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Potential use of only Yb$_2$O$_3$ in producing dense Si$_3$N$_4$ ceramics with high thermal conductivity by gas pressure sintering

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Abstract

Yb$_2$O$_3$ is an efficient sintering additive for enhancing not only thermal conductivity but also the high-temperature mechanical properties of Si$_3$N$_4$ ceramics. Here we report the fabrication of dense Si$_3$N$_4$ ceramics with high thermal conductivity by the gas pressure sintering of $\alpha$-Si$_3$N$_4$ powder compacts, using only Yb$_2$O$_3$ as an additive, at 1900 °C under a nitrogen pressure of 1 MPa. The effects of Yb$_2$O$_3$ content, sample packing condition and sintering time on the densification, microstructure and thermal conductivity were investigated. Curves of the density plotted against the Yb$_2$O$_3$ content exhibited a characteristic ‘N’ shape with a local minimum at 3 mol% Yb$_2$O$_3$ and nearly complete densification below and above this concentration. The effects of the sample packing condition on the densification, microstructure and thermal conductivity strongly depended on the Yb$_2$O$_3$ content. The embedded condition led to more complete densification but also to a decrease in thermal conductivity from 119 to 94 W m$^{-1}$ K$^{-1}$ upon 1 mol% Yb$_2$O$_3$ addition. The sample packing condition had little effect on the density and thermal conductivity (102–106 W m$^{-1}$ K$^{-1}$) at 7 mol% Yb$_2$O$_3$. The thermal conductivity value was strongly related to the microstructure.

Keywords: Si$_3$N$_4$, Yb$_2$O$_3$, gas pressure sintering, grain growth, thermal conductivity

1. Introduction

Silicon nitride (Si$_3$N$_4$) ceramics have been intensively studied over the past four decades for their high-temperature structural applications owing to the excellent mechanical properties of Si$_3$N$_4$ at elevated temperatures. However, little attention was paid to the thermal conductivity of Si$_3$N$_4$ ceramics until Haggerty and Lightfoot pointed out in 1995 that Si$_3$N$_4$ has an intrinsic thermal conductivity of over 200 W m$^{-1}$ K$^{-1}$ at room temperature [1]. A considerable amount of work resulted in significantly increased thermal conductivities of Si$_3$N$_4$ ceramics of above 100 W m$^{-1}$ K$^{-1}$ [2–7]. Enhanced thermal conductivity opens up new technological applications of Si$_3$N$_4$ as substrates for integrated circuits and heat sinks in electronic devices.

Si$_3$N$_4$ has two major crystalline forms, $\alpha$ and $\beta$. The $\beta$ form is more suitable for applications because $\alpha$-Si$_3$N$_4$ is chemically unstable and converts to $\beta$-Si$_3$N$_4$ upon heating and because $\beta$-Si$_3$N$_4$ grains grow in an elongated manner that reinforces the ceramic matrix [8].
Moreover, $\beta$-Si$_3$N$_4$ has substantially higher intrinsic thermal conductivity than $\alpha$-Si$_3$N$_4$ \cite{9}. Owing to the strong covalent bonding between silicon and nitrogen atoms, additives are required to densify Si$_3$N$_4$ ceramics by the liquid-phase sintering \cite{10}. Self-reinforced $\beta$-Si$_3$N$_4$ is commonly produced from an $\alpha$-Si$_3$N$_4$ powder that usually contains a small fraction of $\beta$-phase (e.g. UBE SN-E10), because the $\alpha$–$\beta$ phase transformation promotes the development of large elongated grains. During the sintering, the additives react with the native SiO$_2$ on the surface of Si$_3$N$_4$ particles and with Si$_3$N$_4$ to form an eutectic liquid phase through which densification, $\alpha$–$\beta$ phase transformation and $\beta$-Si$_3$N$_4$ grain growth occur. The sintering additives determine the densification, phase transformation, grain growth and characteristics of the grain boundary phase; thus, the use of effective sintering additives is crucial for improving the thermal and mechanical properties of Si$_3$N$_4$ ceramics.

The key issues in enhancing the thermal conductivity of $\beta$-Si$_3$N$_4$ ceramics are the complete densification, purification of $\beta$-Si$_3$N$_4$ grains and a reduced amount of grain boundary phases; all of which are dependent on the sintering additives and sintering techniques \cite{2, 7}. Dissolved O and Al in the $\beta$-Si$_3$N$_4$ lattice are the two main impurities that lower the thermal conductivity of $\beta$-Si$_3$N$_4$ via phonon-defect scattering, and thus the use of SiO$_2$ and Al$_2$O$_3$ additives should be avoided \cite{4, 11}. To enhance the thermal conductivity, sintering additives should play a dual role of promoting densification and removing lattice oxygen. Among the rare-earth oxides, Y$_2$O$_3$ and Yb$_2$O$_3$ are the most promising additives for enhancing the thermal conductivity of $\beta$-Si$_3$N$_4$ ceramics \cite{12}. Because of its economic advantage over hot isostatic pressing and the improved thermal and mechanical properties compared with Si$_3$N$_4$ ceramics produced by pressureless sintering, gas pressure sintering has been widely used to produce $\beta$-Si$_3$N$_4$ ceramics with high thermal conductivity. In gas pressure sintering, a higher N$_2$ pressure allows the sintering of powder compacts at higher temperatures without significant thermal decomposition. Higher temperatures not only favor $\beta$-Si$_3$N$_4$ grain growth but also make it possible to reduce the amount of sintering additives and to use more stable compounds \cite{3, 6}. However, Yb$_2$O$_3$ or Y$_2$O$_3$ alone is not efficient in producing dense Si$_3$N$_4$ ceramics by gas pressure sintering because of their high melting temperatures and high eutectic temperature with SiO$_2$. Therefore, Yb$_2$O$_3$ or Y$_2$O$_3$ is normally used together with another additive, such as MgO \cite{4, 13, 14}, MgSiN$_2$ \cite{16–18} or ZrO$_2$ \cite{7}.

