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Processing and characterization of ZrB_2–SiC_W ultra-high temperature ceramics

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ABSTRACT

SiC whisker-reinforced ZrB_2 ultra-high temperature ceramics containing 20 vol.% whisker were prepared in the temperature range of 1750–2000 °C by hot pressing. The microstructure and mechanical properties of ZrB_2–SiC_W ultra-high temperature ceramics were examined. The results showed that SiC whiskers were not stable in the ZrB_2 matrix above 1900 °C and degenerated into particles. The sintering temperature for this material system should be lower than 1800 °C to obtain high performance of ZrB_2–SiC_W. Significant improvement in fracture toughness of the material was obtained at 1800 °C using fine ZrB_2 particles compared to ZrB_2 ceramic. The improvement of toughness was mainly attributed to whisker bridging and cracking deflection around whiskers.

1. Introduction

Ultra-high temperature ceramics (UHTCs) include borides, carbides, and nitrides with melting temperatures above 2700 °C [1]. UHTCs have been investigated for high temperature applications, including thermal protection systems for hypersonic aerospace vehicles, high temperature electrodes, and molten metal crucibles [2–5]. Recently, ZrB_2-based ceramics have attracted much attention because of their unique combination of low density, high melting temperature and thermal shock resistance as well as excellent mechanical and chemical stability at high temperatures [6–10].

Generally pressure-assisted sintering techniques at very high temperature (>1900 °C) are required to achieve complete densification of pure ZrB_2 material due to its strong covalent bonding and low self-diffusion coefficient. Several studies have shown that the addition of SiC to ZrB_2 powders has beneficial effects not only on sinterability, but also on mechanical properties and resistance to oxidation [9–12]. Although great efforts have been devoted to enhancing the mechanical properties and much progress has been made recently, the susceptibility to brittle fracture is still a major issue for the use of ZrB_2-based UHTCs. Whisker-reinforced ceramic matrix composites are of promising materials, especially for high temperature applications [13–15]. SiC whiskers, combining high strength, elastic modulus and chemical inertness at elevated temperature, are the main reinforcements incorporated into ceramic materials [14–17]. Unfortunately, few studies on SiC whisker-reinforced ZrB_2 ultra-high temperature ceramics have been reported in open literature.

The purpose of the present study is to investigate the effect of SiC whisker on the mechanical properties of ZrB_2-based UHTCs. The effect of the temperature and characteristic of SiC whisker were also studied.

2. Experimental procedures

Commercially available raw materials were used in this study. The ZrB_2 powders (Northwest Institute for Non-ferrous Metal Research, China) had a purity of >99% and mean particle sizes of 2 and 5 μm, respectively. β-SiC whisker (99% pure, Alfa Aesar, MA, USA) had an average size of 18 μm in length and 1.5 μm in diameter. The powders were attrition milled in polymer-coated bucket charged with ethanol at 180 rpm, using WC balls for 8 h and then dried in a rotating evaporator (Model Rotavapor 205). The rotational speed was restricted in 220 rpm for preventing SiC whiskers from damage (Fig. 1). The as-milled power mixtures were hot-pressed in a boron nitride coated graphite die in the temperature range of 1750–2000 °C for 1 h under a uniaxial load of 30–40 MPa in Ar atmosphere. The precise heating schedule has been described elsewhere [12].

The bulk density of hot pressed billets was determined using the Archimedes' method, while the relative density was estimated by the rule of mixture. Specimens were polished and ultrasonic cleaned. Flexural strength in a three-point configuration was tested on 3 mm × 4 mm × 36 mm chamfered bar, using 24 mm as the span and a crosshead speed of 0.5 mm min^{-1} (Instron-1186, Instron Corporation, Canton, MA). Fracture toughness (K_{IC}) was evaluated using the single edge notched beam method on 20 mm × 4 mm × 2 mm bars, on the same jig used for the flexural strength with a crosshead speed of 0.05 mm min^{-1}. Five samples were used for both fracture toughness and flexural strength tests. The resulting microstructure of polished and fractured sections of the sintered samples were studied by a scanning electron microscopy/energy dispersive spectroscopy (FEI Sirion, Holland). Phase composition was determined via X-ray diffractometry (Rigaku, Japan) using Cu Kα radiation.

