Effect of Different Sintering Additives on the Microstructure, Phase Compositions and Mechanical Properties of Si₃N₄/SiC Ceramics

Hailing Yang, Qinggang Li, Zhi Wang, Mengyong Sun, Hao Wu, and Xin Cheng

Abstract

Y₂O₃ and CeO₂ were chosen as additives to investigate the effect of different additives on the microstructure, composition, phases, and mechanical properties of Si₃N₄/SiC ceramics using pressureless sintering. Si₃N₄/SiC ceramic without additives had a high density, while after adding Y₂O₃ and CeO₂, the density and flexural strength of Si₃N₄/SiC ceramics were significantly decreased due to the increase in porosity. The main phase compositions of the samples were β-Si₃N₄ and SiC. Moreover, the liquid phases Y-Si-O-N and Ce-Si-O-N were observed after adding Y₂O₃ and CeO₂ respectively. It also indicated that for Si₃N₄/SiC composite ceramics, the high aspect ratio β-Si₃N₄ overlapped with each other and closely bonded with the glass phase could improve flexure strength effectively. Besides, the SiC crystal grains mainly existed in the grain boundary, which could inhibit the secondary recrystallization to avoid the decrease of flexural strength caused by the overgrowth of β-Si₃N₄ grains.

Keywords: Silicon nitride (Si₃N₄); Silicon carbide (SiC); Sintering aids; Mechanical properties.

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1. Introduction

Silicon nitride (Si₃N₄) ceramics had been widely applied in the modern industry due to their excellent properties including thermal shock resistance, outstanding anti-corrosion, and good wear resistance. However, the shortcomings of the ceramics such as brittleness, hard machinability, and high sensitivity to internal flaws of materials are the main hindrances to its applications. It has been revealed that adding a second phase (TiC, TiO₂, SiC, BN, etc.) with high hardness and chemical resistance, as the reinforcing phase, could improve the properties of ceramics, such as flexural strength, fracture toughness and creep resistance. For example, silicon carbide (SiC) as reinforcing phase includes whiskers and particles. Kai and Yang et al. obtained the Si₃N₄/SiC composite ceramics with high density and excellent mechanical properties by using the SiC whiskers as a reinforcing phase in the Si₃N₄ matrix. Moreover, many researchers have reported that the SiC nanoparticles were widespread on the grain boundary. The phenomena caused the interlocking of neighboring Si₃N₄ grains and impede grain-boundary sliding, therefore, the hardness, strength, and high-temperature properties such as the creep behavior of ceramics been improved. The sintering methods of preparing the ceramics include spark plasma sintering (SPS), reaction Sintering, etc. As a relatively new sintering technology, SPS could realize the densification of ceramic at a lower temperature. However, the growth of grain is incomplete due to the shorter holding time of SPS, and the equipment is also expensive. In addition, for the reaction sintering method, the sample has low mechanical properties due to the existence of free silicon. In order to industrialize Si₃N₄/SiC ceramics, pressureless sintering was selected as a possible method because it was practical to control the size and shape of the product along with the temperature schedule. Si₃N₄ and SiC belong to covalent compounds, and both the covalent bonding Si-N and Si-C are strong. Thus, the oxides are always added as sintering additives to promote the process of liquid-phase sintering by forming eutectic liquids.
at the low sintering temperature. The liquid phase finally could be reserved as glassy or partially crystalline after cooling, and it usually locates in the junctions of three or two grains.\textsuperscript{[15]} The common sintering additives including MgO, Y$_2$O$_3$, Yb$_2$O$_3$, Al$_2$O$_3$, CeO$_2$, and so on have been reported.\textsuperscript{[13-17]} In addition, different types and quantities of additives have different effects on the materials. Lojanová and Tatarko\textsuperscript{[10,18,19]}, et.al. investigated the effects of different rare-earth oxides RE$_2$O$_3$ (RE = La, Nd, Lu, etc.) on the bending strength and microstructure of Si$_3$N$_4$-SiC and Si$_3$N$_4$ nanocomposites, and it also analyzed the effects of SiC grains on the matrix. It indicated that the additives and surface oxide layers could react and form the liquid phase showing different viscosity, which influenced the mechanical properties of ceramics and the location of SiC grains. Y$_2$O$_3$ and CeO$_2$ have been successfully used as sintering additives for Si$_3$N$_4$. The density and bending strength of the materials were improved obviously within a certain range of contents.\textsuperscript{[14,20]}

