

Habits of Grains in Dense Polycrystalline Solids

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We show here that the boundaries of individual grains in dense polycrystals prefer certain crystallographic habit planes, almost as if they were independent of the neighboring crystals. In MgO, SrTiO₃, MgAl₂O₄, TiO₂, and aluminum, the specific habit planes within the polycrystal correspond to the same planes that dominate the external growth forms and equilibrium shapes of isolated crystals of the same phase. The observations decrease the apparent complexity of interfacial networks and suggest that the mechanisms of solid-state grain growth may be analogous to conventional crystal growth. The results also indicate that a model for grain-boundary energy and structure based on grain surface relationships is more appropriate than the widely accepted models based on lattice orientation relationships.

I. Introduction

THE physical properties of polycrystalline solids depend on the structure of the three-dimension network of internal interfaces. With a few notable exceptions, most of what we know about the network structure and the distribution of three-dimensional grain shapes has been derived from foams or computer simulations with isotropic boundary properties.^{1–3} The purpose of this communication is to report recent measurements of the crystallographic distribution of internal grain surface orientations.

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 interface plane. Electron backscattered diffraction (EBSD) mapping makes it 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^{4,5} or by stereological analysis.^{6,7} Recent measurements of the distribution of grain boundaries in polycrystalline MgO indicate that grains are most frequently bounded by low-energy {100} surface planes.^{5,8} 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. If this approximation holds generally in polycrystalline solids, then an extremely useful simplifying principle emerges: knowledge of 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. A more recent study of SrTiO₃ (cubic, perovskite structure) also has shown that the lowest-energy surfaces dominate the distribution of grain-boundary planes.⁹ In the current communication, we add to the earlier findings new results from TiO₂ (tetragonal, rutile structure), MgAl₂O₄ (cubic, spinel structure), and aluminum (cubic close-packed structure). The result is that the phenomenon originally observed in MgO can be generalized to other polycrystals: the most frequently observed grain-boundary planes are the same planes that dominate the external growth forms and equilibrium shapes of isolated crystals of the same phase.

II. Experimental Procedures

Each sample was annealed at a high homologous temperature before analysis to promote grain growth. Aspects of the sample origin, preparation, and characteristics are summarized in Table I. Crystal orientation maps on planar sections were obtained using an EBSD mapping system (TexSEM Laboratories, Inc., Provo, UT) integrated with scanning electron microscopy (Model XL40 FEG Phillips, Eindhoven, The Netherlands). The orientation maps contained between 5000 and 30000 grains and had a spatial resolution of $\leq 2 \mu\text{m}$. The internal grain-surface orientations of SrTiO₃ were determined by analyzing orientation data from two parallel sections, as described previously.⁹ For the other specimens, the distributions of internal grain surfaces were determined using a stereological analysis of the lines of intersection between the grain-boundary plane and specimen surface.^{6,7} The lines of intersection were determined directly from the orientation maps using a procedure described by Wright and Larsen.¹² In the current communication, we describe only the distribution of internal grain surfaces, indexed in the crystal reference frame, averaged over all misorientations. The procedure for this analysis has been described previously.⁵ 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 $\sim 10^\circ$.

III. Results

The preferred orientations for grain-boundary planes in each polycrystal are illustrated in Fig. 1. In SrTiO₃, internal {100} planes are found with twice the frequency of {111} planes.⁹ Calculations^{13,14} and experimental measurements¹⁰ agree that the

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Table I. Materials

Material	Space group	Grain size (μm)	Final heat ($^{\circ}\text{C}/\text{h}$)	Source/preparation
SrTiO ₃	$Pm\bar{3}m$	90	1650/48	See Ref. 10
MgAl ₂ O ₄	$Fd\bar{3}m$	12	1600/48	RCS Technologies, sintered disk
TiO ₂	$P4_2/mnm$	55	1600/24	See Ref. 11
Aluminum	$Fm\bar{3}m$	30	400/1	Alcoa, commercially pure alloy 1050

