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Demystifying the role of sintering additives with "complexion"

Shen J. Dillon, Martin P. Harmer *

Center for Advanced Materials and Nanotechnology, Lehigh University, 5 East Packer Avenue, Bethlehem, PA 18015, United States

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Abstract

The role of additives has long been a theme in sintering science. Recently, it has been discovered that ceramics may contain multiple different grain boundary phases (complexions) that are chemically induced by certain additives. These complexions are useful in explaining a number of anomalous phenomena associated with sintering, such as abnormal grain growth. The current work investigates how transitions between these complexions occur and at which grain boundaries they are most likely to occur. The number of complexion transitions that occur increases linearly with grain size (grain boundary excess concentration), and exponentially with temperature. The results suggest that grain boundary energy and anisotropy are important in predicting which and how many grain boundaries will undergo such a transition.

Keywords: Grain growth; Al_2O_3; Grain boundaries; Sintering

1. Introduction

The use of sintering additives has been an effective strategy for microstructure control in ceramics. Sir Richard J. Brook performed early pioneering work on both microstructural evolution during sintering, and the optimization of processing and microstructures through the use of additives.[1–16] Prof. Brook's classic work on modeling pore–boundary interactions is a mainstay of sintering and grain growth textbooks.[17] Brook maps[17] have provided an easy and convenient way of visualizing a complex problem. His insight into the subject focused our attention on important ratios; the ratio of the pore to boundary mobility,[17] the ratio of diffusional pre-exponential to activation energy,[18] and the ratio of the relative densification rate to the relative grain growth rate.[19–22] He was the first to recognize the effect of solute drag on the grain growth exponent and its critical effect on microstructural evolution in ceramics.[23] He was helpful in guiding researchers in the field to appreciate the complexity of the sintering problem.[21,24–27] Much of this is well described in his classic review paper on controlled grain growth.[28] He made many important contributions by designing and implementing critical experiments.[8,21,29,30] Of particular note, was his proposed strategy to use hot pressing as a means to study densification without grain growth.[21] He introduced the concept of fast firing as a new processing strategy that has become widely established as an effective approach for producing dense fine-grained ceramics by pressure-less sintering.[19,20] In addition to basic science, he also contributed to developing a number of novel ceramic processing techniques.[31–36]

Despite much progress, however, fundamental mechanisms are still debated even after 50 years of continuous study.[37] Two examples of this are the mechanism(s) for abnormal grain growth, and the classic debate over the role of magnesia as a sintering aid.[37–39] However, the recent discovery of interface "complexions" offers a new perspective and possible solution to such problems.[40,41]

Interface complexions are equilibrium interface 'phases' that have associated thermodynamic properties.[41] Interface complexions have some characteristic equilibrium feature such as; a characteristic solute profile, a crystallographic reconstruction, a common disorder parameter, interfacial film width, etc. Thermodynamics predict that their stability is dependent on temperature, chemistry, and crystallography.[41–44] The well-documented intergranular films in materials such as silicon nitride and silicon carbide are one example of a grain boundary complexion.[45–48] Similar interface complexions have also been observed in zinc oxide,[49] silicon nitride,[50] olivine,[51] silicon carbide,[52] alumina,[53] ruthenates,[54] strontium titanate,[55] barium titanate,[56] aluminum nitride,[57] metal–ceramic interfaces,[58,59] and a nickel–tungsten alloy.[60] Recent work by the authors has shown that six distinctly different grain boundary complexions may exist in alumina, and that several grain boundary complex-

* Corresponding author. Tel.: +1 610 758 4227; fax: +1 610 758 4244.
E-mail address: mph2@lehigh.edu (M.P. Harmer).

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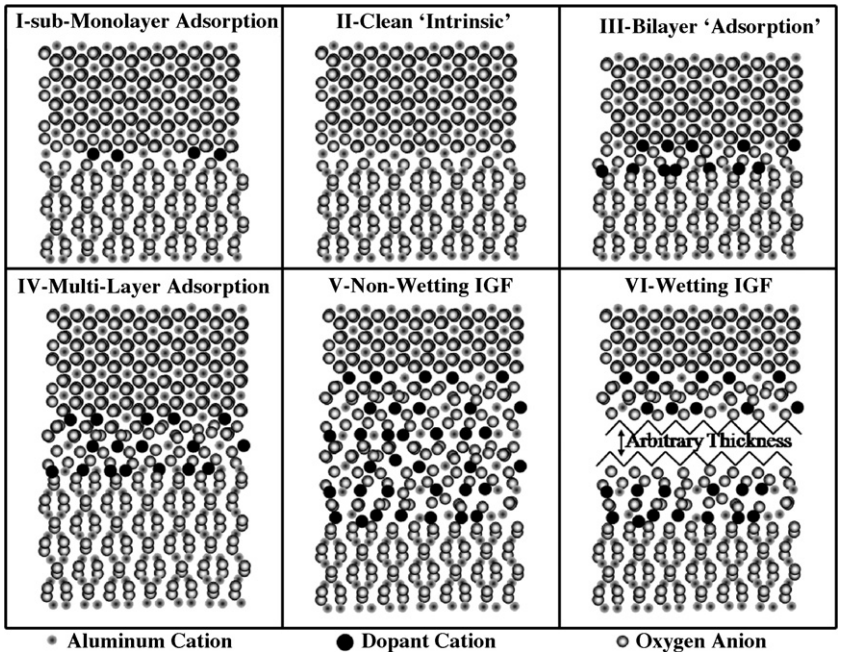

