Crystallographic Distribution of Internal Interfaces in Spinel Polycrystals

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Abstract. Measurements of the grain boundary character distribution in $MgAl_2O_4$ (spinel) as a function of lattice misorientation and boundary plane orientation show that at all misorientations, grain boundaries are most frequently terminated on {111} planes. Boundaries with {111} orientations are observed 2.5 times more frequently than boundaries with {100} orientations. Furthermore, the most common boundary type is the twist boundary formed by a 60° rotation about the [111] axis. {111} planes also dominate the external form of spinel crystals found in natural settings, and this suggests that they are low energy and/or slow growing planes. The mechanisms that might lead to a high population of these planes during solid state crystal growth are discussed.

Introduction

Five parameters are needed to characterize grain boundaries in polycrystalline solids: three can be associated with the lattice misorientation and two with the orientation of the boundary plane. Using electron backscattered diffraction (EBSD) mapping, it is possible to measure four of the five parameters from a single section plane. The fifth parameter, the inclination of the boundary with respect to the section plane, can be determined either by serial sectioning [1,2] or stereological analysis [3,4]. Recent measurements of the distribution of grain boundaries in polycrystalline MgO indicate that grains are most frequently bounded by low energy {100} surface planes [2,5]. Furthermore, the variation of the grain boundary energy with type is, to first order, simply proportional to the variation of the sum of the energies of the two surfaces that comprise the boundary. A more recent study of $SrTiO_3$ (cubic, perovskite structure) also showed that the lowest energy surfaces dominate the grain boundary plane distribution [6].

These observations have two implications. The first is that the surface energy anisotropy, which depends on two parameters, is sufficient for predicting the anisotropy of the grain boundary energy. This is useful because surface energies are easier to measure than grain boundary energies. The second is that the elimination of interfacial area during grain growth is biased toward higher energy grain boundaries so that the population of boundaries is dominated by the lower energy boundaries. This was substantiated by recent three dimensional grain growth simulations of MgO which, when using anisotropic grain boundary energies that approximated the measured energy anisotropy, reproduced the main features of the observed distribution of grain boundary planes [7].

The purpose of the present paper is to examine the distribution of grain boundary planes in $MgAl_2O_4$ (cubic, spinel structure). In the prior work, MgO and $SrTiO_3$ both have low energy {100} planes and these planes dominated the grain boundary population. Spinel was selected because it typically exhibits an octahedral growth form bounded principally by {111} faces and it is therefore expected to show grain boundaries that are most frequently terminated by these same planes. This expectation proved to be correct and in the final section of this paper, possible mechanisms for the predominance of the low energy planes are discussed.

Experimental

A sintered disk of spinel, obtained from RCS technologies, was annealed in air at 1600°C for 48 hours. After this treatment, the average grain size was 12 μm. Crystal orientation maps on a planar section were obtained using an EBSD mapping system (TexSEM Laboratories, Inc.) integrated with a scanning electron microscope (Phillips XL40 FEG). Sixteen maps were obtained, each with an area of 400 μm x 400 μm. Within each map, orientations were recorded at an interval of 2 μm. When combined, these maps contained ~8500 grains. The distributions of grain orientations and misorientations were determined from these data. The five parameter grain boundary character distribution was determined by a stereological analysis of grain boundary traces observed where the grain boundary plane meets the specimen surface [3,4]. Using a procedure described by Wright and Larsen [8], 28,000 traces were extracted from the orientation maps. The traces were analyzed using a previously described procedure to determine the grain boundary character distribution, $\lambda(\Delta g, \mathbf{n})$, which we define as the relative areas of grain boundaries distinguished by their lattice misorientation (Δg) and orientation ($\mathbf{n}$) [2,4]. By separating the three misorientation parameters and the two interface plane parameters, the distribution of grain boundary planes at each misorientation, $\lambda(\mathbf{n}|\Delta g)$, can be plotted on a stereographic projection. Here, the misorientations are selected according to the axis-angle convention by specifying the common axis of rotation, [uvw] and the angle about that axis, θ. The results are presented in multiples of a random distribution (MRD); values greater than one indicate planes observed more frequently than expected in a random distribution. The resolution of the distribution is approximately 10 °.

Results

Based on the EBSD data, the sample exhibited negligible grain orientation texture and only a weak misorientation texture. Grain boundaries with misorientations of less than 10° occurred with a higher than random frequency, as did boundaries with the $\Sigma3$ misorientation (a 60° rotation about [111].) The maximum in the misorientation distribution was about 2 MRD and occurred at $\Sigma3$. The distribution of grain boundary plane orientations, averaged over all misorientations, is illustrated in Fig. 1. Note that the distribution peaks at the {111} orientation. The data show that the ratio of {111} area to {100} area is approximately 2.5. At specific axis-angle combinations, the anisotropy in $\lambda(\mathbf{n}|\Delta g)$ is larger than in the misorientation averaged plot.

