Effect of Graphene on Microstructure and Mechanical Properties of Si₃N₄/SiC Ceramics

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Abstract

Graphene with 0.3% content was added to enhance the fracture toughness of Si₃N₄/SiC ceramics prepared by pressureless sintering. The microstructure, mechanical properties and toughening mechanism of ceramics were investigated. Results showed that the fracture strength significantly increased from 329.11 MPa to 443.19 MPa after adding graphene. The main toughening mechanism of ceramics was crack deflection since the existence of graphene platelets. The main phase compositions of samples were β-Si₃N₄ with a high aspect ratio and SiC located in the grain boundary, and the SiC particles could avoid the excessive growth of β-Si₃N₄ to reduce the strength.

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

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1. Introduction

Graphene, in recent years, has attracted considerable attention in the fields of physics, chemistry and materials due to its excellent properties. Graphene is a monolayer two-dimensional structure assembled by carbon atoms via sp² hybridized bonds, and it has high specific surface area, excellent mechanical and thermal properties.^[1-4] In addition, it also has distinctive electronic properties owing to the microscopic corrugations of surface.^[1] The fracture strength of single graphene sheets is 130 GPa, and the Young's modulus is 1 TPa, according to reports.^[4,5] Therefore, graphene is often used as the reinforced phase to improve the mechanical properties of materials such as polymers,^[6,7] metal matrix composites and ceramics. Khan *et al.*^[7] reported that both the Young's modulus and the stress at 3% strain increase exponentially with the mass fractions above 50 wt. %. There are many of studies have reported that metal-based materials reinforced by graphene were successfully prepared.^[4,8,9] Tian^[4] and Li *et al.*^[8] reported that the mechanical properties

including hardness, compressive, strength and yield strength are enhanced of aluminum matrix composites with the addition of low content graphene. It could be attributed to the homogeneous distribution of graphene in the matrix, the clean and strong interface between the Al matrix and graphene formed via metallurgical bonding.

Graphene is also widely used to toughen ceramic materials because the inherent drawbacks as brittleness of ceramics cannot be ignored.^[10-15] Kim^[10] and Fan^[11] *et al.* studied that fracture toughness and hardness were improved simultaneously by adding graphene nanosheet for the Al₂O₃ ceramics, besides, the dielectric properties were also improved. A few reports with Si₃N₄ have demonstrated that graphene platelets could significantly improve the mechanical properties.^[12-15] Based on microstructural observations of crack paths, connected matrix and protruding graphene were found, which proved that the toughening mechanisms were the crack deflection, crack bridging and pulling out of graphene.^[10-17] In addition, it was found that adding low-content graphene was beneficial to enhance the mechanical properties of composites (not only to ceramics) while the deterioration would be generated with the increase of content due to the agglomeration of graphene platelets.^[4,8,9,15] There are many of studies on pure ceramics strengthened by graphene, while multiphase ceramics are also inadequate. Si₃N₄-based ceramics are widely used as structural components at temperatures because of their high strength, relative chemical stability and corrosion resistance, but the toughness still needs to be improved.^[18-20] The effect of SiC

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Fig. 1 SEM images of raw materials: (a) Si_3N_4 ; (b) SiC .

nanoparticles in $\text{Si}_3\text{N}_4/\text{SiC}$ composite ceramics are to pin grain boundaries, refine grains and inhibit propagation of cracks,^[18,19,21] and rod-like $\beta\text{-Si}_3\text{N}_4$ strengthens ceramic by self-interlocking.^[2,15] This paper purposes to improve toughness by adding graphene. Spark plasma sintering (SPS) is always used to prepare the composites due to its faster heating rates, shorter sintering times, low-pressure and high-quality method.^[14,15,22] However, the $\beta\text{-Si}_3\text{N}_4$ grain growth will be eliminated because of lower temperature and shorter holding time.^[20]

Thus, in this paper, in order to analyze the influence of graphene on the mechanical properties, 0.3% graphene was added to prepare the $\text{Si}_3\text{N}_4/\text{SiC}$ composite ceramic using cold isostatic pressing and pressure less sintering at high temperature. And investigated the strength mechanism of $\text{Si}_3\text{N}_4/\text{SiC}$ ceramic by analyzing the phase composition and microstructure.

