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Ceramics International 32 (2006) 929–934

CERAMICS
INTERNATIONAL

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Effect of sintering additives on microstructures and mechanical properties of short-carbon-fiber-reinforced SiC composites prepared by precursor pyrolysis–hot pressing

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Received 26 January 2005; received in revised form 13 May 2005; accepted 22 July 2005

Abstract

Short-carbon-fiber-reinforced SiC composites were prepared by precursor pyrolysis–hot pressing with $MgO–Al_2O_3–Y_2O_3$ as sintering additives. The effects of the amount of sintering additives on microstructure and mechanical properties of the composites were investigated. The results showed that the composites could be densified at a relatively low temperature of 1800 °C via the liquid-phase sintering mechanism and the composite density and mechanical properties improved with the amount of additives. The amorphous interphase in the composites with more additive content, not only avoided the direct contact of the fibers with matrix, but also improved the fiber–matrix bonding. It proved that the fiber–matrix interphase characteristics played a key role in controlling mechanical properties of the composites.

Keywords: Short-carbon-fiber-reinforced SiC composite; Sintering additives; Microstructures; C. Mechanical properties

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1. Introduction

Silicon carbide (SiC) has been accepted to have considerable potential as an engineering material on the basis of its high temperature strength, stiffness, oxidation resistance, and low density. Over the past years, various kinds of SiC-based composites including particulate-, whisker- and fiber-reinforced SiC composites have been studied extensively [1,2]. Much attention has been focused on continuous fiber-reinforced ceramic matrix. These composites were fabricated by chemical vapor infiltration (CVI), polymer infiltration and pyrolysis (PIP), melt infiltration (MI) and hot-pressing (HP) methods. However, CVI requires only limited handling but it is often time-consuming and the cost of equipment is typically high. The PIP process is also lengthy and requires multiple infiltration stages. The MI has been developed, but it is not efficient in penetrating the fiber tows of dense weaves with matrix materials. Finally, HP technique is fast but it will degrade the fiber reinforcement through treatment at high temperature and pressure [3–9].

Short-fiber-reinforced composites will increasingly be used in a wide range of applications because of their easy adaptability to conventional manufacturing techniques and then low cost of fabrication [10]. The increasing number of applications of short-fiber-reinforced composites makes it more important to understand their mechanical properties, which depend strongly on the interfacial bonding between fiber and matrix. It has been documented that, weak fiber–matrix interfacial bonding in a brittle matrix composite facilitates toughening mechanism, such as interfacial debonding, for fiber pullout to operate. In contrast, a strong interfacial bonding tends to allow a crack to propagate straightly through the fibers, resulting in low fracture toughness [11].

Polycarbosilane (PCS) had been widely used as a precursor polymer for SiC fibers and fiber-reinforced composites. The use of precursor pyrolysis followed by hot press sintering is one of the best techniques to obtain

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doi:10.1016/j.ceramint.2005.07.007

dense ceramic matrix composites. The reaction of Al_2O_3 and Y_2O_3 with the SiO_2 of the pyrolysis products from PCS was responsible for the formation of the liquid phase, which was distributed to the grain boundaries and the fiber–matrix interphase mainly in an amorphous form after sintering. So the degradation of the carbon fibers, which was caused by high sintering temperature, could be avoided [12,13].

In the present work, short-carbon-fiber-reinforced SiC composites with $MgO–Al_2O_3–Y_2O_3$ as sintering additives were prepared by precursor pyrolysis–hot pressing. The effects of amount of sintering additives on microstructures and mechanical properties of the composites were investigated.

2. Experimental procedure

2.1. Fabrication of composites

The average tensile strength and density of the carbon fiber used in this study (Model TX-3, PAN-precursor, Elastic modulus = 220 GPa, Jilin Carbon Group Company LTD. China) were 3.84 GPa and 1.76 g/cm^3, respectively. Polycarbosilane (PCS) (National University of Defense Technology, Changsha, China) was selected as the precursor, whose mean molecular weight and melting point were 1375 and 215–236 °C, respectively. Commercially available β-SiC was used as the starting powder, with an average particle size of ~0.8 μm. MgO, Al_2O_3 and Y_2O_3 were chosen as the sintering additives and a standard additive composition of 67:16:17 mol.% $MgO:Al_2O_3:Y_2O_3$ was used throughout. The carbon fiber volume fraction of the composites was estimated to be about 20 vol.%. The compositions of materials are shown in Table 1.

