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Efficiency of drag mechanisms for inhibition of grain growth in nanocrystalline materials

An attempt is made to assess the efficiency of drag effects by different structural elements of a polycrystal on grain growth. The rate of grain area change is chosen as a measure of stability of a grain structure, and the inhibition of grain growth is pairwise evaluated among all drag effects considered. In aluminium, at temperatures of about 200 °C, triple junction drag was found to be most effective. The derived hierarchy of drag efficiency can be used as an effective engineering tool to assess and compare the role of chemistry and crystal defects on the microstructural stability of nanocrystalline and fine-grained materials.

Keywords: Grain microstructure; Grain growth; Thermal stability; Nanocrystals; Drag effects

1. Definition of drag efficiency

The investigation and design of ultrafine and nanograined materials is one of the particularly promising directions in modern materials science. However, to produce a fine-grained or nanocrystalline material is part of the problem only. It is of equal importance to slow down the process of grain growth since the small grain size generates a large driving force for grain growth. In this study, an attempt is made to compare the efficiency of various potential drag effects. The rate of grain area change, dS/dt, is chosen as a measure for the stability of a 2D grain structure. The change of grain area characterizes grain growth in more detail than the change of grain size, and both can be distinctly different even for the same grain. We confine ourselves to 2D grain growth, as the theories of grain growth are elaborated best for 2D systems. Because we are interested only in a relative efficiency of grain growth drag, the use of a 2D approach is also physically justified.

To define the relative efficiency of grain growth drag due to different drag effects, we will determine a hierarchy of pairwise criteria $\lambda_{i,k}$,

$$\lambda_{i,k} = \frac{\left(\frac{dS}{dt}\right)_i}{\left(\frac{dS}{dt}\right)_k} \qquad (1)$$

which constitutes the ratio of the rate of grain area change for a pair of different drag mechanisms. When $\lambda_{i,k} < 1$, grain growth is controlled by mechanism (i), and the magnitude of $\lambda_{i,k}$ denotes the drag efficiency. The kinetics of growth and dragging are strongly affected by material, temperature and initial microstructure. In this study, we shall confine ourselves to nanocrystalline polycrystals of aluminium-based alloys at temperatures of about 200 °C.

2. Impurity drag

For grain growth controlled by grain boundary kinetics, the rate of grain area change, dS/dt, is expressed by the von Neumann–Mullins relation [1, 2]. The influence of impurities is reflected basically by the grain boundary, mobility $m_b(c)$, where c is the concentration of the impurities. The criterion $\lambda_{imp,0}$ in this case is equal to:

$$\lambda_{imp,0} = \frac{\left(\frac{dS}{dt}\right)_{imp}}{\left(\frac{dS}{dt}\right)_{c=0}} = \frac{\frac{m_b(c)\,\gamma_b\pi}{3}(n-6)}{\frac{m_b\gamma_b\pi}{3}(n-6)} = \frac{m_b(c)}{m_b} \qquad (2)$$

where $\left(\frac{dS}{dt}\right)_{c=0}$ and $\left(\frac{dS}{dt}\right)_{imp}$ are the rates of grain area change in a "pure" metal and in a metal with impurities, respectively. γ_b denotes the grain boundary surface tension as the mobility depends on grain boundary crystallography the best way to define this ratio is to use data for a specific grain boundary in materials with a different amount of impurities. For a <111>-tilt grain boundary (misorientation angle 38.2° (Σ7)) in Al with total impurity content 0.4 ppm and 7.0 ppm, respectively, at 200 °C, $\lambda_{imp,0} = 5 \cdot 10^{-4}$. For a non-special <111>-tilt grain boundary (misorientation angle 40.5°) at the same temperature $\lambda_{imp,0} = 1.7 \cdot 10^{-4}$ [3]. Unfortunately, the number of such experiments is extremely small. On the other hand, the materials science community is interested in an approach which can be applied to a so-called "average" grain boundary. As a rough approximation, we will use a combination of the Burke–Turnbull expression for the grain boundary velocity and the Lücke–Detert approach of impurity drag. The change of grain boundary mobility with impurity concentration yields

