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Short communication

Microstructural evolution of ZrB_2–$MoSi_2$ composites during heat treatment

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

The microstructural evolution of ZrB_2–20 vol% $MoSi_2$ composites during heat treatment with and without pressure at 2000 °C for 1 h in argon was investigated. Results showed the materials exhibited a multiphase layered structure after heat treatment without pressure. From surface to center, the layered structure consisted of (1) a Mo layer, (2) a Si layer, (3) a ZrB_2–$MoSi_2$ layer and (4) a partially $MoSi_2$-depleted ZrB_2 layer. The formation mechanism of layered structure was analyzed. After heat treatment with pressure, the materials with high toughness mainly contained ZrB_2 phase.

Keywords: B. Composites; ZrB_2–$MoSi_2$; Heat treatment; Microstructure

1. Introduction

ZrB_2 ceramics, among the ultra-high-temperature ceramics (UHTCs), is especially promising for high-temperature structural applications, owing to the excellent combination of physicochemical properties such as low density, high melting temperature and thermal conductivity [1]. Pure ZrB_2 is limited by its poor sinterability and oxidation resistance. Considerable studies have shown that SiC or $MoSi_2$ as second phase was very effective to enhance the densification and oxidation resistance. For ZrB_2–SiC system, a lot of studies have been conducted by Groups in the United States, Japan, Italy and China [1–8]. For ZrB_2–$MoSi_2$ system, most studies have been carried out by Groups in the Europe [9–13]. They mainly investigated the densification, microstructure, and properties of ZrB_2–$MoSi_2$ composites produced by different sintering techniques including spark plasma sintering, hot pressing and pressureless sintering. Recently, Mizuguchi et al. investigated the microstructure and grain boundary phase of ZrB_2–$MoSi_2$ by transmission electron microscopy [14]. In addition, Wu et al. obtained ZrB_2–20 vol% $MoSi_2$ composites with elongated ZrB_2 grains and high toughness by reactive hot pressing [15].

As one member of UHTCs family, ZrB_2–$MoSi_2$ will be used in some extreme environments such as oxygen atmosphere and high temperature. The oxidation behavior of ZrB_2–$MoSi_2$ has been investigated in detail [11,12]. However, the effect of high temperature on the ZrB_2–$MoSi_2$ ceramics has not been reported by far. Previously, a lot of investigations have been conducted on the heat treatment effect in several ceramic systems [16–21]. These studies were essentially based on two main purposes. The first purpose of heat treatment is to adjust microstructure and composition, which can better improve properties such as fracture toughness and thermal conductivity [16–18]. For example, thermal conductivity of Si_3N_4 ceramics increased from 44 to 89 W m^{-1} K^{-1} by the decrease in glassy phase and lattice oxygen after the heat-treatment [17]. The second purpose of heat treatment is to evaluate the high-temperature stability and reliability [19–21]. For example, the microstructural stability of the ZrB_2–SiC composites has been evaluated by heat treatment at 2000 °C [21]. Results showed that the ZrB_2 grain growth rate in the ZrB_2–30 vol% SiC was 25 times lower than that for ZrB_2–10 vol% SiC, and the mechanical properties including Vickers' hardness and fracture toughness were not influenced by the heat treatment.

In the present work, the microstructural evolution of ZrB_2–20 vol% $MoSi_2$ composites during heat treatment with and without pressure at 2000 °C for 1 h in argon was investigated. The main aim is to evaluate the microstructural stability of the ZrB_2–$MoSi_2$ at high temperature.

* Corresponding authors.
E-mail addresses: zgyang@fudan.edu.cn, guo1238@126.com (Z.-G. Yang), gjzhang@mail.sic.ac.cn (G.-J. Zhang).

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2. Experimental

The raw materials used were ZrB_2 (D_{50} = 14 μm) and $MoSi_2$ (D_{50} = 3.9 μm). The ZrB_2–$MoSi_2$ composites contained 20 vol% $MoSi_2$. The starting powder mixtures were ball milled for 8 h in acetone using Si_3N_4 balls in a planetary ball mill in nylon containers, and dried by rotary evaporation. The powder compacts were hot pressed at 1850 °C for 60 min under a pressure of 30 MPa in argon atmosphere. The heat treatment of the hot-pressed materials was conducted at 2000 °C for 1 h in argon atmosphere either without or with applied pressure (50 MPa). The hot-pressed ZrB_2–$MoSi_2$ was referred to as ZM. The heat-treated ZrB_2–$MoSi_2$ without pressure was referred to as ZMT, and that with pressure was referred to as ZMTP.

