

The Relative Energies of Normally and Abnormally Growing Grain Boundaries in Alumina Displaying Different Complexions

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Chemically induced grain-boundary structural transitions are well documented in a number of ceramic systems. It has been hypothesized that transitions between distinct structural states, referred to as complexions, are driven by a reduction in the free energy of the grain boundaries. The current work tests this hypothesis by measuring the relative energies of boundaries on normal grains and abnormal grains in the same microstructure, which are known to have different complexions. The complexion transition from the most ordered state reduces the average grain-boundary energy by up to 45%. Similar changes in the energy are not observed for cases when the initial state is a higher order complexion that is more disordered. The results indicate that complexion transitions are influenced by both the change in free energy and the activation energy of the transition and that the dominant factor depends on the specific transition.

I. Background

ABNORMAL grain growth in crystalline materials remains an enigmatic problem. Various causes, such as differences in energy, mobility, particle drag, solute drag, or interface attachment rate between the different boundaries, have been assigned to this process.^{1–9} However, it appears that there is not likely a single explanation for the general problem. In a number of ceramic systems abnormal grain growth has been observed to occur in the presence of an intergranular film.^{10–14} An improved thermodynamic understanding of these films may provide better strategies for controlling microstructure evolution and resultant materials properties in certain systems.

The presence of intergranular films at ceramic grain boundaries has been known for several decades.^{13,15–24} The observation of intergranular films in the 1980s inspired early theoretical work on the subject. Notably, Clarke²⁵ showed that it was possible for grain-boundary films to establish an equilibrium thickness when the forces across the grain boundaries were balanced. There have also been efforts to model these films atomistically.²⁶ Recently, more generalized thermodynamic descriptions of the transition to an intergranular film from a “dry” boundary has been described.^{27–30} There has also been a numerical treatment for the formation of an analogous solid crystalline grain-boundary film, based on the energetics of segregation.³¹ One general assumption of all these models is that, under some conditions, the formation of these films is thermodynamically favorable.

Recent work by Dillon *et al.*,^{9,32} demonstrating that there are multiple grain-boundary transitions which may occur in a polycrystal, shows that the situation is more complex than originally assumed. The intergranular film is just one particular type of grain-boundary “phase” out of a host of possibilities. These grain-boundary “phases” have been termed complexions. Complexions are not phases in the traditional sense because they are stable only in the presence of the abutting bulk phase and do not participate in the Gibb’s phase rule. The general idea is that the macroscopic crystallographic degrees of freedom and chemistry of the grain boundary alone do not fix the microscopic structure or properties. The microscopic degrees of freedom may vary discontinuously as a function of thermodynamic variables such as temperature, pressure, etc. The detailed atomistic structure of every grain boundary is going to be different, and the term complexion has been used to group interfaces with similar characteristic features. For example, boundaries containing monolayers versus bilayers of adsorbate might be considered two different types of complexions. Two different boundaries containing bilayers of adsorbate may be considered the same complexion, even though the details of their structure may differ. Such a description is convenient because the boundaries containing the same complexion may have more similar properties to one another and have stability related to similar thermodynamics arguments.

Grain boundaries in doped alumina have been shown to display any one of five different characteristic complexions.⁹ The intrinsic structure of the pure boundary has been designated as an independent complexion to serve as a reference for kinetics, structure, and properties.⁹ The authors numbered these different types of boundaries I–VI in order of increasing grain-boundary mobility that also correlates with increasing boundary disorder, and we use the same numbering here. The different complexion types in alumina were found to be: I—submonolayer adsorption, II—a “clean” undoped boundary, III—bilayer adsorption, IV—multilayer (trilayer) adsorption, V—an intergranular film, VI—a wetting film. Other complexions such as solid intergranular films, or reconstructed grain boundaries might also exist in different systems or under different circumstances. This numbering system is somewhat specific to alumina, although other materials are expected to exhibit similar behavior (i.e., multiple grain-boundary complexion types).

