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Influence of additives on anisotropic grain growth in silicon nitride ceramics

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Abstract

Tailoring microstructure and composition are critical components for obtaining high-performance silicon nitride (Si_3N_4) ceramics. Anisotropic growth behavior of Si_3N_4 grains can be used to form very elongated grains, which serve to reinforce the matrix analogous to whisker-reinforcement of ceramics. The Si_3N_4 grain morphology is known to be very sensitive to the particular additive used, especially in the case of the oxides of the rare earths (RE) and Group III elements. However, the atomistic mechanisms by which this occurs has not been understood until now. A first-principles model, the differential binding energy, has been developed to characterize the competition between RE and Si for migrating to the β-Si_3N_4 grain surfaces. The theory predicts that, of the RE, La should have the strongest and Lu the weakest preferential segregation to the grain surfaces. Additional calculations define the adsorption sites and their binding strengths for each of the REs on the prismatic plane of the Si_3N_4 grains. These predictions are confirmed by unique atomic-resolution images obtained by aberration-corrected Z-contrast scanning transmission electron microscopy (STEM). The combined theoretical and STEM studies reveal that the elements that induce the greatest observed grain anisotropy are those with the strongest preferential segregation plus high binding strength to the prismatic grain surface. Advances now allow one to use first principles calculations to determine the chemical affinity and bonding of the rare earths, as well as other elements, at the grain interfaces; atomistic factors that actually control the growth anisotropy as opposed to the commonly considered ion size, which at best, only provides a trend.
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1. Background

1.1. Anisotropic grain growth

Inorganic compounds are required to promote the densification at elevated temperatures of silicon nitride (Si_3N_4) ceramics as a result of its very covalent nature and the onset of decomposition in place of melting. These are often oxides (e.g. alumina, magnesia, yttria, rare earth oxides) and are used in combination with the native oxide present in Si_3N_4 powders to form minor phases which exhibit low viscosities at temperatures has below 1800 °C. This promotes densification through liquid-phase mechanisms such as grain solution/reprecipitation processes, which enhance particle rearrangement, and diffusion processes. Tailoring the additives and the amount of additives is employed to diversify processing approaches and to modify the properties of the resultant ceramic.

For instance, over the last decade significant improvements in creep resistance have been gained by tailoring the additives employed [1,2]. Modification of the amount of specific additives have been shown to enhance fracture toughness [3–5] of Si_3N_4 ceramics. The formation of a microstructure consisting of elongated grains in a fine grained matrix can significantly impact on improve mechanical properties of Si_3N_4 ceramics where the elongated grains can function as reinforcements similar to whiskers or fibers in reinforced ceramics [6,7]. Such elongated reinforcing grains in Si_3N_4 ceramics can be introduced by seeding techniques [4,8] and be enhanced by anisotropic grain growth during sintering.

A wealth of experimental data exists that demonstrate the anisotropy in the growth of silicon nitride grains can be significantly altered by the choice of sintering additives, espe-

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cially amongst the rare earth (RE) and Group III elements. Model studies of the growth of silicon nitride grains dispersed in silicon–aluminium–RE oxynitride glass matrices revealed a correlation between the increase in grain aspect ratios with an increase in the ionic radius of the specific rare earth employed [9–11]. Studies of partially sintered mixtures of silicon nitride powder with small additions of silica plus rare earth oxides confirm that such increased grain aspect ratios with increase in rare earth size also occur in monolithic Si_3N_4 ceramics [12]. Apparently, secondary additions such as alumina or magnesia have limited effect on this relationship as a similar increase in aspect ratio with ion size is observed for silicon nitride grains dispersed in silicon (aluminum or magnesium) oxynitride glasses containing selected rare earth or Group III elements [9,13]. When aspect ratios are compared to cation size, the Group III elements appear to exhibit a response that differs from that for the lanthanide series elements, which was suggested to reflect the differences in electronic structure [13].

