Effect of Sintering Aid Composition on the Processing of Si₃N₄/BN Fibrous Monolithic Ceramics

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Si₃N₄/BN fibrous monoliths were prepared with 4 wt% Y₂O₃ added as a sintering aid to the Si₃N₄. Residual carbon, present in the billet before hot-pressing, was shown to influence the final microstructure. The sintering aid glass, known to migrate into the BN cell boundaries during hot-pressing, was not sufficient in quantity to prevent premature shear failure when samples were tested in flexure. Increasing the hot-pressing temperature alleviated this problem. For flexure samples tested at 1400°C, fibrous monoliths fabricated with 4 wt% Y₂O₃ demonstrated linear-elastic loading behavior at a greater stress than fibrous monoliths fabricated with 6 wt% Y₂O₃/2 wt% Al₂O₃ sintering aids.

II. Experimental Procedure

(1) Fibrous Monolith Fabrication

The methods for fabricating fibrous monolithic billets have been described in detail in previous publications. The basic building blocks of fibrous monoliths are small-diameter filaments (~250 μm) composed of Si₃N₄ surrounded by a thin BN layer. The thickness of the outer shell of BN is ~10–20 μm. Fibrous monoliths are composed of hundreds of filaments, giving rise to their "woodlike" architecture.

The cell material of each filament was prepared from Si₃N₄ (SN-E-10, UBE Industries, Yamaguchi, Japan) powders with 4 wt% Y₂O₃ (99.9% pure; ReAction, Johnson Matthey, Ceramics, Downingtown, PA) added as a sintering aid. Hexagonal BN (HCP, Advanced Ceramics, Cleveland, OH), consisting of plateletic particles 7–10 μm in diameter and 0.1–0.3 μm thick, was used to fabricate the cell boundaries in fibrous monoliths. Long, continuous filaments were manufactured by an outside vendor (Advanced Ceramics Research, Tucson, AZ) and wound onto a spool.

A filament-winding approach was used to fabricate 4Y-FMs, based on the method developed by King et al. The uniaxially aligned filaments were warm-pressed at 150°C and 3–4 MPa, creating a 8–9 mm thick "green" billet with a high degree of filament order. A burnout step was needed to remove the polymeric binder from the green billets. The billets were subjected to temperatures varying from 25°C to 700°C for 98 h. As is developed in this paper, a post-binder-burnout heat treatment in air was also performed on two of the billets to remove residual carbon. Billets were hot-pressed at either 1800°C or 1820°C under an applied pressure of 25 MPa for 1 h using a heating rate of 600°C/h. The load was applied when the surface temperature of the die reached 1200°C.

(2) Specimen Fabrication and Testing

The hot-pressed billets were machined to a thickness of 3 mm by removing equal amounts of material from both sides. Samples were cut from these billets using diamond blades (American Diamond Tool, Inc., Buffalo, NY) into 3 mm × 4 mm × 48 mm flexure bars. The tensile surface was always polished through 3 μm prior to testing.

The average modulus of 4Y-FM samples, determined using the acoustic resonance method (Grindosonic, J. W. Lemmens, Inc., St. Louis, MO) was 295 ± 1 GPa. X-ray diffraction (XRD) of pulverized specimens revealed complete transformation of the starting α-Si₃N₄ powder to β-Si₃N₄. The point-fracture method, using a square grid, was used to estimate the volume percentage of secondary phases.

Flexure testing was performed on a screw-driven load frame (Model 4483, Instron Corp., Canton, MA) equipped with a 5 kN load cell and a clamshell furnace (Applied Test Systems, Butler, PA). Material evaluations were made between 25°C and 1400°C. A thermocouple was placed within 5 mm of the sample (and near the mid-span) during testing. A 10 min dwell at ±2°C of the desired testing temperature was achieved before testing. A SiC fixture, with outer and inner spans fixed at 40 and 20 mm, respectively, was used for all tests. All samples were tested at a load rate of 16.7 N/s.
Flexural tests were conducted at a rate of 0.5 mm/min. The work of fracture of each specimen was calculated by determining the area under the load–crosshead deflection curve and dividing it by twice the cross-sectional area of the sample. An apparent stress was calculated using load and the original cross-sectional area, employing the standard specified equation for stress in 4-point loading.

