COMPOSITIONAL DESIGN OF POROUS β-Si₃N₄ PREPARED BY PRESSURELESS-SINTERING COMPOSITIONS IN THE Si-Y-Mg-(Ca)-O-N SYSTEM

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ABSTRACT
Porous β-Si₃N₄ can be microstructurally engineered to provide similar mechanical properties to dense β-Si₃N₄, with the additional benefits of reduced mass. However, while flexural strengths exceeding 1 GPa can be achieved by tailoring the microstructure of the material, through alignment of anisotropic β-Si₃N₄ grains, the porosity levels of such materials are still relatively low (< 15 vol. %). This also requires moderately complex processing techniques to be employed, such as tape-casting and sinter-forging. In the present study, an alternate approach is taken where compositional design is advocated, with the aim of producing a more porous β-Si₃N₄ structure (ideally 20-40 vol. % porosity) with high grain aspect ratios (i.e. >10:1). This approach makes use of a low volume fraction of multiple sintering aids, where each additive plays one or more roles in the sintering behavior of Si₃N₄ (i.e. densification aid, transformation aid and/or whisker growth aid). Compositions are based on various ratios of Y₂O₃:MgO, both with and without CaO additions. Sintering has been conducted in a nitrogen atmosphere (0.1 MPa) between 1400 and 1700°C. The effects of processing parameters (e.g. composition, sintering temperature and time) will be discussed, paying particular attention to microstructure development, including both the densification behavior and α- to β-Si₃N₄ transformation kinetics.

INTRODUCTION
There is increasing interest in the development of porous ceramics for a number of advanced applications, including use as filters, bio-prosthetic implants, bioreactor supports, and lightweight structural materials. Among the materials that are used in such applications, silicon nitride (Si₃N₄) ceramics possess arguably the most favorable combination of mechanical and thermal properties. Several approaches have been developed to prepare β-Si₃N₄ based ceramics with either nano-, micro- or macro-porosity. For the preparation of materials with nano-/micro-porosity, the primary approach involves the selection of a single sintering aid that promotes the α- to β-Si₃N₄ transformation, but has little beneficial effect on densification. Suitable sintering aids include many of the lanthanide or Group IIIB elements (e.g. La₂O₃, Lu₂O₃, Sc₂O₃, Sm₂O₃, Y₂O₃, Yb₂O₃, etc). The result of this approach is to produce materials with extremely fine scale

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porosity, between the individual $\beta$-Si$_3$N$_4$ grains. With this approach, the materials can be expected to retain good mechanical properties, through the attainment of an anisotropic, interlocking $\beta$-Si$_3$N$_4$ grain structure. Extending this approach, through the use of controlled seeding and texture development, strengths in excess of 1 GPa can be achieved for materials with a porosity content of less than 15 vol. %, in combination with high toughness.\(^6,7\)

Alternatively, macro-porosity can be controlled through the addition of fugitive pore formers, which can be either particulate (e.g. starch) or continuous in nature (e.g. open cell foams).\(^8-10\) Recently, novel processes based on suspension freezing have also been developed, where displacement of the ceramic powder occurs at the solidification front, resulting in interconnected porosity after sublimation of the suspension medium (e.g. water, camphene).\(^11\)

The present work reports upon a new approach to develop nano-/micro-porous $\beta$-Si$_3$N$_4$ ceramics through the use of a low volume fraction of multiple sintering additives, where each additive component is chosen to promote one or more of the following functionalities: (1) $\alpha$- to $\beta$-Si$_3$N$_4$ phase transformation, (2) anisotropic $\beta$-Si$_3$N$_4$ grain growth, or (3) densification. This method is partly adapted from the prior work of Pyzik et al in developing tough, in-situ reinforced $\beta$-Si$_3$N$_4$ ceramics.\(^12\) It is possible to present each potential oxide additive on a “functionality map” that highlights the role(s) of that specific additive in sintering $\beta$-Si$_3$N$_4$ ceramics, as shown in Figure 1. In this figure, the position of each additive is dictated by its role(s) in sintering; for example an additive that contributes to each of functions 1-3 will sit in the middle of the triangle, while one that only contributes to one role will sit in that respective corner, etc.

![Figure 1. Schematic Si$_3$N$_4$ sintering aid “functionality map” (adapted in part from ref. 12).](image)

**EXPERIMENTAL PROCEDURES**

All samples in the current work were prepared using Ube SN E-10 $\alpha$-Si$_3$N$_4$ powder, together with the oxides summarized in Table I. The compositions that were prepared in this study are summarized in Table II. In each case, 50 g batches of the appropriate composition were prepared by ball-milling for 24 h in isopropyl alcohol using TZP media, followed by drying and
sieving through a 75 µm mesh stainless steel sieve. The powders were then uniaxially pressed (at ~31 MPa) into 31 mm diameter x 4 mm thick discs, followed by cold-isostatic pressing at ~175 MPa. Sintering of MgO containing samples was conducted within a powder bed comprised of 50 wt. % BN/49 wt. % Si₃N₄/1 wt. % MgO, while the pure Y₂O₃ additives samples were sintered in a mixture of 50 wt. % Si₃N₄/50 wt. % BN. All samples were sintered within a graphite crucible, under a static nitrogen environment (0.1 MPa), at temperatures between 1400 and 1750ºC for a period of two hours. Sintered densities were subsequently determined via immersion in mercury.

