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Short communication

Effect of high temperature heat treatment on ZrB_2–SiC composites added with Yb_2O_3

Wei-Ming Guo[a,b], Zhen-Guo Yang[a,*], Guo-Jun Zhang[b,**]

[a]*Department of Materials Science, Fudan University, Shanghai 200433, China*

[b]*State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Shanghai 200050, China*

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Abstract

ZrB_2-20 vol% SiC composites added with 3 vol% Yb_2O_3 were hot-pressed at 1900 °C, and then heat-treated at 2000 °C in argon. The effect of heat treatment on phase composition, microstructure, and mechanical properties of the composites was investigated. Results showed that the high temperature heat treatment led to the depletion of Yb-containing phases by decomposition or evaporation, the formation of some pores at multiple-grain junctions, significant microstructural coarsening with the increase of ZrB_2 grain size from ~1.9 μm to ~4.8 μm, and the change of fracture mode from mixed inter/transgranular to fully transgranular. In addition, Vickers' hardness, fracture toughness and flexural strength were severely degraded after heat treatment.

Keywords: C. Mechanical properties; ZrB_2–SiC; Yb_2O_3; Heat treatment; Microstructure

1. Introduction

Because of excellent combination of properties such as low density, high melting temperature and thermal conductivity, ZrB_2 ceramics are especially promising for high-temperature structural applications [1]. However, the application of monolithic ZrB_2 is limited by its poor sinterability and mechanical properties. Considerable studies have shown that SiC as second phase was very effective to improve the densification, strength, fracture toughness, and oxidation resistance [2,3].

To lower the sintering temperature and improve the properties, a lot of additives were used in the ZrB_2–SiC composites such as elementary substance (e.g., boron, carbon) [4,5], carbides (e.g., VC, WC) [6,7], nitrides (e.g., AlN, Si_3N_4) [8,9], rare-earth oxides (e.g., Y_2O_3, Yb_2O_3) [10,11], and so on. Several studies have shown that the carbon, boron, or carbides were effective in promoting the densification of ZrB_2–SiC composites by reacting with and removing oxide impurities [4–7]. The addition of Yb_2O_3 could also enhance densification and result in the increase of hardness and fracture toughness [11].

ZrB_2-based composites are often considered to be used in some extreme environments at temperature above 1800 °C. So, it will be very important to investigate the high temperature effect on microstructure and properties of the composites. Some studies on the high temperature effect in several ceramic systems have been conducted by heat treatment method, [12–15]. The main purpose was to evaluate the high-temperature stability of microstructure and composition. For example, the thermal stability of ZrB_2–SiC composites was investigated by heat treatment at 2000 °C in argon [14]. Results showed that the ZrB_2 grain growth rate in the ZrB_2-30 vol% SiC was 25 times lower than that in the ZrB_2-10 vol% SiC, and the high temperature heat treatment had little effect on Vickers' hardness and fracture toughness of ZrB_2–SiC composites. The microstructural evolution of ZrB_2–$MoSi_2$ composites was also studied during heat treatment at 2000 °C in argon [15]. Due to the decomposition of $MoSi_2$ phase, the heat-treated

*Corresponding author. Tel.: +86 21 65642523; fax: +86 21 65103056.
**Corresponding author. Tel.: +86 21 52411080; fax: +86 21 52413122.
E-mail addresses: zgyang@fudan.edu.cn (Z.-G. Yang), gjzhang@mail.sic.ac.cn (G.-J. Zhang).

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composites exhibited multiphase layered structures, which consisted of (1) an outer Mo layer, (2) a subsurface Si layer, (3) a ZrB_2–$MoSi_2$ layer, and (4) an inner partially $MoSi_2$-depleted ZrB_2 layer.

In the present work, the phase composition, microstructure, and mechanical properties of ZrB_2-20 vol% SiC composites doped with 3 vol% Yb_2O_3 were investigated before and after heat treatment.

