Available online at www.sciencedirect.com
SciVerse ScienceDirect
Ceramics International 39 (2013) 449–455
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Fabrication and characterization of SiC whisker reinforced reaction bonded SiC composite

Shuang Li*, Yumin Zhang, Jiecai Han, Yufeng Zhou

Center for Composite Materials, Harbin Institute of Technology, Harbin 150001, China

Received 28 February 2012; received in revised form 15 June 2012; accepted 15 June 2012
Available online 23 June 2012

Abstract

SiC whisker reinforced reaction bonded SiC composites have been developed for fabricating large scale, complex shaped structural components. Here the composites were prepared with the method of slip casting and liquid silicon infiltration at 1650 °C. The distribution, morphology and reinforcing behaviors of the SiC whisker in the composite were investigated. It is revealed that the introduction of SiC whisker increases the porosity of the green body, and accordingly the bulk density of the composite. Whisker pullout can be clearly observed on the fracture surface, implying a moderate bonding strength between the whisker and matrix. After liquid silicon infiltration, the SiC whisker keeps its initial diameter and morphology in the case of 15 wt% whisker. The fracture toughness is enhanced by SiC whisker, reaching the peak value of 4.2 MPa m$^{1/2}$ at the whisker fraction of 20 wt%. Whisker pullout, whisker bridging and crack deflection are considered as the main toughening mechanisms.

Keywords: A. Slip casting; B. Whiskers; C. Mechanical properties; D. SiC

1. Introduction

Reaction bonded silicon carbide (RBSC) ceramic was developed first as a nuclear fuel cladding material in the 1950s. As a promising material it then quickly found its applications in aeronautics, energy, electronics, nuclear and transportation industries. In general, the RBSC is prepared by reaction sintering of SiC/C mixtures or porous carbon with liquid silicon [1–3]. Such a material has the merits of low sintering temperature, short sintering time, full densification and negligible dimensional change compared with the conventional sintered SiC [4,5]. Additionally, due to the high thermal conductivity, low coefficient of thermal expansion (CTE) and good shape capability, the RBSC is believed to be an outstanding candidate for the large scale, complex shaped and ultra-lightweight structural components [6,7]. However, it has been noted that during sintering, a great many pores in the green bodies are filled by highly brittle, discontinuous silicon. This will lower the resistance ability to crack propagation of the RBSC material. Thus, the monolithic RBSC ceramic cannot meet the demands of high reliability and excellent performances, that have to be guaranteed in the application of large scale structural components.

In the past years, many works have been conducted to improve mechanical behavior of RBSC. Most of them focus on the elimination of residual silicon and porosity defects through employment of the fine SiC particles, silicon–metal alloy, boron carbide (B_4C) modifier, and so on [8–11]. Suyama et al. [8] developed high-strength RBSC by controlling the size of residual Si under 100 nm. The flexural strength of the obtained RBSC exceeded 1000 MPa. However, its fracture toughness was only 3.3 MPa m$^{1/2}$. Aroati et al. [9] chose B_4C as the alternative source of carbon, and multimodal size SiC as the matrix to reduce the residual silicon. This approach shows merits of reduced residual silicon, low density and the environment friendship, but renders the flexural strength only ranged from 180 to 280 MPa. Silicon alloyed melt was also used to reduce the volume fraction and particle size of the residual silicon. However, it could not significantly improve the mechanical properties [10]. In summary, the current approaches have only been confined to the particulate reinforcing.

*Corresponding author. Tel./fax: +86 0451-86412236.
E-mail addresses: shuangli1981@gmail.com, 2816361@163.com (S. Li).