The starting powder for the matrix components was prepared by ball-milling of a submicron β-SiC powder, PCS and various kinds of sintering additives with a dispersing agent for 24 h in absolute ethanol using ZrO_2 balls. The short carbon fibers (4–6 mm) were dispersed for 0.5 h in absolute ethanol by ultrasonic waves, then the SiC–PCS additives solution was added to the suspension of fibers. This suspension was further dispersed for 0.5 h by ultrasonic waves to obtain the final slurry. After drying, the prepared green sheets were prepressed into compacts in a graphite die. Finally, the green compacts were hot pressed at 1800 °C under a pressure of 20 MPa in Ar atmosphere (0.5 atm) for 1 h.

Table 1
Compositions of materials

Samples	Additives (wt.%)	PCS (wt.%)
SO5P20	5	20
SO8P20	8	20
SO11P20	11	20
SO14P20	14	20

2.2. Characterization of composites

The bulk densities of the samples were measured according to Archimede's principle with deionized water as the immersion medium. The flexural strength was determined using a three-point bending test on 3 mm × 4 mm × 36 mm bar with a span of 30 mm and a crosshead speed of 0.5 mm/min. For fracture toughness, single-edge notched beam (SENB) test was used with a crosshead speed of 0.05 mm/min and a span of 16 mm. The samples were 2 mm × 4 mm × 20 mm with the notch depth to samples thickness of ~0.25 mm. For all the tests, five or six specimens were tested for each batch of composites.

Characterization of the microstructure was performed by transmission electron microscopy (TEM). The fracture surfaces of the samples were observed by scanning electron microscopy (SEM). The phases contained in the samples were identified by X-ray diffractometry (XRD) with Cu Kα radiation.

3. Results and discussion

3.1. XRD patterns of the composites

XRD patterns of the composites are shown in Fig. 1. α-SiC and YAG ($Y_3Al_5O_{12}$) were seen in the XRD results. It shows that the starting powder β-SiC might have undergone a phase transformation from β to α. The α-SiC crystals were needle-like and could play a role of reinforcing agents similar to that of whiskers.

From the presence of YAG in the composite, it could be concluded that the sintering mechanism in the composites is the liquid-phase sintering. YAG has a melting point of about 1760 °C and it also can improve sinterability and interfacial strength between fiber and matrix [14]. The reason for the

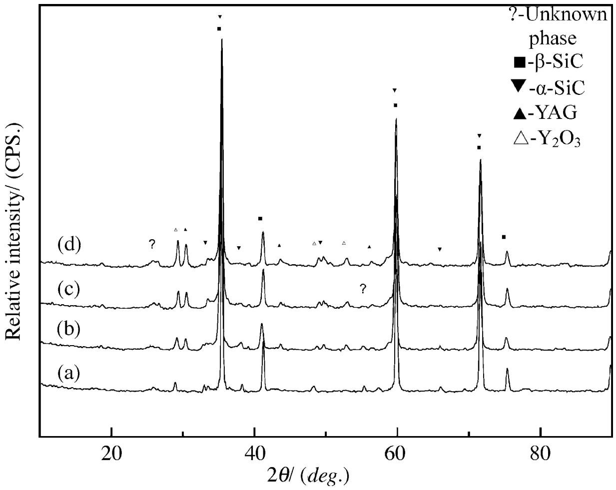

Fig. 1. XRD patterns of C_f/SiC composites: (a) SO5P20; (b) SO8P20; (c) SO11P20; and (d) SO14P20.

increasing amount of YAG with additives in this study is the form alien to a more liquid phase.

The amount of residual Y_2O_3 in the composites also increased with increasing additives. One reason might be that there was no action between Y_2O_3 and SiC below 2000 °C, the other reason was the amount of Al_2O_3 was about equal to that of Y_2O_3.

3.2. Microstructures of composites

Because the β-SiC powder was mainly added to the materials, the matrix could be observed to be mainly composed of the β-SiC through TEM analysis. From the XRD patterns of the composites, the starting powder β-SiC might have undergone a phase transformation from β to α. As the SiC has many polymorphic modifications and the diffraction peak of the different crystal system is seriously overlapped, it is very difficult for us to distinguish different polymorphic modification though the XRD analysis. A small quantity of α-SiC was found in the materials in the process of the TEM test. The orientation of the fault is only one in the hexagon SiC crystal grain, and the fault orientation is more in the cubic. The TEM image and diffraction pattern of the 6H-SiC are shown in Fig. 2.

