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Excess Free Volume of High Angle Grain Boundaries in Aluminum

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Abstract. A new method is introduced to determine the absolute value of the boundary excess free volume. Along with the boundary energy the excess free volume belongs to the major thermodynamic properties of grain boundaries. The method utilizes the dependence of the contact angle at triple junctions of grain boundaries in Al-tricrystals on hydrostatic pressure. We investigated <111> tilt boundaries in the pressure range up to 14 kbar. In particular, for a 40° <111> tilt boundary with 2° twist component the boundary free volume was found to be equal to 5.03×10^{-11} m^3/m^2.

Introduction

A grain boundary is the interface between two differently oriented crystallites of the same phase in a crystalline solid. In order to accommodate the lattice mismatch both crystallites have to expand locally at their interface. This "expansion" of the region where two grains meet is referred to as a grain boundary excess free volume (BFV). Along with the grain boundary energy it belongs to the fundamental thermodynamic properties of grain boundaries and thus, directly correlates with grain boundary properties such as grain boundary diffusion, sliding, wetting, etc. It is also closely releated to the mechanism of grain boundary migration which in turn determines the microstructure evolution in the course of recrystallization and grain growth. The knowledge of the BFV is especially important for fine grained and nanocrystalline systems where it is instrumental for the control of microstructure and properties of such polycrystals.

The concept of BFV was considered previously by several authors. Correlations between the BFV and different boundary properties were analyzed by Knizhnik for <111>, <110> and <100> boundaries in fcc solids [1]. The analysis revealed that similar to grain boundary mobility and diffusivity, the BFV changes non-monotonically with the angle of misorientation and assumes cusps for low Σ orientation relationships. Computer simulation studies by Wolf [2-4] revealed that the boundary free volume is proportional to the boundary energy. Similar results were obtained by Frost [5] for <100> grain boundaries in fcc crystals. The BFV of different grain boundaries in Al and γ-Fe was computed by Stremel et al. [6] using a broken bond model. Recently, the correlation between grain boundary mobility and BFV was examined by Zhang and Srolovitz [7].

There were also some efforts to determine the BFV experimentally [8-10]. Meiser and Gleiter [8] measured the change of misorientation for grain boundary energy cusps by applying a hydrostatic pressure of 7×10^8 Pa. Merkle et al. [9,10] measured the BFV by HRTEM observations of the lattice parameter change in the vicinity of the interface between two grains.

It is worth noting that computer simulations and the mentioned experimental methods utilize the assumption that the grain boundary has a defined width, typically of several interatomic distances. However, the exact boundary width is not known. Furthermore, it can probably not be exactly determined, since the width of the region with lattice distortions can change along the boundary. In

the current paper an experimental method is introduced to determine the BFV without any assumptions on boundary width.

Measurement of Grain Boundary Free Volume

The BFV of a grain boundary V_{gb}^{ex} can be expressed as [11]

$$V_{gb}^{ex} = -\Gamma_0 \Omega_a = \frac{\partial \gamma}{\partial p}, \tag{1}$$

where γ, p and Ω_a are grain boundary energy, pressure and atomic volume, respectively. The parameter Γ_0 has the meaning of autoadsorption on grain boundaries in a pure material and is defined as the difference between the number of atoms in a bicrystal N_a^* and in a single crystal of the same volume N_a per unit area of a boundary: $\Gamma_0 = \left(N_a^* - N_a\right)/\tilde{A}$, where $\tilde{A}$ is the grain boundary area[1].

The proposed method is best realized in specially grown tricrystals where the triple junction is formed by two high angle grain boundaries GB1 and GB2 with equal grain boundary surface energy $\gamma_1 = \gamma_2 = \gamma_b$ (Fig. 1). The third grain boundary has to be a low angle grain boundary, whose surface energy γ_3 can be calculated according to the Read and Shockley approach [12]. The system in Fig. 1 is homogeneous through the thickness of the tricrystal, i.e. the triple junction line is rectilinear and runs perpendicular to the plane of diagram. Since through the thickness all three grain boundaries extend perpendicular to the plane of diagram, the configuration of the grain boundary system in Fig. 1 is quasi-two-dimensional.