The distribution of grain boundary orientations for boundaries with misorientations of 20°, 40°, and 60° about the [111] axis are shown in Fig. 2. The schematic stereogram in 2a is provided as the key, and the symbols have the same meaning as in Fig. 1. Boundary planes perpendicular to the [111] misorientation axis have a pure twist character. The pure tilt boundaries lie along the great circle 90° from the [111] axis and these positions are marked by the black arc in Fig. 2a. The maximum in Fig. 2b corresponds to a pure twist boundary terminated on both sides of the interface by (111) planes. The smaller peaks at $(\bar{1}11)$, $(\bar{1}\bar{1}1)$, and $(1\bar{1}1)$ are mixed boundaries, where the surface of one grain has a {111}-type orientation and the complementary surface is inclined by 20° from this orientation. This accounts for the spreading of the maxima along the direction of the rotation. This is more clearly evident in Fig. 2c, which shows the distribution of planes for boundaries with a 40° rotation about [111]. In this case, the local maxima are clearly split into two peaks; one is a {111}-type orientation and the other is a complementary plane 40° away.

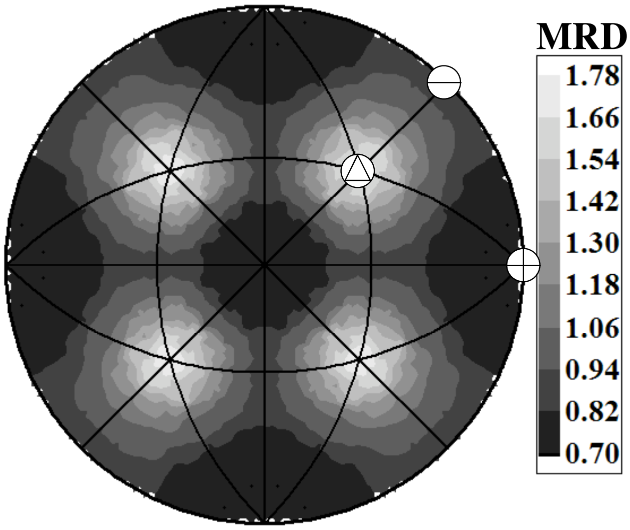

Figure 1. □(**n**), the relative areas of grain boundary planes in spinel, in multiples of a random distribution, plotted in stereographic projection along [001]. The circled triangle, line, and cross denote the (111), (110), and (100) directions, respectively.