Phase composition was determined by X-ray diffraction (XRD, D/max 2550 V, Tokyo, Japan). Microstructures were characterized using scanning electron microscopy (SEM) imaging in an electron probe microanalyzer (JEOL JXA-8100F, Japan) along with energy-dispersive spectroscopy (EDS, Oxford INCA energy) for chemical analysis. The fracture toughness was determined by indentation method using a diamond indenter with a load of 5 kg for 10 s on a polished surface.

3. Results and discussion

3.1. Microstructural evolution without pressure

Fig. 1 shows the microstructures of fracture surface of ZM, ZMT and ZMTP materials. Very few pores were observed for ZM materials, indicating a fully dense hot-pressed ZrB_2–20 vol% $MoSi_2$ at 1850 °C. Many pores were present for ZMT materials (indicated by arrows in Fig. 1(b)). This showed that the ZrB_2–$MoSi_2$ composites might have volatilization or decomposition during high-temperature heat treatment without pressure, resulting in the appearance of pores. In addition, ZMT materials showed obvious coarsening grain growth.

Fig. 2 shows the microstructures of polished cross-section of ZMT materials. It was found that the ZMT materials exhibited a multiphase layered structure. Analysis using SEM/EDS revealed that the layered structure, from surface to center, consisted of (1) a Mo layer; (2) a Si layer; (3) a ZrB_2–$MoSi_2$ layer; (4) a porous layer of ZrB_2 from which $MoSi_2$ had been partially depleted. Based on the layered structure, it was concluded that the $MoSi_2$ phase of the ZrB_2–$MoSi_2$ composites would decompose into Mo phase and Si phase during heat treatment at 2000 °C:

$$MoSi_2 \rightarrow Mo + 2Si \quad (1)$$

Therefore, the formation of some pores in ZMT materials may be attributed to the decomposition of $MoSi_2$ phase during heat treatment. Fig. 3 shows the XRD patterns of ZM, ZMT and ZMTP materials. The peak intensities of $MoSi_2$ phase of ZMT materials decreased obviously compared with that of ZM materials. This indicated that a part of $MoSi_2$ phase disappeared after heat treatment, which was consistent with results of SEM. So, the ZrB_2–$MoSi_2$ composites showed poor high-temperature

