Novel Approaches to the Thermodynamics of Grain Boundaries and Grain Boundary Junctions

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Abstract. Three recent investigations in the field of thermodynamics of grain boundaries and grain boundary junctions are presented.

1. The grain boundary excess free volume (BFV) along with the surface tension belongs to the major thermodynamic properties of grain boundaries. A special technique, recently developed, makes it possible to measure the BFV for practically any grain boundary and provides a way of estimating the grain boundary excess free volume for grain boundaries of different classes with rather high accuracy. The experimental values of the BFV measured for different grain boundaries are compared and discussed.

2. A new approach will be presented that makes it possible to correctly measure the grain boundary triple line tension. For this the topography at an equilibrated triple junction was measured by atomic force microscopy. Preliminary results of grain boundary triple line energy measurements are presented.

3. The problem is discussed whether it is possible to achieve an equilibrium grain size during grain growth in single phase alloys. Various approaches to the problem are considered. It is shown that the most realistic possibility to stabilize the grain size in a polycrystal is by impurities with negative grain boundary adsorption.

The Grain Boundary Excess Free Volume

The grain boundary excess free volume (BFV) along with the surface tension determines the major thermodynamic and kinetic properties of grain boundaries and controls to a large extent the evolution and stability of polycrystals [1-3]. Unfortunately, our knowledge about the BFV is entirely restricted to data generated by computer simulations, which, in turn, are mostly limited to grain boundaries in the vicinity of special (low Σ) misorientations [2–7]. Only a few experimental attempts were undertaken to determine the BFV and their evaluation was based on models, which have to make assumptions on the grain boundary width, which, however, is unknown [8,9]. Meiser and Gleiter [11] applied a hydrostatic pressure of $7 \cdot 10^8$ Pa and measured the change of misorientation for grain boundary energy cusps. Merkle et al. [9,10] derived the BFV from lattice parameter measurements by HRTEM in the vicinity of grain boundaries. The experimental average value of the BFV for all kinds of studies is in the range of $10^{-12} - 10^{-10}$ m^3/m^2. It is stressed, however, that all estimates are based on models with uncertain assumptions on the grain boundary width.

A correct way to determine the BFV for grain boundaries will be presented in the following [11,12]. Let us consider the Gibbs equation for adsorption at interfaces

$$dy = -s^s dT - \sum_{i=1}^{k} \Gamma_i d\mu_i + v^s dp \qquad (1)$$

where s^s and v^s are the entropy and the volume of the surface, Γ_i and μ_i are the adsorption and chemical potential of the ith component, T is the temperature.

In the Gibbs method, in a local sense, $v^s = 0$, and for a single component system Eq. (1) assumes the form

$$dy = -s^s dT - \Gamma_0 d\mu \qquad (2)$$

The parameter Γ_i has the meaning of an autoadsorption at grain boundaries in a pure material. Expressing μ through the thermodynamic characteristics of the volume of the grain and taking into account that $s^s = \Gamma_0 s_a^s$, where s_a^s is the surface excess of the entropy per atom at the boundary surface we arrive at [11]

$$dy = -\Gamma_0 \left(s_a^s - s_a^v \right) dT - \Gamma_0 \Omega_a dp \qquad (3)$$

A grain boundary separates two thermodynamically identical phases, and one peculiarity of grain boundaries consists of the fact that for a system with a grain boundary the number of degrees of freedom is by one greater than for an interphase [10], which is completely determined at constant temperature.

Hence

$$\left(\frac{\partial \gamma}{\partial p} \right)_T = -\Gamma_0 \Omega_a$$

$$\left(\frac{\partial \gamma}{\partial T} \right)_p = -\Gamma_0 \left(s_a^s - s_a^v \right) = -\frac{q}{T} \qquad (4)$$

where q is the specific heat of grain boundary formation.

The grain boundary excess free volume can be expressed from Eq. (4) as:

$$V_{gb}^{ex} = -\Gamma_0 \Omega_a = \frac{\partial \gamma}{\partial p} \qquad (5)$$

It is pointed out that along with grain boundaries also domain walls and liquid foams possess these thermodynamic properties.

