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Abstract
Seeding effects on the microstructure and mechanical properties of single-phase Ca-α-SiAlON ceramics have been investigated. Whereas a small amount of seeds can transform the microstructure from one of fine equiaxed grains to one consisting of many needle-like grains, the highest fracture toughness of 8 MPa · m$^{1/2}$ is not reached until 8% seeding. This contrasts with the much higher seed efficiency in Y-SiAlON, where the peak toughness is reached at 1% seeding. The difference and the general trend of mechanical properties of seeded α-SiAlONs are discussed in terms of α-SiAlON formation and toughening mechanisms.

Comments
Effect of Seeding on the Microstructure and Mechanical Properties of $\alpha$-SiAlON: II, Ca-$\alpha$-SiAlON

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Seeding effects on the microstructure and mechanical properties of single-phase Ca-$\alpha$-SiAlON ceramics have been investigated. Whereas a small amount of seeds can transform the microstructure from one of fine equiaxed grains to one consisting of many needle-like grains, the highest fracture toughness of 8 MPa m$^{1/2}$ is not reached until 8% seeding. This contrasts with the much higher seed efficiency in Y-SiAlON, where the peak toughness is reached at 1% seeding. The difference and the general trend of mechanical properties of seeded $\alpha$-SiAlONs are discussed in terms of $\alpha$-SiAlON formation and toughening mechanisms.

I. Introduction

Compared to yttrium- and rare-earth-containing silicon nitride and SiAlONs, calcium-containing products have a cost advantage by using less expensive raw materials and requiring lower sintering temperatures. In manufacturing self-reinforced $\beta$-Si$_3$N$_4$ ceramics, calcium is also known to promote whisker growth, resulting in needle-like grains of a high aspect ratio. This effect is apparently quite dramatic, because the amount of calcium used for such a purpose is typically in the range of only 0.1–1 wt%. Fracture surfaces of calcium-added self-reinforced $\beta$-Si$_3$N$_4$ show a much higher calcium content than that in the background glasses, indicating a strong tendency for calcium segregation that weakens grain boundaries. In $\alpha$-SiAlON, there is also evidence that calcium promotes the formation of needle-like grains. For example, whereas Ca-$\alpha$-SiAlONs with 4–7 wt% CaO (such as Ca-0809 and Ca-1512; for designation, see the companion paper) have mostly equiaxed grains in the microstructure, compositions with higher calcium contents, up to 14 wt% CaO (Ca-3020), show many elongated grains. Unfortunately, however, ceramics of high calcium and aluminum content also tend to have a large amount of residual glasses, often with AlN polytypes. This in turn results in disappointing properties, such as low hardness (not exceeding 16 GPa), inferior toughness, weak creep strength, and poor chemical resistance.

Recently, we have shown that $\alpha$-SiAlONs of a low calcium content can impart a microstructure with elongated grains when seed crystals are introduced during processing. The resultant ceramics are both hard and tough, with properties roughly comparable to rare-earth containing $\alpha$-SiAlONs. In this paper we report in detail the seeding effects on the microstructure and mechanical properties of Ca-$\alpha$-SiAlON. These results are compared with ones on Y-$\alpha$-SiAlON reported in the companion paper. Through this comparison, we hope to understand the mechanism of seeding and microstructure development in $\alpha$-SiAlONs and to provide a basis for further microstructure optimization for future applications.

II. Experimental Procedure

Experimental procedures used in this study were similar to those described in the companion paper. The main difference here is the composition, which is Ca$_{10}$Si$_7$Al$_2$O$_{12}$N$_{14.8}$. This has been referred to as Ca-1512 in our previous studies, indicating $m = 1.5$ and $n = 1.2$ in the conventional designation of $\alpha$-SiAlON, $M_{10m}Si_{12-4m}Al_{2m+2n}O_{12+4n}N_{16-1.8m}$. SiAlON of this composition is known to be rather stable and can be prepared using Si$_3$N$_4$, AlN, CaCO$_3$ (CS-3NA, Pred Materials, Inc., New York) and Al$_2$O$_3$, as shown in Table I. Samples were hot pressed in nitrogen at either 1900° or 1950°C for 1 h. Full densification was achieved in all cases. The phase purity and the composition were assessed using X-ray diffraction (XRD), which showed reflections that all could be identified with the $\alpha$-SiAlON structure with the lattice parameters listed in Table I.