Nishimura et al \cite{19} have shown that Yb$_2$O$_3$ results in substantially better sinterability than Y$_2$O$_3$. Lee et al \cite{20} have studied the effect of adding Yb$_2$O$_3$ on the microstructural uniformity of gas-pressure-sintered Si$_3$N$_4$. Although they did not present density data, the microstructure suggested that complete densification was achieved in some of their samples. Yb$_2$O$_3$ is also an effective additive for improving the high-temperature mechanical properties of Si$_3$N$_4$ ceramics because of the easy formation of the crystalline Yb$_2$Si$_3$O$_7$N$_2$ phase at the grain boundaries \cite{19, 21}. Thus, we infer that gas pressure sintering can produce dense $\beta$-Si$_3$N$_4$ ceramics with the addition of only Yb$_2$O$_3$, and such ceramics should have high thermal conductivity and excellent high-temperature mechanical properties. These new $\beta$-Si$_3$N$_4$ ceramics are potentially interesting structural and functional materials.

In this work, we studied the synthesis of dense Si$_3$N$_4$ ceramics by gas pressure sintering using only Yb$_2$O$_3$ as an additive. The effects of Yb$_2$O$_3$ content, sample packing condition and sintering time on the densification, phase transformation, grain boundary phase, microstructure and thermal conductivity of the ceramics were investigated.

### 2. Experimental procedure

The starting raw materials were $\alpha$-Si$_3$N$_4$ powder (SN-E10, $\alpha$ > 95 wt%, BET 10.9 m$^2$ g$^{-1}$, 1.29 wt% O, UBE Industries Ltd, Yamaguchi, Japan) and Yb$_2$O$_3$ (purity >99.9%, BET 19.3 m$^2$ g$^{-1}$, Nihon Yttrium Co. Ltd, Tokyo, Japan). The amount of added Yb$_2$O$_3$ was varied in the range of 0.5–7 mol% with respect to Si$_3$N$_4$. The calculated compositions and theoretical densities of the starting powder mixtures are listed in table 1; the SiO$_2$ phase is inherently present on the surface of raw Si$_3$N$_4$ particles. The compositions are also indicated in the phase diagram of the Si$_3$N$_4$–SiO$_2$–Yb$_2$O$_3$ system \cite{22} (figure 1).

The powders were mixed for 1 h using a planetary mill in a Si$_3$N$_4$ jar with Si$_3$N$_4$ balls and methanol as a milling medium. The slurry was dried in a rotary evaporator at 60°C and then in a vacuum oven at 110°C for at least 4 h. A powder mixture of about 3 g was uniaxially pressed in

### Table 1. Calculated compositions and theoretical densities of the starting powder mixtures.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Composition (mol% wt% vol%)</th>
<th>(\rho_{th}) (g cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>94.06/96.22/96.63</td>
<td>5.45/3.29/2.89</td>
</tr>
<tr>
<td>B</td>
<td>93.61/94.89/96.17</td>
<td>5.43/3.26/2.87</td>
</tr>
<tr>
<td>C</td>
<td>92.69/92.29/95.23</td>
<td>5.37/2.29/2.85</td>
</tr>
<tr>
<td>D</td>
<td>91.77/89.78/94.30</td>
<td>5.32/2.23/2.82</td>
</tr>
<tr>
<td>E</td>
<td>89.94/85.01/92.42</td>
<td>5.21/2.11/2.76</td>
</tr>
<tr>
<td>F</td>
<td>86.10/80.55/90.55</td>
<td>5.11/2.00/2.71</td>
</tr>
</tbody>
</table>