Fig. 1. Schematic of the six different grain boundary complexions observed in alumina. These include: submonolayer adsorption, a 'clean' boundary, bilayer adsorption, multilayer adsorption, a non-wetting intergranular film (IGF), and a wetting IGF.

ions may coexist in the same microstructure.[40,41] These grain boundary complexions in alumina are submonolayer adsorption, the clean 'intrinsic' boundary, bilayer adsorption, multilayer adsorption, a non-wetting intergranular film (IGF), and a wetting intergranular film.[41] These six boundaries are listed in order of increasing grain boundary mobility, and are shown schematically in Fig. 1. Each grain boundary complexion has its own associated characteristic average grain boundary mobility (absent significant second-phase drag effects[61–63]), and there is a trend of increasing mobility with increasing disorder within the core of the grain boundary. The coexistence of any two or more complexions within a microstructure is the condition for abnormal grain growth. Certain dopants promote the coexistence of multiple complexions and high mobility complexions, while others stabilize low mobility complexions. The role of magnesia in preventing abnormal grain growth in alumina is to stabilize a single low mobility complexion.[41] In this sense, understanding grain boundary complexions helps to simplify a complex problem. However, it is still not clear how, why and under what conditions *transitions* between different complexions occur.

Prof. Brook was also one of the first researchers to recognize the role of inhomogeneities in the sintering process, and treat them quantitatively.[27,64] Since early work on the subject, abnormal grain growth in alumina has often been attributed to inhomogeneities.[65] There are two principal kinds of inhomogeneities that may exist in a green or sintered body; extrinsic and intrinsic. Extrinsic inhomogeneities are associated with imperfect processing. Poor mixing, chemical segregation during drying, agglomeration, or defects in powder consolidation are examples of cases where inhomogeneities may arise. Intrinsic inhomogeneities are associated with anisotropy in the material.[66]

It has been shown that an inhomogeneous distribution of impurities or dopants in alumina would produce abnormal grains growing where the chemical composition was highest.[67,68] A number of researchers have observed qualitatively that increasing dopant concentration increases the volume fraction of abnormal grains in alumina.[69–72] Some have suggested that there is some 'critical concentration' above which a grain boundary

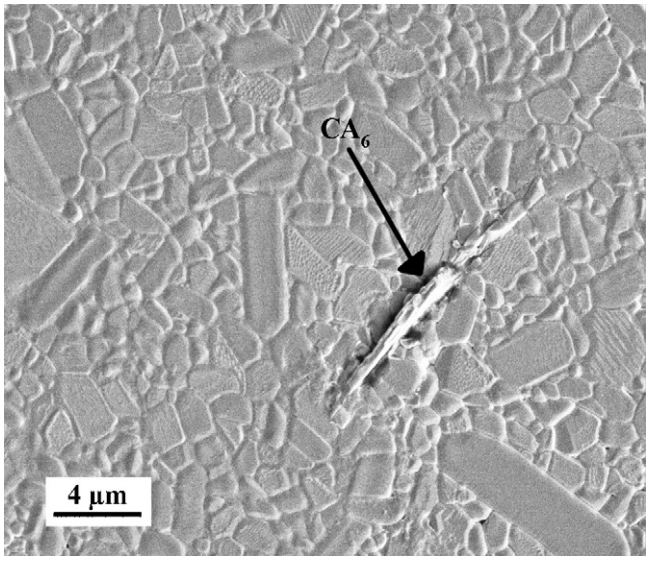

Fig. 2. SEM micrograph of 100 ppm calcia-doped alumina showing a second-phase calcium hexaluminate particle marked by an arrow. All the grain boundaries in contact with this particle will be saturated with calcium, and none of them have become abnormal. However, there are other abnormal grains in the microstructure that are not associated with any visible second phase. This indicates that the presence of a saturated boundary alone will not produce abnormal grain growth in alumina.