Post-sinter microstructure characterization included evaluation using x-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM). The volume fraction of β-Si₃N₄ formed, \( R_β \), relative to residual α-Si₃N₄, was determined from XRD using the following relationship:

\[
R = 1.4434 \left( \frac{I(101)}{I(101)} \right) - 0.4434 \left( \frac{I(101)}{I(101)} \right)^2 100
\]

The aspect ratio of β-Si₃N₄ grains in individual samples was ascertained through room temperature dissolution of small sections of material in concentrated HF solution, followed by filtering of the resulting suspension, dispersion of the particles onto a polished aluminum stub and examination of the dried product in the FE-SEM.

<table>
<thead>
<tr>
<th>Sintering aid</th>
<th>Purity (at. %)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y₂O₃</td>
<td>99.99</td>
<td>Metall rare Earth Ltd., Shenzhen, China</td>
</tr>
<tr>
<td>MgO</td>
<td>99.9</td>
<td>Inframat Advanced Materials, Farmington, CT</td>
</tr>
<tr>
<td>CaO</td>
<td>99.95</td>
<td>Alfa Aesar, Ward Hill, MA</td>
</tr>
</tbody>
</table>

Table I. Summary of the oxide sintering additives used, their purity and supplier.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Composition (wt. %)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si₃N₄</td>
<td>Y₂O₃</td>
</tr>
<tr>
<td>SN5Y</td>
<td>95</td>
<td>5</td>
</tr>
<tr>
<td>SN5YM</td>
<td>97</td>
<td>2.5</td>
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<tr>
<td>SN2YM</td>
<td>97</td>
<td>2</td>
</tr>
<tr>
<td>SNYM</td>
<td>97</td>
<td>1.5</td>
</tr>
<tr>
<td>SN5YM01C</td>
<td>97</td>
<td>2.5</td>
</tr>
<tr>
<td>SN5YM05C</td>
<td>97</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table II. Compositional designations for the porous Si₃N₄ samples prepared in the present work. Note that samples with CaO additions are prepared with a baseline composition of SN5YM.
RESULTS AND DISCUSSION

The influence of additive composition upon densification behavior is shown in Figure 2 for samples prepared with either 5 wt. % Y$_2$O$_3$ additions or varying Y$_2$O$_3$:MgO ratios. It is apparent that Y$_2$O$_3$ alone does not promote densification, as anticipated from prior studies.\textsuperscript{1} When examining the mixed Y$_2$O$_3$:MgO additions, it can be seen that increasing MgO content increases the level of densification. The additive levels for these samples are significantly lower than used for conventional pressureless-sintering of Si$_3$N$_4$-based ceramics to high density.

The use of pure Y$_2$O$_3$ as a sintering aid promotes the transformation of α- to β-Si$_3$N$_4$, particularly above 1600°C, with complete transformation observed at 1700°C (Figure 3). It is apparent that the addition of MgO to the mixture significantly lowers the transformation temperature, such that complete transformation is observed for the 5:1 ratio (SN5YM) when sintering at 1600°C and above. Increasing the relative content of MgO results in a slight reduction in the extent of α- to β-Si$_3$N$_4$ transformation for a given sintering temperature. Previous studies of the rheological behavior of Si-Y-Mg-O-N glasses demonstrates that increasing the Y:Mg ratio results in an increase in the glass transition and softening temperatures.\textsuperscript{14} Such a response may be expected to be reflected in the relative viscosity of such glasses at any given temperature. An increase in viscosity may then be expected to decrease sintered density and increase the α- to β-Si$_3$N$_4$ transformation, as noted in the present case, based on the prior arguments of Hampshire and Jack.\textsuperscript{15}

![Figure 2](image-url)  
Figure 2. Density as a function of sintering temperature for samples prepared with varying ratios of Y$_2$O$_3$:MgO, as well as with single Y$_2$O$_3$ additions.

Figure 4 highlights the microstructural changes occurring when sintering the high Y$_2$O$_3$:MgO ratio SN5YM composition. The transition from the fine, equiaxed α-Si$_3$N$_4$ to the elongated β-Si$_3$N$_4$ structure is clearly apparent at 1600°C and above. As noted earlier, these compositions are essentially fully transformed to β-Si$_3$N$_4$ at this temperature. The effect of Y$_2$O$_3$:MgO ratio upon the sintered microstructure, for a fixed sintering temperature of 1700°C, is shown in Figure 5. Qualitatively, is it is apparent that the β-Si$_3$N$_4$ aspect ratio decreases slightly
with increasing MgO content in the sintered material. As a consequence of this, the higher Y$_2$O$_3$:MgO ratio composition was selected for further study through small additions of CaO which are designed to promote further anisotropic $\beta$-Si$_3$N$_4$ grain growth, as outlined in Figure 1.