\*The amount of native SiO$_2$ on the surface of raw Si$_3$N$_4$ powders was estimated as 2.42 wt% based on the oxygen content of 1.29 wt% provided by the manufacturer, and the raw Yb$_2$O$_3$ powder is assumed to be pure. The component densities used in calculating the theoretical densities of the composites are 3.19 g cm$^{-3}$ for Si$_3$N$_4$, 2.65 g cm$^{-3}$ for SiO$_2$ and 9.28 g cm$^{-3}$ for Yb$_2$O$_3$. \*
a 20-mm-diameter stainless-steel die and then isostatically cold-pressed at 400 MPa. The green density showed a slight increase from 53.4 to 54.5% of the theoretical value with increasing Yb$_2$O$_3$ content from 0.5 to 7 mol%. A boron nitride powder (BN, GP grade, Denki Kagaku Kogyo Co., Tokyo, Japan) was used as the powder bed. We applied two different packing conditions, with samples either placed onto the BN powder bed (SPC-I) or entirely embedded in the BN powder bed (SPC-II). The samples were placed inside a triple-crucible arrangement consisting of a double BN crucible and an outer graphite crucible. The sintering was conducted in a graphite resistance furnace (Multi-500, Fujidempa Kogyo Co. Ltd, Osaka, Japan) as follows: (i) heating to 1000 $^\circ$C within 1 h in vacuum, (ii) pressurizing the furnace to 1 MPa at 1000 $^\circ$C with nitrogen gas, (iii) heating at a rate of 10 $^\circ$C min$^{-1}$ to the final temperature, (iv) cooling at a rate of 10 $^\circ$C min$^{-1}$ to 1200 $^\circ$C and then natural slow cooling to room temperature.

Weight loss was determined from the weight change of the sample during sintering. Bulk density was measured by the Archimedes method in distilled water. Phase identification was conducted on the cross sections of sintered samples by powder x-ray diffractometry (XRD, Model RINT 2500, Rigaku Co., Tokyo, Japan) with CuK$\alpha$ radiation. The microstructure was examined by scanning electron microscopy (SEM, Model JSM-5600, JEOL, Tokyo, Japan) on the fracture surfaces coated with a 30-nm-thick gold layer.

To measure thermal conductivity, disk specimens with diameter of 10 mm and thickness of 3 mm were prepared by grinding the sintered samples. Thermal diffusivity was measured by a laser-flash method (Model TC-7000, ULVAC, Yokohama, Japan). Prior to measurements, the surfaces of the specimens were sputter-coated with a 60-nm-thick gold layer to avoid direct transmission of the laser pulse, followed by a subsequent coating of colloidal graphite to enhance the absorption of the flash energy. Thermal conductivity ($k$) was calculated as

$$k = \rho C_p \alpha,$$

where $\rho$, $C_p$ and $\alpha$ are the bulk density, specific heat and thermal diffusivity of the disk specimen, respectively. A specific heat of 0.68 J (g K$^{-1}$) [6] was adopted in this work.

3. Results and discussion

3.1. Sintering at 1800 $^\circ$C

To investigate the densification, $\alpha$–$\beta$ phase transformation and grain growth at the initial stage of sintering, we interrupted the sintering (SPC-I) when the temperature reached 1800 $^\circ$C without holding the sample at this temperature. This process is hereafter referred to as ‘initial sintering’. Figure 2 reveals that both densification and a phase transformation occurred, consistent with the lowest eutectic liquid temperature of $\sim$1650 $^\circ$C in the Yb$_2$O$_3$–SiO$_2$ system [23] and the findings of
Figure 3. SEM micrographs of fracture surfaces in the samples with (a) 0.5, (b) 1, (c) 3 and (d) 7 mol% Yb$_2$O$_3$ sintered at 1800 °C.

Yang et al [24]. Relative densities of 69–74% were achieved in all samples. The density had a maximum at 1 mol% Yb$_2$O$_3$, decreased with increasing Yb$_2$O$_3$ content, and increased again at 7 mol% Yb$_2$O$_3$. The β-phase fraction was ~70 wt% for ≤3 mol% of Yb$_2$O$_3$ and reached 100% at a higher Yb$_2$O$_3$ content, i.e., the α–β phase transformation was completed earlier than the densification. The highest weight loss of 1.6 wt% upon sintering was observed in the case of 0.5 mol% Yb$_2$O$_3$. The weight loss decreased with increasing Yb$_2$O$_3$ content, and a weight gain occurred at 5 mol% Yb$_2$O$_3$ or higher. The reason for this is discussed below.

When a liquid phase is formed, densification proceeds by particle rearrangement followed by dissolution–reprecipitation [10]. Because the phase transformation occurred, the observed densification should be due to the combination of particle rearrangement and dissolution–reprecipitation. Owing to the limited amount of the liquid phase in this study, the dissolution–reprecipitation process should play a dominant role in the densification. The phase transformation promoted by the addition of Yb$_2$O$_3$ suggests that the dissolution–reprecipitation process is diffusion controlled. The Yb$^{3+}$ cation is primarily a network modifier of Yb–Si–O–N glass allowing the rapid diffusion of Si and N ions through the liquid phase [25]. A higher Yb$_2$O$_3$ content produces a higher volume of the liquid phase; thus, so the solution–reprecipitation process is accelerated resulting in a faster phase transformation.

No crystalline secondary phases could be detected by XRD in the samples with the addition of <7 mol% Yb$_2$O$_3$. However, at 7 mol% Yb$_2$O$_3$, both the Yb$_2$SiO$_5$ (Yb$_2$O$_3$ : SiO$_2$ molar ratio of 1) and Yb$_2$Si$_2$O$_7$N$_2$ (Yb$_2$O$_3$ : SiO$_2$ = 4 : 1) phases were observed. This is consistent with the fact that composition F is located in the Si$_3$N$_4$–Yb$_2$SiO$_5$–Yb$_4$Si$_2$O$_7$N$_2$ compatibility triangle (figure 1(b)).

