Combustion Synthesis of Si$_3$N$_4$-BN-SiC Composites by in-situ Introduction of BN and SiC

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Abstract: Si$_3$N$_4$-BN-SiC composites present desirable potential for engineering applications because of their improved mechanical properties and oxidation resistance. In present work, Si$_3$N$_4$-BN-SiC composites were successfully fabricated by combustion synthesis using Si, Si$_3$N$_4$ diluent, B$_4$C, and Y$_2$O$_3$ as initial powders. BN and SiC were in situ introduced into Si$_3$N$_4$ ceramics by the reaction between Si, B$_4$C, and N$_2$ gas. The obtained Si$_3$N$_4$-BN-SiC composites were composed of elongated β-Si$_3$N$_4$ matrix and hollow spherical composites. The formation mechanism of the hollow spherical microstructure was investigated. The results show that the generated SiC and BN particles and glass phase cover on the raw materials, and hollow spherical microstructure is formed when raw particles are depleted. Furthermore, the impacts of B$_4$C content on the mechanical properties of Si$_3$N$_4$-BN-SiC composites were investigated in detail. The in-situ introduction of BN and SiC is advantageous to the improvement of mechanical properties of the composites to some extent. Si$_3$N$_4$-BN-SiC composites with bending strength of 28-144 MPa, fracture toughness of 0.6-2.3 MPa-m$^{1/2}$, and Young’s modulus of 17.4-54.5 GPa porosity of 37.7%-51.8% were obtained for the samples with 0-20wt% B$_4$C addition.

Key Words: combustion synthesis; Si$_3$N$_4$-BN-SiC composites; in situ introduction; phase compositions; hollow spheres; formation mechanism

Silicon nitride (Si$_3$N$_4$) ceramics have been extensively used as structural and/or functional components in various engineering fields such as filtration, aerospace, and membrane support. It possesses low thermal expansion coefficient, excellent mechanical properties, good thermal shock resistance, and high chemical stability due to its strongly covalent bonds between atoms $^{[1-3]}$. Several technologies can be used to fabricate Si$_3$N$_4$ ceramics, including pressureless sintering$^{[4-5]}$, reactive sintering$^{[6-7]}$, carbothermal synthesis$^{[8]}$, and combustion synthesis (CS) $^{[9-10]}$. Among these approaches, combustion synthesis can achieve rapid and low-cost fabrication of Si$_3$N$_4$ ceramics by the self-propagating of combustion waves using Si as starting material $^{[9]}$.

Compared with Si$_3$N$_4$ ceramics, Si$_3$N$_4$-BN-SiC composites present some improved properties such as lower dielectric constant, lower thermal expansion coefficient, and higher flexural strength, which draws attractive attentions in engineering applications$^{[11-12]}$. The traditional introduction way of an additional phase is to add the required phase into the initial powders$^{[13]}$. However, the introduced phase is difficult to disperse homogeneously into the sintered product. In-situ introduction can solve this difficulty and achieve good interface bonding between the matrix and introduced phases$^{[14]}$. But investigations involving the in-situ introduction of BN or SiC into Si$_3$N$_4$ matrix are limited. Kusunose et al.$^{[15]}$ reported the preparation of Si$_3$N$_4$/BN nanocomposites by hot-pressing the t-BN coated α-Si$_3$N$_4$ powders, t-BN was in situ synthesized by the reducing reaction between boric acid and urea. Zheng et al.$^{[16]}$ used B$_4$C and Si as raw materials to prepare h-BN-SiC composites via their combustion reaction at high-pressure N$_2$ gas (60-120 MPa). Inspired by above-mentioned study, present study is attempting to in situ introduce BN/SiC into Si$_3$N$_4$ matrix by B$_4$C addition. The microstructural evolution of the in-situ fabricated BN/SiC and its effects on the properties of the sintered Si$_3$N$_4$-BN-SiC composites will be studied.