Typical microstructures of the composites with different additives are represented in Fig. 3. It can be concluded that several types of interphases were identified in the composites. One was the direct contact between the fiber and matrix (Fig. 3a). This kind of interphase was so much present in the SO5P20 composite with little additive that the fiber–matrix interfacial bonding was strong and the mechanical properties were lower than other composites with more additives. In addition, there were some voids in the SO5P20 composite, which led to the poor densification. It is apparent that the amount of additives of the SO5P20 composite was insufficient for compact densification.

The second was the amorphous interphase between the fiber and matrix in the composites with more additives (Fig. 3b). The width of amorphous interphase is about 60–70 nm. Its SAD-pattern and EDS-pattern are given in Fig. 4. It can be evidenced from the SAD-pattern that the interphase

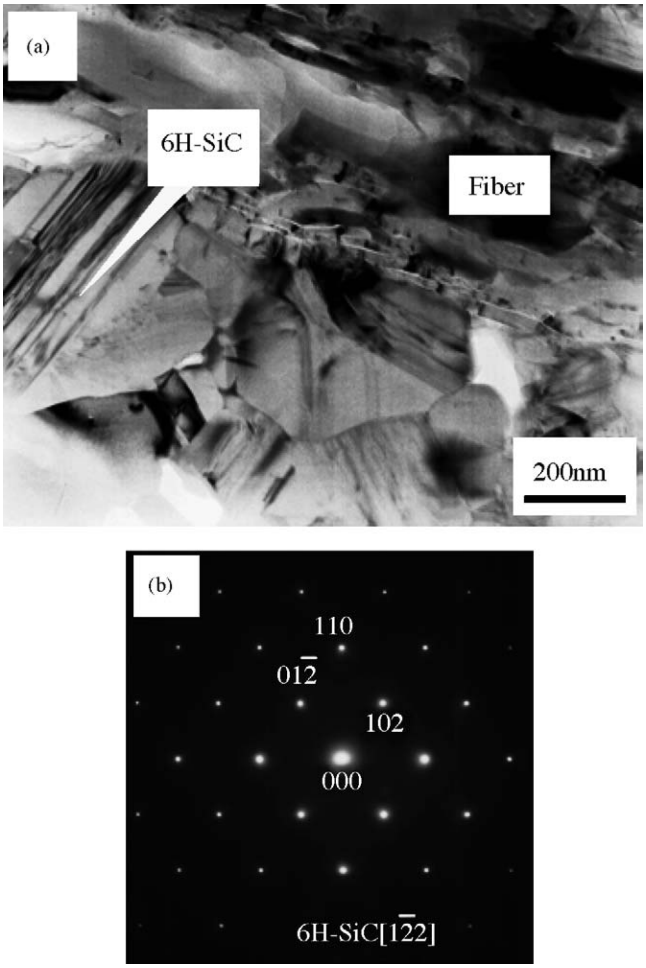

Fig. 2. (a) TEM image of 6H-SiC of SO8P20. (b) Diffraction pattern of 6H-SiC.