$$\lambda_{imp,0} = \frac{m_b(c)}{m_b} = \frac{D_0 \exp\left(-\frac{\left(H_{Dimp} - H_{SD} + H_{int}\right)}{kT}\right)}{N_a B_0 \Omega_a b v \cdot c} \qquad (3)$$

where b is the lattice constant, v the Debye frequency, D_0 the pre-exponential factor of the diffusion coefficient,

H_{Dimp} the activation enthalpy for bulk diffusion of impurity atoms, H_{int} the interaction energy of impurity atoms with the boundary, H_{50} the activation energy N_{a} the number of adsorption sites in the grain boundary, B_0 the pre-exponential factor of the adsorption coefficient, and c the bulk impurity concentration.

For Fe impurities in Al:

$D_0 = 91\ \mathrm{m^2/s}$; $H_{\mathrm{Dimp}} = 2.68$ eV; $H_{\mathrm{SD}} = 1.48$ eV [4];

$H_{\mathrm{int}} = 0.24$ eV [5]; $N_{\mathrm{a}} \approx 5 \cdot 10^{-5}\mathrm{mol/m^2}$;

$\Omega_{\mathrm{a}} \approx 10^{-5}\mathrm{m^3/mol}$; $B_0 \approx 1$; $b = 3 \cdot 10^{-10}$ m; $\nu = 10^{13}$

Here $\mathrm{SD_a}$ is the atomic volume. Then, for $c \approx 10^{-5}$ at 200 °C, $\lambda_{\mathrm{imp},0} \approx 3.6 \cdot 10^{-3}$. It is emphasized that grain boundary adsorption decreases with decreasing grain size and makes impurity drag even less effective.

3. Triple junction drag

Triple junctions are defects on their own and may have a lower mobility than the adjoining grain boundaries. This results in a drag effect, which modifies the von Neumann–Mullins relation [1, 2]. For this effect, we find

$$\lambda_{\mathrm{tj,b}} = \frac{\dfrac{\mathrm{d}S_{\mathrm{tj}}}{\mathrm{d}t}}{\dfrac{\mathrm{d}S_{\mathrm{b}}}{\mathrm{d}t}} = \frac{-m_{\mathrm{tj}}\gamma_{\mathrm{b}}\bar{R}n\sin\left(\dfrac{2\pi}{n}\right)\left[2\sin\left(\dfrac{\pi}{n}\right)-1\right]}{\dfrac{m_{\mathrm{b}}\gamma_{\mathrm{b}}\pi}{3}(n-6)}$$

$$= \lambda_{\mathrm{tj,b}} = \lim_{n\to 6}\frac{\dfrac{\mathrm{d}}{\mathrm{d}n}\left(\dfrac{\mathrm{d}S_{\mathrm{tj}}}{\mathrm{d}t}\right)}{\dfrac{\mathrm{d}}{\mathrm{d}n}\left(\dfrac{\mathrm{d}S_{\mathrm{b}}}{\mathrm{d}t}\right)} = \frac{3}{4}\frac{m_{\mathrm{tj}}\bar{R}}{m_{\mathrm{b}}} = \frac{3}{4}\Lambda \qquad (4)$$

where $\bar{R}$ is the grain size, and Λ is defined by this equation, n is a topological class of a grain.