The detailed understanding of complexions gained in early work has allowed for new experimental investigations into the thermodynamics of the complexion transitions. Recent results for alumina show that the number of complexion transitions that occur within a fixed volume increases exponentially with temperature, and linearly with grain size (i.e., grain boundary excess concentration).³³ This result suggests that chemical composition is not the only relevant thermodynamic variable. It was noted that both the change in free energy associated with a grain-boundary transition and the activation energy barrier associated with the atomic processes necessary to restructure a

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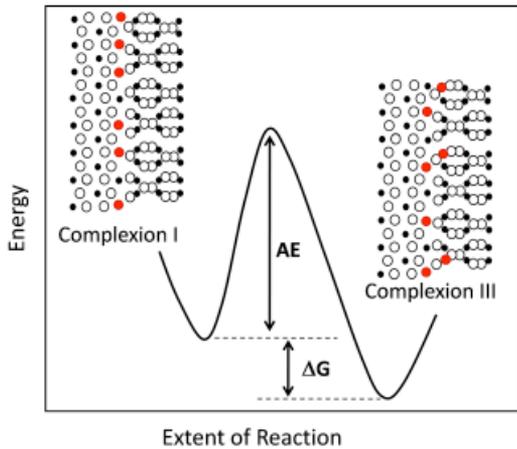


Fig. 1. Schematic energy well diagram showing the transition from complexions I to III along with schematics of the two boundary types.

grain boundary might affect the transitions. This is illustrated in Fig. 1 which schematically depicts a transition from complexion I to complexion III. The activation energy is related to the difference in free energy of the ground state and the free energy of the transition state. The existence of such an activation energy has been suggested previously.³⁴

The aim of the current work is to establish whether there is a difference in the relative free energies of boundaries that have undergone a transition and those that have not. It will also be important to understand the relative influence of the activation energy barrier in these transitions. As a multitude of complexions may exist, there may be numerous different transitions between different types of boundaries. For example, transitions between I and III might display a different behavior than those from III to IV. Each state may have different activation energies, different changes in free energy and different stabilities. Therefore, it will be necessary to experimentally measure the changes in energy related to transitions between different sets of complexions.

To quantify the energy change associated with a grain-boundary transitions, the relative energies of grain boundaries can be measured before and after a transition. The surface dihedral angle of a thermal groove may be used to characterize the energy of a grain boundary relative to the surface energy in isotropic systems. This approach may also be used to compare individual dihedral angles that are crystallographically identical. This technique has been used to identify a discontinuous change in the relative grain-boundary energy of a bismuth-doped copper bicrystal, which was thought to be an indicator of some type of grain-boundary transition.³⁵ By measuring large data sets in real polycrystals, it is possible to neglect anisotropy effects and estimate an average relative energy of the population.^{36,37} In this study, the relative energies of boundary populations that have undergone a transition will be compared with those that have not. The different grain populations in a bimodal microstructure are used to distinguish the complexion types. This is illustrated in Fig. 2. One disadvantage of this approach is that boundary migration after the transition means that the composition and crystallographic character of the boundary we measure is different from the one that underwent the transition. Prior work suggests that the complexion type may be preserved after significant growth, even though the exact chemical composition and crystallographic character may change.^{9,38,39} This result suggests some metastability exists in the system that must be considered. One advantage of this approach is that it allows us to compare distinct populations of boundaries with statistical confidence.

The current study will characterize the relative energies of populations of normal and abnormal grains of different complexion type based on the dihedral angles at thermal grooves. The results will provide insights into the relative driving force

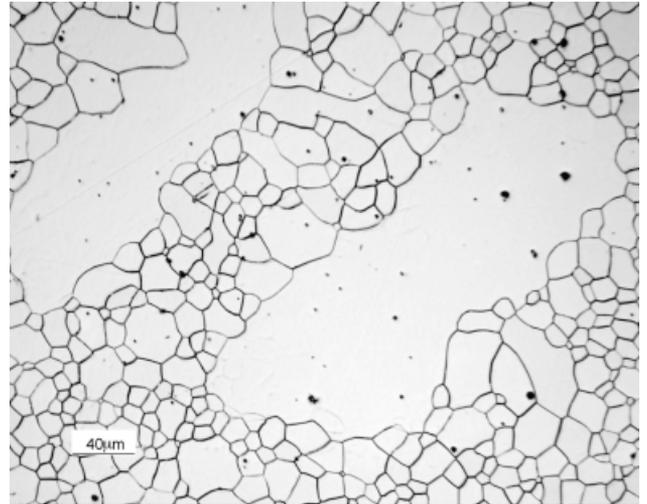


Fig. 2. Optical micrograph showing a bimodal microstructure where the abnormal grain boundaries are generally of a complexion different than the normal grains.

for complexion transitions and the role of activation and metastability in these transitions. The analysis is performed on alumina, which is a model material for such an analysis due to the large amount of preexisting knowledge of this system, its availability in high purity, its tendency to maintain stoichiometry, and its rich variety of complexion transitions.

