PHYSICAL REVIEW B **70**, 144108 (2004)

First-principles study of rare-earth effects on grain growth and microstructure in β-Si_3N_4 ceramics

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(Received 8 June 2004; published 20 October 2004)

Rare earth (RE) and group III oxide additions are frequently used to optimize densification during the processing of ceramics. Silicon nitride ceramics frequently serve as model cases, and in these systems the effects of rare earths are important. Additions often determine the morphology of β-Si_3N_4 crystallites that grow in the multiphase ceramic, thereby affecting the microstructure and mechanical toughness of the ceramic. The influence of different rare earths has recently been experimentally characterized in terms of their effects on grain growth aspect ratios. In the study reported here, a new energy parameter is introduced that provides a first-principles based understanding of these effects. Grain growth aspect ratios measured for various RE additions in silicon nitride correlate well with corresponding *differential binding energies* (DBE) calculated within the partial wave self-consistent field atomic cluster model. The DBE provides a second-difference measure of relative site stabilities of RE vs Si atoms in regions of variable O/N content. The physical mechanism that underlies anisotropic grain growth is found to originate from the site competition between REs and Si for bonding at β-Si_3N_4 interfaces and within the O-rich glass. The different segregation strengths exhibited by rare earth elements in oxynitride glasses are simply a reflection of their different local chemistries in O, N environments. Elements that segregate to the prism planes of the embedded β-Si_3N_4 grains impede the attachment of Si-based silicon nitride growth units, and the extent of this limitation leads to the observed grain growth anisotropy.

DOI: 10.1103/PhysRevB.70.144108 PACS number(s): 68.55.Ln, 71.55.Jv, 73.90.+f, 81.05.Je

INTRODUCTION

Understanding the atomic level effects of additives in multicomponent materials has gained increasing importance in the search for improved control over material properties at the macroscopic level. One such case involves the mechanical properties of silicon nitride and other high temperature structural ceramics. Their properties depend strongly on the distribution of additive elements used as sintering aids to promote their densification.[1] Rare earth oxide additions (lanthanide series and the related group III elements, Y and Sc) are of particular interest, since their effects are both large and variable.[2] Most importantly, through their influence on microstructure, RE additions affect the *toughness*—the resistance of the ceramic to fracture.

Silicon nitride ceramics have become model systems for both theoretical and experimental studies.[3] They have β-Si_3N_4 grains embedded in an (Al- or Mg-modified) silicon oxynitride glass matrix with a microstructure resembling that of whisker-reinforced ceramics. The embedded β-Si_3N_4 rodlike grains are bounded by six *prism planes* and terminated by curved end caps with faceted structure. Growth of the β-Si_3N_4 crystallites is normally very anisotropic. Experiment suggests that growth on the prism planes is reaction rate limited and thus, slow compared to that along the c-axis, which is diffusion controlled and rapid. This leads to grains with large aspect ratios ($\Delta L/\Delta D$, where L is crystal length and D the diameter).[4] The resulting β-Si_3N_4 *grain morphology* is very sensitive to the type of additive,[5,6] as illustrated in Fig. 1 for La and Lu additions. This is a critical factor as it affects the formation of the elongated reinforcing grains that benefit fracture toughness.[7] Additives can also influence the debonding behavior as a crack intersects and deflects around a silicon nitride grain. Since debonding is required to activate the toughening effects of the reinforcing grains,[8,9] its control is also very important in tailoring mechanical behavior.

Traditionally, the aspect ratio is considered to be a function of the rare earth ionic radius. However, as shown in Fig. 2, one finds that this common use of ionic radius alone is insufficient to fully explain the measured effects on grain growth. For example, it is observed that additions from the Ln series lead to smaller aspect ratios in comparison with cations of group III (Sc and Y), although the ionic radii may be the same. The problem is that ionic radius can only reflect size effects whereas an understanding of the influence of additions requires a description of the underlying mechanisms of segregation and chemical bonding. While direct first-principles calculations for these systems are feasible,[10] their scaling behavior and the inherent structural disorder in glassy systems greatly limit their use here. What is needed is a simpler, comparative measure of the relative preference of dopant cations for bonding in environments enriched in one anion over another, relative to the *abundant* cation (Si) of the base system, (β-Si_3N_4 grains act as a large reservoir of Si).