always becomes abnormal.[73,74] It is not surprising then that regions of the material with the highest levels of dopant or impurities may show complexion transitions and abnormal grain growth first.[40] However, even when the concentration is high locally it is still questionable which particular grain boundary might undergo a structural transition necessary to produce abnormal grain growth. The cation diffusivity along a grain boundary of alumina is known to be orders of magnitude higher than its diffusivity across a grain boundary.[75] It is possible that at high temperatures cations segregated to the grain boundaries may be able to redistribute themselves locally, to some extent. Fig. 2 illustrates the difficulty in trying to predict exactly which grain boundaries will become abnormal based solely on considerations of dopant level. In this figure, there is a large calcium hexaluminate second-phase particle (indicated by the arrow) surrounded by normal grains. The grain boundaries of all of these grains should be saturated with calcium, assuming they are in equilibrium with the precipitate they are in contact with. In fact, in order for the precipitate to grow to this size calcium had to diffuse along the grain boundaries of the adjacent alumina grains. While the boundaries of these grains are saturated and have not become abnormal, there are abnormal grains nearby in the microstructure that are not in contact with second phase. While there may be unseen second phase below the surface of the sample, it still does not discount the fact that some saturated grain boundaries do not become abnormal while other saturated grain boundaries do. This figure suggests that inhomogeneities introduced during processing (extrinsic) may not be the only factor affecting complexion transitions. The intrinsic inhomogeneity may play an important role in affecting the local chemistry and grain boundary complexion transition.

Because the presence of abnormal grains and their kinetics are so intimately associated with their particular grain boundary complexion,[41] it is possible to study the distribution of grain boundary complexions in a microstructure by monitoring the distribution of abnormal grains. A quantitative description of this distribution with sintering time, grain size, dopant composition, dopant species, and temperature may provide insight into

