 Silicon Nitride Ceramics with High Thermal Conductivity and Excellent Mechanical Properties Fabricated with MgF₂ Sintering Aid and Post-Sintering Heat Treatment  

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Abstract  
Si₃N₄ ceramics were prepared with MgF₂+Y₂O₃ as sintering aids by means of SPS, assisted by post-sintering heat treatment; these ceramics exhibited high thermal conductivity and excellent mechanical properties. The effect of the introduced MgF₂ content and post-sintering heat treatment on the properties of Si₃N₄ ceramics was investigated in detail. It was found that the introduction of MgF₂ had a positive impact on the growth of large elongated grains and the grain size of the Si₃N₄ ceramics. Compared to Si₃N₄ ceramics with Y₂O₃+MgO as sintering aids, the thermal conductivity, flexural strength and fracture toughness of the Si₃N₄ ceramics with Y₂O₃+MgF₂ as sintering aids were increased by ~19%, 9% and 12.7%, respectively. After post-sintering heat treatments, the thermal conductivity and fracture toughness of the Si₃N₄ ceramics were increased by ~29.9% and 16.2%, respectively. However, the flexural strength of the Si₃N₄ ceramics was reduced by ~10%. The resulting Si₃N₄ ceramics exhibited possessed thermal conductivity of 82.5 W m⁻¹ K⁻¹, flexural strength of 911 MPa and fracture toughness of 8.47 MPa m¹/².  

Keywords: MgF₂ sintering aids; silicon nitride; thermal conductivity; mechanical properties  

I. Introduction  
Ceramic materials are widely applied in electronic packaging substrates. Compared with organic polymer counterparts, ceramics boast significant advantages, such as good thermal conductivity, high insulation performance and chemical stability. The most commonly used heat conduction ceramic substrates at present are Al₂O₃, BeO, SiC and AlN, etc.¹ However, there are still some challenges limiting their wider application. For instance, AlN ceramics may be an excellent substrate candidate, with thermal conductivity usually over 150 W m⁻¹ K⁻¹, however, their poor mechanical performance (such as a flexural strength of 300 ~ 400 MPa) severely hinders their commercial application. Si₃N₄ ceramics possess outstanding mechanical properties as well as high intrinsic thermal conductivity (200 ~ 320 W m⁻¹ K⁻¹), rendering them one of the most promising electronic substrate materials²,³.  

Metal oxides and rare earth oxides (e.g. MgO, Al₂O₃, Y₂O₃, CeO₂, La₂O₃, Yb₂O₃) are generally employed as sintering aids to facilitate the sintering process of Si₃N₄ ceramics. These sintering aids were able to generate liquid phase by reacting with Si₃N₄ and SiO₂, forming a coating on the surface of Si₃N₄ powder at high temperature, which had distinct impact on the performance of Si₃N₄ ceramics⁴,⁵,⁶. Kitayama et al.⁷ reported that the thermal conductivity of Si₃N₄ ceramics was increased along with the decrease in lattice oxygen content in the Si₃N₄ grains. Hayashi et al.⁸ reported that using MgSiN₂ as an additive rather than MgO improved the thermal conductivity of Si₃N₄ ceramics (~15%). These results indicated that, regardless of the fact that the introduced metal oxides promoted sintering, the extra oxygen atom could be easily transferred into the lattice of Si₃N₄ ceramics, which reduced their thermal conductivity. Accordingly, non-oxide sintering aids could be more effective in preventing the extra oxide invading the lattice of Si₃N₄ ceramics, which could consequently improve the thermal conductivity of Si₃N₄ ceramics. Like MgSiN₂, MgF₂ is a non-oxide sintering aid that can supply magnesium ions without increasing the oxygen content in the liquid phase. The presence of alkaline earth ions such as Mg²⁺ usually leads to a decrease in the melting point of silicate glass phase. Compared with MgO, the common oxide sintering additive used for sintering Si₃N₄ ceramics, MgF₂ has another unique characteristic of a low melting point (e.g. the melting points of MgO and MgF₂ are 2800 and 1261 °C, respectively). Hence, the liquid phases can be formed at lower temperature in Si₃N₄ ceramics when MgF₂ is used as a sintering additive compared to in Si₃N₄ ceramics with added MgO. However, there have been only few studies on the fabri-
cation of Si₃N₄ ceramics with high thermal conductivity using MgF₂ as a sintering aid.

