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Viewpoint Paper

Thermodynamics and kinetics of grain boundary triple junctions in metals: Recent developments

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Abstract—This paper assesses the contribution of grain boundary triple junctions to the driving force for grain growth and the "energetic" effect of boundary junctions on grain growth in nanocrystalline materials. The first measurement of grain boundary line tension allows the quantitative estimation of the fraction of the driving force due to boundary triple junctions. For polycrystals with a grain size in the range ~50 nm, it is comparable with the driving force from grain boundaries.

Keywords: Grain boundary triple junction; Triple line energy; Driving force of grain growth

1. Introduction

The traditional concepts of grain growth are based on the assumption of the dominant role of grain boundaries. A most obvious example of such an approach is the well-known von Neumann–Mullins relation for two-dimensional (2D) grain growth. According to this theory, boundary junctions (triple junctions) do not affect grain growth, and their role is reduced to maintaining the thermodynamically prescribed equilibrium angles at the points where boundaries meet. A more recent approach where triple junctions are considered as grain boundary elements with specific kinetic properties was introduced in Refs. [1–4]. Crystallographically defined grain boundary configurations in tricrystals and novel experimental techniques [1,2] have made it possible to study the steady-state motion of grain boundary systems with triple junction and to measure accurately the mobility of the grain boundaries and triple junctions. Moreover, molecular dynamics simulations of triple junction migration were performed for the same geometrical configurations as used in experiment. Overall, the simulations support the experimental observations of non-equilibrium triple junction angles and ascertain a substantial triple junction drag [5].

It was found that the triple junction mobility is finite and may be low. As shown in Refs. [1–4,6] grain boundary triple junctions not only drag grain boundary motion and thus slow down grain growth, but also essentially affect the evolution of grain microstructure during grain growth. When grain growth is controlled by the kinetics of grain boundary migration, grain growth in a 2D polycrystal complies with the von Neumann–Mullins relation. If grain growth becomes governed by the mobility of triple junctions, the kinetics change, and the von Neumann–Mullins relation no longer holds. This is more pronounced the smaller the triple junction mobility. A generalized theory of 2D grain growth, including a limited triple junction mobility, is given in Refs. [1–4]. The dimensionless criterion $\Lambda = \frac{m_{tj}a}{m_b}$, where m_b is boundary mobility, m_{tj} is triple junction mobility, and a is grain size, is the central parameter that controls the behavior of the boundary system. For large Λ (large m_{tj} or large grain size) grain growth is determined by the grain boundary mobility (grain boundary kinetics), and the mean grain size follows the well-known parabolic law $\langle D\rangle \sim \sqrt{t}$, where t is the annealing time. For relatively small Λ, the triple junction mobility dominates the grain growth kinetics (triple junction kinetics), and the size increases linearly with time. It is stressed also that the dihedral angles at the triple junction in a polycrystal are determined by criterion Λ. The generalized von Neumann–Mullins relation [7] can be expressed in terms of Λ:

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$$\dot{S} = \frac{m_b \gamma_b \pi}{3}\left(n\frac{6+\sqrt{3}\Lambda}{2+\sqrt{3}\Lambda} - 6\right) \quad \text{for } n < 6 \tag{1}$$

$$\dot{S} = \frac{m_b \gamma_b \pi}{3}\left[n\left(1 - \frac{6}{\pi \Lambda B}\right) - 6\right] \quad \text{for } n > 6 \tag{2}$$

Here, S is the grain area, $\dot{S} \equiv dS/dt$, n is the number of the triple junctions (neighboring grains), γ_b is the grain boundary surface tension, and $B = -\frac{\sqrt{3}}{\ln \sin \pi/3}$.

Evidently, for $\Lambda \to \infty$ expressions (1) and (2) approach the von Neumann–Mullins relation.

For small values of Λ, conspicuous changes in microstructure evolution during grain growth and of microstructural stability are predicted. The theoretical predictions are supported by the results of computer simulations. In particular, it was demonstrated that the vertex angle Θ at the triple junction can deviate substantially from the equilibrium value when a low mobility of the triple junction hinders the motion of the grain boundaries. In fact, a transition from triple junction kinetics to grain boundary kinetics was observed experimentally [4,6]. In essence, a low triple junction mobility will exert a drag effect on grain boundary motion.