II. Experimental Procedure

Samples of doped and undoped aluminas were prepared by methods described in detail elsewhere.⁹ The major aspects of the processing routes are described below. Alumina (Sumitomo AKP-HP, Sumitomo Chemical, Tokyo, Japan) samples were doped using dopant-cation precursor chemicals dissolved in methanol (Pharmco, Brookfield, CT). These precursor chemicals include calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) (Alfa Aesar, Ward Hill, MA), neodymium nitrate hexahydrate ($\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) (Alfa Aesar), magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (Alfa Aesar), tetraethylorthosilicate (TEOS) ($\text{C}_2\text{H}_5\text{O}_4\text{Si}$) (Alfa Aesar), and yttrium nitrate hexahydrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) (Alfa Aesar). Doped alumina powders were produced in the following compositions; 30 ppm calcia, 200 ppm silica, 500 ppm magnesia, 100 ppm neodymia, and 100 ppm yttria. All of these concentrations are expected to be similar to, in the case of calcia and silica doping, or exceed, in the case of magnesia, yttria, and neodymia, the bulk solubility.^{10,40-43} Observations of nanoscale precipitates in each of the microstructures confirm this fact.

Most samples were vacuum hot pressed under 50 MPa at 1300°C (Astro 1000, Thermal Technology Inc., Santa Rosa, CA), for varying times that were long enough to achieve near theoretical density. A set of silica-, calcia- and yttria-doped samples were also hot pressed at 1200°C for 2 h. This lower temperature processing was performed to avoid complexion transitions that may occur in these materials during hot pressing at higher temperatures. The samples were sectioned and polished to a 1 μm diamond finish. Samples were then annealed at temperatures ranging from 1200° to 2020°C (Centorr S15, Centorr Vacuum Industries, Nashua, NH) in $\text{N}_2-5\%\text{H}_2$. Magnesia-doped samples were annealed in N_2 , to avoid preferential vaporization of the magnesia by hydrogen.⁴⁴

The geometry of thermal grooves was analyzed using an atomic force microscopy (AFM) in contact mode. Line profiles measured perpendicularly across grain boundaries were used to calculate the surface dihedral angle (Ψ_s). This angle may be calculated if its height (d) and width (W) are known explicitly, using Mullins' analysis.⁴⁵ A schematic of a thermal groove is shown in Fig. 3. The dihedral angle is related to the ratio of the

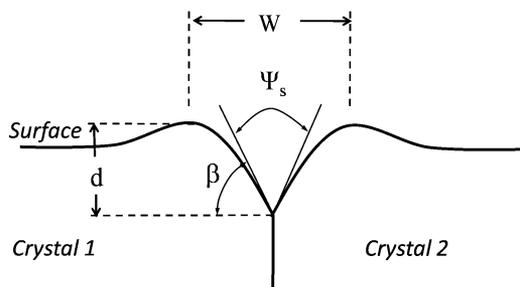


Fig. 3. Schematic of the cross-section of an ideal thermal groove.

grain-boundary energy (γ_{Gb}) to surface energy (γ_s) through the following equation:

$$\gamma_{Gb}/\gamma_s = 2 \cos(\Psi_s/2) \quad (1)$$

This relation is generally true if the surface and grain-boundary energies are isotropic and the tangent to the grain-boundary plane is normal to the surface. The analysis of real thermal grooves is complicated by several facts. The subsurface inclination of a grain boundary in a polycrystal is typically not known, so it is not possible to solve for the relative energies of an individual grain boundary. Surface and grain-boundary anisotropy will affect the measurement of any particular thermal groove, making it difficult to compare any two individual grooves without knowledge of the Wulff shape and grain orientations. However, by measuring a large number of thermal grooves it is possible to characterize the distribution. At least 200 grains of each type (normal and abnormal) were measured for each different sample. The mean of this distribution will average the variations in the surface energy anisotropy and the inclination angle of the grain boundary. It is then possible to compare the mean of two distributions that on average have similar populations of surface normals but different populations of grain-boundary complexions. The surface is important because it provides a common feature that allows the two distinct boundary populations to be compared with. A detailed summary of a technique for measuring dihedral angles in polycrystals by AFM is given by Saylor and Rohrer.³⁶ This work produced similar results to a previously developed reference line method used by Handwerker *et al.*⁴⁶