2. Experimental procedure

The raw materials were ZrB_2 (D_{50}=14 μm, 98.5%, Gongyi Sanxing Ceramics Materials Co. Ltd, Gongyi, China), SiC (D_{50}=0.45 μm, 98.5%, Changle Xinyuan Carborundum Micropowder Co. Ltd, Changle, China), and analytical grade Yb_2O_3 (99.9%, ChemPur, Germany). The composition contained 77 vol% ZrB_2, 20 vol% SiC, and 3 vol% Yb_2O_3. The starting mixture was ball milled for 8 h using acetone and Si_3N_4 balls in a planetary ball mill, and then dried by rotary evaporation. After being dried, the powder compacts were hot pressed at 1900 °C for 1 h under a pressure of 30 MPa in an argon atmosphere. The sintered sample was designated as ZSYb.

The ZSYb was heat-treated at 2000 °C for 3 h without pressure in a flowing argon atmosphere with a heating rate of 50 °C/min. The heat treatment was carried out in graphite heating element resistance furnace. The heat-treated sample was labeled as ZSYb-T.

Phase composition was determined by X-ray diffraction (XRD, *D*/max 2550 V, Tokyo, Japan). Microstructure was characterized by scanning electron microscopy (SEM, Hitachi S-570, Tokyo, Japan). The ZrB_2 grain size was described in terms of the corresponding circular equivalent diameter, and determined using an image analysis software package. Vickers' hardness and fracture toughness were determined by indentation method using a diamond indenter with a load of 10 kg for 10 s on a polished surface. Flexural strength via four-point bending was tested on 2.5 mm × 2 mm × 25 mm bars using 20 mm and 10 mm as outer and inner spans, respectively.

3. Results and discussion

XRD patterns of polished cross-sections of ZrB_2–SiC composites added with Yb_2O_3 before and after heat treatment are shown in Fig. 1. In addition to ZrB_2 and SiC phases, $Yb_2Zr_2O_7$ phase was observed in the ZSYb composites (Fig. 1(a)). The formation of $Yb_2Zr_2O_7$ was due to the reaction of Yb_2O_3 with ZrO_2 impurities on the ZrB_2 powders [11]. The $Yb_2Zr_2O_7$ phase disappeared in the ZSYb-T composites, and Yb_2O_3 and ZrC phases were detected (as shown in Fig. 1(b)). The $Yb_2Zr_2O_7$ phase decomposed into Yb_2O_3 and ZrO_2 phases during high-temperature heat treatment. Due to the graphite-rich heat treatment environment, the ZrO_2 phase converted to ZrC phase [5,11].

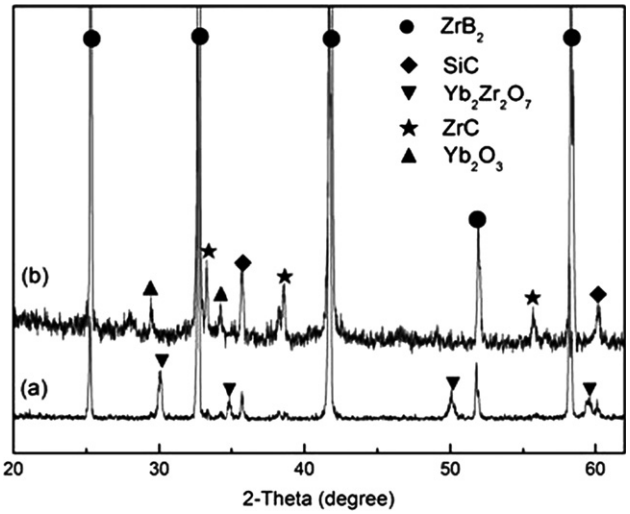

Fig. 1. XRD patterns of ZSYb (a) and ZSYb-T (b) composites.

