EFFECT OF STARTING POWDER CHARACTERISTICS ON DENSITY, MICROSTRUCTURE AND LOW TEMPERATURE OXIDATION BEHAVIOR OF A Si₃N₄ – 8 w/o Y₂O₃ CERAMIC

Susan Schuon and Sunil Dutta
Lewis Research Center
Cleveland, Ohio

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EFFECT OF STARTING POWDER CHARACTERISTICS ON DENSITY, MICRO-
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SUMMARY

The densification and oxidation behavior of Si$_3$N$_4$ - 8 w/o Y$_2$O$_3$ prepared from three commercial starting powders were studied. Bars of SN 402, SN 502, and CP 85/15 were sintered for 3 to 4.5 hours at 1750°C. A second set was hot-pressed for 2 hours at 1750°C. The microstructures were studied by TEM and SEM, densities were determined, and the phase compositions were determined by x-ray diffraction.

Densification and microstructure were greatly influenced by the starting powder morphology and impurity content. Although SN 402 exhibited the maximum weight loss, the highest sintered and hot-pressed densities were obtained with this powder.

All powders had both equiaxed and elongated grains. Sintered bars were composed of beta silicon nitride and n-melilite. In contrast, hot-pressed bars contained beta silicon nitride, H-phase, and J-phase, but no melilite. Yttria distribution in sintered bars was related to the presence of cation impurities such as Ca, Fe, and Mg.

A limited oxidation study at 750°C in air showed no instability in these Si$_3$N$_4$ - 8 w/o Y$_2$O$_3$ specimens, regardless of starting powder.

INTRODUCTION

The inability of Si$_3$N$_4$ powder to readily sinter has led to the use of sintering additives such as MgO and Y$_2$O$_3$. These additives promote the
formation of a liquid phase, thus enabling the Si$_3$N$_4$ powder to be sintered to a high density. Si$_3$N$_4$ - 8 w/o Y$_2$O$_3$ is considered to be one of the most promising compositions.\textsuperscript{1} For example, commercial hot-pressed Si$_3$N$_4$ - 8 Y$_2$O$_3$ (NCX-34\textsuperscript{a}), exhibits good strength and creep resistance at elevated temperatures (1300 to 1400°C).

As a general rule, the strength of a ceramic increases with increasing density. In this study, the effects of Si$_3$N$_4$ starting powder morphology and cation impurity level on the densification of Si$_3$N$_4$ - 8 Y$_2$O$_3$ ceramics was investigated for three commercial Si$_3$N$_4$ powders. Densification processes evaluated included both pressureless sintering and hot pressing. Since cracking and severe oxidation have been observed in some lots of NCX-34 at 600 to 900°C\textsuperscript{2,3}, the oxidation behavior of Si$_3$N$_4$ - 8 Y$_2$O$_3$ ceramics prepared in this study was evaluated at 750°C.

**EXPERIMENTAL PROCEDURE**

Three commercial powders, SN 402**, SN 502**, and CP 85/15*** were selected for this study. Eight w/o Y$_2$O$_3$ was added to all three powders. Batches of 100 grams were wet milled in polyethylene bottles for 17 hrs using alumina balls and ethanol. The alumina pick up was less than 1 w/o for a 200 gram ball charge with a 100 gm powder charge. After milling, the slurry was dried on a heated aluminum plate and sieved through a 60 mesh sieve to break up agglomerates.

To make pressureless sintered specimens, twenty gram portions of mixed powder were cold formed into rectangular blocks of 7.6 by 2.5 by 0.64 cm. by

* Norton Company hot pressed Si$_3$N$_4$ - 8 Y$_2$O$_3$
** GTE Sylvania, Towanda, PA
*** KBI, Reading, PA
Die pressing. The compacts were then isostatically pressed in rubber bags at a pressure of 414 MPa. The isostatically pressed bars were then sintered in a cold-wall furnace equipped with tungsten heating elements. The sintering was conducted at 1750°C for 3 to 4.5 hrs under a nitrogen pressure of one atmosphere. After sintering, the compacts were furnace cooled and weighed.

For hot pressing, eighteen gram portions of mixed powder were placed in a graphite die coated with boron nitride. Hot pressing was carried out at 1750°C for 2 hrs in one atmosphere of nitrogen under a hydraulically applied load of 276 MPa. After hot pressing the compacts were furnace cooled.

Both the sintered and hot pressed blocks were machined into test bars 2.54 by 0.64 by 0.32 cm. The bars were ground with a 220 grit diamond wheel to a final surface finish of 8-10 microinches rms.

Densities were determined on the machined test bars by physical as well as by pycnometric methods. Microstructural characterization was done by optical microscopy and by scanning and transmission electron microscopy, while phase analysis was carried out by X-ray diffraction. Yttria distribution was determined by scanning transmission electron microscopy.