We developed a special technique that makes it possible to measure the BFV for practically any grain boundary and provides a way of estimating the BFV for grain boundaries of different classes with high accuracy. The central idea of this technique can be understood from Fig. 1 [12]. A specially grown tricrystal is composed of two high angle grain boundaries GB1 and GB2 with equal grain boundary surface energy $\gamma_1 = \gamma_2 = \gamma$ (Fig. 1) and a low angle twist grain boundary GB3 with surface energy γ_3 that can be calculated according to the Read and Shockley approach [12]. (The elastic energy of a screw dislocation (apart from the dislocation core energy) is not affected by the hydrostatic pressure, since a screw dislocation represents a state of pure shear. In our consideration we neglect any influence of torque terms.). In equilibrium, enforced by two notches (Fig.1), the contact angle 2θ reflects the balance between the energies of boundaries GB1, GB2, and GB3 at the given temperature and pressure

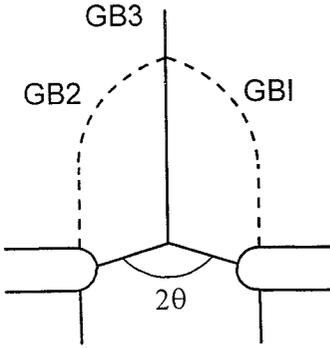$$2\gamma \cos \theta = \gamma_3 \qquad (6)$$

Fig. 1. Grain boundary geometry to determine the BFV: the grain boundary system with triple junction attains an equilibrium configuration at the notches introduced from the lateral surfaces of the tricrystal.

Finally,

$$V_{gb}^{ex} = \gamma \ \frac{\sin\theta}{2\cos^2\theta} \ \frac{\partial\theta}{\partial p}$$

(6)

The quantities θ, $\dfrac{\partial\theta}{\partial p}$ and γ in Eq. (6) can be determined experimentally.

The experiments were carried out on asymmetrical 40° <111> tilt grain boundaries. The two asymmetrical 40° <111> tilt grain boundaries (GB1 and GB2) were superimposed by a rotation around an axis perpendicular to the grain boundary plane by an angle ψ of 2°. The third grain boundary (GB3) was therefore a low angle twist boundary with a rotation angle of 4° and the rotation axis <110>. Similar experiments were carried on asymmetrical 39° <110> tilt grain boundaries. Also, a grain boundary system comprised of two 40° <111> tilt grain boundaries (GB1 and GB2) and an 80°<111> tilt boundary (GB3) was investigated.
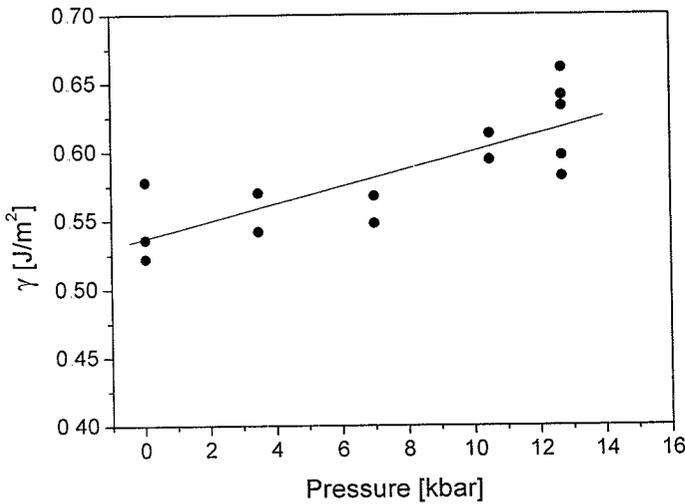

Fig. 2. Pressure dependence of the grain boundary surface tension for a tricrystal with two 40°<111> tilt grain boundaries (GB1 and GB2) [12].

The samples were annealed at 630 °C for 60 min under a hydrostatic pressure up to 14 kbar. The temperature of annealing and the pressure were kept constant within ±1°C and ~±0.1kbar.

