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Refractory $\alpha$-SiAlON Containing $\text{La}_2\text{O}_3$

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Refractory α-SialON Containing La$_2$O$_3$

Abstract
Refractory Y-α-SialON with elongated grain morphology was obtained by utilizing La$_2$O$_3$ as a densification aid, which resulted in excellent room-temperature and high-temperature strength. Room-temperature strength of 1000 MPa was achieved when La$_2$O$_3$ was augmented by adding Y$_2$O$_3$ or removing AlN. With only La$_2$O$_3$, a temperature-independent strength of 800–950 MPa was maintained up to 1100°C, then gradually decreasing by 25% when reaching 1300°C. The R-curve measurements of fracture toughness showed relatively little dependence on microstructure, consistent with a strong interface that suppresses grain boundary decohesion. Compared with other densification aids such as SiO$_2$, Al$_2$O$_3$, Sc$_2$O$_3$, Y$_2$O$_3$, and Lu$_2$O$_3$, a finer microstructure was obtained by using La$_2$O$_3$. High nitrogen content in the residual La–Si–Al–O–N glass in equilibrium with the nitrogen-rich α-SialON is suggested to be the cause of these findings.

Comments
Refractory \(\alpha\)-SiAlON Containing \(La_2O_3\)

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Refractory \(Y\)-\(\alpha\)-SiAlON with elongated grain morphology was obtained by utilizing \(La_2O_3\) as a densification aid, which resulted in excellent room-temperature and high-temperature strength. Room-temperature strength of 1000 MPa was achieved when \(La_2O_3\) was augmented by adding \(Y_2O_3\) or removing \(Al_2O_3\). With only \(La_2O_3\), a temperature-independent strength of 800–950 MPa was maintained up to 1100°C, then gradually decreasing by 25% when reaching 1300°C. The R-curve measurements of fracture toughness showed relatively little dependence on microstructure, consistent with a strong interface that suppresses grain boundary decohesion. Compared with other densification aids such as \(SiO_2\), \(Al_2O_3\), \(Sc_2O_3\), \(Y_2O_3\), and \(Lu_2O_3\), a finer microstructure was obtained by using \(La_2O_3\). High nitrogen content in the residual La-Si-Al-O-N glass in equilibrium with the nitrogen-rich \(\alpha\)-SiAlON is suggested to be the cause of these findings.

I. Introduction

Silicon nitride ceramics for structural applications at temperatures \(>1000°C\) must withstand grain boundary deformation under stress. To achieve this objective, the selection of densification aids that leave a refractory liquid/glass after densification is of great importance.1,2 Yttria is an excellent densification additive for silicon nitride. Indeed, the original patent on yttria-added silicon nitride was entitled “Heat Resistant Silicon Nitride Ceramics with the Nominal \(\alpha\)-SiAlON Composition of \(M_{12/3}\) \(Si_{12-n}Al_{12-n}O_{16-n}N_{16-n}\) (\(M\) is \(Y\) or \(Lu\), \(m\) = 1.5, \(n\) = 1.2, referred to as \(Y1512\) and \(Lu1512\), respectively) were densified with \(La_2O_3\), \(Y_2O_3\), \(Lu_2O_3\), \(Sc_2O_3\), \(Al_2O_3\), and \(SiO_2\) as sintering aids. They were prepared from \(Si\), \(Al_2O_3\), \(Y_2O_3\), \(Sc_2O_3\), \(Al_2O_3\), and \(SiO_2\) to confirm the unique attributes of \(La_2O_3\).

II. Experimental Procedure

Ceramics with the nominal \(\alpha\)-SiAlON composition of \(M_{m/3}\) \(Si_{12-n}Al_{12-n}O_{16-n}N_{16-n}\) (\(M\) is \(Y\) or \(Lu\), \(m\) = 1.5, \(n\) = 1.2) were densified with \(La_2O_3\), \(Y_2O_3\), \(Lu_2O_3\), \(Sc_2O_3\), \(Al_2O_3\), and \(SiO_2\) as sintering aids. They were prepared from \(Si\), \(Al_2O_3\), \(Y_2O_3\), \(Sc_2O_3\), \(Al_2O_3\), and \(SiO_2\) to confirm the unique attributes of \(La_2O_3\).

