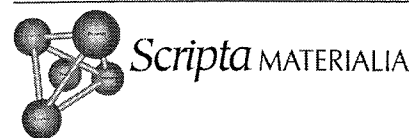




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Unexplored topics and potentials of grain boundary engineering

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Abstract

We propose to generalize the concept of grain boundary engineering by taking into account grain boundary phenomena and behaviour beyond a structure (low Σ)-energy relationship. In particular pressure effects due to the grain boundary free volume, segregation, and junction drag are addressed.

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1. Introduction

The concept of grain boundary engineering (GBE) was first introduced and mainly promoted by Palumbo, Aust and Watanabe [1–3]. It is based on the philosophy that the properties of a material can be influenced by changing the fraction of special (low Σ) boundaries, in face-centered cubic materials in particular first order twin boundaries. This fraction can be changed by appropriate thermomechanical processing. In this contribution we propose to generalize the concept of GBE. In our understanding GBE comprises all aspects which determine the choice of physical, chemical, thermal and mechanical treatments of a material to obtain a polycrystal with a desired distribution of interfacial characteristics, i.e., grain boundaries and their junctions with specific properties. Below we will elucidate some theoretical approaches and ideas which can provide new avenues for the development of GBE.

2. Grain boundary free volume and the stability of polycrystals

The grain boundary excess free volume (BFV) is a fundamental property of grain boundaries. It is the property

that controls the reaction of a polycrystal to an applied hydrostatic pressure. A thermal treatment under high hydrostatic pressure will drive a polycrystal to favor grain boundaries of low BFV. As will be shown, this issue is of great importance for the stability of ultrafine grained and nanocrystalline materials.

The BFV along with the surface tension belongs to the major thermodynamic properties of grain boundaries. The BFV determines the stability of a grain structure and the kinetics of grain growth of polycrystals under high stresses [4,5]. The magnitude of the excess free volume determines the driving force that tries to “squeeze” grain boundaries out of a polycrystal. On the other hand the BFV influences processes which are accompanied by the generation of vacancies like grain growth [6,7]. As shown in Refs. [4,5] the BFV is released into the bulk when the total grain boundary area is reduced during grain growth. Excess vacancies increase the free energy of a system and thereby reduce the driving force for grain growth. The BFV determines the rate of deceleration of grain growth. Note that this produces a generalized thermodynamic force which influences (decelerates) exactly the kinetic process by which vacancies are generated. This effect is even more pronounced in thin films on a substrate where the BFV causes an “equilibrium grain size” beyond which no grain growth occurs [8,9].

In other words, the BFV determines to a large extent the evolution and stability of polycrystals. At low external

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pressure the BFV slows down grain growth, at high pressure its influence is more complex. However, it can be said with confidence that under pressure a system will first try to remove grain boundaries with large free volume.

Unfortunately, our knowledge about the grain boundary excess free volume is restricted to data of computer simulations [10–12], which, in turn, is limited to grain boundaries with special misorientation. There is only one experimental study [13] where the excess free volume of grain boundaries was estimated from measurements of the location of cusps in the energy–misorientation relationship of grain boundaries in silver at ambient pressure and at a hydrostatic pressure of 7×10^8 Pa [13]. (Their estimation of the BFV was 10^{-10} – 10^{-8} cm³/cm².)

A thermodynamically correct way of the experimental determination of the BFV was put forward in Refs. [14,15]. The authors proposed to use the Gibbs adsorption equation to measure the BFV

$$d\gamma_b = -s^s dT - \sum_i \Gamma_i d\mu_i \quad (1)$$

To make this approach more understandable it should be noted that the grain boundary excess number of atoms can be considered as an adsorption at grain boundaries in a one-component system, which we shall call auto adsorption Γ_0 .

