Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 36 (2010) 1787–1790

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Fabrication of SiC_w reinforced ZrB_2-based ceramics

Yiguang Wang *, Miao Zhu, Laifei Cheng, Litong Zhang

National Key Laboratory of Thermostructure Composite Materials, Northwestern Polytechnical University, Xi'an 710072, China

Received 23 December 2009; received in revised form 5 January 2010; accepted 2 March 2010
Available online 21 May 2010

Abstract

ZrB_2-based ceramics with SiC_w were produced by hot pressing at 1750 °C for 1 h from mixed powders after adding liquid polycarbosilane. The obtained ZrB_2-SiC_w composites had toughness up to 7.57 MPa $m^{1/2}$, which was much higher than those for monolithic ZrB_2, SiC particles reinforced ZrB_2 composites, and other ZrB_2–SiC_w composites directly sintered at high temperatures. The added liquid polycarbosilane could reduce the sintering temperatures and restrict the reaction of matrix with whisker, which led to fewer damages to the whisker and high fracture toughness.

Keywords: A: Sintering; B: Whiskers; C: Toughness and toughening

1. Introduction

Zirconium diboride (ZrB_2), one of the ultrahigh temperature ceramics (UHTCs), has many excellent properties such as high melting point, good chemical stability, and high strength, which make it suitable for high temperature structural applications [1–6]. By adding SiC particles to ZrB_2, the resultant ZrB_2–SiC ceramics have better strength and oxidation resistance than ZrB_2 ceramics alone [1,4–8]. However, the intrinsic brittleness of ceramics results in the catastrophic failure and poor thermal shock resistance of ZrB_2-based ceramics, which limit their engineering applications. Many efforts have been made to improve their toughness [9–11]. SiC whisker (SiC_w) with high orientation has been used to reinforce ceramics like ZrO_2, Al_2O_3, Si_3N_4, TiB_2 and $MoSi_2$ [11–18]. In the last few years, SiC_w reinforced ZrB_2 ceramics have been intensively studied [11,19,20]. However, SiC_w reinforced ZrB_2 ceramics did not show much higher toughness than the un-reinforced one [11,19,20]. This is due to the following two reasons: firstly, the sintering temperatures for the ZrB_2-based ceramics are as high as 1800–2200 °C [1–3,7–8]. At such high temperatures, the partial damage of SiC_w results in the degradation of its toughness. Secondly, SiC will react with the oxide impurity (ZrO_2) on the surface of ZrB_2 particles during sintering at high temperatures [20], which leads to further degradation of SiC_w.

In order to fully fulfill the function of SiC_w, low temperature sintering of ZrB_2 is required as well as restricting the reactions between ZrO_2 and SiC_w. Our previous study [21] indicated that addition of polycarbosilane (PCS) to the starting powders can reduce the sintering temperatures to as low as 1750 °C. Moreover, the PCS can provide carbon and SiC during pyrolysis at high temperatures [7–8,21]. These pyrolytic products can remove the oxides impurities on the surface of ZrB_2 particles [7–8,21], which might prevent ZrO_2 from reacting with SiC_w. In this paper, ZrB_2–SiC_w powders impregnated with PCS were hot-pressed at 1750 °C. The fracture toughness of these ceramics was measured, and their microstructures were characterized. The reinforced mechanism in the ZrB_2–SiC_w–PCS system was discussed based on these results.

2. Experimental procedure

ZrB_2 powder (99.9% purity, 0.5 μm, Beijing Mountain Technical Development Center for Non-ferrous Metals, China), SiC_w (99% purity, Alfa Aesar, MA, USA), and liquid polycarbosilane (PCS, Xia Men University, China) were used as the starting materials. The SiC_w has an average diameter of 1.5 μm and a length of about 18 μm. The PCS is the precursor of SiC ceramics, and its pyrolysis process was described elsewhere [22]. The mixture of ZrB_2 and SiC_w was ball-milled

---

* Corresponding author. Tel.: +86 29 88494914; fax: +86 29 88494620.
E-mail address: wangyiguang@mail.nwpu.edu.cn (Y. Wang).

