Capillarity Vector Reconstruction of the Relative Energies of [0001] Tilt Boundaries in Alumina

D. M. Saylor, K. W. Cherry, and G. S. Rohrer

Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA, 15213-3890, USA

Keywords: grain boundaries, capillarity vector, Al_2O_3, grain boundary energy.

Abstract. We have measured the geometry and crystallography of the grain boundaries that form 124 triple junctions in a specimen of polycrystalline alumina. Each of these triple junctions is comprised of [0001] tilt boundaries which were assumed to be in local thermal equilibrium. By using the capillarity vector reconstruction method, we determined the energies of these boundaries as a function of the tilt angle and the grain boundary plane. The results show that for misorientations less than 25°, the relative energy increases with the misorientation angle, reaches a maximum, and then decreases as the $\Sigma 3$ misorientation is approached at 60°. Furthermore, the energy anisotropy caused by changes in the grain boundary plane is nearly as large as that caused by changes in misorientation.

1 Introduction

The physical and chemical properties of grain boundaries are known to be anisotropic. It has been pointed out that for a microstructure whose interfacial junctions are in local equilibrium, the mesoscale structure of the grain boundary network contains an imprint of the grain boundary properties [1]. By measuring the geometry and crystallography of the three interfaces that meet at tri-grain junctions, and assuming that Herring's [2] condition for local equilibrium is satisfied, it is possible to determine the anisotropy of the grain boundary free energy. In this paper, we reconstruct the relative grain boundary energies from microstructural observations using the capillarity vector reconstruction method, as originally described by Morawiec [3]. This method has previously been used to reconstruct the anisotropy of the surface energy of magnesia from thermal groove

data [4]. In the present paper, we apply the same technique to extract relative grain boundary energies from observations of tri-grain junctions, referred to as triple junctions.

We consider a grain boundary's character to be determined by its crystallographic lattice misorientation and the boundary plane. The number of distinct grain boundary characters expected in a sample with random texture is very large, and this has made it challenging to characterize their diversity and establish character-property correlations [5]. In the present case, we have avoided the problem by considering a sample with strong crystallographic and morphological texture so that there are only two degrees of freedom and the space of populated characters is significantly reduced. The sample has platy grains, with the basal plane aligned perpendicular to the sample normal so that there is a [0001] axial texture that is approximately 100 times random at maximum and most of the boundary planes are parallel to the sample normal [6]. Because of this, there are a significant number of boundaries that can be represented by a single <0001> misorientation axis and a boundary plane whose normal is perpendicular to this axis. Therefore, the boundaries we consider here are all of tilt character so that the misorientation and the boundary plane are each described by a single angular parameter. Because of the triad parallel to <0001>, all distinct misorientations (tilts) are between 0 and $\pi/3$ and all boundary plane normals (inclinations) are between 0 and $2\pi/3$.

2 Experimental Details

The sample used in this study was produced by Brandon's group as described previously [6]. Secondary electron (SE) images of grain boundary triple junctions were obtained in a Philips XL40 FEG scanning electron microscope (SEM) with the stage at 0° tilt. The images were captured at 20,000x magnification such that only one triple junction appeared in each image (an example is shown in Fig. 1). After collecting the SE images, the sample stage was tilted to an angle of 60° and electron backscattered diffraction patterns (EBSPs) were obtained for the grains bounding each characterized triple junction. The EBSPs were automatically indexed using TSL analysis software to obtain the grain orientations, and the indexing solution for each pattern was checked manually. Grain orientations from OIM tend to have systematic errors associated with them for a variety of experimental reasons, such as misalignment in the SEM or incorrect pattern center. The systematic errors were corrected by rotating the data such that the peak of the <0001> pole figure was centered about the sample normal. Each

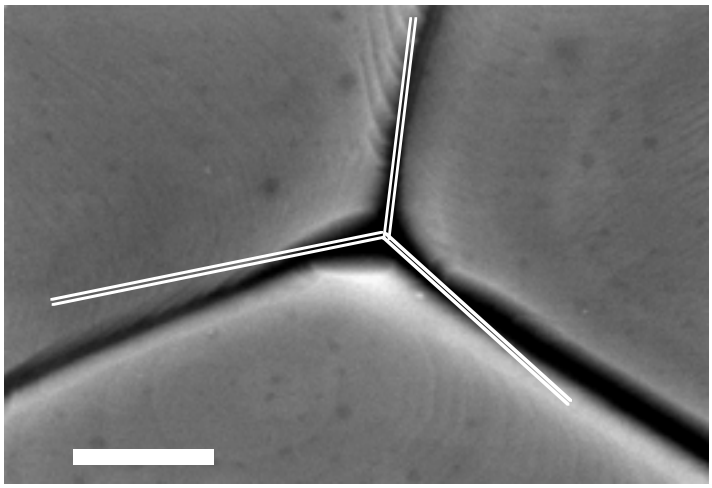

Fig.1. Secondary electron image typical of those used in the analysis. Lines drawn on the image are used to determine the dihedral angles and the in plane angles. The scale bar in lower left is 3 μm.

image was corrected such that the pixel to micron ratio was identical along the x and y axes. The corrected images were then used to manually measure the in-plane dihedral angles, as illustrated in Fig. 1.

