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Effect of diamond doping on carbothermal reduction reaction and properties of Si₃N₄ ceramics

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ABSTRACT

Si₃N₄ ceramics were sintered at 1900°C for 12 h with Y₂O₃ and MgSiN₂ as sintering aids under 1 MPa nitrogen pressure. The effects of diamond with different particle sizes (1,2 μm) as carbon source on the microstructure, thermal properties and carbothermal reduction behavior of Si₃N₄ ceramics were systematically studied. The results show that the carbothermal reduction process introduced by diamond significantly reduces the oxygen content and increases the N/O ratio of the secondary phase at the grain boundary. Among them, the sample with 1μm diamond (SNC-1) showed the best reaction efficiency: the fine-grained diamond had a higher specific surface area and stronger reactivity, which promoted the uniform carbothermal reduction reaction and effectively removed the oxygen impurities at the grain boundary. In the final dense Si₃N₄ ceramics, although the strength of the SNC-1 sample with 1 μm diamond is slightly sacrificed, with the decrease of grain boundary oxygen content, the content of β-Si₃N₄ increases, the grain morphology develops into a rod shape and the size is obviously coarsened, forming a microstructure that is more conducive to heat conduction. Therefore, SNC-1 achieves a balance between thermal conductivity and mechanical properties, and improves thermal conductivity while maintaining high strength. This is of great significance for the application scenarios that pursue the synergy of high thermal conductivity and good mechanical properties.

Keywords

Si₃N₄ ceramics; Diamond; Thermal conductivity; Mechanical properties;
Microstructure

1、Introduction

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With the rapid advancement of global energy transition and smart grids, the enhancement of power semiconductor device performance and the assurance of reliability have become key driving forces for the advancement of renewable energy technologies [1, 2]. In this background, the selection of packaging materials plays a crucial role. Ceramic substrates possess exceptional high thermal conductivity and robust mechanical strength, stand out among semiconductor packaging materials, making them one of the preferred materials to propel the development of renewable energy technologies [3-5].

Silicon nitride (Si_3N_4) ceramics exhibit good theoretical thermal conductivity, outstanding electrical insulation, high strength, and excellent thermal shock resistance, have been regarded as a favorable candidate for packaging materials in power semiconductor devices[6]. Hirosaki et al.[7] demonstrated through molecular dynamics calculations that the thermal conductivity of β - Si_3N_4 single crystals in the a and c directions are 170 and 450 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, respectively. Nevertheless, due to the influence of lattice defects (vacancies, impurities, dislocations, etc.) and microstructure (grain size, porosity, intergranular phases, etc.), the experimental thermal conductivity of Si_3N_4 ceramics is much lower than the theoretical value [8, 9]. Among all the influencing factors, lattice oxygen is the main impurity affecting the thermal conductivity. Si_3N_4 ceramics primarily transfer heat through phonon vibrations. O solid solution into the Si_3N_4 lattice, replacing the positions of N and creating Si vacancies, which leads to lattice distortion. This lattice distortion strongly scatters phonons, shortening their mean free path and reducing the thermal conductivity of Si_3N_4 ceramics. The formation of oxygen impurities is primarily attributed to the silicon dioxide (SiO_2) oxide layer on the surface of the Si_3N_4 powder and the oxide sintering additives introduced. To mitigate the negative impact of lattice oxygen on thermal conductivity, researchers have adopted various strategies, including reducing the oxygen content of the raw powder through carbothermal reduction [10, 11], prolonged heat treatment at high temperatures to promote grain growth, purification, and reduce lattice defects [12], and using non-oxide sintering additives to decrease oxygen content in the liquid phase [13-15]. Among the methods mentioned above, the carbothermal reduction method has been shown to be efficacious in reducing oxygen levels in raw materials. Nevertheless, research in this field is relatively limited and still deficiency.

The introduction of carbon into ceramic systems can effectively react with surface

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oxides, decreasing the content of liquid phase oxygen impurities and improving thermal conductivity. Li et al.[11] used 5 mol% carbon powder, and Yb₂O₃ and MgO as sintering additives to fabricate Si₃N₄ ceramics, successfully reducing the oxygen content from 1.54 to 1.18wt%. Compared to the samples without carbon addition, the thermal conductivity enhanced 25%. Similarly, Fan et al. [10] added 1wt% and 2wt% of carbon, using Y₂O₃ and MgO as sintering additives. The thermal conductivity of Si₃N₄ ceramics increased to 101 W·m⁻¹·K⁻¹, while the sample without adding carbon was only 67 W·m⁻¹·K⁻¹. These improvements can be explained by effectively reducing the liquid phase oxygen content through carbothermal reduction, which in turn reduces the formation of lattice oxygen, thereby increasing the thermal conductivity. Above findings highlight the substantial potential of carbon doping to enhance the thermal performance of ceramic materials. Furthermore, due to the various structures of carbon, these different carbon structures exhibit different physicochemical properties. However, there has been no comprehensive study has been conducted on the specific effects of different carbon structures (such as diamond, graphene, and graphite) on the thermal conductivity of Si₃N₄ ceramics.