It was shown in Refs. [7,8] that the influence of grain boundary junctions (triple line and quadruple junctions in three-dimensional (3D) polycrystals) drag on grain growth kinetics can be described in terms of Λ. The rate of 3D grain growth can be expressed as

$$\frac{d\langle D\rangle}{dt} = \frac{m_b P}{\left(1 + \frac{1}{\Lambda_{qp}} + \frac{1}{\Lambda_{tj}}\right)} \tag{3}$$

where $P = \frac{2\gamma_b}{R}$ is the driving force for continuous grain growth. Here, $1/R$ is the grain boundary curvature. For simplicity, assume $R \approx \langle D\rangle$, Λ_{qp} and Λ_{tj} are the quadruple point and triple junction criteria, respectively [8]. Note that the reciprocal value of Λ, i.e., $\frac{1}{\Lambda}$ is a measure of the drag effect of a given junction on grain growth. With $D(t=0) = D_0$, integration of Eq. (3) yields

$$\frac{1}{2}\left(\langle D\rangle^2 - \langle D_0\rangle^2\right) + \frac{m_b}{m_{tj}}\left(\langle D\rangle - \langle D_0\rangle\right) + \frac{m_b}{m_{qp}}\ln\frac{\langle D\rangle}{\langle D_0\rangle} = 2\gamma_b m_b t \tag{4}$$

However, triple junction drag is not the only triple junction effect on grain growth and grain microstructure evolution. Another influence stems from the energy of the triple junction lines, their line tension γ^l. Actually, the excess energy of boundary junctions *along with the grain boundary energy* constitute the driving force for grain growth.

The following will show how to measure the triple junction line tension and, finally, how much this energy contributes to the driving force for grain growth will be assessed.

2. Measurement of grain boundary triple line energy

The problem of triple line energy was discussed in a speculative way by Gibbs [9], who came to the conclusion that the excess free energy of a triple line between fluid phases might be positive or negative. McLean [10] contended that triple junctions should always have a positive energy. Using computer simulation, Srinivasan et al. [11] came to the conclusion that a negative triple line energy is possible, whereas Van Swygenhoven et al. [12] found that the triple line tension obtained in the simulation studies was always positive. Nishimura [13] and Fortier et al. [14] tried to measure the triple line tension. They approximated the crater at the triple junction by a tetrahedron and estimated the energy of the triple line to be of the order or 5×10^{-7} J/m.

A thermodynamically correct approach is given in Refs. [15,16]. It is based on the equilibrium of four line tensions at their point of intersection, the grain boundary triple line and three triple lines at the bottom of the thermal grooves of the joining boundaries (Fig. 1). The term $u(r)$ mathematically describes the profile of the groove root as a function of r, where the vector $r = (x, y)$ denotes the planar coordinates of a point on the groove root (Fig. 1a). The origin of the coordinate system is attached to the point of intersection of the three groove roots and the triple line. Moreover, it is assumed that the surface tension is independent of the crystal orientation.

From the equilibrium of the four line tensions, it follows for the triple line tension

$$\gamma^l = \gamma^{IS}_{1-2}\sin\zeta_{1-2} + \gamma^{IS}_{1-3}\sin\zeta_{1-3} + \gamma^{IS}_{2-3}\sin\zeta_{2-3} \tag{5}$$

where γ^l and γ^{IS}_{i-j} are the grain boundary triple junction line tension and the line tension of the triple lines at the bottom of the thermal groove, respectively, and ζ_{i-j} are the angles of each groove root of the corresponding grain boundary at the center of the triple junction:

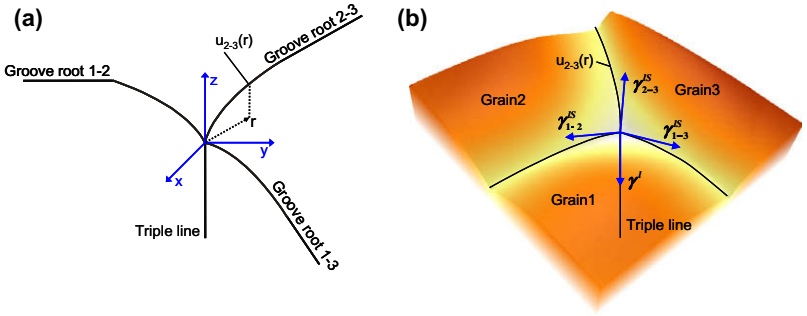

Figure 1. (a) Schematic 3D view of the line geometry at a triple junction. (b) AFM 3D view of the line tension equilibrium at a triple junction [16].