Refractory \(\alpha\)-SiAlON that

We reckon that, in developing refractory nitride ceramics, while it is desirable to employ densification aids that yield an oxyxynitride liquid/glass with high N content and high glass transition temperature \(T_g\), the high viscosity of such liquid/glass inevitably presents some difficulty in sintering and microstructure development. In fact, highly refractory silicon nitride ceramics need to be hot isostatically pressed to achieve high density, and they also tend to have relatively low fracture toughness because of strong interface and lack of elongated grains.21–24 Generally, \(T_g\), viscosity, and hardness linearly increase with \(FS\).25–28 While the coefficient of thermal expansion (CTE) decreases with \(FS\).25,26 For this reason, La-containing glasses have the lowest \(T_g\), modulus, viscosity, and the largest CTE among all RE-containing glasses of comparable compositions.20 On the other hand, as low FS cations cause less distortion of the glass structure,29,30 \(La_2O_3\)-containing glasses are more stable and have the highest N solubility (up to about 25 at.% \(N\)).33 Among all \(La_2O_3\)-containing glasses. These features suggest that \(La_2O_3\)-containing liquid may facilitate densification because of lower \(T_g\) and viscosity, yet after densification and SiAlON precipitation, the remaining La-glass may be enriched in N and thus highly refractory. For \(\alpha\)-SiAlON, the effect should be especially pronounced since, unlike most other RE\(^3+\), \(La^{3+}\) is too large to enter the \(\alpha\)-SiAlON lattice.31 This forces \(La^{3+}\) to remain in the sintering liquid and, later, in the residual glass, so that its effect on grain boundary is undulated. In addition, unlike other larger RE, \(La\) does not form melilite (\(Lu_2SiO_5N_3\)).32 which is a common intermediate phase during densification of \(\alpha\)-SiAlON that depletes liquid and impedes densification. In short, \(La_2O_3\) may indeed possess some very favorable attributes as a densification aid for refractory \(\alpha\)-SiAlON, which motivated the present study.

In the following, we first document the microstructure development in \(Y\)-\(\alpha\)-SiAlON using \(La_2O_3\) as a sintering aid. We then describe the mechanical performance of these ceramics to assess the interfacial properties at various temperatures. We lastly compare \(La_2O_3\) with other densification aids, including several sesquioxides and \(SiO_2\), to confirm the unique attributes of \(La_2O_3\).

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The powder was placed in a graphite die and hot pressed in a graphite resistance furnace. Hot pressing was performed in a N₂ atmosphere (1 atm) at a uniaxial pressure of 30 MPa. The heating rate was 15 °C/min, followed by holding at 1900 °C for 1 h and cooling with the furnace (approximately 50 °C/min down to 1500 °C). For one composition, holding time at 1900 °C was varied from 0 to 5 h to compare the effect of coarsening (see note “w” in Table I). In the case of Lu1512, holding at 1900 °C was replaced with two-step annealing, first at 1800 °C for 4 h, then 1900 °C for 1 h (see note “x” in Table I), in order to promote microstructure coarsening without risking decomposition. In all runs during hot pressing the chamber was filled with N₂ and mechanical pressure was applied at 1000 °C after holding for 1 h in vacuum at this temperature to remove absorbed organic residues from the powder surface. Full density (99.9%) was achieved in all cases. For the purpose of glass crystallization some hot-pressed samples were also annealed at various temperatures (1300–1550 °C) for 20 h at 1 atm N₂ (see note “y” in Table I).

Phase analysis of ceramics was performed by X-ray diffraction (XRD) using CuKα radiation. Microstructure of hot-pressed samples was characterized using a scanning electron microscope (SEM) on fractured surfaces or polished sections. The R-curves of the same materials were recorded by in situ observation of crack propagation in bars (approximate dimensions \( L \times W \times H = 30 \text{ mm} \times 2 \text{ mm} \times 3 \text{ mm} \)) cut from the hot-pressed samples and loaded in four-point bending with an outer span of 20 mm and inner span of 10 mm. The experimental details were reported elsewhere. The flexural strength was measured using bars (\( L \times W \times H = 30 \text{ mm} \times 2 \text{ mm} \times 1.5 \text{ mm} \)) with edges chamfered at 45° and tensile surface polished down to 1 µm. Samples placed on ceramic roller bearings were loaded in three-point bending with a span of 12.5 mm at a displacement rate of 0.2 mm/min.

