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Quantitative measurements of grain boundary excess volume from HAADF-STEM micrographs

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ABSTRACT

A novel approach for quantitative measurements of grain boundary (GB) excess volume has been developed using correlative analytical transmission electron microscopy (TEM) and successfully demonstrated for several simulated symmetrical [100] tilt GB configurations as well as for the experimental case of an Al bicrystal containing a near Σ13 GB with an additional twist component. The reliability and precision of this new approach is analyzed and the limitations are discussed.

1. Introduction

Grain boundaries (GBs) with their specific atomic structure have a significant impact on a wide range of physical properties (mechanical, electrical or diffusional) of polycrystalline materials. GBs are typically classified with respect to the misorientation angle, θ, of the abutting grains; that is, (i) low-angle boundaries with $\theta \leq 15^\circ$ and (ii) high-angle boundaries with $\theta > 15^\circ$ [1]. Low-angle GBs are composed of dislocations. The above mentioned critical value for $\theta = 15^\circ$ corresponds to the largest angle for which the dislocation-based model applies [2]. Read and Shockley [3] have developed such a model describing the accommodation of the misorientation between the abutting grains by arrangements of edge dislocations. One of the fundamental parameters for the characterization of GBs is their volume expansion ε_{GB}, i.e. the amount of excess volume in the GB [4]. It has been shown that the GB excess volume is correlated with the GB energy [5,6] and has thus an influence on transport and thermodynamic properties of GBs such as diffusion and/or segregation [7]. The GB excess volume (per unit area A) of low-angle GBs can be described according to Wolf [5,8] as:

$$\varepsilon_{GB} \equiv \frac{\delta V(\theta)}{A} = \sin\theta[\delta V_c - \delta V_s \ln(\sin\theta)]/|\boldsymbol{b}| \quad (1)$$

where δV_C is the excess core volume per unit length of a dislocation, δV_S is the related strain-field contribution (per unit length), θ is the misorientation angle between the grains and **b** is the Burgers vector. For FCC materials low-angle GBs with misorientation angles $\theta < 15^\circ$ are composed of dislocations with Burgers vectors $\mathbf{b} = [100]$. Accordingly, low-angle GBs with misorientation angles around 90° are composed of dislocations with Burgers vectors of the type $\mathbf{b} = -½\,[110]$ [3,9].

High-angle GBs are typically characterized by periodic structure units [10] using structural unit cells that differ from crystal unit cells. The excess volume of high-angle GBs can be derived from the basics of thermodynamics, see e.g. Ref. [4]. Bishop and Chalmers [11] determined the excess volume of high-angle GBs, V_F, as a parameter expressing the change in volume of a polycrystalline material together with the change of GB area (A) at constant temperature (T), pressure (P), number of atoms (n_i) and composition (x). The equilibrium state can be described as:

$$V_F = \left(\frac{\partial V}{\partial A}\right)_{T,P,n_i,x} nm^3 per\ nm^2 \quad (2)$$

Atomistic calculations for gold and copper crystals using the

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latter approach were performed by Wolf [5,8,12] with different interatomic potentials (embedded-atom method (EAM) and Lennard-Jones (LJ)) as input. In that work [8] (i) an almost linear relationship between the GB excess volume and the GB energy was found and, (ii) an equally good correlation of the number of broken nearest-neighbor bonds per unit area with the GB energy was observed. Moreover, a recent comprehensive survey of computed GBs properties reported also a rough correlation between the GB energy and the GB excess volume; however, the correlation is not sufficiently strong to predict energy from excess volume [8,13].

Quite a number of excess volumes have been calculated for different types of GBs [5,13,14]. These values are summarized in Table 1. However, there is a lack of experimental data. This motivates the interest in an experimental approach to measure the excess volume contributions of specific GBs. Recently, high-precision differential dilatometry was used to determine the release of the excess volume upon annealing of ultra-fine grained materials (Table 1) [15,16]. In this approach the fact is utilized that due to grain growth, the release of the excess volume out of the grain boundaries can be estimated from the differential length change of an ultra-fine grained specimen compared with a coarse-grained reference sample. However, this method inherently provides only an integral value averaged over a large number of different species of GBs present in ultra-fine grained polycrystals. In a different approach using the pressure dependence of the GB energy, the GB excess volume was determined in Al tricrystals for selected individual GBs [4].

Local techniques using transmission electron microscopy (TEM) micrographs have also been tested to quantify the GB expansion. It has been suggested that the component of the rigid-body translation, which represents the volume expansion of a particular GB, may be suitable for solving this problem [17]. For this purpose, Moiré fringes [17], α-fringes [18], Fresnel fringes [19–22] or lattice fringes [23–25] (see Table 1) were applied to measure the rigid-body displacements and thus to extract the information about the GB expansion.