In this study, in order to investigate the effect of both SiC and rare-earth oxides on mechanical properties of Si$_3$N$_4$/SiC composite ceramics, using Si$_3$N$_4$ and SiC particles as raw materials, 3 wt.% rare earth oxides Y$_2$O$_3$ and CeO$_2$ as additives respectively to prepare samples by pressureless sintering method. Furthermore, the microstructure and phase compositions were also analyzed, which might provide evidence to reveal the relationships between the sintering additives and the mechanical properties.

2. Materials and method
2.1 Sample preparation
Si$_3$N$_4$ powders (α-phase 92 %, β-phase 8 %, Shanghai Shuitian Technology Co., LTD., Shanghai, China), Chemical Composition and Content of Si$_3$N$_4$ were shown in Table 1) were used as the matrix materials and SiC powders (average particle size 2 μm, purity > 99.9 %, Shanghai ST-Nano Technology Co. Ltd., China) were used as reinforcement in this study. The proportion of Si$_3$N$_4$ and SiC is 95 : 5. Rare earth oxides Y$_2$O$_3$ (purity > 99.95 %, Ganzhou Jin Chengyuan new materials Co. LTD., Jiangxi, China) and CeO$_2$ (< 50 nm, purity > 99.95 %, Aladdin reagents Co. LTD., Shanghai, China) were added as sintering additives respectively, both the content of Y$_2$O$_3$ and CeO$_2$ is 3 wt.%. The samples with different additives were named SC, SCY, and SCC, respectively. The detailed information is shown in Table 2. Fig. 1 showed the XRD pattern (Fig. 1(a)) and SEM micrograph (Fig. 1(b)) of Si$_3$N$_4$ powders, and Fig. 1 indicated that the main crystal phase of particles was α-Si$_3$N$_4$ and some of the powders were agglomerating. SEM image and grain diameter distribution map of SiC powders were shown in Fig. 2. It showed that the agglomeration of SiC particles was observed (Fig. 2(a)), and the average particulate diameter was around 5 μm. Rare-earth oxides Y$_2$O$_3$ and CeO$_2$ particles were spherical with obvious agglomeration as shown in Figs. 3(a) and (b), and both of them had particle sizes less than 50 nm. The mixtures were ball-milled in ethanol for 12 h, followed by drying for 15 h at 85 ℃ and then sieving through 250 mesh. Afterward, the green body was formed by the cold isostatic pressing method under 200 MPa for 2 min. Then under the nitrogen atmosphere, materials were sintered at 1950 ℃ for 1.5 h without pressure.

2.2 Characterization
The densities (ρ) and apparent porosity (P) of samples were measured by the Archimedes method. The flexure strength via the three-point bending test using electromechanical universal testing machine (CMT5150, China) and the samples were machined into rectangle bars with a size of 3.0 mm×4.0 mm×36.0 mm; the support distance of 30.0 mm and a cross-head speed of 0.5 mm/min was used. After the three-point bending test, the microstructure on the fracture surface of the samples was observed by Scanning Electron Microscope (SEM, JSM-6510LV, JEOL, Tokyo, Japan). Crystalline phases of raw materials and sintered samples were identified by X-ray diffractometry (XRD, D8-ADVANCE, Bruker, Karlsruhe, Germany) with Cu Kα radiation. In addition, Transmission Electron Microscope (TEM, JEM-2100, JEO, Tokyo, Japan) was used to further to determine the microstructure, particle morphology and composition of the materials.

![Fig. 1](image-url) (a) XRD pattern of Si3N4 powders; (b) SEM image of Si3N4 powders.
Table 1. Chemical composition and content of silicon nitride.