Compositions and phase analysis of the samples studied are listed in Table I. In all cases, the concentration is referred to in weight percent.

III. Results and Discussion

(1) Microstructure Control of La₂O₃-Added α-SiAlON

Microstructure of α-SiAlON (Y1512) was systematically varied by varying the amount of La₂O₃, AlN, seeds, and annealing time. Y1512 ceramics containing 0.25% seeds and densified with different amounts of La₂O₃ are shown in Fig. 1. As increasing La₂O₃, the grain size became smaller, but a tendency toward growing more elongated grains also developed. The observation of grain refinement is surprising as the literature of silicon nitride is replete with references that associate coarser microstructures with more sintering aids/liquid. However, similar observations of finer matrix grain sizes with increasing sintering aids, often accompanied by abnormal grain growth, have been previously reported for α-SiAlONs. Other microstructure aspects of La₂O₃-added α-SiAlON followed a more predictable trend. For example, as more seed crystals were added to Y1512 ceramics containing 2% La₂O₃ shown in Fig. 2, the number of large, elongated grains proliferated, causing an apparent coarsening of the microstructure. A strong texture due to the alignment of elongated grains on the hot-pressed plane also developed, which caused the XRD intensity ratio of 210 and 102 peaks to linearly increase from about 2.5 for unseeded ceramic to 9.5 at 10% seeding (this ratio equals 1 if there is no texture). Annealing was effective in causing grain growth too. As shown in Fig. 3, with increasing holding time at 1900 °C during hot pressing, microstructure coarsened and very large, elongated grains became commonplace.

Adjustment of AlN amount in the composition provided an effective way to influence the microstructure. This is because the effective amount of oxide sintering aid decreases with the amount of AlN. For example, starting with the nominal composition of Y1512 plus 2 wt% La₂O₃, a 5 wt% deficit in AlN brings the actual composition close to that of Y1110+3 wt% Y₃O₅+2 wt% La₂O₃+native SiO₂, i.e., having more than twice the amount of oxide aids as before (2 wt% La₂O₃ and native SiO₂). Conversely, the same nominal composition but with 5 wt% excess in AlN leaves little oxide additive, as the actual composition is close to that of Y1912–3 wt% Y₂O₃+2 wt% La₂O₃+native SiO₂. As shown in Fig. 4, Y1512 with AlN deficit contained large, rod-like grains, which were mostly absent when AlN was in excess. The micrographs in Fig. 5 confirmed that an appreciable amount of glass was present when AlN was in deficit, the amount was much less in nominal Y1512 sintered with 2 wt% La₂O₃, and almost absent when AlN was in excess. Therefore, regardless of the unusual character of La₂O₃ the different microstructures in Fig. 4 were most likely because of the different amount of densification liquid affected by adjusting AlN excess/deficit. Low glass ceramics became increasingly transparent as the amount of residual glass decreased while maintaining a high density. One example is shown in Fig. 6 for a transparent Y1512 ceramic that contained 0.25% La₂O₃ and 0.25% seeds.

(2) Mechanical Properties of La₂O₃-Added Y1512 Ceramics

As the ceramic microstructure coarsens, the R-curve typically rises reflecting the increasing fracture resistance owing to grain pullout. This effect was found to be relatively weak in all the
ceramics densified using La$_2$O$_3$. For example, although grain refinement (owing to increasing La$_2$O$_3$) shown in Fig. 1 caused a corresponding decrease of R-curves in Fig. 7(a), microstructure coarsening (owing to increasing seed) shown in Fig. 2 also caused a decrease of R-curves in Fig. 7(b), and a similar coarsening (owing to annealing) shown in Fig. 3 caused an initial rise, then a fall of R-curves in Fig. 7(c).

Fig. 2. Fracture surfaces of Y1512 with different amounts of seeds, (a) 0%, (b) 1%, (c) 4%, and (d) 10%, all containing 2% La$_2$O$_3$ (refer to Fig. 1(b) for comparison with 0.25% seed).

Fig. 3. Fracture surfaces of Y1512 hot pressed with holding at 1900°C for (a) 0 h and (b) 5 h. All materials contained 2% La$_2$O$_3$ and 1% seeds (refer to Fig. 2(b) for comparison with 1 h holding).