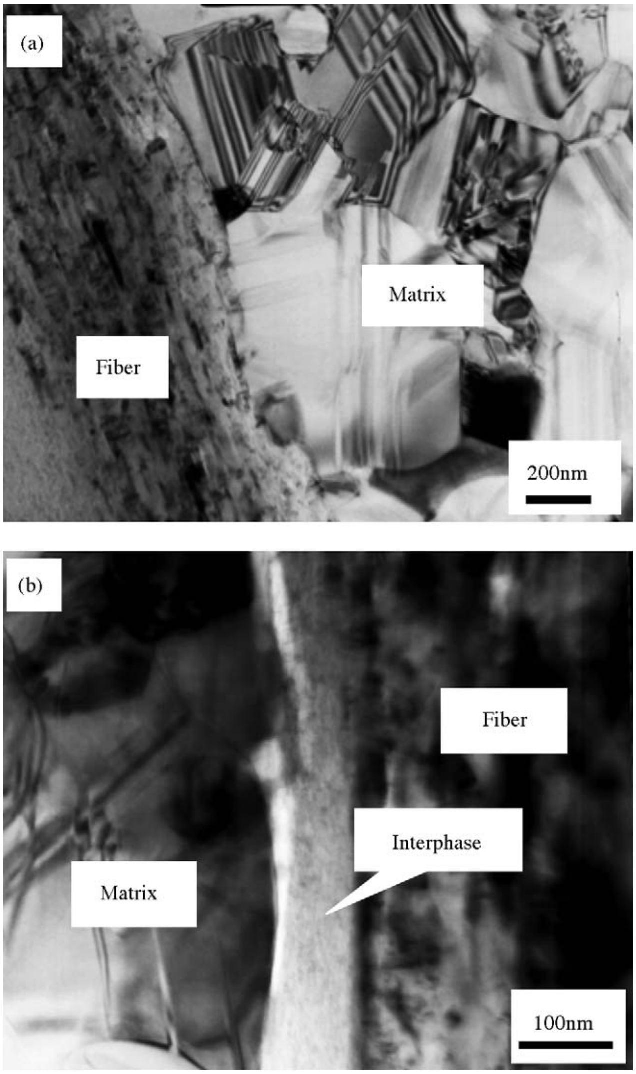

Fig. 3. TEM images of the C_f/SiC composites with different content of additives: (a) SO5P20 and (b) SO14P20.

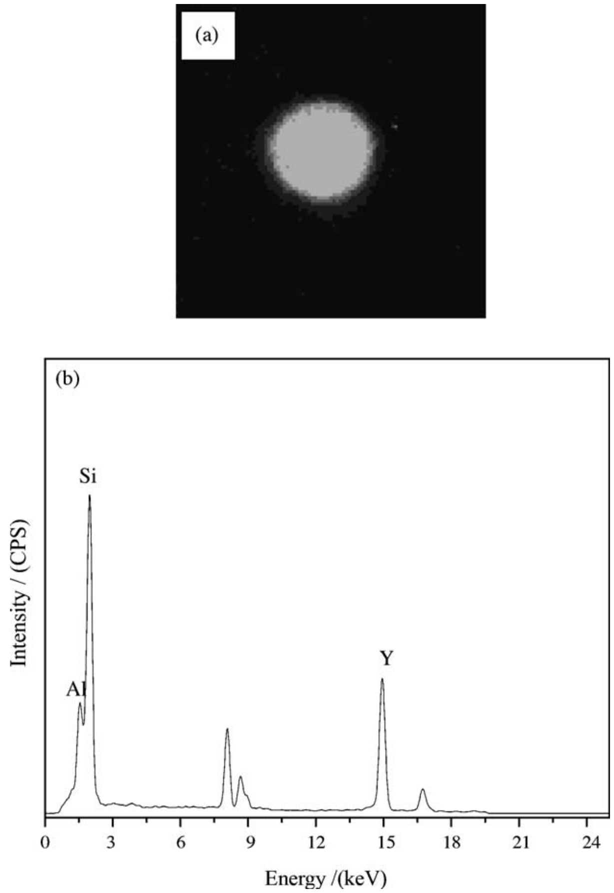

Fig. 4. (a) SAD-pattern of the interphase of SO14P20. (b) EDS-pattern of the interphase of SO14P20.

was amorphous. The EDS characterization showed that the amorphous interphase consisted Y and Al elements. It is proposed that in the composites sintered at temperature above 1750 °C, the reaction of Y_2O_3, Al_2O_3 with the pyrolysis products from the PCS and the oxides on the SiC grains is responsible for the formation a liquid phase, distributed at the fiber–matrix interphase mainly in an amorphous form after sintering [15]. It is well known that the fiber–matrix interfacial characteristics play a critical role in controlling the fracture properties of the composites [16]. This kind of interphase not only avoided the direct contact of the fibers with matrix but also improved the fiber–matrix bonding and realized the pullout function of carbon fiber. So it could be concluded that the composites with more liquid phase and interphase exhibited easier densification and higher mechanical properties.