The experimental procedure is based upon previously described methods.³⁶ To summarize, three measurements of each groove were used to calculate an average dihedral angle and a standard deviation. A scan resolution between 5 and 10 nm per pixel was used. An example of a thermal groove of a normal and abnormal grain profile are shown in Fig. 4. In each case, thermal grooves of the normal grains are measured adjacent to those of the abnormal grains. The local chemistry should be more consistent by sampling adjacent boundaries. For some samples, the population of abnormal grains was rather small and a limited number of boundaries could be sampled.

The radius of curvature of the AFM tip is known to introduce artifacts into the data. Saylor and Rohrer.³⁶ detailed the specific case of thermal groove geometries and calculated the error as a function of the groove width and the surface inclination angle β , which is the complementary angle to the half-angle of the dihedral. The use of the AFM to characterize thermal grooves always underestimates the surface dihedral angle. Fortunately, this error is systematic and does not create trends in the data. Instead, each population may be shifted in the same direction but by different amounts. The maximum errors in each case were found to produce <1% change in the relative energies so this effect may be ignored in this study.

The determination of specific complexion type is based primarily on the observed grain growth kinetics correlated with the previously measured kinetics that had been related to grain-

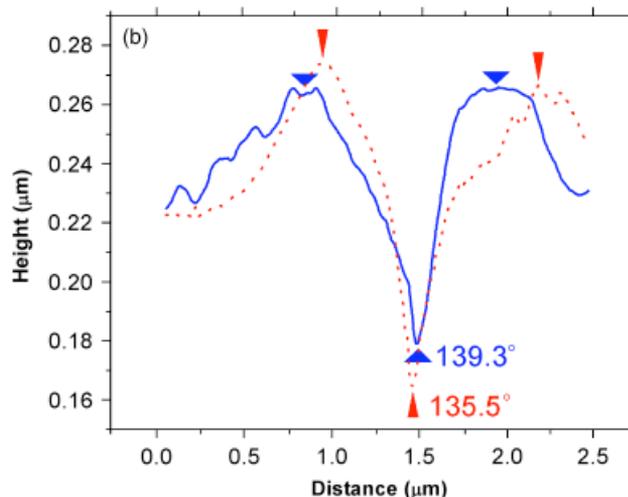
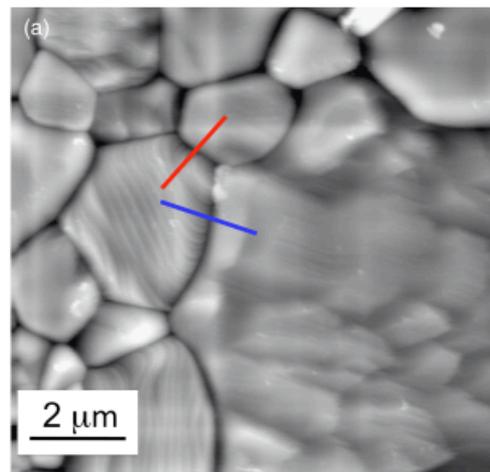


Fig. 4. (a) An atomic force microscopic scan of an abnormal grain surrounded by several normal grains in neodymia-doped alumina with lines marking the locations of profiles that are shown in (b).

boundary structure through high-resolution transmission electron microscopy (TEM).⁹ In fact, many of the same samples from the previous study were reanalyzed, in order to reduce ambiguities. Samples were studied which exhibited primarily one type of grain-boundary complexion for the normal grains. Normal and abnormal are relative terms that describe how grains behave with respect to the rest of the distribution. Boundaries of normal grains in any given doped alumina do not have to be of any specific complexion, however it has been possible to determine which complexion the boundaries at normal grains exhibit by characterizing both their kinetics and atomistic structure. It is not possible to characterize every normal boundary by TEM, but prior work shows that the vast majority of grains in the normal microstructures have consistent boundary complexions. There may also be multiple different types of complexions that abnormal grain boundaries exhibit. In alumina, the majority of the abnormal grains will be of the next complexion type in the sequence, because the occurrence of transitions follows an exponential relationship.³³ This exponential relationship between complexion transitions and temperature also explains why a large group of normal grains may contain the same complexion in a certain temperature range. The grain-boundary mobility advantage associated with a complexion transitions means that only a small fraction (a few percent) of the boundaries must undergo such a transition in order for the associated grains to consume the entire microstructure. For this study all of the abnormal grain boundaries were grouped together as exhibiting complexions that are of higher order than the normal grains, because they have all undergone a grain-boundary