For seeding, we selected seed crystals that have a similar average area/volume as those used for seeding Y-$\alpha$-SiAlON ceramic in the companion paper. These seeds were prepared using the method described elsewhere. A scanning electron microscope (SEM) image of such seed crystals is shown in Fig. 1. Their essential structures and geometric parameters are summarized in Table II. The lattice parameters of seeds determined using XRD, also listed in Table II, are very similar to those of the ceramics of the overall composition of Ca-1512 (Table I). Various amounts of seeds from 1–16 wt% were used to control the microstructure. The maximum amount here is much larger than that used in the companion paper (5%) because peak toughening was achieved at a larger amount, as will become clear later.

Microstructures were studied by SEM using polished sections normal to the hot-pressing axis. Molten KOH was used for etching. Further details of the characterization and mechanical testing methods were described in the companion paper. Strength was measured in three-point bending using samples of dimensions 30 mm $\times$ 2.5 mm $\times$ 2.5 mm finished with 400 grit diamond wheel grinding. An outer span of 13 mm and a crosshead speed of 0.5

<table>
<thead>
<tr>
<th>Table I. Composition and Lattice Parameters of Ca-1512 Ceramic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>Composition of starting powder (wt%)</td>
</tr>
<tr>
<td>Si$_3$N$_4$ (1.24% oxygen)</td>
</tr>
<tr>
<td>AlN (0.88% oxygen)</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
</tr>
<tr>
<td>CaCO$_3$</td>
</tr>
<tr>
<td>Lattice parameters of ceramic</td>
</tr>
<tr>
<td>$a$ (Å)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
</tr>
</tbody>
</table>
mm/min were used. Both resistance (R-curve) and single-edge-notched-beam (SENB) fracture toughness were measured in four-point bending. Bars of 30 mm × 3.5 mm × 2 mm, with their tensile surfaces lying parallel to the hot-pressing plane, were used for both measurements. The initial crack of ~40%–60% of total bar height was introduced using a thin blade, then followed by wire sawing to achieve a tip radius of 10 μm. In the R-curve measurement, the load was increased in small increments to allow in situ monitoring of crack extension. In the SENB toughness measurement, the load was increased until the specimen failed and the initial crack length was used for toughness determination.

III. Results

(1) Microstructure of 1900°C Ceramics

Microstructures of Ca-1512 ceramics hot pressed at 1900°C are shown in Fig. 2. The unseeded material (Fig. 2(a)) contains only small grains with a low aspect ratio (AR). The effect of seeding is clear. With only 1% of seed crystals added, the ceramic (Fig. 2(b)) developed a bimodal distribution of grains, comprising some very long needles embedded in a matrix of fine grains. With a gradual increase in the seed amount (Fig. 2(c)), the length of the needle-like grains decreases as their number increases. At the highest level of seeding, 16%, there is evidence of (large) grain coalescence, as seen from the presence of blocky grains with greatly increased widths (Fig. 2(d)). It is also easy to see core-shell structures in these large grains, which reveals seed crystals (Fig. 2(e)).

For a quantitative analysis, we measured the dimensions (length and width) and surface area of 600–1000 grains and calculated their AR. This was performed in a semiautomated way using “Image Tool” software (University of Texas Health Science Center, San Antonio, TX). Grain area and grain width distributions, in terms of their area fractions on the micrographs, are presented in Figs. 3 and 4, respectively. They show a clear difference between unseeded and seeded microstructures. In the unseeded microstructure, the grain area and width have a narrow distribution at small sizes. In the seeded microstructure, the distribution is much broader and the long tail in the distribution clearly corresponds to the population of large needle-like grains.