Then the value of the BFV for a 40°<111> tilt grain boundary could be extracted according to Eq. (6) and the experimental data presented in Fig. 2. It was found that $V_{gb}^{ex} = 6.4 \cdot 10^{-11}$ m³/m². For 39° <110> tilt grain boundaries the value of the BFV was equal to $V_{gb}^{ex} = 11.0 \cdot 10^{-11} m^3 / m^2$. To check the obtained results the pressure dependence of the equilibrium vertex angle θ was measured for a grain boundary system of two 40°<111> tilt grain boundaries as GB1 and GB2 and an 80°<111> tilt boundary as GB3. Due to crystal symmetry 80°<111> corresponds to -40°<111>, and

the grain boundary energy of GB3 should be the same as the energy of GB1 and GB2. The measured angle was about 120° in the whole pressure range and, hence $\left(\dfrac{\partial \theta}{\partial p}\right)_T = 0$, as expected.

It is noted that the quantity $V_{gb}^{ex} = -\Gamma_0 \Omega_a$ defines the absolute value of the BFV, which does not depend on the grain boundary model used, in particular it does not depend on the grain boundary width. The approach put forward opens up new fields of experimental research. In particular, it makes it possible to determine the border between low and high angle boundaries.

Grain Boundary Junctions

While triple junction kinetics (mostly the motion of triple junctions) has been subject of investigations, especially in recent years [10-14], the thermodynamics properties of triple junctions, for instance, their line tension, is still *terra incognita*.

Although Gibbs discussed the possibility that the excess free energy of a triple line (among fluid phases) might be negative [15], McLean [16] contended that triple lines should have a positive free energy because "the atoms at grain boundary junctions, being under the influence of three instead of two competing forces, are in positions of still higher free energy". Srinivasan et al. [17] studied quantitatively the excess energy of a grain boundary triple line by means of atomistic simulation using molecular dynamics. It was found that the excess energy of a triple line might be negative or positive.

The authors are aware of only one experimental study of the triple line energy. Fortier and co-workers [18] stated that the excess line energies of triple junctions must always be positive. Representing the local geometry at a triple junction as an irregular tetrahedron, the authors of [18] estimated the minimum triple line tension for Cu as 5×10^{-7} J/m. However, as shown in [19,20], the geometry at the intersection of a triple line with the surface − the triple junction crater − is curved and cannot be represented as a pyramid. The theoretical background of a correct experimental measurement of triple line tension is given in [19,20].

The topography of a triple junction crater after thermal annealing is formed by three grain boundaries which meet in a way schematically shown in Fig. 3.
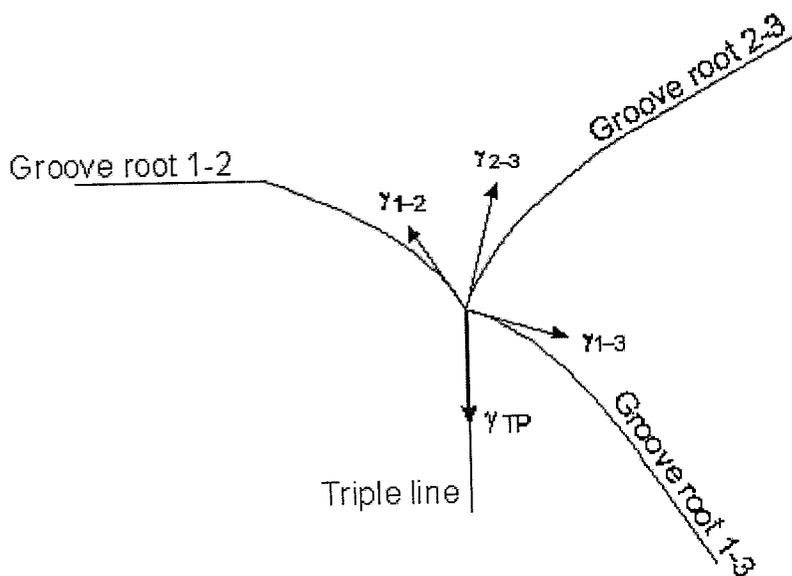

Fig. 3. Schematic 3D-view of the line tension equilibrium at e triple junction.