Samples with 0.5 or 1 mol% Yb$_2$O$_3$ had ~65 wt% β-phase and mostly consisted of fine equiaxial grains with only a few elongated β-Si$_3$N$_4$ grains (figures 3(a) and (b)). This illustrates that no significant β-Si$_3$N$_4$ grain growth occurred. The β-phase content was similar upon the addition of 3 mol% Yb$_2$O$_3$; however, most grains became elongated, and β-Si$_3$N$_4$ crystallites larger than several micrometers can be seen in figure 3(c). At 7 mol% of Yb$_2$O$_3$, the phase transformation was completed, almost all β-Si$_3$N$_4$ grains became elongated (figure 3(d)), and the grain size was larger than that in 3 mol% samples. The promotion of β-Si$_3$N$_4$ grain growth upon increasing Yb$_2$O$_3$ content is similar to the findings of Park et al [21]. These results suggest that both the phase transformation and grain growth are dominated by the diffusion-controlled solution–reprecipitation mechanism.

3.2. Sintering at 1900 °C

3.2.1 Weight loss, bulk density and bulk color. As shown in figure 4(a), the weight loss increased with increasing holding time regardless of the Yb$_2$O$_3$ content. However, the effect of Yb$_2$O$_3$ content on the weight loss appeared to depend on the holding time. For 2 h holding, the weight loss decreased with increasing Yb$_2$O$_3$ content, and a similar result was obtained
Figure 4. (a) Weight loss and (b) relative density as a function of Yb$_2$O$_3$ content for the samples sintered at 1900 °C (holding times 2 and 12 h) under different sample packing conditions (SPCs). All density measurements were conducted immediately after taking samples out of the furnace.

The weight gain at a Yb$_2$O$_3$ content of 5 mol% or higher was attributed to the chemical dissolution of nitrogen gas in the oxynitride liquid through substitution for bonded oxygen via the reaction [28, 29]

$$N_2 + Si + (O) \rightarrow 2 (N) + SiO.$$  (3)
The addition of Yb$_2$O$_3$ increases the contents of oxynitride liquid and dissolved nitrogen. Meanwhile, the SiO vapor generated by reaction (3) can inhibit the progress of reaction (2) and thus reduce the weight loss.

As shown in figure 4(b), the relative density increased with increasing Yb$_2$O$_3$ content from 0.5 to 1 mol%, remained constant between 1 and 2 mol%, sharply decreased from 2 to 3 mol% and increased again at higher Yb$_2$O$_3$ concentrations. Density depended on the sintering time, particularly for Yb$_2$O$_3$ content of 5 and 7 mol%. For 7 mol% Yb$_2$O$_3$, it increased with sintering time from 86% (2 h) to 97% (12 h), reaching nearly complete densification. Once the phase transformation is completed, the further densification is due to the combination of Ostwald ripening and coalescence via the solution–precipitation process. Moreover, the embedded condition did not affect the density when Yb$_2$O$_3$ addition was ⩾ 5 mol% but significantly increased it at < 5 mol%.

The embedded condition allowed the samples with 1–2 mol% Yb$_2$O$_3$ to achieve relative densities of > 95% after holding for 12 h.

During the sintering, the sample interacts with the reduced atmosphere and thus usually exhibits either a porous or dense outer surface layer, depending on the processing parameters. A direct and simple approach to understanding this feature is to measure the density of samples before and after surface grinding.

Before being ground into disk specimens with 10 mm diameter and 3 mm thickness for thermal conductivity measurements, the sintered samples had diameters of 14.4–15.5 mm and thicknesses of 5.0–6.2 mm. The grinding allowed the samples to achieve relative densities of > 97% and even 100% with the addition of < 3 mol% Yb$_2$O$_3$ (figure 5(a)); for example, the sample with 2 mol% Yb$_2$O$_3$ sintered under SPC-I showed a large increase in relative density from ~88 to ~100%. This result is attributed to the removal of open pores by grinding (figure 5(b)); this indicates that these samples had at least two layers—a dense inner layer and a porous surface layer. In the case of 3 mol% Yb$_2$O$_3$ addition, the grinding led to an increase in relative density from 73 to 77% under SPC-I but a decrease from 87 to 80% under SPC-II. However, at 7 mol% Yb$_2$O$_3$, grinding led to a very slight decrease in relative density (~97%, figure 5(a)) regardless of the packing condition, suggesting the formation of a dense outer surface layer.