To determine the correlation between the needle-like grains and the seeds introduced, we analyzed the upper end (i.e., the tail) of the above distributions. Because the largest grain areas seen in the unseeded ceramics are 1.35 μm² (Fig. 3 at 0% seeding), this value is set as the cut-off beyond which all the grains are considered to be produced from seeds. The areal number density of the large grains thus defined, and their average length, width, aspect ratio, and grain area, as well as their total area fraction, are tabulated in Table III for comparison. Also shown is the estimated areal number density of seed crystals in the ceramics, assuming an average area of 0.34 μm² per seed (see Table II). We can see that the number density of (needle-like) grains within the tail is initially (1% and 2% seeding) comparable to that of seed crystals. This would suggest an approximate one-to-one correspondence between seed crystals and elongated grains. As the amount of seed crystals increases (e.g., 4% and 8%), the number of seeds begins to exceed that of large grains. This indicates that not every seed crystal could nucleate a needle-like grain. At the largest amount of seed crystals used (16%), the number density of needle-like grains actually decreases. This is accompanied by an increase of their average grain area and an abrupt increase of the scatter in width, which results from the coalescence of some grains in this ceramic (Fig. 2(d)). Overall, the total area fraction of needle-like grains in the tail distribution remains nearly constant at ~0.42, but the relative scatter of their dimensions (grain area, width, length, and AR), defined by the ratio of standard deviation to the mean, is the smallest at 4% and 8% seeding and markedly higher at lower and higher seed concentrations (Fig. 5). This implies that the bimodal microstructure, having interlocking needle-like grains in a fine-grain matrix, is more uniform at 4% and 8% seeding. The above analysis was also repeated using width distributions (Fig. 4). Very similar results (not shown here) were obtained if the cutoff is taken as 0.8 μm, which is about the largest grain width in the unseeded microstructure.

(2) Microstructure of 1950°C Ceramics

Ceramics sintered at 1950°C exhibit microstructure coarsening and some abnormal grain growth (Fig. 6). In both unseeded and seeded microstructures, however, the same qualitative trend seen in 1900°C ceramics (from fine grains for unseeded material, to bimodal distribution with a few large elongated grains at 1%–2% seeding, to a larger number of elongated but shorter grains at 4%–16% seeding) is again observed, albeit at a coarser level. Grain coalescence forming blocky grains (marked by arrows in Fig. 6(c)–(d)) also takes place in both 8% and 16% seeded ceramics. Otherwise, microstructures shown in Fig. 6(a)–(d) are quite similar to those shown in Fig. 2(a)–(d).

(3) Mechanical Properties

R-curves of ceramics hot pressed at 1900°C are shown in Fig. 7(a). The unseeded material exhibits an essentially flat R-curve. With 1%–2% of seed crystals, the toughness increases but the slope of R-curves is not significantly altered. With the amount of seed crystals increased to 4% and 8%, steeper R-curves emerge, then approaching a plateau after a crack length of ~100 μm. Peak toughening is achieved at 8% seeding when the plateau K₁ₚ is ~8 MPa m¹/₂. At 16% seeding, the toughness actually decreases. This trend is confirmed by SENB toughness measurements. The SENB toughness Kₑ is shown in Fig. 8 for the ceramics hot pressed at 1900°C and it reaches a peak of 6.4 MPa m¹/₂ at 8% seeding.

To further assess the effect of microstructure on the mechanical properties, strength and hardness values are shown in Table IV for unseeded ceramics and 4% seeded ceramics sintered at the two temperatures (1900°C and 1950°C). The highest strength is achieved...
in 4% seeded ceramic hot pressed at 1900°C. Both strength and strength variation are improved by seeding. The Vickers hardness (measured under 10 kg load) decreases slightly in the seeded ceramics hot pressed at 1900°C, although the measured value of 19 GPa is still higher than those reported in the literature for other single-phase Ca-SiAlON compositions. Hot-pressing at 1950°C, however, lowers the hardness further. Thus, grain coarsening has an adverse effect on hardness, suggesting relatively weak grain-boundaries in this ceramic. We note that in the seeded ceramics, grain coarsening at 1950°C is not as severe, in relative terms, as in unseeded ceramics. This explains why, in the seeded ceramics, the hardness decrease caused by higher hot-pressing temperature is less apparent.