0272-8842/$36.00
http://dx.doi.org/10.1016/j.ceramint.2012.06.047

An alternative is to add SiC whisker. SiC whisker is characterized by high tensile strength, high elastic modulus and good thermal stability at elevated temperature. With the high aspect ratio, SiC whiskers can effectively toughen the ceramic matrix composites via various toughening mechanisms, such as whisker pullout, whisker bridging, whisker debonding and crack deflection [12,13]. To obtain high toughness values with SiC whisker incorporation, three obstacles have to be resolved: the aggregation of whisker due to the high aspect ratio, the degradation of the whisker during the sintering, and the bonding strength between whisker and the matrix [14]. Ball milling is usually used to disperse whiskers into the matrix during the preparation. Some reduction of the whisker length may be caused by the high impact, but a heavy aggregation of whiskers cannot be induced The siliconization of carbon is a typical exothermic reaction, which leads to a high local temperature even up to 2200 °C. So the prevention of high temperature degradation of whisker is a key factor for the toughening performance. A moderate bond strengthening is also necessary such that the whisker pullout and whisker debonding are allowed. SiC whisker has been used in a wide range of ceramics, such as Al_2O_3, ZrB_2, ZrO_2 and mullite. However, the RBSC ceramic strengthened and toughened by SiC whisker has attracted little attention so far.

The present work aims at improving the microstructure and mechanical behavior of RBSC. The SiC whisker was introduced into SiC/C suspensions to produce whisker reinforced RBSC composites. Slip casting and liquid silicon infiltration (LSI) were combined to prepare the large scale, complex shaped components. The whisker fraction ranged from 10 to 25 wt%. The effects of SiC whisker on microstructure and mechanical properties were investigated. The morphology changes of SiC whisker after LSI were evaluated.

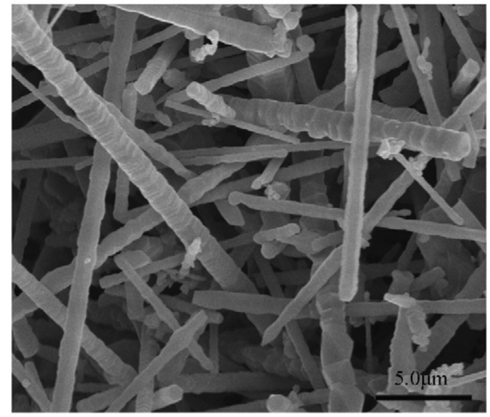

Fig. 1. SEM image of the starting silicon carbide whiskers.

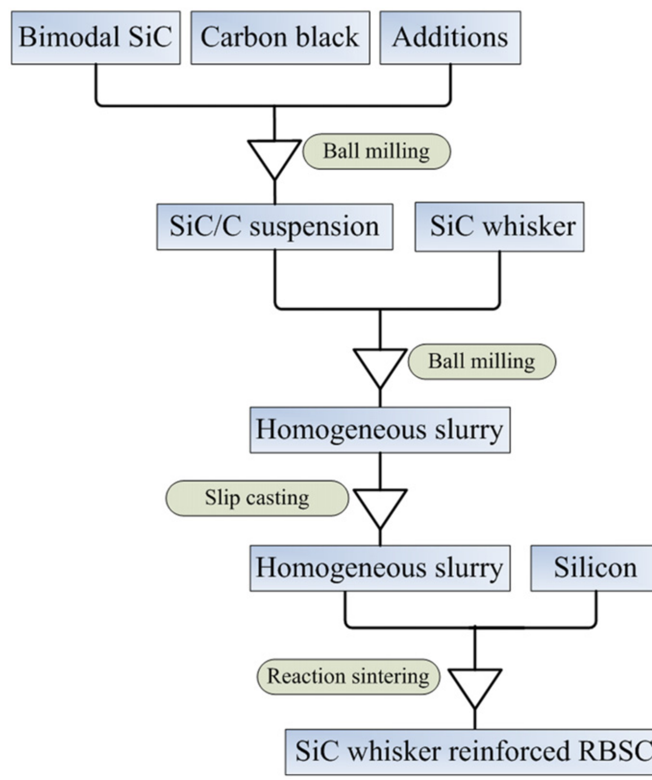

Fig. 2. Fabrication process for the SiC whisker reinforced RBSC composites.

2. Experimental procedure

2.1. Raw materials and fabrication

β-SiC whiskers (99% pure, stable up to 1900 °C, Alfa Aesar, MA, USA) are characterized with an average length of 18 μm and diameter of 1.5 μm. A burl profile on the whisker surface was observed, as shown in Fig. 1. Two commercial SiC powders (α-SiC, purity 98.5%, Huanyu, Zibo, China) with sizes of 60 and 10 μm were chosen. Carbon black was introduced as carbon resource in LSI.

