Elimination of Grain Boundary Glass in $\alpha$-Sialon by Adding Aluminium

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Elimination of Grain Boundary Glass in α-Sialon by Adding Aluminium

Abstract
The elimination of residual glass in hot-pressed Y-α-SiAlON was demonstrated by varying the nitride composition. This was readily achieved by adding excess aluminium nitride (AlN), while the addition of excess Si₃N₄ had little effect. The amount of excess AlN required for this purpose increased with increasing Al and O content in α-SiAlON, and was higher if α-SiAlON contained larger interstitial cations. These results were explained by the thermodynamics of α-SiAlON precipitation. The elimination of liquid also led to suppressed grain growth, refined microstructure, and improved oxidation resistance. Grain coarsening by post-sintering annealing was required to obtain high fracture toughness.

Comments
The elimination of residual glass in hot-pressed Y-α-SiAlON was demonstrated by varying the nitride composition. This was readily achieved by adding excess aluminum nitride (AlN), while the addition of excess Si3N4 had little effect. The amount of excess AlN required for this purpose increased with increasing Al and O content in α-SiAlON, and was higher if α-SiAlON contained larger interstitial cations. These results were explained by the thermodynamics of α-SiAlON precipitation. The elimination of liquid also led to suppressed grain growth, refined microstructure, and improved oxidation resistance. Grain coarsening by post-sintering annealing was required to obtain high fracture toughness.

I. Introduction

Coring, referring to the compositional gradient in the solidified microstructure, is commonly seen after a multicomponent liquid is cooled to form a solid solution. It is also found in α-SiAlON1–3 and β-Si3N4/α-SiAlON,6 both are solid solutions requiring liquid-phase sintering. An example of coring in α-SiAlON is provided in Fig. 1, which shows diffraction patterns of α-SiAlON grains from crushed ceramics. These grains had been washed by a solvent (KOH), which removed the glass coating and gradually exposed the grain cores. As the core became more exposed, the diffraction pattern shifted to lower angles, indicating an increase in lattice parameters and an enrichment of m in the α-SiAlON composition \( M_{(n/2)Si_{3}N_{4}-(m/2)Al_{2}O_{3}N_{m}Si_{3}N_{4}} \), where M (an interstitial cation) is Y in this case. Thus, the local composition is non-uniform and clearly different from the overall composition. This is actually a common situation in α-SiAlON and β-Si3N4/α-SiAlON, for this reason, even nominally “single-phase” compositions may form two or more phases after solidification.

The problem of coring is especially relevant for α-SiAlON. Because of its ability to incorporate cations M (Li, Ca, Y, Ln) into the crystal lattice, α-SiAlON was thought to be capable of resorbing all the transient M-rich liquid after sintering. This would have removed grain boundary glass that forms from the residual liquid, which is a common cause for the poor high-temperature strength and oxidation resistance of many ceramics. Indeed, β-Si3N4 containing a small amount of α-SiAlON “scavenger” was found by Wada and Ukyo7 to have exceedingly high strength (1000 MPa) even at 1400°C. However, as pointed out by Rosenflanz,8 in all other α-SiAlON ceramics some glassy phase in the amount of 5–15 vol% is present in the microstructure, even though the diffraction patterns may have revealed only single-phase α-SiAlON. The existence of such glass can be readily verified by inspecting the micrographs of “single-phase” α-SiAlON, in which liquid phase exceeding ~5 vol% is usually visible because of its high M content that gives a bright contrast.9–13 The residual glass increases the creep rate in these otherwise hard and tough ceramics.8,14–20

Rosenflanz8 further showed that glass-free α-SiAlON with superior creep resistance could, after all, be obtained if an extra (20–30 wt%) amount of Si3N4/AlN (AlN) was added to the starting composition. In retrospect, we believe his results can be interpreted using the concept of chemical equilibrium. Because of the relatively lower stability of α-SiAlON at lower temperature, its formation is typically delayed so that from the transient liquid β-SiAlON, M-rich intermediate compounds (including AlN polytypes, M melilite, and J phase, etc.), and α-SiAlON of a non-nominal composition form first.21–24 (The complexity of the α-SiAlON system, including 13 equilibrium tetrahedra of α-SiAlON with the aforementioned compounds, was extensively studied by Sun et al.25.) As the formation of α-SiAlON requires sources of Si, Al, and M, once they are tied up in the intermediate compounds, these compounds will experience diminished driving force to dissolve. Therefore, complete precipitation of α-SiAlON is difficult, and “unreacted” liquid remains. We further believe that, according to Le Chatelier’s principle, the injection of more Si3N4 and AlN reactants as Si and Al sources should favor the formation of α-SiAlON, which could explain Rosenflanz’s finding. In this study, we will show that, for the above purpose, the addition of extra AlN is much more effective than the addition of extra Si3N4, which can be understood by refining the equilibrium argument after taking phase distribution into account. The effect of excess AlN on the microstructure and properties of α-SiAlON ceramics will also be examined.