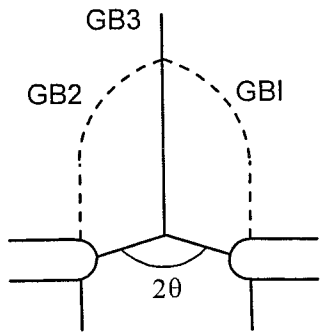

Fig. 1. Grain boundary geometry to determine the BFV: the grain boundary system with triple junction attains an equilibrium configuration at the notches introduced from the lateral surfaces of the tricrystal.

The grain boundaries will move in order to reduce the length of GB1 and GB2 whereas GB3 is extended. When the boundaries arrive at the notches (Fig. 1), boundary motion will cease and force equilibrium at the triple junction will be established. In this equilibrium the contact angle 2θ reflects the balance between the energy of boundaries GB1, GB2 and GB3 at the given temperature and pressure

$$2\gamma_b \cos\theta = \gamma_3 \tag{2}$$

The relationship between the contact angle and the hydrostatic pressure can be obtained by substitution of Eq. (2) into Eq. (1)

[1] Since $N_a^* < N_a$, the autoadsoption is negative by definition

$$2\frac{\partial\gamma_b}{\partial p}\cos\theta - 2\gamma_b \sin\theta\frac{\partial\theta}{\partial p} = \frac{\partial\gamma_3}{\partial p} \tag{3}$$

According to Read and Shockley [12] a low angle grain boundary can be represented by a periodic arrangement of lattice dislocations. In particular, a low angle twist grain boundary is represented by sets of screw dislocations. 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. The energy of the dislocation core does not exceed 10% of the total energy of the dislocation. It can be therefore assumed that the energy of a low angle twist grain boundary does not change with an increase of hydrostatic pressure.

If the grain boundary GB3 in Fig. 1 is a low angle twist boundary and $\partial\gamma_3/\partial p \cong 0$, Eq. (3) can be re-written as

$$2\frac{\partial\gamma_b}{\partial p}\cos\theta - 2\gamma_b \sin\theta\frac{\partial\theta}{\partial p} = 0, \tag{4}$$

and accounting for Eq. (2) we arrive at

$$V_{gb}^{ex} = \gamma_3 \frac{\sin\theta}{2\cos^2\theta}\frac{\partial\theta}{\partial p} \tag{5}$$

According to Eq. (5), the BFV can be obtained from the measurement of the pressure dependence of the equilibrium vertex angle at the boundary triple junction (Fig. 1).

Experimental Details

The experiments were carried out on high purity aluminum (99.999%). Figure 2 shows the geometrical configuration of investigated tricrystals. The two asymmetrical 40° <111> tilt grain boundaries (GB1 and GB2) were superimposed by a rotation around the 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 rotation angle of 4° and rotation axis <110>. Also, the grain boundary system with two 40° <111> tilt grain boundaries (GB1 and GB2) and 80°<111> tilt boundary (GB3) was investigated. The tricrystals were grown from specially oriented seeds in a horizontal Bridgman furnace. The orientation of the crystallographic axes of the crystals was measured by the Laue back-reflection method. After crystal growth the triple junction was generated with a special technique [13]. Prior to annealing the samples were electrolytically polished to improve the surface quality.

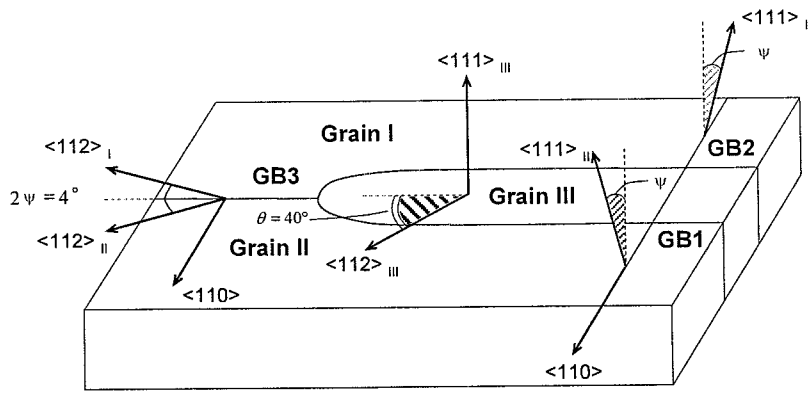

Fig. 2. Geometry of tricrystals used in experiment.

