Effect of Heat-Treatment on Microstructure and Thermal Conductivity of Spark-Plasma-Sintered Silicon Nitride Ceramics

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$\alpha$-Si$_3$N$_4$ ceramics were sintered at a low temperature of 1773 K by using a spark-plasma-sintering method. Some of the ceramics were further heat-treated at different temperatures from 1773 K to 2173 K for 1 hour, to study the effect of heat-treatment on the microstructure and the thermal conductivity of the ceramics. The results show that the heat-treatment at temperatures above 1873 K can increase the thermal conductivity greatly. During the heat-treatment, the $\alpha$-Si$_3$N$_4$ transforms into $\beta$-Si$_3$N$_4$ and the $\beta$-Si$_3$N$_4$ columnar crystal grows up largely as the heating temperature increases, but the phase transformation and the growth of the $\beta$-Si$_3$N$_4$ columnar crystal does not seem to have an obvious effect on the thermal conductivity of the ceramics. [Received August 4, 2003; Accepted December 18, 2003]

Key-words : Si$_3$N$_4$, SPS, thermal conductivity, ceramics, heat-treatment

1. Introduction

Silicon nitride has an excellent mechanical properties and a high intrinsic thermal conductivity just as high as that of aluminum nitride,$^{11}$ it is considered as a perfect candidate for manufacturing power electronic substrate. A lot of research work has been done recently on the silicon nitride ceramics for increasing their thermal conductivity.\(^2\)-\(^{11}\) the heat-treatment at high temperatures such as over 2273 K for a long time was proved to be an effective means for increasing thermal conductivity of the ceramics. This was attributed to the $\beta$-Si$_3$N$_4$ grain growth,$^{2\text{-}4\text{}}$ to the phase transformation from $\alpha$ to $\beta$-Si$_3$N$_4$,\(^1\) and to the purification of the $\beta$-Si$_3$N$_4$ crystals,\(^1\) but which is the main reason of the improvement of the thermal conductivity still remains unclear.\(^7\)

The effect of heat-treatment at relatively low temperatures under 2073 K was scarcely ever studied, because that it is difficult to consolidate the ceramics at the lower temperature by conventional methods. However the phase transformation from $\alpha$-Si$_3$N$_4$ to $\beta$-Si$_3$N$_4$ and the growth of the $\beta$-Si$_3$N$_4$ columnar crystals mainly proceed at the temperature range from 1773 K to 2073 K, the low temperature range is more important to the study of the relationship between microstructure and the thermal conductivity of the ceramics. Nishimura reported that silicon nitride ceramics can be densified at low temperatures by a spark-plasma-sintering (SPS) method.\(^1\) In the present work, silicon nitride ceramic samples are sintered at 1773 K by using the SPS method, and some of the samples are reheated at different temperature from 1773 K to 2173 K, to study the effect of heat-treatment at the lower temperature on the microstructure and the thermal conductivity of the ceramics, and also the relationship between the microstructure and the thermal conductivity.

2. Experimental

Commercial $\alpha$-Si$_3$N$_4$ powder (Table 1, Tsinghua Founder Co., Ltd., China) was ball-milled with 5 wt% Y$_2$O$_3$ powder (99.5 wt% pure, Kunshan Chemical Industry, China) and 3 wt% MgO powder (98 wt% pure, Tianjin Chemicals center, China) as sintering additives in ethanol for 24 hours. The slurry was dried in an evaporator at a temperature of 328 K and the cakes remained were crushed to pass through a 100-mesh sieve. The mixed powders were then filled into a carbon die 12 mm in diameter, and they were heated to 1773 K and cooled down immediately in a spark-plasma-sintering equipment (SPS-1050, Sumitomo coal mining Co. Ltd.) for sintering. The heating rate was 1.7, 2.5 and 5 K/sec respectively and the pressure applied during sintering was 25 MPa. The ceramic pellets sintered were 12 mm in diameter and 3 mm in thickness.

Some of the ceramic pellets were reheated to 1773 K, 1873 K, 1973 K, 2073 K and 2173 K respectively and they were kept at the temperature for 1 hour in a 1 MPa nitrogen atmosphere.

The surface of the samples as-sintered and heat-treated at different temperatures was ground, and the bulk densities ($\rho$) of the samples were measured by the Archimedes’ method. The relative density of the ceramics was calculated by using the theoretical density of 3.23 g/cm$^3$. The thermal diffusivity ($\alpha$) of the samples was measured at room temperature by a laser flash method using a thermal constant analyzer (JR-II, South China University of Technology). The thermal conductivity ($\kappa$) was calculated from the eq. (1), using a reported specific heat of 0.7 J/K·g.$^7$

\[
\kappa = \rho C_p \alpha.
\]

Phase identification of the samples was performed by X-ray diffraction (XRD) method, using a diffract meter (Cu target, Philips X’ Pert MPD, Netherlands). The microstructure of the samples was studied by using a scanning electronic microscope (SEM) (SCAN4100, Hitachi S-4100, Japan).