(100) plane has the minimum energy. For the case of MgAl₂O₄, the data show that internal {111} planes occur with more than twice the frequency of {100} planes. This is in agreement with the free surfaces of naturally occurring spinels, which are typically dominated by {111} planes.¹⁵ The most frequently observed twin and cleavage plane in spinel is also (111). Surface energy calculations, on the other hand, have yielded ambiguous results.^{16,17} Early calculations have concluded that the (111) plane has the lowest energy,¹⁶ whereas more recent calculations indicate a minimum at the (100) orientation.¹⁷ Even so, the habits of the grains in the polycrystal are consistent with the habits of spinel crystals observed in natural settings.

Tetragonal TiO₂ (rutile) crystals display {110}, {100}, {101}, and {111} facets. The cleavage planes are {110} and {100}, and twins are found on {101} planes.¹⁸ Calculations identify the minimum energy surface as (110), whereas the (100) and (101) surfaces have higher energies.¹⁹ The internal surfaces of the rutile polycrystal show the same trend (see Fig. 1(c)): {110} planes are the most abundant, followed by {100}, {111}, and {101}. This is the only noncubic system investigated to date, and the uniaxial symmetry about the [001] direction is distinct from the other three distributions. The minimum in the distribution occurs at the [001] orientation, consistent with its absence on growth habits and the theoretical result that it has the highest energy.¹⁹

The cohesive forces in MgO, SrTiO₃, MgAl₂O₄, and TiO₂ are dominated by long-range electrostatic interactions. Aluminum has been examined as an example of a crystalline material with short-range cohesive interactions. Here, internal {111} planes are preferred. The (111) surface has the highest coordination number of any plane in this structure, and observations of microscopic cavities in aluminum suggest that this is the plane of minimum energy.²⁰ The predominance of internal planes with low surface energy, observed in all the materials, suggests that the grain boundaries made up of these planes also have a low energy. The grain-boundary energy must be equal to the sum of the energies of the two free surfaces on each side of the boundary, minus a binding energy that results from the bonds formed when the two surfaces are brought together.²¹ Thus, the current observations suggest that variations in the binding energy are small compared with the variations in the surface energy. The relationship between surface energy and grain-boundary population is also reflected in the magnitude of the deviation from random in the distributions of internal surfaces. Aluminum, which is thought to have the smallest surface energy anisotropy of the materials studied, deviates less from random than the other materials. These findings are consistent with previous reports that the grain-boundary population is correlated more strongly to the grain-boundary plane orientation than to the lattice misorientation.^{8,9}