II. Experimental Procedure

When using \( M_{2}O_{3} \) along with Si3N4 and AlN as source materials, the composition achievable for α-SiAlON is limited to \( n \geq 0.4+0.5m \), after taking into account the oxygen content in Si3N4 (1.26 wt%) and AlN (0.82 wt%) in the formulation. Therefore, three lowest oxygen compositions, Y1009, Y1512, and Y2014, with (m, n) = (1.0, 0.9), (1.5, 1.15), and (2.0, 1.4), respectively, that form “single phase” α-SiAlON were the focus of this study. Other selected compositions of different (m, n) and M were also examined for comparison. To these base compositions different amounts of AlN and/or Si3N4 were included, as summarized in Table I that lists the sample compositions and phase analysis. The starting powders used were Si3N4 (SN-E10, UBE Industries, Ube, Japan), AlN (Type F, Tokuyama Soda Co., Burlingame, CA), Y2O3 (99.995%, APS 25–50 nm, Alfa-Johnson Mathew Co., Ward Hill, MA), and \( Al_{2}O_{3} \) (AKP50, Sumitomo Chemical America, New York, NY). To all compositions Y1512 single crystals in the amount of 1% were added as seeds to control the microstructure. These seeds were prepared using the procedure reported elsewhere.26,27

Powder mixtures were attrition milled for 2 h at 600 rpm in anhydrous isopropanol with high purity Si3N4 milling media, in

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phases (e.g., Nd2AlO3N) resulting from binary reactions be-

Y-poor boundary (Y1009, Y1012) also had SEM analysis. The samples of the compositions located near the AlN and Y/Ln oxides were detected by either XRD or different amounts of grain dissolution. The increase of peak intensities at washing with KOH solution for (upper) 60 h, and (lower) 120 h to cause cases XRD indicated that The results of phase analysis are summarized in Table I. In all applied at 1000 pressure) at a uniaxial pressure of 30 MPa. The pressure was achieved in all cases. To coarsen the microstructure, post-hot-

pressing annealing of some samples was conducted in a gas-pressure-sintering (GPS) furnace at 1950 1 h after reaching 1900 C, then cooling with the furnace C/min, followed by holding for 1 h after reaching 1900 C, then cooling with the furnace (~50 C/min down to 1500 C). Full density (99% +) was achieved in all cases. To coarsen the microstructure, post-hot-

pressing annealing of some samples was conducted in a gas-pressure-sintering (GPS) furnace at 1950 C for 4 h at 10 MPa of nitrogen pressure.

Phase composition was characterized by X-ray diffraction (XRD) using pulverized samples and CuKα radiation. Micro-

structure characterization of sintered samples was performed on fractured as well as polished sections using an optical micro-

scope and a scanning electron microscope (SEM), which was also used for energy-dispersive X-ray spectroscopy (EDX) element-

al mapping. The R-curves of the hot-pressed materials were recorded by in situ observation of crack propagation in bars (approximate dimensions 30 mm x 2 mm x 3 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 details of these experimental procedures were reported elsewhere.16

III. Results

The results of phase analysis are summarized in Table I. In all cases XRD indicated that α-SiAlON was the major phase. No phases (e.g., Nd2AlO3N) resulting from binary reactions between AlN and Y/Ln oxides were detected by either XRD or SEM analysis. The samples of the compositions located near the Y-poor boundary (Y1009, Y1012) also had β-Si3N4 as a second phase, while others, such as the ones in the center of the solubility region (Y1512) or near the Y-rich boundary (Y2014), had AlN polytypes (21R and 27R) with an amount that increased with the amount of extra AlN. Unreacted AlN was detected too when the amount of extra AlN was large. The above phase compositions might not be the equilibrium ones; certainly the AlN and 21R/27R polytype could evolve toward the more AlN-rich polytype 2H. However, in our experience, this did not happen in any reasonable amount of holding time (e.g., 4 h), probably because of lack of residual liquid as will become clear later. Much longer holding time or higher temperature (above 1900 C) tends to cause decomposition of the samples.