<table>
<thead>
<tr>
<th>Material</th>
<th>α phase</th>
<th>β phase</th>
<th>Fe</th>
<th>Al</th>
<th>O</th>
<th>C</th>
<th>Si</th>
<th>BET</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si₃N₄</td>
<td>92</td>
<td>8</td>
<td>0.04</td>
<td>0.03</td>
<td>1.1-1.4</td>
<td>0.18-0.25</td>
<td>0.1-0.2</td>
<td>10-10.9 m²/g</td>
</tr>
</tbody>
</table>

Fig. 2 (a) SEM image of SiC powders; (b) Particle size distribution of SiC powders.

Table 2. Designations and corresponding composition of the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Component concentration (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si₃N₄: SiC</td>
</tr>
<tr>
<td>SC</td>
<td>95:5</td>
</tr>
<tr>
<td>SCY</td>
<td>95:5</td>
</tr>
<tr>
<td>SCC</td>
<td>95:5</td>
</tr>
</tbody>
</table>

3. Results and discussion
3.1 Densification behavior and mechanical properties
Figure 4 was the macroscopic morphology of Si₃N₄/SiC ceramics after sintering at 1950 °C. It is obvious that the color of the samples had been changed; the sample SC was shown black, while the sample SCY and SCC were shown gray-white after adding Y₂O₃ and CeO₂. It is widely known that Y₂O₃ and CeO₂ are common sintering additives, which could form the eutectic solution with oxide on the surface of Si₃N₄, the difference of absorption spectra for different materials results in different colors of the sample surface. The main properties of the samples were shown in Table 3, and the relationship of density, porosity, and flexure strength was drawn clearly in Fig. 5. From Fig. 5, it was not difficult to see that sample SC without admixture had higher density after sintering, and the porosity of SC was less than 0.5 percent, which was indicating that the sample SC had been fully sintered. The pores of SC discharged from the body through the grain boundary, in the process of sintering, resulting in the densification of the material.

However, after adding Y₂O₃ and CeO₂, the porosities of SCY and SCC were increased significantly resulting in lower densities and mechanical properties, which were contrary to

Fig. 3 SEM images of rare earth oxides: (a) Y₂O₃, (b) CeO₂.
expectations. From SEM (Fig. 6), it was found that the two samples had many macropores and micropores, and the micropores were mainly formed by overlapping of $\beta$-Si$_3$N$_4$. Generally, sintering additives promote liquid phase sintering through dissolution and precipitation mechanisms.[18] Besides, according to previous reports, the type and content of sintering additives affect the amount and viscosity of the liquid, which in turn affect densification, grain coarsening, and mechanical properties of Si$_3$N$_4$ as well as influence the stability of SiC.[1] Therefore, it can be speculated that the formation of macropores is included for several reasons. The first is the decomposition of partial silicon nitride to some extent at high temperatures, which is promoted by the addition of sintering additives. After adding additives, the sintering temperature could be decreased and the liquid phase generated. The air produced by the decomposition of Si$_3$N$_4$ could get trapped by the liquid phase, and it was left eventually in the matrix due to the rapid cooling rate or the high viscosity of the liquid. The second is that the silicon carbide particles and rod-like $\beta$-Si$_3$N$_4$ can impede the flow of liquid phases leading to the aggregation of Si$_3$N$_4$ and the liquid phases cannot fill the macropores. And another possibility was that the additive loss (bloating) during annealing at high temperatures caused the increase in the pores quantity.[6,21] When the porosity is high in ceramics, it will become the main factor to reduce the flexural strength since the increase of defects. Furthermore, the densification behavior and mechanical properties of SCY and SCC ceramics could be influenced by sintering temperature, sintering time, and the additional amount of additives, which are the research targets in the future.

It can be seen that the trend of porosity in the materials was converse with the flexure strength (Fig. 5), which is consistent with other studies.[20,22] The ceramic with lower porosity indicated that there were fewer internal defects and more grain boundaries, which explained the high strength of the material. Therefore, the flexure strength of SC was significantly higher than SCY and SCC. It can be concluded that the additives Y$_2$O$_3$ and CeO$_2$ were beneficial to improve the porosity of materials. The factors influencing the strength could be analyzed from the internal structure and the crystal phase composition of materials. The action mechanisms for flexure strength will be described in more detail below.