Such a consideration is possible for grain boundaries due to the availability of an additional degree of freedom.¹

In this case, at $T = \text{const.}$ Gibbs adsorption equation takes the form [15]

$$d\gamma_b = -\Gamma_0 \Omega dp \quad (2)$$

where Ω is the atomic volume, and p is an external pressure. Hence

$$\left(\frac{\partial \gamma_b}{\partial p}\right)_T = -\Gamma_0 \Omega \quad (3)$$

The special technique developed in Ref. [16] makes it possible to measure the BFV for practically any grain boundary and provides a way of estimating the BFV with high accuracy. So, for a 40° (111) tilt grain boundary with additional 2° twist component $\Gamma_0 \Omega = -(5.4 \pm 0.5) \times 10^{-11}$ m³/m². It is noted that the quantity $\Gamma_0 \Omega$ defines the absolute value of the BFV which does not depend on the grain boundary model used, for instance, on the grain boundary width.

Knowing Γ_0 , the BFV for a sample and thus, the “squeezing” force can be found. Indeed, in the framework of a uniform grain boundary model for a polycrystal with a mean grain radius R the grain boundary excess free volume ΔV can be represented as

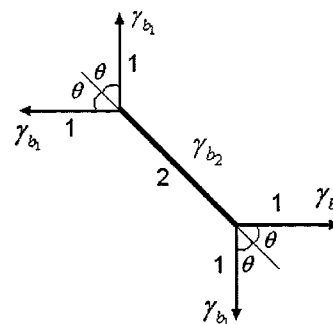


Fig. 1. Diagram of two identical triple junctions of a polycrystal.

$$\Delta V = \frac{3}{2R} \Gamma_0 \Omega \quad (4)$$

The squeezing force, i.e., the force which tries to expel a grain boundary from a system acting on a grain boundary under the pressure p is²

$$P_{\Delta V} = \frac{3}{2R} p \Gamma_0 \Omega \quad (5)$$

It is emphasized that this driving force acts on a grain boundary as a volume of different density and is not necessarily directed towards the centre of curvature like a capillary force. Most likely, this driving force will manifest itself as an increased grain boundary surface tension.

It is interesting to consider in this context how different grain boundaries behave under high pressure. The point is that at $p = 0$ the equilibrium at triple junctions is dictated by the grain boundary surface tension only. By applying a pressure the equilibrium conditions are changed abruptly. The physical features of such situation are best demonstrated by the following example. For simplicity we consider two triple junctions which connect grain boundaries 1 and 2 with surface tensions γ_{b1} and γ_{b2} , respectively (Fig. 1). The equilibrium at zero pressure is described by the relation $2\gamma_{b1} \cos \theta = \gamma_{b2}$. If pressure is applied the equilibrium needs to adjust. Let us assume that the new value of $\gamma_{b2} > 2\gamma_{b1}$. Apparently, in this case the triple junctions will move along grain boundary 2 towards each other, eliminating grain boundary 2. This example may not describe the only possible mechanism of removing grain boundaries with higher energy from the polycrystal. Nevertheless, it is obvious that thermal treatment under high pressure will remove grain boundaries with large BFV from a polycrystal.

¹ There is no sense in considering such a problem for an interface boundary, inasmuch as at constant temperature such a system is completely determined.

² It is stressed that there is, in principle, no reason for the boundary density not to be higher than the density of the bulk of a grain; traditionally it is assumed that the interface has a lower density than the bulk. However, we contend that there is also a physical indication that the bulk density is higher than the boundary density. Otherwise, annealing under high pressure should, in accordance with the Le Chatelet principle, increase the total grain boundary area, i.e., lead to grain refinement.

3. Grain growth in high magnetic fields: a means to generate a distribution of equally mobile boundaries

Grain boundary motion in a magnetic field can be considered as the motion of an electric conductor in a magnetic field [17]. The dissipation of energy due to the induced electromotive force depends strongly on the velocity of grain boundary migration. Therefore, a thermomagnetic treatment permits us to select grain boundaries with low mobilities, i.e., to generate polycrystals with a more stable grain microstructure.