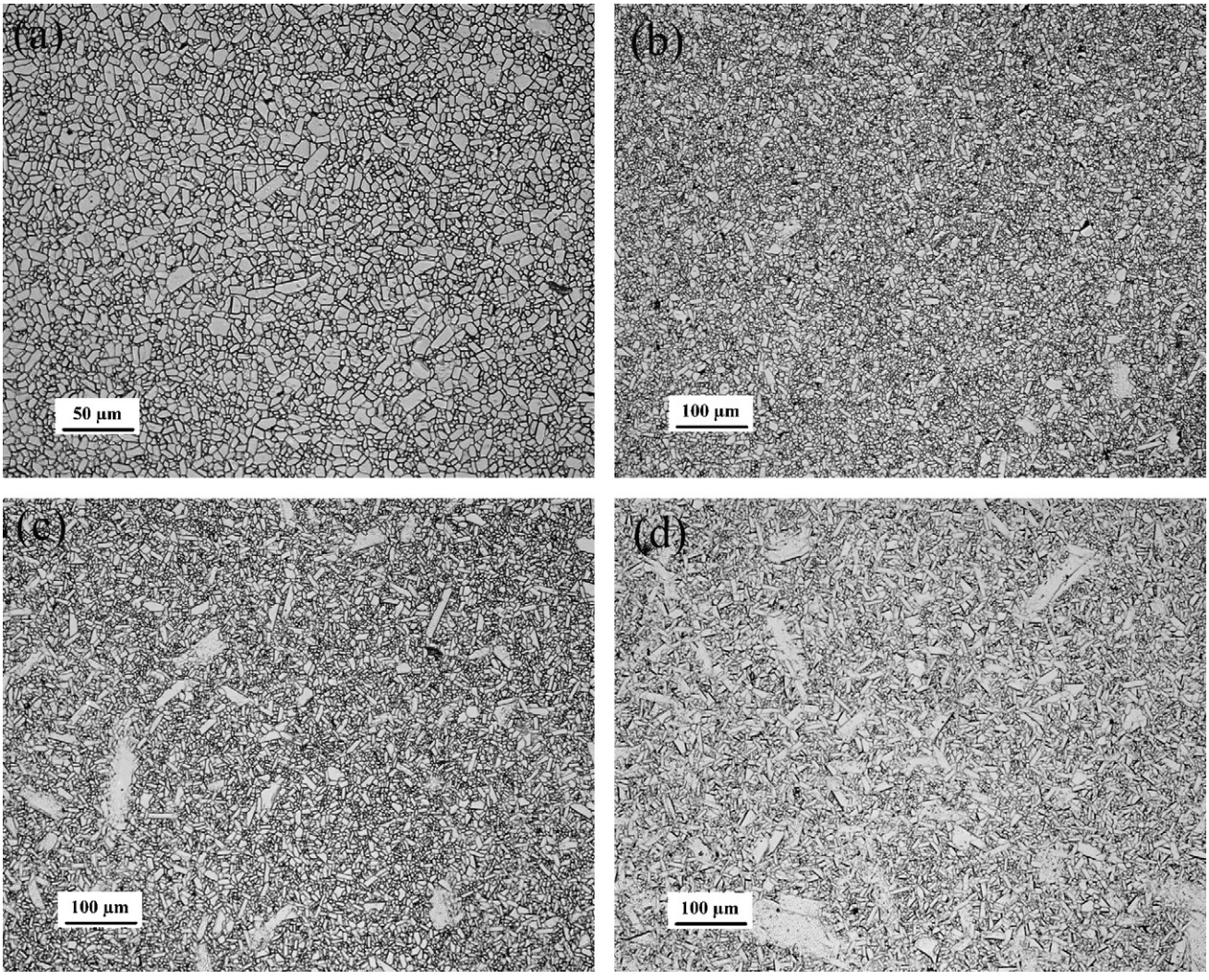

Fig. 3. Representative optical micrographs of 30 ppm calcia-doped alumina grown to equivalent normal grain size (9 μm) at (a) 1400 °C, (b) 1475 °C, (c) 1550 °C, and (d) 1625 °C.

understanding which grains are likely to undergo a complexion transition (i.e. abnormal grain growth). This paper attempts to quantitatively understand transitions between complexions, the cause of these transitions, and their relation to inhomogeneities. We hope this work adds insight into a field that Prof. Brook has made great contributions to, and carries on his themes of understanding the role of additives, inhomogeneities, and providing simplification of a complex problem.

2. Experimental procedure

Silica (SiO_2) doped alumina (α-Al_2O_3) samples were prepared in nominal composition of 200 ppm. Alumina powder (Sumitomo, AKP-50 99.995%, Sumitomo Chemical, Tokyo, Japan) was mixed with tetraethylorthosilicate (Alfa Aesar, Ward Hill, MA) in methanol, dried and calcined. Calcia (CaO) doped alumina samples were prepared in the nominal compositions of 30 and 100 ppm. Alumina powder was mixed with calcium nitrate ($Ca(NO_3)_2$-$4H_2O$) (Alfa Aesar Puratronic 99.9995%, Alfa Aesar) in alcohol, dried, and subsequently calcined. All powders were processed in a class 1000 clean room in acid washed polytetrafluoroethylene and polyethylene containers. Samples were hot pressed at 50 MPa, for 2 h at 1300 °C (Astro 1000, Thermal Technology Inc., Santa Rosa, CA). Samples were annealed at temperatures ranging from 1325 to 1675 °C (Centorr S15, Centorr Vacuum Industries, Nashua, NH). Grain growth data from a previous study was used to calculate sintering times for calcia-doped alumina that would produce an equivalent normal grain size in each sample at different temperatures.[61] 30 ppm calcia-doped alumina was annealed to produce a normal grain size of 9 μm, and 100 ppm calcia-doped alumina was sintered to produce a grain size of 3.5 μm. This was done so that samples at different temperatures would have an equivalent grain boundary excess composition of calcia (neglecting the weak temperature dependence of solubility in alumina). Previous studies have shown that unimpinged abnormal grain boundaries separate from second-phase particles and excess solute leaving them entrapped within the abnormal grain, rather than pushing it in front of the grain. This indicates that the equivalent grain boundary excess concentration for equivalent normal grain size will be valid regardless of the volume fraction of abnormal grains. Other samples were annealed for various times to determine the number density of abnormal grains as a function of grain size. Heating and cooling rates of 100 °C/min were used. Ten low magnification images were taken randomly using a light optical microscope. The number of abnormal grains in each image was counted by hand. Measurements of normal grain size were performed using the linear intercept method.

Electron back scatter diffraction (EBSD) was performed in the FEI XL30 using the TSL system which included a digiview camera and the OIM data collection software (TexSEM, EDAX, Mahwah, NJ). EBSD was performed at 20 kV with the sample tilted to 70°. Samples for the transmission electron microscopy (TEM) (Jeol 2200FS, Jeol USA Inc., Peabody, MA) were prepared using a focused-ion beam microscope (FEI DB235, FEI Company, Hillsboro, Oregon).