A somewhat different R-curve behavior is observed in ceramics hot pressed at 1950°C (Fig. 7(b)). The unseeded ceramic has a rising R-curve that reaches a plateau of 6 MPa m^{1/2} after 100 μm of crack propagation. All seeded ceramics, however, have similar R-curves that continue to rise even when the crack growth is as
much as 800 μm. Values of $K_R$ lie in the range of 7.5–8.5 MPa m$^{1/2}$ at 200 μm crack growth. Values of SENB fracture toughness at 1950 °C (Fig. 8) are higher than those at 1900 °C and have a broad maximum at ~8% seeding.

IV. Discussion

(1) Seed-initiated Growth

As in Y-SiAlON, seeds of the Ca-α-SiAlON composition that is identical to the final ceramic composition are stable and effective in initiating α-SiAlON precipitation and growth. This stability is evidenced by the approximate one-to-one correspondence between seed crystals and elongated grains when the amount of seeds is small (Table III, at 1% and 2%). Therefore, it allows the microstructure of Ca-SiAlON to be effectively controlled by seeding as in Y-SiAlON. In the following, we make a more detailed comparison between the calcium and yttrium systems to shed light on the mechanisms that control microstructure evolutions in these ceramics.

The comparison is made for the same processing conditions (hot pressed at 1900 °C) and similar seeds (S-1 in the companion paper, with a comparable size and shape as seeds used in this study). In both systems, whereas unseeded ceramics have mostly fine equiaxed grains, seeded ceramics contain elongated grains. Peak toughening occurs when elongated grains form a highly interlocked microstructure. There are, however, several differences between microstructures of the two SiAlONs. First, the total area fraction of elongated grains in the calcium system (~40%–45%) is somewhat smaller than that in the yttrium system (~47%–55%). This suggests that the effectiveness of seeding is lower in Ca-SiAlON than in Y-SiAlON. Second, peak toughening with highly interlocked microstructure occurs at ~4%–8% seeding in Ca-SiAlON, compared with 1% seeding in Y-SiAlON (Fig. 8), suggesting that the optimal microstructure is achieved after different microstructure evolution. Third, while grain impingement at high seed concentrations generally causes a decrease in the size and number density of elongated grains, in Ca-SiAlON needle-like grains also coalesce to form large blocky grains. This could be caused by the higher seed concentrations in Ca-SiAlON. Fourth, elongated grains in seeded Ca-SiAlON tend to have a higher AR and smaller grain width than in seeded Y-SiAlON, suggesting a stronger growth anisotropy in Ca-SiAlON. The following discussion addresses the likely origins of these differences, except the optimal microstructure, which is discussed in the next section when we consider toughening mechanisms.

To understand the above results, we first note that the grain size of unseeded Ca-α-SiAlON (0.5 μm, Fig. 2a) is smaller than that of unseeded Y-α-SiAlON (0.8 μm, Fig. 2(a) of the companion paper) when both were hot pressed at 1900 °C. Such grain size difference has been attributed to the different driving force for α-SiAlON precipitation, with a larger driving force associated with a finer grain size because of more favorable nucleation statistics in the solution/reprecipitation process. Compared with Y-α-SiAlON, the driving force for forming Ca-α-SiAlON appears to be higher. This is based on the size of their respective compositional range of the α-SiAlON single phase in the phase diagram, which is larger for Ca-SiAlON. So the grain size of unseeded ceramics is expected to be smaller in Ca-SiAlON. This assessment of different driving force is also supported by our experience (not reported here) that Ca-α-SiAlON forms at a lower temperature (~1500 °C at 50% transformation) than Y-α-SiAlON (~1650 °C at 50% transformation) during hot pressing.

The large driving force for α-SiAlON formation in the calcium system means that there is probably a strong competition in the seeded ceramics between seed-initiated growth and "homogeneous" SiAlON precipitation (onto α-Si$_3$N$_4$ particles instead of artificial α-SiAlON seeds). Most likely, the latter precipitation leads to the fine grains, which form the matrix of the seeded ceramic that also contains large elongated grains produced from the seeds. Once this happens, the remaining driving force for further grain growth is capillary in nature, which is much smaller. Meanwhile, the higher stability of Ca-α-SiAlON precipitates