Furthermore, the aspect ratios of both α-SiAlON seeds grown in a oxynitride glass and α-SiAlON ceramics increased with the size of individual additive cations, which included separate additions of lithia and calcia, as well as ytterbia, yttria or neodymia [14,15]. Thus, it appears that the effect of size of selected cations on grain anisotropy occurs for a wide range of cations, regardless of the aluminum and oxygen solute content of the Si_3N_4-based grains. However while these trends are informative, the size of the additive cation, in and of itself, provides no insight into the mechanism(s) that control grain growth. As noted above, this is a non-trivial point as the formation of elongated reinforcing grains can be a critical step in the development of toughened Si_3N_4-based ceramics [4] and the composition of the additives can alter the toughening response [3,5].

1.2. Mechanisms of grain growth

The formation of elongated hexagonal cross-sectioned grains with curved end caps are typically observed in β-Si_3N_4 and β-SiAlON ceramics. The shape of the end caps is acknowledged to represent a diffusion-controlled *c*-axis growth process (e.g. Ref. [16]). Analysis of compositional effects on diffusion-controlled growth has been addressed via the Stokes–Einstein equation where the diffusion coefficient is inversely proportional to the compositional-dependent viscosity of the intergranular amorphous phase. In the range of 800–1100 °C, the viscosity of bulk Si–RE–Al and Si–RE–Mg oxynitride glasses of fixed compositions is known to increase as the size of the rare earth decreases [17–19]. At the same time, there is evidence that the nitrogen solubility of bulk Si–Me–RE oxynitride glasses increases slightly as the size of the RE ion increases [20], which leads to an increase in viscosity. However, the viscosities of glasses decrease substantially as the temperature rises and very low viscosities are asymptotically reached at higher temperatures. For example, the viscosity of an aluminosilicate glass decreases well below the working point at 1200 °C and is thus quite fluid; while fused silicas only reach the softening point where they flow under their own weight at ∼1550 °C, Fig. 1. The Si–RE–Mg oxynitride glasses exhibit strongly temperature dependent viscosities like

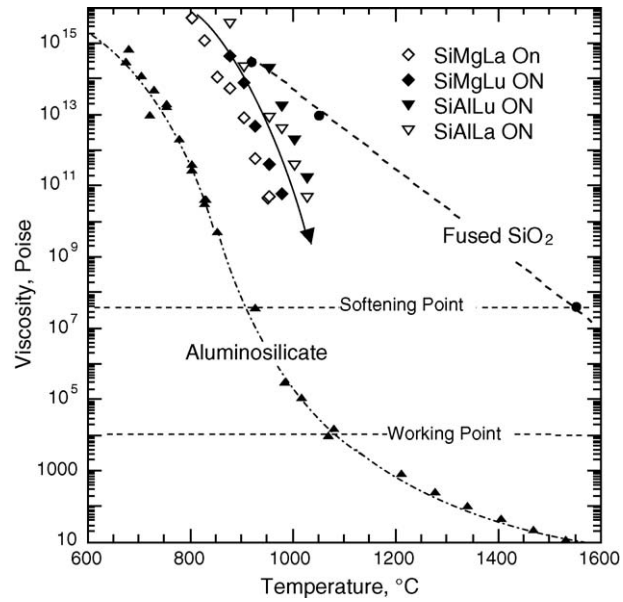

Fig. 1. Except for pure silica, the viscosity of oxide and oxynitride glasses decrease rapidly with increase in temperature and the effects of composition in multi-component oxynitride glasses become indistinguishable at temperature of ∼1200 °C. Hence, diffusion in oxynitride glasses would not be expected to vary significantly at typical sintering temperatures (>1700 °C).

that of the aluminosilicate glass; also their viscosities become less distinguishable with increasing temperatures. Projections of the existing data suggest that the viscosity of either oxynitride glass would be well below the working point above 1400 °C. The Si–RE–Al oxynitride glasses exhibit similar viscosity trends with increasing temperature. Thus at the temperatures used in grain growth studies (e.g. ≥1600 °C), one would expect little difference in the diffusivities among any of the oxynitride amorphous phases present in the typical Si_3N_4 ceramic. This is consistent with the findings of many of the grain growth studies that show growth rates in the *c*-axis (or longitudinal axis) direction of the grains are not sensitive to the rare earth employed.