Spark plasma sintering (SPS)⁹,¹⁰ is an efficient sintering technique that enables the fast densification of ceramics over short time scales. Compared with conventional sintering, spark plasma sintering can result in densification at much lower sintering temperatures. The sintering temperature with SPS is usually about 100–200 °C lower than that with conventional sintering.¹¹

In the present work, we report on the fabrication of Si₃N₄ ceramics with high thermal conductivity and high excellent mechanical properties by means of SPS, assisted by post-sintering heat treatment. Commercially available α-Si₃N₄ powder was used as the raw material, and a mixture of Y₂O₃ and MgF₂ was used as the sintering additive. The effect of MgF₂ and the post-sintering heat treatment on the thermal conductivity and mechanical properties of the resulting Si₃N₄ ceramics was investigated in detail.

II. Experiments

(1) Raw materials

A commercial α-Si₃N₄ powder (α-Si₃N₄ > 95%, d_{52} = 0.5 μm, oxygen content < 1.4 wt%, Jinseng ceramics technology Co., Ltd., Jiangsu, China) was used as the starting raw material. MgF₂ (Sinopharm Chemical Reagent Beijing Co., Ltd.), MgO (Sinopharm Chemical Reagent Beijing Co., Ltd.) and Y₂O₃ (Sinopharm Chemical Reagent Beijing Co., Ltd.) were employed as the sintering aids.

(2) Experiment procedure

The α-Si₃N₄ powder was mixed with 5 wt% of Y₂O₃ and certain amount of MgF₂ or MgO in absolute ethyl alcohol, as shown in Table 1, and ball-milled with Si₃N₄ ceramic balls for 12 h. The obtained mixture was dried in an oven at 50 °C for 6 h, and then sieved through an 80-mesh nylon fine screen. The resultant powders were placed into a graphite mold (30 mm in diameter), and sintered by means of SPS (1050T, Japan) at 1600 °C with a dwell time of 5 min.

The samples were then placed into a graphite crucible covered with a powder mixture of Si₃N₄ (50 wt%) and BN (50 wt%), and maintained at 1850 °C for 3 h under 1 MPa nitrogen atmosphere in a furnace (HIGH-MULTI 5000, Japan).

III. Results and Discussion

(1) Effect of the sintering additives on the sintering behavior

Table 2 shows the bulk density, true porosity, thermal conductivity, flexural strength and fracture toughness of the samples with different sintering additives. It seems that, with the increase of the MgF₂ content (Y₂O₃ is fixed at 5 wt%), the thermal conductivity, flexural strength and fracture toughness of the samples are firstly increased and then decreased. When the introduced MgF₂ reaches 4 wt%, the thermal conductivity is the highest at 63.5 W·m⁻¹·K⁻¹. At the same time, the flexural strength and fracture toughness are also reached the highest values, which are 1015 MPa and 7.29 MPa·m¹/², respectively.

Fig. 1(a-d) show typical SEM images of the polished and plasma-etched surface of sample Y5F0, Y5F2, Y5F4 and Y5F6, respectively. It can be observed that relatively small grains and obvious pores exist within the sample Y5F0. It is known that in the sintering of Si₃N₄ ceramics the sintering aids react with Si₃N₄ and SiO₂ coated on the surface of Si₃N₄ powder to generate the liquid phase at high temperatures. If a small amount of the sintering aid is added, the gaps between the Si₃N₄ grains cannot be fully filled by the liquid phase formed, which hinders the diffusion and growth of silicon nitride crystal grains. With the increase of MgF₂ content, ample liquid phase is generated and gradually fills the pores completely. The size of the Si₃N₄ grains and the density at the pores of the sample Y5F6 are the largest. The microstructures of sample Y5F6 are typical features of those of a fully densified material.

