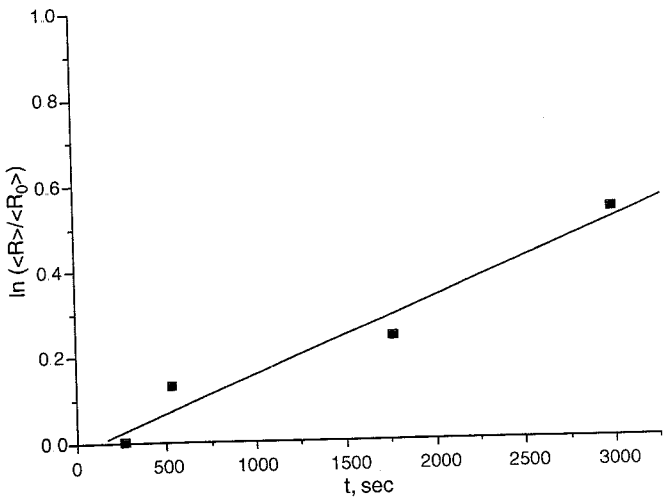

Fig. 9. Logarithm of the mean grain size $\ln(\frac{\langle R\rangle}{\langle R_0\rangle})$ vs. annealing time t for nanocrystalline Al at 600 °C. The experimental data are taken from Ref. [12].

commonly the measured grain growth rate will be a result of a superposition of the influence of different structural elements. In this case we can utilize another scenario. The mean rate of grain growth in nanocrystals was measured as a function of the annealing time [12]: $V = 5 \times 10^{-12}$ m/s; $\langle R\rangle = 55 \times 10^{-9}$ m. The values of the reduced mobility of high-angle boundaries and triple junctions were extracted from Ref. [14], where the motion of grain boundary systems with triple junctions in Al doped with impurities had been studied. The concentration dependency of grain boundary and triple junction mobility was extrapolated to ~5% of the total impurity concentration. This concentration corresponds to the impurity content in the experiments reported in Ref. [14]. For the system of high angle boundaries at 540 °C $A_b = m_b\gamma_b = 2 \times 10^{-14}$ m^2/s; $A_{tj} = m_{tj}a\gamma_b = 4 \times 10^{-15}$ m^2/s, where a is the grain size in the experiments [14], $a = 10^{-3}$ m and $m_{tj}\gamma_b = 4 \times 10^{-12}$ m/s, respectively. The criterion $\Lambda = \frac{m_{tj}\langle R\rangle}{m_b} = 10^{-5}$. The grain growth rate and the mean grain size at 540 °C amount to 5×10^{-12} m/s and $\langle R\rangle \approx 55 \times 10^{-9}$ m, respectively [12]. With Eq. (15) we arrive at

$$1 + \frac{1}{\Lambda} + \frac{1}{\overline{A}_{qp}} = 7.3 \times 10^4 \tag{17}$$

and

$$\overline{A}_{qp} = \frac{m_{qp}\langle R\rangle^2}{m_b} = \frac{\gamma_b m_{qp}\langle R\rangle^2}{\gamma_b m_b} = \frac{A_{qp}}{A_b} = 1.4 \times 10^{-5} \tag{18}$$

where $A_{qp} = m_{qp}\gamma_b\langle R\rangle^2$ defines the extended mobility of a quadruple junction.

We obtain for this extended quadruple junction mobility at 540 °C

$$A_{qp} = m_{qp}\gamma_b\langle R\rangle^2 = 2.8 \times 10^{-19}\ \text{m}^2/\text{s}$$
$$m_{qp}\gamma_b = 9 \times 10^{-5}\ \text{s}^{-1} \tag{19}$$

The magnitude of $m_{qp}\gamma_b$ obtained in this calculation compares well with results of a direct estimation (see Eq. (16)). Eqs. (16)–(19) allow us to find the critical mean grain size $\langle R_{cr}\rangle$, above which the dragging influence of triple junctions on grain growth will exceed the effect of quadruple points

$$\langle R_{cr}\rangle = \frac{m_{tj}\gamma_b}{m_{qp}\gamma_b} = 5 \times 10^{-8}\ \text{m} \tag{20}$$

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