$$\sin\zeta_{i-j} = \sin\left(\arctan\left.\frac{\partial u_{i-j}}{\partial r}\right|_{r=0}\right) = \left.\frac{\frac{\partial u_{i-j}}{\partial r}}{\sqrt{1+\left(\frac{\partial u_{i-j}}{\partial r}\right)^2}}\right|_{r=0} \tag{6}$$

The line tension of the triple lines γ^{IS}_{i-j} is determined by comparing the dihedral angle at the root of a flat and a curved grain boundary groove (Fig. 1). In particular, close to the point of intersection, the groove roots will be curved. In the case where the grain boundary remains flat but the root of the grain boundary groove is curved [16], one must take into account an additional term, which is principally equivalent to the Laplace pressure for 3D curved grain boundary surfaces. Therefore,

$$\gamma_B - \gamma^{IS}\frac{\frac{\partial^2 u}{\partial r^2}}{[1+(\frac{\partial u}{\partial r})^2]^{3/2}} = 2\gamma_S\cos\frac{\xi}{2} \tag{7}$$

where γ_B and γ_S are the grain boundary surface tension and the crystal surface tension, respectively. The dihedral angles denoted by ξ have the same meaning as θ in the classical equation of the thermal grain boundary groove, $\gamma_B = 2\gamma_S\cos\frac{\theta}{2}$, but are significantly different in value owing to the curvature of the grain boundary groove root.

As shown in Ref. [16], the necessary parameters to extract the triple line tension can be derived from atomic force microscopy (AFM), such as the grain boundary groove angles, the groove root angles at the curved part of the grain boundary and the curvature of the groove roots. Such an experiment was carried out on a copper tricrystal. For the line tension of the grain boundary groove root, this yielded $\gamma^{IS} \cong (17.0 \pm 7.0)\times 10^{-9}$ J/m and, for the grain boundary triple junction, this yielded $\gamma^{l} = (6.0 \pm 3.0)\times 10^{-9}$ J/m [16]. Moreover, a more detailed thermodynamic analysis shows that the triple line and the grain boundary free surface energy are positive under equilibrium conditions.

3. Triple line contribution to the driving force for grain growth

It is obvious that the driving force for grain growth contributed by grain boundary triple junctions can be expressed as

$$P_{tj} = \sum_i L_i\cdot\gamma^l_i \tag{8}$$

where L_i is the total length per unit volume of boundary triple junctions with line energy (line tension) γ^l_i.

As shown in Ref. [17] for a uniform triple junction model, i.e., all triple junctions are of equal energy γ^l, the total length $\bar{L}_{tj}$ per unit volume is

$$\bar{L}_{tj} \cong \frac{36}{\pi\langle D\rangle^2} \tag{9}$$

where $\langle D\rangle$ is the mean grain diameter.

Then the driving force exerted by grain boundary triple junctions P_{tj} is equal to

$$P_{tj} = \frac{36\gamma^l}{\pi\langle D^2\rangle} \tag{10}$$

However, the driving force for continuous grain growth due to grain boundary curvature $1/R$ reads

$$P_b = \frac{2\gamma_b}{\langle R\rangle} \approx \frac{2\gamma_b}{\langle D\rangle} \tag{11}$$

where one assumes $R \approx \langle D\rangle$.

The total driving force from grain boundaries and triple junctions reads

$$P = \frac{2\gamma_b}{\langle D\rangle} + \frac{36\gamma^l}{\pi\langle D^2\rangle} \tag{12}$$

The ratio $\frac{P_{tj}}{P_b} = \frac{18\gamma^l}{\pi\gamma_b} = a$ defines the grain size for which the grain boundary and triple junction contribution to the driving force are equal. Apparently, in a polycrystal with mean grain size smaller than a, the triple line energy is larger than the grain boundary excess energy. To evaluate the magnitude of a, one needs to know the line tension of the grain boundary triple junction (see previous section).

For a random triple line in polycrystalline Cu, measurements rendered $\gamma^l \approx 6.0\times 10^{-9}$ J/m. Taking $\gamma_b \approx 0.6$ J/m^2 for the grain boundary surface tension in Cu, one arrives at $a \approx 55$ nm. In other words, up to a mean grain size of ~55 nm, the driving force stemming from triple junctions is larger than that of the boundaries. As a consequence, a correct examination of grain growth in nanocrystalline materials, at least up to a mean grain size equal to a, cannot be performed if the driving force of triple junctions is not taken into account.