(3) Characterization methods

The bulk density of the samples was determined with the Archimedes method. The phase compositions were analyzed by means of X-ray diffraction (D8-Advance, Bruker, Germany). Quantitative analysis of α- and β-Si₃N₄ phases was performed with an X’Pert Highscore report program. The samples were polished and then plasma-etched with CF₄ gas for 30 s in plasma etching apparatus (L-451D-L, Anelva reactive ion etching system). The microstructures were observed under a field emission scanning electron microscope (SEM; MERLIN VP Compact, Germany). The thermal conductivity (k) at room temperature (RT) was calculated according to:

\[ k = \alpha \cdot C_p \]
of the grains is increased, which leads to a larger fraction of large elongated grains and improved contact between the Si₃N₄ grains, making the samples fully dense without obvious pores (Fig. 1(b) and(c)). Accordingly, the thermal conductivity, flexural strength and fracture toughness of the samples are profoundly enhanced. However, when the amount of MgF₂ reaches up to 6 wt%, the excessive addition of sintering aid favors a lot of glassy phase at the grain boundary, which could reduce the thermal conductivity and mechanical properties of the ceramic¹³,¹⁴.

![Fig. 1: Representative SEM images of the polished and plasma-etched surface of different samples: (a) sample Y5F0, (b) sample Y5F2, (c) sample Y5F4, (d) sample Y5F6, (e) sample Y5O4, (f) sample Y5F4 after post-sintering heat treatments.](image)

**Table 2: The typical performances of the as-prepared samples.**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Bulk density (g·cm⁻³)</th>
<th>True porosity (%)</th>
<th>Thermal conductivity (W·m⁻¹·K⁻¹)</th>
<th>Flexural strength (MPa)</th>
<th>Fracture toughness (MPa·m¹/₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y5F0</td>
<td>3.04±0.07</td>
<td>6.4±2.1</td>
<td>26.5±3.2</td>
<td>456±45</td>
<td>5.54±0.27</td>
</tr>
<tr>
<td>Y5F2</td>
<td>3.13±0.02</td>
<td>3.6±0.6</td>
<td>43.2±1.9</td>
<td>902±79</td>
<td>6.29±0.19</td>
</tr>
<tr>
<td>Y5F4</td>
<td>3.19±0.02</td>
<td>1.3±0.6</td>
<td>63.5±3.2</td>
<td>1015±87</td>
<td>7.29±0.21</td>
</tr>
<tr>
<td>Y5F6</td>
<td>3.17±0.01</td>
<td>2.1±0.3</td>
<td>55.6±3.9</td>
<td>989±92</td>
<td>6.98±0.33</td>
</tr>
<tr>
<td>Y5O4</td>
<td>3.15±0.02</td>
<td>3.3±0.6</td>
<td>53.2±2.9</td>
<td>930±81</td>
<td>6.47±0.25</td>
</tr>
<tr>
<td>Y5F4H</td>
<td>3.22±0.01</td>
<td>0.6±0.3</td>
<td>82.5±3.1</td>
<td>911±47</td>
<td>8.47±0.31</td>
</tr>
</tbody>
</table>

* Y5F4H: the sample Y5F4 after post-sintering heat treatments
In comparison, MgO is used as the sintering aid to substitute MgF₂ in the sample Y5F4, and corresponding results are shown in Table 2. The experimental results show that the bulk density, thermal conductivity and mechanical properties of sample Y5F4 are higher than those of sample Y5O4, indicating that the MgF₂ sintering aid is more beneficial to the grain growth and performance improvement of Si₃N₄ ceramics than MgO.

Fig. 2 shows the typical x-ray diffraction (XRD) pattern of samples Y5O4 and Y5F4, revealing the major phase of β-Si₃N₄ with a small amount of α-Si₃N₄. The grain boundary existed in the sample in the form of glass phase. The quantitative analysis revealed that the β : α ratio of sample Y5F4 was 98.1 : 1.9, which was higher than the β : α ratio (96.8 : 3.2) of sample Y5O4. These results indicated that the MgF₂ is also an excellent sintering additive compared to the traditional sintering additive of MgO. It is well known that lattice oxygen is regarded as the dominant extrinsic factor governing the thermal conductivity of Si₃N₄ ceramics, and the sintering additive is also the main source of lattice oxygen. Hence, compared to the as-fabricated samples with oxide sintering additives, fewer extra oxygen atoms coming from the sintering additives are introduced into the lattice, resulting in a higher thermal conductivity of the Si₃N₄ ceramics.

