Influence of grain boundary energy on the nucleation of complexion transitions

Stephanie A. Bojarski,[a] Martin P. Harmer[b] and Gregory S. Rohrer[a,*]

[a]Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA
[b]Department of Materials Science and Engineering, Lehigh University, Bethlehem, PA 18015, USA

To test the effect of grain boundary energy on the nucleation of a transition from a low mobility to a high mobility grain boundary complexion, polycrystalline yttria-doped alumina was sandwiched between two single crystals of sapphire. Thermal groove measurements showed that the distribution of grain boundary energies at the single crystal–polycrystal interface is biased by the single crystal orientation. When annealed above the critical temperature for the complexion transition, the high mobility complexion preferentially nucleated at the higher energy interface.
© 2014 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

It has recently been found that the structure and chemistry of a grain boundary can change abruptly as certain thermodynamic parameters are varied and this can lead to changes in the properties of the boundary, such as the energy and mobility [1]. For example, below a critical temperature, a monolayer of adsorbed impurities might be segregated to a grain boundary and above this temperature a bilayer of impurities might be stable [2]. These distinguishable states are now referred to as complexions [1–3]. While complexions have been characterized in a variety of materials, including metals [4], semiconductors [5] and ceramics [6], the most extensively studied complexions are found at the grain boundaries of doped aluminas [2]. In this case, the observations show that, when the temperature is changed, the transformation from one complexion to another is not immediate, or at least does not happen immediately at every grain boundary [7]. This suggests that the transformation from a metastable complexion to a stable complexion is limited by a nucleation energy barrier and/or that different types of grain boundaries have different transition temperatures. It has been hypothesized that higher energy grain boundaries have a lower nucleation energy barrier for the transformation and therefore transform first, or

that they have a lower critical temperature for the transformation [2,8,9]. Either of these two circumstances would lead to a mixture of transformed and untransformed boundaries at a constant temperature. The goal of this paper is to describe an experiment designed to test the hypothesis that grain boundaries with higher relative energies preferentially undergo complexion transitions.

Our experiment uses a unique sandwich-like sample, as shown schematically in Figure 1. The sample consists of a doped alumina polycrystal sandwiched between two single crystals of sapphire with known orientations. Grain boundary energies vary with the grain boundary plane orientation [10]. Therefore, the single crystals bias the distribution of grain boundary plane orientations at the single crystal–polycrystal interface and, with it, the distribution of grain boundary energies [11]. So, by using a sapphire crystal that has a surface orientation associated with high energy boundaries on one side and a crystal with an orientation associated with low energy boundaries on the other side, distinct grain boundary energy distributions will be created at the two single crystal–polycrystal interfaces. If the chemical potential of yttria, the temperature and the pressure are constant throughout the sample, the grain boundary energy is the only variable parameter. According to the hypothesis stated above, the transition to a higher mobility complexion should occur preferentially at the interface with a relatively higher energy.

---

* Corresponding author. Tel.: +1 412 268 2696; fax: +1 412 268 3113; e-mail: gr20@andrew.cmu.edu
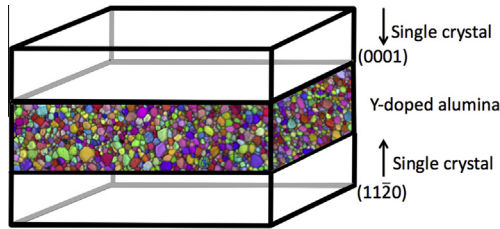
Figure 1. Schematic illustration of the sandwich sample. A polycrystalline Y-doped alumina polycrystal is sandwiched between two sapphire crystals of different orientation and diffusion bonded in a hot press or spark plasma sintering furnace.

For this experiment, we employ Y_2O_3-doped Al_2O_3. This pseudo-binary system is selected because there is already considerable documentation about the complexion transition in this system [12]. Based on a previous study of the grain boundary character distribution of yttria-doped alumina, it was concluded that grain boundaries with (0001) orientated planes have higher energies than those with $(11\bar{2}0)$ or $(\bar{1}012)$ orientations [13]. Using this knowledge, we will test the idea that grain boundary energy influences the nucleation of the complexion transition by comparing the grain growth behavior at the higher energy (0001) plane with growth at the lower energy interfaces under the same conditions.