After cutting, the cross sections of all samples exhibited an inhomogeneous color. This inhomogeneity depended on the Yb$_2$O$_3$ content, sintering time and sample packing condition, as shown in figure 6. With the addition of 1 mol% Yb$_2$O$_3$, the bulk color changed from dark gray to light gray and then to white from inside to outside. The embedded condition led to an increase in the thickness of the dark gray inner layer from ~58 to ~78% of the sample thickness. With the addition of 7 mol% Yb$_2$O$_3$, the bulk color changed from inside to outside in the sequence very dark gray, gray, white, gray. The embedded condition led to an increase in the thickness of the very dark gray inner layer from ~26 to ~48% of the sample thickness. If we assume that the very dark gray layer and gray layer constitute the whole inner region, then the thickness of the inner layer increased from ~68 to ~75% of the sample thickness in the SPC-II sample. The largest thickness was about 500 µm for the white surface layer and ~200 µm for the outermost gray surface layer, which corresponded to ~10 and ~4% of the sample thickness, respectively.

The gray color in Si$_3$N$_4$ ceramics is primarily associated with the formation of free Si at the grain boundaries during sintering [30, 31]. The following three reactions in the

\[
\begin{align*}
\text{(i)} & \quad \text{Si} + 3\text{N}_2 \rightarrow \text{Si}_3\text{N}_4 \\ 
\text{(ii)} & \quad \text{Si} + \text{N}_2 \rightarrow \text{SiN} \\ 
\text{(iii)} & \quad \text{Si} + \text{O}_2 \rightarrow \text{SiO}_2
\end{align*}
\]
Sample surface

Table 2. XRD identification results of crystalline secondary phases in the samples sintered at 1900 °C (holding times 2 and 12 h) under different sample packing conditions (SPCs).

<table>
<thead>
<tr>
<th>Yb$_2$O$_3$ content (mol%)</th>
<th>Crystalline secondary phases (intensity$^*$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SPC-I, 1900 °C–2 h</td>
</tr>
<tr>
<td>0.5</td>
<td>Yb$_2$Si$_2$O$_4$N$_2$(×)</td>
</tr>
<tr>
<td>1</td>
<td>Yb$_2$Si$_2$O$_4$N$_2$(×)</td>
</tr>
<tr>
<td>2</td>
<td>Yb$_2$Si$_2$O$_4$N$_2$(×), Yb$_2$Si$_2$O$_4$((×))</td>
</tr>
<tr>
<td>3</td>
<td>Yb$_2$Si$_2$O$_4$N$_2$(×××), Yb$_2$Si$_2$O$_4$(×)</td>
</tr>
<tr>
<td>5</td>
<td>Yb$_2$Si$_2$O$_4$N$_2$(×××), Yb$_2$Si$_2$O$_4$(×)</td>
</tr>
<tr>
<td>7</td>
<td>Yb$_2$Si$_2$O$_4$N$_2$(×××), Yb$_2$Si$_2$O$_4$(×)</td>
</tr>
</tbody>
</table>

$^*$ ××× = major content, ×× = small content, × smaller content, (×) = traces.

Figure 7. SEM micrographs showing the typical three-layer structure in the sintered sample with 7 mol% Yb$_2$O$_3$ regardless of the SPC.

The formation of free Si in gas-pressure-sintered Si$_3$N$_4$ was demonstrated by the weight increase during the second stage of sintering under a nitrogen pressure of 5 MPa when a BN crucible was used [29]. The gray color becomes darker with increasing amount of free Si. The stability of free Si formed in the oxynitride liquid upon cooling depends on the diffusion rate of nitrogen through the bulk Si$_3$N$_4$ ceramic. In the open-pore region, the diffusion path is sufficiently short for nitrogen to bond with Si or directly with SiO to form Si$_3$N$_4$, thus resulting in a white color. Density data and SEM observation confirmed that the dark gray layer was the dense oxynitride liquid have been proposed to account for the formation of free Si in gas-pressure-sintered Si$_3$N$_4$ [31]:

$$3\text{SiO}_2 + \text{Si}_3\text{N}_4 \rightarrow 6\text{SiO} + 2\text{N}_2;$$

$$\text{Si}^{4+} + 2e^- \rightarrow \text{Si}^{2+};$$

$$\text{SiO} \rightarrow \text{Si} + \text{SiO}_2.$$
3.2.2 Crystalline secondary phases. No $\alpha$-$\text{Si}_3\text{N}_4$ phase was detected by XRD in all samples sintered at 1900 $^\circ$C, indicating a complete phase transformation. In addition to the major $\beta$-$\text{Si}_3\text{N}_4$ phase, crystalline secondary phases were observed in all samples. The identification results are summarized in table 2. In the case of 2 h holding under SPC-I, only Yb$_5$Si$_2$O$_7$N$_2$ (among the possible Y-Si phases) was observed for 0.5 and 1 mol% Yb$_2$O$_3$, and both Yb$_5$Si$_2$O$_7$N$_2$ and Yb$_4$Si$_2$O$_7$ (Yb$_2$O$_3$: SiO$_2$ = 1:2) were detected at >2 mol% Yb$_2$O$_3$, with Yb$_2$Si$_2$O$_7$N$_2$ being predominant. More Yb$_5$Si$_2$O$_7$N$_2$ was formed at a higher Yb$_2$O$_3$ content. In the case of 12 h holding under SPC-I, both the Yb$_5$Si$_2$O$_7$N$_2$ and Yb$_4$Si$_2$O$_7$ phases were observed for 2–5 mol% Yb$_2$O$_3$, and the Yb$_5$Si$_2$O$_7$N$_2$ phase was again dominant. At 3 and 7 mol% Yb$_2$O$_3$, in addition to the Yb$_5$Si$_2$O$_7$N$_2$ and Yb$_4$Si$_2$O$_7$ phases, the Yb$_2$Si$_3$O$_7$N$_2$ phase appeared, and it dominated the Yb$_5$Si$_2$O$_7$N$_2$ phase at 7 mol% of Yb$_2$O$_3$. In the case of 12 h holding under SPC-II, only the Yb$_5$Si$_2$O$_7$N$_2$ phase was observed for 0.5 and 1 mol% Yb$_2$O$_3$, and both the Yb$_5$Si$_2$O$_7$N$_2$ and Yb$_4$Si$_2$O$_7$ phases were present at >2 mol% Yb$_2$O$_3$, similar to the case of 2 h holding under SPC-I.

