Processing and mechanical properties of silicon carbide-based ceramics doped with short zirconia fibers

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SiC ceramics doped with five ratios of ZrO2 short fibers (0, 5, 10, 15, 20 vol.%) were fabricated via hot pressing at 1800°C for 60 min under a pressure of 50 MPa. The bending strength and fracture toughness were improved by ZrO2 short fibers additives except SiC/20 vol.% ZrO2. Moreover, the SiC/15 vol.% ZrO2 possessed the bending strength of 553 ± 30 MPa and fracture toughness of 7.4 ± 0.4 MPa m1/2, respectively. However, the relative density decreased. The relative density of pure SiC sample was 94.18%, and the hardness decreased from 13.01 to 12.13 GPa with the increase of the ZrO2 short fiber additive. The ZrC peak was detected in X-ray diffraction patterns, which is the result of the reaction between ZrO2 fibers and SiC.

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Key-words : ZrO2 short fibers, Mechanical properties, Phase compositions microstructures

[Received September 7, 2015; Accepted March 14, 2016]

1. Introduction

As structural materials, SiC ceramics have aroused a great deal of concerns in the electronics, machinery, and aviation industries because of their great mechanical strength, high hardness, high thermal conductivity, lower physical density, and low coefficient of thermal expansion.1-5 SiC ceramics possess superior anti-oxidation properties due to the self-sealing performance of SiO2 during the oxidation process of SiC.6-8 However, the applications of SiC ceramics are restricted by low bending strength and fracture toughness.9,10 Moreover, the most intractable issue is the appropriate method to obtain a dense sample. The problem of the low fracture toughness can be overcome through designing and preparing composites reinforced with fibers, whiskers, or particles.10,11 The toughness of the ZrB2-SiC-ZrO2 ceramic ranged from 6.3 to 7.6 MPa m1/2, corresponding to an increase of approximately 134% compared with the reported results of monolithic ZrB2, and an increase of 46% was found for ZrB2-SiC composites.12 The fracture toughness and bending strength of ZrB2 matrix are obviously increased with the addition of SiC particles and whiskers.13 Short fibers reinforced ceramics have some advantages, such as lower costs and easy of production. Many research studies have indicated that SiC was employed as a second phase as a stabilizer.14,15 In the present study, ZrO2 short fibers were doped into the SiC matrix to improve the mechanical properties of the composites.

ZrO2 fibers were considered due to their high melting point (2600°C), high temperature resistance (2200°C), strong oxidation resistance, good anti-corrosion, and low thermal conductivity.16 ZrO2 fibers were used to improve mechanical properties of Al2O3 ceramics because of the deflection and the bridging of micro-cracks in the interface of zirconia toughened alumina (ZTA) composites.11,13-15 The mechanical properties of Si3N4 ceramics can be enhanced through adjustment of the content of ZrO2 powders.18 Carbon fibers were used to fabricate fiber reinforced composites via vacuum hot pressing, which could realize high efficiency and accuracy control to prepare high density and good crystallinity materials. The bending strength and anti-oxidation of ceramic composites were intensified simultaneously.19

In this study, ZrO2 short fibers reinforced SiC composites were fabricated via vacuum hot pressing. The mechanical properties and microstructures of the obtained composites were studied in detail.

2. Experimental procedure

2.1 Materials

ZrO2 short fibers (diameter 4 μm, length 600 μm, purity > 99.0%, SPN Co. Ltd., Shaoxing, China) and SiC powders (4H-SiC, particle size 1 μm, purity > 99.0%, STNANO Co. Ltd., Shanghai, China) were mixed at volume fraction ratios of 0, 5, 10, 15, and 20% of ZrO2 short fibers; these samples were denoted as 1, 2, 3, 4, and 5, respectively. The experimental procedure was shown in Fig. 1. Figure 2 shows SEM images of SiC powders with three different enlargement factors; the grain sizes were found to be homogeneous. The SEM images of ZrO2 short fibers (Fig. 3) exhibited an almost symmetrical diameter for every fiber.