Yttrium-doped alumina powder was prepared by mixing pure alumina powder (Puratronic, Alpha Aesar 99.995% pure) with 500 ppm $Y(NO_3)_3 \cdot 6H_2O$ (Alpha Aesar, Ward Hill, MA). Sapphire single crystals ($10 \times 10 \times 0.5$ mm) were purchased (MTI Corp, Richmond, CA) and thoroughly cleaned to avoid contamination. The sandwich sample was organized in a graphite die such that 1.5 g of Y-doped alumina powder was interfaced with the graphite plunger and the (0001) oriented sapphire was then laid parallel to the die with the polished side of the crystal oriented upward. About 4 g of Y-doped alumina powder was then layered onto the (0001) oriented sapphire, a $(11\bar{2}0)$ orientated sapphire single crystal was placed on top of the powder, with the polished side oriented downward, and covered with another 1.5 g of Y-doped alumina powder before inserting the ram. After uniaxial pressing, the samples were spark plasma sintered (Thermal Technologies, LLC, Santa Clara, CA) using the following thermal treatment: a ramp of $100\,°C\,min^{-1}$ to $800\,°C$ at a pressure of 10 MPa for an initial calcination dwell of 45 min, followed by an additional $100\,°C\,min^{-1}$ ramp to $1300\,°C$ and sintering at 50 MPa for 30 min. For comparison, a second set of samples was produced in a hot press. For this experiment, the alumina powder was doped with 100 ppm yttria and a (0001) oriented sapphire crystal was paired with a $(\bar{1}012)$ oriented crystal. The sample was constructed as described above and then sintered by hot isostatic pressing in a vacuum at less than 10 MPa (Astro 1000, Thermal Technology Inc., Santa Rosa, CA) for 60 min to achieve near theoretical density.

Orientation data was collected on a Quanta 200 field emission scanning electron microscope with OIM EDAX Delphi software configured with TSL analysis (EDAX Inc, Mahwah, NJ). The EBSD step size was roughly one-tenth the average grain size, the accelerating voltage was 15 kV and the working distance was

10 mm. Contact atomic force microscopy topographs were recorded using a SolverNext NT-MDT atomic force microscope (NT-MDT, Zelenograd, Moscow) and Pyrex-nitride tips (Contact mode, Nanoworld, Neuchâtel, Switzerland). The topographic images were taken with a step size of 10 nm and a field of view of 5–20 μm.

The orientation maps in Figure 2a and b show the microstructure of the samples after densification. The regions of constant orientation on the left and right sides are the edges of the single crystals. The polycrystalline material between the single crystals is dense, about 2.5 mm thick, and shows a normal distribution of grain sizes, with an average size of 1.0 μm. The single crystal surfaces do not remain perfectly flat because they sinter with the alumina powder. However, the interfaces did not advance significantly into the polycrystal, and it was assumed that the average orientation of the interface was maintained. The polycrystal along the (0001) and $(\bar{1}012)$ orientated interfaces had a similar appearance.

To evaluate the grain boundary energy distributions in the as-sintered state, the sample was thermally grooved in air at $1350\,°C$ for 15 h. At least 100 individual boundaries were analyzed along both the (0001) and $(11\bar{2}0)$ planes. Following the procedures described by Saylor and Rohrer [14] and Dillon et al. [15], which adapt the original Mullins [16] analysis for the half angle of the groove, the grain boundary to surface energy ratio was determined for all of the grooves. For each boundary, a mean dihedral angle determined from multiple measurements of the same groove. Cumulative distribution plots for the measured dihedral angles and the relative grain boundary energies at the (0001) and $(11\bar{2}0)$ interfaces are compared in Figure 3(a). As expected from an earlier study of the grain boundary character distribution [13], the interface with the $(11\bar{2}0)$ orientation has a lower mean energy (0.55) than the one with the (0001) orientation (1.15). Furthermore, the standard deviation of the higher energy interface (0.30) is larger than that of the lower energy interface (0.21). Random boundaries spatially separated from the single crystals by at least two grains have an intermediate average energy (0.71). This indicates that the single crystals bias the energy distribution so that grain boundaries at the (0001) interface have, on average, higher energies than random boundaries and that those at the $(11\bar{2}0)$ interface have lower energies than random boundaries.