The samples were heat treated at a temperature of 630°C for 60 min at a hydrostatic pressure up to 14 kbar. The temperature of annealing was kept constant within ±1°C. The samples were exposed to high pressure by a pressurized nitrogen gas atmosphere. The pressure was kept constant within ± 0.05 kbar in the pressure range up to 4 kbar and within ±0.15 kbar in the pressure range exceeding 4 kbar. At the end of annealing the decompression of the experimental cell resulted in a rapid cooling of the sample. Therefore, it can be assumed that the measured value of the contact angle reflects the situation under high pressure.

The center grain of the tricrystal was notched by two straight cuts with an electrical discharge machine in order to arrest the boundary during annealing (Fig. 1). For the measurement of the vertex angles at the triple junctions SEM micrographs of the respective samples were used (Fig. 3b).

Results

Figure 3 shows the SEM micrograph of an investigated grain boundary system in a tricrystal after 1 hour annealing at 630°C and 10.5 kbar. The measured pressure dependence of the vertex angle 2θ is shown in Fig. 4.

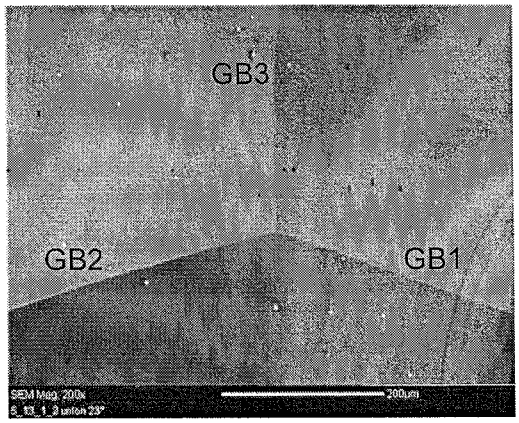

Fig. 3. SEM image of investigated grain boundary system after annealing.

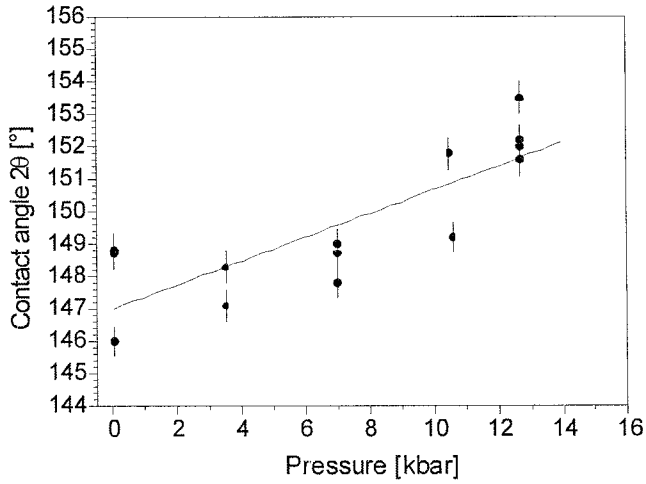

Fig. 4. Equilibrium vertex angle at the triple junction 2θ vs. hydrostatic pressure.

Generally, the relationship between the grain boundary surface tension and the pressure is not known. The experimentally measured dependency of the contact angle on the pressure in Fig. 4 can

be approximated by the linear function $\theta = \theta_0 + \partial\theta/\partial p \cdot p$, where θ_0 =73.5° and $\partial\theta/\partial p = 3.19\times10^{-11}$ are obtained by linear regression.

The energy γ_3 of the grain boundary GB3 can be calculated according to the following equation [12]

$$\gamma_3 = \gamma^{4°\text{twist}} = 2\frac{Gb}{4\pi}\vartheta(A - \ln\vartheta) = 0.265 \text{ J/m}^2, \quad (6)$$

where $b = 2.86\times10^{-10}$ m is the Burgers vector, G =26.4 GPa is the shear modulus in Al, $\vartheta = 2\psi = 4°$ is the misorientation angle of the low angle twist grain boundary, $A = 0.5$ is a constant of integration, which is determined by the energy of the dislocation core [14]. With this value the BFV of a 40°<111> tilt grain boundary could finally be calculated from Eq. (5) and was found to be equal to $V_{gb}^{ex} \cong 5.03\times10^{-11}$ m^3/m^2.

It is worth noting that no model assumptions like grain boundary width in HRTEM measurements or the size of a simulation box in atomistic simulations were necessary to determine the boundary free volume by the introduced method.