![Grain size distribution](image)
implies a lower solubility of their constituents in the surrounding liquid, thereby slowing the diffusion kinetics further. Thus, only the more potent seed crystals, presumably those larger ones, are able to rapidly grow into the liquid and the surrounding fine-grain matrix, whereas the less potent seed crystals grow more slowly and may not yield large grains of a distinct, needle-like shape. This explains why seeding efficiency appears to be less in Ca-SiAlON. In comparison, in Y-SiAlON, “homogeneous” precipitation has a smaller driving force and presents less competition. Therefore, all the seeds are effective in initiating growth, which is driven by the transformation of the free energy of $\alpha$-SiAlON formation (from $\alpha$-Si$_3$N$_4$ and the constituents) that persists for a longer duration. This explains why there is apparently a one-to-one correspondence between seed crystals and large grains even in the “saturation” microstructure in Y-SiAlON. It also explains why the area fraction of large grains is somewhat larger in Y-SiAlON than in Ca-SiAlON. In addition, because fewer seeds are needed to achieve a comparable microstructure in Y-SiAlON, the probability for grain coalescence is lower and fewer blocky grains tend to form.

Regarding the different grain shapes in the two systems, we note that in the literature of $\alpha$-Si$_3$N$_4$ with rare-earth oxide additives, it has been reported that the aspect ratio increases with the ionic radius of the rare-earth cation. This trend has been further correlated to the observation of a stronger segregation of larger cation at the grain boundary that results in increased grain boundary thickness. Together, they suggest that cation segregation may poison the interfacial kinetics on the prismatic surfaces of silicon nitride grains, so that the growth anisotropy becomes more severe as the tendency for cation segregation increases. From the literature, it is also known that calcium segregates strongly in $\alpha$-SiAlON. If the same trend occurs in $\alpha$-SiAlON ceramics, it would explain why elongated grains have a higher aspect ratio in Ca-SiAlON than in Y-SiAlON. This aspect of interfacial segregation could also be of importance to mechanical properties in that it impacts the interfacial strength and toughness that control grain debonding during grain pullout. Further investigation of this aspect to compare Ca-SiAlON and Y-SiAlON, as well as $\alpha$-SiAlON, $\beta$-Si$_3$N$_4$, and $\beta$-SiAlON, is warranted.

The effects described above are applicable to ceramics hot pressed at 1950$^\circ$C; however, at this temperature, the growth kinetics is obviously faster than at 1900$^\circ$C. This results in the development of larger grains, shifting the grain-size distribution to larger sizes. The abnormal grain growth that takes place at this temperature could be the result of reduced driving force of larger grains toward Ostwald ripening. As explained by Yoon et al., a reduced driving force tends to accentuate kinetic disparity among different growth facets, hence abnormal grain growth.

### Table III. Large Grains and Their Average Characteristics

<table>
<thead>
<tr>
<th>Amount of seed (%)</th>
<th>Number of seeds</th>
<th>Number of grains</th>
<th>Area fraction</th>
<th>Area, $A$ ($\mu$m$^2$)</th>
<th>Width, $W$ ($\mu$m)</th>
<th>Length, $L$ ($\mu$m)</th>
<th>AR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>49</td>
<td>59</td>
<td>0.45</td>
<td>$5.74 \pm 6.14$</td>
<td>$1.30 \pm 0.65$</td>
<td>$5.33 \pm 3.38$</td>
<td>4.20 $\pm 1.90$</td>
</tr>
<tr>
<td>2</td>
<td>95</td>
<td>85</td>
<td>0.41</td>
<td>$3.75 \pm 3.32$</td>
<td>$1.04 \pm 0.38$</td>
<td>$4.50 \pm 2.45$</td>
<td>4.47 $\pm 1.77$</td>
</tr>
<tr>
<td>4</td>
<td>192</td>
<td>113</td>
<td>0.41</td>
<td>$5.55 \pm 1.26$</td>
<td>$1.11 \pm 0.29$</td>
<td>$3.26 \pm 1.32$</td>
<td>3.07 $\pm 1.30$</td>
</tr>
<tr>
<td>8</td>
<td>382</td>
<td>144</td>
<td>0.41</td>
<td>$2.22 \pm 1.10$</td>
<td>$0.97 \pm 0.22$</td>
<td>$3.52 \pm 1.20$</td>
<td>3.53 $\pm 1.44$</td>
</tr>
<tr>
<td>16</td>
<td>764</td>
<td>100</td>
<td>0.43</td>
<td>$3.28 \pm 2.95$</td>
<td>$1.06 \pm 0.58$</td>
<td>$3.96 \pm 1.95$</td>
<td>3.97 $\pm 1.53$</td>
</tr>
</tbody>
</table>

