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Fabrication and characterization of a new-style structure capillary channel in reaction bonded silicon carbide composites

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ABSTRACT

A new-style structure capillary channel was fabricated by using boron carbide powder mixtures with an appropriate multimodal particle size distribution to promote the liquid silicon infiltration in reaction bonded silicon carbide composites. Two types of core–rim structure were observed and the secondary SiC produced in the siliconisation reaction existed in two forms: nucleating on the original SiC and occupying the original positions of the residual silicon. The size of the secondary SiC in the latter form was in a range of tens to hundreds nanometers. These nano-sized SiC grains and the additive of fine boron carbide particles refined the crystalline structure and broke up the residual silicon phase into small pieces. Using this method, the microstructure was refined and the mechanical properties improved significantly. The lowest residual silicon volume fraction was 4.0% and the flexural strength and fracture toughness reached peak values of 526 ± 21 MPa and 6.2 ± 0.4MPa m$^{1/2}$, respectively.

1. Introduction

Reaction bonded silicon carbide (RBSC) composites are excellent ceramic materials with nearly full densification for a wide range of applications, e.g., light armor, fusion reactor and semiconductor part [1–4]. In the typical RBSC composite fabrication process [5–7], the porous SiC/C preform is infiltrated with liquid silicon utilizing the capillary action of the liquid silicon. The newly-formed β-SiC, which is produced by reacting liquid silicon and carbon source, nucleates on the original α-SiC. Consequently, the original α-SiC and the newly-formed secondary β-SiC form a continuous three-dimensional ceramic skeleton structure. Finally, the residual pores in the sintered body are filled with the residual silicon. Based on the above process, the reaction bonding process has many merits, such as low sintering temperature and low processing cost, short sintering time and near net shape. The RBSC composites are composed of α-SiC, β-SiC and residual silicon. Among them, the residual silicon with low melt point (~1410 °C), high brittleness (≤1 MPa m$^{1/2}$) and inferior flexural strength (≤100 MPa) is bad for the service temperature and the mechanical performance of the composites [8–11]. Therefore, it is of great importance to reduce the residual silicon content and the size of the silicon phase.

Compared with SiC, boron carbide has a lower density and better mechanical properties [12–17]. In the RBSC composites fabrication process, boron carbide was usually added into the green body to improve the mechanical properties and act as an alternative source of carbon. For instance, Han et al. [18] found that the residual silicon content was dramatically reduced by adding boron carbide into the preform. Nevertheless, the analysis did not determine the reasons for this tendency and the achieved improvement in mechanical properties was rather limited, with the highest flexural strength of 300 ± 50 MPa. Aroati et al. [2] fabricated RBSC composites with a lower amount of residual silicon (10.6 vol.%) using boron carbide as an alternative source of carbon, thereby eliminating the need for the environmentally unfriendly pyrolized organic compounds. However, the amount of the secondary β-SiC was limited, resulting in the formation of a discontinuous three-dimensional ceramic skeleton structure. The highest flexural strength reached 270 ± 18 MPa. The simplest way to reduce the residual silicon content is to increase the carbon content in the preform. Plenty of secondary β-SiC, which is produced in the siliconisation reaction between carbon source and liquid silicon, not only bonds the original α-SiC but also fills the residual pores in the sintered body. This process ultimately results in low residual silicon volume fraction. However, the high volume expansion due to the siliconisation reaction between carbon source and liquid silicon easily blocks the capillary channels. These blocked capillary channels affect the liquid silicon infiltration and then lead to an incomplete sintering. In the case of improving carbon content, it is significant to find a new

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way to promote the liquid silicon infiltration. In our previous work [19], carbon fibres were used as carbon source to reduce the volume fraction of the residual silicon, reaching the minimum value of about 8%. Moreover, no newly-formed β-SiC nucleated on the boron carbide composite particle in the reaction bonding process and this result showed the introduction of boron carbide particles promoted the liquid silicon infiltration. Therefore, it becomes possible to improve the carbon content with the additive of boron carbide particles.

To further reduce the residual silicon content and investigate the sintering behavior of boron carbide in the RBSC composites, we introduced boron carbide powder mixtures with an appropriate multimodal particle size distribution into SiC/C slurry. Suitable mixture ration was acquired by adding varying contents of carbon black and mixed boron carbide particles into the preform. Validated by the experiments, the new-style structure capillary channels, which were composed of the multimodal particle size distribution of boron carbide particles, proved beneficial for the liquid silicon infiltration process. The reaction between carbon black and liquid silicon was complete after the liquid silicon infiltration (LSI). We studied the formation mechanism of the new-style structure of capillary channels and the effect of boron carbide on the microstructure and the mechanical properties of the RBSC composites. Finally, the volume fraction of the residual silicon decreased to 4.0%.

