Preparation and Mechanical Property of Short Carbon Fiber Reinforced Silicon Carbide Matrix Composites

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Abstract: In this study, high-strength silicon carbide (SiC) matrix composites reinforced by short carbon fiber (Csf) (SiC/Csf) were fabricated by slip casting and reaction sintering. The effects of the dispersant (tetramethylammonium hydroxide, TMAH) content and mixing time on the viscosity of the slurry were investigated. In addition, the influences of the volume fraction of Csf and particle size of SiC powder on the mechanical property were also studied. It is found that the viscosity of slurry with 0.1wt% TMAH is the lowest and the mixing time is preferably controlled at 6 h. The composites with 35vol% Csf shows the highest flexural strength of (412±47) MPa. The composites with 5μm SiC powder achieves the highest flexural strength of (387±40) MPa. Grain composition demonstrates that the sample prepared by a mixture of 5 and 50μm SiC powder at a ratio of 2 to 1 shows relatively excellent mechanical properties with the flexural strength up to (357±41) MPa.

Key words: Csf/SiC composites; slip casting; reaction sintering

SiC ceramics have excellent properties such as high strength, high hardness and wear resistance, leading to lots of researches on its preparation methods and properties in recent years[1-3]. As reported by previous literature, the flexural strength of the SiC ceramics prepared by Suyama using the reaction sintering method has exceeded 1000 MPa[4]. However, the inherently high brittleness and large density (3.20 g/cm3) of SiC ceramics limit its application in many fields, including aerospace that requires high-strength and lightweighted structure design. Therefore, high-strength fiber was introduced into SiC ceramics to prepare high-strength, high-fracture, low-density SiC matrix composites[5-8].

Currently, carbon fiber, carbon nanotube, SiC fiber, and the like are generally used as the reinforcing phase. For example, Zhu, et al[9] introduced SiC fiber into 2.5D fiber preforms and prepared SiC matrix composites by polymer impregnation and pyrolysis. The mechanical properties were excellent and the flexural strength could reach 441 MPa. Gbadeyan, et al[10] reported that multi-walled carbon nanotube and chopped carbon fiber were combined to enhance composites, demonstrating that the uniform dispersion and synergy of carbon fiber and multi-walled carbon nanotubes enabled a more stable structure. However, the costly SiC fiber and carbon nanotube mentioned in the above literatures give a restriction on the practical application. Therefore, many researchers use cheaper carbon fiber as the reinforced phase of SiC matrix ceramics.

Chen, et al[11] reported long carbon fiber reinforced SiC matrix composites prepared by chemical vapor infiltration had superior performances and the flexural strength can reach (375±10) MPa. Later further improvement has been made by growing SiC nanowires in situ in the SiC matrix, which greatly enhanced the mechanical properties of the composites reinforced by longer carbon fiber. However, relatively obvious orientation was observed in long carbon fiber reinforced composites due to the special manufacturing process of the green body, resulting in certain limitations in practical applications. Therefore, it is considered to use short carbon fiber (Csf) as reinforcement to obtain a uniform and isotropic SiC matrix composites (Csf/SiC composites)[12-16].

The Csf used in SiC matrix composites in the above literatures are relatively long and difficult to disperse homogeneously in SiC matrix, which goes against the isotropy and uniformity of the composites. The shape of the composites obtained by the common sintering methods is simple, such as hot press sintering and spark plasma sintering, which makes the subsequent processing
more difficult and further tends to introduce defects into the material during the processing. Moreover, carbon fiber is easily oxidized under the high temperature required in sintering. Therefore, this study proposes to introduce micron-sized Csf as reinforcing phase into the SiC ceramic by slip casting and reaction sintering to obtain SiC composites with high performance and complex shape under low temperature. The effects and mechanism of volume fraction and size of SiC particles on the properties of composites were investigated in order to highly improve the performance of Csf/SiC composites.