DIFFERENTIAL BINDING ENERGY MODEL

In this study, a simple *differential binding energy* model is introduced that can distinguish the segregation behavior of

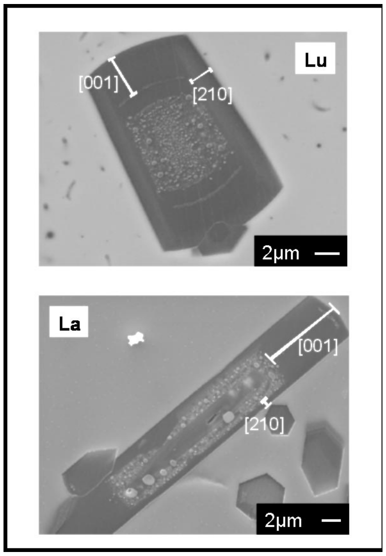

FIG. 1. $\boldsymbol{\beta}$-Si_3N_4 grain morphologies showing cooling bands that give a measure of grain growth rate along the *c*-axis and on the prism planes. Growth along [−210] (prism surface) for La doping is very limited relative to that of Lu.

rare earths without explicit large-scale calculations. Clearly, a chemical gradient exists between the silicon nitride surface and O-coordination sites in the surrounding glassy oxynitride phase. Differences in bond strengths of RE elements within locally different environments are quantified through the ground state energetics calculated from first principles for atomic cluster models of the various structures. When referenced to the behavior of the abundant cation, Si, the variation in effects of RE additions becomes clear. The model builds on the finding that even atomic clusters of minimal size can describe differences in energetics at the large scale, e.g. as found in s,p bonded metals and the transition metal series.[11]

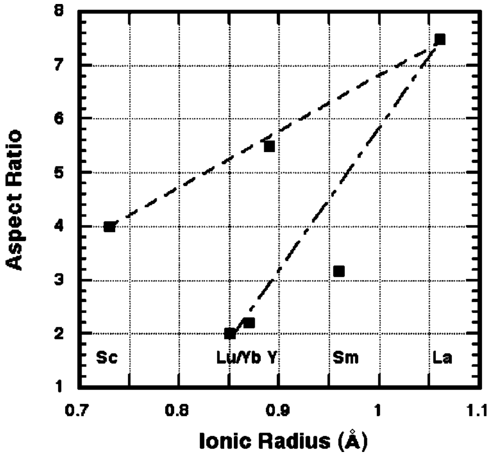

FIG. 2. Mean aspect ratios for $\boldsymbol{\beta}$-Si_3N_4 grains in 60Si-20RE-20Mg oxynitride glass matrix plotted vs ionic radii. Lanthanides and group III elements follow different trend lines, suggesting that the ionic radius is insufficient as an indicator of grain growth.

First, it is necessary to address the population distribution of rare earths in the ceramic, if we are to understand *how* they affect the growth of β-Si_3N_4 grains within the ceramic. Rare earth cations can bind within the oxynitride glassy phase of triple-junction pockets, within nanometer thick intergranular films (IGF) and at the glass or IGF/β-Si_3N_4 grain interfaces. As chemical preferences affect segregation, so bond strengths lead to differences in dopant behavior and their effects. In order to quantify cation bond site preferences, the binding energies for REs and Si in different hosts are calculated for small fragment atomic clusters chosen to represent possible first-shell coordination spheres at different sites in the chemically-graded environment. The local density equations[12] are solved from first-principles using the full potential partial wave self-consistent field atomic cluster method.[13] This technique is an all-electon linear variational method using numerical orbital basis functions and partial wave expansions for the charge density and potentials. Total energies are calculated from the self-consistent electronic structure and wave functions. Then *second* energy differences, separately calculated for different environments, are formed as a measure of the relative strength of RE-O and RE-N bonds, referenced to those of the abundant competing species, Si, in environments enriched in oxygen (glass phase) or nitrogen (at the β-Si_3N_4/glass interface). The *differential binding energy* for Si and RE cations in a compositionally graded O,N environment is defined in general by