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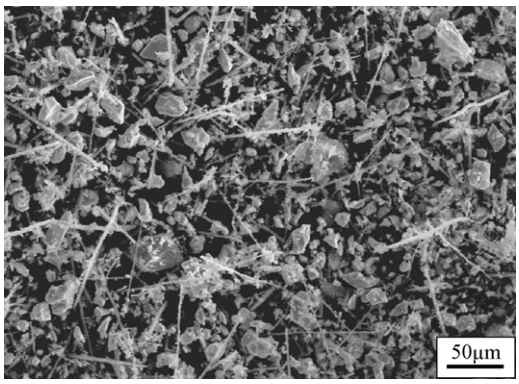

Fig. 1. Milled materials.

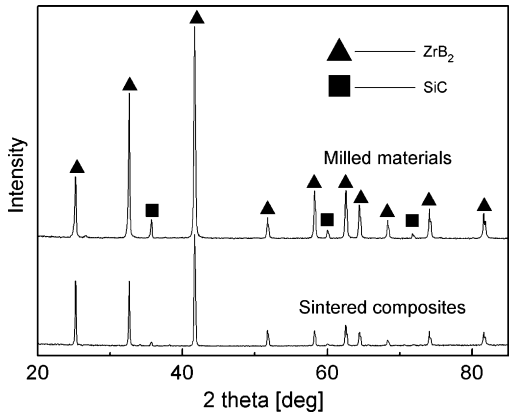

Fig. 3. XRD patterns of ZrB_2–SiC_W milled materials and sintered composites.

3. Results and discussion

The bulk density of the ZrB_2–20 vol.% SiC_W composites hot-pressed at 2000 °C was 5.44 g/cm^3, which corresponds to 98.6% of the theoretical density estimated with the rule of mixture. The flexural strength and fracture toughness of ZrB_2–SiC_W composites at room temperature are 510 ± 25 MPa and 4.05 ± 0.20 MPa m$^{1/2}$, respectively. However, the flexural strength and the fracture toughness of SiC whisker-reinforced ZrB_2 were not significantly increased compared with those without reinforcements. The values of flexural strength and the fracture toughness are similar to those of SiC particle reinforced ZrB_2 composites. Amazingly, SiC whiskers have been degenerated into particles (Fig. 2). Furthermore, the microstructure of the SiC whisker reinforced ZrB_2 composite is very similar to that of the SiC particle reinforced (not shown).

SiC whiskers were homogeneously distributed after milling as shown in Fig. 1. However, no appreciable SiC whisker was observed in the SEM micrographs neither for the polished surface nor for fracture surface of ZrB_2–SiC_W composites (Fig. 2), indicating that the transformation of SiC whiskers occurred during the fabrication process. The main reasons associated to disappearance of SiC whisker may include: (a) fragmentation of whisker due to applied pressure; (b) chemical reaction between whisker and matrix; (c) instability of SiC whisker in ZrB_2 matrix. The XRD profiles from the mixed powders and hot pressed material are shown in Fig. 3. According to the XRD patterns, only ZrB_2 and SiC phases are observed in both the mixed powders and the obtained composites, which indicates that there is no appreciable chemical reaction between whisker and matrix in sintering process. Thus, the assumption of reaction between SiC whisker and ZrB_2 particle as primary cause for the failure of SiC whisker can be ruled out, since no new phase was detected.

Many SiC whiskers were found in ZrB_2–10 vol.% SiC_W–40 vol.% ZrC composites (not shown), which were prepared at the same conditions as ZrB_2–SiC_W composites. It is significant to note that the initial SiC whisker content in the ZrB_2–SiC_W–ZrC composites is only half of that of ZrB_2–SiC_W composites. In contrast, no SiC whisker was observed in ZrB_2–SiC_W composites though it contained a larger SiC whisker content than the ZrB_2–SiC_W–ZrC composites. Given the difference of the SiC whisker content and the same sintering processing used by two type of composites, the disappearance of whiskers in the ZrB_2–SiC_W composites due to fragmentation of whisker is unlikely since same applied pressure was used. Therefore, the disappearance of the SiC_W is most likely due to the instability of the SiC whisker in ZrB_2 at this temperature. However, the thermophysical properties of SiC whisker at high temperatures, especially at temperature above 2000 °C, are very limited in open literature. To better understand the thermal stability of SiC whisker at high temperature, loose SiC whiskers were processed in the same heating rate a dwell time of 1 h at 2000 °C. The basic morphology of

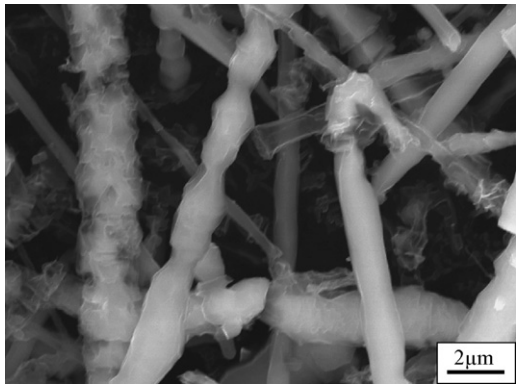

Fig. 4. SEM micrograph of the heat-treated SiC whiskers.