The third is the interphase between the starting β-SiC powder and PCS-derived SiC. The average grain size of PCS-derived SiC was as small as about 200 nm. It was reported that pyrolysis of PCS at 1000 °C yields an amorphous powder, and crystallization begins above 1200 °C. Very fine crystals of β-SiC of about 100–200 nm in diameter are obtained [17]. In this study those nanocrystals PCS-derived SiC almost lay on the surface of the particles of starting powder β-SiC, so they could play a role of filling up the void and improve the relative density of the composites.

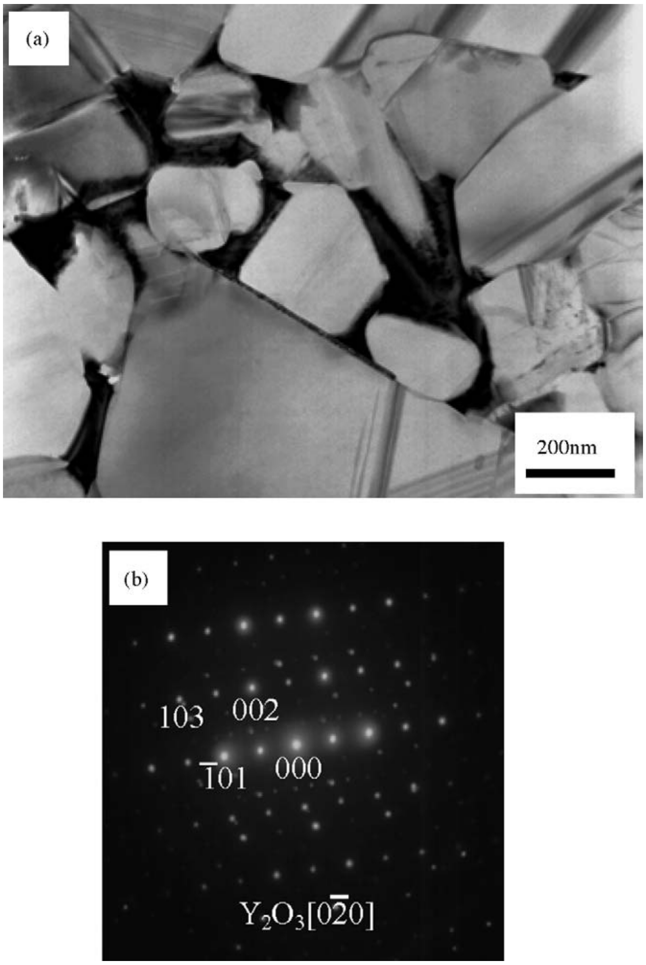

Fig. 5. (a) TEM image of the interphase of SO14P20. (b) Diffraction pattern of Y_2O_3.

In addition, the remaining Y_2O_3 almost lay on the surface of the particles of PCS-derived SiC nanocrystals. As shown in Fig. 5a, the Y_2O_3 phase is black. The diffraction pattern of the Y_2O_3 is shown in Fig. 5b. Based on the TEM analysis, it was apparent that this segregation phenomenon of Y_2O_3 was common in the composites with more additives. This probably had influence on the mechanical properties of the composites.

From these results it is clear that suitable amount of additive is necessary for the better control of fiber–matrix interphase and to improve mechanical properties of the composites.

3.3. Mechanical properties of composites

The mechanical properties of the composites are given in Fig. 6. It was reported that bending strength of polycarbosilane-added SiC fabricated by hot pressing was higher than that of SiC ceramic without polycarbosilane, where the former had much finer grain size than the latter

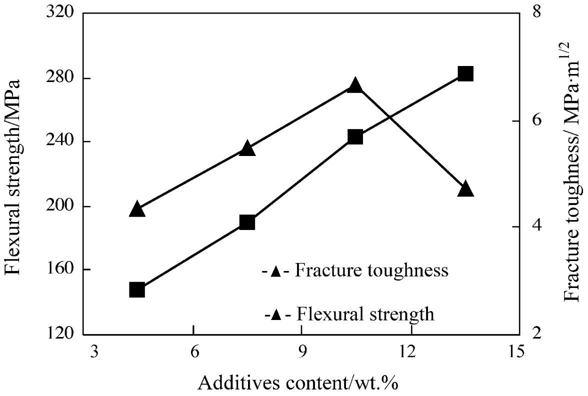

Fig. 6. Flexural strength and fracture toughness as a function of sintering additives content.