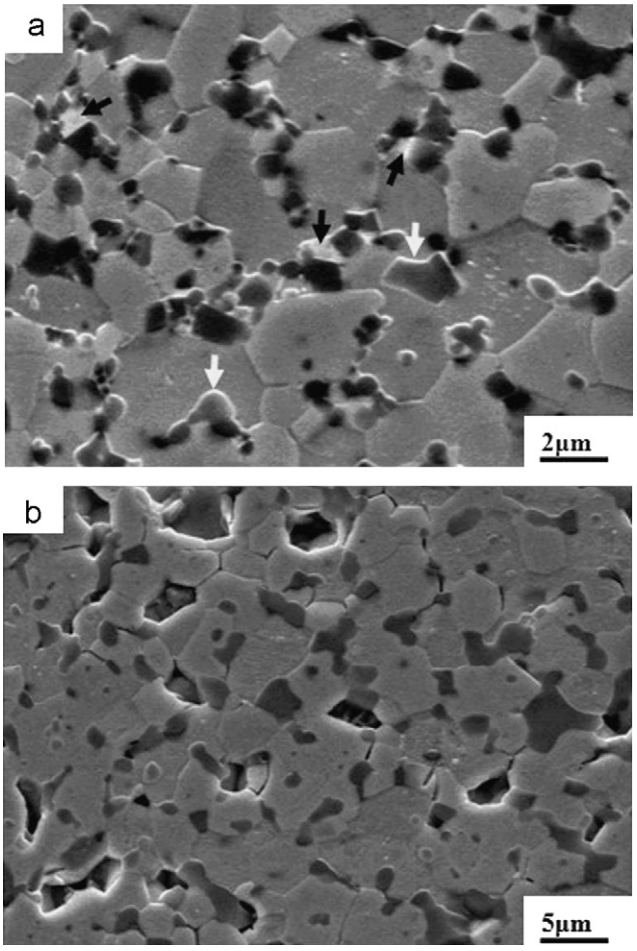

Fig. 2. Microstructure of polished cross-sections of ZSYb (a) and ZSYb-T (b) composites. Note the variation in magnification between the images.

Microstructure of polished cross-sections of ZrB_2–SiC composites added with Yb_2O_3 before and after heat treatment is shown in Fig. 2. In addition to gray ZrB_2 and black SiC phases, white phases were observed in the

ZSYb composites. It was noted that there were two types of white phase. The first type was located at multiple-grain junctions, as indicated by black arrows in Fig. 2(a). Our previous study has shown that the white phase at multiple-grain junctions was $Yb_2Zr_2O_7$ phase confirmed by XRD and EDS analysis [11]. The second type was present on the surface of SiC grains, as indicated by white arrows in Fig. 2(a). Studies on liquid-phase-sintered SiC have shown that the rare-earth oxides Re_2O_3 (such as Y_2O_3, Yb_2O_3) could react with SiO_2 on the SiC particle to form the silicate phase (Re–Si–O) in the grain boundary of SiC grains [16,17]. In this study, the Yb_2O_3 could react with SiO_2 on the SiC and B_2O_3 on the ZrB_2 to form Yb–Si–B–O phase. Due to the high vapor pressure, however, the B_2O_3 at high temperature had rapid evaporation. So, the white phase on the surface of SiC grains might be Yb–Si–O phase in the ZSYb composites.

As shown in Fig. 2(b), the two types of white phases disappeared in the ZSYb-T composites, and many pores were observed at multiple-grain junctions. The high temperature heat treatment led to the escape of Yb-containing phases ($Yb_2Zr_2O_7$ and Yb–Si–O) by decomposition or evaporation. The above XRD result also confirmed the decomposition of $Yb_2Zr_2O_7$ phase during heat treatment (Fig. 1(b)). Earlier studies on Si_3N_4 ceramics added with Yb_2O_3 have shown that the Yb-containing phases could be depleted by evaporation at high temperature [18,19]. The depletion of Yb-containing phases led to the formation of some pores in the ZSYb-T composites.