In this work, Y₂O₃-MgSiN₂ were used as sintering additives, and different carbon crystal structure (including different particle sizes diamond, graphene and graphite), were added to prepare Si₃N₄ ceramics. The effects of carbon crystal structure on the densification process, microstructural evolution, thermal conductivity, and mechanical properties of Si₃N₄ ceramics were systematically investigated.

2. Experimental procedure

2.1 Raw materials

The starting materials used were α -Si₃N₄ (SN-E10, O=1.21wt%, UBE Industries, Japan). The sintering additives including Y₂O₃ (Y103888, purity $\geq$ 99.99wt%, Shanghai Aladdin Biochemical Technology Co., Ltd., China), MgSiN₂ (CX-M02, Qingdao PORCELAIN NEW Material Co., Ltd, China), were incorporated to promote liquid-phase sintering of Si₃N₄ ceramics. This study focuses on exploring the effect of carbon source size in the micron range close to the characteristic size of the substrate. We strategically selected two representative particle sizes of diamond, 1 μ m and 2 μ m, to reveal its nonlinear effects on carbothermal reduction reaction, microstructure and properties of silicon nitride ceramics.

Table 1

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Nomenclature of Si₃N₄ ceramic specimens and the content of sintering additives incorporated

	Si ₃ N ₄ (mol%)	Y ₂ O ₃ (mol%)	MgSiN ₂ (mol%)	1μm Diamond powder(wt%)	2μm Diamond powder(wt%)
SN-0	93	2	5	0	0
SNC-1	93	2	5	2	0
SNC-2	93	2	5	0	2

The detailed ratio information was shown in **Table 1**. The SEM images of the Si₃N₄ powder were shown in **Fig. 1**. **Fig. 1(a)** showed that the majority of the Si₃N₄ powder is in an agglomerated state. **Fig. 1(b)** revealed the presence of a few β-Si₃N₄ grains interspersed among the α-Si₃N₄ grains, indicating that both α-Si₃N₄ and β-Si₃N₄ grains coexist in the starting powder.

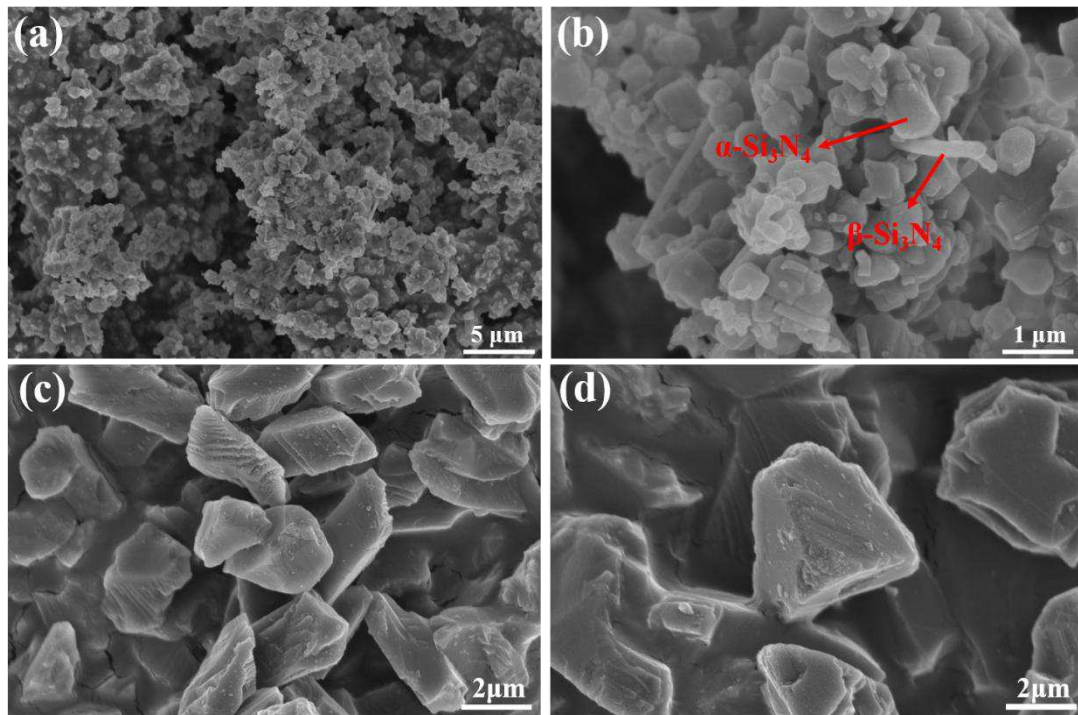


Fig. 1 SEM images of raw materials and additives; (a) and (b) are the SEM images of silicon nitride at different magnifications, (c) 1.0 μm Diamond powder, (d) 2.0 μm Diamond powder

The characteristics of diamond particles of different grain sizes were shown in Fig. 1(c) and (d). **Fig. 1(c)** presented diamond powder with an average grain size of 1 μm, exhibiting sharp shapes and a smaller particle spacing. The SEM of 2 μm diamond powder, as shown in **Fig. 1(d)**, showed that larger grain size and more dispersed distribution.