1 Experimental procedure

The initial powders were Si powder (Peixian Tiannayuan Silicon Materials Co., Ltd., Jiangsu, China; purity≥99.99%; $d_{50}=4.1$ μm), Si$_3$N$_4$ powder (Yantai Tomley Hi-Tech Advanced Materials Co., Ltd., Shandong, China; purity≥99.9%; α-phase content=42.3wt%; $d_{50}=22$ μm), B$_4$C powder (Dalian Jinma Boron Technology Group Co., Ltd, Shandong, China; purity≥99.99%; $d_{50}=1.5$ μm), and Y$_2$O$_3$ powder (Yuelong
New Material Co., Ltd, Shanghai, China; purity≥99.999%; \( d_{50} = 5.04 \mu m \). The weight ratio of initial powders was determined as Si: Si\(_3\)N\(_4\): B\(_4\)C: Y\(_2\)O\(_3\) = 40: (60-\( \chi \)) : \( \chi \) : 2 (\( \chi \)=0, 5, 10, 15, and 20, respectively). The samples were named SBC00, SBC05, SBC10, SBC15, and SBC20 according to the weight ratio of B\(_4\)C, respectively. To obtain homogeneous mixtures, the ceramic powders were ball-milled for 3 h in ethyl alcohol with a ball/charge weight ratio of 2:1. After dried and sieved through a 150 \( \mu m \) (100 mesh) screen, each homogeneous mixture was cold-pressed into a rectangular compact (40 mm\( \times \)40 mm\( \times \)10 mm) at 10 MPa. The obtained compact was immersed into a powder bed (homogeneous mixture of 40wt% Si and 60wt% Si\(_3\)N\(_4\)) and ignited under 5 MPa N\(_2\) atmosphere. Schematic diagram of the reactor and detailed preparation process was mentioned in previous work\(^{[17]}\).

The reaction temperature was obtained from the W-Re5/26 thermocouple immersed into the powder bed. Rectangular bars with the dimensions of 3.0 mm\( \times \)4.0 mm\( \times \)36.0 mm were prepared to measure the bending strength and Young's modulus by three-point bending method (Instron-3443, Instron, USA). Fracture toughness was tested by single-edge notched beam method (SEBN) on pre-notched bars (3.0 mm\( \times \)6.0 mm\( \times \)30.0 mm). The microstructure of the sample was observed by scanning electron microscope (SU-1000, Hitachi, Japan) and transmission electron microscope (JEM-2100F, JEOL Company, Japan). The phase composition of the sample was performed by XRD (Diffractor meter D8, Bruker, Germany), and the content of each crystalline phase was calculated based on the XRD results. The open porosity of sintered sample was determined by the Archimedes method in the distilled water. The total porosity (\( P \)) was calculated from the measured bulk density (\( \rho_b \)), theoretical density (\( \rho \) calculated based on the phase content of each phase) using following equation: \( P = 1 - \rho_b/\rho \).

### 2 Results and Discussion

The possible reactions during the fabrication process are shown in Eq. (1-2). Both the reactions are exothermic, but the adiabatic temperature of reaction (2) is reported to be lower than that of reaction (1)\(^{[18-19]}\). It meets the experimental results as shown in Table 1, the measured reaction temperature decreases from 1850 °C to 1765 °C with the increase of B\(_4\)C content. Meanwhile, the reaction time increases with the B\(_4\)C content increasing, it can be ascribed to the generation of SiC and BN which restrain the propagating of combustion wave as an inert phase.

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\begin{align*}
3\text{Si(s)} + 2\text{N}_2(g) &\rightarrow \text{Si}_2\text{N}_3(s) \quad (1) \\
\Delta G^0 &= -725.615 \text{ kJ} \\
\text{Si(s)} + 2\text{N}_2(g) + \text{B}_4\text{C}(s) &= \text{SiC}(s) + 4\text{BN}(s) \quad (2) \\
\Delta G^0 &= -914.459 \text{ kJ}
\end{align*}
\]