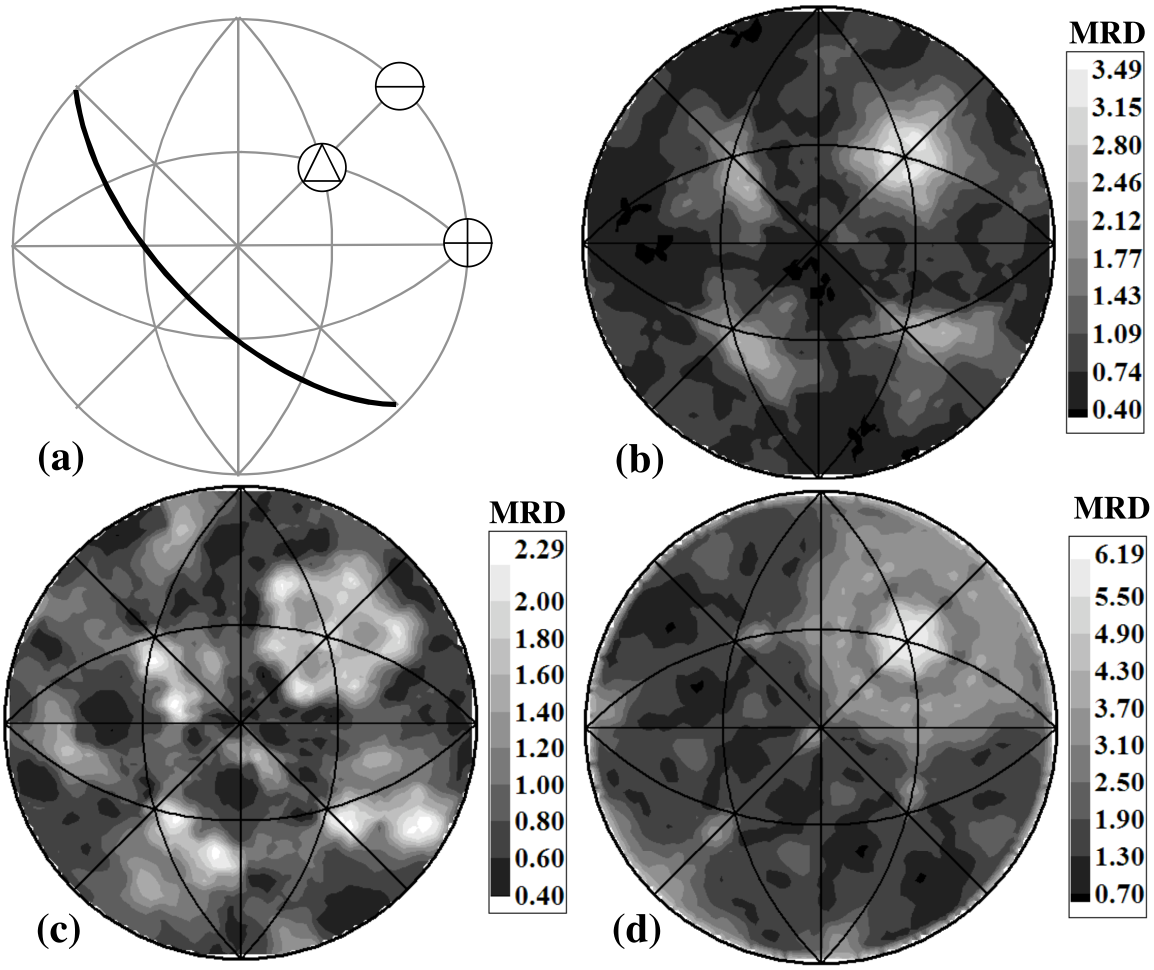

Figure 2. Distribution of grain boundary planes in spinel for [111] misorienations. (a) Schematic (see text for description) (b) □(**n**|20°/[111]), (c) □(**n**|40°/[111]), (d) □(**n**|60°/[111]).

The maximum in the five parameter distribution occurs for the pure twist configuration of the □3 misorientation, as illustrated in Fig. 2(d). In cubic close packed metals, this boundary is usually referred to as the coherent twin and is distinguished because the atoms in the interface plane can occupy positions such that their nearest neighbors are identical to those in the bulk structure; only the next and more distant neighbor configurations vary. Note that for □(**n**|20°/[111]) and □(**n**|40°/[111]), there are similar populations at (111), $(\bar{1}11)$, $(\bar{1}\bar{1}1)$, and $(1\bar{1}1)$. However at □(**n**|60°/[111]), the population of the twist configuration at (111) is much larger than the other three, suggesting that the special geometry makes it distinct from (111) twist boundaries at other angles.

The preference for grain boundaries terminated on {111} planes is also found for other misorientation angles. In Fig. 3, the distribution of grain boundary planes is shown for misorientations about the [100], [110], and [952] axes. The [952] boundary is added to show an example of a general boundary with the lowest possible symmetry in the space of boundary plane orientations. In this case, the boundary normals have only inversion symmetry and the entire hemisphere is required to represent the distribution. The preference for {111} grain boundary planes is illustrated by the broad maxima at all four {111} variant orientations in each of the plots.