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Fig. 1. Experimental procedure for fabrication of SiC/ZrO2 composites.
and elliptical section. The XRD pattern of the mixed materials was displayed in Fig. 4; only SiC and ZrO$_2$ peaks were observed.

2.2 Processing of composites

SiC powders and ZrO$_2$ short fibers with various proportions were distributed by ethyl alcohol as the dispersion medium in a ball mill (TENCAN powder Co. Ltd., Shanghai, China) operated for 2 h at 159 rps. The homogeneous mixtures were dried at 60°C in a drying oven and then mingled with moderate polyvinyl alcohol (PVA) to obtain uniform powders, which were selected by a 40 mesh screen size griddle. The prepared mixture powders were placed for 24 h after pelleting to allow for uniform diffusion and then were packaged into a graphite die. Finally, the graphite die containing the powders were placed into a hot press furnace with the air pressure reduced to 8.0 $\pm$ 1 MPa before heating. The heating produce involved a heating rate of 10°C/min below 1200°C and 5°C/min between 1200–1800°C. A pressure of 50 MPa was maintained for 60 min at 1800°C. The cooling procedure was set to 10°C/min from 1800°C to room temperature, and the load was not removed until the die temperature reduced to below 500°C.

Sintered samples were cut into several strips with the shape size of 35 mm $\times$ 4 mm $\times$ 3 mm and chamfer of 0.3 mm. The bending strength was tested by electronic universal testing machine (CMT5105 100 KN, China) with a crosshead speed of 0.5 mm/min and span of 30 mm. The density and porosity of the sintered composites were characterized by X-ray diffraction (XRD) with Cu K$_\alpha$ radiation to observe the phase compositions of the composites. The morphology of the composites were studied by scanning electron microscope (SEM, FEI QUANTA FEG250, USA).

3. Results and discussion

The five groups of samples marked as 1, 2, 3, 4, and 5 were fabricated by 0, 5, 10, 15, and 20 vol.% ZrO$_2$ short fibers, respectively, into SiC ceramics. Figure 5 describes the fracture surface of the pure SiC (1st group). The 1st composite exhibited a compact structure and homogeneous grains that certified SiC could be successfully manufactured via a high sintering temperature of 1800°C and a pressure of 50 MPa. The SEM images of the fracture surfaces of 2nd, 3rd, 4th, and 5th specimens are shown in Figs. 6–9. The fracture surfaces of 2nd sample showed a relatively dense structure in Fig. 6. Nevertheless, there was no distinct different between the SEM images of the 2nd sample and the pure SiC sample. It may be caused by the following reason. Firstly, ZrO$_2$ fibers may be smashed during the ball milling process. This process explains why rare fibers were presented in Fig. 6. Second, some fibers cracked because of the volume shrinkage during the process of hot pressing. In addition, ZrO$_2$ fibers and the matrix may undergo a chemical reaction. With the increase of the number of ZrO$_2$ fibers, the rupture surfaces of the fibers could be found in the SEM images, as indicated by the arrows in Figs. 7–9. The size of ZrO$_2$ fibers was greater than SiC, which caused the mismatch of the interface between the two materials and reduced the relative density and hardness of the composites. In addition, short fibers act as barrier to restrict
Fig. 5. SEM of the fracture surfaces of the 1st sample.

Fig. 6. SEM of the fracture surfaces of the 2nd sample.

Fig. 7. SEM of the fracture surfaces of the 3rd sample.

Fig. 8. SEM of the fracture surfaces of the 4th sample.