| Sample | Reaction temperature/°C | Reaction time/s | Open porosity/% | Total porosity/% | Bending strength/MPa | Fracture toughness/(MPa m\(^{1/2}\)) | Young's modulus/GPa |
|--------|--------------------------|-----------------|-----------------|------------------|-------------------------|----------------------------------|---------------------|
| SBC00  | 1850±15                  | 16±3            | 51.8±1.0        | 52.0             | 120±12.0                | 2.2±0.4                          | 49.5±1.6            |
| SBC05  | 1825±20                  | 18±5            | 47.3±0.5        | 48.5             | 144±8.4                 | 2.3±0.2                          | 54.5±1.7            |
| SBC10  | 1795±12                  | 21±2            | 43.3±0.6        | 47.5             | 108±5.0                 | 1.7±0.2                          | 46.2±3.0            |
| SBC15  | 1778±20                  | 26±5            | 42.3±0.5        | 46.9             | 30±7.4                  | 0.7±0.2                          | 18.5±2.1            |
| SBC20  | 1765±14                  | 30±3            | 37.7±1.7        | 45.2             | 28±3.9                  | 0.6±0.1                          | 17.4±1.2            |
The properties of the sintered samples are shown in Table 1, the open porosity of sample SBC00 is 51.8%. With the increase of B\textsubscript{4}C content, the open porosity of the sample decreases apparently. When the B\textsubscript{4}C content is 20wt\%, the open porosity of the obtained Si\textsubscript{3}N\textsubscript{4}-BN-SiC composites is 37.7%. The significant decrease in porosity can be attributed to the higher volume expansion (170%) of reaction (2) than that of nitridation of Si (21.2%)\textsuperscript{[16]}, more pores are filled by the generated SiC and BN grains. However, the calculated total porosity based on the XRD results is higher than open porosity, especially for samples prepared with higher B\textsubscript{4}C content. On one hand, closed pores are formed with increasing addition of B\textsubscript{4}C as discussed above. On the other hand, B\textsubscript{4}C might form glass phase with native SiO\textsubscript{2} film and Y\textsubscript{2}O\textsubscript{3} during the high-temperature CS process, the theoretical density calculated based on the XRD results is higher than the actual value of sample, thus leading to the increasing total porosity. This behavior could be proven from the calculated content of each phase by XRD. According to the law of conservation of mass of reaction (2), the content of the generated BN and SiC should be higher than the calculated content. It illustrates that B\textsubscript{4}C partially forms glass phase instead of BN and SiC after CS process, which could not be detected by XRD.
To investigate the reaction mechanism of the CS process, transmission electron microscope (TEM), high-resolution transmission electron microscope (HRTEM), energy dispersive spectroscopy (EDS) analysis, and selected area electron diffraction (SAED) are conducted on sample SBC10 and the results are shown in Fig. 3. The results demonstrate that the hollow sphere is a mixture of polycrystalline phase and amorphous phase. The crystalline phase should be BN and SiC combining the XRD analysis in Fig. 1. The amorphous phase consists of multiple elements including B, C, Si, N, and a little amount of O. On one hand, it has the characteristics of SiBCN ceramics. It is well known that SiBCN ceramics have two compositions of amorphous SiC$_x$N$_{4-x}$ ($x=1-4$) and graphite-like BN(C). The above-mentioned broadening of BN peak is due to the formation of amorphous BN(C). On the other hand, the amorphous phase contains evident glass phase combining the SEM image. The formation of the hollow spher-
ical microstructure may originate from the comparatively low N\textsubscript{2} gas pressure and the formation of glass phase. At the initial stage of the combustion reaction, eutectic liquid phase, and small BN and SiC particles are formed and cover on the surfaces of raw particles, but the small BN flakes could not grow up because of the low N\textsubscript{2} gas pressure and restriction of liquid phase. As the reaction proceeding, the newly formed products continue to cover on the surfaces thus forming hollow spheres when raw particles are depleted. Ultimately, eutectic liquid phase forms glass phase during the rapid cooling of CS process.