0272-8842/$36.00 © 2010 Published by Elsevier Ltd and Techna Group S.r.l.
doi:10.1016/j.ceramint.2010.03.006

for 5 h in a nylon vial with ethanol as the grinding medium. After mixing, the slurry was dried in a vacuum oven. PCS was diluted by acetone and then mixed with ZrB_2–SiC_w powders uniformly. The weight ratio of PCS to ZrB_2 was varied from 0 to 1:7. The ZrB_2–SiC_w–PCS slurry was gradually dried by continuous stirring. The resulting mixed powders were then put into a graphite die, followed by hot pressing at 1750 °C for 1 h under a uniaxial pressure of 28 MPa in vacuum.

The morphologies and microstructures of the sintered ceramics were observed by scanning electron microscope (SEM, JEOL 6700F, Tokyo, Japan). The densities of specimens were measured by the Archimedes method with distilled water as medium. The flexural strength was measured using a three-point bending test (SANS CMT 4304, Sans Testing Machine, Shen Zhen, China) with a span of 20 mm. At least three samples with a dimension of 25 mm × 3 mm × 2.5 mm were used for the test. The loading rate was 0.5 mm/min. The toughness of ceramics was measured by single-edge notched beam (SENB) method. Its value was calculated based on the following equation [23]:

$$K_{1c} = \sigma_c\sqrt{a}Y = \frac{P_c S}{BW^{3/2}} f\left(\frac{c}{W}\right)$$

where P_c is the critical load, S the support span (20 mm in present study), B the width of samples (2.5 mm), W the height of the samples (5 mm), c the notch length (c/W is about 0.5). $f(c/w)$ can be expressed as the following [23]:

$$f\left(\frac{c}{W}\right) = 2.9\left(\frac{c}{W}\right)^{1/2} - 4.6\left(\frac{c}{W}\right)^{3/2} + 21.8\left(\frac{c}{W}\right)^{5/2} - 37.6\left(\frac{c}{W}\right)^{7/2} + 38.7\left(\frac{c}{W}\right)^{9/2}$$

3. Results and discussion

Previous study [7–8,21] indicated that PCS could greatly reduce the sintering temperature. However, the volatile products from PCS deteriorate the density of ceramics, thereby the strength of the final products. In order to get dense ZrB_2–SiC_w ceramics, different contents of PCS were used in the sintering process. The bulk density and flexural strength of