As an example of α-SiAlON located near the M-poor phase boundary, Y1012 contained glass pockets that are visible in Fig. 2(a). Similar to the report of Rosenflanz, simultaneous ad-

dition of both Si3N4 (10%) and AlN (5%) almost completely removed the glass pockets (Fig. 2(b)). On the other hand, ad-

dition of Si3N4 (20%) alone had little effect on the amount of glass; instead, it merely caused the formation of β-Si3N4 and some 21R (Fig. 2(c)). In contrast, the addition of AlN (5%) almost completely removed the glass pockets (Fig. 2(d)), while leaving some 21R as the second phase.

As an example of α-SiAlON located in the center of the single-phase region, Y1512 also contained glass pockets that are visible in Fig. 3(a). The addition of 10% AlN appeared to have completely removed the glass pockets (Fig. 3(c)). After a post-
sintering heat treatment at 1950 C for 4 h, grain coarsening caused the residual glass to concentrate at fewer grain junctions rendering them visible (Fig. 3(d)), but the amount of glass was quite small in comparison with unmodified Y1512 after the same heat treatment (Fig. 3(b)). A further visualization of the very different microstructures of these samples was afforded by SEM micrographs of fracture surfaces (Figs 3(e–h)). It is clear that the addition of AlN is very effective in not only eliminating the residual glass but also reducing the grain size and suppressing the growth of elongated grains. Using EDX elemental mapping, we

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### Table I. Composition and Phase Content of Selected Samples Used in this Work

<table>
<thead>
<tr>
<th>Base composition</th>
<th>+ Si3N4 (wt%)</th>
<th>+ AlN (wt%)</th>
<th>Second phases</th>
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<tbody>
<tr>
<td>Y1009</td>
<td></td>
<td>β’ (m), 21R (tr)</td>
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</tr>
<tr>
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<td></td>
</tr>
<tr>
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<td></td>
<td>21R (vw), AlN (w)</td>
<td></td>
</tr>
<tr>
<td>Y1110 0, 1, 2, 5</td>
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</tr>
<tr>
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<td></td>
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</tr>
<tr>
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</tr>
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</tr>
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<td>Y2014</td>
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</tr>
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<tr>
<td>Yb2014 10</td>
<td></td>
<td>27R (m), AlN (m)</td>
<td></td>
</tr>
</tbody>
</table>

1After hot pressing, sample was GPS annealed at 1950 C for 4 h.
27R(Al15O32Si3), 21R(6Al15Si3O32), and 15R(Al15O32Si3O32) are AlN polytypes. β’ is β-SiAlON (z = 2), K is kyanite (Al2O3:Sip).
vs, very strong; s, strong; m, medium; w, weak; vw, very weak; tr, trace; GPS, gas-pressure-sintering.
found that the dark areas in Fig. 3(b) were rich in Al, poor in Si, and depleted of Y, as expected for the AlN polytype. The matrix contained Y and had an Al/Si ratio of 0.29 (Fig. 4), in agreement with the expected Al/Si ratio, \( \frac{(m+n)}{(12-m-n)} = \frac{2.7}{9.3} = 0.29 \), for the Y1512 composition.

To determine the minimal amount of extra AlN required to completely eliminate residual glass in \( \alpha \)-SiAlON, we added 1%–10% of extra AlN to several base compositions; 1%, 2%, and 5% to Y1110; 1%, 2%, 5%, 7%, and 10% to Y1512; 5% to Y1009 and Y1311; and 10% to Y1813 and Y2014. The results based on SEM examination are summarized in Fig. 5, which indicates that the required AlN amount increases with increasing \( m \)-value. In the case of Y1009, there were very few glass pockets even without extra AlN (Fig. 6(a)). In comparison, Y2014 (Fig. 6(b)) still contained a large number of glass pockets, which remained even after 10% AlN addition (Fig. 6(c)). Based on the comparison of Y1009 (Fig. 6(a)) and Y1012 (Fig. 2(a)), we may also state that SiAlON compositions with \( n > 0.4 + 0.5m \) will require even more AlN to eliminate the residual glass.

The above observations were verified in selected compositions using other rare earth M. Yb 2014, just like Y2014, contained a large amount of glass that could not be eliminated by 10% extra AlN. Nd1009 (Fig. 7(a)), which has lower phase stability than Y1009, contained more glass than Y1009 (Fig. 6(a)). In fact, it still had considerable residual glass left after 5% addition of AlN (Fig. 7(b)).