Compared with other common oxide sintering additives used for sintering Si₃N₄ ceramics, the MgF₂ has another unique characteristic of a low melting point (e.g. the melting points of MgO and MgF₂ are 2800 and 1261 °C, respectively). The displacement as a function of temperature during SPS for sample Y5F4 and sample Y5O4 are shown in Fig. 3. It seems that shrinkage occurs at 1200 °C and at 1350 °C for the samples with MgF₂ and MgO as the sintering aids, respectively, verifying that the MgF₂ facilitates the formation of liquid phase at a lower temperature. Above these temperatures, the sample containing MgF₂ reached a plateau at 1500 °C with a displacement of 5.2 mm whereas the sample containing MgO only reached a displacement of 2.86 mm. This shows that the MgF₂-containing sample densified much faster than that containing the MgO additive. The bulk density of the sintered samples is presented in Table 1. The higher bulk density of 3.1697 g·cm⁻³ was obtained for the sample containing MgF₂. The lower bulk density of 3.1453 g·cm⁻³ was obtained for the sample containing MgO. Thus, the sample containing MgF₂ has higher density than the equivalent MgO-containing samples. Furthermore, the fluorine-containing liquids allow a higher solubility of the nitrogen with regard to oxide-containing liquids. Hanifi et al. have reported on the effect of fluorine content on the solubility of the nitrogen in Ca-Si-Al-O-N compositions and found that the maximum nitrogen content of 40 eq% can be obtained at 1 eq% F. Hence, the tiny fluorine content coming from MgF₂ still contributes to the increase in solubility of nitrogen. Table 3 details the fluorine content of the as-prepared samples. The grain boundary existed in the samples in the form of glass phase. With the increase in MgF₂ content, the fluorine content is also increased in the grain boundary glass phase. The effect of fluorine addition on the structure of silicate glasses has been investigated and it has been shown that fluorine can bond to silicon as Si-F, in glasses containing both F and N, the network terminating effect of fluorine induces significant reductions in both glass melting temperatures and glass transition temperatures. Consequently, the formed liquid using MgF₂ as a sintering additive provides more time for completion of the phase transformation from α to β than that with MgO. A longer transformation process from α→β phase would promote grain growth, which results in the purification of Si₃N₄ and increase of Si₃N₄-Si₃N₄ contiguity (shown in Fig. 1(c) and (e)), offering higher thermal conductivity in the samples with MgF₂ than with MgO as a sintering additive.

Table 3: The fluorine content of the as-prepared samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Fluorine content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y5F0</td>
<td>0</td>
</tr>
<tr>
<td>Y5F2</td>
<td>0.63±0.16</td>
</tr>
<tr>
<td>Y5F4</td>
<td>1.73±0.18</td>
</tr>
<tr>
<td>Y5F6</td>
<td>2.25±0.21</td>
</tr>
<tr>
<td>Y5F4H</td>
<td>0.32±0.12</td>
</tr>
</tbody>
</table>

Table 2 lists the typical flexural strength and fracture toughness of sample Y5F4 and Y5O4, suggesting that sample Y5F4 exhibits higher fracture toughness than sample Y5O4, which could be mainly attributed to the fact that the MgF₂-doped sample has a larger fraction of elongated grains than MgO-doped counterparts. These large elongated grains can improve the fracture toughness by facilitating toughening mechanisms such as crack deflection and crack bridging. The flexural strength of sample Y5F4 is also higher than that of sample Y5O4, which could be mainly ascribed to the fact that the MgF₂-doped sample has a higher bulk density than MgO-doped counterparts.
The effect of post-sintering heat treatment

Although SPS exhibits certain advantages, such as accelerating the diffusion of atoms in the sintering process, the short sintering time generally leads to some structural defects in the ceramics. To obtain a better performance, post-sintering heat treatment is necessary. The properties of sample YSF4 before and after post-sintering heat treatment are shown in Table 2. This suggests that the density, thermal conductivity, flexural strength and fracture toughness of sample YSF4 have been profoundly improved after the post-sintering heat treatment. The thermal conductivity is enhanced up to 82.53 W·m\(^{-1}\)·K\(^{-1}\), with an increase of ~29.9% caused by the post-sintering heat treatment.