It is worth mentioning that the valence of Yb is +3 in Yb$_5$Si$_2$O$_7$N$_2$ and +2 in Yb$_5$Si$_3$O$_7$N$_2$. The formation of Yb$_5$Si$_2$O$_7$N$_2$ is attributed to the following reaction:

$$\text{SiO}_2 + 4\text{Yb}_2\text{O}_3 + \text{Si}_3\text{N}_4 \rightarrow 2\text{Yb}_4\text{Si}_2\text{O}_7\text{N}_2.$$  

(7)

Wills et al [32] reported the production of Yb$_5$Si$_3$O$_7$N$_2$ in reactions between Si$_3$N$_4$ and lanthanide oxides. Tanaka et al [33] also reported Yb$_5$Si$_3$O$_7$N$_2$ formation in MgSiN$_2$ hot-pressed with Yb$_2$O$_3$ and Si$_3$N$_4$ and explained it by the following reaction between Si$_3$N$_4$ and Yb$_2$O$_3$:

$$5\text{Yb}_2\text{O}_3 + 3\text{Si}_3\text{N}_4 \rightarrow 3\text{Yb}_5\text{Si}_3\text{O}_7\text{N}_2 + 4\text{YbN} + \text{N}_2.$$  

(8)

Although no YbN phase was detected by XRD, the formation of Yb$_5$Si$_3$O$_7$N$_2$ in this study probably results from reaction (8). However, it is unclear why Yb$_5$Si$_3$O$_7$N$_2$ was formed only under SPC-I.

Yang et al [24] also observed only Yb$_5$Si$_2$O$_7$N$_2$ among the possible yttrium-silicon phases in porous Si$_3$N$_4$ sintered with 1.0–7.5 wt% Yb$_2$O$_3$. Park et al [21] reported a transformation from Yb$_5$Si$_2$O$_7$ to Yb$_5$Si$_2$O$_7$N$_2$ in hot-pressed Si$_3$N$_4$ with increasing Yb$_2$O$_3$ content from 4 to 8 wt%; however, only Yb$_5$Si$_2$O$_7$N$_2$ was detected at a higher Yb$_2$O$_3$ content. Our results indicate that the formation of the Yb$_5$Si$_2$O$_7$N$_2$ phase is independent of the Yb$_2$O$_3$ content upon sintering at 1900 $^\circ$C. We interpret this observation in terms of the evaporation of native SiO$_2$ from the surface of Si$_3$N$_4$ particles, which is most likely to shift the starting composition to within the Si$_3$N$_4$–Yb$_5$Si$_2$O$_7$–Yb$_5$Si$_2$O$_7$N$_2$ compatibility triangle. During the rapid sintering at 1800 $^\circ$C, the minimum evaporation of SiO$_2$ allows the formation of crystalline secondary phases in accordance with the compatibility triangle.

![Figure 8. SEM micrographs of fracture surfaces of the samples with (a) 1, (b) 3 and (c) 7 mol% Yb$_2$O$_3$ sintered at 1900 $^\circ$C (holding time 2 h) under SPC-I.](image-url)

3.2.3 Microstructure. Figure 7 reveals the typical three-layer structure formed in the sintered samples with 7 mol% Yb$_2$O$_3$. The structure is characterized by a dense inner region, followed by a porous surface layer of ~500 $\mu$m thickness and an outermost dense surface layer of ~200 $\mu$m thickness. This layering correlates with the inhomogeneous coloration presented in figure 6.

As shown in figure 8, in the case of 2 h holding under SPC-I, the samples with 1 and 3 mol% Yb$_2$O$_3$ exhibited the
finest and coarsest microstructures, respectively. Almost all large grains were elongated in samples with 1 and 7 mol% Yb$_2$O$_3$; the elongated grains have a similar width of $\sim 4 \mu m$ and length of $\sim 40 \mu m$ in these two samples. The structure of the 1 mol% Yb$_2$O$_3$ sample was most bimodal, that is, it had the largest size difference between the fine matrix and the large elongated grains.