1 Experiment

1.1 Materials
The Csf used in the experiment is 400-mesh (37 µm) chopped fiber (12KT300, Yancheng Xiangsheng Carbon Fiber Co., Ltd.). The specification of short carbon fiber is about Φ7 µm×50 µm, and the basic properties are shown in Table 1. The α-SiC powders with different diameters (5, 10, 20 and 50 µm) are produced by Shanghai Shangma Abrasives Co., Ltd. Tetramethylammonium hydroxide (TMAH, 25% aqueous solution, Shanghai Aladdin Biochemical Technology Co., Ltd.) acts as dispersant. Polyvinylpyrrolidone (PVP, model K29-32, molecular weight 58000, Admas company) and polyvinyl alcohol (PVA, molecular weight 44.05, 1788 low viscosity, Shanghai Aladdin Biochemical Technology Co., Ltd.) are used as binder. The silicon powder used in the reaction sintering process is of high purity.

1.2 Preparation of composites
The SiC powder and the Csf were mixed with various additives in a certain ratio by planetary ball miller with deionized water and SiC balls as the mixing medium. The mixed slurry was injected into the prepared mold after vacuum degassing, and the green body was dried and molded at room temperature with the water absorbed by the gypsum board. After 24 h, the obtained green body was released from the mold followed by completely drying at 40 °C. Then the green body was kept at 900 °C for 30 min to remove the organics. The debonded green body was embedded in silicon powder and sintered at 1650 °C. The prepared sample was obtained followed by post-processing and performance testing.

1.3 Performance characterization
The bulk density and porosity of the composites were tested by the Archimedes Drainage Method. The microstructure of the composites was observed using a scanning electron microscope from Feiner. The rheological properties of freshly prepared slurry were tested on a rotary rheometer (MCR 72, Anton Paar, Austria). The flexural strength was measured on a universal testing machine (Instron-5566, UK) using a three-point bending method with the sample size of 3 mm×4 mm×36 mm, the span of 30 mm, and loading rate of 0.5 mm/min. Each set of data was tested by 5 sample strips.

2 Results and discussion

2.1 Factors affecting the rheology of the slurry
The viscosity of the slurry has a significant influence on the dispersibility of the raw material, the yield of the slurry, the efficiency of the injection molding, and the molding effect of the green body. In this experiment, tetramethylammonium hydroxide (TMAH) was used as the dispersant, and the influence of TMAH content and mixing time on the viscosity of the slurry was studied.

As shown in Fig. 1, the viscosity of the slurry with 0.1wt% TMAH is the lowest and the viscosity tends to increase with TMAH content. Since TMAH is a strongly basic cationic inorganic electrolyte, an ionization reaction occurs when TMAH is added in an aqueous solution. The charged dispersant adsorbed on the surface of the powder enhances the electrostatic repulsion between the particles, improving the dispersion stability of the powder and reducing the viscosity of the slurry according to the electrostatic stabilization mechanism. Excessive dispersant increases the ion concentration in the slurry and lowers thickness of the double electron layer on surface of the particle, thereby increasing viscosity of the slurry.
The apparent porosity and bulk density of the C_{sf}/SiC green body with different TMAH are demonstrated in Fig. 2. The composites with 0.1wt% TMAH has the lowest apparent porosity and the highest bulk density. Fig. 3 is the SEM images of the composites with different contents of TMAH. Considering the relatively more uniform and disordered dispersion of C_{sf} and SiC particles in samples with 0.1wt% and 0.3wt% TMAH than that with 0.05wt%, it is concluded that higher TMAH content is helpful to homogeneous microstructure and isotropic behaviors. However, excessive TMAH (0.5wt% in this work) results in higher viscosity, going against the uniform dispersion of C_{sf} and SiC.

The rheological properties of the slurry have a crucial influence on the injection molding, and the lower slurry viscosity contributes to the process of grouting. Table 2 is the formula table to study the effect of the mixing time on the composites.

It can be seen from Fig. 4 that the viscosity of the slurry changes significantly with the mixing time. Longer mixing time helps to lower the viscosity of the slurry. But excessively long mixing time will result in more fragmented carbon fiber under the impact of SiC powder, which will weaken the enhancement of the reinforcing phase. What’s more, batching feeding under the same mixing time can slightly reduce the viscosity of the slurry because the slurry mixed in batches is more uniform.