The stability of hot pressed specimens at intermediate temperatures was studied. Machined test bars 2.54 by 0.64 by 0.32 cm were heated in air at 750°C. After 200 hrs at temperature, the bars were weighed and the oxide scales were characterized by X-ray diffraction.

RESULTS AND DISCUSSIONS

Powder Characterization

Commercially available Si₃N₄ powders vary considerably in particle size, particle shape, phase composition and impurity levels. The morphologies and crystallinity of the powders for the present study are shown in Figure 1.
SN 402 powder was totally amorphous. SN 402 powder particles are spherical and often agglomerated, with individual particles sizes ranging from 0.05 to 1.0 μm. SN 502 powder was about 60 percent crystalline and 40 percent amorphous, as shown in Figure 1(b). The amorphous fraction consisted of rounded particles ranging from 0.05 to 1.0 μm as in SN 402, while the crystalline fraction consisted of acicular particles with diameters ranging from 0.03 to 0.05 μm and with variable lengths. The crystalline fraction of the powder contained about 95 percent α-Si₃N₄ and 5 percent α-Si₃N₄. In contrast, CP 85/15 powder was totally crystalline and consisted mostly of angular particles ranging in diameter from 0.05 to 6.0 μm (Figure 1(c)). Particles were about 85 percent α-Si₃N₄ and 15 percent α-Si₃N₄.

Oxygen contents and impurity levels of the three commercial Si₃N₄ powders also varied considerably. While SN 402 and SN 502 powders had low levels of cation impurities as shown in Table 1, CP 85/15 had relatively high levels of impurities such as Al, Ca, and Fe. The oxygen contents of the SN 402, SN 502 and CP 85/15 were 2.66 percent, 2.17 percent and 1.75 percent, respectively, compared with a theoretical oxygen content for Si₃N₄ - 8 w/o Y₂O₃ of 1.70 percent. Hot pressed NCX-34 has cation impurity levels similar to those determined for SN 502 powder, except for high tungsten levels, 1 to 2 w/o, in NCX-34.¹

The BET surface areas of the three starting powders were 11.84 m²/gm for SN 402 powder, 4.83 m²/gm for SN 502 powder, and 3.95 m²/gm for CP 85/15 powder.

Cold-Isostatic Pressing

Prior to sintering, SN 402, SN 502, and CP 85/15 powder mixes were cold-isostatic pressed (CIP) at 483 MPa. The lowest CIP density, 1.4 gm/cc, was obtained with the amorphous SN 402 powder, which consisted of spherical particles. The CIP density of SN 502 powder was 1.5 gm/cc, slightly higher than...
that of SN 402. The highest CIP density, 2.2 gm/cc, was obtained with CP 85/15 powder, which consisted of angular, platy particles. The densities are plotted in Figure 2.

Each type of CIP bar had a distinctive fracture surface, which reflected starting powder morphology as shown in Figure 3. In SN 402 and SN 502 bars, individual particles are distinguishable, indicating a large amount of open porosity. In contrast, the individual particles are somewhat difficult to distinguish in CP 85/15 fracture bars due to greater mechanical agglomeration and more numerous particle contacts.

Densification

Sintering

The CIP bars were sintered in nitrogen for 3 hours or 4.5 hours at 1750°C. After 3 hours, the density of SN 402 bars increased from about 1.4 gm/cc to about 1.8 gm/cc, as shown in Figure 2. The density of SN 502 bars increased from 1.55 gm/cc to 1.90 gm/cc. On the other hand, the density of CP 85/15 bars decreased slightly during sintering, from 2.0 gm/cc to 1.95 gm/cc. This decrease in density was also observed by Galasso and Veltri\(^3\).

Sintering for 4.5 hours did not improve the final densities of CP 85/15 and SN 502 bars. However, longer sintering time did increase the density of SN 402 CIP bars, from about 55 percent of the theoretical density of 3.28 gm/cc to about 94 percent theoretical density. In comparison, NCX-34, which is hot pressed, has a density of about 98 percent of theoretical.

The results were not in accord with the general rule that the higher the green density, the higher the final density of the end product. For example, SN 402 powder exhibited the lowest green density (1.4 gm/cc) but also exhibited the highest sintered density (3.1 gm/cc). CP 85/15 powder had the highest
green density (2.0 gm/cc), but exhibited a slight decrease in sintered density (to 1.85 gm/cc). These observations suggest that densification of Si₃N₄ powder compacts depends more on the powder reactivity than initial green density. The higher surface area of the SN 402, about twice that of the other powders, provided greater reactivity and enhanced sintering. However, in all cases, densification was facilitated by formation of a liquid phase with Y₂O₃ at the sintering temperatures.