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2.2 Preparation

According to the designed experimental composition, the raw materials such as Si_3N_4 powder, diamond and sintering additives required for the experiment were weighed into the ball mill tank by using a precision electronic balance. The powder was mixed by a ball milling process at 300 rpm for 3 h, with anhydrous ethanol as the dispersion medium and Si_3N_4 balls as the ball-milling medium. The volume fraction of the mixed slurry and the balls should not exceed 2/3 of the tank capacity. After ball milling, the ball-milled slurry was dried at 60 °C in a vacuum drying oven and screened by using a 100-mesh sieve. Subsequently, the mixtures were uniaxially pressed in a steel die at 20 MPa, followed by cold isostatic pressing at 200 MPa to further increase the relative density of the green compacts. Finally, the samples were sintered at 1900°C for 12 h under 1 MPa N_2 . The preparation process of the sample is shown in Fig. 2.

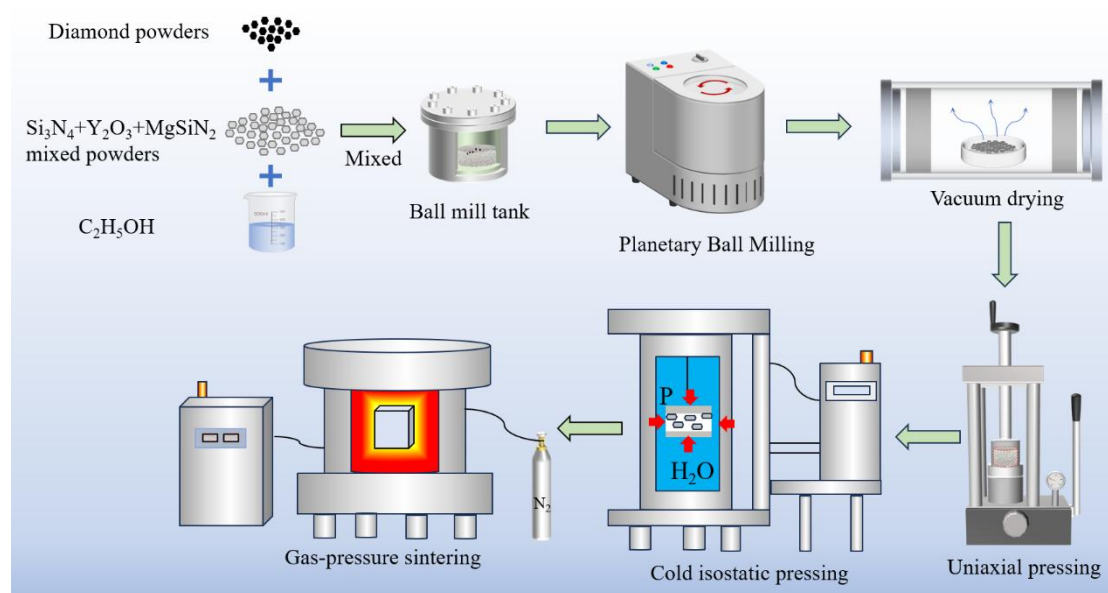


Fig. 2 Flow chart of preparation process

2.3 Characterization

The density was measured by Archimedes method, requiring that the samples be fully immersed in deionized water. The relative density was calculated from the ratio of theoretical density to the measured density. The microstructural features of the polished sample surface were observed with scanning electron microscope (SEM, SU8010, Hitachi) and the phase identification were analyzed via X-ray diffraction (XRD, Rigaku Smart Lab, Japan). The interface was analyzed using a transmission electron microscope (TEM, Talos F200S, FEI, USA) equipped with energy dispersive spectrometer (EDS, MICROSCOPEI PORT SU8100, USA). Rectangular bars with

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dimensions 3×4×36mm were tested on a universal testing machine (UTM4103, Shenzhen SANS testing machine Co. Ltd, Shenzhen) to take average value as the flexural strength by the 3-point bending method, with a span of 30 mm and a loading rate of 0.5 mm/min. The fracture toughness (K_{IC}) of the samples was calculated by indentation method. The test surface of every specimen was ground and polished to the mirror-like. The measurement of Vickers hardness and fracture toughness were conducted by using the indentation testing equipment (SCV-50A/T, Shandong Shancai TEST Instrument Co. LTD, China) at a load of 196.2 N and a dwell time of 15 s. The crack morphology and crack propagation paths were observed using SEM. The K_{IC} was calculated using the Shetty equation [16]:

$$K_{IC} = 0.0899(H \times P / 4l)^{0.5}$$

where H is the Vickers hardness, l is the length of the indentation crack and P is the indentation load. The final results of Vickers hardness and fracture toughness were obtained from the mean value of least five indentations at different places.