From the equilibrium of the four line tensions (i.e. three groove roots and triple line) it follows for the triple line tension

$$\vec{\gamma}^l = \vec{\gamma}_{1-2} + \vec{\gamma}_{1-3} + \vec{\gamma}_{2-3} \qquad (7)$$

or

$$\gamma^l = \gamma_{1-2} \sin \zeta_{1-2} + \gamma_{1-3} \sin \zeta_{1-3} + \gamma_{2-3} \sin \zeta_{2-3} \qquad (7')$$

where ζ_{1-2} ζ_{1-3}, and ζ_{2-3} are the angles of the groove roots of the corresponding grain boundaries at the center of the triple junction. The three groove roots have a curvature in the vicinity of the triple junction and remain straight far away from this point. The three line tensions of the three grain boundaries are indicated in Fig. 3 by γ_{i-j} with the indices i and j denoting the two grains on both sides of the grain boundary. The equilibrium condition for grain boundaries and two crystal surfaces in the vicinity of the root of the groove should include an additional term, which takes into account the influence of the Laplace curvature on the line tension γ^l [19,20]:

$$\gamma_B - \gamma^l \frac{\dfrac{\partial^2 u}{\partial r^2}}{\left[1 + \left(\dfrac{\partial u}{\partial r} \right)^2 \right]^{3/2}} = \gamma_{S1} \sin \xi_1 + \gamma_{S2} \sin \xi_2 \qquad (8)$$

where $u(r)$ describes the profile of the groove root as a function of its lateral location r. Eqs. (7) and (8) comprise the basis of the approach proposed in [20]. This approach can be used to estimate the line tension in polycrystalline copper under the following assumptions [20,21]:

(1) The grain boundaries are perpendicular to the crystal surface.
(2) The surface tensions of the crystal surfaces are independent of crystal orientation. So
$$\gamma_{S1} = \gamma_{S2} = \gamma_S = 1.75\,J/m^2 \quad [22].$$
(3) Torque terms [10] are neglected.

Atomic force microscopy (AFM) of the grain boundary grooves in the vicinity and far away from the triple line (Fig. 4) provides us with all necessary information on the grain boundary groove angles, the groove root angles at the center of the triple junction, and the curvature of the groove roots [20,21]. As an example an AFM image and respectively surface profiles measured perpendicular to the grain boundary grooves are presented in Fig. 4.

First experiments on polycrystals indicate that the triple line tension may be positive or negative [20]. Measurements on triple junctions with defined geometry and crystallography have to corroborate these preliminary results.