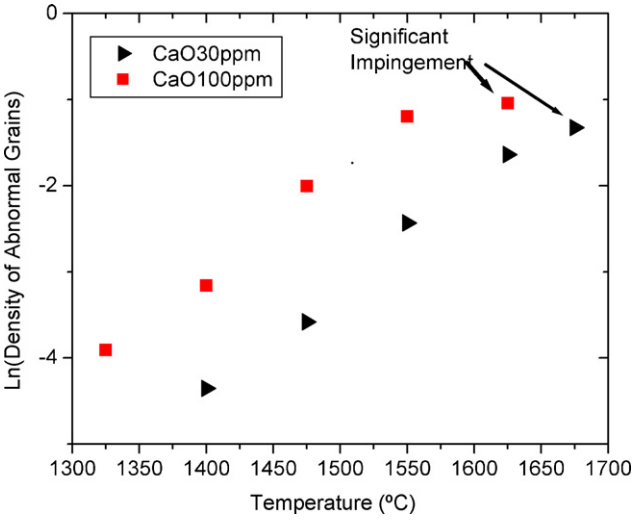

Fig. 4. Plot of the number density of abnormal grains versus temperature for two different constant excess grain boundary compositions in alumina doped with different levels of calcia, which shows an exponential dependence. These samples had an average grain size of 3 and 9 μm for the 30 and 100 ppm calcia-doped samples, respectively.

3. Results and discussion

Representive microstructures of 30 ppm calcia-doped alumina are shown in Fig. 3. Fig. 4 shows the number density of abnormal grains for two different constant excess grain boundary compositions (i.e. equivalent average normal grain sizes) in alumina doped with different levels of calcia. The solubility of calcia in alumina is thought to be near 30 ppm so the excess grain boundary composition in this alumina should be much less than that of the 100 ppm calcia-doped alumina. This is reflected in the fact that the number density of abnormal grains in the 100 ppm calcia-doped alumina is always higher for any given temperature. The density of abnormal grains increases exponentially with increasing temperature up until the point of impingement.

The increase in the number density of abnormal grains is linear with grain size (Fig. 5). The number density was normalized by dividing the measured density by the average volume of the abnormal grain. This was done to account for stereological considerations about the probability of cross-sectioning through a

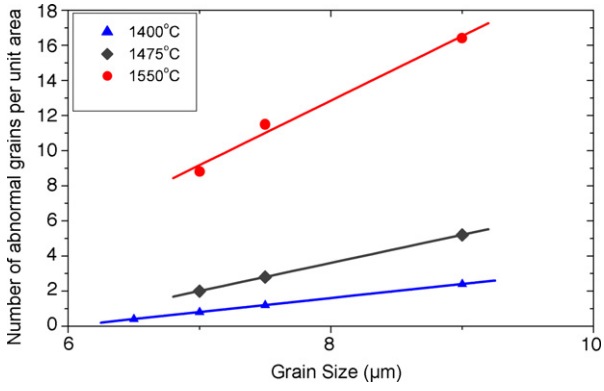

Fig. 5. Plot of the number density of abnormal grains versus grain size, which shows a linear dependence.

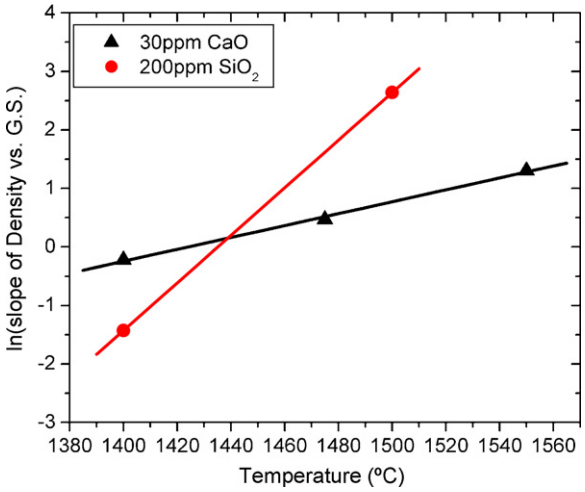

Fig. 6. Plot of the slope of each line of number density versus grain size (Fig. 5) versus temperature, for 200 ppm silica-doped alumina and 30 ppm calcia-doped alumina.

particular grain. The slope of each line of number density versus grain size increases exponentially with increasing temperature, as shown in Fig. 6. The slope of the line for calcia-doped alumina in this figure is in agreement, within error, with the slope of the line in Fig. 4. The grain boundary excess composition is directly proportional to the grain size up to the grain boundary saturation limit. This indicates there is a general trend in the data that the number density of abnormal grains increases linearly with increasing grain boundary excess concentration and exponentially with temperature for any particular grain boundary excess concentration.