2. Materials and method

2.1 Sample Preparation

Si_3N_4 powders (α -phase 92 %, β -phase 8 %, Shanghai ST-Nano Technology Co., Ltd., Shanghai, China) and SiC powders (purity > 99.9 %, Shanghai ST-Nano Technology Co. Ltd., China) were used as starting powders, and the weight

ratio of Si_3N_4 and SiC is 95:5. As shown in Fig. 1, the average diameter of Si_3N_4 was 5 μm and the SiC was 2 μm , there were no obvious agglomeration for Si_3N_4 (Fig. 1(a)) and SiC particles (Fig. 1(b)), respectively. Graphene was added as additive, and two groups of samples were prepared with the content of 0% and 0.3% graphene, which were named SC and SCC, respectively. The micrograph of graphene was shown in Fig. 2, the graphene was a two-dimensional material composed of a single layer of carbon atoms with a transparent folded surface. The common out-of-plane distortion of graphene, wrinkling (Fig. 2 (a) and (b)) and rippling (Fig. 2 (c)), could be observed.

The mixtures were ball-milled in ethanol for 12 h, followed by drying for 15 h at 85 $^{\circ}\text{C}$, and then sieving through 250 mesh. The microtopography of mixtures for SC and SCG as illustrated in Fig. 3, the SiC and Si_3N_4 distributed evenly across the surface of graphene layers which was conducive to the formation of uniform body. Afterward, the green body was formed by the cold isostatic pressing method under 200 MPa for 2 min. Finally, under the nitrogen atmosphere, the composite ceramics were obtained by sintering at 1950 $^{\circ}\text{C}$ for 1.5 h without pressure.

Fig. 2 SEM and TEM images of graphene: (a) SEM; (b) Low- and (c) higher-magnification TEM images of graphene.

Fig. 3 SEM images of mixed powders: (a) SC without graphene; (b) SCG with graphene.

2.2 Characterization

Archimedes method was used to measure the densities (ρ) and apparent porosities (P) of samples. The flexural strength was determined via the three-point bending tests using electromechanical universal testing machine (CMT5150, China) on $3.0 \text{ mm} \times 4.0 \text{ mm} \times 36.0 \text{ mm}$ test specimens with 30.0 mm support distance and 0.5 mm/min crosshead speed. X-ray diffractometry (XRD, D8-ADVANCE, Bruker, Karlsruhe, Germany) analysis was used to identify the crystalline phases of raw materials and sintered samples in a 2θ range of 10° to 80° using Cu K α radiation. Scanning Electron Microscope (SEM, JSM-6510LV, JEOL, Tokyo, Japan) was used to observe the microstructure on the fracture surface of ceramics. In addition, the interfaces, particle morphology and composition information of the materials were further investigated by Transmission Electron Microscope (TEM, JEM-2100, JEOL, Tokyo, Japan).

3. Results and discussion

3.1 Densification and mechanical property

The density, porosity and flexural strength of samples were shown in Table 1. It was not difficult to see that both sample SC without admixture and SCG with graphene had high density after sintering, and the porosities of SC and SCG were less than 0.5 percent, which indicated that both samples were completely sintered. In the sintering process, the pores of samples move to the grain boundary gradually from the inside of the grain, and then discharge at the grain boundary, resulting in the densification of materials.^[23] As well known, it is usually accepted that the flexural strength of ceramics is inversely proportional to the porosity, and the higher the porosity, the lower the flexural strength.^[23-25] However, the flexural strength of material was significantly improved after adding graphene. As shown in Table 1, the porosity of sample SC and SCG was very similar, while the flexural strength of SCG (adding graphene), compared with SC, increase from 329.11 to 443.19 MPa, which indicated that adding graphene was conducive to significantly improve the mechanical property of composite ceramics. The strengthening mechanism would be explained from the microstructures and compositions in the next chapter.

Table 1. Mechanical properties of $\text{Si}_3\text{N}_4/\text{SiC}$ composite ceramics.

Samples	Additives	Density(ρ) (g/cm ³)	Porosity (P) (%)	Flexural strength (MPa)
SC		3.0485	0.4192	329.11
SCG	graphene	3.0012	0.4118	443.19

3.2 Phase composition and microstructure

The phase compositions of the matrix were $\beta\text{-Si}_3\text{N}_4$ and SiC as shown in Fig. 4 revealed by XRD analysis. Moreover, the $\alpha\text{-Si}_3\text{N}_4$ crystal phase was not be observed indicating that the $\alpha\text{-}\beta$ phase transformation was complete for two samples at high temperature. It was not observed the characteristic peaks of graphene for sample SCG, although graphene was added in the experiment. Perhaps the 0.3% content of graphene was so small that it is not detected.

Fig. 4 XRD diagram of $\text{Si}_3\text{N}_4/\text{SiC}$ composites.