We will restrict ourselves to the value of $\lambda_{\mathrm{tj,b}}$ for the average topological class of a 2D system, namely for $n = 6$. An important property of Eq. (4) is its explicit dependency on grain size. Grain boundary triple junction mobility has been explored very poorly, even less than grain boundary mobility. We will use the experimental data given in reference [7] for a triple junction, TJ1, formed by three 40°<111> tilt grain boundaries in pure Al. For $\bar{R} = 10^{-8}$ m at 200 °C and 300 °C, we obtain $\Lambda = 10^{-12}$ and $\Lambda = 10^{-10}$, respectively. For another investigated triple junction, TJ2, formed by the same tilt boundary system (with different misorientation angles), we arrive for $\bar{R} = 10^{-8}$ m and 200 °C and 300 °C at $\Lambda = 10^{-11}$ and $\Lambda = 10^{-8}$, respectively. This yields the efficiency of triple junction drag $\lambda_{\mathrm{tj,b}}$ for $\bar{R} = 10^{-8}$ m

$$\lambda^{\mathrm{TJ1}}_{\mathrm{tj,b}}(200^{\circ}\mathrm{C}) \approx 10^{-12} \quad \text{and} \quad \lambda^{\mathrm{TJ2}}_{\mathrm{tj,b}}(200^{\circ}\mathrm{C}) \approx 10^{-11}$$

$$\lambda^{\mathrm{TJ1}}_{\mathrm{tj,b}}(300^{\circ}\mathrm{C}) \approx \cdot 10^{-9} \quad \text{and} \quad \lambda^{\mathrm{TJ2}}_{\mathrm{tj,b}}(300^{\circ}\mathrm{C}) \approx 10^{-8}$$

Obviously, triple junctions cause a powerful drag for grain growth in nanosystems.

4. Vacancy drag

Owing to the loss of excess volume during grain growth, vacancies are generated to temporarily compensate the volume change. This leads to a drag effect during grain growth. The effective mobility of grain boundaries during grain growth, influenced by the injected vacancies, can be expressed as [8, 9]:

$$m_{\mathrm{beff}} = \frac{V_{\mathrm{eff}}}{P} = \frac{1}{36}\cdot\frac{\bar{R}D_{\mathrm{SD}}}{NkTZ(\beta\delta)^2} \qquad (5)$$

where $P = \dfrac{3}{2}\cdot\dfrac{\gamma}{\bar{R}}$ is the driving force for grain growth δ the grain boundary Heidner and β the relative free grain boundary volume is the driving force for 3D grain growth, which we consider for a 2D system. The difference in the numerical coefficient is of the order of unity and will be disregarded.) Then, for the desired criterion $\lambda_{\mathrm{vac,b}}$, we arrive at:

$$\lambda_{\mathrm{vac,b}} = \frac{m_{\mathrm{b,eff}}\gamma_{\mathrm{b}}\pi(n-6)/3}{m_{\mathrm{b}}\gamma_{\mathrm{b}}\pi(n-6)/3} = \frac{1}{36}\cdot\frac{D_{\mathrm{SD}}}{A_{\mathrm{b}}}\frac{\bar{R}\gamma_{\mathrm{b}}}{NkTZ(\beta\delta)^2} \qquad (6)$$

where A_{b} is the reduced mobility of grain boundaries: $A_{\mathrm{b}} = m_{\mathrm{b}}\gamma$. For pure Al at 300 °C, using the experimental data of grain boundary mobility presented in [5], we obtain $\lambda_{\mathrm{vac,b}} \approx 10^3\bar{R}$, and for $\bar{R} \approx 10^{-8}m$ this yields $\lambda_{\mathrm{vac,b}} \approx 10^{-5}$.