For any particular grain boundary there is some level of excess dopant concentration necessary to induce a transition. It is known that pure undoped alumina does not undergo any complexion transitions up to 99% of the melting temperature.[75] As the grain size increases the grain boundary excess increases, which increase the probability that some individual grain boundary will reach the level of excess necessary to induce a transition. This explains the linear relationship between the number density of abnormal grains and the grain size. However, for some grain boundaries the grain boundary excess level required to induce a transition may be above the saturation limit and a precipitate will form before a transition may occur.

The idea that a 'critical concentration' is the only criterion for a grain boundary transition and abnormal grain growth is proved false by the temperature dependence of the number density of abnormal grains. If there were a critical concentration then the number density of abnormal grains would be constant for a constant grain boundary excess concentration, regardless of the temperature.

The results also contradict a theory that has grown in popularity lately, that abnormal grain growth in alumina, doped in the parts/million levels, is nucleation limited interface controlled.[38] The theory does not predict such a temperature dependence or grain size dependence of the number density of abnormal grains. The current authors have previously shown theoretically that nucleation limited interface controlled abnormal grain growth theory may not be applied to single phase and pseudo-single phase alumina.[39] The current experimental evidence along with other experimental evidence further discounts the theory.

The activation energy for the transitions is 1002 and 257 kJ/mol for silica-doped alumina and calcia-doped alumina, respectively. The underlying source of this apparent activation energy is not obvious. There are two factors that may affect the measured activation energy for a grain boundary complexion transition. There is the activation energy barrier associated with the grain boundary transitioning from one stable state to another through some intermediate state (ΔE), and there is the temperature dependence of the free energy of the two different complexions that describes which is more stable (which results from temperature dependence of ΔG). This is shown schematically in Fig. 7. The thermodynamics of such a transition have been described theoretically by Tang et al.,[42–44] based on a modification of Cahn's critical point wetting theory.[76] They predict that for any particular temperature the likelihood of a grain boundary transition increases with increasing misorientation and dopant concentration. They also predict that for a particular dopant concentration the lower misorientation boundaries will transition at higher temperatures and vice versa.[42–44] It may be more general to consider grain boundary energy rather than misorientation because the inclination of the grain boundary plane is likely to be a critical factor.[66,77] In this case, the likelihood of a transition should increase with increasing grain boundary energy. Saylor et al.[78] have shown experimentally that the density of boundaries of a particular energy increases exponentially with decreasing grain boundary energy. The work of Tang et al.[42] and Saylor et al.[78] predicts exactly what we see experimentally, that the number of abnormal grains will increase exponentially with increasing temperature. At any particular temperature, there may be a grain boundary energy above which all boundaries having those energies will go through a transition. This is shown schematically in Fig. 8, where $T_2 > T_1$ and that the number of grain boundaries that undergo a transition is equivalent to the area under the curve. Similar ideas have been proposed for the effect of anisotropy on wetting.[79] The idea that the probability of a grain boundary transition is intimately related to its grain boundary energy is supported by evidence from previous studies such as; low energy basal planes are the least likely to undergo a transition in calcia-doped alumina,[61] and that low-energy bicrystal boundaries are less likely to transition than high-angle grain boundaries in real microstructures.[80,81] Several previous stud-

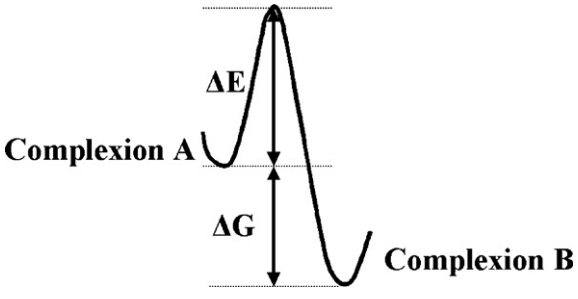

Fig. 7. Simple schematic of an energy barrier to a grain boundary transition.