The sample containing the (0001) and $(11\bar{2}0)$ oriented crystals was then heated in air for 8 h at $1500\,°C$, which is above the temperature at which a grain boundary complexion transition is expected [13]. The sample was then polished to a 0.05 μm diamond finish and thermally grooved at $1400\,°C$ for 15 h in air. Orientation maps of this sample are illustrated in Figure 2(c) and (d). After the high temperature anneal, there is a bimodal grain size distribution in the bulk of the polycrystal, where the average size of grains smaller than 10 μm was 3.2 μm and the average size of grains larger than 10 μm is was 19.8 μm. However, there is also a distinct difference between the two interfaces. The microstructure along the (0001) interface contains nearly all larger grains, but the microstructure along the $(11\bar{2}0)$ interface contains mostly smaller grains. Both single crystals grew into the polycrystal, where
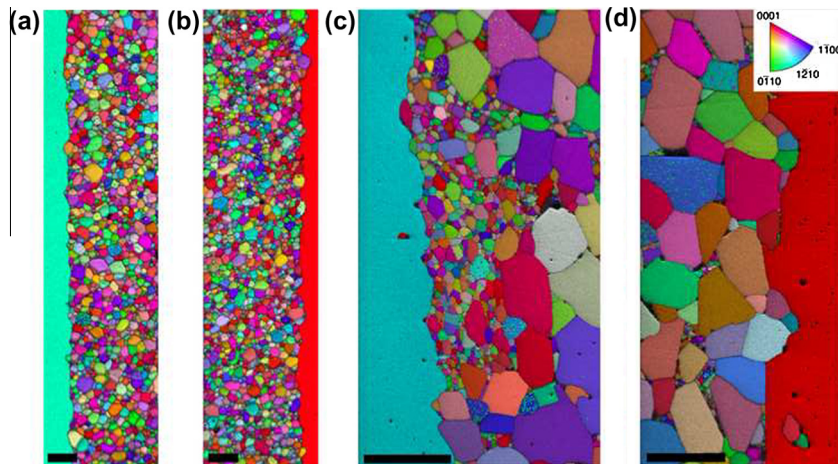
Figure 2. Orientation maps of cross-sections of the sandwich samples. The shading is a combination of the crystal orientation perpendicular to the viewing axis (see the key in the upper right portion of (d)) and image quality, where darker shading indicates relatively lower image quality. (a) Near the interface with the $(11\bar{2}0)$ plane and (b) near the (0001) plane (b) in the as-consolidated sample. (c) and (d) are also near the $(11\bar{2}0)$ and (0001) planes, respectively, but were recorded after annealing at 1500 °C for 8 h. The lengths of the scale bars are (a) 5 μm, (b) 5 μm, (c) 50 μm and (d) 45 μm.

the (0001) oriented crystal advanced 38 μm and the $(11\bar{2}0)$ oriented crystal advanced 29 μm. The maps in Figure 2(c) and (d) are characteristic of the entire interface. Note that in a control experiment, to test the influence of the current direction in the SPS apparatus, one sample was prepared with the sapphire crystals in the opposite order, so that current flowed in the opposite direction with respect to the high and low energy interfaces. The result was the same, indicating that the current direction does not influence the result. The sample that paired the (0001) oriented crystal with the $(\bar{1}012)$ oriented crystal, annealed at 1550 °C in a hydrogen/nitrogen environment for 18 h, behaved similarly. In this case, the distances that the two interfaces moved during the anneal were measured. The (0001) orientated interface moved six times further (about 70 μm) than the $(\bar{1}012)$ interface under the same conditions, implying that the mobility was 36 times greater.

The relative grain boundary energies for the sample pairing the (0001) and $(11\bar{2}0)$ interfaces were measured after the heat treatment, and the cumulative distributions are shown in Figure 3(b). As before the anneal, the (0001) plane has a higher energy than the $(11\bar{2}0)$ plane. However, the grain boundary energy of the (0001) interface decreased by 19% (mean energy = 0.93, standard deviation = 0.37) and the energy of the $(11\bar{2}0)$ interface decreased by 27% (mean energy = 0.40, standard deviation = 0.21).

