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Unexplored topics and potentials of grain boundary engineering

L.S. Shvindlerman [a,b], G. Gottstein [a,*]

[a] Institut für Metallkunde und Metallphysik, RWTH Aachen, D-52056 Aachen, Germany
[b] Institute of Solid State Physics, Russian Academy of Science, Chernogolovka, Moscow distr. 142432, Russia

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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.

Keywords: Grain boundary; Grain boundary excess free volume; Mobility; Grain boundary thermodynamics; Magnetic field

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

* Corresponding author.
E-mail address: gottstein@imm.rwth-aachen.de (G. Gottstein).

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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} cm^3/cm^2.)

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

$$d\gamma_b = -s^s dT - \sum_i^k \Gamma_i d\mu_i \tag{1}$$

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]

$$d\gamma_b = -\Gamma_0 \Omega dp \tag{2}$$

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

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

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° ⟨1 1 1⟩ tilt grain boundary with additional 2° twist component $\Gamma_0\Omega = -(5.4 \pm 0.5) \times 10^{-11}\ m^3/m^2$. 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

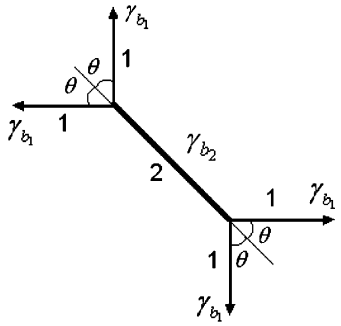

Fig. 1. Diagram of two identical triple junctions of a polycrystal.

$$\Delta V = \frac{3}{2R}\Gamma_0 \Omega \tag{4}$$

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 is[2]

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

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_{b_1} and γ_{b_2}, respectively (Fig. 1). The equilibrium at zero pressure is described by the relation $2\gamma_{b_1} \cos\theta = \gamma_{b_2}$. If pressure is applied the equilibrium needs to adjust. Let us assume that the new value of $\gamma_{b_2} > 2\gamma_{b_1}$. 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.