Fig. 4. Microstructure of Y1512 with AlN at (a) 5% excess and (b) 5% deficit. All samples contained 2% La$_2$O$_3$ and 1% seeds. Rod-like grains (marked with arrows) more numerous in (b) due to more liquid (see Fig. 5).
Although a detailed study of the grain size (length and diameter) distributions, as was done in Zenotchkine et al.,\textsuperscript{13} would be necessary to understand the variation of the R-curve behavior of different microstructures in this SiAlON series, one reason that grain coarsening causes relatively small increase in fracture toughness could be because of a strong interface. An examination of crack paths, such as the one shown in Fig. 7(d), did not find crack deflection between grains when the incident angle was high or when the grains were large. These results strongly suggest that the grain/glass interface at the grain boundaries was relatively strong in these ceramics, making it difficult to have grain pullout. There are other examples in the ceramic literature, in which a coarse microstructure with rod- or plate-like grains is not accompanied by high fracture toughness. For instance, SiC with plate-like grains has strong interface and low fracture toughness when sintered using B/C as sintering additives,\textsuperscript{31,42} even though the same ceramic sintered with Al\textsubscript{2}O\textsubscript{3}/Y\textsubscript{2}O\textsubscript{3}\textsuperscript{43} or, more markedly, with Al/B/C,\textsuperscript{41,42,44} has a weak interface and high fracture toughness. Presumably, despite the fact that La\textsubscript{2}O\textsubscript{3} allows highly elongated grains to develop, the interface is still strong enough so that intergranular decohesion is difficult. In such a case, a coarser microstructure can actually lead to a lower toughness because of the increasing debonding length required for grain pullout.

Another remarkable property of the La\textsubscript{2}O\textsubscript{3}-added α-SiAlONs is their outstanding strength at high temperatures. This is illustrated in Fig. 8 for an Y1512 ceramic with 2% La\textsubscript{2}O\textsubscript{3} and 1% seeds. The stress-displacement curves in three-point bending showed no stiffness softening up to 1000°C, and only modest (∼25%) softening and strength degradation up to 1300°C. Meanwhile, inelastic deformation as reflected in the downward curvature at higher load became apparent only at 1400° and 1500°C. In fact, we have tested all the Y1512+La\textsubscript{2}O\textsubscript{3} compositions in Table I, with different compositions (amounts of La\textsubscript{2}O\textsubscript{3}, seeds, and AlN) and heat treatments (various holding time at 1900°C during hot pressing and various 20 h holding temperatures between 1300° and 1550°C after hot pressing), and found that their strength at 1300°C was always around 600±25 MPa. This implies that La-rich grain boundary glass is rather refractory.

Compared with R-curves and high-temperature strength, the strength and hardness at room temperature of this series of ceramics were more sensitive to the microstructure. As shown in Fig. 9, there is a small increase in hardness as the microstructure refines, because of either increasing amount of La\textsubscript{2}O\textsubscript{3} (see Fig. 1) or decreasing amount of seeds (see Fig. 2). This suggests microstructural hardening, which is frequently seen in ceramics due to dislocation barriers at grain boundaries. In our experience, it could also arise from grain boundary cracking at the edge of the indent that tends to amplify the apparent indent size, and such cracking is of an extent commensurate with the grain size. Regarding strength, it increased with the amount of oxide densification aid/liquid, either from La\textsubscript{2}O\textsubscript{3} addition or AlN deficit, as shown in Fig. 10. This trend probably reflects different flaw populations in different ceramics, the lowest in those that contain more sintering aid. However, some secondary effect of microstructure on toughness may also have played a role.

### (3) Comparison of La\textsubscript{2}O\textsubscript{3} and other Sintering Aids

To compare La and other cations in their role of microstructure development and grain boundary strength, we studied Y1512 and Lu1512 using various M\textsubscript{2}O\textsubscript{3} oxides as densification aids. Among them are oxides of Y and Lu, which enter the crystal lattice of α-SiAlON, as well as oxides of Sc and La, which do not. Also compared were Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2}. The amount of oxide addition was kept at 2 wt% in all cases, which amounted to a higher volume percent for lighter oxides (SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, Sc\textsubscript{2}O\textsubscript{3}, and Y\textsubscript{2}O\textsubscript{3}) than La\textsubscript{2}O\textsubscript{3} (heavier) and especially Lu\textsubscript{2}O\textsubscript{3} (heaviest).