$$\boldsymbol{\delta}_{\text{Si,RE}} = \Delta E_{\text{Si-O}} - \Delta E_{\text{Si-N}} - (\Delta E_{\text{RE-O}} - \Delta E_{\text{RE-N}}).$$

For the choice of reference hosts used here, with the RE in local sixfold and fourfold O and N-coordination, respectively,

$$\boldsymbol{\delta}_{\text{Si,RE}} = \Delta E_{\text{SiO}_6} - \Delta E_{\text{Sin}_4} - (\Delta E_{\text{REO}_6} - \Delta E_{\text{REN}_4}),$$

where ΔE_{IJ} is the binding energy of cation I (Si or RE), in an anion environment, J, that models oxygen-rich or nitrogen-rich host sites in the ceramic. For a RE in an octahedral O environment, the binding energy is

$$\Delta E_{\text{REO}_6} = E_{\text{REO}_6} - E_{\text{O}_6} - E_{\text{RE}},$$

where E_K is the calculated total energy for the relaxed system, K. The expression for $\boldsymbol{\delta}$ is thus a difference of binding energies for two cations (RE and Si) in two anion environments (O and N), with different coordination preferences. The type of chemical gradient for which this construct applies contains no other strong perturbations within the O-rich and N-rich regions. This is expected to be the situation within the subnanometer region at the amorphous film/silicon nitride interface.

Since $\boldsymbol{\delta}$ is based upon a *second* energy difference, corrections (e.g., due to cluster size) are largely self-canceling. The connection with segregation energies is apparent, since $\boldsymbol{\delta}$ is a difference of segregation energies for a pair of cations and host sites of different O, N composition and coordination. The calculated energy differential, $\boldsymbol{\delta}_{\text{Si,RE,}}$ quantifies the difference in chemical preferences of the rare earth for O vs N bonding, *relative to that of Si*. The advantage of this reference is that the sign of $\boldsymbol{\delta}$ separates RE according to their bond preference with O vs N. This follows since in the special case RE=Si, $\boldsymbol{\delta}=0$, indicating Si experiences no driving force from competition with itself. Of course, the competition is important for other cations, such that for RE with $\delta > 0$ site-occupancy in the O-rich glass is enhanced, while cations with $\delta < 0$ are more likely to bind at the N-rich interfacial region of the embedded grains. *Thus, δ measures the energy contribution to the rare earth segregation due to the competition between the RE and Si for anion bonding*.

The choice of "representative" host clusters is guided by the need for a measure of O and N- "attractiveness" for the rare earth. While the choice is largely intuitive, specific data on the population distribution of rings[14] in glassy SiO_2 (i.e., sixfold), and the tetrahedral coordination at a growing nitride interface guide the selection used here. Results with larger clusters are consistent in separating the behavior of La and Lu with regard to Si, but the placement of intermediate REs is more sensitive to cluster details. For example, inclusion of a second anion shell in the reference clusters yields δ values placing Y very close to Lu. Clearly, with δ values calculated from assumed structural models (which is, at present, necessary for glasses), there is the possibility that the anion attractiveness can be masked by other bonding factors. However, within the choice of host clusters used here, results are quite systematic. For example, allowing mixed O, N content for the composition of the hosts maintains the calculated trend in δ from element to element with only a change in slope of the trend line as the host composition is changed.