Grain orientations were parameterized in terms of Eulerian angles, (ϕ_1,Φ,ϕ_2), from which the misorientation for any pair of grains can be determined. Because alumina is trigonal, there are 6 x 6 x 2 = 72 symmetrically equivalent grain misorientations. Thus, for grains with orientations $\mathbf{g_1}$ and $\mathbf{g_2}$, we consider misorientations $\Delta\mathbf{g}=(\mathbf{C_i g_1})(\mathbf{C_j g_2})^{-1}$ and $\Delta\mathbf{g}=(\mathbf{C_j g_2})(\mathbf{C_i g_1})^{-1}$, where the $\mathbf{C_i}$ are the symmetry operators for this crystal system. Therefore, the misorientation, θ, is $\cos^{-1}[(\mathrm{tr}(\Delta\mathbf{g})-1)/2]$ and we define the fundamental zone of misorientation space as that for which θ is as small as possible and the misorientation axis, $n_i=\varepsilon_{ijk}\Delta\mathbf{g_{jk}}/2\sin(\theta)$, is such that $n_3 \geq 0$, $n_1 \geq 0$, and $(n_2/\ n_1)^2 \leq 1/3$. To characterize the boundary plane, we define the tilt angle, ρ, to be the angle between the boundary plane normal and <1000>. When determining a tilt angle for each boundary, we are obliged to select one of the two adjoining crystal orientations as the reference frame. Since the calculated values of $\Delta\mathbf{g}$ that fall in the fundamental zone of misorientation space always arise from the same combinations of non-inverted and inverted orientations, we select the non-inverted orientation as the reference frame.

To reconstruct the grain boundary energy, we assign to each interface a capillarity vector, $\breve{\xi}$, as defined by Hoffman and Cahn [7,8]. The component of the

capillarity vector normal to the interface is equal in magnitude to the boundary energy, γ, such that $\breve{\xi} \times \hat{l} = \gamma \hat{t}$, where $\hat{t}$ is the unit vector that lies in the interface plane and points in a direction perpendicular to and away from the line of intersection of the three interfaces ($\hat{l}$). The component of the capillarity vector in the plane tangent to the interface that is related to the change in γ with orientation given by $(\partial\gamma / \partial\beta)_{\max}\hat{t}_0$, where $\hat{t}_0$ points in the direction of maximum increase of γ and, β is the right handed angle of rotation about $\hat{l}$, which is measured from a reference direction. This is a measure of the so-called torque force that is normal to the interface and urges it to rotate about the line of intersection. In other words, $\breve{\xi} \times \hat{l} = (\partial\gamma / \partial\beta)\hat{n}$. Using our experimental observations of $\hat{n}$, $\hat{l}$, and the dihedral angles, we can assume that the Herring equilibrium equation applies $((\breve{\xi}^1 + \breve{\xi}^2 + \breve{\xi}^3) \times \hat{l} = 0$, where the superscripts label the three interfaces at the triple junction) and determine a set of capillarity vectors that most nearly satisfies this condition at each triple junction. The details of the capillarity vector reconstruction method have been described in previous publications [3, 4].

In treating the data, it was assumed that all grains had a perfect [0001] orientation with respect to the sample normal. In fact, there was some scatter about this pole. Grains with surface normals more then 15° from [0001] were excluded from the analysis. The preliminary data set discussed here is made up of 124 triple junctions. The domain of grain boundary characters is discretized in such a way that the resolution is limited to 12°.

3. Results and discussion

The results of the relative grain boundary energy reconstruction are illustrated in Fig. 2. Here, the data are represented in a density plot where relatively low energies correspond to black and relatively higher energies are white. The results illustrate two general trends. First, the relative energy increases with the misorientation angle in the range of $0 < \theta < 25°$. Second, the relative energies maximize at intermediate misorientation angles ($25° < \theta < 40°$) and decrease as the misorientation approaches 60°. The two trends are consistent with conventional theory regarding low angle boundaries and boundaries near coincident site lattice (CSL) orientations [9,10]. At low misorientations, the tilts can be accommodated by edge dislocations parallel to [0001] and, the relatively lower energy of boundaries with a near 60° misorientation are expected because there is a Σ3 CSL boundary at this point.