Conversely, it is apparent that the *a*-axis (or diametrical) growth rate is typically much slower in comparison to that for *c*-axis growth and is quite sensitive to the rare earth or Group III cation present. The observed behavior suggests attachment/interface limited growth on the prismatic plane rather than diffusion limited growth, a conclusion of numerous studies (e.g. [12,13,21–26]). Various observations also indicate that the prismatic planes that bound the hexagonal rod-like silicon nitride grains appear to be quite smooth. Electron microscopy observations show that the prismatic surfaces can be atomically flat. Attachment of Si (and N), which controls the growth velocity, is seen to be determined by the population of surface ledges/steps. Processes whereby additives adsorbed on the surface would be expected to also impede the attachment of Si and N to the prismatic plane and decrease the growth velocity along *a*-axis.

As noted, the changes in grain aspect ratios are often related to the ionic radius of the "rare earth" ions as shown in Fig. 2. Why would ionic size by itself affect growth—easier for smaller ion to fit into interstices at the grain surface? For ions of the same

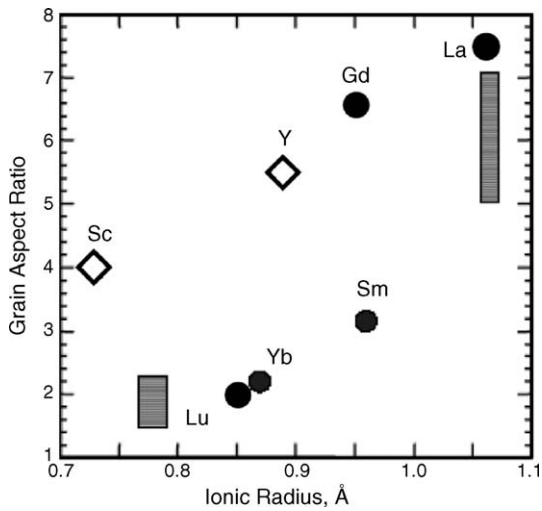

Fig. 2. General trends in the anisotropy of silicon nitride grains that are not subject to impingement effects in the presence of various rare earth and Group III additions. Note the lack associated effects for the lanthanide (●) and Group III (◊) series.

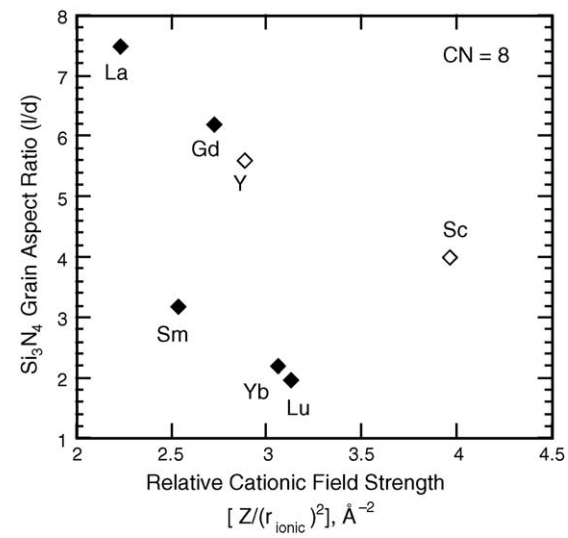

Fig. 3. Aspect (grain length to diameter) ratios for silicon nitride grains grown in a 60Si–20RE–20Mg–78O–22N (equiv.%) glass matrix [12] correlated with cationic field strength (lanthanides-filled symbols, group III-open symbols). The calculated relative cationic field strength is based on +3 valence cations that have fixed coordination with the same eight (8) anions and reflects only the differences in cation radius. The correlation of the grain aspect ratio with the relative field strength (or similarly with ionic radius) is suggestive but inconsistencies appear among the rare earths.