The silicon carbide and carbon black powders combined with plasticizer and dispersant were ball-milled in deionized water using SiC media. After 12 h of ball-milling, a uniform SiC/C suspension was obtained. Before adding to the suspension, the SiC whisker was pre-dispersed by ultrasonication and mechanical homogenization with carboxy methylcellulose (CMC, molecular weight 20,000, GONSO, Shanghai, China) as dispersant. Subsequently, the dispersed SiC whisker was ball milled with the obtained SiC/C suspension for 2 h. The ball milling speed was restricted to 180 rpm to protect the SiC whisker from damage. After mixing, the slurry was vacuumed and then poured into the plaster mold to obtain the green body. The resulting green body was dried at room temperature and then sintered via LSI in vacuum at 1650 °C for 60 min. During sintering, the silicon was placed on top of the green body. The processing procedure is shown in Fig. 2.

2.2. Characterization

Microstructure of the polished and the fracture surfaces were observed by scanning electron microscopy (SEM, QUANTA 200, FEI, USA). Before examining, the polished surface was etched by HF/HNO_3 acid mixture. Crystal structure of the composite was analyzed by X-ray diffraction (XRD, Rigaku, Dmax-rb). Bulk density of the specimens was measured by the Archimedes method. Flexural strength test was carried out with a crosshead speed of 0.5 mm/min and a span of 30 mm. The tested bars with a dimension of 3 mm × 4 mm × 36 mm were polished by a diamond slurry of 2 μm. Fracture toughness was evaluated using a single edge notched beam (SENB) test with a crosshead speed of 0.05 mm/min and a span of 20 mm. The tested bars were in the dimension of 2 mm × 4 mm × 22 mm with a notch of 2 mm in depth and 0.02 mm in width. All data were averages of five tests for each specimen. A Vickers indenter was used on polished surface with 19.6 N as applied load for 15 s to observe the crack propagation.

3. Results and discussion

3.1. Microstructure

Due to the high aspect ratio and low diameter, SiC whiskers are subjected to aggregation in the slurry. Many efforts have been made to realize a uniform dispersion of whiskers into the SiC/C suspensions. From the green body shown in Fig. 3, the SiC whiskers were uniformly dispersed into the matrix. The whisker length was reduced to appropriate 15 μm because of the high speed impact during ball mixing. In view of the reinforcing performance, the milling time and milling speed should be controlled, so as to avoid whisker from damage.

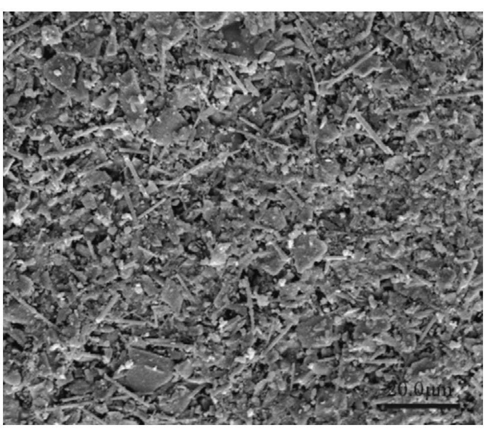

Fig. 3. SEM image of the green body formed in slip casting.

Fig. 4 exhibits the microstructures of the polished (Fig. 4(a)) and fracture surfaces (Fig. 4(b)) of the composite with whisker fraction of 15 vol%. The polished surface consists of three main phases — SiC particle, SiC whisker and residual silicon. It is difficult to distinguish whisker from the matrix due to its same composition with the SiC matrix. By the obscure edges, the whiskers that distributed on the polished surface were observed, as shown in (Fig. 4(a)). Additionally, the whiskers preserve the initial diameter inspite of the high temperature degradation. Thus, it is concluded that the siliconization reaction did not degrade the whisker during the sintering. Whisker pullout can be observed on the fracture surface, as shown in Fig. 4(b). The white arrows indicate the SiC whisker; the black arrows represent the holes resulted from the whisker pullout. Such a significant whisker pullout is beneficial to the fracture toughness due to the consumption of fracture energy. Moreover, the random orientation of the linear SiC whiskers further confirms the uniform distribution of whiskers in the matrix. This uniformity is in favor of the isotropy of the thermal and mechanical properties of the RBSC composite.