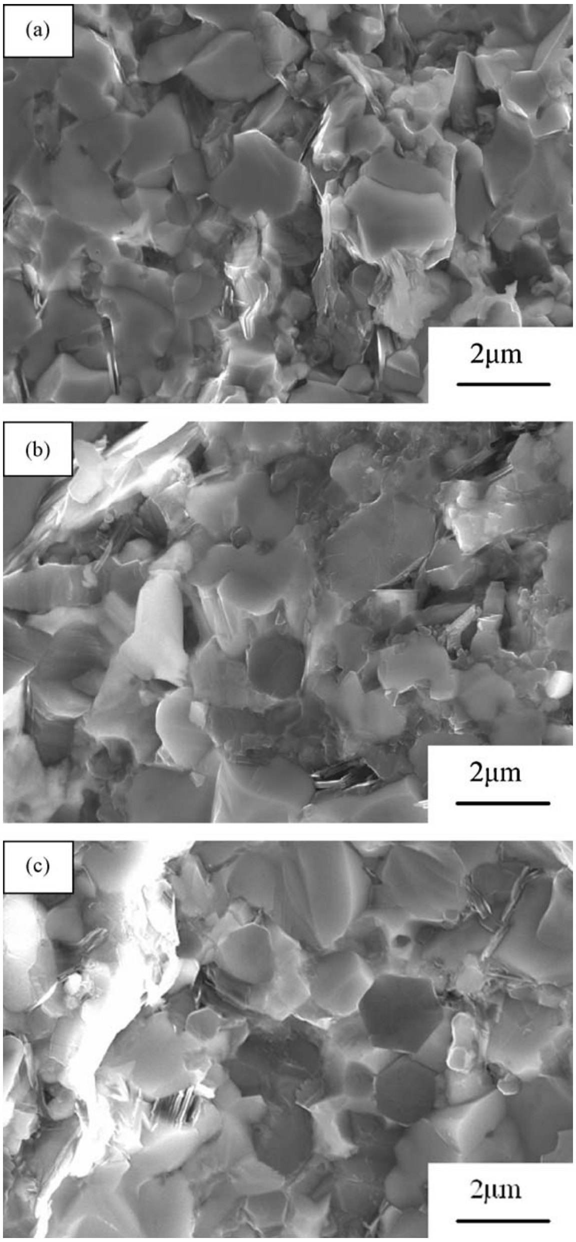

Fig. 2. SEM micrograph of the fracture surface of ZrB_2–SiC_w–ex-PCS ceramics with different PCS contents. (a) No PCS, (b) 14.3% PCS, (c) 9.1 wt% PCS.

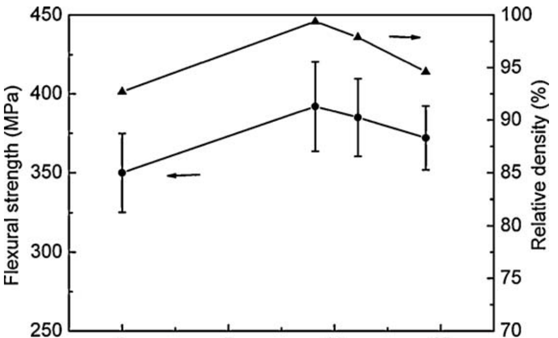

Fig. 1. Flexural strength and relative density of ZrB_2–SiC_w–ex-PCS ceramics obtained with different PCS contents.

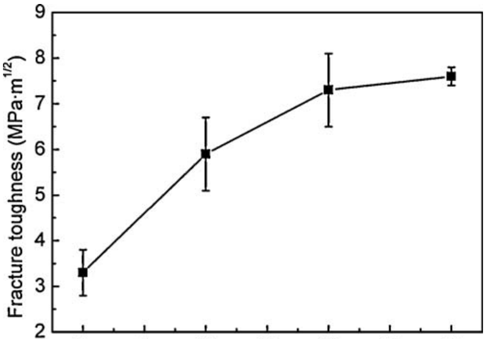

Fig. 3. Fracture toughness of ZrB_2–SiC_w–ex-PCS ceramics with different SiC whisker contents.

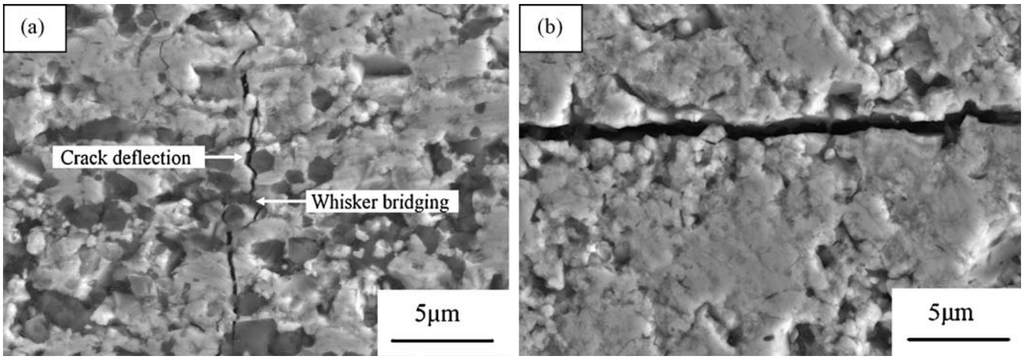

Fig. 4. SEM micrographs of indentation-induced crack propagation on a polished surface of (a) ZrB_2–SiC_w and (b) ZrB_2–ex-PCS.

sintered ceramics as a function of PCS content are shown in Fig. 1. It can be seen that the relative density and flexural strength of the ceramics first increases with increasing the PCS amount, go through a maximum for around 9.1 wt% added PCS and decreases beyond. When there is no PCS or PCS content is not enough, the ZrB_2–SiC_w ceramics cannot be fully densified (Fig. 2a) because the sintering temperature (1750 °C) is too low to get fully dense ceramics. More PCS means more volatile products during sintering, which will cause pores in ceramics (Fig. 2b). The 9.1 wt% of PCS is an optimal content in present study. By this addition of PCS, fully dense ZrB_2–SiC_w ceramics can be obtained (Fig. 2c).