\( R \)-curve measurements shown in Fig. 8 for Y1512 revealed that the AlN addition resulted in a lower fracture resistance because of the finer microstructure and lack of elongated grains. Grain coarsening at 1950°C for 4 h was able to improve the fracture resistance, even at a very high AlN amount. The flexural strength was 670 MPa for the unmodified Y1512, 600 MPa for Y1512+10% AlN, and 580 MPa for the latter after coarsening. The reduced amount of glass in \( \alpha \)-SiAlON/AlN composites also led to a significant improvement in the oxidation resistance (Fig. 9). In fact, some of our AlN-rich \( \alpha \)-SiAlON showed similar or better oxidation resistance than commercial \( \beta \)-Si3N4 (SN282 of Kyocera, containing Lu2O3 as sintering aid). Further details of the oxidation study will be reported elsewhere.

**IV. Discussion**

(1) **Strategy to Eliminate Residual Glass**

At the later stage of liquid-phase sintering, \( \alpha \)-SiAlON precipitation and liquid consumption typically proceed by the following reaction:

\[
\text{M-rich liquid + } \beta \text{-SiAlON + AlN-polytype } \Rightarrow \alpha \text{-SiAlON}
\]

in which the reactants are, respectively, the source of M, Si, and Al for \( \alpha \)-SiAlON.\(^{21,22}\) As we mentioned in the introduction, these intermediate phases are more stable than their counterparts in the starting powders (\( \text{M}_2\text{O}_3, \beta \text{-Si}_3\text{N}_4, \) and AlN, as sources of M, Si, and Al, respectively). Therefore, the driving force for the reaction is much lower than that of

\[
\text{M}_2\text{O}_3\text{-rich liquid + Si}_3\text{N}_4 + \text{AlN } \Rightarrow \alpha \text{-SiAlON}
\]

and it will be further decreased if the \( \alpha \)-SiAlON is of a relatively low stability composition (e.g., with larger M).\(^{28,29}\) Previously, Rosenflanz and Chen have shown that a lower driving force dictates slower transformation kinetics, for example if \( \text{Si}_3\text{N}_4 \) in (2) is of a higher stability (\( \beta \)-type versus \( \alpha \)-type).\(^{5}\) We now propose that this can be countered by providing extra reactants (\( \text{Si}_3\text{N}_4 \) and especially AlN) that effectively increase the driving force. The elevated driving force then favors \( \alpha \)-SiAlON precipitation and liquid consumption, thus eliminating the residual glass.

Accordingly, \( \alpha \)-SiAlON compositions near the phase boundary or with a larger M are expected to have more residual glass because of their lower \( \alpha \)-SiAlON stability. It is also obvious that
the liquid amount increases with the M and O content, thus the amount of extra AlN addition required for eliminating residual glass should increase. Together, these two considerations can qualitatively rationalize our observations on the relation between composition and glass amount. Specifically, higher $m$ and $n$ values (implying higher M and O content) have more residual glass, which requires more AlN addition to eliminate it. So does a larger M (implying lower $\alpha$-SiAlON stability).

Our results are consistent with those of Rosenflanz$^8$ who used simultaneous Si$_3$N$_4$ and AlN addition to eliminate residual glass. This is because, compositionally, the sum of $\alpha$-SiAlON and Si$_3$N$_4$ is equivalent to another $\alpha$-SiAlON of a lower $m$ (and

**Fig. 3.** Scanning electron microscope (SEM) backscattered electron mode images of (a) Y1512, (b) Y1512 after 4 h at 1950°C, (c) Y1512+10% AlN, and (d) Y1512+10% AlN after 4 h at 1950°C. Glass pockets appear as white spots, dark regions are AlN polytype 27R. Corresponding SEM micrographs of fractured surfaces of (a–d) are shown in (e–h).
a slightly lower $n$ composition. Therefore, the net effect of Rosenflanz’ $\text{Si}_3\text{N}_4+\text{AlN}$ addition is the same as AlN addition, after the effect of $m/n$ downshift is considered. However, our experiments also found that AlN addition is much more effective than $\text{Si}_3\text{N}_4$ addition for the purpose of eliminating residual glass. To understand why, we need to take into account the stoichiometry and microstructure of $\alpha$-SiAlON.