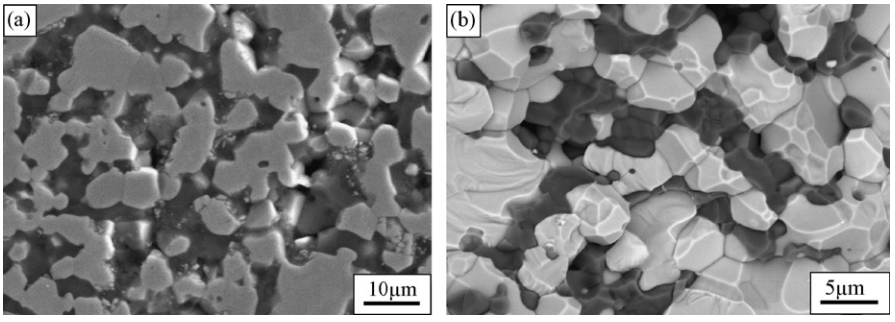

Fig. 2. SEM micrographs of the polished (a) and fracture (b) surface of ZrB_2–SiC_W composites.

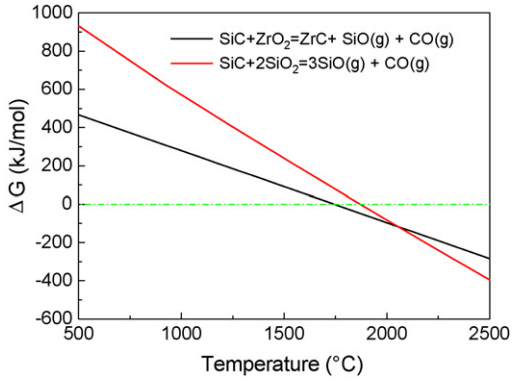

Fig. 5. Gibbs free energies of reactions (1) and (2) as a function of temperature.

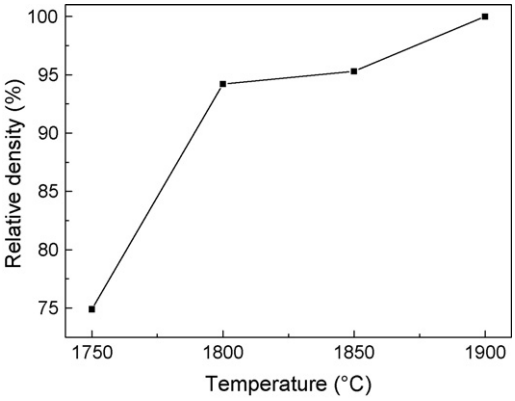

Fig. 6. Theoretical density vs. temperature.

SiC whiskers were retained at 2000 °C though some of them showed moderate degradation (Fig. 4).

In fact, oxides impurity (SiO_2, ZrO_2 and B_2O_3) exist on the surfaces of the SiC whiskers and the ZrB_2 particles. At high temperatures, these oxides would be reacted with SiC whiskers resulting in significant degradation of the SiC whiskers as shown in Fig. 2

$$SiC + 2SiO_2 = 3SiO(g) + CO(g) \quad (1)$$

$$SiC + ZrO_2 = ZrC + SiO(g) + CO(g) \quad (2)$$

The Gibbs free energies ΔG_T° of reactions (1) and (2) at different temperatures ranging from 500 to 2500 °C are calculated and shown in Fig. 5. The reactions (1) and (2) will be favorable at 1870 and 1750 °C, respectively. Therefore, a lower hot-pressing temperature should be employed for the preparation of ZrB_2–SiC_W ultra-high temperature ceramics in order to prevent SiC whiskers from significant degradation.