The specimen with 15 wt% whisker addition was etched by HF/HNO_3 acid mixture to remove the residual silicon. After the acid etching, the SiC whisker on the polished surface was observed. As shown in Fig. 5, the whiskers maintain the burl profile on the surface, implying their excellent stability at high temperature. This stability is an important factor for the reinforcing performance of SiC whisker in the RBSC composite. In addition, more pores were observed in the vicinity of the whiskers than those in other regions. They were derived from the removal of residual silicon by acid etching. So, SiC whisker incorporation leads to an increase of residual silicon in local regions.

The whisker pullout on the fracture surface is shown in Fig. 6. The broad arrows indicate whiskers that were

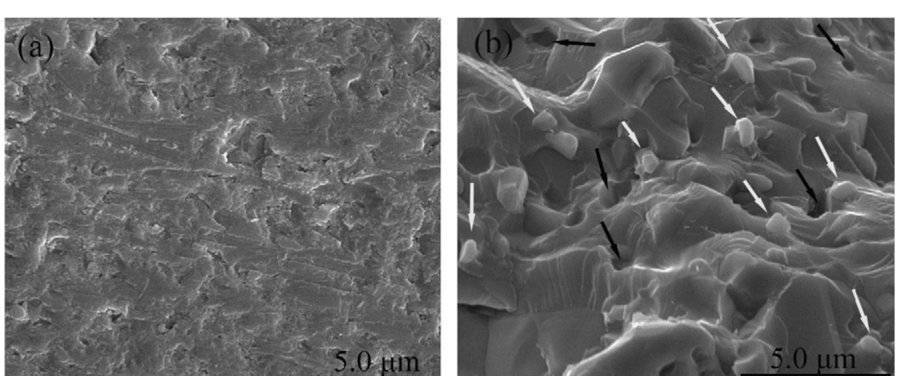

Fig. 4. SEM images of the SiC whisker reinforced RBSC with whisker fraction of 15 wt%: (a) the polished surface and (b) the fracture surface.

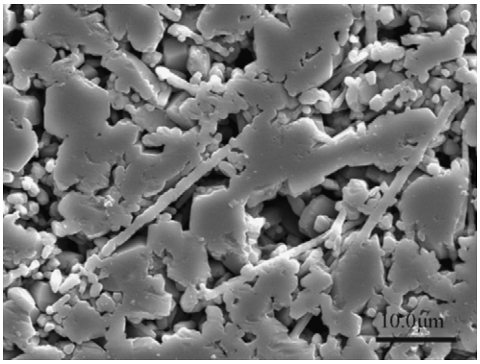

Fig. 5. SEM image of the polished surface (15 wt% whisker) etched with HF/HNO_3 acid mixture.

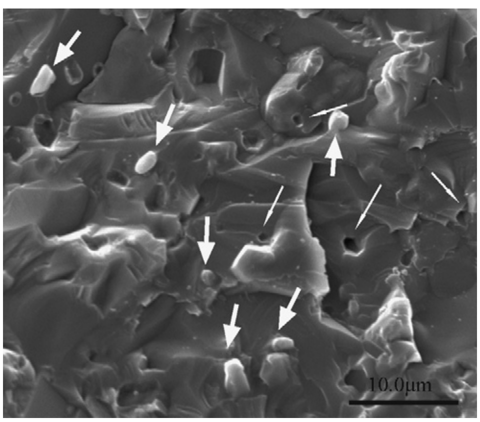

Fig. 6. SEM images for the whisker pullout on the fracture surface of the composites, in which the broad arrows indicate whiskers pulled out from the matrix, and the fine arrows indicate holes due to whisker pullout.

pulled out from the matrix. The fine arrows correspond to holes that originated from the whisker pullout. The pullout of SiC whisker indicates that the bonding of the SiC whisker and the matrix is somewhat weak with respect to the strength of whisker. The whisker pullout is considered as the main toughening mechanism in RBSC composite. Compared with the conventional SiC fiber reinforcement, the pullout length of SiC whisker is short. This short length is ascribed to the shorter starting length and lower tensile strength of SiC whiskers.