It is common knowledge that the atomic structure of grain boundaries is different from the structure of the grain interior. The electronic structure of grain boundaries is much less understood. Nevertheless, it may be safely suggested that the electronic structure of a grain boundary is different from the structure in the interior of the adjacent crystals. In this case, the migration of a grain boundary can be considered as the motion of an electric conductor. This leads to the generation of an electric field in accordance with Faraday's law. The induced electrical current (Ohm's law) generates its own magnetic field H_G (Biot-Savart-Laplace law). The directions of the induced current and the magnetic field H_G are determined by Lenz' rule in such a way that the generated magnetic flux counteracts the imposed magnetic field, which corresponds to an electromotive force. Due to this dissipation of energy the driving magnetic force decreases. This idea was put forward in Ref. [17] where the theory of electromagnetic drag in the course of grain boundary motion in a magnetic field has been treated. All approaches considered in Ref. [17] predict a decrease of the effective grain boundary mobility. The magnitude of the effect depends on the orientation of the magnetic field with respect to the crystal axes and therefore depends on the direction of motion, except for symmetrical tilt boundaries. A quantitative assessment was performed for grain boundary motion in bicrystals of Bi. The conductivity of Bi is very low, so the contribution of the dragging forces is rather small as well. Nevertheless, for other diamagnetic metals the influence of the electromotive forces can be appreciable.

We would like to draw the attention of the reader to one aspect of this theory. As shown in [17], the magnitude of electromagnetic drag strongly depends on the velocity v of grain boundary motion. So, the Lenz dragging force F which is associated exclusively with the magnetic field induced by grain boundary motion is proportional to v^2 , the Joule dragging force F_{Joule} due to the conversion of magnetic energy into Joule heat is proportional to v^4 [17].

The corresponding change of grain boundary mobility for typical diamagnetic metals yields

$$10^{-4} \leq \frac{\Delta m_{\text{Joule}}}{m} \leq 10^{-2} \quad (6)$$

The inequality (6) is arrived at by using the magnitude of the velocity of grain boundary motion in Bi bicrystals [18], while the velocity of small regions of a grain boundary

during grain growth might be significantly larger. By this is meant that grain growth in a magnetic field will suppress especially the growth of fast grain boundaries, and thus, make the grain boundary distribution more uniform with respect to velocity (mobility).

4. Equilibrium grain size. Is it feasible?

At first glance the title of this section seems to challenge thermodynamic principles. However, alloy systems differ from a pure material. We will try to show that there is, in principle, the possibility to stabilize the grain size in a polycrystal with negative adsorption.

It is textbook knowledge that grain boundaries are non-equilibrium elements of a polycrystalline structure and, therefore, there is no equilibrium grain size. Kirchheim [19,20] put forward the interesting idea that, although impossible in pure materials, the desired effect can be achieved in alloys. Let us consider the problem for a binary solution in the framework of Gibbs interfacial approach. We will treat the free energy ΔG of a polycrystal with total grain boundary area \mathcal{S} as the sum of two terms. The first one defines the energy of formation of a bulk solid solution, while the second term constitutes the grain boundary energy, i.e., the product of grain boundary area \mathcal{S} and grain boundary surface tension γ

$$\Delta G = \Delta G_{\text{sol}}(c_2) + \gamma(c_2)\mathcal{S} \quad (7)$$

where c_2 is the concentration of impurities in the bulk of the grains. Grain boundaries in Gibbs approach are geometrical surfaces, their volume is equal to zero. The effective impurity concentration in the bulk can be expressed as

$$c_2 = \frac{V_0 c_2^0 - \Gamma_2 \mathcal{S}}{V_0} \quad (8)$$

where V_0 is the volume of the sample, $V_0 c_2^0$ is the total amount of impurities in the sample, and Γ_2 is the impurity adsorption at grain boundaries. Exactly this concentration should be used when the bulk-free energy of a solid solution is evaluated.