Seedless Y1512-containing La\textsubscript{2}O\textsubscript{3} (Fig. 11(a)) had a distinctly finer microstructure than the one containing Y\textsubscript{2}O\textsubscript{3} (Fig. 11(b)).
For ceramics with 1% seeds, we compared Y1512 sintered with La$_2$O$_3$ (Fig. 11(c)) or Sc$_2$O$_3$ (Fig. 11(d)), and again found a much finer microstructure for the former. For Lu1512, we compared ones sintered with La$_2$O$_3$ (Fig. 11(e)) or Lu$_2$O$_3$ (Fig. 11(f)), using a hot-pressing schedule (1800°C for 4 h and 1900°C for 1 h) designed to promote grain growth without causing decomposition. Although large elongated grains were obtained in both cases, the matrix grain size was smaller with La$_2$O$_3$ addition. Thus, compared to oxides that are lighter or heavier, regardless of whether the cation M entering a-SiAlON or not, La$_2$O$_3$ addition always resulted in a finer microstructure. Lastly, compared to Al$_2$O$_3$ (Fig. 11(g)) and SiO$_2$ (Fig. 11(h)), both being lighter oxides, La$_2$O$_3$ addition (Fig. 11(c)) again yielded a finer microstructure.

The strength of the interface at room temperature is compared using the R-curves of Y1512 and Lu1512, shown in Fig. 12(a) with different densification aids. The ceramics with La$_2$O$_3$ had a distinctly lower R-curve in both series, suggesting a stronger interface of La-containing grain boundary. This was supported by observation of crack path: the crack path was the smoothest for La-added materials and the roughest (with many zigzag features) for SiO$_2$-added materials (Fig. 12(b)), in agreement with the R-Curve data. The refractoriness of residual glass at high temperature is compared using the strength of the above ceramics at various temperatures, shown in Fig. 13. As mentioned previously, the strength of La-containing a-SiAlON at

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**Fig. 7.** Fracture resistance curves (R-curves) of Y1512 with (a) different amount of La$_2$O$_3$ and 0.25% seeds, (b) different amount of seeds and 2% La$_2$O$_3$, and (c) different amount of holding time at 1900°C and 2% La$_2$O$_3$ plus 1% seeds. (d) Propagation of indentation crack (from left to right) through large grains in material with 1% seeds and 2% La$_2$O$_3$ (optical micrograph).

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**Fig. 8.** Stress–displacement curves of Y1512 with 2% La$_2$O$_3$ and 1% seed. Downward curvature at high stress observed above 1300°C due to plastic deformation.

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**Fig. 9.** Hardness of Y1512 increases with microstructure refinement because of decreasing amount of seeds at 2% La$_2$O$_3$ or increasing amount of La$_2$O$_3$ at 0.25% seeds.
Complementary metal nitrides: following exchange reaction between these oxides and their
tations of silica and alumina are mutually commutable due to the
(h) and mechanical properties (Figs. 12 and 13). As the addi-
ics behave similarly in terms of microstructure (Figs. 11(g) and
in ceramics of high strength at both room temperature and high
1 Y1512 increases with increasing
sintering liquid because of increasing amount of La2O3 at 0.25% seeds or decreasing amount of AlN at 2% La2O3 and 1% seeds.

Fig. 10. Room-temperature strength of Y1512 increases with increasing sintering liquid because of increasing amount of La2O3 at 0.25% seeds or decreasing amount of AlN at 2% La2O3 and 1% seeds.