The thermal diffusivity was obtained by the laser flash (LFA 467 Hyper flash, NETZSCH Instruments Co. Ltd., Selb, Germany) analysis on disks of size $\Phi 10 \times 2$ mm. The thermal conductivity (K) was calculated using the following equation:

$$K = \rho C_p \alpha$$

where ρ is the bulk density, α is the thermal diffusivity, and the specific heat capacity (C_p) was taken as a fixed value of $0.68 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ [17].

3. Results and discussion

3.1 Densification

The density of Si₃N₄ samples were shown in **Table 2**. Due to the different characteristic of diamond powders, the density values of samples were different as well. The density of SNC-2 was undesirable, reasonably because the reaction activity of the 2 μ m diamond powder was weak. There is a close inverse correlation between grain size of particle and reaction activity. The bigger the particle size, the smaller the specific surface area. Particle with low specific surface area was not prone to chemical reactions. As a result, the 2 μ m diamond powder couldn't effectively take part in the carbothermal reduction reaction, the residual diamond powder (2 μ m) hindered the densification process.

Table 2

The density, average grain size and performance data of β -Si₃N₄ ceramics were

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prepared by diamond with different particle sizes.

	Bulk density(g/cm ³)	Relative density (%)	Average grain size (μm)	Area ratio of grain boundary phase (%)
SN-0	3.14	98.17	1.94	3.21
SNC-1	3.13	97.71	2.05	2.67
SNC-2	2.89	90.23	1.77	3.01

3.2 Phase composition and microstructure

The XRD patterns of the sintered samples with different particle sizes of diamond added were shown in **Fig. 3**. α - Si_3N_4 diffraction peaks were not detected, suggesting α - Si_3N_4 completely transformed into the β - Si_3N_4 (PDF#33-1160) after sintering. Additionally, $\text{Y}_2\text{Si}_3\text{O}_3\text{N}_4$ was found in all samples, which is a typical intergranular phase in Si_3N_4 ceramics, predominantly formed by the reaction of Y_2O_3 in the sintering additives with Si_3N_4 , as shown in the reaction Eq. (1) [18, 19]. Studies have shown that the presence of $\text{Y}_2\text{Si}_3\text{O}_3\text{N}_4$ positively contributes to enhancing the thermal conductivity of Si_3N_4 ceramics [20]. However, the MgO-containing phases are not detected and considered to be dissolved in the liquid phases of Si_3N_4 samples.

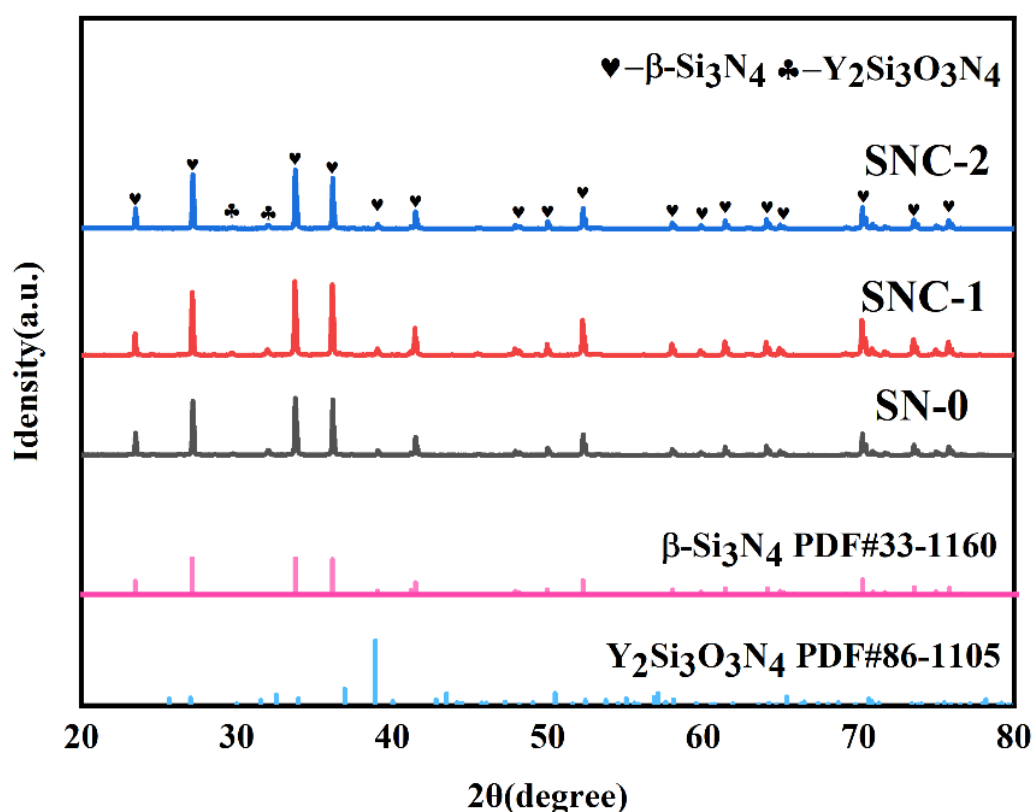
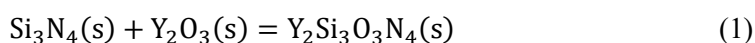