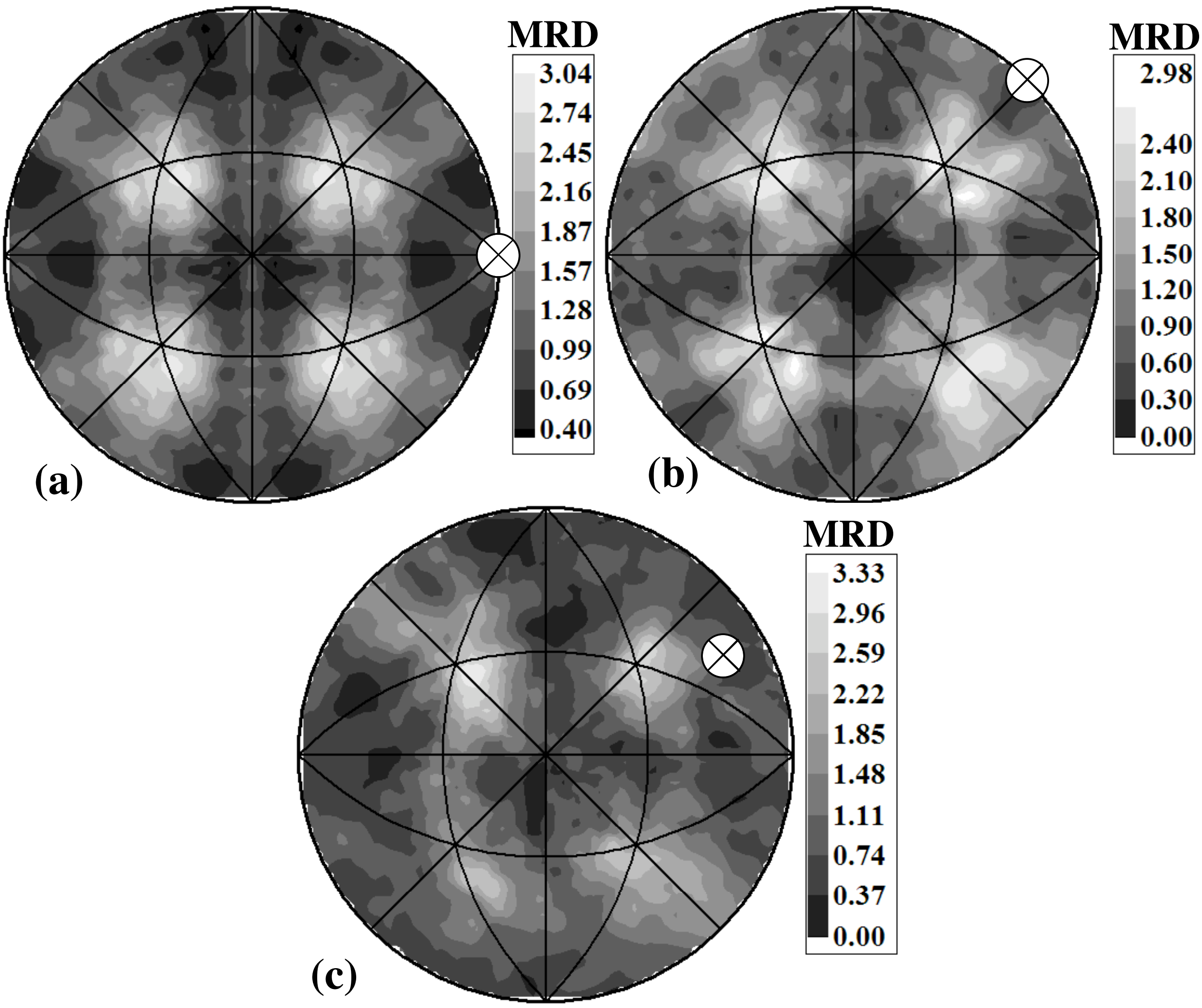

Figure 3. Distributions of grain boundary planes in spinel. (a) □(**n**|15°/[100]), (b) □(**n**|20°/[110]), and (c) □(**n**|20°/[952]). In each case, the reference frame is the same as used in Fig. 2 and the circle with the x shows the position of the misorientation axis.

Discussion

The high populations of {100} grain boundary planes in MgO and $SrTiO_3$ have been quantitatively compared to the measured surface energies, which show minima at these orientations [5,6]. Comparable measurements of the surface energy anisotropy of spinel are not available. However, it is known that {111} planes typically dominate the free surfaces of naturally occurring spinels. The most frequently observed twin and cleavage plane in spinel is also (111) [9]. Calculations of the surface energy have yielded ambiguous results [10,11]. Early calculations concluded that the (111) plane has the lowest energy [10], while more recent calculations indicate a minimum at the (100) orientation [11]. Assuming that the more recent calculation is more accurate, then the equilibrium crystal shape of spinel should have large (100) facets. Even if this is the case, the grains we have examined here are growth forms and the high population of {111} planes is consistent with the habits of spinel crystals observed in natural settings.

While the results show that grains in spinel prefer {111} habit planes, the topology of the network demands the simultaneous presence of non-habit planes. For example, since the average number of faces on a grain (13-14) is greater than the multiplicity of the {111} planes, and grain boundaries always have some curvature, it is necessary to introduce non-habit planes in the interfacial network. Furthermore, if there is a low index plane on one side of the boundary, then the plane on the other side is determined by the lattice misorientation and for an arbitrary misorientation, the adjoining surface is most likely to be a non-habit plane. Because of these geometric constraints, it would be incorrect to think of grains in spinel as a collection of self-similar octahedra bounded by {111} planes.