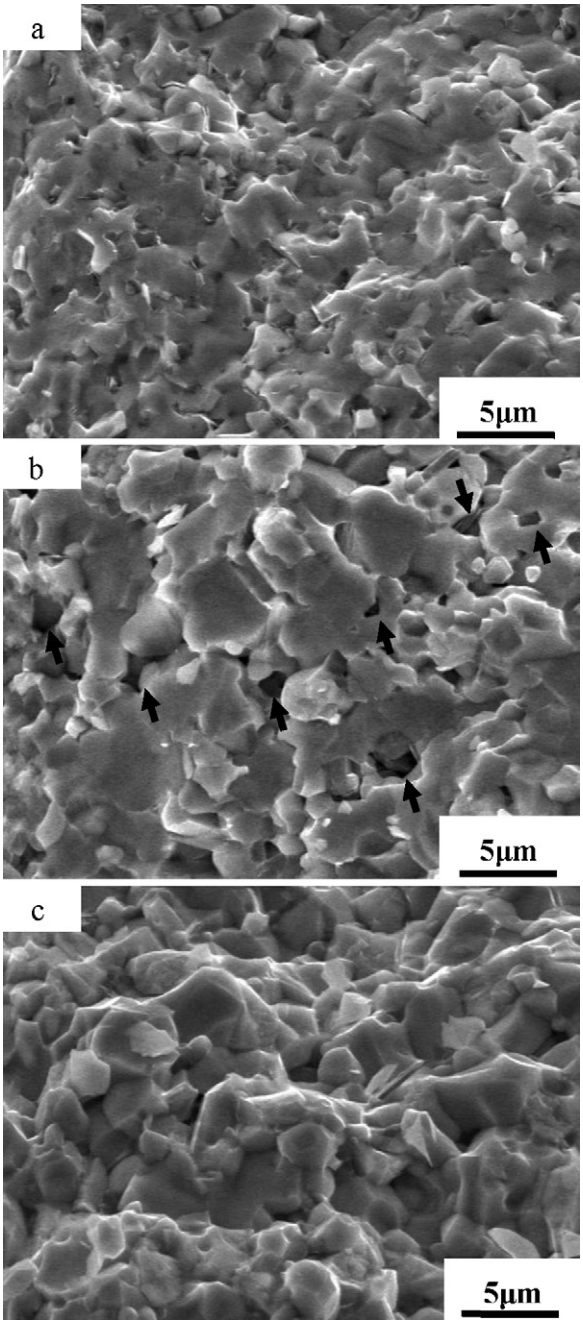

Fig. 1. Microstructures of fracture surface of ZM (a), ZMT (b) and ZMTP (c) materials.

stability. For another important system of ZrB_2-based composites, previous study showed that the ZrB_2–SiC had microstructural coarsening during heat treatment without pressure at 2000 °C, whereas the densification and phase composition had no obvious difference [21].

To understand the formation mechanism of the layered structure of ZMT materials, schematic diagram of microstructural evolution of ZrB_2–$MoSi_2$ composites during heat treatment without pressure is shown in Fig. 4. At initial stage of heat treatment, the $MoSi_2$ close to surface firstly decomposed into Mo phase and Si phase which would diffuse to external surface. As a result, the outer Mo layer and subsurface Si layer