As shown in figure 9, in the case of 12 h holding, the microstructure was unaffected by the sample packing condition but was affected by the Yb$_2$O$_3$ content. The samples with 1 and 7 mol% Yb$_2$O$_3$ were dense, whereas the 3 mol% Yb$_2$O$_3$ material was porous; the 1 mol% Yb$_2$O$_3$ sample had the coarsest and the most bimodal microstructure, whereas the 7 mol% Yb$_2$O$_3$ sample exhibited the finest microstructure. In the sample with 1 mol% Yb$_2$O$_3$, the largest elongated grains had a width of about 17 $\mu m$ and length $\sim 100 \mu m$. These results indicate that the abnormal grain growth of $\beta$-Si$_3$N$_4$ was significantly promoted by the addition of 1 mol% Yb$_2$O$_3$ but hindered by the addition of 7 mol% Yb$_2$O$_3$. With the addition of 3 mol% Yb$_2$O$_3$, the $\beta$-Si$_3$N$_4$ grains grew in a normal manner. This is similar to the effect of MgSiN$_2$ addition on the microstructure development of Si$_3$N$_4$ when Y$_2$O$_3$ is used as an additive [34].

The above results indicate that after the $\alpha$–$\beta$ phase transformation is complete, the grain growth of $\beta$-Si$_3$N$_4$ is determined by the amount and size of the large elongated $\beta$-Si$_3$N$_4$ grains, specifically, by the difference in size between the large $\beta$-Si$_3$N$_4$ grains and the matrix grains [35, 36]. If the difference exceeds a critical value, then abnormal grain growth occurs; normal grain growth is observed otherwise. The exaggerated grain growth in the samples with $< 3$ mol% Yb$_2$O$_3$ compared with samples having $> 3$ mol% Yb$_2$O$_3$ is due to the enhanced bimodal microstructure that developed in the early stage of sintering. With the addition of $3 \text{ mol}\% \ Yb_2O_3$, normal grain growth dominates, resulting in a strong porous skeleton composed of elongated grains of similar size. The steric impingement effect hinders and even stops the densification when the amount of liquid phase is insufficient [34, 37].

### 3.2.4 Thermal conductivity

As shown in figure 10(a), the samples sintered under SPC-I had the highest thermal diffusivity of $0.59 \text{ cm}^2 \text{s}^{-1}$ at 0.5 mol% Yb$_2$O$_3$. The thermal diffusivity generally decreased with the Yb$_2$O$_3$ content, except for the 3 mol% Yb$_2$O$_3$ sample which also exhibited the lowest density of <80% (figure 5(a)). In the samples sintered under SPC-II, the thermal diffusivity was almost independent of the Yb$_2$O$_3$ content and had a value of $\sim 0.45 \text{ cm}^2 \text{s}^{-1}$, except for the 3 mol% Yb$_2$O$_3$ sample. The effect of the sample packing condition on the thermal diffusivity was dependent on the Yb$_2$O$_3$ content. With the addition of $< 3 \text{ mol}\% \ Yb_2O_3$, the embedded condition led to a large reduction in thermal diffusivity, and this reduction became more significant with decreasing Yb$_2$O$_3$ content. However, with the addition of $\geqslant 3 \text{ mol}\% \ Yb_2O_3$, the sample packing condition had little effect on the thermal diffusivity.

As shown in figure 10(b), in the samples sintered under SPC-I the thermal conductivity had the highest values of $115-119 \text{ W m}^{-1} \text{K}^{-1}$ at Yb$_2$O$_3$ contents of 0.5–2 mol% and exhibited the lowest value of $67 \text{ W m}^{-1} \text{K}^{-1}$ at 3 mol% Yb$_2$O$_3$. When the Yb$_2$O$_3$ content was further increased to 7 mol%, the thermal conductivity reached $102 \text{ W m}^{-1} \text{K}^{-1}$. Under SPC-II, at low Yb$_2$O$_3$ contents of 0.5–2 mol% the thermal conductivity was significantly reduced to near $100 \text{ W m}^{-1} \text{K}^{-1}$. However, at higher Yb$_2$O$_3$ contents of $\geqslant 3 \text{ mol}\%$, the thermal conductivities were close to the values.
Porosity is known to lower the thermal conductivity of ceramics. Only the samples with 1, 2 and 7 mol% Yb2O3 were almost fully densified, whereas those with other amounts of Yb2O3 were more porous. Considering that most pores are closed and isolated and assuming that the thermal conductivity of pores is zero, the thermal conductivity without pores, $\kappa_{c0}$, can be calculated using the following modified Maxwell equation [38]:

$$\kappa_{c0} = \kappa_c \frac{2 + V_p}{2(1 - V_p)},$$  \hspace{1cm} (9)

where $\kappa_c$ is the thermal conductivity of the ceramic sample and $V_p$ is the porosity, given by $V_p = 1 - \phi$ (relative density). The thermal conductivities corrected for porosity are added in figure 10(b). The correction compensated for the decrease at 3 mol% Yb2O3, resulting in a more regular dependence.