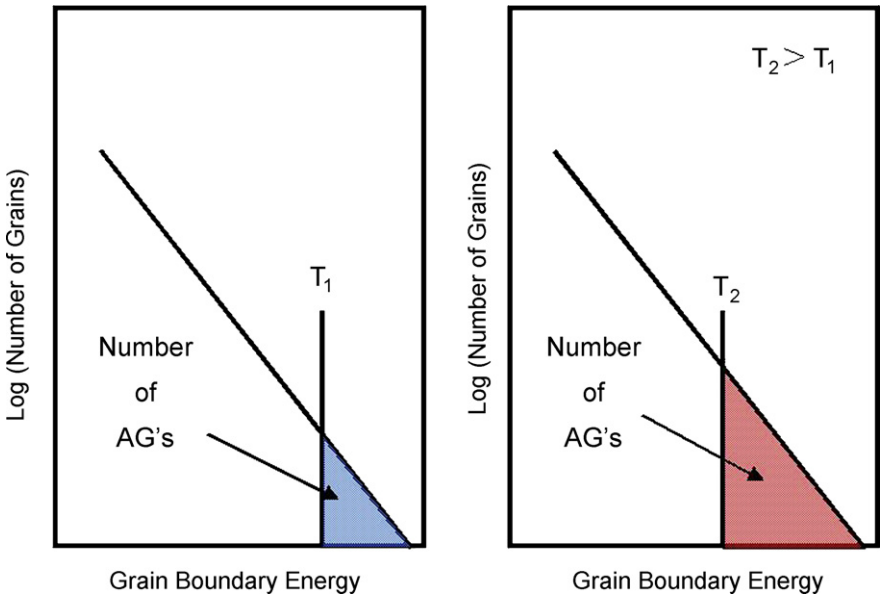

Fig. 8. Schematic showing how a linear increase in temperature produces an exponential increase in the number density of abnormal grains by decreasing the critical grain boundary energy necessary to produce a transition.

ies have shown that high-energy planes and grain boundaries show the highest levels of dopant segregation.[66,82–84] This effect also increases the likelihood of a grain boundary transition for high-energy grain boundaries relative to low energy grain boundaries. This suggests that intrinsic inhomogeneities in interfacial energy and dopant concentration at a particular boundary due to anisotropy are the major effect in complexion transitions.

However, it is known that after a grain boundary transition, a single abnormal grain samples various misorientations and grain boundary planes as it consumes multiple neighboring grains. The fact that an abnormal grain continues to grow after the initial grain boundary character is lost suggests that the true activation energy associated with transitioning from one complexion to another (ΔE) is not trivial. Small grains are often found entrapped within a large abnormal grain. EBSD indicates that these grains are low-angle misorientations or near coincident site lattice boundaries (Fig. 9a), and transmission electron microscopy indicates that the intergranular film associated with the abnormal growth of the large grain has dewet this entrapped grain (Fig. 9b). This result shows that it is possible for a grain boundary to transition back to its more ordered structure, but that the associated driving force (i.e. change in free energy) must be large. This is supported by previous results from Luo et al.[85] who showed that such a reverse transition took weeks to occur. A reverse transition may be less likely to occur because the higher concentration of solute in the more disordered boundary must be removed before such a transition may occur. This imposes a thermodynamic barrier to reverse transitions, in that there is an energy that must be overcome to either nucleate a precipitate or dissolve solute in the lattice above its solubility limit. This means that the activation energy associated with a reverse transition would be greater than that of the initial grain boundary

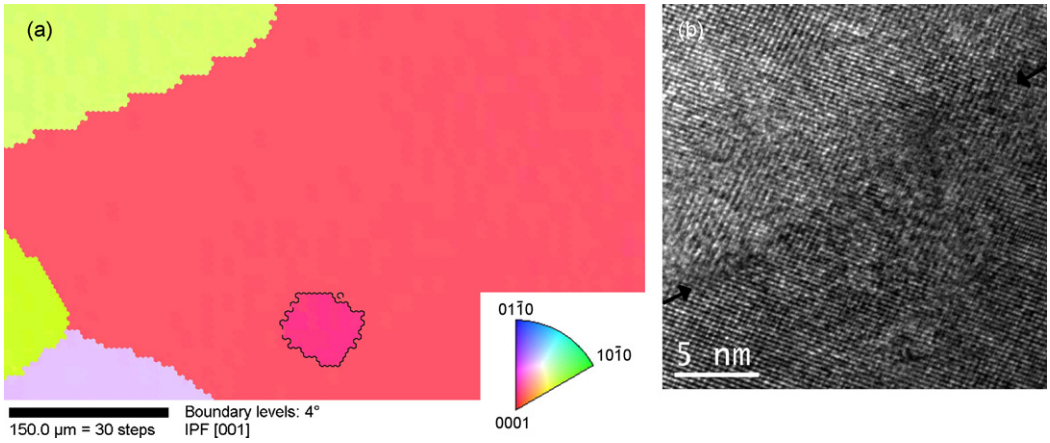

Fig. 9. (a) Orientation image maps of a small grain entrapped (outlined) in large abnormal grain. In (a) the entrapped grain is a low-angle boundary (~4°). (b) HRTEM micrograph of a near Σ1 (low-angle) grain boundary, which shows no evidence of any intergranular film, which indicates that this boundary was dewetted by the film on the abnormal grain. The boundary is indicated by the arrows, and is difficult to see because it is a low-angle boundary.