**Weight loss**

Substantial weight losses occurred on sintering at 1750°C. SN 402 bars had the maximum weight loss, about 21 percent of their green (CIP) weight; SN 502 bars had a loss of about 6.4 percent, while the weight loss in CP 85/15 bars was about 10.2 percent. However, SN 402 bars, in spite of having the highest weight loss, sintered to the highest final density. On the other hand, SN 502 bars had minimum weight loss but sintered to the lowest final density. The large weight loss in SN 402 bars during sintering is attributed to thermal decomposition of amorphous, submicron, Si₃N₄ particles at the external surface of the bars.

**Hot pressing**

The three Si₃N₄ powder types were hot pressed at 1750°C for 2 hrs in one atmosphere of nitrogen under an applied pressure of 276 MPa. The purpose of hot pressing was (1) to determine the maximum densities that could be achieved with different types of Si₃N₄ starting powders for comparison with sintered products, and (2) to prepare high density samples for study of the intermediate temperature oxidation behavior. The densities of all three powders hot
pressed for 2 hrs at 1750°C are compared with the densities of samples sintered for 3 hrs at 1750°C in Figure 4. The highest density (3.2 gm/cc) was observed in SN 402 powder followed by CP 85/15 (3.05 gm/cc) and SN 502 powder (2.75 gm/cc). In all cases, the hot pressed densities were significantly higher than the sintered densities, confirming the advantage of hot pressing for achieving high density ceramics.

Microstructure

The microstructures of both sintered and hot pressed Si$_3$N$_4$ bars were examined by transmission and scanning electron microscopy. These microstructures are shown in Figures 5 to 8. All Si$_3$N$_4$ bars had duplex grain structures containing both equiaxed and elongated grains. Approximate grain size ranges and aspect ratios are listed in Table 2.

The sintered SN 402 bar had a large population of equiaxed grains 0.05 to 0.5 μm in diameter and a small population of elongated grains 0.5 to 10.0 μm in length. The grain size range of sintered CP 85/15 bars was found to be uniform (Figure 5(c)). Both equiaxed and elongated grains were less than 1 μm in width.

Hot pressed SN 402 bars, shown in Figure 6(a), had finer grains than did sintered SN 402 bars. On the other hand, hot pressed SN 502 and CP 85/15 bars had grain size ranges which were approximately equivalent to those of sintered bars. Of the three different types of powders, the fully crystalline CP 85/15 powder exhibited the most uniform grain size.

The fracture surfaces of samples sintered for 3 hrs are shown in Figure 7. These samples had a partially developed grain structure with interconnected pores, consistent with their intermediate densities as shown in Figure 2. In comparison, fracture surfaces of hot pressed samples, shown in Figure 8,
have more or less well developed grain structure with disconnected pores, typical of high density structures associated with more complete sintering.

Phase determinations on sintered and hot pressed bars were done by X-ray diffraction. Differences in phase composition were found between sintered and hot-pressed bars. Sintered bars, regardless of starting powder, contained α-Si₃N₄, n-melilite (Y₂Si₃N₄O₃) and a vitreous phase SN 502 and CP85/15 hot-pressed bars contained α-Si₃N₄, H-phase (Y₁₀Si₇O₂₂N₄), and J-phase (Y₄Si₂O₇), while SN 402 hot-pressed bars contained α-Si₃N₄ and other secondary phases. Limited observations indicated that these phases are also found in NCX-34.⁴

The microchemical segregation of yttria, the sintering aid, was found to vary with the cation impurity content of the three starting powders possibly due to lowering of the melting point of yttria phase by the impurities. As shown in Figure 9, CP 85/15 sintered powder, which had the highest cation impurity content, had the greatest yttria segregation (Figure 9(c)) while SN 402 sintered powder, with the lowest cation impurity content, had a very uniform yttria distribution (Figure 9(a)).

Oxidation in Air at 750°C

After 200 hours continuous exposure at 750°C, no cracking or scaling was observed in hot-pressed SN 402, SN 502, or CP 85/15 bars as shown in Figure 10(a). Weight gain after 200 hours was negligible. These results are in contrast to the observations by Brennan⁵, who reported severe cracking and oxidation of a similar Si₃N₄-Y₂O₃ ceramic, NCX-34, during exposure to air at 750°C for 48 hours, as shown in Figure 10(b). This instability in NCX-34 has been attributed to carbon contamination⁶ or tungsten contamination⁷ during milling. In contrast, no tungsten contamination was observed in materials of this study. Only a small amount of cristobalite was detected.
the surface of the SN 502 bar. Cristobalite was not observed on the SN 402 and CP 85/15 bars.