[18]. The reason for the lower strength of the composite obtained in this study may be attributed to the carbon fibers which were not well distributed.

The SO5P20 composite was observed to display much lower mechanical properties, which was attributed to the fact that little liquid phase was formed and the fiber–matrix interfacial bonding was too strong. It can be seen from the Fig. 6 that the flexural strength was improved by increasing the amount of additives. This result indicated that when the amount of sintering additives is increased, a relatively high-volume fraction of liquid might be formed at sintering temperatures. Then the viscosity of liquid phases decreased and the solution precipitation process of SiC was also improved.

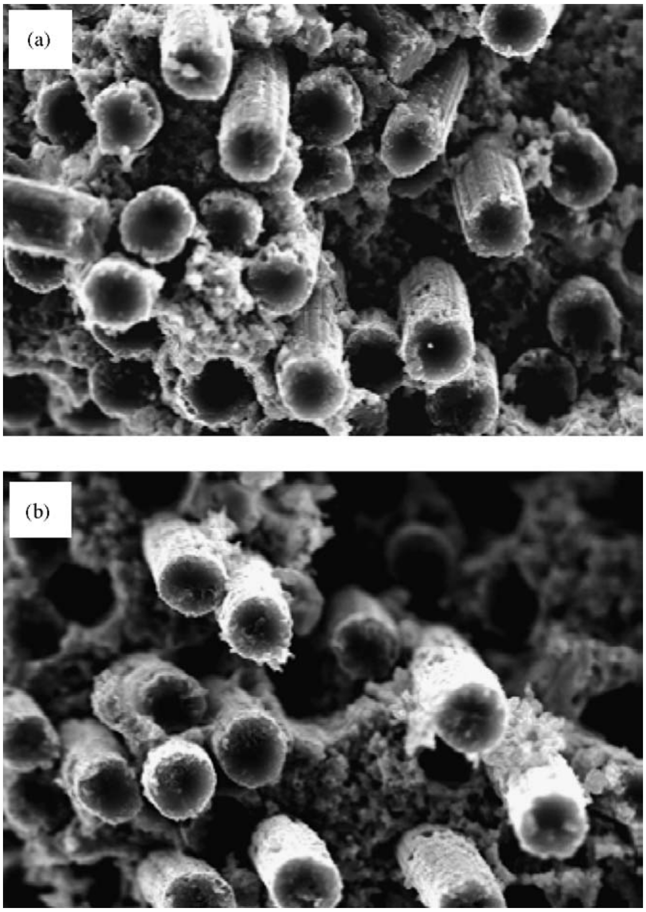

Fig. 7. Fracture surfaces of the composite: (a) SO8P20 and (b) SO11P20.

The highest fracture toughness, 6.64 MPa m$^{1/2}$ was obtained for the composites with 11 wt.% additives. This could be explained by the fact that an appropriate fiber–matrix interfacial bonding was obtained, which facilitated the debonding and pullout of the fibers. The great decrease in fracture toughness of the SO14P20 composites, despite an improvement in flexural strength was mainly attributed to the too strongly bonded fiber–matrix interphase. It proved that too strong a bond was probably beneficial for the flexural strength but harmful for fracture toughness. The fracture behavior of the composites was of completely brittle nature. The result showed that the fiber–matrix interphase characteristics played a key role in controlling mechanical properties of the composites.

The SEM fracture surfaces images of the composites sintered at 1800 °C are shown in Fig. 7. They show that the prevalent toughening mechanism operating in the composites are debonding and pullout of the fibers. A smooth surface of the pullout fiber from the composites suggested a suitable temperature for this kind of composites. It was expected that the temperature and the liquid phase did not result in degradation of the carbon fiber. Work on the effect of liquid phase on the mechanical properties of fibers is now in progress.

4. Conclusions

Short-carbon-fiber-reinforced SiC composites which were prepared by precursor pyrolysis–hot pressing with $MgO–Al_2O_3–Y_2O_3$ as sintering additives, can be densified at a relatively low temperature of 1800 °C via the liquid-phase sintering mechanism. The composite density and mechanical properties were improved by increasing the amount of additives. Amorphous interphase in the composites with more additive content can improve the fiber–matrix bonding. The present study confirms the fiber–matrix interphase characteristics play a key role in controlling mechanical properties of the fiber-reinforced composites.

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