valence, one can propose that ionic radius gives an indication of the cationic field strength, which is employed in glass studies to give some indication of the bond strength between specific cations and anions in terms of the effects on the glass strength. The cationic field strength, which is based upon the cation's valence divided by the square of its radius, provides an estimate of the potential dipole strength for a given cation coordinated with a given number of anions in fully ionic-bonded crystalline systems. One can argue that those cations with higher relative field strengths would be more strongly bound to the grain's prismatic surface and would more effectively limit grain growth. However, one is left to deal with variations in coordination number as well as any covalent bonding for the different additive cations. The cationic field strength has also been used to approximate the donor/acceptor characteristics of a cation to obtain a relative ranking of its acid–base character. One can argue that an acidic Si_3N_4 grain surface would have increasing attraction for cations with greater basic character thereby suggesting some trends in segregation behavior [27]. Unfortunately, while there is a general correlation between the field strengths of the cations and the silicon nitride grain aspect ratios, there are also ambiguities that are unaccounted for, as shown in Fig. 3. In this case, one is left to answer the question as to why Sm, Yb, and Lu result in much smaller grain aspect ratios as compared to Group III and other rare earth elements. Thus, while ionic radius or cationic field strength may provide some sort of rough ranking of the effects of various additive cations, a much more complete understanding requires greater insight into the mechanisms that cause the grain growth to be modified by the additives.

The results to date do indicate that segregation of additive cations to the grain surfaces can be a factor in the *a*-axis growth rates. One of the more important observations conducted on Si_3N_4 grain clusters embedded in Si–RE–Al oxynitride glasses revealed that not only was anisotropic grain growth promoted with La as compared to with Yb, but the La content increased in the film between grains as compared that to out in the glass and the opposite behavior was found for Yb [11]. Further evidence for the association of rare earth elements with growth normal to the prismatic planes is noted by their presence within internal transient growth bands associated with cyclic heating and cooling grain growth anneals of silicon nitride grains embedded in Si–Al–RE oxynitride glasses [28].

In recent studies of the growth of silicon nitride grains embedded in the Si–RE–Mg oxynitride glasses, it was suggested that there must be greater adsorption of the RE at the prismatic surface as the RE ion size increased [13]. Kitayama et al. [12,21] had also suggested that attachment of the rare earths at the prismatic plane surface of silicon nitride grains might be important. In support of this, they referred to molecular orbital calculations by Nakayasu et al. [29] where an increase in the bond density deduced from a population analysis of the occupied states was taken to indicate an enhancement of the covalent bond around the RE when it resides at the grain interface. However, this bond density decreased as the ionic radius of the RE increased, and this was taken to imply that the magnitude of the bond strength between a rare earth and the silicon nitride prismatic plane increased with decrease in rare earth ion size. The weakening of the RE interface bond was then suggested to impede *a*-axis growth by reducing the stability of the prismatic plane. Interestingly, the calculations considered the association of the RE at a nitrogen-terminated prismatic plane and provided some insights into possible chemical bonding effects on interfacial processes. However, we know that the concentration of La increases within the thin intergranular films between grains as compared to that in the surrounding glass matrix while the reverse is true for Yb [11], which appears to be inconsistent with the above results. A number of issues remained to be addressed. Does the RE pref-

erentially segregate to the grain interface? Does the RE have preferred adsorption sites at the interface and how strongly is it bound? How does this vary with the specific RE?

2. Methodology

The fully dense silicon nitride ceramics investigated consisted of three compositions including the following sintering additives to silicon nitride powder (E-10 grade, UBE Industries, Japan): 1.97 wt.% MgO + 8.68 wt.% Lu_2O_3, 1.98 wt.% MgO + 7.97 wt.% Gd_2O_3, and 2.00 wt.% MgO + 7.23 wt.% La_2O_3 (see Ref. [4] for processing details). The slight differences in amounts of additives reflect the need to maintain compositions at the same point in the phase diagram (same composition in equiv.%) for rare earths of significantly different atomic masses.

Atomic-resolution images were taken with a dedicated 300 kV (VG Microscopes, HB603U) scanning transmission electron microscope equipped with aberration corrector (Nion Co.), providing a minimum probe diameter of about 0.6 Å. The specimens for scanning transmission electron microscopy (STEM) were prepared as follows. The bulk material was mechanically polished to about 50 μm thick using a precision polishing system (Allied High Tech Products, Inc., TechPrep), and then dimpled (Gatan Inc., Model 656) to a thickness less than 10 μm before ion-beam thinning. In the ion-beam thinning process (Gatan Inc., Model 691), the initial accelerating voltage of a argon ions was 4.5 kV with an incident beam angle of 7°, and was gradually decreased to 2 kV as thinning progressed. Finally, a low-voltage ion thinning (1 kV) was applied to minimize surface damage (Fischione Instruments Inc., Model 1010). A thin amorphous carbon film (∼3 nm) was deposited onto each sample to avoid charging effects.