Fig. 5 shows the microstructure of the flexural fractured surfaces of the $\text{Si}_3\text{N}_4/\text{SiC}$ ceramics. The surfaces of samples SC and SCC were very dense, but the surface appearance showed very difference as shown in Fig.5 (a) and (c). At high-

Fig. 5 SEM micrographs of the fractured surfaces of SC((a), (b)) and SCG ((c), (d)).

resolution, there were many pores and bumpy like gully with disordered distribution on the surface of SC as shown in Fig. 5 (b). The morphology is mainly due to grain pullout and intergranular fracture of the rod-like β - Si_3N_4 particles (represented by arrows) during the fracture process, which is also reflect the main fracture mechanisms. However, after adding graphene, the surface of SCG exhibited the layered structure with a directionality. From Fig. 5 (d), the fracture occurred mainly at the interface between graphene and ceramics matrix, the graphene platelets were embedded in the matrix. This phenomenon of graphene sheets being pulled out along the interface during fracture may be the main reason for the enhancement of SCG strength.

TEM was used on sample SCG to fully analyze the crystal phase composition and structure of samples. The structure of SCG was compact, and there are a large number of β - Si_3N_4 grains (proved by the interfacial spacing value (Fig. 6 (b)) was 0.62 nm) with high aspect ratio that contacted closely with glass phases. The structure of β - Si_3N_4 is beneficial for the improve of strength due to its self-toughening effects such as pull-out and elastic bridging, while the size is too large can reduce the strength of ceramics.^[2,15,26] Fukasawa, *et.al.* studied the grain will be enhanced with the increase of sintering temperature.^[27] In this paper, $\text{Si}_3\text{N}_4/\text{SiC}$ ceramics were prepared with high sintering temperature, the SiC particles with irregular shape were observed in the grain boundary, which has an inhibitory effect on the secondary recrystallization of Si_3N_4 grains to avoid the overgrowth of grains as reported.^[20] In Fig. 6 (a), it also appeared that graphene was embedded in the matrix, which was consistent with the described before in Fig. 5 (d). The role of graphene and SiC would be described detailly in the next chapter.

3.3 Strengthening mechanisms

Fig. 7 was the schematic graphics of phases compositions. For sample SC (Fig. 7(a)), the SiC grains were mainly located at the junction of Si_3N_4 grain phases to pin grain boundaries. Studies show that the crack energy will be reduced when the crack tip touched the SiC hard particles, and then the crack stop propagating, or the crack deflection occurs.^[18-21,28] On the other hand, SiC could inhibit the overgrowth of β - Si_3N_4 grains to reduce the appearance of large grains and get the β - Si_3N_4 with high aspect ratio in the matrix. That made the microstructure more uniform and conducd to improve the strength of matrix by self-strengthen mechanism as mentioned before. As shown in Fig. 7(b), for sample SCG, the graphene sheets became in contact with multiple particles because of its high specific surface area and formed strong bonding

Fig. 6 TEM picture of the sample SCG: (a) TEM images; (b) HRTEM images.

Fig. 7 Schematic graphics of phase composition in $\text{Si}_3\text{N}_4/\text{SiC}$ ceramics: (a) SC; (b) SCG.

interfaces with $\beta\text{-Si}_3\text{N}_4$. It also could be found in SEM and TEM. When external force acts on the body, the crack will extend within the matrix and produce crack branching during this progress. Then, with the crack tips reach the interface between graphene and the matrix, the crack will deflect and extend along with the interface due to the excellent strength of graphene. Therefore, the material had to overcome stronger friction in this process to break up, and finally the graphene which perpendicular to the plane of the fracture surface was pulled out and tucked and wrapped around matrix grains, which explained why the surface showed the layer structure. Hence the main toughening mechanisms of SCG include crack branching and crack deflection caused by graphene besides those discussed in the SC above, which similar with that reported by Kvetkova and Walker *et al.*^[2,13,16] This also explained why the flexural strength of SCG, compared with SC, was significantly improved after adding graphene.

4. Conclusions

The influences of graphene on the mechanical and microstructure of $\text{Si}_3\text{N}_4/\text{SiC}$ composite ceramics were investigated. The results showed that the fracture strength of SCC whose porosity was similar to SC can be improved significantly after adding graphene with the value increase from 329.11 to 443.19 MPa. The main crystal phases of ceramics were $\beta\text{-Si}_3\text{N}_4$ and SiC, the graphene was not detected through XRD since the low content of graphene in the sample SCC. The main toughening mechanisms of SC were grain pullout and intergranular fracture caused by $\beta\text{-Si}_3\text{N}_4$, while after adding graphene, the main mechanism of SCC was crack deflection at graphene interface with the matrix. Besides, the SiC particles located in the grain boundary could avoid adverse effects on the strength due to the oversize $\beta\text{-Si}_3\text{N}_4$ grains. The influences of graphene content on mechanical properties were not been discussed, which is our following work.

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Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable

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