3.2. Bulk density and mechanical properties

The SiC whisker reinforced RBSC composite consists of SiC and Si phases, and so the bulk density indicates the mass fraction of Si. The bulk density as a function of whisker fraction is illustrated in Fig. 7. Compared with the monolithic RBSC, the bulk density is decreased by the whisker incorporation, resulting from the increase of residual silicon of low density (Si: 2.4 g/cm^3, SiC: 3.2 g/cm^3). The average length of the SiC whisker is 18 μm from the supplier; however, a higher length of 30 μm was observed in the SEM image. The introduction of SiC

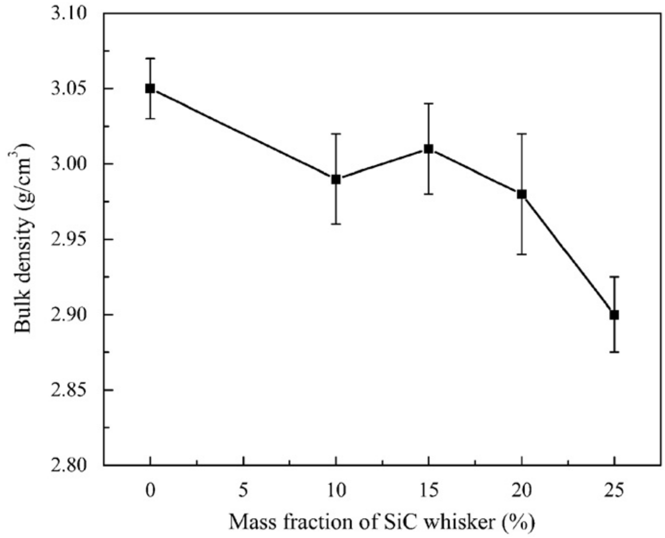

Fig. 7. Bulk density of the whisker reinforced RBSC composite as a function of whisker fraction.

whisker reduces the stacking density of the SiC particles, and thus leads to high porosity of the green body. Driven by capillary pressure, the liquid silicon infiltrates and fills up all the excessive pores in the green body. So the increase of whisker leads to a high fraction of silicon, and consequently a low bulk density. At the whisker fraction of 25 wt%, the bulk density declines to 2.91 g/cm^3. This value is lower than that of the monolithic RBSC ceramic (3.05 g/cm^3).

The specimen with 15 wt% whisker corresponds to a high bulk density of 3.03 g/cm^3, which is higher than that of 10 wt% whisker. This exception is ascribed to the complete siliconization of carbon and filling of residual pores by residual silicon. In this investigation, the soaking time is 2 h for the reaction sintering. Due to the high stacking density and infiltration difficulty, it is speculated that the carbon phase still exists in the material with 10 wt% whisker. However, the trace carbon phase cannot be detected by XRD analysis.

Composition of the polished surface was investigated by XRD analysis, as shown in Fig. 8. Apparently, all the composites consist of both SiC and Si phases. With increase of the whisker fraction, the peak intensity of Si phase becomes stronger, indicating a fraction increase of Si in the composite. This increase is in agreement with the decrease of bulk density with the increase of SiC whisker.

Variations of the flexural strength and fracture toughness are shown in Fig. 9 with whisker fraction in the range from 0 to 25 wt%. The flexural strength increases in the initial stage, reaching the peak value of 310 MPa at the whisker fraction of 15 wt%. Because of the increase of residual silicon, the flexural strength is reduced when the whisker is further increased. It is noticed that both the maximum values of flexural strength and bulk density occur at the same whisker fraction.

The fractures toughness increases from 3.1 MPa m$^{1/2}$ (monolithic RBSC ceramic) to 4.2 MPa m$^{1/2}$ (whisker fraction of 20 wt%). This improvement indicates that some toughening phenomena occur by the whisker incorporation. Owing to the incomplete infiltration and the increase of residual silicon with high brittleness, the fracture toughness is degraded at a whisker fraction of 25 wt%.