First-principles calculations were carried out in the partial-wave self-consistent-field method [30] using the Vosko–Wilk–Nusair exchange-correlation model. This is a linear variational full-potential all-electron technique for solving the local density equations using numerical atomic orbital basis sets. Total energies and forces on the atoms are calculated independently.

3. Results and discussion: observations and first principles analysis of adsorption

In order to gain detailed insights into the role of additives on the observed anisotropic grain growth, a series of theoretical studies were initiated to understand the distribution of selected rare earths in Si_3N_4 ceramics, based upon the underlying electronic structure. A first-principles theory (differential binding energy or DBE) model was developed to calculate the chemical preference of additive elements in competition with silicon for nitrogen-rich (i.e. grain surfaces) versus oxygen-bearing (i.e. in the midst of the intergranular film and/or near the triple point pockets) regions in the microstructure of Si_3N_4 ceramics [31]. This approach made use of the fact that analysis of intergranular films has revealed that oxygen, as well as nitrogen, is present within the amorphous films and triple point pockets as detected in the current and earlier studies [32,33].

The DBE is evaluated by first calculating the binding energies for REs and Si in various atomic fragment host clusters chosen to represent possible first-shell coordination spheres at different sites in the chemically different local environments present. The local density equations [34] are solved from first-principles using the full potential partial wave self-consistent field atomic cluster method [30]. Second energy differences, calculated separately for different O- and N-rich clusters, measure the relative strength of RE–O and RE–N bonds, respectively, as referenced to those of the competing matrix cation, Si. The fragment host clusters are selected to simulate bonding environments where oxygen (1) resides (amorphous intergranular phase) and (2) is essentially excluded (at the Si_3N_4 grain interfaces). Selecting simple tetrahedral and octahedral reference hosts for O and N, respectively, the DBE is defined as

$$\delta_{\mathrm{Si,RE}} = (\Delta E_{\mathrm{REO_6}} - \Delta E_{\mathrm{REN_4}}) - (\Delta E_{\mathrm{SiO_6}} - \Delta E_{\mathrm{SiN_4}}) \quad (1)$$

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

$$\Delta E_{\mathrm{REO_6}} = E_{\mathrm{REO_6}} - E_{\mathrm{O_6}} - E_{\mathrm{RE}} \quad (2)$$

where E_{K} is the calculated total energy for the relaxed system, K.

From these first-principles calculations, one finds that the preference for segregation to a nitrogen-rich region should decrease across the lanthanide series in the order from La to Gd to Lu. Comparing the grain aspect ratios achieved with various rare earth additions with the calculated DBE for each element reveals a consistent trend of decreasing grain aspect ratio as the DBE value for the rare earth/Group III additive decreases, i.e. the element is predicted to have increasing preference for segregating to the grain surfaces with their high nitrogen concentrations, Fig. 4.

Also note that experiments show that the presence of Mg versus Al in the system has little effect on the grain aspect ratios even though at intermediate temperatures the glass viscosities are higher in the Al-bearing glasses, Fig. 1. As noted earlier, the viscosities are not likely to be significantly different at the temperatures used in grain growth experiments due to the rapid decrease in viscosity as the temperature increases. The results in Fig. 4 indicate that these two secondary cations have, at best, a minor role in diametrical growth; thus, the DBE predictions are expected to be applicable to both Si_3N_4 and SiAlON ceramics.