Fig. 4 shows typical SEM images of the fractured surfaces of sample YSF4 before and after post-sintering heat treatment, revealing that sample YSF4 possesses a larger fraction of elongated grains and sharper grain boundary edges after post-sintering heat treatment. This result indicated that tiny $\beta$-Si$_3$N$_4$ grains dissolved constantly and then reprecipitated at the surface of larger $\beta$-Si$_3$N$_4$ grains during the process of post-sintering heat treatment. As a result of this solution-reprecipitation mechanism, the $\beta$-Si$_3$N$_4$ grains become larger and the number of defects can also be reduced. It is well known that phonons play a dominant role in the heat transport of Si$_3$N$_4$ at room temperature. Phonon scattering arising from lattice defects is widely believed to be a major factor in degrading the thermal conductivity of Si$_3$N$_4$ ceramics. Fig. 1(c) and (f) show representative SEM images of polished and plasma-etched surfaces of sample YSF4 before and after post-sintering heat treatment, revealing the amount and distribution of grain boundary phases within these two samples. The sample after post-sintering heat treatment has fewer grain boundary phases and a higher number of Si$_3$N$_4$-Si$_3$N$_4$ contacts. The weighing results show that the weight loss of sample YSF4 after post-sintering heat treatment is 0.75%. The x-ray fluorescence analyses reveal that the magnesium content in the inside of sample YSF4 before and after post-sintering heat treatment is 1.2 wt% and 0.44 wt%, respectively. According to the report by Y. Zhou, the grain boundary phase can diffuse to the surface of Si$_3$N$_4$ ceramics, accompanied with grain growth, and evaporate during the long post-sintering time at 1900 °C. After the post-sintering heat treatment, only a few grain boundary phases covered the grain, while the majority of grain boundary phases resided at multigrain junctions. Hence, the reduced defects caused by grain growth and fewer grain boundary phases are the reason for the significant increase in the thermal conductivity of sample YSF4 after the post-sintering heat treatment. Owing to the larger amount of elongated grains in the samples induced by the post-sintering heat treatment, the fracture toughness is improved by toughening mechanisms of the large elongated grains. After the post-sintering heat treatment, the flexural strength is decreased by ~10%, which is 910.52 MPa, owing to the coarsening of the microstructure.
At present, the highest value of thermal conductivity of silicon nitride has been reported at 177 W m⁻¹ K⁻¹ by Y. Zhou. In this work, the silicon nitride was fabricated via a route of sintering of reaction-bonded silicon nitride (SRBSN), using Y₂O₃/MgO as additives. Although the value of thermal conductivity is high enough, the lengthy post-sintering time (60 h) and the poor flexural strength (460 MPa) lessen the prospect of application. Hence, the silicon nitride ceramics with high thermal conductivity and excellent mechanical properties fabricated with Y₂O₃/MgF₂ sintering aids possess an enormous advantage.

IV. Conclusions

The MgF₂ introduced as a sintering aid plays a significant role in the fabrication of Si₃N₄ ceramics with improved performance. The thermal conductivity, flexural strength and fracture toughness of Si₃N₄ ceramics reach ~63.5 W m⁻¹ K⁻¹, 1015 MPa and 7.29 MPa m⁻¹/², respectively, which are increased by 19%, 9% and 12.7% compared to the values of the counterparts with MgO as a sintering additive.

The post-sintering heat treatment has an important effect in improving the performance of Si₃N₄ ceramics, giving them more elongated grains with sharp grain boundary edges. The thermal conductivity and fracture toughness of Si₃N₄ ceramics after the post-sintering heat treatment reached 82.5 W m⁻¹ K⁻¹ and 8.47 MPa m⁻¹/², respectively. The flexural strength was 911 MPa, i.e. a ~10% decrease after the post-sintering heat treatment.

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References