### Table 3. Mechanical properties of Si$_3$N$_4$/SiC composite ceramics.

<table>
<thead>
<tr>
<th>Samples</th>
<th>additives (%)</th>
<th>Density($\rho$) (g/cm$^3$)</th>
<th>Apparent porosity (P) (%)</th>
<th>Flexure strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td></td>
<td>3.0485</td>
<td>0.4192</td>
<td>329.11</td>
</tr>
<tr>
<td>SCY</td>
<td>Y$_2$O$_3$</td>
<td>2.2923</td>
<td>21.33</td>
<td>170.79</td>
</tr>
<tr>
<td>SCC</td>
<td>CeO$_2$</td>
<td>2.2666</td>
<td>22.75</td>
<td>143.71</td>
</tr>
</tbody>
</table>

Fig. 5 Effect of additives on the density, porosity and flexure strength of composite.

### 3.2 Phase transformation and microstructure

#### 3.2.1 SEM and XRD analysis

The microstructure of the fracture surface of Si$_3$N$_4$/SiC composite materials was shown in Fig. 6. Compared with the sample SCY and SCC, SC had a denser fracture surface with fewer pores without adding any additives, which was consistence with Fig. 5. The rod-like pores left by the $\beta$-Si$_3$N$_4$ with high aspect ratio on the fracture surface of SC (Fig. 6(b)) indicated that the strengthening mechanism was crack deflection, and the crack path along the grains induced the growth of the crack with more twists and turns.[18,23] The
Interweave of $\beta$-$\text{Si}_3\text{N}_4$ grains and glass phase could effectively improve the mechanical properties of materials. For SC samples without adding sintering additives, the growth of $\beta$-$\text{Si}_3\text{N}_4$ crystal was controlled by diffusion due to the lack of liquid phase, and the fine grain of $\beta$-$\text{Si}_3\text{N}_4$ formed at the relatively slow diffusion rate of silicon and nitrogen. In addition, previous research has shown that the overlapping structure of $\beta$-$\text{Si}_3\text{N}_4$ crystals with a high aspect ratio, by bridging and pullout, is beneficial to improve the strength of materials, while the oversized grains with high width have a negative effect on the strength.\textsuperscript{[2,24]} SiC dispersion particles in the $\text{Si}_3\text{N}_4$/SiC ceramics could inhibit the secondary recrystallization of $\beta$-$\text{Si}_3\text{N}_4$ crystals.\textsuperscript{[8]} Thus, the size of $\beta$-$\text{Si}_3\text{N}_4$ grains would not be too large, so as to decrease the mechanical properties. This might explain why sample SC had high flexure strength. For SCY and SCC, after adding $\text{Y}_2\text{O}_3$ and $\text{CeO}_2$, dissolution and precipitation mechanisms played a major role. With the increase in temperature, the liquid phase formed, and then the particles dispersed in the liquid phase moved and rearranged under the action of the capillary force. The smaller particles dissolved and deposited on the surface of large particles through the liquid phase mass transfer, and the grains grow up. It can be seen from Fig. 6 that the porosity increased obviously, and the structure was loose, which explained why the flexure strength decreased after adding the sintering aids. It could also be found that the flexure strength of SCY was slightly higher than SCC. This may be because, for the aspect ratio of $\beta$-$\text{Si}_3\text{N}_4$, the sample SCY was greater than SCC, and the $\beta$-$\text{Si}_3\text{N}_4$ crystal of SCC showed a short columnar. For all the samples, the fracture surface of the samples displayed the intergranular fracture as a whole, particularly in SC and SCC. Besides, the phenomenon that the crystal grains were pulled out from the matrix was also observed in SC and SCY. In summary, the strengthening mechanism of composites could be attributed to intergranular fracture, grain pullout, and SiC dispersion strengthening.