Observations by Wang et al. [28] revealed that concentration of Yb and La, which are not soluble in the β-Si_3N_4 lattice, occur within the growth bands aligned parallel to the prismatic planes during cyclic grain growth anneals. In grain growth studies involving several rare earth and Group III cations, Satet and Hoffmann found that preferential plasma etching occurred at the boundaries of these growth bands consistent with segregation of the additive cations to the grain interfaces [13] in La and Lu samples companion to those studied herein. The question remains as to what are the critical aspects of the presence of these elements

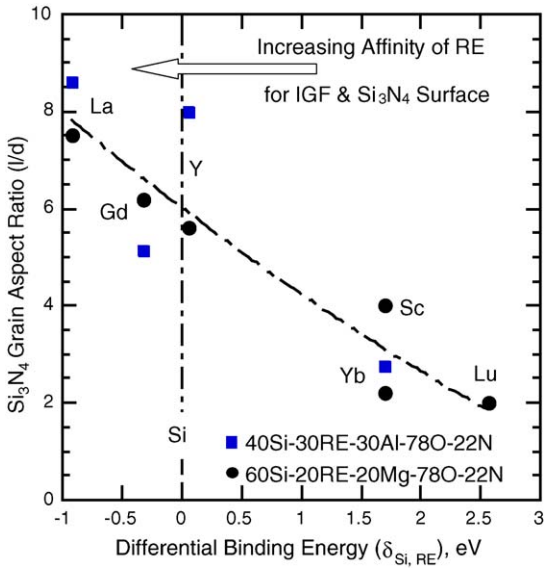

Fig. 4. The degree of anisotropic grain growth represented by the increase in grain aspect ratio (length/diameter) follows the increasing preference of the additive element to segregate to the Si_3N_4 grain surface as represented by the differential binding energies. Note the DBE values of the additive elements are referenced against that of silicon. Elements with larger positive DBE values than Si prefer to reside in regions containing oxygen while those with negative DBE values have a preference of the nitrogen-terminated Si_3N_4 grain surfaces, even more so than Si.

that would influence an attachment-limited process as expected for the smooth prismatic grain surfaces with few steps for attachment. On the other hand, the macroscopically rounded shape of the *c*-axis cap on the grains should provide many surface steps for Si attachment even in the presence of RE segregation consistent with the negligible RE effects on *c*-axis growth (e.g. Refs. [13,16]).

The REs compete with Si for O and N bonds, and the DBE model differentiates the anion preferences of the REs relative to Si for oxygen and nitrogen bonds. Small high symmetry clusters were used as a reference database to simply identify the energy dependence of RE/single element bonding in calculating the DBE. On the other hand, this model does not account for important details about the bonding sites for REs on the prismatic plane. In order to explore the specifics of interfacial RE binding, structure models of the N-terminated prism plane surface were constructed and the energy and forces for each adsorbed RE atom were calculated within the partial-wave method. Minimization of the total energy was achieved by relaxation of the RE position to experience near-zero forces calculated from the solutions to the wave equations [30,34]. The host cluster for the calculations corresponds to the repeating surface unit cell of the prism plane. For RE adsorption on this surface, multiple local minima exist. For La, Gd and Lu adsorption on the nitrogen-terminated prismatic plane, there are two stable sites for each of the repeating surface units. These sites can be occupied by each of the RE species with much higher binding energies than that for Si. For La, there is also a third site, with weaker binding energy but still larger than that of Si. While the calculated adsorption site locations are not too different in the case of La, Gd and Lu, reflecting more a characteristic of the surface than details of the adsorbate electronic structure, the DBE theory [31] suggests that differences in the occupation of these sites can be expected. Thus, based on the DBE predictions, La can freely associate with N-rich sites; however, Lu is not expected to be prevalent at or near the nitrogen-terminated grain surfaces as it favors O-bonding. As a result, the predicted low preference to segregate to the grain surfaces suggests that only a small population of less energetic second adsorption sites is likely to be occupied by Lu.

While these predictions give a very plausible explanation of the observed grain growth results, both in terms of segregation and adsorption of the rare earths, verification of the suggested differences in decoration of the prism planes was lacking. Direct imaging is not a simple task, as one requires atomic level resolution in the region of interfaces between crystalline and amorphous phases. Recent advances in aberration corrected STEM now allow one to resolve the adsorption of individual addition rare earth ions at the grain surfaces in ceramics containing amorphous oxynitride intergranular phases containing a combination of magnesium plus La [35].