complexion transition, relative to the normal grain boundaries, at some point during the microstructural evolution.

III. Results

The distributions of dihedral angles for normal and abnormal grain boundaries in neodymia-doped alumina are shown in Fig. 5. For neodymia-doped alumina (Fig. 5(a)), the transition from complexion I to more disordered complexions produces a reduction in the average grain-boundary energy, outside the experimental error. For silica-doped alumina (Fig. 5(b)), the transition from complexion IV to more disordered complexions does not, on average, produce a significant change in energy outside of the experimental error. Table I shows the median dihedral angles of boundaries with different complexions and the percentage change in average relative energy associated with the specific complexion transition. There is a clear trend that transitions from complexion I to other complexions produces a reduction in the average relative grain-boundary energy.

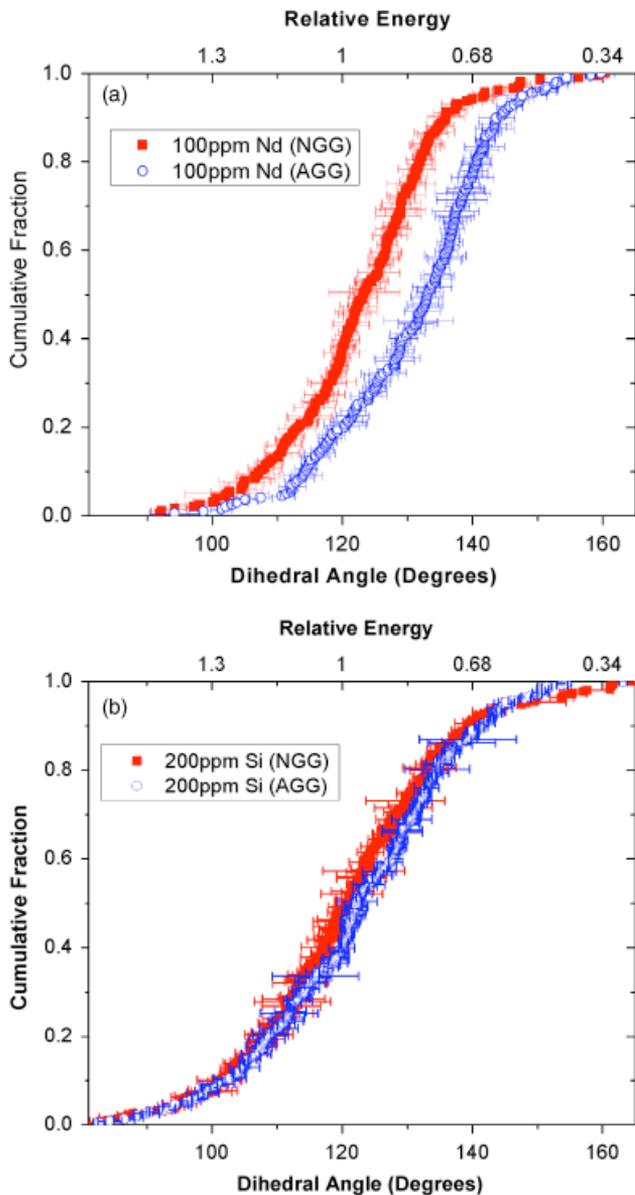


Fig. 5. Cumulative distribution of dihedral angles in (a) neodymia-doped alumina annealed at 1400°C with normal (complexion I) and abnormal (complexion III) grain boundaries, and (b) silica-doped alumina annealed at 1750°C with normal (predominantly complexion IV) and abnormal (complexions V and VI) grain boundaries.