Fig. 5 shows the relationship between the apparent porosity and the bulk density of slurries with different mixing times and feeding mode. It can be obtained that as the mixing time increases, the apparent porosity decreases gradually. On the one hand, the SiC particles in the slurry collide with each other, resulting in smaller SiC particles filling the voids. On the other hand, the generated C_{sf} debris by the collision of SiC particles also serves to reduce the porosity. Considering the largest bulk density of the green body, mixing time of 6 h should be adopted to obtain a slurry with low viscosity and good performance, which is favorable for the slurry forming and reaction sintering.

### 2.2 Effect of C_{sf} volume fraction on the properties of composites

In order to explore the effect of different volume content of C_{sf} on the performance of composites, three compositions were designed: 30vol%, 35vol%, and 40vol%, respectively. In this part, 5 μm SiC powders were mixed with C_{sf} to prepare the composites. In addition, other same components are listed as follows: 0.3wt% aqueous solution of TMAH, 2wt% PVP, and 0.6wt% PVA solution. As shown in Table 3, with C_{sf}
increasing, the bulk density of the green body decreases, mainly resulting from that the density of the Csf (1.76-1.80 g/cm$^3$) is lower than that of SiC (3.20 g/cm$^3$). Furthermore, the increase of Csf content leads to a significant "bridging" of the fibers, which brings about a larger sample porosity. The bulk density of the green body containing more Csf is relatively larger under the condition of constant solid content.

Fig. 6 gives the flexural strengths of the prepared Csf/SiC composites with different content of Csf. It can be concluded that the composites with 35vol% Csf shows the largest flexural strength, namely (412±47) MPa. However, with the further increase of Csf (40vol%), the flexural strength of Csf/SiC composites decreases. It is considered that the excessive Csf reduces the packing coefficient of SiC particles and larger pores are generated in the green body during slip casting, which in turn causes a large amount of molten silicon to fill the excess pores during sintering. The increase in the brittle free silicon content weakens the flexural strength of the composites.

Table 3  Physical and mechanical properties of composites with different short carbon fiber contents

| Volume Fraction/% | Green body Apparent porosity/% (g·cm$^{-3}$) | Sintered bulk Apparent porosity/% (g·cm$^{-3}$) |
|-------------------|---------------------------------------------|---------------------------------------------|
| 30                | (46.09±0.25) (1.26±0.01) (1.17±0.26) (3.06±0.02) |
| 35                | (47.14±0.46) (1.19±0.01) (0.38±0.12) (3.08±0.007) |
| 40                | (45.08±1.20) (1.16±0.03) (1.17±0.23) (3.01±0.01) |

Fig. 6 Variation of flexural strength of composites as a function of the carbon fiber volume fraction

2.3 Effect of SiC particle size and particle size matching on the properties of composites

In order to explore the effect of SiC particle size on the properties of composites, SiC powders with different particle sizes (5, 10, 20 and 50 μm, the mass ratio of two kinds of SiC powder was 2 : 1) were mixed with Csf. In addition, the solid content of the slurry was 70wt% and the volume fraction of Csf was 35vol%, wherein 0.3wt% TMAH aqueous solution and 2wt% PVP were added. The apparent porosity and bulk density of the Csf/SiC composites are shown in Table 4.

It can be seen from Table 4 that as the particle size of SiC increases, the apparent porosity of the green body gradually decreases, but the apparent porosity of the sample increases. The Csf/SiC composites prepared from 5 μm SiC fine powder has an low apparent porosity of 0.95%. The bulk density of the green body gradually increases, and the bulk density after sintering is similar.

Fig. 7 indicates the flexural strength of composites with different particle sizes after reaction sintering. It can be seen from the figure that the flexural strength of Csf/SiC composites prepared from 5 μm SiC powder is the largest, which is (387±40) MPa. As shown in Fig. 8, it is concluded that all the Csf/SiC composites contain certain residual silicon, and the material defects (as indicated by the arrows) are found in Csf/SiC composites prepared by 50 μm SiC powder. Microcracks will develope when materials are under stress, whose causes severe performance degradation. It can be seen from Fig. 8 that the residual silicon in Csf/SiC composites prepared by 5 μm SiC powder is the smallest one among those four composites. Considering that microcracks tend to propagate in the location of silicon whose strength is lower than that of SiC, smaller silicon will effectively hinder the development trend of microcracks, helping to withstand the destruction. It is consistent with the theory mentioned in the literature\cite{4} that the smaller size of the residual silicon leads to the greater flexural strength of the composites.
Table 4  The bulk density and apparent porosity of green body and the sintered bulk containing SiC with different particle sizes