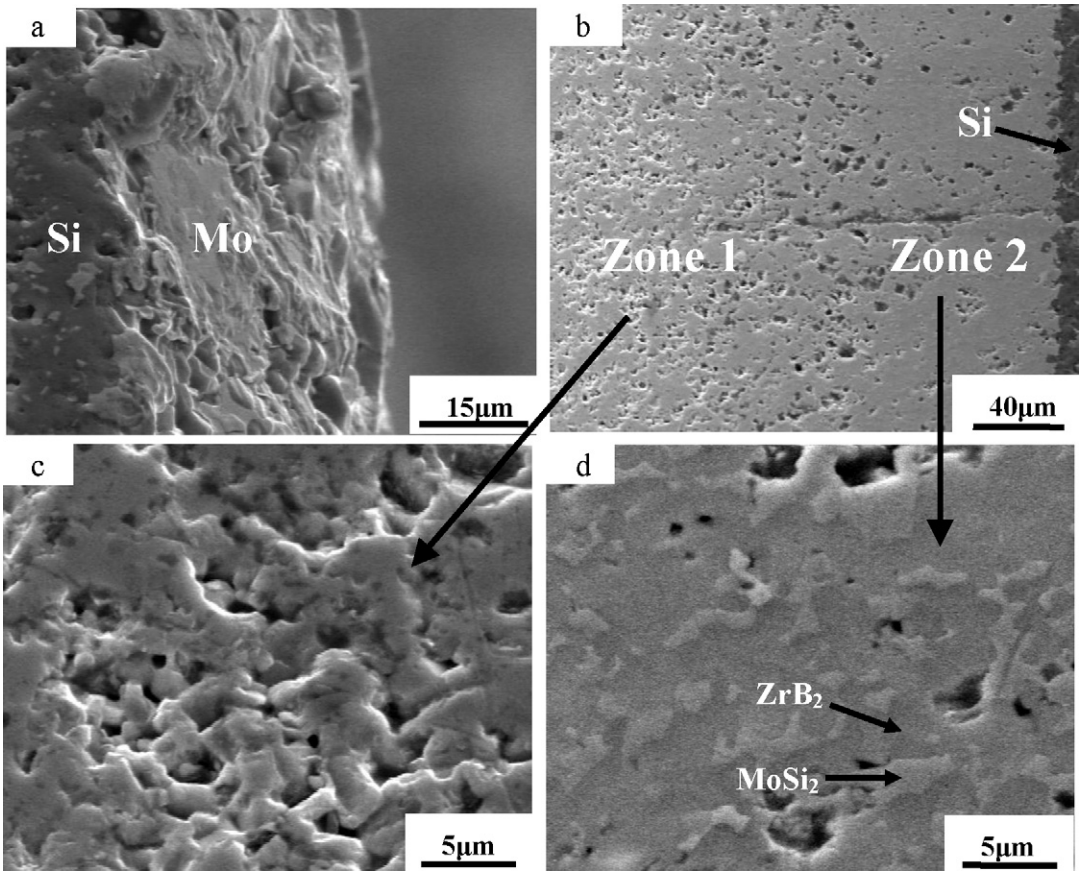

Fig. 2. Microstructures of polished cross-section of ZMT materials: (a) close to the surface, (b) below the surface, (c) high magnification of zone 1, and (d) high magnification of zone 2.

were formed on the surface of ZrB_2–$MoSi_2$ composites. Below the Si layer, a porous layer of ZrB_2 was formed due to the decomposition of $MoSi_2$. This microstructure is shown schematically in Fig. 4(b). With heat treatment going on, the $MoSi_2$ phase close to center of composites started to decompose into Mo phase and Si phase. Due to the presence of dense subsurface Si layer, newly formed Mo phase and Si phase were hard to diffuse outwards and present in porous ZrB_2 layer, which is shown schematically in Fig. 4(c). Then, the Mo phase reacted with Si phase to re-form $MoSi_2$ phase:

$$Mo + 2Si \rightarrow MoSi_2 \quad (2)$$

Consequently, the porous ZrB_2 layer was filled with newly formed $MoSi_2$ phase, and became dense again. This final microstructure is shown schematically in Fig. 4(d).

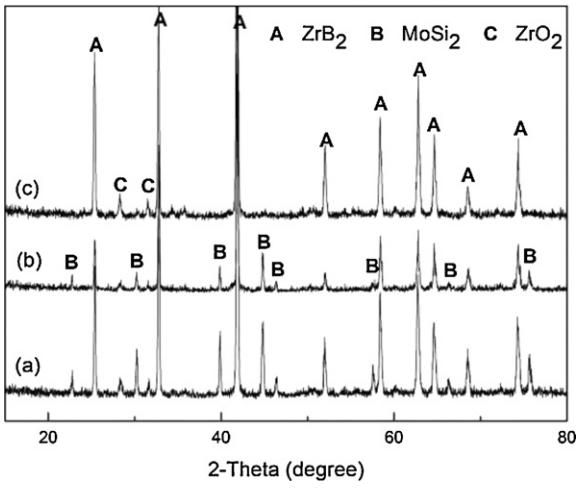

Fig. 3. XRD patterns of ZM (a), ZMT (b) and ZMTP (c) materials.

3.2. Microstructural evolution with pressure

At 2000 °C, heat treatment with pressure resulted in 50% height reduction. ZrB_2–$MoSi_2$ composites exhibited superplastic deformation. The XRD pattern showed that no $MoSi_2$ phase was detected in the ZMTP materials (Fig. 3). The applied pressure promoted the complete decomposition of $MoSi_2$ phase during heat treatment. In spite of decomposition of $MoSi_2$ phase, no pores were observed for ZMTP materials (Fig. 1(c)). This might be because pores were eliminated by plastic deformation. Carefully microstructural observation showed that the ZrB_2 grains in the ZMTP materials were bigger than that of ZM materials, but smaller than that of ZMT materials (Fig. 1). The presence of applied pressure during heat treatment helped to inhibit the ZrB_2 grain growth. Similar result was also obtained by Zhan et al. for heat-treated silicon carbide [22]. They indicated that annealing with applied pressure inhibited grain growth of SiC compared with annealing without pressure.