Subsequent transitions from more disordered complexions do not produce a statistically significant reduction in energy, or even produce an increase in the average energy. In calcia-doped alumina, the abnormal grains grow in a plate-like morphology with a preference for large basal planes. These basal planes are the least likely to undergo a complexion transition in this system. It is found that the grain boundaries made up of at least one basal plane have, on average, lower grain-boundary energies than the rest of the population of normal grains. The basal planes are of the same complexion as the normal grain boundaries and are different from the other crystallographic planes on the same abnormal grain.

IV. Discussion

The surface dihedral angles of grain boundaries have been correlated with a particular average mobility. From knowledge gained through previous investigations in these systems, it is possible to correlate these kinetics with complexion type. In this way, the average dihedral angles have been correlated with complexion type. While the direct results of the study relate kinetics and energy, there is no correlation between these two parameters. The initial increase in mobility occurs along with a decrease in energy, but subsequent increases in mobility do not. The behavior is best interpreted in terms of the associated complexions. The discussion will consider the effects of segregation on grain-boundary energy, the effect of the complexion transitions on boundary energy, complexion metastability, the source of the activation barrier for complexion transitions, and experimental difficulties in determining these thermodynamic quantities.

Distributions of dihedral angles of thermal grooves in undoped alumina have been measured previously. The median values of dihedral angle in these two studies correspond well with the current results for undoped alumina.^{36,37} The undoped alumina had the highest relative energy of any of the aluminas observed. Dopants will affect the energies of both the surface and the grain boundary. It is only possible to say with certainty that doping reduces the energy of the grain boundary relative to the energy of the surface. Segregation may arise due to different effects whose nomenclature varies amongst different fields. In the current work, we define two types of segregation; equilibrium segregation and enrichment. Equilibrium segregation occurs when the solute segregates in order to minimize the energy of the interfaces to which it is segregating. Enrichment occurs when solute is present in excess of solubility and must be accommodated by partitioning the solute to interfaces or second-phases, and does not necessarily contribute to reducing the interfacial energy. In the present case, dopant levels are in excess of bulk solubility, as determined by the presence of precipitates, and it is possible that either or both may occur. It is often difficult to separate the two effects experimentally. Equilibrium surface segregation, driven by a reduction in the surface energy, may occur while thermally etching a polished surface, but surface enrichment, which would increase the energies, should not. If the surface energies of the doped samples are less than or equal to the undoped, then the grain-boundary energies in these systems must be reduced by doping.

Three factors complicate the interpretation of the major results (i.e., relating complexions and boundary energy). First, because we are measuring the energy of high mobility grain boundaries after they have migrated, the crystallographic character of the boundaries we observed were not the same as the one that underwent the complexion transition.

Second, it is expected that the enrichment and equilibrium segregation concentration of two different complexions will vary with both the crystallographic character of the grain boundary and complexion type. The concentration of solute in the boundary immediately after a complexion transition occurs is not necessarily the amount present after significant grain growth has occurred. This grain growth may drive further enrichment of the transitioned boundary because the system is saturated

Table I. The Mean Relative Energies of Different Grain-Boundary Complexions Occurring as Normal and Abnormal Grains in Doped and Undoped Alumina Annealed at Different Temperatures

Chemistry	Temperature (°C)	Complexion	Relative energy	% energy change (complexion transition)
Undoped	1400	II (NGG)	1.11	
	2020	II (NGG)	1.08	
100 ppm-Nd ₂ O ₃	1400	I (NGG)	0.95	-16
	1400	III (AGG)	0.8	
100 ppm-Y ₂ O ₃	1400	I (NGG)	0.57	-46
	1400	III (AGG)	0.31	
500 ppm-MgO	1400	I (NGG)	1.07	-26
	1700	III (NGG)	0.79	
30 ppm-CaO	1200	I (NGG)	0.82	-20
	1200	III (AGG)	0.69	
200 ppm-SiO ₂	1200	I (NGG)	0.68	-10
	1200	III (AGG)	0.61	
30 ppm-CaO	1400	III (NGG)	1.02	0.1
	1400	IV+ (AGG)	1.02	
	1400	III (Basal plane)	0.77	
200 ppm-SiO ₂	1400	III (NGG)	0.65	9.5
	1400	IV (AGG)	0.71	
200 ppm-SiO ₂	1750	IV (NGG)	0.98	-1.7
	1750	V+ (AGG)	0.96	

with solute. The difference in solute concentration of boundaries with different complexions in a saturated system has been measured experimentally.^{41,47} This implies that the measured energy may not necessarily represent the energy immediately following the transition, which was the driving force for the transformation.