Fig. 3 XRD patterns of Si_3N_4 ceramics doped with diamond of different sizes sintered at 1900 °C for 12 h



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The microstructures of the polished surfaces and grain size of all the Si_3N_4 samples were shown in **Fig. 4**. Due to the different characteristics of diamond, samples presented different microscopic morphology. A large number of pores can be observed in SNC-2 (**Fig. 4c**), which is in good concordance with the result of density value (**Table 2**). It illustrated that large size particle of diamond ($\geq 2\mu\text{m}$) is not suitable as carbon source of Si_3N_4 ceramics in carbothermal reduction reaction. It can be seen that primarily equiaxed grains in SN-0 sample (**Fig. 4a**), and only a small fraction of large elongated grains can be observed as well. The average grain size of SN-0 was $1.94\mu\text{m}$. Furthermore, a few abnormally grown, high aspect ratio rod-shaped $\beta\text{-Si}_3\text{N}_4$ grains and a majority of fine equiaxial grains can be found in SNC-1(**Fig.4b**).

In addition, diamond powder ($1\mu\text{m}$) could accelerate the carbothermal reduction reaction and consume the oxygen of Si_3N_4 ceramics, which improve N/O ratio of liquid phase. The high N/O ratio was favorable to the nucleation and growth of $\beta\text{-Si}_3\text{N}_4$ via a dissolution-precipitation mechanism [21, 22]. Thus, the average grain size of SNC-1 were larger than that of SN-0. In conclusion, $1\mu\text{m}$ diamond powder is more effective in promoting growth grains.

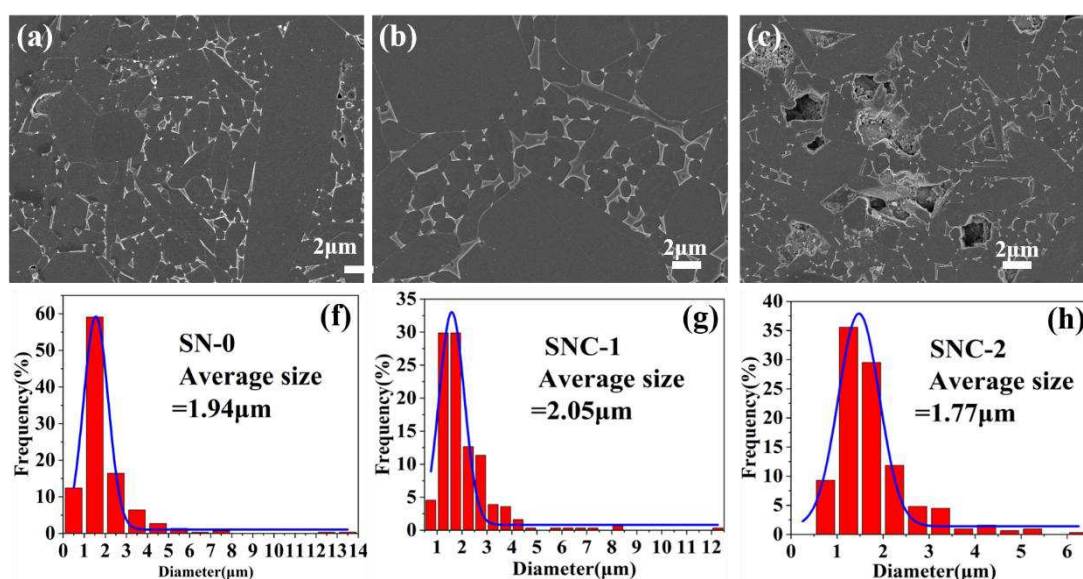


Fig. 4 SEM micrographs of the polished and plasma-etched surfaces and grain size: (a) and (f) belong to SN-0, (b) and (g) belong to SNC-1, (c) and (h) belong to SNC-2.

3.3 Mechanical properties of Si_3N_4 ceramics

The bending strength of SN-0, SNC-1, SNC-2 were depicted in **Fig. 5(a)**. It can be seen from **Fig. 5(a)**, the values of SN-0, SNC-1, SNC-2 were 670 MPa, 588.5 MPa, 299 MPa, respectively. The SEM images of fracture morphologies were shown in **Fig.**

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6(a-c). The bending strength of SNC-2 was the lowest because of undensification, and there were many pores in fracture morphology of SNC-2 (**Fig. 6c**), which becomes initiation points for crack propagation under external loading. The bending strength of SNC-1 was relative lower than SN-0, which were related with the microstructure of samples. These abnormally grown β - Si_3N_4 grains served as significant structural defects, reducing the bending strength of the SNC-1[23]. This is in line with the typical fine grain strengthening mechanism, that is, grain refinement brings more grain boundaries and effectively hinders crack propagation. However, the microstructure evolution path of SNC-1 sample with $1\mu\text{m}$ diamond was changed. Although the grain coarsening and rod-like grain development driven by carbothermal reduction reaction weaken the fine grain strengthening effect to a certain extent, resulting in a decrease in strength to 588.5 MPa, this slender rod-like grain morphology is conducive to grain bridging, which may have a positive impact on the fracture toughness of the material. **Fig. 5(b)** showed a strong negative correlation between bending strength and grain size. On the basis of Hall-Petch relation, there was a negative relation between mechanical property and grain size [24].