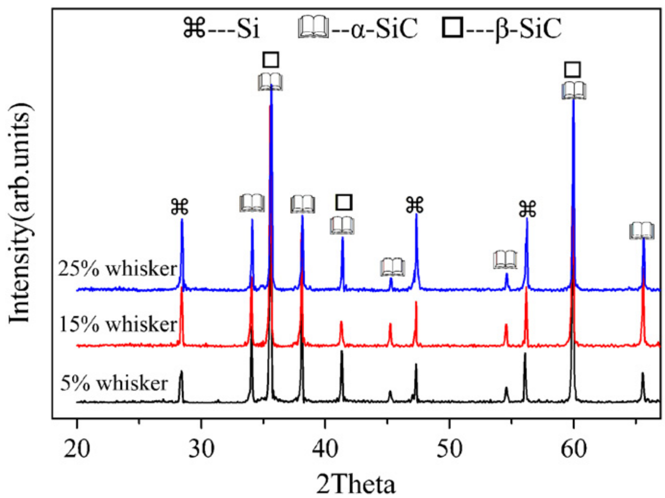

Fig. 8. XRD patterns for the samples with different whisker fractions ranging from 5 to 25 wt%.

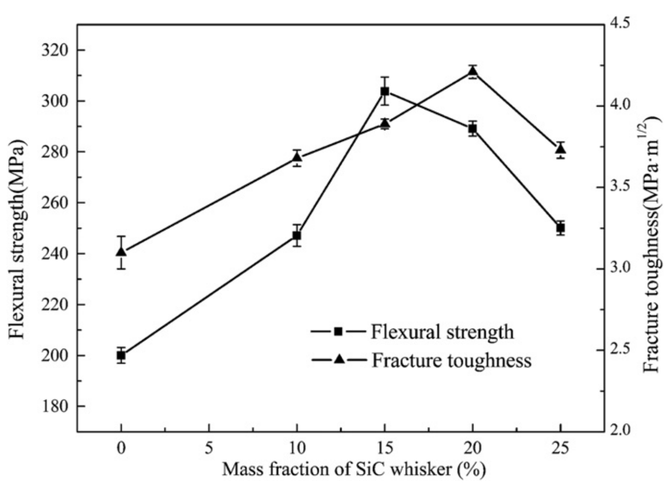

Fig. 9. Flexural strength and fracture toughness as a function of SiC whisker fraction in the RBSC composites reaction sintered at 1650 °C.

The improvement of fracture toughness derives from whisker pullout, whisker bridging and crack deflection. As shown in Fig. 6, a mass of whiskers was pulled out from the matrix when loading. Due to the high strength and high elastic modulus of SiC whisker, the whisker pullout is believed to consume extensive fracture energy. In addition, the surface displays the coexistence of intergranular and transgranular fracture. The cleavage plane originates from the fracture of Si, indicating the strong bonding strength between the SiC particles and residual Si. Coarse SiC particles are difficult to be distinguished from the surface; however, it is speculated that the main fracture mode is intergranular because of the high hardness of SiC and high brittleness of Si [15]. The newly formed β-SiC particles (with diameter of several microns) show a typical intergranular fracture.

To further explain the toughening mechanisms, cracks were introduced from Vikers' indentation on the polished surface of the composite. The general direction of crack propagation is indicated by the black arrow in Fig. 10. Whisker debonding and bridging are shown, respectively, in Fig. 10(a) and (b). The crack is deflected by the whisker, as shown by the white arrow in Fig. 10(a). This implies a weak interface between the whisker and the matrix. Significant deflections occurred in the wake of the crack, which was caused by the intergranular fracture of SiC particle. Whisker bridging is also a common toughening mechanism for whisker reinforced RBSC composite (Fig. 10(b)). With regard to whisker bridging, the SiC whiskers consume fracture energy by spanning wakes of the cracks, and consequently improve fracture toughness of the composite. In addition, the siliconization of carbon forms β-SiC particles, which grow on the edge of the starting α-SiC particles and construct skeleton of the ceramics. Some other fine β-SiC particles of several microns (Fig. 5) are also responsible for the improved flexural strength and fracture toughness.