complexion transition. Either the precipitation or dissolution of the excess solute is also kinetically limited processes. The time it takes them to occur may be longer than the time it takes to grow through a grain that forms an unstable boundary with the growing abnormal grain. This suggests that the abnormal grains may be metastable due to thermodynamic and kinetic limitations. Additionally, there is no theoretical explanation as to why the energy barrier (ΔE) to a grain boundary transition would be as significantly different for different chemistries as the measured activation energies for silica- and calcia-doped alumina. While the valence is different, it might be expected that calcia, which is the larger cation, might produce a larger energy barrier to a transition. Both boundaries have similar mobilities, so it is not expected that the diffusivity of either species in the alumina grain boundary would be significantly different. This suggests that the energy barrier (ΔE) is not controlling the measured activation energy. In all, it is inferred that that while the true activation energy associated with the energy barrier to a grain boundary transition (ΔE) is non-trivial, the measured activation energy is more associated with the change in free energy between the initial and final state (ΔG) and the distribution of grain boundary energies.

It has long been known that dopants in alumina have an effect on the distribution of grain boundary energies. Most notably magnesia is well known to decrease the energy of all boundaries and produce a more isotropic distribution.[82,86] This decrease in grain boundary energy might also explain why magnesia-doping suppresses grain boundary transitions and prevents abnormal grain growth in alumina. The measured temperature dependence of the number density of abnormal grains may be somewhat representative of the distribution of grain boundary energies and might be correlated with measures of the grain boundary character distribution.

For a typical type of abnormal grain that is 10 times the size of the normal grains, only 0.1% of the grains must become abnormal for the microstructure to be completely consumed by abnormal grains. When the number density of abnormal grains is 0.01% they are not very significant in the measure of an average grain size, but a factor of 10 increase in the number density produces a complete transition of the whole microstructure. With a high activation exponential such as the one observed for silica-doped alumina, it appears that the transition occurs at some 'critical temperature'. Such a critical temperature has been observed in previous studies, but is likely due to a similar exponential behavior. The number of grains that undergo a transition in a typical microstructure that contains the occasional abnormal grain may be on the order of 1 in 10,000 to 1 in 1,000,000. The nucleation of a single abnormal grain for single crystal conversion,[87] as has been demonstrated previously, is literally a 1 in a billion event.[88] This indicates that the formation of an abnormal grain is a rather rare event, even when they are present throughout the microstructure. The seven degrees (5 macroscopic +2 microscopic) of freedom of the grain boundaries allow for the possibility of a large number of distinct grain boundaries. Because the temperature dependence of the density of abnormal grains fits exponential behavior there is some probability that an abnormal grain may form even at very low temperatures. Practically, the lower limit of temperature at which any abnormal grain may form is then determined by the energy of the highest energy grain boundary possible. Understanding this lower limit is of particular importance in applications where the presence of a single abnormal grain or high diffusivity complexion is not acceptable. A technologically significant example of this is in thermally grown alumina oxide scales on high-temperature superalloys in turbine engines.[89] Here a single complexion transition may produce a locally high oxidation rate, introducing a locally high growth stress, and cause spalling.

In order to achieve the level of microstructural control required to reproducibly induce a 1 in a billion event, it is critical to understand the influence of chemistry on the distribution of grain boundary energies. To design a toughened microstructure where there are large plate-like abnormal grains dispersed amongst small normal grains, it is necessary to select a dopant that produces a very anisotropic grain boundary energy distribution, which will promote anisotropic grain growth and produce a low apparent activation energy for the number density of abnormal grains that will allow normal and abnormal grains to coexist over a wide temperature range. In order to suppress grain boundary transitions all together it is important to select a dopant that lowers the energy of all of the grain boundaries. However, if it is only important to achieve a unimodal grain size distribution than it is sufficient to choose a dopant that promotes grain boundary isotropy. This ability to predict and control transitions between different grain boundary complexions through the use of chemistry and temperature is the foundation of kinetic engineering of materials. Our goal of understanding the effects of temperature and chemistry on processing materials is in the tradition and spirit of Sir Richard J. Brook, and this paper is dedicated to him on the occasion of his 70th birthday.

4. Conclusions

The number density of abnormal grains (i.e. complexion transitions) increases linearly with grain boundary excess dopant concentration, and exponentially with temperature. Both the distribution of chemistry and the distribution of grain boundary energies, due to anisotropy, are important in predicting which grain boundaries undergo a complexion transition. The results indicate that low energy grain boundaries are the least likely to undergo a disordering transition. High-energy grain boundaries are, then, most likely to undergo a disordering complexion transition. These disordered complexions may then be metastable, due to the presence of a high concentration of solute. The number of transitions that occur in a particular microstructure is typically low. The highest temperature at which no abnormal grains will form will be defined by the energy of the highest energy grain boundary.

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