Perhaps the most interesting feature of the results is that the variation of the energy along the boundary plane axis is almost as large as those along the misorientation axis. For boundaries with misorientations less than 25°, as the boundary plane rotates away from <1000>, the energy increases. Previously, relative grain boundary energies for alumina were determined using a thermal groove technique and the dispersion of the energies for boundaries with similar misorientations was nearly as large as the total variation in energy [11,12]. The current observations confirm the idea that the energy of a boundary varies with both its misorientation (θ) and its inclination (ρ). At the $\Sigma 3$ misorientation (θ=60°), we expect minima in the relative energies at ρ = 30° and ρ = 90°, where lattice points that actually fall on the boundary plane maximize coincidence. There are minima near both of these orientations that, considering the limited resolution of this reconstruction (12°), might be ascribed to this special boundary. By accumulating more data, we plan to increase the resolution of the reconstructed grain boundary energy and establish a more detailed relationship between grain boundary character and energy.

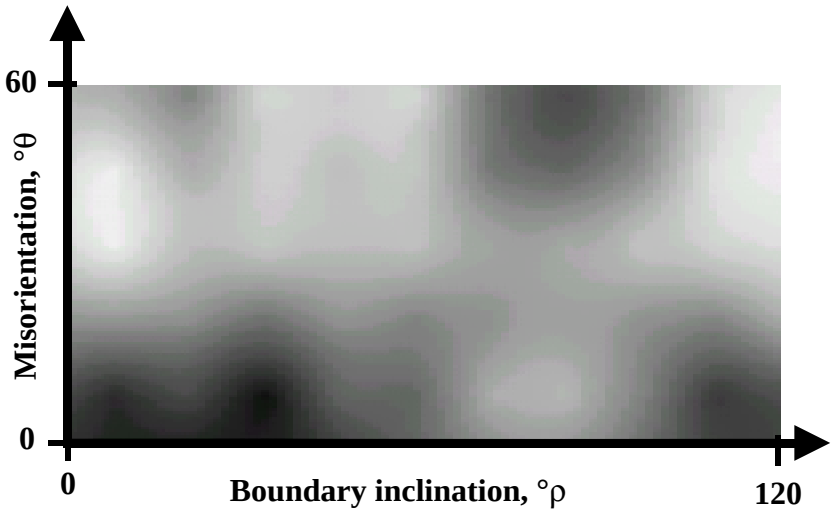

Fig. 2. The reconstructed relative grain boundary energy, as a function of misorientation and inclination. The darkest points represent the lowest relative energy (0.9) and the lightest represent the highest (1.02).

4. Summary

Geometric and crystallographic data obtained from triple junctions in a textured alumina polycrystal have been used to determine the relative energies of [0001] tilt boundaries using the capillarity vector reconstruction method. The data show anticipated variations both at low misorientations and near the Σ3 misorientation. Furthermore, the energy anisotropy derived from changes in the boundary inclination are almost as large as that derived from the lattice misorientation.

Acknowledgement

This work was supported primarily by the MRSEC program of the National Science Foundation under award number DMR-0079996.

References

[1] B.L. Adams, D. Kinderlehrer, W.W. Mullins, A.D. Rollett, and S. Ta'asan, *Scripta Mater.*, 38, 1998, pp. 531-536.
[2] C. Herring in The Physics of Powder Metallurgy, edited by W.E. Kingston, McGraw Hill, New York, 1951, pp. 143-79.
[3] A. Morawiec, *Acta Mater.*, 48, 2000, pp. 3525-32.
[4] D.M. Saylor and G.S. Rohrer, *Interface Science*, 9, 2001, pp. 33-44.
[5] D.M. Saylor, A. Morawiec, B.L. Adams, and G.S. Rohrer, *Interface Science*, 8, 2000, pp. 131-140.
[6] T. Carisey, I. Levin, and D.G. Brandon, *J. Euro. Ceram. Soc.*, 15, 1995, pp. 283-9.
[7] D.W. Hoffman and J.W. Cahn, *Surface Science*, 31, 1972, pp. 368-388.
[8] J.W. Cahn and D.W. Hoffman, *Acta Met.*, 22, 1974, pp. 1205-1214.
[9] W.T. Read and W. Shockley, *Phys. Rev.*, 78, 1950, pp. 275-289.
[10] D. G. Brandon, *Acta Metall.* 14, 1966, pp. 1479-84.
[11] D.M. Saylor and G.S. Rohrer, *J. Amer. Ceram. Soc.* 82, 1999, pp. 1529-1536.
[12] S.J. Glass, V.R. Vedula, D.M. Saylor, and G.S. Rohrer, in "Proceedings of ICOTOM-12", edited by J. Szpunar, NRC Research Press, Ottawa, 1999, pp. 1489-1494.