If there is an equilibrium grain size, then there is a defined value of total grain boundary area where the free energy of the sample becomes minimal, i.e., $\frac{d\Delta G}{d\mathcal{S}} = 0$ at $T = \text{const}$.

$$\frac{d\Delta G}{d\mathcal{S}} = V_0 \frac{d\Delta G_{\text{sol}}(c_2)}{d\mathcal{S}} + \mathcal{S} \frac{d\gamma(c_2)}{d\mathcal{S}} + \gamma(c_2) \quad (9)$$

However, we will show that the right-hand side of Eq. (9) cannot be equal to zero. The derivative $d\Delta G/d\mathcal{S}$ can be represented as

$$\frac{d\Delta G}{d\mathcal{S}} = V_0 \frac{d\Delta G_{\text{sol}}(c_2)}{dc_2} \frac{dc_2}{d\mathcal{S}} + \frac{d\gamma(c_2)}{dc_2} \frac{dc_2}{d\mathcal{S}} + \gamma(c_2) \quad (10)$$

For positive adsorption ($\Gamma > 0$), when the concentration of impurities at grain boundaries is higher than in the bulk, and taking into account Eq. (8), the derivatives $\frac{d\Delta G_{\text{sol}}(c_2)}{dc_2}$, $\frac{dc_2}{d\mathcal{S}}$, $\frac{d\gamma(c_2)}{dc_2}$ are negative. So, all terms on the right-hand side of

Eq. (10) are positive, which renders the existence of a minimum, strictly speaking, of an extremum, impossible. For this we tacitly assumed that the grain boundary surface tension γ is positive as well. If γ were negative, however, the system would be forced to become totally dispersed, down to molecular and atomic dimensions. So, in the framework of Gibbs interfacial approach for positive adsorption there is no equilibrium grain size.

However, Eq. (10) might have a solution for negative adsorption ($\Gamma < 0$), when the boundary concentration is lower than in the bulk of a grain, and the boundary surface tension rises with impurity concentration. In this case, an increase of the impurity concentration in the sample decreases the free energy of the solid solution, but increases at the same time the boundary surface tension. (One can see, that in this case both derivatives $\frac{dc_2}{dS}$ and $\frac{d\gamma}{dc_2}$ are positive.) For such type of adsorption the effect of equilibrium grain size is theoretically possible, although this type of adsorption has never been observed. Nevertheless, it cannot be ruled out in principle.

For a grain boundary model with a certain boundary thickness δ Eq. (7) can be re-written as

$$\Delta G = (V_0 - \delta S)\Delta G_{\text{sol}}(c_2) + \gamma(c_2)S \quad (11)$$

and the impurity concentration c_2 is, in turn, a function of total grain boundary area and grain boundary thickness

$$c_2 = \frac{V_0 c_2^0 - c_2^b S \delta}{V_0 - S \delta} \quad (12)$$

where c_2^b is the impurity concentration in the grain boundary.

When $R \gg \delta$ the relations (11) and (12) reduce to Eqs. (7) and (8), respectively. A negative term of the order of $\delta \Delta G_{\text{sol}}$ arises on the right-hand side of $\frac{d\Delta G}{dS}$ when R tends to δ . However, in this limit the uncertainty of the grain boundary width δ is rather large.

One can see from Eqs. (7) and (8) that even if the grain boundary surface tension γ_b is assumed to be equal to zero [19], ΔG does not assume a minimum. In other words, even at $\gamma_b = 0$ the driving force for grain growth is not zero. Obviously, a heterogeneous cellular structure—grains separated by walls with increased impurity concentration—does not conform with the concept of an equilibrium polycrystal.

As a result, we can state with reasonable confidence that for positive adsorption the thermodynamic analysis does not confirm the possibility of an equilibrium grain size in a polycrystal. There is a theoretical potential for such a phenomenon for negative adsorption.