The DBE model is formulated to apply over the range of the chemical gradient in which the cation resides. This is well-suited for the gradient between the nitride interface and several atomic diameters into the adjacent glass. Clearly, perturbations within the gradient are outside the scope of this scheme, since only end points of the segregation path are treated. For similar reasons, the model would need extension for applications to diffusion within a lattice.

Experiment shows that Si_3N_4 solubility in oxynitride melts containing RE (and Al) increases with "ionic radius," i.e., from Lu to La, and that higher N-concentrations are stable in the structurally diffuse regions of the glass/Si_3N_4 interface.[15] The tetrahedral structure at the nitride interface and the high concentration of N in the diffuse interfacial layer determine the choice of the host cluster model of the interface. The DBE model itself and the choice of reference hosts are separate issues, i.e., the energetics could be obtained from other sources. Similarly, generalization to other systems is straightforward.

RESULTS: RARE EARTHS IN SILICON NITRIDE CERAMICS

In this simple application of the DBE to effects of rare earths on the grain growth of β-Si_3N_4, binding energies with relaxation were calculated for selected REs sixfold coordinated within a generic O-rich (octahedral) site in the glass and fourfold tetrahedral coordinated in N cluster models at the silicon nitride interface, where the glassy layer is relatively N-enriched. Increasingly positive values of the differential binding energy corresponds to an increasing population density of sites with RE coordination in the O-rich oxynitride glass. Increasingly negative values of the DBE then predicts an increasing population density of RE coordination with nitrogen sites, e.g., the N-terminated surfaces of β-Si_3N_4. The second-differential nature of the DBE assures that it measures the relative stability of the RE in the various available host sites.

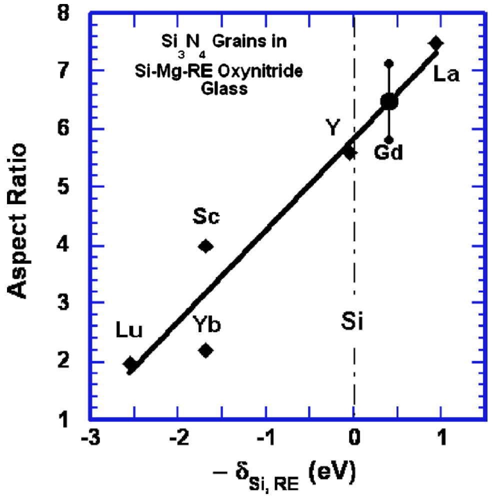

FIG. 3. Experimental aspect ratios plotted vs calculated differential binding energies. The Si reference DBE ($\delta = \mathbf{0}$) separates elements that effectively complete with Si to bind at nitride interfaces ($\delta < \mathbf{0}$) and those that can bond within the glass ($\delta > \mathbf{0}$) with Si as a competitive cation. The calculated value for δ (−0.37 eV) and predicted range of the aspect ratio are also shown for Gd (unmeasured).

Through controlled and systematic experimentation, grain growth behavior has been measured for most important rare earth additives to silicon nitride.[3] Plotting the measured aspect ratios vs corresponding calculated values for δ in Fig. 3, it is clear that the correlation of δ with grain growth is very good, correcting the discrepancies found in comparisons with ionic radii (Fig. 2). Calculated energy differentials, δ, for Sc, Y, La, Yb, and Lu, systematically increase from La ($\delta < \mathbf{0}$) to Y ($\delta \sim \mathbf{0}$) to Lu ($\delta > \mathbf{0}$). The largely positive values for δ reflect the oxyphilic character of the series, indicating that in each case except La, the RE's preference for bonding with O over N exceeds that of Si, for which δ is zero by definition. Rare earths for which $\delta > \mathbf{0}$ effectively compete with Si for O-rich environments and are favored to occupy sites in the glass.