2. Experimental procedures

2.1. Sample fabrication

Commercial α-SiC powder with an average particle size of 14 μm (98.1% purity, Zhucheng Co., Ltd., China), boron carbide powders with an average particle size of 1.5, 7 and 14 μm, respectively (97.5% purity, Mudan Jang Co., Ltd., China), carbon black (N330, Tianyishiji Co., Ltd., China) and phenolic resin with a carbon yield of 45% (Blue Star Co., Ltd., China) were used as original raw materials. First, the phenolic resin was dissolved in absolute alcohol (at a ratio 1 g/40 ml) to form a homogeneous solution. The SiC powder, the boron carbide powder, the carbon black and the phenolic resin solution were then ball milled in a planetary mixer (QM-3S4P, China) for 4 h at a milling speed of 200 r/min using agate balls (ball to powder weight ratio 2:1). Finally, alcohol was removed from the homogenous slurry to obtain a dry powder. The green bodies were compacted at a pressure of 180 MPa for 120 s. Then, the prepared preforms were infiltrated with liquid silicon at 1600 °C in vacuum for 30 min. The sintered bodies were cut into parallelepipeds with dimensions of 50 mm × 3 mm × 4 mm and 25 mm × 3 mm × 4 mm for the fracture toughness measurements and three-point bending tests, respectively. The surfaces of the samples were prepared employing a standard metallographic procedure that included a polishing with a 0.5 μm diamond paste and chamfering as the last step. In order to study the morphology of the samples in more detail, the samples were etched with a 1HF:7HNO$_3$ solution to remove the residual silicon. Seven sets of samples with different starting material ratios were prepared as shown in Table 1.

Table 1
Nomenclature used to distinguish the prepared RBSC composite samples and raw material composition.

Constitution	Designation
SiC + 20 wt.% C + 15 wt.% mixed[a] B$_4$C + 12 wt.% phenolic resin	RB^{a}2015
SiC + 20 wt.% C + 25 wt.% mixed[a] B$_4$C + 12 wt.% phenolic resin	RB^{a}2025
SiC + 20 wt.% C + 35 wt.% mixed[a] B$_4$C + 12 wt.% phenolic resin	RB^{a}2035
SiC + 25 wt.% C + 35 wt.% mixed[a] B$_4$C + 12 wt.% phenolic resin	RB^{a}2535
SiC + 25 wt.% C + 45 wt.% mixed[a] B$_4$C + 12 wt.% phenolic resin	RB^{a}2545
SiC + 20 wt.% C + 25 wt.% mixed[b] B$_4$C + 12 wt.% phenolic resin	RB^{b}2025
SiC + 20 wt.% C + 35 wt.% mixed[b] B$_4$C + 12 wt.% phenolic resin	RB^{b}2035

[a] Mixed B$_4$C particles of different sizes with 14 μm:7 μm:1.5 μm mass ratio of 5:3:2.

[b] Mixed B$_4$C particles of different sizes with 14 μm:7 μm:1.5 μm mass ratio of 2:3:5.

2.2. Characterization technique

The bulk densities of the samples were determined utilizing the Archimedes principle. The microstructure of the samples was studied by scanning electron microscopy (SEM, VEGA IIXMU, Czech Republic), combined with energy-dispersive X-ray spectroscopy (EDS, OXFORD 7718, United Kingdom). The residual silicon volume fractions were obtained by using the image analysis software DT2000. The flexural strength was determined by performing three-point bending tests, with the crosshead speed set to 0.5 mm/min. The fracture toughness was evaluated using a single-edge notched beam and a crosshead speed of 0.05 mm/min. The presented data corresponds to the average value calculated from five different measurements.

3. Results and discussion

3.1. Fabrication of new-style structure capillary channels

In the typical RBSC composites fabrication process, the porous SiC/C preform is infiltrated with liquid silicon utilizing the capillary action of the liquid silicon. As soon as liquid silicon flows into the porous preform, the siliconisation reaction takes place. Newly-formed secondary β-SiC gradually bonds the original α-SiC. The width of the capillary channel decreases as the reaction progress. With carbon source content increasing, the amount of the secondary SiC increases. As a result, the capillary channels become blocked and some residual carbon remains in the RBSC composites, resulting in the performance degradation. The processes of formation, development and disappearance are shown in Fig. 1. Fig. 1(a) reveals the formation of the capillary channel. According to the dissolution–precipitation mechanism [20,21], the carbon gradually dissolves in the liquid silicon, and the carbon activity gradient within the silicon causes a rapid diffusion of carbon away from the dissolution sites. The carbon diffuses to locally cooler sites (i.e., the original SiC particles) until a supersaturation occurs in the silicon and then precipitates as an epitaxial secondary SiC coating. Fig. 1(b) shows the secondary SiC precipitates from the C–Si solution and grows on the original SiC. As shown in Fig. 1(c), the secondary SiC bonds the original SiC and the capillary channel becomes blocked.

Efforts can be made in the following aspects to improve the situation. One of the simpler ways is to widen the capillary channel. It means an increasing gap among the original particles. Although the widened capillary channel promotes the liquid silicon infiltration, it must lead the residual silicon content to increase. On the other hand, the siliconisation reaction takes place as soon as the liquid silicon flows into the preform and the liquid silicon viscosity is quite high initially but falls with increasing temperature [22]. Improving the sintering temperature is beneficial for the liquid silicon infiltration process, but the effect still remains limited. In addition, high sintering temperature means high requirement on sintering equipment and high cost. In the previous works [2,19,23,24], no secondary SiC nucleated on the boron carbide composite particles. Therefore, we attempt to fabricate a new-style structure capillary channel by using a multimodal boron carbide particle size distribution. The new-style structure capillary channels pervade the whole preform and maintain stability until the final stage of the LSI process. Fig. 2 shows the process of the LSI and the new-style structure capillary channels. As shown in Fig. 2(a), the red circles represent the original SiC and the black dots represent the carbon black. The blue circles with different sizes correspond to the multimodal

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