The fracture toughness of fully dense ZrB_2–SiC_w–PCS ceramics as a function of SiC_w content is shown in Fig. 3. It can be seen that the fracture toughness increases with the increase in the content of SiC_w. The ZrB_2–PCS ceramics without SiC_w have a fracture toughness 3.25 MPa $m^{1/2}$, close to the reported values in the literature [7,8]. With the addition of SiC_w, the fracture toughness of ZrB_2-based ceramics is obviously enhanced. When the content of SiC_w is over 20 vol.%, the fracture toughness is over 7.33 MPa $m^{1/2}$, more than twice that of ZrB_2–PCS ceramics, and almost 50–70% larger than ZrB_2–SiC_p (4.0–4.4 MPa $m^{1/2}$ in references [1,5,9,24]). Compared with the reported fracture toughness of ZrB_2–SiC_w (5.97–6.0 in literature [11,20]), the value of our ZrB_2–SiC_w ceramics is about 25% higher. It is believed that the low sintering temperature and reduced surface reactions between SiC_w and ZrO_2 on the surface of ZrB_2 particles are the reason. As shown in Fig. 2c, the SiC_w still has hexagonal cross-section, without obviously being destroyed during sintering process, while the SiC_w treated at 1800 °C changed its shape [20].

To understand the toughening mechanism, the indentation cracks for ZrB_2–SiC_w and ZrB_2–PCS are compared in Fig. 4. The extensive interactions between cracks and whiskers are obvious (Fig. 4a). The cracks are deflected and bridged by the whiskers. The crack propagation with such interactions will consume more energy than the process without interactions. The fracture toughness is thus improved.

4. Conclusion

ZrB_2–SiC_w ceramics were produced from mixed powders impregnated with PCS by hot pressing at 1750 °C and 28 MPa. The PCS reduces the sintering temperature and the reactions between SiC_w and ZrO_2 on the surface of ZrB_2 particles, which protects SiC_w from being damaged during sintering process. The SiC_w can fully fulfill its function to deflect and bridge the cracks. The fracture toughness of ZrB_2–SiC_w thus increases. Its value is about twice higher than that of monolithic ZrB_2, and about 70% higher than that of ZrB_2–SiC_p. Since SiC_w is less damaged during sintering process, the toughness of ZrB_2–SiC_w in present work is about 25% higher than the reported data of ZrB_2–SiC_w.

Acknowledgements

This work is financially supported by the Chinese Natural Science Foundation (Grant #90716023) and by the Research Fund of State Key Laboratory of Solidification Processing (NWPU), China (Grant #21-TP2007).

References

[1] W.G. Fahrenholtz, G.E. Hilmas, I.G. Talmy, J.A. Zaykoski, Refractory diborides of zirconium and hafnium, J. Am. Ceram. Soc. 90 (5) (2007) 1347–1364.

[2] F. Monteverde, A. Bellosi, S. Guicciardi, Processing and properties of zirconium diboride-based composites, J. Eur. Ceram. Soc. 22 (2002) 279–288.

[3] A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, Pressureless sintering of zirconium diboride, J. Am. Ceram. Soc. 89 (2) (2006) 450–456.

[4] S.R. Levine, E.J. Opila, M.C. Halbig, J.D. Kiser, M. Singh, J.A. Salem, Evaluation of ultrahigh temperature ceramics for aeropropulsion use, J. Eur. Ceram. Soc. 22 (2002) 2757–2767.

[5] A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, D.T. Ellerby, High-strength zirconium diboride-based ceramics, J. Am. Ceram. Soc. 87 (6) (2004) 1170–1172.

[6] Y.J. Yan, Z.R. Huang, S.M. Dong, D.L. Jiang, Pressureless sintering of high-density ZrB_2–SiC ceramic composites, J. Am. Ceram. Soc. 89 (11) (2006) 3589–3592.