5. Grain boundary junctions or how correlate grain boundary mobility is determined in systems of different dimensionality

In spite of substantial progress in bicrystal techniques, grain growth in polycrystals is still the dominant source

of our knowledge of grain boundary motion and its major parameter—grain boundary mobility m_b . However, the value of the reduced mobility $m_b \cdot \gamma = A_b$, extracted from experimental data of grain growth depends on the drag effect of grain boundary junctions. The most noticeable discrepancy between free boundary motion and junction-dragged motion, as reflected by A_b , should be observed for fine grained and nanocrystalline materials.

In the past, grain growth was the only source of grain boundary mobility data. Grain growth and grain boundary motion were practically synonymous. Such assumption was supported by theoretical analysis. The von Neumann–Mullins relation [15] proved that grain growth in a 2D system is controlled by the mobility of grain boundaries if the mobility of triple junctions is infinite. The development of experimental techniques to observe single grain boundary migration in bicrystals made the concept of grain boundary mobility physically meaningful. The main goal of these studies was to establish an experimental basis for the construction of a fundamental theory of grain growth, and the conspicuous achievements of bicrystal physics made these hopes well founded. However, there is no isolated boundary in polycrystals, rather boundaries are connected by triple junctions, and this has serious consequences for the validity of the von Neumann–Mullins relation. Besides, an infinite mobility of triple junctions would cause an infinite junction velocity for any non-zero driving force. Replacing “infinite mobility” by “sufficiently large mobility” does not remove the problem, because of the dragging effect of triple junctions, which can be quantified by the dimensionless criterion A [15,21]:

$$A = \frac{m_{ij} a}{m_b} \quad (13)$$

where m_{ij} and m_b are triple junction and grain boundary mobility, respectively, and a is the grain size. Small values of A correspond to a strong dragging influence of the triple junction. In the course of grain growth the vanishing grains will by necessity pass through a phase where their size and, hence, the criterion A are small and the dragging effect is large. Such a situation will not arise for growing grains. Special measurements proved that it is possible to measure the mobility of individual triple junctions [22,23], and their mobility was found to be not only finite but rather small.

In 3D polycrystals apart from the mentioned structural elements—grain boundaries and triple junctions—grain boundary quadruple junctions are also present. So far, nobody knows how these structural elements affect grain boundary motion. Quite recently a novel concept to determine the mobility of quadruple junctions was put forward [24]. It was shown [24] that the influence of a quadruple junction configuration on triple junction motion and, consequently, on grain boundary motion can be described by a similar dimensionless criterion A_{qp}

$$A_{qp} = \frac{m_{qp}a}{m_{ij}} \quad (14)$$

m_{qp} is the mobility of a quadruple junction.

It is easy to see that the influence of quadruple points on the motion of triple junctions and, in turn, on grain boundaries is qualitatively similar to the effect of triple junctions. In other words, the strongest influence of quadruple junctions should be observed for a small grain size.

In conclusion, the most unconstrained motion of grain boundaries can be observed in bicrystals.³ Next in order of “the degree of freedom of grain boundary motion” are 2D systems. They contain grain boundaries and grain boundary triple junctions. Grain boundary migration in such systems is slowed down by the triple junctions and, therefore, the extracted mobility of grain boundaries should be smaller than the mobility measured in bicrystal experiments. Finally, in 3D systems grain boundary motion is influenced by both triple junctions and quadruple points.

Therefore, we contend that experimentally measured grain boundary mobilities in bicrystals, 2D and 3D systems will decrease with the degree of dimension. Comparing the grain boundary mobility in these systems may become one way of extracting the dragging effect of triple and, especially, quadruple junctions.

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³ True, there are triple junctions in bicrystal as well, so-called “surface triple junctions”. However, their influence is small and remains constant in the process of boundary motion [25].