Two features important to grain growth behavior were noted for observations where the electron beam was parallel to the prismatic surface and the [0 0 0 1] zone axis. First, the images are consistent with a nitrogen-terminated surface and the prismatic planes were atomically flat over dimensions equivalent to many unit cells, making Si attachment difficult. It has been assumed that this smoothness of the surface makes adsorption more difficult than an atomically rough service, because there are fewer bond sites. Note the STEM observations also do not reveal any obvious differences in the density of ledges or steps on the prismatic grain surfaces for the rare earths used in this study. Thus, the change in diametrical growth involving the prismatic planes still involves smooth surfaces in each case; thus, one must look to the differences in adsorption behavior of the rare earths.

Second, the predicted specific repeating sites along the trace of the nitrogen-terminated prismatic plane were occupied by La with the two most stable sites being always filled and the third more meta-stable site being filled at least two thirds of the time! These observations and predictions are in excellent agreement, and one sees that many sites on the smooth prismatic grain surfaces are occupied by La and the calculated La bonds to the nitrogen-terminated prismatic surface are quite strong. This provides an initial insight as to why La has the greatest impact on impeding diametrical grain growth.

The next step required that one determines how the atomic level distribution of different rare earths vary using STEM observations on Si_3N_4 ceramics containing magnesia plus either lutetia or gadolinia to obtain a cross-section of the effects of the rare earths on grain growth. Lu was selected as it represents the opposite end of the lanthanide spectrum from La, and the mid-row member, Gd (selected from DBE results to closely mimic Yb). Again it was found that the prismatic grain surfaces viewed edge-on were atomically flat over extended distances with nitrogen-terminated features in the case of each rare earth additive. As noted in representative STEM images viewed along

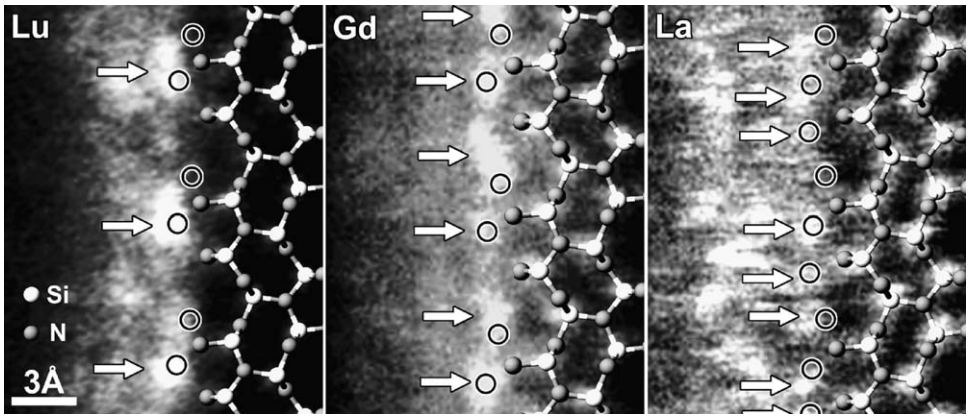

Fig. 5. Aberration-corrected scanning transmission electron microscopy images of rare earth atoms adsorbed along the nitrogen-terminated prismatic surfaces of Si_3N_4 grains viewed along the [0 0 0 1] axis. The Si_3N_4 lattice is superimposed on the atom columns in the grain that appears on the right-hand side of each image; the amorphous intergranular film is located on the left-hand side of each image. The open circles represent the calculated position for the adsorbing element for each additive. The dark regions represent a concentration of this element in each image.

the [0 0 0 1] zone axis each of the rare earths is found in the first cation row adjacent to the nitrogen-terminate prismatic grain surface, Fig. 5, as reflected by the bright spots in these STEM images. These spots represent regions of high intensity due to the accumulation of the rare earths, whose high and increasing z-values result in greater intensity. In the typical case La can be difficult to detect. However, the current aberration correction produces not only greater spatial resolution but also provides greater beam intensity allowing La to be resolved albeit not as well as the higher z-elements—Gd and Lu. One can observe that there is an increase in the number of sites occupied by the rare earths going from Lu to Gd to La. Recall that the first-principles calculations indicated that site occupancy on the prismatic grain surfaces is expected to increase in the order of Lu to Gd to La and the predicted RE adsorption sites are indicated by the open circles in each image. As noted, La fills the two most stable sites and frequently fills the third site, Gd fills the two stable sites, and Lu preferentially fills only the most stable of the two sites, consistent with its tendency to bond with oxygen away from the grain surfaces. Thus, the current STEM observations are consistent with the predictions [31]. In addition, separate observations on comparable Si_3N_4 ceramics containing a combination of magnesium plus either La or Lu found similar adsorption behavior at the prismatic surfaces of the silicon nitride grains [36–38].