As listed in Table 1, the mechanical properties of the obtained Si\textsubscript{3}N\textsubscript{4}-BN-SiC composites fluctuate with different contents of B\textsubscript{4}C addition. Compared to the monolithic Si\textsubscript{3}N\textsubscript{4} ceramics, the composites prepared with 5wt\% B\textsubscript{4}C has higher bending strength of 144 MPa and higher Young's modulus of 54.5 GPa. These improvements mainly result from the decrease of porosity of the sample according to the well-known negative relationship between bending strength and porosity of porous material\cite{23}. Additionally, the generated BN and SiC grains may also benefit the mechanical properties of composites because of their pinning effects within the grain boundary. But the fracture toughness of composites does not show apparent increase. It could be ascribed to the introductions of BN and SiC grains, resulting in more lattice defects in Si\textsubscript{3}N\textsubscript{4} grains. The elongated Si\textsubscript{3}N\textsubscript{4} grains become new crack sources, which is unfavorable to the fracture toughness of composites. With the further increase of B\textsubscript{4}C content, the porosity of the obtained Si\textsubscript{3}N\textsubscript{4}-BN-SiC composites decreases continuously from 47.3\% to 37.7\%, but their mechanical properties, including bending strength, Young's modulus, and fracture toughness, degrade sharply. These behaviors indicate that the variation of microstructure is the predominated factor degrading the mechanical properties. On the one hand, the introduction of hollow spheres instead of elongated Si\textsubscript{3}N\textsubscript{4} grains presents lower mechanical properties than that of Si\textsubscript{3}N\textsubscript{4} ceramics with elongated morphology. On the other hand, the growth of Si\textsubscript{3}N\textsubscript{4} growth was restrained because of the introduction of B\textsubscript{4}C and the consequent generation of BN and SiC. Therefore, the degraded average aspect ratio is also a significant factor decreasing the mechanical properties of the Si\textsubscript{3}N\textsubscript{4}-BN-SiC composites according to the theory of crack deflection\cite{24}.

3 Conclusion

In this research, Si\textsubscript{3}N\textsubscript{4}-BN-SiC composites with hollow spherical microstructure were successfully fabricated by combustion synthesis. The microstructural evolution of the in-situ introduced BN/SiC and its impacts on the properties of the obtained Si\textsubscript{3}N\textsubscript{4}-BN-SiC composites were studied. As the B\textsubscript{4}C content increases, the reaction temperature decreases and the porosity of sintered sample decreases evidently. Besides, the nitridation of Si phase transition from α-Si\textsubscript{3}N\textsubscript{4} to β-Si\textsubscript{3}N\textsubscript{4}, and growth of β-Si\textsubscript{3}N\textsubscript{4} grains are suppressed with the introduction of B\textsubscript{4}C. Therefore, residual Si and α-Si\textsubscript{3}N\textsubscript{4} are detected for samples prepared with high B\textsubscript{4}C content. The bending strength and Young's modulus of the obtained Si\textsubscript{3}N\textsubscript{4}-BN-SiC composites increase firstly and then decrease with the B\textsubscript{4}C content increasing because of the decreasing porosity and degradation of microstructure. Optimal mechanical properties with bending strength of 144 MPa, fracture toughness of 2.3 MPa-m\textsuperscript{1/2}, and Young's modulus of 54.5 GPa are achieved when B\textsubscript{4}C content is 5wt\%.

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原位引入 BN-SiC 燃烧合成 Si₃N₄-BN-SiC 复合材料

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摘 要：Si₃N₄-BN-SiC 复合材料以其良好的力学性能和抗氧化性能而具有良好的工程应用前景。研究以 Si、Si₃N₄ 稀释剂、B₄C 和 Y₂O₃ 为原料, 采用燃烧合成法成功制备了 Si₃N₄-BN-SiC 复合材料。通过 Si、B₄C 和 N₂ 气之间的反应, 在 Si₃N₄ 陶瓷中原位引入 BN 和 SiC。制备的 Si₃N₄-BN-SiC 复合材料由长棒状的 β-Si₃N₄ 和空心球形复合材料组成。实验研究了空心球微结构的形成机理, 结果表明, 生成的 SiC、BN 颗粒及玻璃相覆盖在原料颗粒上, 当原料颗粒反应完全时, 形成空心球形微结构。进一步研究了 B₄C 含量对 Si₃N₄-BN-SiC 复合材料力学性能的影响。原位引入 SiC 和 BN 在一定程度上可以提高复合材料的力学性能。当 B₄C 添加量为 0~20wt% 时, 获得了抗弯强度为 28~144 MPa、断裂韧性为 0.6~2.3 MPa-m²/³, 该结果表明 Si₃N₄-BN-SiC 复合材料的力学性能。