<table>
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<th>Base composition</th>
<th>Sintering aid, wt%</th>
<th>Seed, wt%</th>
<th>Secondary phases1</th>
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<tr>
<td>Y1512</td>
<td>2 La2O3</td>
<td>0</td>
<td>27R (vw)</td>
</tr>
<tr>
<td>Y1512</td>
<td>2 Lu2O3</td>
<td>0</td>
<td>27R (tr)</td>
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<td>0.25</td>
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<td>27R (tr)</td>
</tr>
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<td>0, 0.25, 0.5, 1, 2, 4, 6, 8, 10</td>
<td>27R (vw)</td>
</tr>
<tr>
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<td>2 La2O3</td>
<td>0, 0.25, 0.5, 1, 2, 4, 6, 8, 10</td>
<td>27R (ww)</td>
</tr>
<tr>
<td>Y1512*</td>
<td>2 La2O3</td>
<td>1</td>
<td>27R (ww), 12H (ww)</td>
</tr>
<tr>
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<td>21R (w)</td>
</tr>
<tr>
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<td>1</td>
<td>27R (ww), AlN(w)</td>
</tr>
<tr>
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<tr>
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</table>

1 Only secondary phases are listed, while α-SiAlON was the major phase. 2 Hot-pressed at 1900°C for 4 h, followed by 1900°C for 1 h. 3 Hot-pressed at 1900°C for 0–5 h. 4 Annealed, after hot pressing, for 20 h at either 1300, 1350, 1400, 1450, 1500, or 1550°C. vs, very strong; s, strong; m, medium; w, weak; vw, very weak; tr, traces; 27R(8AlN:SiO2), 21R(6AlN:SiO2) and 12H(5AlN:SiO2) are AlN polytypes, S–La7.58(SiO4)6O2 (JCPDS 76-0338). Powders were ball milled for 2 h and hot pressed at 1900°C for 1 h unless otherwise noted.

1300°C remained at about 600 MPa, which is now found valid for both Y1512 and Lu1512. In comparison, the strength of ceramics containing oxides of Sc, Y, Lu, Al, and Si as densification aids had a strength around 400 MPa or lower at 1300°C. These data suggest that, at least up to 1300°C, La-containing glass is stronger than other glasses.

4 The Unique Characteristics of La-Containing Glass

It is clear that La2O3 is an effective densification aid that results in ceramics of high strength at both room temperature and high temperature. On the other hand, ceramics with alumina and silica behave similarly in terms of microstructure (Figs. 11(g) and (h)) and mechanical properties (Figs. 12 and 13). As the additions of silica and alumina are mutually commutable due to the following exchange reaction between these oxides and their complementary metal nitrides:

\[
\text{SiO}_2 + \text{AlN} = \text{SiN}_4 + \text{Al}_2\text{O}_3
\]

it is not surprising that their effects are similar. For a quantitative comparison, note that 2 wt% of La2O3 addition is equivalent to the addition of 8 mol% LaO1.5 (M = 163 g/mol) to Y0.5SiO3Al2.7O1.3N14.8 (M = 605 g/mol), 2 wt% of SiO2 is equivalent to the addition of 20 mol% of SiO2 (M = 60 g/mol) to the same SiAlON, and 2 wt% of Al2O3 is equivalent to the addition of 23 mol% of AlO1.5 (M = 51 g/mol) to the SiAlON. Therefore, there is only a small shift in the overall nominal Si/Al ratio (9.3:2.7), by +2% (9.5:2.7) for SiO2 addition, −8% (9.3:2.93) for Al2O3 addition, and none for La2O3 addition. However, the 2 wt% oxide addition increases the overall oxygen content more significantly but also very differently, by 35% with SiO2 addition, 30% with Al2O3 addition, and only 10% with La2O3 addition. This comparison makes it evident that the alumina and silica additions should have a similar effect, whereas at the same weight percent the addition of La2O3 modifies the composition (oxide mole fraction and O/N ratio) much less. Yet, despite the large influence of SiO2 addition on the composition, we found the minimum amount of oxide addition required to yield fully dense bodies was the same, being about 1 wt% for both SiO2 and La2O3 (data not shown). This means that La2O3 is a more effective densification aid on both a molar and volume basis. Compared with other sesquioxides, Sc2O3, Y2O3 (both much lighter), and Lu2O3 (heavier), we recall that La2O3 addition yielded stronger ceramics at all temperatures. Thus, it is clear that La2O3, as a densification additive, is both special and highly beneficial.

The smaller matrix grain size and the stronger interface of La2O3-added ceramics are also noteworthy. In particular, the refinement of microstructure with increasing amount of La2O3 addition (Fig. 1), in contrast to the common experience that more liquid and oxide addition promotes microstructure coarsening, is interesting. In the case of SiO2 addition, we also found that the matrix grain size decreased as the amount (1–4%) of SiO2 increased (data not shown), but this was accompanied by the emergence of some very coarse grains. Similar observations of refinement of matrix grains as the amount of sintering additives was increased were reported in the literature of α-SiAlON.