III. Results and Discussion

(1) Processing Trials of 4Y-FMs

An overview of the billets fabricated for this study is shown in Table I. Two problems arose during the early attempts to fabricate fibrous monoliths using 4 wt% Y2O3 sintering aids. These were (1) formation of melilite, Y2O3·Si3N4, a secondary phase subject to extreme oxidation near 1000°C, and (2) weak BN cell boundaries. The origin and resolution of these two problems are discussed presently.

(A) Formation of the Melilite Phase: Billet 4Y-FM-1 was hot-pressed at 1800°C for 1 h. Density measurements averaged 99.1% of the theoretical density of 3.04 g/cm³ for this composition of fibrous monolith (assuming 80 vol% Si3N4 cells and 20 vol% BN cell boundaries). XRD of pulverized samples, shown in Fig. 1, indicated the presence of β-Si3N4, h-BN, and Y2O3·Si3N4, commonly referred to as melilite. Melilite, a quaternary phase formed by the reaction of Si3N4 and Y2O3, was originally thought to be highly refractory. However, early researchers did not realize that while the melilite phase is very refractory at 1400°C, it undergoes severe oxidation in the 900°–1100°C temperature range because of the large stresses that develop in the surface scale during oxidation. The reaction equation is

\[
Y_2O_3·Si_3N_4 + 3O_2 \rightarrow Y_2Si_2O_7 + SiO_2 + 2N_2
\]

where melilite transforms to yttrium silicate and cristobalite. The specific volume increase associated with this reaction is ~30%. As a result of the volume change, the oxidation product does not form a protective layer on the surface of the Si3N4, but cracks instead, exposing new oxidized Si3N4. This process continues until complete failure occurs.

Figure 2 presents the phase diagram for Si3N4-Y2O3-SiO2. Starting powders that would fix compositions in the Si3N4-Y2O3-Si3N4-YSiO2N region (triangle I) are to be avoided because of the formation of melilite. The Si3N4-Y2Si2O7-Si2N2O region (triangle II) is more desirable, because the reaction products demonstrate excellent oxidation resistance. From the phase diagram, ~2.4 wt% SiO2 is required to put the reaction products in compatibility triangle II. Because 3 wt% SiO2 exists in this Si3N4 powder, melilite should not be formed during hot-pressing. However, the diffraction pattern in Fig. 1 shows that this is not the case.

<table>
<thead>
<tr>
<th>Billet</th>
<th>Post-binder-burnout heat treatment</th>
<th>Melilite observed</th>
<th>Hot-press temperature (°C)</th>
<th>Relative cell-boundary strength</th>
<th>Cell-boundary glassy phase (vol%)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4Y-FM-1</td>
<td>No</td>
<td>Yes</td>
<td>1800</td>
<td>Weak</td>
<td>Not measured</td>
<td>3.01 ± 0.01</td>
</tr>
<tr>
<td>4Y-FM-2</td>
<td>Yes</td>
<td>No</td>
<td>1800</td>
<td>Weak</td>
<td>7 ± 1.5</td>
<td>3.04 ± 0.01</td>
</tr>
<tr>
<td>4Y-FM-3</td>
<td>Yes</td>
<td>No</td>
<td>1820</td>
<td>Strong</td>
<td>12 ± 2.3</td>
<td>3.04 ± 0.01</td>
</tr>
</tbody>
</table>
One of the consequences of using polymers during the fabrication of fibrous monoliths is the residual carbon concentration after binder burnout in flowing nitrogen. Hampshire and Jack\textsuperscript{25} showed that when Y\textsubscript{2}O\textsubscript{3}-doped Si\textsubscript{3}N\textsubscript{4} is hot-pressed, the final products are dependent upon the initial oxygen and carbon concentrations. The carbon reacts with the SiO\textsubscript{2} present on the Si\textsubscript{3}N\textsubscript{4} powder according to:

\[
\text{SiO}_2 + \text{C} \rightarrow \text{SiO} + \text{CO} \tag{2}
\]

where the SiO\textsubscript{2} concentration needed to avoid formation of melilite is vaporized. Thus, it appears that the carbon leftover after binder burnout is reacting with the surface SiO\textsubscript{2} during hot-pressing, depleting the Si\textsubscript{3}N\textsubscript{4} powders of SiO\textsubscript{2} and forming melilite.