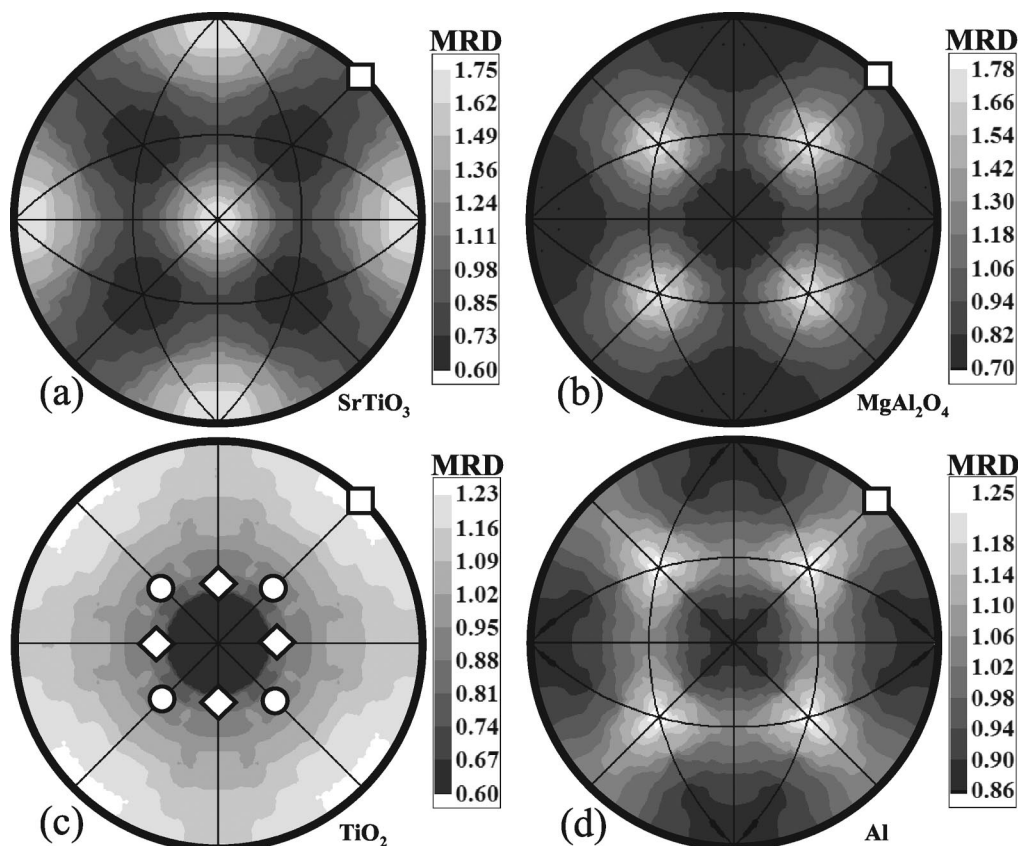


Fig. 1. Distribution of grain-boundary planes averaged over all misorientations for (a) SrTiO₃, (b) MgAl₂O₄, (c) TiO₂, and (d) aluminum. Data are shown in stereographic projection along [001], which is in the center of each projection. [110] direction is marked with a square in each projection. In (c), the directions normal to the {101} surfaces are marked with white diamonds, and the directions normal to the {111} surfaces are marked with white circles.

IV. Discussion

The average grain habits described here should be thought of as growth forms rather than equilibrium shapes. Therefore, it is not justified to assume an exact inverse correlation between the observed distribution of planes and the surface energy anisotropy. However, we should also recognize that the slow-growing faces found on crystal habits typically correspond to low-energy surfaces, and, in this way, we can explain the tendency for certain low-energy planes to be preferred on grain shapes.

Although the results show that grains in polycrystals display preferred habit planes, the topology of the network demands the simultaneous presence of nonhabit planes. For example, because the average number of faces on a grain^{12,13} is greater than the multiplicity of the habit planes, and these planes have some curvature, it is necessary to introduce nonhabit 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 nonhabit plane. Because of these geometric constraints, it is incorrect to think of the polycrystal as a collection of self-similar shapes. The preferred grain habits and the topological requirements do, however, constrain the possible crystal arrangements, and this affects all materials properties that depend on the interfacial connectivity. Furthermore, any physical property that is anisotropic also is influenced by these constraints on local arrangements.²²

The fact that internal grain surfaces have the tendency to take the same orientations as external crystal surfaces suggests that grains in polycrystals might grow by mechanisms analogous to those of crystals growing in a vapor or liquid phase. This idea has a significant impact on the conventional theory of grain growth, which assumes that the rate of growth or shrinkage of a grain is determined only by its size.²³ In fact, the rate at which a given grain grows or shrinks is 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.²⁴ According to this theory, mobility is controlled by the availability of donor and receptor sites on each 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.

V. Conclusions

Observations of internal surfaces in MgO, SrTiO₃, MgAl₂O₄, TiO₂, and aluminum lead us to conclude 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. Therefore, if the surface energy anisotropy of a phase, or even its natural habit, is known, it is possible to predict the distribution of

internal interfaces in a dense polycrystal of the same material. The results also suggest a simple relationship between the surface and grain-boundary energy and indicate that solid-state grain growth might occur by mechanisms analogous to those that govern the growth of crystals in liquid or vapor phases.

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