The above observations support our hypothesis in Section I about the special attributes of La, which could arise because of its large ionic size and low FS. Inasmuch as liquid viscosity decreases with decreasing FS, we expect La-containing melt to be the least viscous among all RE-containing melts. This could explain why La2O3 is an effective densification aid. On the other hand, the N solubility and the glass-forming region of oxynitride
Fig. 11. Scanning electron microscopy micrographs of fracture surfaces of Y1512 without seeds containing 2% (a) La$_2$O$_3$ or (b) Y$_2$O$_3$; Y1512 with 1% seeds containing 2% (c) La$_2$O$_3$ or (d) Sc$_2$O$_3$; Lu1512 without seeds containing 2% (e) La$_2$O$_3$ or (f) Lu$_2$O$_3$, and Y1512 with 1% seeds containing 2% (g) Al$_2$O$_3$ or (h) SiO$_2$ (also referring to (c) to compare with 2% La$_2$O$_3$). Y1512 was hot pressed at 1900°C for 1 h; Lu1512 was hot pressed at 1800°C for 4 h followed by 1900°C for 1 h to promote grain growth.
glasses both increase with the size of RE cation. Thus, a more stable, La-containing liquid at the end of α-SiAlON precipitation should be richer in N. This could suppress grain growth and provide superior high-temperature strength, as an N-rich oxynitride glass is generally more viscous and refractory. This argument is consistent with several other observations in the literature. For example, Sun et al. found that La2O3 addition to Yα-SiAlON promoted sintering but retarded the formation of α-SiAlON. This could be because of the initially low viscosity that promoted sintering, and the later higher liquid stability that provided a smaller driving force for phase transformation (from Si3N4 to α-SiAlON). In the other limit of ionic size of RE oxides, Lu2O3 and Yb2O3 are used to obtain highly refractory α-Si3N4 partly because their oxynitride liquid can be easily crystallized This is understandable because Lu- and Yb-containing glasses are more viscous and stronger in view of the higher FS of these cations, but they also have poorer stability, thus easy to crystallize, which further reduces the liquid amount and strengthens the grain boundary. In contrast, our attempt to crystallize La-glass in Y1512 densified with 2 wt% La2O3 in the temperature range 1300–1500 °C showed only limited crystalline phase formation (isostructural with La silicate, see note “J” in Table I). This occurred in a narrow temperature range of 1300–1450 °C, and it had little impact on the high-temperature strength. Therefore, the La-containing glass is apparently too stable to be substantially crystallized at the volume present, in support of the above argument.

Lastly, the tendency for La to encourage growth of elongated grains has also been observed in the present study. As mentioned in the Section I, this is generally attributed to the stronger tendency for interfacial segregation at the grain prism surface for lower FS cations. However, even if such segregation occurred in our materials, it had little effect on the debonding strength of the grain boundary at room temperature. This aspect requires further understanding but is beyond the scope of the present study.

### IV. Conclusions

(1) Lanthanum oxide is a good densification aid for α-SiAlON, allowing densification, promoting the abnormal
growth of elongated grains, while refining the grain size of the matrix.

(2) $\alpha$-SiAlON sintered with La$_2$O$_3$ is highly refractory maintaining strength up to 1300°C, with no evidence of inelastic deformation preceding failure. High N content in the residual La-Si-Al–O–N glass in equilibrium with the N-rich $\alpha$-SiAlON is suggested to be the cause of this finding.

(3) By careful tailoring of microstructure, $\alpha$-SiAlON sintered with La$_2$O$_3$ additive can achieve high hardness (HV10 $\approx$ 20–21 GPa) and high strength from room temperature (~1000 MPa) to 1300°C (~600 MPa). While higher room temperature strength may be achieved via other additives, the strength retention at high temperature is the best when using La$_2$O$_3$.

(4) Relatively high toughness (reaching 7 MPa·m$^{1/2}$ in R-curve) may be obtained in La$_2$O$_3$-added $\alpha$-SiAlON with the presence of some elongated grains in the microstructure. However, further toughness improvement is limited in this series of ceramics owing to the relatively strong grain/glass grain boundary interface.

References