On the basis of this good correlation of δ with experiment, the physical model of the DBE suggests a likely *mechanism* for the effects of REs on grain growth. As δ increases ($> \mathbf{0}$), the population distributions of Sc, Yb, and Lu are expected to uniformly increase in oxygen-rich regions (the glass) and decrease in N-rich regions (e.g., the nitride growth layer), in comparison to the distribution of Si. Rare earth bonding in the glass does not limit grain growth, rather it effectively increases the population of sites at the grain surfaces available to Si, in effect enhancing prism plane growth. Conversely, the population distribution for La ($\delta < \mathbf{0}$) is indicated to have relatively greater weight in the N-rich growth layer at the β-Si_3N_4 grain interfaces, with a reduction of the La/Si ratio in the glass. The bonding of La with the N-terminated surfaces is strong, hindering the attachment of Si to the growing prism planes, reducing the reaction rate for diametrical growth and increasing the aspect ratio. This effect is expected to be more dramatic on the slowly growing prism planes where growth is intrinsically slow. To be sure, the mechanism affects all interfaces of the growing grain, but on the faceted surfaces normal to the *c*-axis, which display an intrinsically higher growth rate, the dopant-induced reduction is far less limiting than on the prism planes. As a result, those REs having population distributions that increase the RE/Si ratio at Si_3N_4 interfaces produce larger aspect ratios than those with smaller populations there.

As shown in Fig. 3, yttrium has the second largest probability for interfacial segregation. However, since Y falls close to the Si reference ($\boldsymbol{\delta} \sim 0.0$), it is indicated to be somewhat ambivalent with regard to site occupancy. It has a very small driving force (relative to that of Si) for segregation to the interface. Reported TEM data[16] does suggest that Y segregation to silicon nitride interfaces is weak, but the low atomic number of Y ($Z=39$) makes detection difficult. In order to circumvent this experimental limitation, as well as assess the predictive capability of the DBE, the calculated value of $\boldsymbol{\delta}$ for Gd is included in Fig. 3. Gd ($Z=64$) will be much easier to detect than Y, and Gd may be indicative of Y's behavior since their differential binding energies are not too different.

CONCLUSION

The segregation preferences described within the DBE model are critical in explaining the RE-dependent anisotropy in grain growth: chemically induced RE segregation and adsorption on the prism planes leads to a reduction in the reaction rate for $\boldsymbol{\beta}$-Si_3N_4 growth. A poisoning of these interfacial planes by La has been empirically proposed earlier.[6] The DBE model verifies this and provides the atomic level mechanism by which such poisoning occurs. This description deduced from the DBE model is also consistent with other experimental observations. For example, in EELS measurements of elemental concentrations across an IGF in Yb- and La-doped silicon nitride,[6] the RE/Si signal ratios in the glass, compared to within the N-enriched IGF, were 2/1 for Yb and 1/2 for La. The differential binding energy model explains this in terms of RE/Si population ratios being higher at the interfacial layer for La, but higher within the glass for Yb.

More recent *Z*-contrast microscopy carried out on the La-doped samples used in this study indeed confirm that La segregates strongly into the IGF and bonds with N atoms of N-terminated $\boldsymbol{\beta}$-Si_3N_4 prism surfaces.[17] This verification for the behavior of La predicted by the differential binding energy model is significant to the validity of the model in its broader description of *how* additives segregate within the oxynitride glass in silicon nitride, and thereby influence grain growth and interfacial strength. This model provides a link between the chemical bonding of the additive in the ceramic and the observed properties. The significance of this is best realized in the fact that such understanding is essential to achieving atomic level *control* of the microstructure and mechanical properties of future generation ceramics.

ACKNOWLEDGMENTS

Research supported by the Division of Materials Sciences and Engineering, U. S. Department of Energy, under Contract DE-AC05-00OR22725 with UT-Battelle, LLC and the European Community "Growth" Program, NANOAM Contract No. GRD2-200-3030351. The authors thank I. M. Anderson, C.-L. Fu, and J. R. Morris for helpful comments on this manuscript.

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