Fig. 9. SEM of the fracture surfaces of the 5th sample.
The fracture toughness expressed an increasing tendency for all samples except the 5th sample, and the highest value of 553 ± 30 MPa was observed in the 4th sample. The ZrO2 fibers and SiC powders were distributed uniformly in the sintered composites, according to the SEM images. According to the SEM in Fig. 8, the section of ZrO2 fibers was uniform, and the diameter of SiC was equally distributed; as a result, the highest binding energy of interface corresponded to the 4th sample. In addition, Li et al. reported that ZrO2 would change its crystal structure from the tetragonal phase (t-phase ZrO2) to the monoclinic phase (m-phase ZrO2) at 1170°C. During the transition process, the volume and geometry of ZrO2 would change, thereby absorbing the energy from the system. Consequently, it will prevent the crack grown to enhance the toughness and strength of ceramics.18) In the present experiments, the change mentioned in the aforesaid theory of ZrO2 fibers acted as an intensive element to reinforce the mechanical properties of the composites. However, when the amount of ZrO2 fibers increase, the mixed materials become aggregated or pocket-like, thereby reducing the toughness and strength of the SiC/ZrO2 composites. In addition, the porosity of the composites was influenced by the phase change of ZrO2. The higher ratio of ZrO2 fibers additives, the more non-uniform the composites became. Therefore, the excellent microstructure and outstanding interfacial adhesion of the 4th sample enabled the new phase of ZrC.22) In the present study, ZrO2/SiC composites were successfully fabricated via vacuum hot pressing at 1800°C for 60 min under a pressure of 50 MPa with 0, 5, 10, 15, and 20% of ZrO2 short fibers in volume. According to the analysis of the SEM images, the sample of pure SiC had the densest microstructure. The relative density of the composites became smaller when more ZrO2 fibers were added, and the highest relative density of 94.18% was found for pure SiC. The ZrC phase, which was produced by the reaction of ZrO2 and SiC, was discovered in the XRD patterns of the composites. The fracture toughness and bending strength increased with the addition of fibres up to 20% ZrO2 fibres, in contrast to the change of the relative density with the addition of fibres. The SiC/15% ZrO2 composites presented the best mechanical properties, with the bending strength of 553 ± 30 MPa and the fracture toughness of 7.4 ± 0.4 MPa-m1/2. The hardness would be higher if more ZrO2 fibres were added. Consequently, the 1st sample exhibited the highest value of 13.01 ± 0.11 GPa among these composites.

### Table 1. Mechanical properties of SiC/ZrO2 composites

| Samples | Relative density (%) | Hv (GPa) |σb (MPa) |KIC (MPa·m−1/2) |
|---------|----------------------|----------|---------|----------------|
| 1       | 94.18                | 13.01 ± 0.11 | 508 ± 31 | 6.2 ± 0.5     |
| 2       | 93.69                | 12.61 ± 0.10 | 511 ± 25 | 6.5 ± 0.3     |
| 3       | 91.82                | 12.55 ± 0.08 | 548 ± 28 | 6.9 ± 0.8     |
| 4       | 84.45                | 12.38 ± 0.11 | 553 ± 30 | 7.4 ± 0.4     |
| 5       | 82.27                | 12.13 ± 0.12 | 514 ± 24 | 6.7 ± 0.4     |

X-ray diffraction patterns of these five specimens sintered at 1800°C with the pressure of 50 MPa for 60 min were shown in Fig. 10. The peaks of the SiC and ZrO2 representing the main phases and the impurity phase ZrC appeared in the XRD patterns of the 2nd, 3rd, 4th and 5th samples. The reaction between ZrO2 and SiC during the process of hot pressing promoted the formation of the new phase of ZrC:22)

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2ZrO_2 + 3SiC \rightarrow 2ZrC + 3SiO (g) + CO (g) \tag{1}
\]

SiO was formed as gaseous materials that were not detected via XRD. However, ZrC was detected in the XRD pattern of the 1st sample; the most probable source of ZrO2 was from the ball mill. The peaks of ZrO2 were ascending with the increase of the volume ratio variation trend of generally, which was in agreement with the predicted result. However, the peaks of SiC were opposite to the peaks of ZrO2. The highest peak of SiC was observed in the 1st sample, indicating that the sample had the highest degree of crystallization. Hence, the 1st sample with the greatest degree of crystallinity exhibited the highest hardness value, in accord with the measured value.