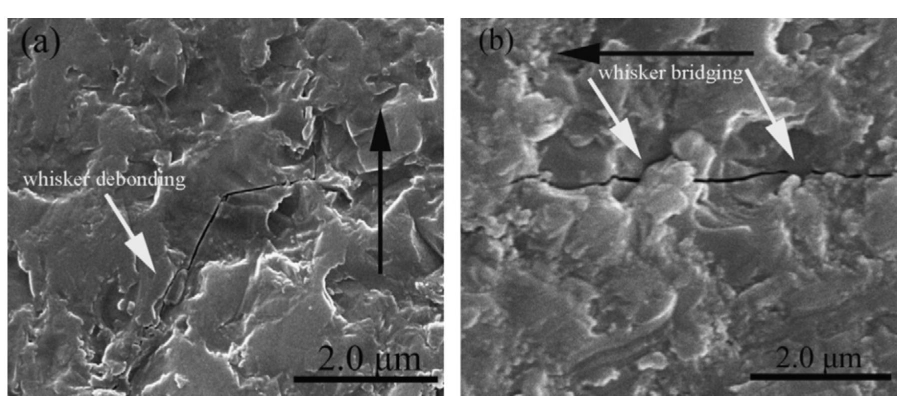

Fig. 10. SEM images for crack deflection and bridging of the SiC whisker reinforced RBSC composite: (a) 10 wt% whisker and (b) 20 wt% whisker.

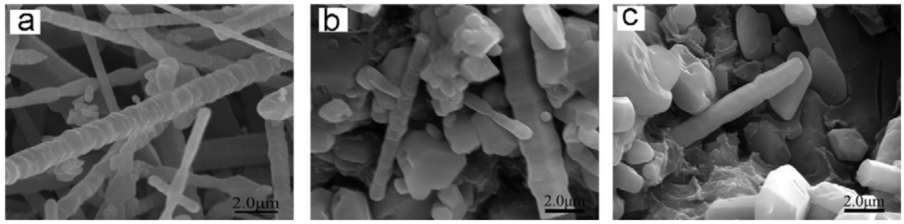

Fig. 11. SEM images showing the morphological variation of SiC whisker: (a) the starting SiC whisker, (b) RBSC with 15 wt% whisker and (c) RBSC with 25 wt% sintered at 1650 °C.

3.3. Morphology variation of SiC whisker

The siliconization of carbon is a typical exothermic reaction, resulting in high temperature in local region during the LSI [16,17]. Thus, the morphology changes of SiC whisker with whisker fraction were investigated. Morphology of the starting SiC whisker is shown in Fig. 11(a). The diameter of the whisker ranges from 1 to 2 μm with a significant burl profile on the whisker surface. At a whisker fraction of 15 wt%, the whisker represents a similar morphology with the starting whisker, as shown in Fig. 11(b). Inspite of high temperature degradation during LSI, the whisker can still preserve the original burl profile. This stability is beneficial for toughening of the composite for the high sliding friction during whisker pullout. Compared with the former two, for the composite with 25 wt% whisker addition, a disappearance of the burl profile occurs, as shown in Fig. 11(c). As mentioned above, the composite with 25 wt% whisker is of low density for the excess residual silicon. So, it is speculated that the excess molten silicon infiltrated into the green body rapidly and reacted with carbon simultaneously. As the temperature in the vicinity of the whisker was very high, partial β-SiC on the whisker surface dissolved into the molten silicon. As a result, the burl profile on the whisker surface disappeared.

4. Conclusions

SiC whisker reinforced RBSC composite was prepared by a combination of slip casting and reaction sintering. The SiC whisker keeps the initial diameter and the burl profile on the surface at the whisker fraction of 15 wt%. This structural stability is of great importance for whisker reinforcing. At whisker fraction of 25 wt%, the burl profile disappears due to the dissolution of SiC into the liquid silicon. The whisker incorporation leads to an increase of porosity in the green body, and then a decrease of bulk density.

Compared with the monolithic RBSC ceramic, the flexural strength is improved by the whisker introduction. However, the increment is small due to the increase of residual silicon. The fracture toughness of the composite is enhanced with whisker fraction ranging from 0 to 20 wt%; subsequently, it declines due to the increase of the residual silicon and the incomplete infiltration. The enhancement of fracture toughness is ascribed to whisker pullout, whisker bridging and crack deflection. To further develop the reinforcing performance of SiC whisker, it is necessary to reduce the residual silicon in the sintered body. So, further investigation should focus on the porosity reduction of the green body.