ZrB_2 and SiC showed grain growth after heat treatment. Due to the clustering of two or more SiC grains in the composites, it was difficult to determine the effective SiC particle size. Accordingly, only ZrB_2 grain growth was analyzed. The measured average ZrB_2 grain size is summarized in Table 1. The ZrB_2 grain size increased from ~1.9 μm to ~4.8 μm in the ZrB_2–SiC composites doped with Yb_2O_3 after heat treatment at 2000 °C for 3 h. In our previous study on ZrB_2–SiC composites without Yb_2O_3, the ZrB_2 grain size increased from ~2.5 μm to ~3.3 μm after heat treatment at 2000 °C for 3 h [14]. It was found that the heat treatment induced more significant grain growth in the Yb_2O_3-doped ZrB_2–SiC composites. The rapid grain growth was mainly attributed to two factors: (1) the presence of pores and (2) the evaporation of Yb-containing phases. The formation of pores reduced the pinning effect on inhibition of grain growth. The escape of Yb-containing phases promoted the grain growth by evaporation–condensation mechanism.

Fig. 3 shows the microstructure of fracture surfaces of ZrB_2–SiC composite added with Yb_2O_3 before and after heat treatment. The ZSYb-T composites had some pores (Fig. 3(b)), which further confirmed the decomposition or evaporation of the ZSYb composites during heat treatment. The fracture mode of ZSYb composites was mixed inter/transgranular, and that of ZSYb-T composites was fully transgranular. The heat treatment caused the removal of Yb-containing phases, and strengthened the grain boundaries, which led to the change of fracture mode.

Mechanical properties of ZrB_2–SiC composites added with Yb_2O_3 before and after heat treatment are also summarized in Table 1. The Vickers hardness of ZSYb was ~20.2 Gpa, whereas that of ZSYb-T was ~15.2 Gpa. The heat treatment decreased the hardness. Typically, the ceramics with larger grain sizes or more porosity have lower hardness [20]. As shown in Fig. 2, the heat treatment

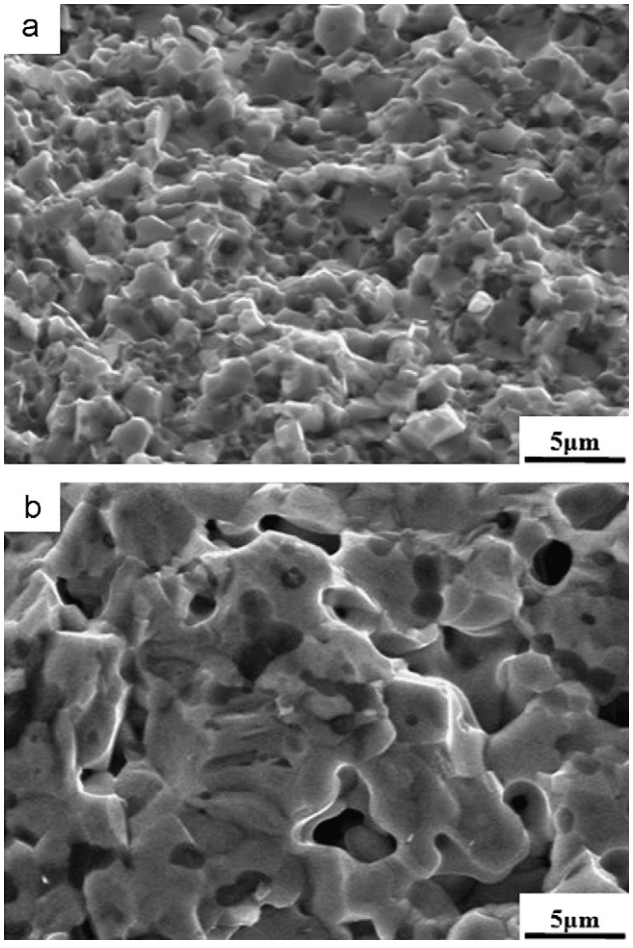

Fig. 3. Microstructure of fracture surfaces of ZSYb (a) and ZSYb-T (b) composites.

Table 1
Measured ZrB_2 grain size and mechanical properties of ZSYb and ZSYb-T composites.