Measurements of the BFV provide a way to estimate the material density in the region of a grain boundary. The ratio of a "grain boundary density" ρ_b and in the bulk of a crystal ρ_0 is equal to $\rho_b/\rho_0 = 1 + \Gamma_0\Omega_a/\delta$, where δ is a boundary width. Assuming $\delta = 10^{-9}$ m, ρ_b/ρ_0 amounts 0.95.

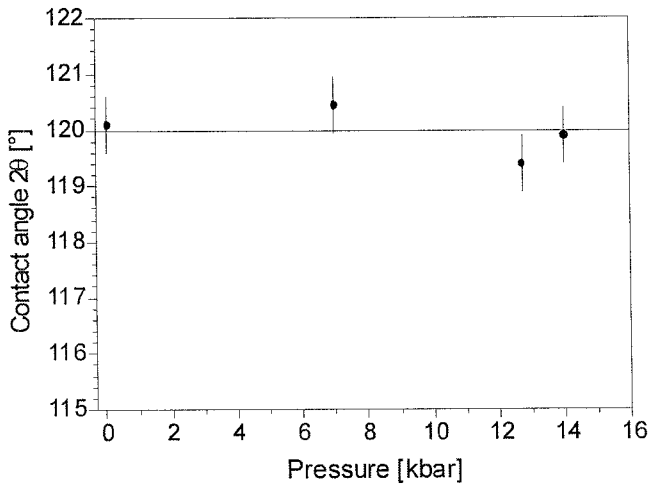

Fig. 5. Equilibrium vertex angle 2θ vs. hydrostatic pressure for tricrystal with two 40°<111> tilt grain boundaries (GB1 and GB2) and 80°<111> tilt boundary (GB3).

If the grain boundary system with junction consists of grain boundaries with similar properties, the surface energy of all of them should equally rise with increasing pressure. In this situation the vertex angle at the junction must be independent of pressure. To check this point the pressure dependence of the equilibrium vertex angle was measured for a grain boundary system composed 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 results of the measurements are shown in Fig. 5. As expected, no pressure dependence was observed. The measured angle was about 120° in the whole pressure range.

Summary

A special technique to determine the absolute value of the BFV is introduced. An important feature of this technique is that no assumptions on grain boundary width are necessary. The BFV was derived from the dependence of the vertex angle at the triple junction of grain boundaries in Al-tricrystals on hydrostatic pressure. This dependence was measured for a boundary system composed of two high angle grain boundaries and a 4°<110> twist grain boundary in the pressure range up to 14 kbar. For a 40° <111> tilt boundary with 2° twist component the boundary free volume was found to be equal to 5.03×10^{-11} m^3/m^2.

The proposed method provides a new avenue of obtaining quantitative information on important thermodynamic properties of grain boundaries.

Acknowledgments

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References

1. G. S. Knizhnik, Poverhnost: Fizika, Khimia, Mehanika Vol. 5 (1981), p. 50
2. D. Wolf, Scripta Metall. Vol. 23 (1989), p. 1913
3. D. Wolf, J. Appl. Phys.. Vol. 68 (1990), p. 3221
4. D. Wolf, Acta Metall. Mater. Vol. 38 (1990), p. 781
5. H. J. Frost, M. F. Ashby, F. Spaepen, Scripta Metall. Vol. 14 (1980), p. 1051
6. M. A. Stremel, A. L. Markovich, Poverhnost: Rentgenovskie, Sinhrotronnii i Neitronnii Issledovaniya Vol. 1 (1997), p. 85
7. H. Zhang, D. J. Srolovitz, to be published
8. H. Meiser, H. Gleiter, R. W. Mirwald, Scripta Metall. Vol. 14 (1980), p. 95
9. K. I. Buckett, K. L. Merkle, Ultramicroscopy Vol. 56 (1994), p. 71
10. K. L. Merkle, R. Csencsits, K. L. Rynes, J. P. Withrow, P. A. Stadelmann, J. of Microscopy Vol. 190 (1998), p. 204
11. G. Gottstein, L. S. Shvindlerman: *Grain Boundary Migration in Metals. Thermodynamics, Kinetics, Applications* (CRC Press, 1999), p. 310
12. W. T. Read, W. Shockley, Phys. Review Vol. 28 (1950), p. 275
13. D. Mattissen, PhD Thesis, RWTH Aachen, Shaker Verlag, Aachen, 2004
14. J. H. van der Merwe, Proc. Phys. Soc Vol. A63 (1950), p. 616