Acknowledgments

This study was financially supported by "the Fundamental Research Funds for the Central Universities" (Grant no. HIT.KLOF.2010024) and Program for the New Century Excellent Talents in University (NCET-10–0069).

References

[1] J. Martínez Fernández, A. Muñoz, A.R. de Arellano López, F.M. Valera Feria, A. Domínguez-Rodríguez, M. Singh, Microstructure-mechanical properties correlation in siliconized silicon carbide ceramics, Acta Materialia 51 (2003) 3259–3275.
[2] Q.W. Huang, L.H. Zhu, High-temperature strength and toughness behaviors for reaction-bonded SiC ceramics below 1400 °C, Materials Letters 59 (2005) 1732–1735.
[3] F. Varela-Feria, J. Ramírez-Rico, A. de Arellano-López, J. Martínez-Fernández, M. Singh, Reaction–formation mechanisms and microstructure evolution of biomorphic SiC, Journal of Materials Science 43 (2008) 933–941.
[4] A. Sayano, C. Sutoh, S. Suyama, Y. Itoh, S. Nakagawa, Development of a reaction-sintered silicon carbide matrix composite, Journal of Nuclear Materials 271–272 (1999) 467–471.
[5] S.P. Lee, Y. Katoh, J.S. Park, S. Dong, A. Kohyama, S. Suyama, H.K. Yoon, Microstructural and mechanical characteristics of SiC/SiC composites with modified-RS process, Journal of Nuclear Materials 289 (2001) 30–36.
[6] Y.M. Zhang, J.H. Zhang, J.C. Han, X.D. He, W. Yao, Large-scale fabrication of lightweight Si/SiC ceramic composite optical mirror, Materials Letters 58 (2004) 1204–1208.
[7] S.W. Guo, G.Y. Zhang, L.B. Li, W.Y. Wang, X.Z. Zhao, Effect of materials and modelling on the design of the space-based lightweight mirror, Materials and Design 30 (2009) 9–14.
[8] S. Suyama, T. Kameda, Y. Itoh, Development of high-strength reaction-sintered silicon carbide, Diamond and Related Materials 12 (2003) 1201–1204.
[9] S. Aroati, M. Cafri, H. Dilman, M.P. Dariel, N. Frage, Preparation of reaction bonded silicon carbide (RBSC) using boron carbide as an alternative source of carbon, Journal of the European Ceramic Society 31 (2011) 841–845.
[10] M. Esfehanian, J. Guenster, J.G. Heinrich, J. Horvath, D. Koch, G. Grathwohl, High-temperature mechanical behavior of carbon–silicide–carbide composites developed by alloyed melt infiltration, Journal of the European Ceramic Society 28 (2008) 1267–1274.
[11] P.A. Lessing, A.W. Erickson, D.C. Kunerth, Thermal cycling of siliconized-SiC at high temperatures, Journal of Materials Science 36 (2001) 1389–1394.

[12] S. Guicciardi, L. Silvestroni, M. Nygren, D. Sciti, Microstructure and toughening mechanisms in spark plasma-sintered ZrB_2 ceramics reinforced by SiC whiskers or SiC-chopped fibers, Journal of the American Ceramic Society 93 (2010) 2384–2391.
[13] G.M. Song, Y. Zhou, Y. Sun, T.C. Lei, Modelling of combined reinforcement of ceramic composites by whisker and transformation toughening, Ceramics International 24 (1998) 521–525.
[14] P.F. Becher, Ceramics: Whisker Toughening, in: K.H.J. Buschow, W.C. Robert, C.F. Merton (Eds.), Encyclopedia of Materials: Science and Technology, Elsevier, Oxford, 2001, pp. 1116–1118.
[15] M. Wilhelm, M. Kornfeld, W. Wruss, Development of SiC–Si composites with fine-grained SiC microstructures, Journal of the European Ceramic Society 19 (1999) 2155–2163.
[16] N.R. Calderon, M. Martínez-Escandell, J. Narciso, F. Rodríguez-Reinoso, The combined effect of porosity and reactivity of the carbon preforms on the properties of SiC produced by reactive infiltration with liquid Si, Carbon 47 (2009) 2200–2210.
[17] R.M. Sullivan, A model for the oxidation of carbon silicon carbide composite structures, Carbon 43 (2005) 275–285.