To investigate the effect of temperature on the microstructure of ZrB_2–SiC_W composites, different hot pressing temperatures were employed ranging from 1750 to 1900 °C. Densification and sintering temperature are two contradictory factors for the preparation of ZrB_2–SiC. The introduction of Si_3N_4 has succeeded in improving both the density and mechanical properties of ZrB_2-based UHTCs [18]. Therefore, we used silicon nitride as a sintering aid (5 vol.%) to improve the powder sinterability of zirconium diboride at lower temperatures. The relative density of the hot pressed composites remarkably increased as the temperature increased from 1750 to

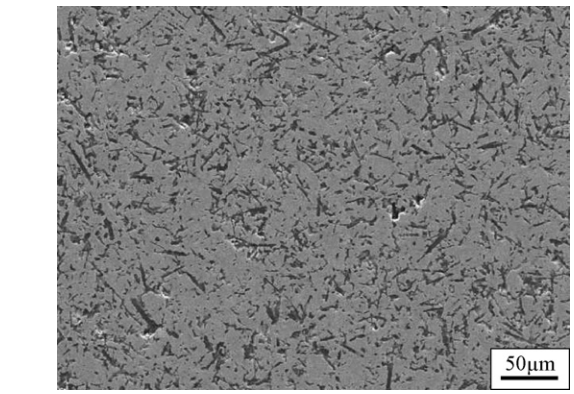

Fig. 8. SEM micrograph from a polished cross-section of the ZrB_2–SiC_W hot-pressed at 1800 °C.

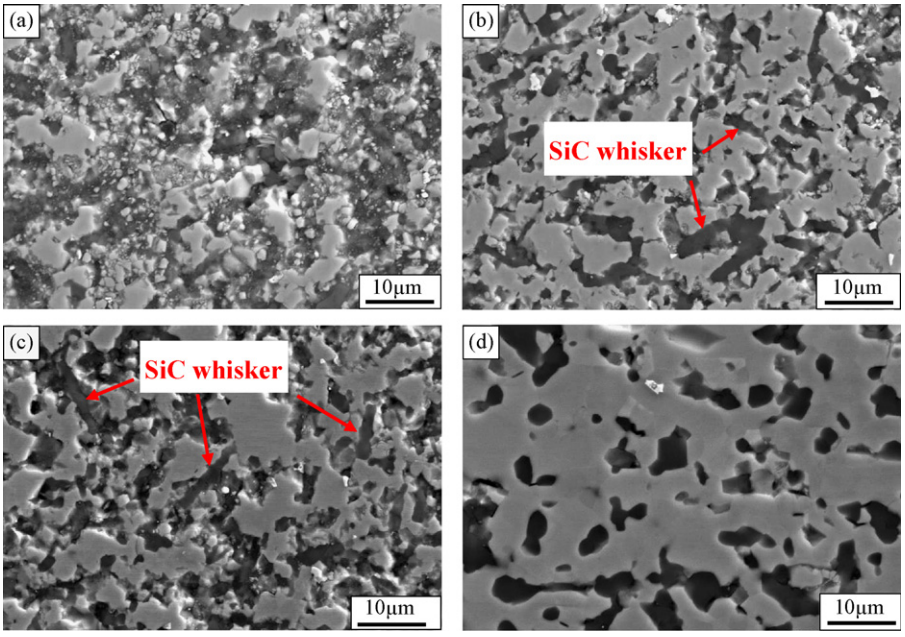

Fig. 7. SEM micrographs of ZrB_2–SiC_W composite sintered at different temperatures: (a) 1750 °C; (b) 1800 °C; (c) 1850 °C; (d) 1900 °C.

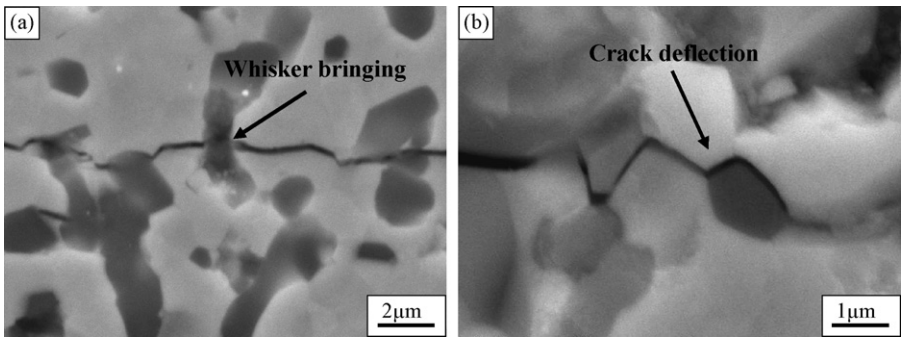

Fig. 9. SEM micrograph of the crack propagation from the Vickers indentation for the ZrB_2–SiC_W hot-pressed at 1800 °C: (a) whisker bridging and (b) crack deflection.