The final major complication is associated with the fact that we are attempting to measure a change in energy of a transition, but we have no ability to measure the activation term in this transition. Often average activation energies may be measured directly from temperature dependencies, but in this case it is expected the critical temperature at which a transition will occur is a function of macroscopic degrees of freedom associated with the grain boundary (grain-boundary character). Therefore, the presence of an anisotropic grain-boundary character distribution induces a temperature dependence even absent an activation barrier.⁴⁸ This relation has been derived theoretically,^{9,27,28} discussed by the authors in relation to other experiments,³³ and is exemplified by calcia-doped alumina where there is a significant difference in the transition behavior of the basal plane as compared with grain boundaries comprised of other planes.³⁸ Additionally, the activation energy is likely to be a function of grain-boundary character.

In a relatively untextured sample, such as the aluminas studied here, there is no particular orientation relationship between any particular abnormal grain and grains elsewhere in the microstructure that do not intersect it. When an abnormal grain grows it will randomly intersect surrounding grains creating boundaries whose character is somewhat random (a crystallographic growth preference may fix two of the five macroscopic parameters that characterize the grain boundary). This is the common paradox associated with abnormal grain growth in many systems. If abnormal growth results from any factor that is correlated with the specific boundaries around the abnormal grain, then how does it persist as it consumes its neighbors absent any significant crystallographic texture? This question is difficult to answer without introducing either some critical barrier that only the abnormal grain may overcome, such as a nucleation barrier or second-phase depinning, or relying on some metastability that allows the abnormal boundary to persist. Because the distribution of misorientations across the abnormal grain boundaries is somewhat random after significant growth, it is likely that a similar distribution of misorientations may be found in the normal population. This is especially true of the relatively equiaxed normal and abnormal grains in the silica-

and yttria-doped aluminas observed. If the distribution of grain-boundary misorientations is not drastically impacted then the energy differences or lack of should relate directly with the complexions present. The interesting result is that if the energy of the abnormal grains is significantly lower than the normal grains then some reasonable fraction of the normal grains must be metastable relative to a transition. This is evidence that metastability in a certain complexion type may exist. Alternatively, if the abnormal grain-boundary energies are greater than or equal to those of the normal grains then most of the abnormal grain boundaries will be metastable relative to the complexions on the normal boundaries. It is suspected that in the latter case the abnormal grain boundaries would originally have transitioned to a lower energy, but later become metastable as they grow through the neighboring grains.

These results indicate that the activation barrier is a major limiting effect in determining which boundaries will undergo the first complexion transition (I–III). For the higher order transitions (III–VI), the occurrence of a specific grain-boundary character where the transition is thermodynamically stable should be the major factor in determining which boundaries undergo a transition. Although, it is quite obvious that both conditions, a reduction in energy and overcoming an activation barrier, must be satisfied in order for a transition to occur.

There are two likely contributors to the metastability of a higher order complexion. As discussed above, the saturation level for grain-boundary enrichment or equilibrium segregation of the two different complexions may be different, with the more ordered complexion likely having a lower saturation level. After the abnormal grain has grown significantly its boundaries will become enriched in solute relative to the more ordered complexions. To transition back to an ordered complexion, this solute must either precipitate or dissolve into an already saturated lattice. Either process will require energy and will increase the activation energy for a reverse transition relative to the initial transition. Therefore, complexion transitions are not thermodynamically reversible after appreciable growth. The second source of metastability is related to the first, because both of these processes will be kinetically limited. For example, there will be a finite time required to diffuse all of the excess solute to a precipitate. During this time the grain will also be growing and the boundaries will be accumulating more solute. This may lead to a steady-state where metastability is maintained. It has been observed, previously, that low-angle boundaries that are typically low-energy may induce a reverse complexion transition to a

more ordered grain boundary.³³ This suggests that if the driving force is large enough a reverse transition will occur.