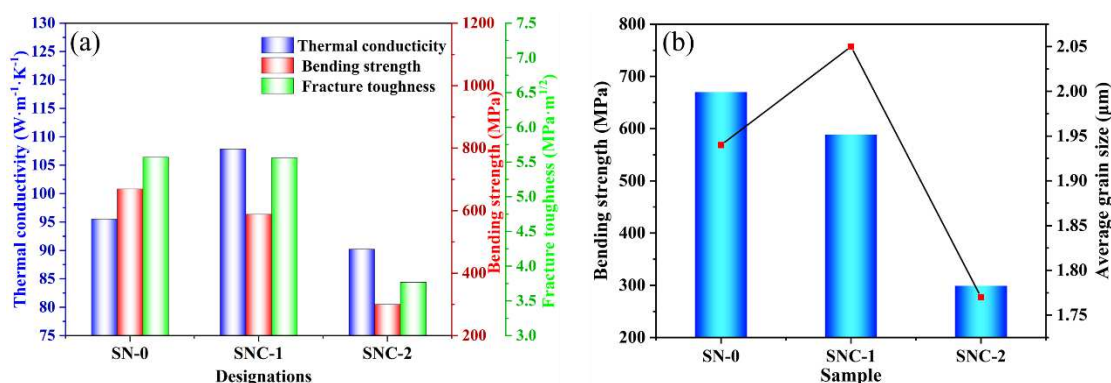


Fig. 5 (a) The thermal conductivity, bending strength and fracture toughness of diamond-doped Si_3N_4 ceramics with different particle sizes. (b) The correlation between bending strength and grain size.

The fracture toughness of samples could be found in **Fig. 5(a)** as well. The fracture toughness of SN-0, SNC-1, SNC-2 were $5.57 \text{ MPa}\cdot\text{m}^{1/2}$, $5.56 \text{ MPa}\cdot\text{m}^{1/2}$, $3.77 \text{ MPa}\cdot\text{m}^{1/2}$, respectively. This was benefited from the presence of larger grains, SNC-1 and SN-0 exhibited the highest fracture toughness. The value of SNC-2 was unsatisfactory on account of undensification. In order to analyze detailedly the toughening mechanism of Si_3N_4 ceramics, the crack extension paths of Si_3N_4 ceramics doped with diamond of different particle sizes were evaluated, as shown in **Fig. 6(d-f)**. It can be observed that

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SN-0 and SNC-1 exhibit crack deflection and bridging phenomena. The large columnar grains enhance toughness by bridging the main crack and promoting crack deflection mechanisms. The tortuous crack propagation path and crack branching were observed in **Fig. 6(d-e)**, which preventing crack defects by forming a new surface, absorb more energy, and improve the overall toughness of the material [25-28]. In contrast, as shown in **Fig. 6(f)**, SNC-2 showed a smooth crack propagation path. It contained a substantial number of large, unevenly distributed pores, which served as channels for rapid crack propagation, thereby accelerating the fracture process. Furthermore, the pores could cause cracks to propagate along the pore boundaries or directly into the pore interior, leading to the lowest fracture toughness.