To evaluate this hypothesis, the residual concentration of carbon was significantly reduced before hot-pressing by a post binder-burnout heat treatment in air. Figure 3 shows the results of a thermogravimetric test, conducted in flowing air, used to establish the temperature where carbon was oxidized. The test sample was taken from a billet after a typical binder burnout run in nitrogen and was composed of \~99.2 wt\% ceramic powder and \~0.8 wt\% residual carbon. Upon heating, there was an initial weight loss of 0.3 wt\% that was likely the result of absorbed moisture in the sample. The sharp decline in weight observed near 400\degree C and continued through 550\degree C was due to oxidation of the residual carbon. The weight of the sample began to increase beyond 700\degree C, indicating that oxidation of the powders was occurring. Based on these results, a post binder-burnout schedule was developed that included a 24 h dwell at 400\degree C in flowing air.

A second fibrous monolith billet, 4Y-FM-2, was fabricated by inserting the post binder-burnout treatment between the binder burnout and hot-pressing steps. The residual carbon concentration was found to be 0.13 ± 0.01 wt\% following this post binder-burnout treatment. Following this additional process step, this billet was hot-pressed under identical conditions as 4Y-FM-1. None of the deleterious melilite was observed in XRD patterns of a sample from 4Y-FM-2, as shown in Fig. 4.

(B) Weak Cell Boundaries in 4Y-FM Billets: A fully dense 4 wt\% Y\textsubscript{2}O\textsubscript{3} monolithic Si\textsubscript{3}N\textsubscript{4} billet was fabricated using a 1 h hot-press at 1800\degree C and 25 MPa. Based on this understanding, identical hot-pressing conditions were used to fabricate 4Y-FM-2. The average density of this billet was 3.04 g/cm\textsuperscript{3}, equivalent to the theoretical density. However, this billet was not structurally sound, because it was easy to flake off individual cells of Si\textsubscript{3}N\textsubscript{4}. Figure 5(a) shows the results of a flexure test run at 25\degree C on a sample machined from this billet. Based on the flexural response and observations of the failed sample, it was deduced that shear-initiated failure occurred at the midplane of the specimen. Failure analysis revealed that the initial crack originated in the BN cell boundary, an indication that the cell boundary was very weak compared with the strength of the cells.
Billet 4Y-FM-3 was fabricated at an increased hot-pressing temperature of 1820°C. Like 4Y-FM-2, samples cut from billet 4Y-FM-3 exhibited theoretical densities. However, it was not possible to flake off individual cells of Si₃N₄ from the surface, suggesting a stronger cell boundary. Figure 5(b) presents the 25°C flexure results for a sample cut from 4Y-FM-3. The stress versus crosshead deflection curve and fractured specimen both indicated that failure initiated on the tensile surface in the Si₃N₄ cells.

The presence of a secondary phase in the BN is the likely reason for the stronger cell boundaries displayed by 4Y-FM-3. Previous research26 has shown that the sintering aid glass formed in the Si₃N₄ cells flows into the BN cell boundaries during hot-pressing and resides there upon cooling. An example of the cell-boundary glassy phase is shown in Fig. 6, a backscattered SEM image of a cross section of a 4Y-FM-2 sample near the intersection of three cells. A bright phase, previously shown to have the same composition as the residual glassy phase between the grains of Si₃N₄, is clustered at the intersection of the three filaments. 26 Cross-sectional analysis of samples cut from 4Y-FM-2 indicates the amount of glassy phase present in the cell boundary is relatively low, only 7 ± 1.5 vol%. A 12 vol% glass is measured in the cell boundary of 4Y-FM-3. Thus, increasing the hot-pressing temperature has increased the amount of glassy phase that has flowed into the BN cell boundary during processing. The increased amount of glass in the cell boundary seems to have increased its strength, so that failure is now favored first in the Si₃N₄ cells rather than in the BN cell boundary.

(2) Effect of Sintering Aid Composition on the Mechanical Properties of Si₃N₄/BN Fibrous Monoliths

The following section addresses the effect of varying sintering aid composition on the mechanical properties of fibrous monoliths. The mechanical results of 4Y-FM-3 are compared to a less-refractory fibrous monolith, in which the sintering aids added to the Si₃N₄ cells are 6 wt% Y₂O₃ and 2 wt% Al₂O₃. Samples cut from these billets are designated as 6Y/2Al-FMs and represent a composition of fibrous monoliths that have been extensively studied. Previous research indicated that Al₂O₃ additions to Y₂O₃-doped Si₃N₄ decreased its flexure strength at elevated temperatures.7 Table II lists the results of the flexure tests. The mechanical behavior of 6Y/2Al-FMs is compared to individual samples from 4Y-FM-3. Because of the limited number of specimens, the discussion focuses on failure modes and load–deflection response.