In the present study, we describe an approach to determine first of all the relative density changes [26] between GBs and grain interiors from conventional high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of individual GBs and subsequently to calculate their corresponding excess volumes. The reliability of this novel approach is discussed with respect to segregated solute atoms, oxide layers and sample thickness. It is shown that the method developed here offers a rather simple and extremely versatile approach to obtain reliable data for the GB density for a wide range of materials and microstructures.

2. Calculations

Symmetrical [100] tilt GBs in Al were generated using atomistic simulations. These are in detail: two low-angle GBs indicated as $\Sigma1^{\Delta}$ and $\Sigma1^{*}$with misorientation angles below 15° having [100] type Burgers vectors, one low-angle GB with a misorientation angle around 90° having a [110] type Burgers vector indicated as $\Sigma1^{+}$, six high-angle GBs indicated as Σ13, Σ17, Σ37, Σ41, $\Sigma5^{(031)}$ and $\Sigma5^{(021)}$; the superscripts denote the different GB planes. The interatomic potential of Al [27] in an embedded atom model [28] was used together with the LAMMPS software [29,30] to perform molecular dynamics (MD) simulations. The relaxed atomic positions were subsequently taken as input for the simulation of HAADF-STEM images using the Kirkland code [31]. For the simulations the parameters of an FEI Titan 80–300 TEM were employed. Since the HAADF-STEM intensity in zone axis condition may be strongly affected by channeling [32], the GB structures were tilted 5° off the zone axis for the HAADF simulations.

Information about the local density changes was calculated from the simulated structures and the generated HAADF-STEM images. The dark-field intensity I/I_0 contains information about the mass thickness $\rho{\cdot}t$ [26]:

$$\frac{I}{I_0}=\left[1-\exp\left(-\frac{N_A\cdot\sigma\cdot\rho\cdot t}{A}\right)\right]=\left[1-\exp\left(-\frac{\rho\cdot t}{\chi_k}\right)\right]$$
$$\text{and for small arguments}: \quad \frac{I}{I_0}\cong\frac{\rho\cdot t}{\chi_k} \tag{3}$$

where N_A is the Avogadro's number, σ is the total scattering cross-section, ρ is the density, t is the foil thickness and A is the atomic weight. χ_k is the contrast thickness, which is defined as $A/(N_A{\cdot}\sigma)$. For experimental data, an acquired electron energy loss (EEL) signal allows calculation of the specimen foil thickness t from the low-loss spectral region [33]. Using Eq. (3) the relative density change (normalized to the intrinsic density of the material present in the grain interiors) can be expressed:

$$\frac{\Delta\rho}{\rho}=\frac{\rho^{GB}(x)-\rho^{GI}(x)}{\rho^{GI}(x)}=\frac{I^{GB}(x)\cdot t^{GI}(x)\cdot\chi_k^{GB}}{I^{GI}(x)\cdot t^{GB}(x)\cdot\chi_k^{GI}}-1 \tag{4}$$

where ρ^{GI}, ρ^{GB} are the mass densities of the grain interior (GI) and the GB, I^{GI}, I^{GB} are the HAADF intensities, χ_k^{GI}, χ_k^{GB} are the contrast thicknesses and $t^{GI}(x)$, $t^{GB}(x)$ are the corresponding local foil

Table 1
Compilation of GB excess volumes ε_{GB}.

Method	GB type	ε_{GB}/nm	Reference
Moiré patterns	Au Σ3	0.056	Matthews et al. [17]
Fresnel fringes	Cu Σ3	0.001 ± 0.004	Wood et al. [19]
Fresnel fringes	Cu Σ3	0.012 ± 0.002	Boothroyd et al. [20]
Lattice fringe	Au Σ11	0.0028–0.0033	Merkle et al. [23–25]
Molecular dynamics	Cu*	0.009–0.08	Wolf [5,8,12]
	Au*	0.005–0.03	Wolf [5,8,12]
Molecular dynamics	Ni Σ5	0.039–0.042	Srolovitz [37]
Thermodynamics	Al***	0.064	Shvindlerman et al. [4]
Differential dilatometry	Ni**	0.032–0.035	Steyskal et al. [15]
Differential dilatometry	Ni**	0.039	Reglitz et al. [16]
computed HAADF-STEM intensities	Al*	0.005–0.047	Current work
computed HAADF-STEM intensities	Al ≈ Σ13	0.048 ± 0.005	Current work
measured HAADF-STEM intensities	Al ≈ Σ13	0.051 ± 0.01	Current work

*Excess volume determined for the whole range of symmetrical tilted [100] GBs.
**Excess volume experimentally determined by averaging over many GBs.
***Excess volume determined for asymmetrical 40° < 111 > tilt boundaries.