5. Particle drag

In general, two types of particle drag effects on grain growth drag can be considered: the drag by small mobile particles and by large immobile particles. However, the grain size in nanostructures is so small that it is difficult to imagine the existence of large immobile particles which are comparable in size with the grains. That is why we will consider only drag by particles moving jointly with the grain boundaries. The effective mobility of a grain boundary moving together with particles is [5]:

$$m_{\mathrm{eff}} = \frac{m_{\mathrm{p}}(r_0)}{n_0} \qquad (7)$$

where $m_{\mathrm{p}}(r_0)$ is the mobility of particles of radius r_0, and n_0 is the number of particles per unit area of the boundary, respectively. The approach used above and the results derived in [10] yield

$$\lambda_{\mathrm{part,b}} = \frac{m_{\mathrm{beff}}}{m_{\mathrm{b}}} = \frac{m_{\mathrm{p}}(r)}{n}\cdot\frac{1}{m_{\mathrm{b}}} = \frac{2}{3}\cdot\frac{\delta}{r^2}\cdot\frac{D_{\mathrm{S}}\Omega_{\mathrm{a}}}{kTm_{\mathrm{b}}}\cdot\frac{c_{\mathrm{B}}-c_{\mathrm{A}}}{c_0-c_{\mathrm{A}}} \qquad (8)$$

D_{S} is the interface difference coefficient. Using the values ($\delta = 10^{-9}$ m; $D_{\mathrm{s}} \approx +10\ \mathrm{m^2s^{-1}}$ [11]; $\Omega_{\mathrm{a}} \approx 10^{-5}\ \mathrm{m^3mol^{-1}}$; $\gamma_{\mathrm{b}} \approx 1\mathrm{J\,m^{-2}}$; $T = 573$ K; $c_{\mathrm{B}} \approx 1$, $c_{\mathrm{A}} \approx 10^{-4}$; $c_0 \approx 10^{-3}$ and $A_{\mathrm{b}} \approx 10^{-10}\ \mathrm{m^2s^{-1}}$ [5] we arrive at $\lambda_{\mathrm{part,b}} \simeq \dfrac{10^{-15}\ \mathrm{m^2}}{r^2}$.

Evidently, only sufficiently "large" particles will exert an efficient drag on moving grain boundaries in nanocrystalline systems.

It is of particular interest to compare the relative efficiency of particle and triple junction drag on grain growth. We will consider the most favourable condition for particle drag, which occurs at the highest possible velocity of their joint motion with the grain boundary, i. e., when the force acting on the particle is equal to the bonding force between the particle and the boundary: $V = m_{\mathrm{p}}(r_0)\,f_{\mathrm{p}}(r_0)$, $f_{\mathrm{p}}(r_0) = \dfrac{3}{2}\pi r_0\gamma_{\mathrm{b}}$.

In this case, we obtain the effective mobility of the grain boundary migrating together with the particles at their high-

est joint mobility

$$m_{\mathrm{beff}} = \frac{V}{P} = \pi m_{\mathrm{p}}(r_0)\, r_0 \bar{R} \tag{9}$$

Consequently, the relative drag efficiency on grain growth by triple junctions and mobile particles can be expressed as:

$$\lambda_{\mathrm{tj,p}} = \frac{3}{4}\frac{m_{\mathrm{tj}}\bar{R}}{m_{\mathrm{beff}}} = \frac{3}{4}\frac{m_{\mathrm{tj}}}{\pi m_{\mathrm{p}}(r_0)\, r_0} \tag{10}$$

With the values of the parameters used in Eq. (8), and the reduced triple junction mobility $\gamma_{\mathrm{b}} m_{\mathrm{tj}} \approx 5.6 \cdot 10^{-13}\,\mathrm{ms}^{-1}$ [7] for 300 °C in Al, we finally arrive at:

$$\lambda_{\mathrm{tj,part}} \approx 2 \cdot 10^{15} r^3 \tag{11}$$

As a result, triple junction drag becomes comparable to particle drag only for $r \sim 10^{-5}$m, in other words for very large particles.

6. Conclusions

The relative efficiency of the drag effect of different structural elements in polycrystalline microstructures was considered. Triple junction drag was found to be most effective for microstructural stabilization of very fine-grained microstructures in the range of the used parameters. The derived hierarchy of dragging efficiency can be utilized as an effective tool to assess the contribution of the various mechanisms for microstructure stability of fine-grained and nanostructured materials.

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