(A) Effect of Sintering Aid Composition at 25°C: The 25°C flexural response of the two compositions of fibrous monoliths was very similar. Figure 7 presents a side view of 4Y-FM-3 after testing. The fracture behavior is similar to that observed in 6Y/2Al-FMs.1 As expected, varying the sintering aid composition seems to have little effect on the room-temperature mechanical properties of fibrous monoliths.

(B) Effect of Sintering Aid Composition at 1000°C: The flexural response and microscopic investigations of both compositions of fibrous monoliths tested at 1000°C indicated that tensile-initiated failure was observed in 6Y/2Al-FMs, while shear-initiated failure was observed in the 4Y-FM sample. The difference in failure mode was a consequence of the smaller amount of cell-boundary glassy phase present in 4Y-FM-3 as compared with 6Y/2Al-FMs. 6Y/2Al-FMs contained 19 vol% cell-boundary glassy phase compared to 12 vol% for 4Y-FMs. The general trend observed when shear-initiated failure is favored over tensile-initiated failure is a reduction in the overall strength of the sample. Thus, shear failure is to be avoided by having sufficient glassy phase (>16–18 vol%) in the BN cell boundaries.

(C) Effect of Sintering Aid Composition at 1400°C: The characteristic stress–deflection curves for specimens of both sintering aid compositions tested at 1400°C are presented in Fig. 8. It is evident that the 6Y/2Al-FM sample exhibits nonlinear stress–deflection behavior at 65 MPa, well before tensile

\[\text{Table II. Comparison of Flexure Strength for Two Fibrous Monoliths}^{\dagger}\]

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Fibrous monolith composition</th>
<th>Strength (MPa)</th>
<th>Work of fracture (J/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>6Y/2Al-FM</td>
<td>510 ± 87</td>
<td>7400 ± 1350</td>
</tr>
<tr>
<td></td>
<td>4Y-FM-3</td>
<td>553</td>
<td>6700</td>
</tr>
<tr>
<td>1000</td>
<td>6Y/2Al-FM</td>
<td>440 ± 110</td>
<td>7800 ± 2100</td>
</tr>
<tr>
<td></td>
<td>4Y-FM-3</td>
<td>390</td>
<td>4800</td>
</tr>
<tr>
<td>1400</td>
<td>6Y/2Al-FM</td>
<td>176</td>
<td>3200</td>
</tr>
<tr>
<td></td>
<td>4Y-FM-3</td>
<td>293</td>
<td>3000</td>
</tr>
</tbody>
</table>

\(^{\dagger}\) Different compositions of sintering aids added to the Si₃N₄ cells.27
fracture initiates in the Si₃N₄ cells. The fibrous monolith made with 4 wt% Y₂O₃ is linear elastic to 280 MPa before failing from tensile-initiated cracks in the cells. This response is expected in 4Y-FMs, because the glassy phase formed from the sintering aids (as manifested in the Si₃N₄ cells) is more refractory.

IV. Conclusions

A completely dense, 4 wt% Y₂O₃/Si₃N₄/BN fibrous monolith has been fabricated in an effort to improve the high-temperature properties of fibrous monoliths. At 1400°C, the 4Y-FM exhibited elastic behavior through 280 MPa, whereas considerable nonlinear loading behavior was observed in the less-refractory-composition fibrous monolith.

The presence of residual carbon following binder burnout was found to be responsible for the formation of Y₂O₃-Si₃N₄, a phase known to undergo severe oxidation between 900°C and 1100°C. XRD results indicated that Y₂O₃-Si₃N₄ was not formed during hot-pressing if residual carbon was removed prior to hot-pressing with an additional binder-burnout processing step at 400°C in air. Furthermore, the small volume percentage of sintering aids used limited the amount of sintering aid glass that migrated to the cell boundary during hot-pressing, resulting in fibrous monoliths with extremely weak cell boundaries. Increasing the hot-press temperature by 20°C, to 1820°C, resulted in an increased percentage of glassy phase in the cell boundary and, thus, stronger cell boundaries.

Ultimately, increasing the refactoriness of the glassy phase by adjusting the sintering sintering aid composition improves the high-temperature performance of fibrous monoliths at 1400°C. The problem is that increasing the refactoriness of the Si₃N₄ often involves using less sintering aid. The result is that less glassy phase is available to migrate into the cell boundary during hot-pressing. This favors shear initiation at temperatures <1400°C, which can significantly reduce the strength of a fibrous monolith in the intermediate temperature ranges (1000°C–1300°C).

References