The observations support the hypothesis that complexion transitions nucleate preferentially at higher energy grain boundaries. After annealing for a fixed time and temperature, there are more large grains along the higher energy interface, indicating that these interfaces transformed to a high mobility complexion in advance of those at the lower energy interface. There are two possible mechanisms that might explain these observations. The first is that each type of boundary might have a different critical temperature for the transformation. If higher energy grain boundaries transform at lower temperatures, then one can imagine that, at a fixed temperature, some boundaries are metastable and transform to the higher mobility complexion and that

lower energy boundaries are stable, with the lower mobility complexion, and do not transform. Because there are more high energy boundaries at the (0001) interface, more boundaries transform and there are more large grains. The second possibility is that the nucleation energy barrier for the complexion transition is affected by the grain boundary energy, with higher energy boundaries having a smaller barrier. Therefore, after a fixed time, higher energy boundaries are more likely to transform. Again, because there are more high energy boundaries at the (0001) interface, a higher fraction of the boundaries are expected to have high mobilities and more large grains should be found.

In prior work, the energy change associated with this complexion transition was measured to be 46% [12]. In the current experiment, the energy decreases were 19% for the (0001) interface and 27% for the $(11\bar{2}0)$. While these decreases are smaller, it should be noted that only boundaries around very large grains, presumed to be transformed, were sampled in the previous work. In the current work, all boundaries along a given interface were sampled, meaning that the result is an average of the energies of the transformed and untransformed boundaries.

The measured energies decreased at both interfaces, which suggests that the complexion transition was relatively widespread, even though the large grains were not detected everywhere. It is worth emphasizing that we are comparing the characteristics of distributions, both of which include a mixture of transformed and untransformed grain boundaries. The differences in the distributions reflect different proportions of the transformed and untransformed boundaries. Furthermore, using the size of a grain as an indicator of the transition can potentially be misleading. In fact, it has been observed in Ca-doped yttria that the grain boundaries in the vicinity of a very large grain can have low energies associated with the transition, but have not yet have achieved the characteristically large size [17]. Furthermore, isolated boundaries with high mobility will not lead to the characteristic grains with abnormal size; for the entire grain to grow abnormally large, it is reasonable
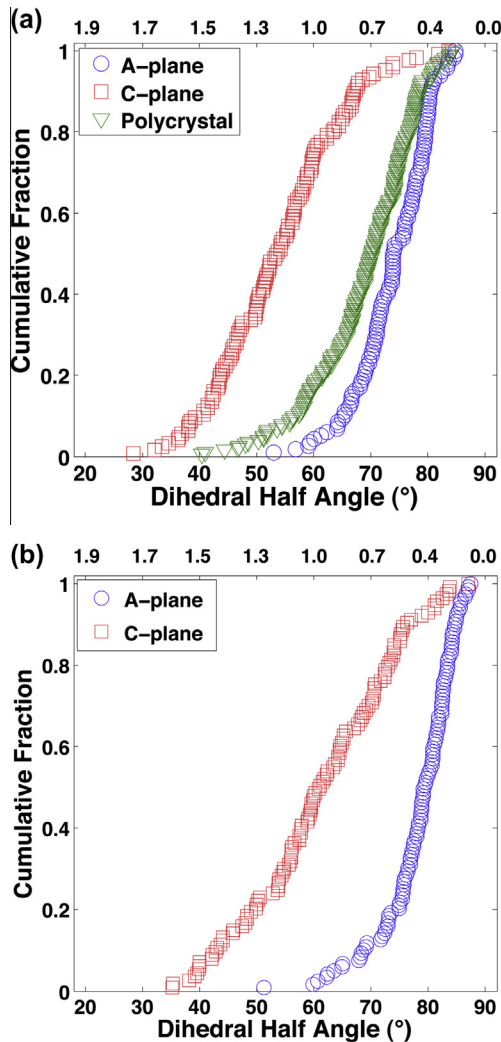
Figure 3. Cumulative distributions of relative grain boundary energy for (a) the sample that was thermally grooved immediately after SPS and (b) the sample annealed for 8 h at 1500 °C inducing AGG. The points indicate the mean of at least three measurements at each boundary.

two grains grow into one another [18]. Therefore, even though the mean energy decreases, this does not preclude the formation of new, high energy boundaries during the normal course of microstructural evolution.