(A) Stoichiometry: While the formation of $\alpha$-SiAlON requires Si, Al, and M, charge consideration (implicit in the formula $\text{M}_{m/3}\text{Si}_{12-(m+n)}\text{Al}_{m+n}\text{O}_{16-2n}\text{N}_{-2n}$) dictates that the incorporation of $\text{M}^{m+}$ and $\text{Al}^{3+}$ (which replaces $\text{Si}^{4+}$) should be in the ratio of 1:3. As no such restriction applies between M and Si, the addition of a sufficient amount of AlN is clearly more critical than $\text{Si}_3\text{N}_4$ addition for the removal of M-rich liquid.

(B) Microstructure: In the composition that has only extra $\text{Si}_3\text{N}_4$, the amount of AlN polytypes was quite small (Fig. 2(c) and Table I). As a result, lacking local sources of Al, reaction (1) could not proceed to the full extent throughout the sample, thus much residual glass still remained. In contrast, in the composition with extra AlN, the source of Al is assured by the relative abundance of AlN polytypes that are well dispersed (e.g., Figs. 2(b), (d) and 3(c)), and the source of Si may simply come from previously formed non-equilibrium $\alpha$-SiAlON that is obviously abundant.

The stoichiometric effect of AlN can also be rationalized by considering the precipitation of $\alpha$-SiAlON from a hypothetical M–Si–Al–O–N glass. As the initial concentration of Al is much lower than that of Si, the addition of AlN will shift the overall Al/Si ratio more than the addition of $\text{Si}_3\text{N}_4$. The stability of aluminosilicate glasses is likely to be maximal at an intermediate Al content. Therefore, too high an Al/Si or N/O ratio in the liquid in the presence of excess AlN could destabilize the glasses, forcing the precipitation of $\alpha$-SiAlON.

(2) Refractory SiAlON and $\text{Si}_3\text{N}_4$

The experiments of Rosenflanz and ours both found improved oxidation resistance in the nitride-modified ceramics. The simultaneous addition of $\text{Si}_3\text{N}_4$ and AlN in the amount that Rosenflanz prescribed is equivalent to the subtraction of $\text{M}_2\text{O}_3$ from the overall composition. This, in turn, is equivalent to the reduction of sintering aids, which is a common strategy used in the silicon nitride field to improve the refactoriness of the ceramics. In our experiment, the addition of AlN removed $\text{SiO}_2$ from the
that it is the residual glass that is vulnerable to oxidation attack. In this respect, the superior oxidation resistance of AlN-added α-SiAlON and low-oxide-additive β-Si₃N₄, both having very little residual glass, has the same microstructural origin.

V. Conclusions

1. The addition of AlN reduces the amount of residual glassy phase in α-SiAlON. This is attributed to the promotion of α-SiAlON precipitation by providing an extra driving force, which is made readily available with a uniform dispersion of AlN polytypes. In addition, the consumption of SiO₂ by AlN-polytype formation may deplete the oxygen content and destabilize the liquid, further shifting the reaction equilibrium toward the formation of α-SiAlON phase and reducing the amount of glass.

2. Glass elimination in low m and n α-SiAlON, which has less residual liquid even when unmodified, can be readily achieved by adding a few weight percent of AlN. Compositions with large m and n and those with large interstitial cations (such as Nd) require a much larger amount of extra AlN to eliminate the glass.

3. The addition of extra Si₃N₄ to the low-m Y-α-SiAlON compositions leads to the formation of αβ composite but has little effect on the amount of residual glass. This is because of the poor availability of AlN or AlN polytypes, which provide the source of Al for α-SiAlON formation.

4. AlN addition refines the microstructure of α-SiAlON by reducing the liquid content and increasing liquid viscosity. This leads to a lower fracture toughness and strength. However, grain coarsening by post-sintering annealing can restore some fracture toughness.

5. AlN-added α-SiAlON ceramics have superior oxidation resistance. This refutes the notion that presence of Al is detrimental to the refractoriness of silicon nitride ceramics. Instead, it reaffirms the direct connection between residual glass and refractoriness.

References


Fig. 7. Scanning electron microscope backscattered electron images of (a) Nd1009 and (b) Nd1009 + 5% AlN. The amount of glass in (a) is more than in Y1009 in Fig. 6(a). The amount of glass in (b) is more than in Y1012 + 5% AlN in Fig. 2(d).

Fig. 8. R-curves of Y1512 with different amounts of AlN. Fracture toughness is reduced with increase in AlN content because of inhibited grain growth. This problem may be partially overcome by annealing at higher temperature (1950 C).

Fig. 9. Thickness of oxide layer on Y1512 and Y1512 + 10% AlN as a function of time in O₂–NaNO₃ (300 ppm) at 1100°C (courtesy of Dr. H. Du).
March 2006

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