4. Macroscopic description of grain growth in nanocrystalline materials

On the basis of Eqs. (3) and (11), the kinetic equation of grain growth can be written as

$$\frac{d\langle D\rangle}{dt} = \frac{m_b\left(\frac{2\gamma_b}{\langle D\rangle}+\frac{36\gamma^l}{\pi\langle D\rangle^2}\right)}{1+\frac{m_b}{m_{tj}\langle D\rangle}+\frac{m_b}{m_{qp}\langle D^2\rangle}} \tag{13}$$

After integration, one arrives at:

$$\frac{1}{2}\left(\langle D^2\rangle - \langle D_0^2\rangle\right) + \left(\frac{m_b}{m_{tj}} - a\right)\left(\langle D\rangle - \langle D_0\rangle\right) + \left(a^2 - \frac{m_b}{m_{tj}}a + \frac{m_b}{m_{qp}}\right)\ln\frac{\langle D\rangle + a}{\langle D_0\rangle + a} = 2\gamma_b m_b t \tag{14}$$

One can see that, for $a \to 0$, Eq. (14) transforms into Eq. (4).

The classical relation without junction and drag effects reads

$$\frac{1}{2}\left(\langle D^2\rangle - \langle D_0^2\rangle\right) = 2\gamma_b m_b t \tag{15}$$

If no drag but the junction line energy is taken into account, one obtains

$$\frac{1}{2}\left(\langle D^2\rangle - \langle D_0^2\rangle\right) - a\left(\langle D\rangle - \langle D_0\rangle\right) + a^2\ln\frac{\langle D\rangle + a}{\langle D_0\rangle + a} = 2\gamma_b m_b t \tag{16}$$

The junction drag decreases dramatically with progressing grain growth (see curve for Eq. (4)). It is obvious

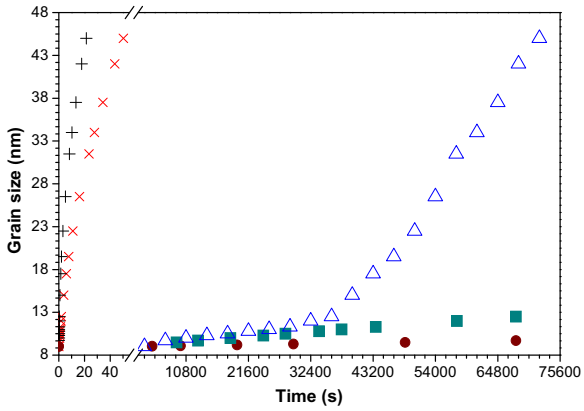

Figure 2. Grain growth in nanocrystalline Pd [18]. The triangles represent the experimental results. The designations for different approximations, ● Eq. (4) and ■ Eq. (14), take the influence of the triple junctions and the quadruple points into account, in contrast to × Eq. (15) and + Eq. (16), where the drag effect of the junctions was neglected.

that the additional driving force due to triple junctions dramatically speeds up grain growth in agreement with experimental results.

This description was applied to the experimental data of grain growth in nanocrystalline Pd [18]. The values of grain boundary mobility and surface tension given in Ref. [18] were used. The mobility of triple junctions and quadruple points were roughly estimated from the experimental curve. The mobility of the quadruple points m_{qp} was about $2.4 \times 10^{-6}\,\mathrm{m^2/Js}$, derived from the first experimental points (Fig. 2) using Eq. (14) and assuming that $\frac{1}{\Lambda_{tj}} = \frac{m_b}{m_{tj}\langle D\rangle} \approx 0$. The mobility of the triple junction $m_{tj} \approx 1.5 \times 10^{-14}\,\mathrm{m^3/Js}$ was extracted using the experimental points in the midsection of the experimental curve, where the drag effect stems mostly from the triple junctions. Unfortunately, the triple junction line tension for Pd is unknown. Instead, the measured value for Cu were used, assuming that the ratio γ^l/γ_b may be considered as constant.

The computed results are presented in Figure 2. Evidently, if the triple junction drag is not taken into account, the rate of grain growth is extremely high (Fig. 2, Eqs. (15) and (16)), which is not surprising for such a small grain size.

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