Grains with area larger than 1.35 $\mu$m$^2$—the largest grain in unseeded ceramic. Estimated by multiplying the image area by the amount of seed (%), then dividing it by the average area per seed. Number density is based on per 1000 $\mu$m$^2$.
(2) Mechanical Properties of In Situ Composites

The measured mechanical properties are in good correlation with the microstructures observed and follow some general trends in both Ca-SiAlON and Y-SiAlON ceramics. Materials consisting of only fine equiaxed grains (unseeded ceramic) exhibit a flat R-curve with a correspondingly low value of fracture toughness. Such ceramics have relatively low strength and relatively high strength variation. Low fracture strength and fracture resistance are also known for both α and β-SiAlONs with this kind of microstructure. Needle-like grains can be definitely associated with rising R-curves and higher $K_{IC}$, as well as higher strength with lower strength deviation (i.e., a higher Weibull modulus). With increasing annealing temperature, larger grains and blocky grains begin to appear. They tend to increase the toughness but at the cost of a lower strength. (Strength data of 1950°C Y-SiAlON ceramics also follow this trend but were not shown in the companion paper.)

To explain these results, we first note that the peak toughness is slightly less in Ca-SiAlON than in Y-SiAlON. We suggest that this is partly related to the smaller average grain area in Ca-SiAlON (2–5 \( \mu \text{m}^2 \)) in Ca-SiAlON vs. 16.5 \( \mu \text{m}^2 \) in Y-SiAlON, both at 1% seeding and hot pressed at 1900°C. The importance of grain area is also suggested by the comparison of ceramics hot pressed at different temperatures. As the grain size coarsens from 1900°C to 1950°C, the fracture toughness and R-curve generally rise, as seen in Figs. 7–8.

Toughening mechanisms in self-reinforced SiAlON ceramics include crack deflection, crack bridging, and grain pullout, the last being the most important, however, it must be initiated by crack deflection and debonding. Crack deflection is controlled by...
the intergranular phase and should be the same in all ceramics of the same composition regardless of microstructure. Grain pullout is a frictional process that operates until the entire grain is pulled out or until the total frictional traction (which increases with the grain length) reaches the grain strength, on which the bridging grain breaks and the crack proceeds forward. According to the latter mechanism, toughness should increase with the volume fraction of pullout grains, the grain width, and the AR (up to a certain value beyond which the toughness is independent of the AR).26,27 Indeed, in Y-SiAlON the peak toughness is reached when the volume fraction of elongated grains is the highest (e.g., see Fig. 2 of the companion paper). In Ca-SiAlON, however, when the peak toughness is reached at 4%–8% seeding, none of the above microstructure metrics (volume fraction of elongated grains, grain width, and AR) reach the maximum value (see Table III). Thus, while the pullout mechanism is likely to operate in Ca-SiAlON, these microstructure metrics, or at least their statistical averages, are not the only factors that control the peak fracture toughness. Instead, as shown in Fig. 5, it is the smallest relative microstructure variation that features the optimal microstructure for peak fracture resistance. This strongly suggests that the uniformity of the microstructure with elongated grains should be an important consideration.

The uniformity of the microstructure is influenced by the AR of grains. Because Ca-SiAlON tend to have narrower, more elongated grains than Y-SiAlON, this difference is central to the understanding of why the peak toughness is reached at a higher seeding level in the calcium system. This is illustrated in Fig. 9 using two schematic microstructures. Both microstructure contain the same number of seeds (at the same locations), the same growth orientations of the elongated grains, and the same area fraction of such grains; the only difference being the grain width (differing by a factor of two) and the average AR. It is clear that the microstructure with narrower grains (Fig. 9(b)) is less uniform than the other (Fig. 9(a)); for example, the relative grain length distribution is much wider in Fig. 9(b). Also note that the microstructure of Fig. 9(a) is relatively uniform already, and