The thermal conductivity of dense $\beta$-Si3N4 ceramics is determined by the $\beta$-Si3N4 grains and grain boundaries [11]. The secondary phases consist of isolated glassy pockets located at the triple grain boundary junctions and the continuous grain boundary film located between the grains. The grain boundary phases have thermal conductivity of as low as $\sim 1$ W m$^{-1}$ K$^{-1}$, and thus should lower the overall value. The thermal conductivity is enhanced by the purification of $\beta$-Si3N4 grains and by lowering the amount of secondary phases. The grain growth allows the dissolution of the less pure small $\beta$-Si3N4 grains and the precipitation of the purer large $\beta$-Si3N4 grains through the liquid phase, thus enhancing the thermal conductivity of $\beta$-Si3N4 grains. Not only the amount, but also the distribution of the secondary phases affects the thermal conductivity—a continuous distribution has a more adverse effect than localization in the form of isolated glass pockets [39, 40]. The thermal conductivity is reduced with the increasing thickness and amount of the grain boundary film [18, 41]. According to the observed microstructure, the decrease in thermal conductivity with increasing Yb2O3 content is attributed to the increasing amounts of secondary phases and the grain boundary film, as well as the higher concentration of lattice defects in the $\beta$-Si3N4 grains, similar to our previous results for MgSiN2 addition [34]. Because the average grain size is larger than 1 $\mu$m in all cases, the effect of grain size on thermal conductivity should be less important in the present work.

As the sample packing condition had no effect on the grain size, the purification of $\beta$-Si3N4 grains is responsible for the change in thermal conductivity. The results of our previous studies suggest that the embedding condition had a strong effect on the removal of lattice oxygen by reaction (2) and thus on the thermal conductivity of $\beta$-Si3N4 ceramics [42]. The embedded condition suppresses the evaporation of SiO, which is indicative of decreased weight loss, thereby lowering the thermal conductivity. The sample packing condition did not change the weight loss in the case of $\leq 3$ mol% Yb2O3 addition, but slightly increased the weight loss for samples with $> 3$ mol% Yb2O3 (figure 4(a)). This result can be understood from the microstructure: the samples with $< 3$ mol% Yb2O3 had a porous outermost surface, making the removal of lattice oxygen by reaction (2) very sensitive to the sample packing condition. SPC-I promoted the removal of lattice oxygen and thus enhanced the thermal conductivity in comparison with SPC-II. However, samples with $> 3$ mol% Yb2O3 exhibited a dense outermost surface, making the removal of lattice oxygen less sensitive to the sample packing condition; thus, the thermal conductivity remained unchanged. SPC-II suppressed the evaporation of SiO generated by reaction (2) and thus enhanced the densification, as evidenced by the large increase in the thickness of the dark-gray inner layer (figures 6(a) and (c)). Under SPC-I, the unchanged weight loss is attributed to the nitridation of SiO in the outer porous surface region. The embedded condition hindered the removal of lattice oxygen and thus lowered the thermal conductivity. Nevertheless, the embedded condition was efficient in producing high densities of $> 95\%$ of the theoretical value and thermal conductivities of $\sim 100$ W m$^{-1}$ K$^{-1}$ upon the addition of 1–2 mol% Yb2O3. From a commercial viewpoint, the adoption of embedded...
conditions is recommended for producing dense Si$_3$N$_4$ ceramics with high thermal conductivity (>100 W m$^{-1}$ K$^{-1}$) via gas pressure sintering, and the recommended Yb$_2$O$_3$ content is either 1–2 mol% or ≥7 mol%.

5. Conclusions

(1) Curves of the density of Si$_3$N$_4$ ceramics plotted against Yb$_2$O$_3$ content exhibited a characteristic ‘N’ shape with a local minimum at 3 mol% and complete densification at lower and higher Yb$_2$O$_3$ concentrations.

(2) Both the α→β phase transformation and β-Si$_3$N$_4$ grain growth were dominated by the diffusion-controlled dissolution–recrystallization mechanism and were promoted at the early stage of sintering by increasing the Yb$_2$O$_3$ content. At the final stage of sintering, the amount and size of large elongated β-Si$_3$N$_4$ grains dominated the grain growth, thereby resulting in enhanced abnormal grain growth with decreasing Yb$_2$O$_3$ content.

(3) The thermal conductivity of pore-free Si$_3$N$_4$ decreased with increasing Yb$_2$O$_3$ content for non-embedded samples but slightly increased when the samples were entirely embedded in BN powder during the sintering.

(4) The sample packing condition had no significant effect on the grain size but a strong effect on the thermal conductivity. Embedding decreased the thermal conductivity from 115–119 W m$^{-1}$ K$^{-1}$ to about 100 W m$^{-1}$ K$^{-1}$ when 0.5–2 mol% Yb$_2$O$_3$ was added, whereas the thermal conductivity was constant at 106 W m$^{-1}$ K$^{-1}$ when 7 mol% Yb$_2$O$_3$ was added. This is due to the formation of an outer porous surface and an outer dense surface in the former and latter cases, respectively.

(5) Our results suggest that dense Si$_3$N$_4$ ceramics with high thermal conductivity and high good-temperature mechanical properties can be produced by gas pressure sintering with the addition of only Yb$_2$O$_3$.

References

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