It can be seen that the main phase compositions of the composite materials were $\beta$-$\text{Si}_3\text{N}_4$ and SiC (Fig. 7). Besides,

**Fig. 6** Microstructure of $\text{Si}_3\text{N}_4$/SiC composites cross-section.
α-Si$_3$N$_4$ crystal phase was not observed, indicating that the α-β phase transformation was complete at high temperature. For sample SCY and SCC, the sintering additives Y$_2$O$_3$ and CeO$_2$ will react with the SiO$_2$ oxide film formed at the particle surface at high temperature so that the ternary system of Si$_3$N$_4$- Y$_2$O$_3$-SiO$_2$ and Si$_3$N$_4$-CeO$_2$-SiO$_2$ formed. The crystal phases Y-Si-O-N and Ce-Si-O-N indicated in Fig. 7 were generated from the liquid phase during cooling. The liquid phases could reduce the sintering temperature of the materials and promote the α-β phase transformation as previously stated. Besides, the Y$_2$SiO$_3$ phase was also observed in sample SCY.

![XRD pattern of Si$_3$N$_4$/SiC composite ceramics.](image)

**Fig. 7** XRD pattern of Si$_3$N$_4$/SiC composite ceramics.

### 3.2.2 TEM analysis

TEM with a higher resolution microscope was used on sample SCC to fully analyze the crystal phase composition and structure of it, as shown in Fig. 8. Many pores and β-Si$_3$N$_4$ grains with a low aspect ratio were observed in Fig. 8(a). Moreover, there were many internal defects in sample SCC, which may be formed by the decomposition of Si$_3$N$_4$ at the high temperature without external force, or by the failure of energy release during the rapid cooling as mentioned before. This verified the conclusion mentioned before and further analyzed the reason why the bending strength decreased after adding CeO$_2$. As shown in Fig. 8(b), the interplanar spacing was 0.62 nm proving that the phase was β-Si$_3$N$_4$, which was consistent with the results of XRD. The liquid phase (indicated by the arrow in Fig. 8(b)) formed by the SiO$_2$ oxide film of the Si$_3$N$_4$ surface and sintering aids could be observed clearly, and it was located at the junction of two or more grain phases. Moreover, the SiC grains with irregular shapes were identified in the grain boundaries. Many kinds of research have shown that SiC grains have an inhibitory effect on the secondary recrystallization of Si$_3$N$_4$ grains and the inhibition effect increases with the increase in size. Therefore, the β-Si$_3$N$_4$ grains would not grow too large to reduce the strength of materials.

### 4. Conclusions

The influences of Y$_2$O$_3$ and CeO$_2$ additives on the mechanical and microstructure of Si$_3$N$_4$/SiC composite ceramics have been investigated, and the impact of SiC on the material structures has also been studied. The sample SC obtained by using pressureless sintering without additives had high flexure strength and density. The main phases were β-Si$_3$N$_4$ and SiC, and the β-Si$_3$N$_4$ with a high aspect ratio, which could combine with the glass phase closely to improve the flexure strength. After adding Y$_2$O$_3$ and CeO$_2$, respectively, the flexure strength of samples SCY and SCC decreased obviously due to the increase of porosity. The increase of porosity was related to the liquid phases which were formed by the SiO$_2$ oxide film and sintering aids, and it also could be influenced by the decomposition of silicon nitride at high temperatures. In addition to β-Si$_3$N$_4$ and SiC crystal phases, the Y-Si-O-N and Y$_2$SiO$_3$ phases were found in sample SCY, and the Ce-Si-O-N phase was found in SCC. In addition, SiC particles located in the grain boundary of ceramics could inhibit the secondary recrystallization of the grains effectively, and avoid adverse effects on the strength of materials due to the oversize β-Si$_3$N$_4$ grains. The influences of additive content and sintering temperature will be research targets in the future.

![TEM pictures of the sample SCC: (a) TEM image; (b) HRTEM image.](image)

**Fig. 8** TEM pictures of the sample SCC: (a) TEM image; (b) HRTEM image.
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Conflict of Interest
There is no conflict of interest.

Supporting Information
Not applicable.

References

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