In summary, measurements of the relative grain boundary energies at the interfaces between single crystals of sapphire and a Y-doped alumina polycrystal show that the grain boundaries at the $(11\bar{2}0)$ interface have lower average energies than those at the (0001) interface. After annealing at 1500 °C, the transformation to the high mobility complexion is more extensive at the higher energy (0001) interface. Measurements of the relative grain boundary energy after the high temperature anneal show that the relative energies decreased, consistent with a complexion transition. Furthermore, the greater number of large grains at the high energy (0001) interface indicates that more boundaries transformed there at an earlier time. Overall, the results show that complexion transitions are more probable at higher energy grain boundaries. Further, the fact that two metastable complexions can coexist at a single temperature suggests that the transformation is governed by a nucleation and growth process, and that the transformation kinetics may obey the conventional kinetic laws that govern bulk phase transformations.

to assume that it must have and sustain a critical number of high mobility boundaries. So, even if some grain boundaries transition to a high mobility complexion in areas with small grains, this does not alter the conclusion that more boundaries at the higher energy interface transform at an earlier time and this led to the observation of more large grains.

The cumulative distribution of relative boundary energies at the $(11\bar{2}0)$ oriented crystal interface in the as-sintered sample have a relatively symmetric normal cumulative distribution. However, when heated for 8 h at 1500 °C, the highest 20% of measured boundaries are still greater than the average of the untransformed dataset, and the maxima are the same within uncertainty. In other words, even though the mean of the partially transformed distribution is 27% less than the mean of the original pre-transformation sample, the highest energy boundaries in the tail appear to remain. This underscores the fact that we are not looking at the same boundaries before and after, and that, as the microstructure evolves, new boundaries that sample the entire range of energies are constantly being created when

[1] P.R. Cantwell, M. Tang, S.J. Dillon, J. Luo, G.S. Rohrer, M.P. Harmer, Acta Mater. 62 (2014) 1–48.
[2] S.J. Dillon, M. Tang, W.C. Carter, M.P. Harmer, Acta Mater. 55 (2007) 6208–6218.
[3] W.D. Kaplan, D. Chatain, P. Wynblatt, W.C. Carter, J. Mater. Sci. 48 (2013) 5681–5717.
[4] J. Luo, H.K. Cheng, K.M. Asl, C.J. Kiely, M.P. Harmer, Science 333 (2011) 1730–1733.
[5] S.L. Ma, K.M. Asl, C. Tansarawiput, P.R. Cantwell, M.H. Qi, M.P. Harmer, J. Luo, Scripta Mater. 66 (2012) 203–206.
[6] S.L. Ma, P.R. Cantwell, T.J. Pennycook, N.X. Zhou, M.P. Oxley, D.N. Leonard, S.J. Pennycook, J. Luo, M.P. Harmer, Acta Mater. 61 (2013) 1691–1704.
[7] S.J. Dillon, M.P. Harmer, J. Eur. Ceram. Soc. 28 (2008) 1485–1493.
[8] M. Tang, W.C. Carter, R.M. Cannon, Phys. Rev. B 73 (2006) 024102.
[9] M. Tang, W.C. Carter, R.M. Cannon, Phys. Rev. Lett. 97 (2006) 075502.
[10] G.S. Rohrer, J. Mater. Sci. 46 (2011) 5881–5895.
[11] S.J. Dillon, H. Miller, M.P. Harmer, G.S. Rohrer, Int. J. Mater. Res. 101 (2010) 50–56.
[12] S.J. Dillon, M.P. Harmer, G.S. Rohrer, J. Am. Ceram. Soc. 93 (2010) 1796–1802.
[13] S.A. Bojarski, M. Stuer, Z. Zhao, P. Bowen, G.S. Rohrer, J. Am. Ceram. Soc. 97 (2014) 622–630.
[14] D.M. Saylor, G.S. Rohrer, J. Am. Ceram. Soc. 82 (1999) 1529.
[15] S.J. Dillon, M.P. Harmer, G.S. Rohrer, Acta Mater. 58 (2010) 5097–5108.
[16] W.W. Mullins, J. Appl. Phys. 28 (1957) 333–339.
[17] S.A. Bojarski, J. Knighting, S.L. Ma, W. Lenthe, M.P. Harmer, G.S. Rohrer, Mater. Sci. Forum 753 (2013) 87–92.
[18] S.J. Dillon, G.S. Rohrer, Acta Mater. 57 (2009) 1–7.