Stability of Granular Microstructures

The stability of a grain microstructure is an important issue and of special interest for nanocrystalline materials. It is textbook knowledge that grain boundaries are non-equilibrium elements of a crystalline structure and thus, it is principally impossible to establish an equilibrium grain size. However, for a system with impurities the situation is different from pure materials. Kirchheim [23] put forward the interesting idea, that an equilibrium grain size can be attained in alloys due to adsorption of impurities, if they reduce the grain boundary surface tension to zero. Moreover, Kirchheim et al. [24] as well as Krill, Birringer et al. [25] stated that the grain boundary surface tension can even be negative so that a thermodynamically stable polycrystalline
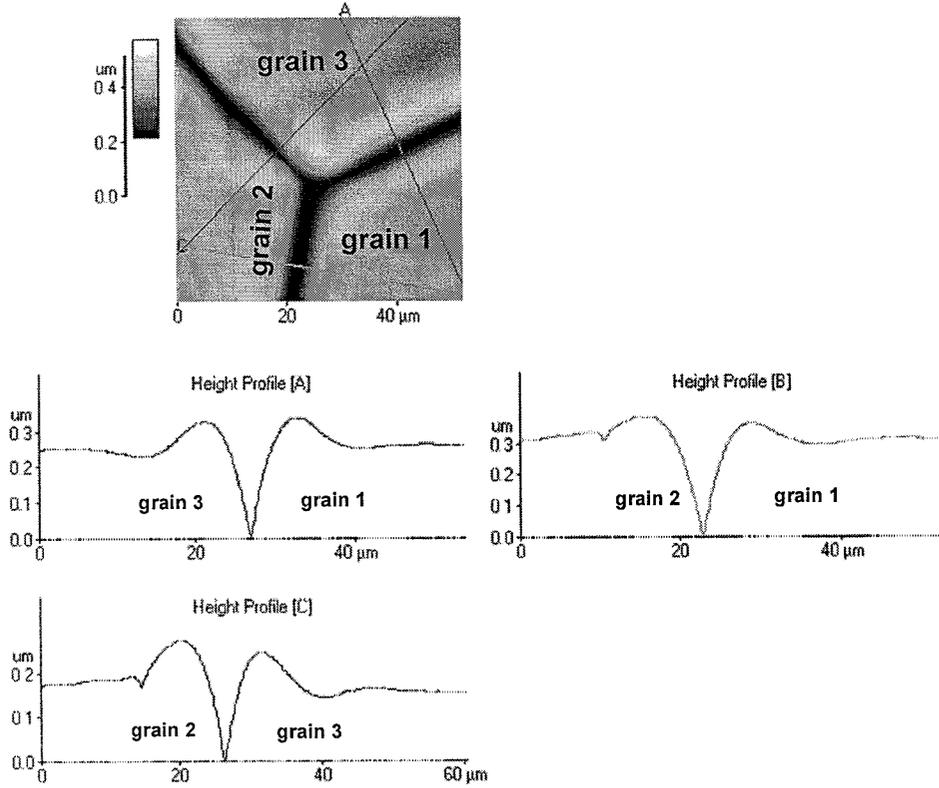
Fig. 4. Profiles perpendicular to the grain boundary grooves (AFM measurements) [20].

microstructure can be established. For a binary solution in the framework of Gibbs interfacial approach the problem was examined more generally in [26]. The free energy ΔG of a polycrystal with total grain boundary area S can be considered as a sum of two terms. The first one defines the energy of formation of a bulk solid solution while the second term constitutes the total grain boundary energy, i.e., the product of grain boundary area S and the grain boundary surface tension γ:

$$\Delta G = \Delta G_{sol}\left(c_2\right) + \gamma\left(c_2\right)S \tag{9}$$

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

$$c_2 = \frac{V_0 c_2^0 - \Gamma_2 S}{V_0} \tag{10}$$

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

For an equilibrium grain size, if it exists, the derivative $\dfrac{d\Delta G}{dS}$ must equal zero at $T = \text{const}$

$$\frac{d\Delta G}{dS} = V_0 \frac{d\Delta G_{sol}\left(c_2\right)}{dc_2}\frac{dc_2}{dS} + \frac{d\gamma\left(c_2\right)}{dc_2}\frac{dc_2}{dS} + \gamma\left(c_2\right) \tag{11}$$

For positive grain boundary energy and positive adsorption ($\Gamma > 0$), when the concentration of impurities at grain boundaries is higher than in the bulk, the derivatives $\dfrac{d\Delta G_{sol}(c_2)}{dc_2}, \dfrac{dc_2}{d\mathbb{S}}, \dfrac{d\gamma(c_2)}{dc_2}$ in Eq. (11) are negative. So, all terms on the right-hand side of (11) are positive, what renders the existence of a minimum, strictly speaking, of the extremum, impossible.

So, in the framework of Gibbs interfacial approach for positive adsorption and boundary energy there is no equilibrium grain size. However, Eq. (11) has a solution for negative adsorption ($\Gamma < 0$), when the boundary concentration is lower that in the bulk and the boundary surface tension grows with rising impurity concentration. In this case an increase of the impurity concentration in a sample decreases the free energy of the solid solution, but at the same time increases the boundary surface tension. For such type of adsorption an equilibrium grain size is theoretically possible. As can be seen from Eq. Eq. (11), an equilibrium grain size is possible for positive adsorption, but for negative γ as well. However, there is an essential difference between these two approaches. There is no experimental evidence so far that the grain boundary energy can be negative, except for the observation that grain growth in nanocrystalline materials is often arrested, which, however may be due to several reason. By contrast, a negative adsorption in metals was discussed and quantitatively considered [27].

Acknowledgment

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