| Particle size/µm | Green body | Sintered bulk |
|------------------|------------|---------------|
|                  | Apparent porosity/% | Bulk density/(g·cm⁻³) | Apparent porosity/% | Bulk density/(g·cm⁻³) |
| 5                | (44.61±0.49) | (1.26±0.01) | (0.95±0.62) | (3.01±0.02) |
| 10               | (43.88±1.05) | (1.28±0.02) | (1.10±0.48) | (2.99±0.02) |
| 20               | (42.29±2.30) | (1.32±0.06) | (2.03±1.13) | (2.96±0.04) |
| 50               | (40.46±0.07) | (1.35±0.004) | (2.20±1.72) | (2.99±0.07) |

In the slurries, the raw material particles spatially influence each other, and the mechanism is complicated in which the spherical SiC particles and the elongated Csf interact with each other. Therefore, in order to explore the effect of the size of SiC particles on the performance, the composites with different grain compositions were prepared.

Table 5  Bulk density and apparent porosity of green body and sintered bulk with different grain compositions

| Particle size/µm | Green body | Sintered bulk |
|------------------|------------|---------------|
|                  | Apparent porosity/% | Bulk density/(g·cm⁻³) | Apparent porosity/% | Bulk density/(g·cm⁻³) |
| 50/10            | (42.73±1.48) | (1.35±0.07) | (0.79±0.11) | (3.04±0.03) |
| 10/5             | (44.37±0.21) | (1.27±0.004) | (0.72±0.10) | (3.05±0.01) |
| 20/5             | (43.46±0.66) | (1.28±0.01) | (1.05±0.18) | (3.06±0.01) |
| 50:5             | (41.88±0.78) | (1.34±0.02) | (0.86±0.26) | (3.04±0.02) |

Fig. 7  Flexural strength of Csf/SiC composites containing SiC with different particle sizes

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Fig. 8  SEM image of sintered composites containing SiC with different particle sizes: (a) 5 µm; (b) 10 µm; (c) 20 µm; (d) 50 µm

Table 5 shows the bulk density and apparent porosity of the composites with different grain compositions. From the table, it can be seen that as the particle size of the SiC powder in the green body increases, the apparent porosity in the green body slightly decreases, and the bulk density of the green body tends to increase. The apparent porosity of the composites after the reaction sintering is relatively low.

Fig. 9  Flexural strength of composites with different grain compositions

The composites with 5 and 50 µm SiC powders demonstrate the highest flexural strength, reaching (357±41) MPa. It can be concluded that in the conducted experiments, the 5 µm SiC powders filled into the slurry containing 50 µm SiC powders and Csf, can significantly increase the bulk density of SiC and the space occupancy rate, promoting the penetration of molten silicon. What's more, it also helps to reduce the content and the size of residual silicon to improve the performance of the Csf/SiC composites.

3  Conclusions

1) The content of TMAH and the mixing time of the slurry have great influence on the rheological property of the slurry. 0.1wt% of TMAH helps to make the slurry with the lowest viscosity. The right rheological properties of the slurry are obtained, and the damage of carbon fiber can be avoided greatly when the raw materials are mixed for 6 h.
2) When the volume fraction of C_{sf} is 35vol%, the flexural strength of the prepared C_{sf}/SiC composites can reach (412±47) MPa. When the volume fraction of C_{sf} is too high, the packing coefficient of SiC particles reduces with porosity increasing, resulting in a higher content of free silicon and weakened performance of the composite material.

3) The residual silicon in the composites prepared by the 5 µm SiC particles has small size, and the performance reaches (387±40) MPa. After the SiC particles of different particle diameters grading, it is found that the composite material with 5 and 50 µm SiC powder exhibits more excellent performance.

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