![Figure 3](image)

Figure 3. The fraction of $\beta$-Si$_3$N$_4$ formed during sintering of Y$_2$O$_3$/MgO additive compositions between 1400 and 1700ºC, and Y$_2$O$_3$ additive compositions between 1500 and 1750ºC.

The effects of small CaO additions on the sintering behavior of the highest Y$_2$O$_3$:MgO ratio composition, when sintering at 1650ºC for 2 hours, are summarized in Table III. Even small CaO contents produce a significant increase in densification, although the porosity content after sintering still exceeds 25 vol. %. It may be expected that CaO additions will further lower the glass viscosity at typical sintering temperatures, resulting in increased densification.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Weight loss (%)</th>
<th>Sintered density (g.cm$^{-3}$)</th>
<th>Nominal retained porosity (vol. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SN5YM</td>
<td>2.52</td>
<td>2.15</td>
<td>33.2</td>
</tr>
<tr>
<td>SN5YM01C</td>
<td>1.33</td>
<td>2.28</td>
<td>28.9</td>
</tr>
<tr>
<td>SN5YM05C</td>
<td>1.37</td>
<td>2.29</td>
<td>28.8</td>
</tr>
</tbody>
</table>

Table III. The effects of CaO additions upon the sintering behavior of the baseline composition SN5YM at 1650ºC.

The primary aim of incorporating small CaO additions is to promote the growth of anisotropic $\beta$-Si$_3$N$_4$ grains during sintering. Measurement of grain dimensions, following their extraction from samples sintered at 1650ºC, demonstrates that CaO incorporation does increase the grain aspect ratio (Figure 6). It is apparent from this figure that aspect ratios greater than 25:1 can be achieved with additions of CaO to the 5:1 ratio Y$_2$O$_3$:MgO composition. It can also be
seen that there is an increase in the maximum grain widths and lengths, which is further reflected in a quantitative manner in Table IV. Table IV demonstrates a mean aspect ratio of ~10.8:1 is obtained for the CaO-free material, which is increased by approximately 12 % when 0.5 wt. % CaO is added. Saito et al\textsuperscript{16} and Satet and Hoffmann\textsuperscript{17} both measured lower mean grain aspect ratios of 4-6:1 for dilute $\beta$-Si$_3$N$_4$ grains growing in Si-Y-Mg-O-N glasses, which may represent the sensitivity of growth to the Y:Mg ratio within the glass or simply a dilution or porosity effect.

Figure 4. SEM images of microstructural evolution for the composition SN5YM (i.e. Y$_2$O$_3$:MgO ratio of 5:1) at sintering temperatures between 1500 and 1700\degree C. The change from equiaxial $\alpha$-Si$_3$N$_4$ to elongated $\beta$-Si$_3$N$_4$, with increasing temperature, is readily apparent.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Length ($\mu$m)</th>
<th>Width ($\mu$m)</th>
<th>Aspect ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>SN5YM</td>
<td>3.84</td>
<td>0.355</td>
<td>10.8</td>
</tr>
<tr>
<td>SN5YM05</td>
<td>4.17</td>
<td>0.345</td>
<td>12.1</td>
</tr>
</tbody>
</table>

Table IV. The mean $\beta$-Si$_3$N$_4$ length, width and aspect ratio for $\beta$-Si$_3$N$_4$ samples prepared with a Y$_2$O$_3$:MgO ratio of 5:1, both without and with 0.5 wt. % CaO addition. Mean values are the average of measurements on 100 extracted $\beta$-Si$_3$N$_4$ grains for each composition.
Figure 5. SEM micrographs of the structure of compositions SN2YM (i.e. $Y_2O_3$:MgO ratio of 2:1) and SNYM (i.e. $Y_2O_3$:MgO ratio of 1:1) sintered at 1700°C. From the figure, it is qualitatively apparent that increasing the $Y_2O_3$:MgO ratio increases the grain aspect ratio (c.f. SN5YM sintered at 1700°C in Figure 4).

Figure 6. The measured length-width and aspect ratio-width distributions for $\beta$-Si$_3$N$_4$ grains in compositions SN5YM and SN5YM05C sintered at 1650°C. The measured distributions are plotted on the same scale for direct comparison.
CONCLUSIONS
The current study has demonstrated that porous $\beta$-Si$_3$N$_4$ based ceramics can be prepared using a low volume fraction of multiple sintering additives (i.e. Y$_2$O$_3$, MgO and CaO). This approach has potential benefits over prior methods to prepare porous Si$_3$N$_4$ ceramics in that the additives can be selected based on their specific “functionality” during sintering (e.g. densification aid, transformation aid, whisker growth agent, etc.). It has been shown that through this approach, the density (porosity) can be tailored, and that high aspect ratios can be achieved through the addition of oxides known to promote $\beta$-Si$_3$N$_4$ whisker growth. This work is currently being extended to assess the effects of alternate lanthanide/Group IIIB oxides, as replacements for Y$_2$O$_3$, and to evaluate the resulting mechanical behavior of these materials. Combined compositional and microstructural design approaches are also being evaluated, in order to further promote high aspect ratio $\beta$-Si$_3$N$_4$ whisker growth.

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REFERENCES