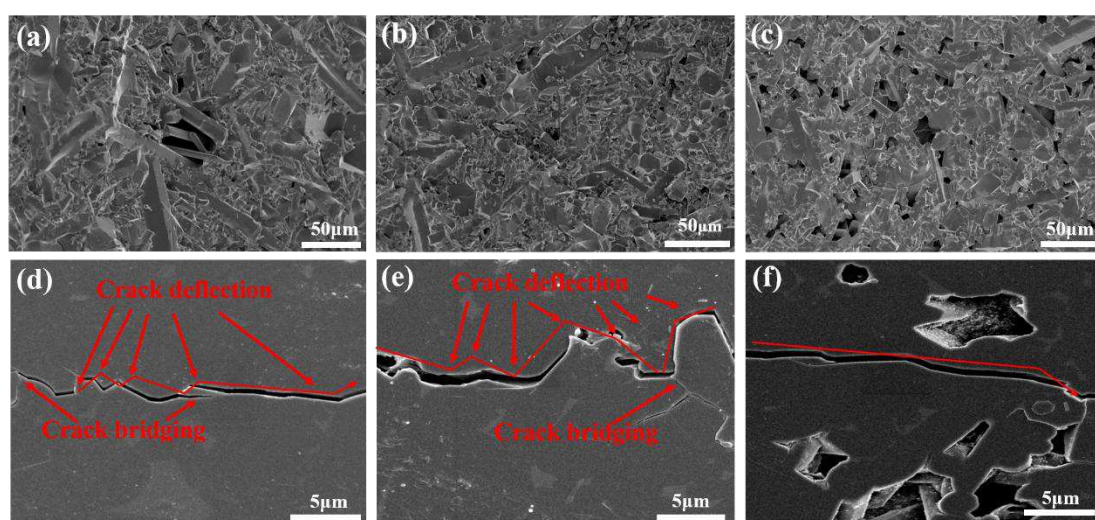


Fig. 6 (a)-(c) SEM micrographs of the Si_3N_4 ceramics fracture and (d)-(f) crack propagation paths on polished surface of Si_3N_4 ceramics: (a) and (d) belong to SN-0, (b) and (e) belong to SNC-1, (c) and (f) belong to SNC-2.

3.4. Carbothermal reduction mechanism and thermal conductivity of Si_3N_4 ceramics

The thermal conductivity of Si_3N_4 ceramics was shown in Figure 5(a). The thermal conductivity values of SN-0, SNC-1, and SNC-2 were $95.51 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, $107.85 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, $90.23 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, respectively. Among them, SNC-1 exhibits the highest thermal conductivity, which is mainly attributed to the occurrence of carbothermal reduction reaction. As illustrated in Figure 7(a), the carbothermal reduction reactions represented by Eqs. (2)-(3) are thermodynamically favorable at temperatures above 1500°C and under standard atmospheric pressure (1 atm) [18, 30, 31]. As shown in figure 7(b), during the sintering process, the addition of diamond as a carbon source promoted the

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elimination of SiO₂ in the sample Si₃N₄. At high temperature, diamond as a reducing agent captures oxygen in SiO₂, forming CO gas and generating highly active gaseous SiO. In addition, the high N₂ pressure of 1 MPa is conducive to the formation of Si₃N₄ by reaction (2), which significantly reduces the oxygen impurities in the liquid phase. It is well known that lattice oxygen is one of the main defects affecting the thermal conductivity of silicon nitride ceramics. Therefore, it is particularly critical to obtain Si₃N₄ with high thermal conductivity by reducing the oxygen content. More importantly, the decrease in oxygen content alleviates the grain-boundary pinning effect, thereby facilitating grain growth. Consequently, SNC-1 possesses the largest average grain size among all samples, accompanied by a reduced number of grain boundaries. Since grain boundaries are primary sources of phonon scattering, this coarse-grained, fewer-boundary microstructure effectively suppresses phonon scattering, endowing SNC-1 with the highest thermal conductivity.

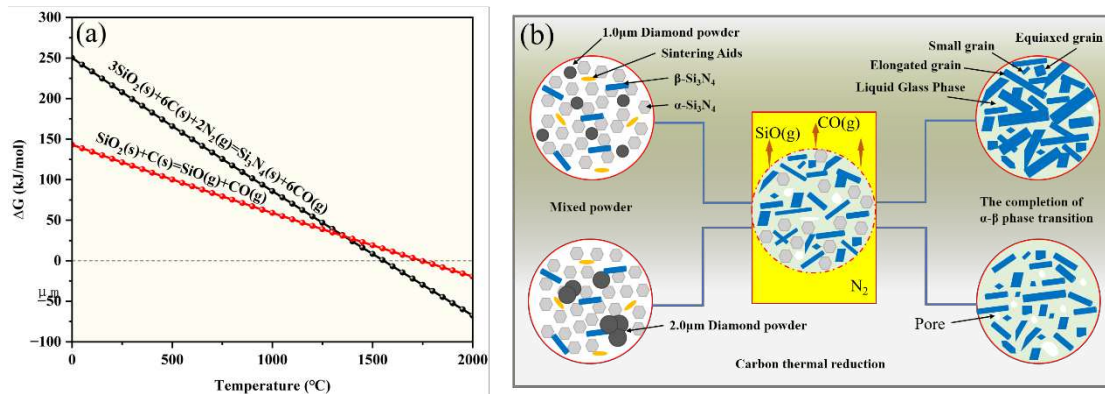
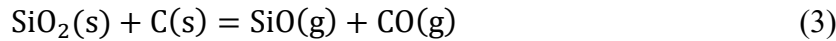
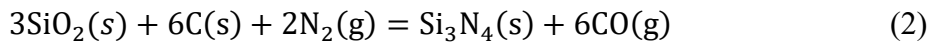


Fig. 7 (a)Standard Gibbs free energy versus temperature for the chemical reactions of Eqs. (2)–(3). (b) Carbothermal reduction mechanism of diamond with different particle sizes.