Sample	ZrB_2 grain size (μm)	Hardness (GPa)	Toughness (MPa $m^{1/2}$)	Strength (MPa)
ZSYb	1.9 ± 0.4	20.2 ± 0.3	4.9 ± 0.2	871 ± 51
ZSYb-T	4.8 ± 0.7	15.2 ± 0.7	3.1 ± 0.5	403 ± 69

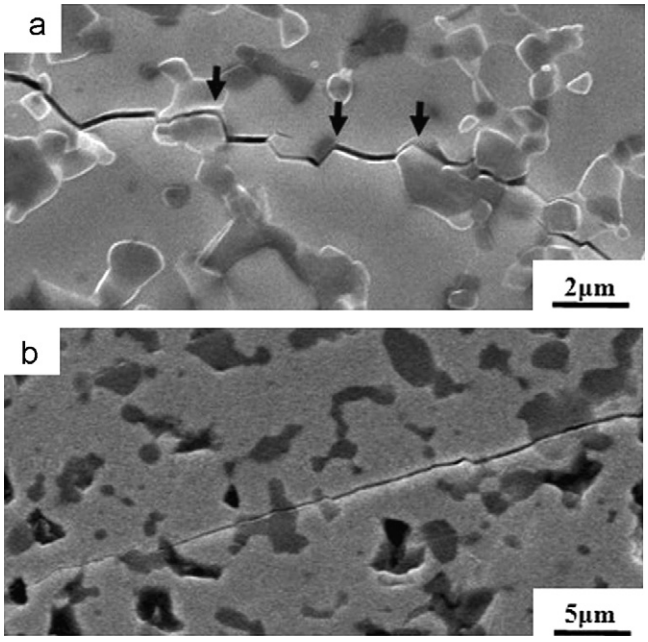

Fig. 4. Paths of some Vickers-indentation-induced cracks on polished sections of ZSYb (a) and ZSYb-T (b) composites. Note the variation in magnification between the images.

led to the formation of pores and significant grain growth. So, the ZSYb-T had lower hardness.

Fracture toughness of ZSYb was ~4.9 MPa $m^{1/2}$, which was higher than that of ZSYb-T (~3.1 MPa $m^{1/2}$). The high temperature heat treatment decreased the fracture toughness. The paths of some Vickers-indentation-induced cracks on polished sections of the ZSYb and ZSYb-T are shown in Fig. 4. SEM observations of crack propagation demonstrated the existence of crack deflection in the ZSYb (as indicated by black arrows in Fig. 4(a)), which led to higher measured fracture toughness. However, the indentation crack in the ZSYb-T was straight (Fig. 4(b)). The heat treatment induced the change in the fracture mode from mixed inter/transgranular to fully transgranular (Fig. 3(a) and (b)). The transgranular fracture demonstrated the disappearance of crack deflection. So, the ZSYb-T composites had lower fracture toughness.

Flexural strength values of ZSYb and ZSYb-T were ~871 MPa and ~403 MPa, respectively. After heat treatment at 2000 °C for 3 h, the flexural strength decreased significantly. The flexural strength of brittle materials is related to grain size and some defects (machining damage during sample preparation, porosity, etc.) [20,21]. The increase of grain size or the presence of defects could decrease the flexural strength. In the present work, the heat treatment led to significant grain growth and the formation of large pores. So, the ZSYb-T composites had lower flexural strength.

4. Conclusion

The effect of heat treatment at 2000 °C in argon on phase composition, microstructure, and mechanical properties of hot-pressed ZrB_2-20 vol% SiC composites added with 3 vol% Yb_2O_3 was investigated. The high temperature heat treatment led to the depletion of Yb-containing phases by decomposition or evaporation, the formation of some pores at multiple-grain junctions, significant microstructural coarsening with the increase of ZrB_2 grain size from ~1.9 μm to ~4.8 μm, and the change of fracture mode from mixed inter/transgranular to fully transgranular. The formation of pores and microstructure coarsening led to the decrease of Vickers' hardness from ~20.2 Gpa to ~15.2 Gpa and flexural strength from ~871 MPa to ~403 MPa. Due to the change of fracture mode, the fracture toughness also decreased from ~4.9 MPa $m^{1/2}$ to ~3.1 MPa $m^{1/2}$.

Acknowledgments

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