Due to the presence of many pores, fracture toughness of ZMT has been not tested. The fracture toughness of ZM and

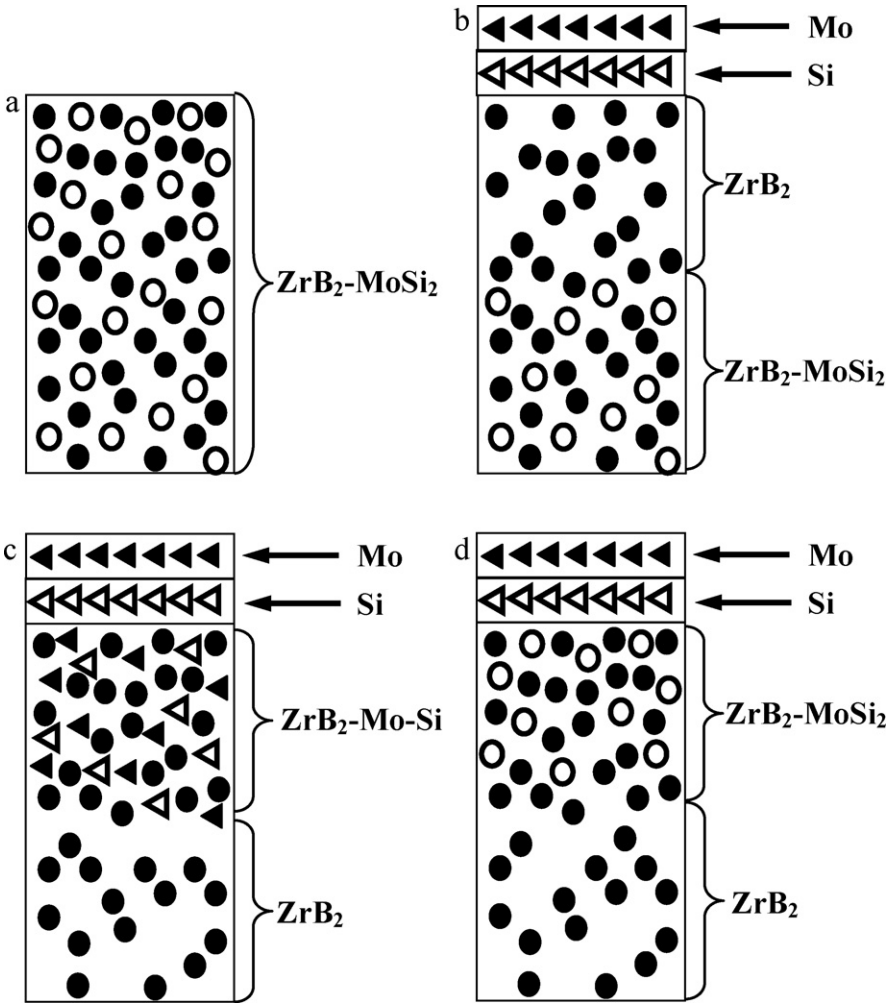

Fig. 4. Schematic diagram of microstructural evolution of ZrB_2–$MoSi_2$ composites during heat treatment without pressure: (a) without heat treatment, (b) initial stage of heat treatment, (c) intermediate stage of heat treatment, and (d) final stage of heat treatment.

ZMTP materials were 2.69 ± 0.30 MPa $m^{1/2}$ and 4.33 ± 0.35 MPa $m^{1/2}$, respectively. As shown in Fig. 1, transgranular fracture of ZM and predominantly intergranular fracture of ZMTP indicated that the indentation crack path in the ZMTP would more tortuous. So, the fracture toughness of ZMTP materials showed great increase compared with that of ZM materials.

4. Conclusion

The microstructural evolution of ZrB_2–20 vol% $MoSi_2$ composites during heat treatment with and without applied pressure at 2000 °C for 1 h in argon atmosphere was investigated. After heat treatment without pressure, the materials exhibited a multiphase layered structure. From surface to center, the layered structure consisted of (1) a Mo layer, (2) a Si layer, (3) a ZrB_2–$MoSi_2$ layer and (4) a porous layer of ZrB_2 from which $MoSi_2$ had been partially depleted. After heat treatment with pressure, the materials with high fracture toughness mainly contained ZrB_2 phase. The presence of applied pressure during heat treatment inhibited the ZrB_2 grain growth compared with that without pressure.

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