So the picture that evolves is that the degree of segregation of the additive cation to the grain surfaces is determined by the chemical bond preference of the RE for oxygen versus nitrogen as silicon competes for bonding with these anions. As such the DBE model explains the observed trend for the increase in RE segregation to the interfacial region as one goes from Lu to La, and for these species this trend also correlates with RE ion size. The local density calculations of the adsorption behavior provide specific information on the RE/interface coordination and relative stabilities of RE surface occupancies. At the same time the DBE results also show that the extent to which predicted sites are occupied depends upon the preference of the RE to migrate to the grain surface region.

Experimentally, it is clear that diametrical growth is slowed, but not halted, by the larger RE elements. Thus, the key issue is how difficult it is for silicon to displace the additive element from the grain surface. It is necessary to also assess how readily the RE desorbs from the grain surface as grain growth at high temperatures is dependent on desorption kinetics. These depend exponentially on the energy for the RE to desorb from the interface into the adjacent glassy film. The desorption rate of the RE versus kT thus sensitively depends on the RE/interface bond strength, as well as the bond strength of the RE within the glass. The DBE theory compares the energy preference of each RE for N versus O referenced against that of Si for N or O. This provides at least a semi-quantitative determination of how readily the RE at the nitrogen-terminated surface can be displaced into the oxygen-bearing intergranular film by Si. From this one notes that Lu prefers oxygen while Gd and La have increasing preference for nitrogen. As such, desorption will occur more readily in the order La to Gd to Lu, which yields increasing attachment of Si to the nitrogen-terminated prismatic plane in that same order. It is the respective increase in interfacial binding energy from Lu to Gd to La that dominates the respective diminishment in the diametrical grain growth and the resultant increase in the anisotropy in grain shape.

4. Conclusions

From a basic understanding of the atomic-level effects of additions, there is promise of more scientific design strategies for tailoring the anisotropic grain growth desired for toughened self-reinforced silicon nitride-based ceramics. The present theoretical studies developed the concept of the driving forces on competing cations in a chemical gradient. A new quantity (differential binding energy) was derived as a measure of the energy change of a cation (e.g. La, Gd, Lu) between environments defining the gradient (e.g. in N-rich compared with O-rich regions), referenced with respect to that of the majority cation (e.g. Si in silicon nitride ceramics, where Si_3N_4 crystallites are surrounded by the amorphous silica-rich phase). The quantity showed excellent correlation with measured grain growth aspect ratios for a series of rare earth-doped nitrides, and explained observed differences in growth morphologies in terms of the bond site sta-

bilities of the rare earth at interfaces of the nitride and amorphous films. First-principles local density calculations then defined the specific adsorption properties of the rare earth adsorbed at the nitride interface.

Observations of the RE-doped silicon nitride intergranular films (amorphous film thickness < 1.0 nm) clearly show the RE within the film and as an adsorbed layer with specific coordination with the nitride N-terminated prism plane. The actual differences in the adsorption behavior for the three selected rare earths are in remarkable agreement with the theoretical predicted response. The resulting strength of RE segregation, and in particular the adsorption/desorption energetics at the nitride surface, correlates directly with the impediment of diametric grain growth. Thus, the chemical preference of the dopant for adsorption on the prismatic grain surface determines its effect on the anisotropic grain growth in Si_3N_4 ceramics. These results now identify guidelines to control ceramic toughening at the atomic-scale by selective choice of dopant additions using theoretical calculations as opposed to empirical methods. These findings and newly established grain growth models also should help understanding the dopant controlled microstructure evolution in a wide range of liquid phase sintered materials.

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