Table IV. Fracture Strength and Indentation Hardness of Some Ca-1512 Ceramics

<table>
<thead>
<tr>
<th>Amount of seed (%)</th>
<th>Sintering temperature (°C)</th>
<th>σ (MPa)</th>
<th>Vickers hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1900</td>
<td>763 ± 67</td>
<td>20.4 ± 0.4</td>
</tr>
<tr>
<td>4</td>
<td>1900</td>
<td>863 ± 48</td>
<td>19.2 ± 0.7</td>
</tr>
<tr>
<td>0</td>
<td>1950</td>
<td>565 ± 51</td>
<td>18.6 ± 0.8</td>
</tr>
<tr>
<td>4</td>
<td>1950</td>
<td>723 ± 30</td>
<td>18.7 ± 0.7</td>
</tr>
</tbody>
</table>

Fig. 7. R-curves of Ca-1512 seeded with various amounts (%) of seed crystals: (a) 1900°C and (b) 1950°C.

Fig. 8. Comparison of SENB fracture toughness of Y-1512 and Ca-1512 seeded with various amounts of seed crystals and processed at different temperatures.

Fig. 9. Two schematic microstructures with elongated grains growing in the same orientations from the same set of seeds. Grain width in (b) is half that of (a) but same area fraction of elongated grains is maintained in both microstructures.
Further seeding will not improve the uniformity because there is little unoccupied space left for growing new, elongated grains. In contrast, the microstructure of Fig. 9(b) could become more uniform if more seeds are placed in regions of very low grain density to produce new elongated grains. This means that a higher seeding level is required to reach the maximum uniformity for systems with narrower and more elongated grains.

Next consider a crack in these microstructures. Because cracks tend to seek the region of the least fracture resistance (i.e., where there are fewest elongated grains) to propagate, the toughness of the microstructure of Fig. 9(b) should be considerably less than the model prediction, which assumes a uniform distribution of bridging grains. It is then obvious that the peak toughness is not reached until the maximum microstructure uniformity is obtained. In view of the influence of grain width on the development of uniform microstructures, it is also obvious that in Ca-SiAlON (having narrower grains), a higher seeding level is needed to reach the peak toughness.

The pullout mechanism does explain why ceramics sintered at a higher temperature tend to have a higher toughness. In the pullout process, the frictional work (at the same AR) increases with the sliding distance, thus elevating the total fracture resistance. It is therefore not surprising that ceramics sintered at 150°C are tougher than those obtained at lower temperatures. A rising R-curve is indeed observed (Fig. 7b) for unseeded ceramic because of the presence of a small number of larger grains formed by abnormal grain growth. However, the abnormal grain growth by itself is not sufficient to provide a significant fraction of reinforcing large, elongated grains. When seeds are added, the larger grains that initiated growth on such seeds may later act as nuclei for abnormal grain growth, thereby promoting toughening further. The reinforcing grains developed in this way are so large (some exceeding 50 μm) that bridging length may exceed 1000 μm, which is the longest crack propagation distance in our experiments. This explains why steady-state R-curves were not observed in the 150°C ceramics. The toughening mechanism here may also involve elastic strain bridging that becomes effective with very large grains.

Finally, the coarser microstructures are known to be more prone to sintering defects and possibly shrinkage microcracks. In our study, we also found them to have R-curves with a somewhat lower initial slope that should reduce the criticality for unstable crack propagation. Both could lead to a slightly lower strength of the 150°C ceramics.

V. Conclusions

(1) In situ toughened Ca-α-SiAlONs with microstructures tailored by seeding have been obtained. Peak toughness reaches 8 MPa√m at 8% seeding, which yields a relatively uniform microstructure of a maximum number of elongated grains with an intermediate aspect ratio.

(2) During nucleation and growth of Ca-α-SiAlON, seed crystals of α-SiAlON compositions are stable and can initiate α-SiAlON growth. However, they face a strong competition from native α-Si3N4 nuclei because of the initially large driving force for precipitation. As a result, except at low concentrations, not all seed crystals are able to grow into large elongated grains.

(3) The optimal toughness and strength is found in ceramics with an intermediate grain size. Very large grain materials have impressive R-curves still rising after 1 mm of crack propagation, but they tend to have low strengths, mitigating their toughness advantage.

References