The measured data for the relative energies of boundaries that have and have not undergone a transition indicate that, for alumina, the transition from complexions I to III produces a reduction in the average grain-boundary energy. However, subsequent transitions do not produce a measurable reduction in energy or may even increase the average grain-boundary energy. For a transition to occur at the original boundary, there must be a reduction in energy. After some growth of the abnormal grain the boundaries may either be stable or metastable depending on which transition has occurred. For the first transition from complexions I to III, the activation energy associated with restructuring the grain boundary should be the major limiting effect in the transition. This suggests that it is difficult to rearrange atoms in the grain-boundary core. This complexion starts as a submonolayer and transitions to a bilayer. Solute initially sits in large cage sites in the grain-boundary core and must adsorb onto the faces of the adjacent grains. This process must be accompanied by reordering of the local bonding and structure, which produces an activation barrier. In subsequent transitions this activation energy and atomic reordering is not the most pronounced limiting effect.

These results may be explained in the context of recently developed thermodynamic models describing grain-boundary complexion transitions.^{27–29,49,50} Generally, these models have considered the thermodynamic balance on a grain boundary where gradients in crystallography, orientation, and chemistry at the boundary drive disordering and the free energy penalty of disorder and long-range van der Waals forces favor ordering. The first structural disordering transition (complexions I–III) should be driven by a reduction in the misorientation energy penalty associated with the grain boundary. This is the primary premelting or prewetting transition, and is expected to be associated with a relatively large reduction in grain-boundary energy. Alternatively, the energy differences amongst complexions III–VI are likely due to the long-range interfacial forces and layering effects. It is expected the energy differences and the activation energies are smaller between these complexions. While the activation barrier is not the major limiting effect in influencing the occurrence of higher order complexion transitions, it is still not trivial. If there were no barrier, the grain boundary would be free to thicken continuously, and monotonically with increases in grain size. This is not observed to occur in alumina,^{9,38,39} but may be possible in other systems.¹⁴ Fully understanding the details of this process will require detailed atomistic modeling.

Previous measurements, of the number density of abnormal grains that form as a function of temperature, show an exponential dependence.³³ These measurements were made on samples that had transitioned from complexion III to higher order complexions. A transition between complexions should have an associated activation barrier and reduction in free energy that is the driving force for the transition (ΔG). Exponential temperature dependencies may result from two distinct sources. Activation limited processes will have an exponential dependence due to the form of the Boltzmann distribution. The second case is more complicated. The critical temperature at which a boundary is susceptible to a complexion transition will be a function of grain-boundary character ($\Delta G = f(T, \text{GBCD})$). The relationship between a grain-boundary's energy and its occurrence in the population is an exponential with low-energy boundaries occurring in a greater frequency than high-energy boundaries.^{51,52} Results of theory and experiments suggest that low energy boundaries are less susceptible to complexion transitions.^{9,27,28} At low temperatures there are a small number of high-energy boundaries that are susceptible to complexion transitions. As the temperature increases, the number of susceptible boundaries increases exponentially due to the nature of the grain-boundary character and energy distributions. Therefore, the grain-boundary energy anisotropy may lead to an exponential temperature dependence. It is likely that both effects will have some influence

on the behavior of polycrystals. However, the experimental results suggest that for transitions from complexions I to III, in alumina, the major limiting effect on the temperature dependence is the activation barrier and that higher order transitions are mainly influenced by the grain-boundary anisotropy. These experimentally observed exponential temperature dependencies might distinguish complexion transitions from other proposed mechanisms for abnormal grain growth, such as solid-state wetting⁸ or two-dimensional nucleation limited growth⁷ that do not predict such a relationship.

The current results provide some of the first experimental insights into the complex nature of complexion transitions. The data should be useful in developing and validating new theory, which will be necessary for fully understanding the nature of complexion transitions and abnormal grain growth. To develop predictive models for complexion transitions, it will be necessary to understand the relative roles of the activation barrier and crystallographic anisotropy.

V. Conclusions

The surface dihedral angles of normal and abnormal grain boundaries containing different complexions have been characterized to determine their relative energies. The complexion behavior has been determined based on transport kinetics and established relationships between the two phenomena. Complexion transitions can reduce the free energy of a grain boundary by as much as 45%. In some cases a reduction in the energy was not observed, but this may be because the observations were made long after the transition had occurred, and grain-boundary migration altered the chemistry and crystallography of the boundaries. The results suggest that both the activation energy and the crystallographic character of a specific boundary are both important in complexion transitions. One of these two effects may dominate depending on the nature of the complexion transition.

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