CONCLUDING REMARKS

The experimental work reported in this study has shown that significant differences exist in particle size, particle shape, and impurity content of three commercially available silicon nitride powders. Sintered densities approaching 3.1 gm/cc (95 percent of theoretical) were obtained only with the amorphous SN 402 powder; this high density was attributed to the high surface area nature of the powder. On the other hand, the presence of cation impurities such as Ca, Fe and Mg in fully crystalline CP 85/15 powder did not promote significant densification during sintering. The amorphous powder (SN 402) exhibited a greater weight loss than the other powders; this was probably due to the greater surface area of the 402 powder and the associated thermal decomposition of amorphous, submicron particles at the external surface of the compacts. Duplex grain structures were observed in both sintered and hot pressed materials.

In a limited oxidation study, no instability was observed in hot pressed Si₃N₄ - 8 w/o Y₂O₃ prepared from three different commercial powders (SN 402, SN 502, CP 85/15) and exposed in air at 750°C.

REFERENCES


Table 1. Trace Element Impurity Analysis of Silicon Nitride Powders.

<table>
<thead>
<tr>
<th>Element</th>
<th>SN 402</th>
<th>SN 502</th>
<th>CP 85/15</th>
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<tr>
<td>Al</td>
<td>&lt;30</td>
<td>50</td>
<td>3000</td>
</tr>
<tr>
<td>C</td>
<td>(a)</td>
<td>410</td>
<td>2600</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;30</td>
<td>50</td>
<td>140</td>
</tr>
<tr>
<td>Ca</td>
<td>&lt;30</td>
<td>130</td>
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<td>Cr</td>
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<tr>
<td>Zr</td>
<td>&lt;30</td>
<td>100</td>
<td>180</td>
</tr>
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</table>

(a) Not analyzed

Table II – Grain Size Ranges and Aspect Ratios of Hot-Pressed and Sintered Si3N4 – 8 w/o Y2O3

<table>
<thead>
<tr>
<th></th>
<th>Hot Pressed</th>
<th>Sintered</th>
</tr>
</thead>
<tbody>
<tr>
<td>SN 402</td>
<td>Small grains 0.05 - 0.5 ( \mu m ); aspect ratio, 1:2.5 to 1:5.</td>
<td>Small grains, 0.05 - 0.3 ( \mu m ); aspect ratio, 1:2.5 to 1:5.</td>
</tr>
<tr>
<td></td>
<td>Large grains usually elongated, width 0.5 to 1.5 ( \mu m ); aspect ratio 1:3 to 1:5.</td>
<td>Large grains equiaxed, 0.5 to 10.0 ( \mu m ).</td>
</tr>
<tr>
<td>SN 502</td>
<td>Equiaxed, 0.1 to 10.0 ( \mu m ); elongated, width 0.12 to 1.2 ( \mu m ) aspect ratio 1:3 to 1:5.</td>
<td>Equiaxed 0.15 to 10.0 ( \mu m ); elongated, width 0.2 to 0.8 ( \mu m ); aspect ratio 1:2 to 1:4</td>
</tr>
<tr>
<td>CP 85/15</td>
<td>Equiaxed, 0.15 to 0.6 ( \mu m ); elongated, width 0.3 to 1.0 ( \mu m ); aspect ratio 1:2.5 to 1:4.</td>
<td>Equiaxed, 0.2 to 0.6 ( \mu m ); majority elongated grains, width 0.1 to 0.4 ( \mu m ), aspect ratio 1:2 to 1:4.</td>
</tr>
</tbody>
</table>
Figure 1 - Transmission electron micrographs of three commercial silicon nitride powders
Figure 2 - Density of silicon nitride + 8wt% yttria cold isostatically-pressed (CIP), sintered for 3 hrs at 1750°C (3h), and sintered for 4.5 hrs at 1750°C.
Figure 3: Fracture surface of cold-isostatically pressed $\text{Si}_3\text{N}_4$ containing 8 wt% $\text{Y}_2\text{O}_3$. 

(a) SN402.

(b) SN502.

(c) CP8515.
Figure 4. - Density comparison of silicon nitride + 8w/o yttria sintered (S) for 3 hrs at 1750°C and hot-pressed (HP) for 2 hrs at 1750°C.
Figure 5: TEM of silicon nitride + 8 wt% Y₂O₃ sintered for 3 hours at 1750°C.
Figure 6: HIP of $SnP_2$ + 8 w/o $Y_2O_3$ hot-pressed for 2 hours at 1760°C.
Figure 9. Microchemical distribution of strontium in sintered Sr2Y2O4·8w/o Y2O3 ceramics.
(a) CPBS/15, SN502, SN502 AFTER 200 HR AT 750° C.

(b) NCX-34 Si$_3$N$_4$ (BILLET F338355) AFTER 48 HR AT 730° C.

Figure 10. - Three hot-pressed silicon nitride + 8 wt. yttria bars oxidized in air.