3. Results and discussion

Figure 1 shows the relative densities of the samples as-sintered and after heat-treatment at different temperatures. The as-sintered samples have a relative density of 89% to 92%, showing that the silicon nitride ceramics can be consolidated at the relatively lower temperature by the SPS method, and

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>$\alpha$-Si$_3$N$_4$ (wt%)</td>
<td>95.3</td>
</tr>
<tr>
<td>$\beta$-Si$_3$N$_4$ (wt%)</td>
<td>4.3</td>
</tr>
<tr>
<td>Si (wt%)</td>
<td>0.3</td>
</tr>
<tr>
<td>Particle size ($\mu$m)</td>
<td>0.07-2.3</td>
</tr>
<tr>
<td>Delta D50 ($\mu$m)</td>
<td>0.474</td>
</tr>
<tr>
<td>D50 ($\mu$m)</td>
<td>0.425</td>
</tr>
</tbody>
</table>

Table 1 Technical Data of Si$_3$N$_4$ Powder
that the change in the heating rate only has a little influence on the consolidation of the ceramics. After the heat-treatment at 1773 K, the densities of the samples sintered at different heating rate increase to 94%, showing that the densification proceeds quite slowly at the temperature. The silicon nitride ceramics become fully densified only after the heat-treatment at the temperature above 1873 K, the relative densities of the samples increase to over 99%.

Figure 2 shows SEM images at the fracture surface of the samples as-sintered and heat-treated at different temperatures from 1773 K to 2173 K. The XRD patterns of the samples are shown in Fig. 3. The as-sintered sample comprises a lot of nodules, that is, the α-Si₃N₄ powders are fired into rounded grains and the grains are sintered together during the spark-plasma-sintering. After the heat-treatment at 1773 K, a lot of fine crystals precipitate from the nodular grains, the ceramics are sintered more densely, but there are still a lot of small voids existing in the ceramics. β-Si₃N₄ columnar crystals are formed during the heat-treatment at 1873 K, and the ratio of the β-Si₃N₄ increases as the heat-treatment temperature increases as shown in Fig. 3. After the heat-treatment at the temperatures over 2073 K, all of the α-Si₃N₄ changes to β-Si₃N₄ and the β-Si₃N₄ columnar crystals grow up largely.

Figure 4 shows the thermal conductivity of the samples as-sintered and heat-treated at different temperatures. The thermal conductivity of the as-sintered ceramics is lower than 20 W/mK, quite lower than that of the ceramics sintered at a higher temperature by other conventional sintering methods. It increases only a little after the heat-treatments at temperatures under 1873 K, even though the ceramics become fully densified and β-Si₃N₄ columnar crystals are formed during the heat-treatment at 1873 K, which means that the densification and the formation of the β-Si₃N₄ columnar crystals scarcely have any influence on the thermal conductivity of the ceramics in this case. The thermal conductivity of the ceramics increases greatly after the heat-treatment at temperatures over 1873 K. At the same time the number of the β-Si₃N₄ columnar crystals increases and the size of the columnar crystals grow up, but it does not seem that there is a simple relationship existing between the microstructure and the thermal conductivity, because that the thermal conductivity of the ceramics increases almost linearly as the heating temperature increases, there is not a distinct change in the thermal conductivity after the heat-treatment at 2073 K where the β-Si₃N₄ columnar crystals grow up quickly; and also that the thermal conductivity continuously increases after the heat-treatment at the temperatures above 2073 K, even though the silicon nitride ceramics change thoroughly to β-Si₃N₄ at 2073 K. The change in the thermal conductivity can not be simply attributed to the phase transformation from α-Si₃N₄ to β-Si₃N₄ or to the formation and growth of the β-Si₃N₄ crystals.
4. Conclusions

1) The thermal conductivity of the silicon nitride ceramics sintered by the SPS method is lower than 20 W/mK. The heat-treatment under 1873 K has scarcely any influence on the thermal conductivity of silicon nitride ceramics, but it does have at the temperatures over 1873 K. The thermal conductivity of the ceramics increases almost linearly as the heat-treatment temperature increases above 1873 K. It reaches 65 W/mK after the heat-treatment at 2173 K.

2) The phase transformation from α-Si₃N₄ to β-Si₃N₄ occurs and some columnar β-Si₃N₄ crystals are formed during the heat-treatment at 1873 K. A distinct change in the size of the columnar β-Si₃N₄ crystals occurs and all of the α-Si₃N₄ transforms into β-Si₃N₄ after the heat-treatment at 2073 K. But the phase transformation and the growth of the cellular β-Si₃N₄ crystal does not seem to have any obvious influence on the thermal conductivity of the ceramics. Further studies are still necessary to elucidate the mechanism of the thermal conductivity of the ceramics.

References