[7] X.J. Zhou, G.J. Zhang, Y.G. Li, Y.M. Kan, P.L. Wang, Hot pressed ZrB_2–SiC–C ultra high temperature ceramics with polycarbosilane as a precursor, Mater. Lett. 61 (2007) 960–963.

[8] S.M. Zhu, W.G. Fahrenholtz, G.E. Hilmas, Enhanced densification and mechanical properties of ZrB_2–SiC processed by a preceramic polymer coating route, Scripta Mater. 59 (2008) 123–126.

[9] W.B. Tian, Y.M. Kan, G.J. Zhang, P.L. Wang, Effect of carbon nanotubes on the properties of ZrB_2–SiC ceramics, Mater. Sci. Eng. A 487 (2008) 568–573.

[10] F.Y. Yang, X.H. Zhang, J.C. Han, S.Y. Du, Mechanical properties of short carbon fiber reinforced ZrB_2–SiC ceramic matrix composites, Mater. Lett. 62 (2008) 2925–2927.

[11] X.H. Zhang, L. Xu, S.Y. Du, J.C. Han, P. Hu, W.B. Han, Fabrication and mechanical properties of ZrB_2–SiC_w ceramic matrix composite, Mater. Lett. 62 (2008) 1058–1060.

[12] P.F. Becher, G.C. Wei, Toughening behavior in SiC-whisker-reinforced alumina, J. Am. Ceram. Soc. 67 (1984) C267–C269.

[13] G.C. Wei, P.F. Becher, Development of SiC-whisker-reinforced ceramics, Am. Ceram. Soc. Bull. 62 (2) (1985) 298–304.

[14] A. Bellosi, G. De Portu, Hot-pressed Si_3N_4–SiC whisker composites, Mater. Sci. Eng. A 109 (1989) 357–362.

[15] G.Y. Lin, T.C. Lei, S.X. Wang, Y. Zhou, Microstructure and mechanical properties of SiC whisker reinforced ZrO_2 (2 mol% Y_2O_3) based composites, Ceram. Int. 22 (1996) 199–205.

[16] C.A. Wang, Y. Huang, H.X. Zhai, The effect of whisker orientation in SiC whisker-reinforced Si_3N_4 ceramic matrix composites, J. Eur. Ceram. Soc. 19 (1999) 1903–1909.

[17] L.Y. Zheng, Y.P. Jin, P.X. Li, High-temperature mechanical behavior and microstructure of SiC-whisker-reinforced $MoSi_2$ composites, Comp. Sci. Technol. 57 (1997) 463–469.

[18] J. Deng, X. Ai, Microstructure, Mechanical properties of hot-pressed TiB_2–SiC_w composites, Mater. Res. Bull. 33 (1998) 575–582.

[19] X.H. Zhang, L. Xu, W.B. Han, P. Hu, L. Weng, J.C. Han, S.Y. Du, Microstructure and properties of silicon carbide whisker reinforced zirconium diboride ultra-high temperature ceramics, Solid State Sci. 11 (2009) 156–161.

[20] P. Zhang, P. Hu, X.H. Zhang, J.C. Han, S.H. Meng, Processing and characterization of ZrB_2–SiC_w ultra-high temperature ceramics, J. Alloys Compd. 472 (2009) 358–362.

[21] M. Zhu, Y.G. Wang, Pressureless sintering ZrB_2–SiC ceramics at low temperatures, Mater. Lett. 63 (2009) 2035–2037.

[22] H.B. Li, L.T. Zhang, L.F. Cheng, Y.G. Wang, Z.J. Yu, M.H. Huang, H.B. Tu, H.P. Xia, Polymer–ceramic conversion of a highly branched liquid polycarbosilane for SiC-based ceramics, J. Mater. Sci. 43 (2008) 2806–2811.

[23] American Society for Testing Materials (ASTM 399-74). Standard test method for plan-strain fracture toughness of metallic materials. E399-74. Philadelphia, PA, ASTM, 1983, pp. 923–936.

[24] J.R. Fenter, Refractory diborides as engineering materials, SAMPE Q. 2 (1971) 1–15.