1800 °C, and then slightly increased with further increase of temperature (Fig. 6). Fig. 7 presents the microstructure of ZrB_2–SiC_W composites at different temperatures. The material was not well densified at the temperature of 1750 °C, which is consistent with the lower relative density measured for this material, which was 74.9%. A large amount of porosity was also observed for hot pressed composites both at 1800 and 1850 °C as a sintering aid was introduced. Fully dense ZrB_2–SiC_W composites were obtained by hot-pressing at 1900 °C. However, SiC whiskers were not observed at 1900 °C, suggesting that they are unstable at this temperature. This result indicated that the hot-pressing temperature for preparation of ZrB_2–SiC_W should be lower than 1900 °C. Apparently, the contradiction between densification and degradation of SiC whisker is a major issue for present material since higher temperature is beneficial for densification, whereas it is harmful to the performance of the SiC whisker.

It is well known that the use of fine powders has beneficial effects on the densification of ZrB_2–SiC, thereby a fine ZrB_2 powder (2 μm) was also chosen as starting material in this study. Fig. 8 shows SEM micrograph from a polished surface of the hot-pressed ZrB_2–SiC_W composite using fine ZrB_2 powder: it reveals a nearly full-dense ZrB_2–SiC_W composite and that the majority of SiC whiskers were retained after hot pressing. Moreover, the SiC whiskers were homogenously distributed in ZrB_2 matrix as can be seen in Fig. 8. The measured fracture toughness of ZrB_2–SiC_W composite was 6.0 ± 0.30 MPa $m^{1/2}$, which is ~71% higher than that of the ZrB_2 ceramic without SiC whisker and is also higher than SiC particle reinforced ZrB_2 composite. Fig. 9 shows the path of a crack produced by Vickers indentation on the polished surface of the hot-pressed ZrB_2–SiC_W composite. Whisker bridging and crack deflection were observed for the composite. Fracture surface examined by SEM shows some whiskers were pulled out and a predominantly transgranular matrix fracture mode (Fig. 10). However, the majority of SiC whiskers were fractured directly and the whisker pullout is very limited. High interfacial bonding strength of ZrB_2–SiC_W interface and the decreased strength of SiC whisker are probably responsible for the limited whisker pullouts. The increase in fracture toughness of the ZrB_2–SiC_W composite was mainly due to SiC whisker bridging and crack deflection. The control of whisker/matrix interfaces and the densification without degradation of SiC whisker for this material will be made in future work. Other densification methods should be taken into account in the future for fabrication this composite with high performance, such as spark plasma sintering due to rapid densification resulting in reduced damage of SiC whisker.

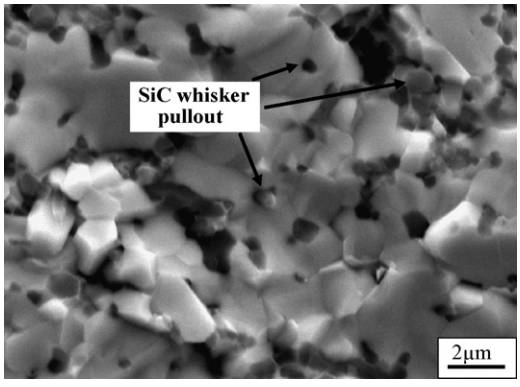

Fig. 10. SEM micrograph of the fracture surface of ZrB_2–SiC_W hot-pressed at 1800 °C.

4. Conclusions

The flexural strength and fracture toughness at room temperature of ZrB_2–SiC_W composites hot-pressed at 2000 °C are 510 ± 25 MPa and 4.05 ± 0.20 MPa $m^{1/2}$, respectively. However, the addition of SiC whiskers to the ZrB_2 matrix did not significantly increase the flexural strength and fracture toughness compared to those for the monolithic ZrB_2 due to the damage of SiC whiskers. Further study shows that SiC whiskers were not stable in ZrB_2 matrix above 1900 °C and degenerated into SiC particles. The sintering temperature for this material system should be lower than 1800 °C to obtain high performance of ZrB_2–SiC_W. A nearly full-dense ZrB_2–SiC_W composite was obtained at 1800 °C using fine ZrB_2 particles. The fracture toughness of ZrB_2–SiC_W composite was 6.0 ± 0.30 MPa $m^{1/2}$, which is ~71% higher than that of ZrB_2 ceramic without SiC whisker and also higher than SiC particle reinforced ZrB_2 composites. The toughness mechanism was mainly attributed to whisker bridging and cracking deflection around whiskers.

Acknowledgements

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