### Acknowledgements
Authors appreciate the financial support of the National Natural Science Foundation of China under the Grant No. 51372099, the Natural Science Foundation of Shandong Province (Grant no. ZR2012EMI05) and the Doctoral Fund of University of Jinan (XBS1310). Authors also appreciate the financial supported by Program for Scientific research innovation team in Colleges and universities of Shandong Province.

### References
1) N. Padmavathi, P. Ghosal and K. K. Ray, Compos. Sci. Technol., 106, 55–59 (2015).
2) S. X. Bai, R. Wang and M. Li, Ceram. Int., 41, 5644–5647
3) R. H. Dong, W. S. Yang, P. Wu, M. Hussain, Z. Y. Xiu, G. H. Wang and P. P. Wang, Mater. Charact., 103, 37–41 (2015).
4) Y. Li, F. P. Huang and Z. H. Liang, Ceramics, 5, 36–41 (2007).
5) W. Chai, Q. F. Deng, Y. Y. Wang, Z. Li and J. L. Yuan, Light Industry Machinery, 30, 117–120 (2012).
6) N. I. Baklanova, O. I. Kiselyova, A. T. Titov and T. M. Zima, J. Eur. Ceram. Soc., 28, 1687–1696 (2008).
7) C. X. Hu and X. F. Yu, Journal of Wudang (Natural Sciences), 18, 52–55 (1998).
8) Q. G. Fu, J. P. Zhang, Z. Z. Zhang, H. J. Li and C. Sun, Trans. Nonferrous Met. Soc. China, 23, 2113–2117 (2013).
9) G. S. Tian, S. Li and Z. P. Xie, J. Chin. Ceram. Soc., 12, 1520–1527 (2014).
10) M. A. Sharif and H. Suyoshi, Ceram. Int., 35, 349–358 (2009).
11) D. Scitini, L. Pienti, D. D. Fabbriche, S. Guicciardi and L. Silvestroni, Ceram. Int., 40, 4819–4826 (2014).
12) J. Lin, X. H. Zhang, Z. Wang and W. B. Han, Scr. Mater., 64, 872–875 (2011).
13) D. J. Chen, L. Xu, X. H. Zhang, B. X. Ma and P. Hu, Int. J. Refract. Met. Hard Mater., 27, 792–795 (2009).
14) L. Silvestroni, E. Landi, K. Bejtka, A. Chiodoni and D. Sciti, J. Eur. Ceram. Soc., 35, 4377–4387 (2015).
15) B. Malmal Moshaghion, A. L. Ortiz, D. Gómez-Garcia and A. Domínguez-Rodríguez, J. Eur. Ceram. Soc., 33, 1395–1401 (2013).
16) L. M. Hu, F. Gao and W. Chen, J. Synth. Cryst., 38, 265–270 (2009).
17) S. Feng, Z. Wang, Y. S. Ding and G. P. Shi, Journal of University of Jinan (Sci. & Tech), 27, 123–126 (2015).
18) J. Li, C. Li, H. Xia, F. Liu, Y. Li, L. Yang and F. Yang, Rare Met. Ceram. Carbides, 40, 38–47 (2012).
19) J. Lin, Y. Huang and H. A. Zhang, Ceram. Int., 40, 16811–16815 (2014).
20) H. L. Tang, X. R. Zeng, X. B. Xiong, L. Li and J. Z. Zou, Tribology International, 42, 823–827 (2009).
21) J. Lin, Y. Huang and H. A. Zhang, Ceram. Int., 41, 2690–2698 (2015).
22) N. P. Vafa, M. S. Asl, M. J. Zamharir and M. G. Kakroudi, Ceram. Int., 41, 8388–8396 (2015).