In contrast, SNC-2 has the lowest thermal conductivity. Although the carbothermal reduction reaction also occurs in SNC-2, due to the large size of 2 μm diamond particles, the reaction area around them is relatively concentrated, and the formation of SiO (g) may be concentrated around the particles, resulting in residual pores; these pores act as secondary-phase defects that severely impede heat conduction. For SN-0, despite the absence of diamond addition, its intrinsic density and grain size still ensure relatively good thermal conductivity. However, its grain refinement is more pronounced than that of SNC-1, resulting in stronger grain-boundary scattering and thus a lower thermal

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conductivity than that of SNC-1.

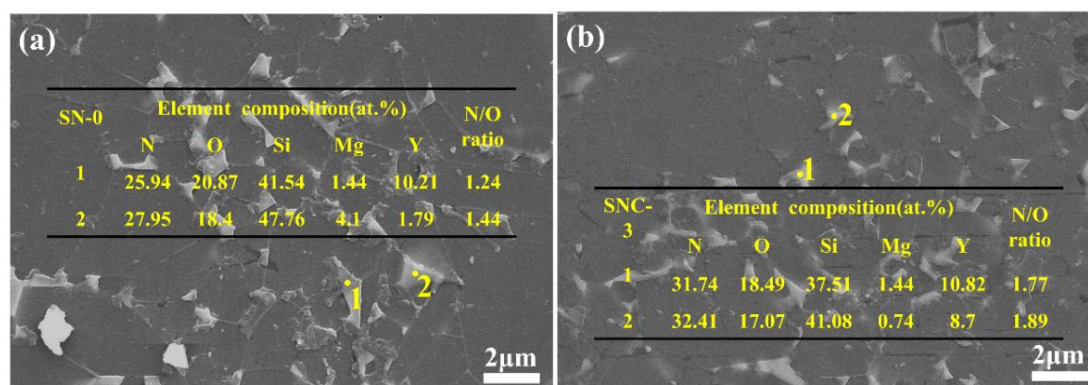


Fig. 8 The surface SEM and intergranular element content of Si_3N_4 ceramics: (a) SN-0, (b) SNC-1.

It also just because of carbothermal reduction reaction of SNC-1 and SNC-2, the oxygen content of these samples was lower than SN-0. In order to further verify this point, the elemental analyses were employed for the grain boundary phases of the SN-0 and SNC-1 samples, as shown in **Fig. 8(a-b)**, respectively. The corresponding EDS results for the liquid phase marked points are listed in the table of **Fig. 8**. Compared to SN-0, the liquid phase in SNC-1 showed a lower oxygen content. This finding confirmed that the carbothermal reduction process contributes to the reduction of oxygen content and the increase in the N/O ratio in the liquid phase.

4、Conclusions

The effects of diamond powders with different particle sizes (1, 2 μm) on the carbothermal reduction reaction, properties and microstructure of Si_3N_4 ceramics were systematically studied. Due to carbothermal reduction reaction, oxide layer (SiO_2) on the surface of Si_3N_4 powder can react with carbon to produce $\text{SiO}(\text{g})$ and $\text{CO}(\text{g})$, which decreased the oxygen content of Si_3N_4 ceramics and increased N/O ratio of liquid phase. Because of suitable particle size and regular granular structure, diamond powder (1 μm) has the ability to accelerate the carbothermal reduction reaction and promote grain growth. Consequently, SNC-1 achieves the highest thermal conductivity ($107.85 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$). While the diamond-free sample SN-0 exhibits the highest bending strength (670 MPa) due to fine-grain strengthening, SNC-1 maintains a competitive strength of 588.5 MPa, reflecting a balanced trade-off between mechanical integrity and thermal performance. In contrast, the addition of 2 μm diamond (SNC-2) leads to incomplete reaction and residual porosity, resulting in significant degradation of both

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bending strength (299 MPa) and thermal conductivity ($90.23 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$). These results show that by controlling the addition of fine diamond particles ($1\mu\text{m}$), effective microstructure control can be achieved by carbothermal reduction during the sintering process of Si_3N_4 ceramics, so as to achieve the best synergistic effect between high thermal conductivity and excellent mechanical properties. In summary, carbothermal reduction reaction could be an effective method of obtaining good thermal conductivity and excellent mechanical properties in Si_3N_4 ceramics, which is important in ceramic substrate field.

CRedit authorship contribution statement

Wenlei Jia: Date Curation, Formal Analysis, Investigation, Writing-Original Draft, Writing-Review & Editing; **Rencong Geng:** Investigation, Methodology, Supervision, Visualization; **Ping Yang:** Conceptualization, Funding Acquisition, Resources, Supervision, Validation, Writing-Review & Editing; **Mingwei Li:** Validation; **Wenhan Qi:** Visualization; **Ju Zhou:** Formal Analysis, Investigation; **Yihua Yue:** Funding Acquisition, Resources; **Shiqi Li:** Investigation; **Jiao Han:** Project Administration, Supervision; **Yiming Zeng:** Conceptualization, Formal Analysis, Supervision, Writing-Review & Editing.

Declaration of competing interest

The authors declare that they have no competing financial interests or personal relationships that could have appeared to influence work reported in this paper.

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Date availability

The data will be available upon reasonable request from corresponding authors.

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