Measurements of the grain boundary plane distribution in TiO_2 and Al polycrystals yield similar results [12]. Low index planes thought to have relatively low energies or slow growth rates are the same planes that have high populations. Starting from a random grain orientation distribution and a random grain boundary character distribution, it is interesting to imagine how particular grain boundary habit plane distributions can develop. As grain boundary area is dissipated, new grains constantly come in contact and new boundaries are continuously created. Starting from a random grain orientation distribution, it does not seem possible that the impingement of randomly oriented grains can lead to a grain boundary character distribution related to boundary energies. On the other hand, the boundary elimination process might be weighted toward the elimination of higher energy boundaries. Grains shrink by losing sides and cascading from a higher topological class to a lower one, until reaching some terminal state where the grain collapses. Smith [13] first suggested that the shortest boundaries are eliminated preferentially. If the area of each grain face is inversely related to its energy, then the highest energy faces are the smallest and they will be eliminated preferentially. Thus, if all types of grain boundaries are created with equal probability, but higher energy boundaries are eliminated with a probability that is proportional to their area, then the population of lower energy boundaries will be higher than that of the high energy boundaries.

An alternate explanation for the observation that internal grain surfaces have the tendency to take the same orientations as external crystal surfaces is that grains in polycrystals grow by mechanisms analogous to those of crystals growing in a vapor or liquid phase. This idea is significantly different from the conventional theory of grain growth which assumes that the rate of growth or shrinkage of a grain is determined only by its size [14] In fact, the rate at which a given grain grows or shrinks will be influenced by the fraction of its bounding area made up of slow moving habit planes. Elementary theories of grain boundary motion depict thermally activated atom transfer across the interface [15]. According to this picture, mobility is controlled by the availability of donor and receptor sites on either side. Low energy facets tend to have low densities of such sites (with possible additional barriers to the thermally activated formation of such sites) and may therefore control the mobility, independent of the facet on the other side of the boundary. On the other hand, current thinking casts doubt on diffusive transfer mechanisms and favors of an atomic shuffle mechanism [16]. It is currently not clear how interface structure would influence migration rates controlled by this mechanism.

Summary

The internal grain surfaces in polycrystalline spinel are dominated by {111} planes. These are the same habit planes that appear on mineralogical specimens of spinel and, therefore, are thought to be the slow growing faces. The results add to a mounting body of data indicating that the habit of a phase in contact with itself (but misoriented) is not substantially different from its habit when in contact with a gas or liquid phase. The results also suggest that the mechanisms by which grains grow in dense polycrystalline compacts might be analogous to those governing the growth of isolated crystals.

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References

[1] V. Randle and H. Davies: Ultramicroscopy Vol. 90 (2001), p. 153

[2] D.M. Saylor, A. Morawiec, and G.S. Rohrer: Acta Mater. Vol. 51 (2003) 3663.

[3] D.M. Saylor and G.S. Rohrer: J. Amer. Ceram. Soc. Vol. 85 (2002) 2799.

[4] D.M. Saylor, B.S. El Dasher, B.L. Adams, G.S. Rohrer: Met. Mater. Trans. In press.

[5] D.M. Saylor, A. Morawiec, and G.S. Rohrer: Acta Mater. Vol. 51 (2003) 3675.

[6] D.M. Saylor, B.S. El-Dasher, T. Sano, and G.S. Rohrer: J. Amer. Ceram. Soc. In press.

[7] J. Gruber, D.C. George, A.P. Kuprat, G.S. Rohrer, and A.D. Rollett: this volume.

[8] S.I. Wright and R.J. Larsen: J. Micro. Vol. 205 (2002) 245.

[9] H.A. Miers: Minerology, 2nd Edition (Macmillan and Co., Ltd, London, 1929).

[10] C.M. Fang, S.C. Parker, and G. de With: J. Am. Ceram. Soc. Vol. 83 (2000) 2082.

[11] R.K. Mishra and G. Thomas: J. Appl. Phys. Vol. 48 (1977) 4576.

[12] D.M. Saylor, B.S. El Dasher, Y. Pang, H.M. Miller, P. Wynblatt, A.D. Rollett, and G.S. Rohrer: J. Amer. Ceram. Soc. In press.

[13] C.S. Smith: in Metal Interfaces (ASM, Cleveland, OH, 1962) p. 65.

[14] M. Hillert: Acta Met. Vol. 13 (1965) 227.

[15] D. Turnbull: J. Metals Vol. 3 (1951) 661.

[16] G. Gottstein and L.S. Shvindlerman: Grain Boundary Migration in Metals (CRC Press, Boca Raton, FL, 1999).