Fabrication and mechanical properties of self-toughening ZrB₂–SiC composites from in-situ reaction

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Abstract: Self-toughening ZrB₂–SiC based composites are fabricated by in-situ reactive hot pressing. The effect of sintering additive content on the microstructure and mechanical properties of the composites is investigated. Microstructure observation found that the in-situ reactive hot pressing could promote the anisotropic growth of ZrB₂ grains and the formation of interlocking microstructure. Such microstructure could improve the mechanical properties, especially, for the fracture toughness. The improved mechanical properties could be attributed to the self-toughening structure related to the ZrB₂ platelets and the formed interlocking microstructure, which could trigger various toughening mechanisms such as grain pull-out, crack bridging, crack deflection, and crack branching, providing the main contribution to the high fracture toughness.

Keywords: ultrahigh temperature ceramic; in-situ reaction; interlocking microstructure; mechanical property

1 Introduction

In recent decades, ultrahigh temperature ceramics (UHTCs) are attracting more and more attention with the development of space and industrial applications. As a special class of highly refractory materials, UHTCs have been accepted for potential use as thermal protection structures in next-generation space vehicles, as well as in critical ground-based applications such as refractory linings and cutting tools [1,2]. Zirconium diboride (ZrB₂), a member of UHTCs, is the most studied candidate because of its unique combination of relatively low density, superior strength, and high hardness [3–5]. Especially, by adding SiC to ZrB₂, the sintering ability,

mechanical properties, and oxidation resistance of ZrB₂ can be further improved [6,7]. However, like all brittle materials, limited fracture toughness and sensitivity to slow or subcritical crack growth are still the major barriers to the wide engineering applications of ZrB₂–SiC based ceramics.

Considerable research efforts have been prompted to improve the toughness of ZrB₂–SiC based ceramics. By adding whiskers, nanotubes, graphene, or fibers with high strength and high elastic modulus into the ceramic matrix, the fracture toughness of ZrB₂–SiC based composites has been effectively improved [8–11]. However, the application of these reinforcements was still limited to some extent due to the low volume fraction of introduction, difficulties in densification, dispersion in the matrix, and high cost [12].

Recently, the concept of microstructure tailoring was proposed to improve and optimize the properties

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of MB₂ (transition metal diboride) based composites in UHTC field [1]. Motivated by the results of Si₃N₄ ceramics [13,14], a unique self-reinforced interlocking and textured microstructures are preferred, which could not only prevent the formation of flaw clusters, but also increase the opportunity for crack bridging and deflection, thereby resulting in both improved strength and fracture toughness [15,16]. Accordingly, ZrB₂–SiC based composites with a unique interlocking microstructure have been densified by pressureless sintering [16]. The ZrB₂ grains exhibit plate-like morphologies when being sintered above 2100 °C. However, the high sintering temperature resulting in large grain size may decrease the mechanical properties of composites to some extent, especially the fracture strength. Some other researchers have shown that the in-situ reactive hot pressing process can be used as an alternative method to fabricate materials with some novel microstructures under relative low sintering temperature [17–19]. Using elementals Zr, B, Mo, and Si as raw materials, ZrB₂–MoSi₂ composites with platelet ZrB₂ grains were fabricated by reactive hot pressing at 1800 °C [20]. The fracture toughness of the composites was improved owing to the partially textured structure with in-situ platelet ZrB₂ grains. Therefore, the in-situ reaction is thought to have potential advantages for the fabrication of ZrB₂–SiC based composites with tailored microstructure to improve the mechanical properties.

In the present work, ZrB₂–SiC based composites were fabricated from in-situ reactive hot pressing. The anisotropic growth of ZrB₂ grain was promoted and a unique self-toughened interlocking microstructure was formed. The X-ray diffractometer (XRD) and field-emission scanning electron microscope (FE-SEM) with an energy dispersive spectrometer (EDS) were applied to analyze the phase composition and microstructure. Besides, the flexural strength and fracture toughness were measured and the relationship between the mechanical properties and the microstructure was studied.

2 Experimental procedure

ZrSi₂ powder (average particle size: 5 μm, purity > 99%, supplied by Shanghai Bohan Co., Ltd., China), B₄C powder (average particle size: 2–3 μm, purity > 99%, supplied by Aladdin Co., Ltd., China), and carbon black (average particle size: 40 nm, purity >

99%, supplied by Alfa Aesar Co., Ltd., China) were used as the raw materials to prepare ZrB₂–SiC based composites based on the following reaction:

Five different compositions of raw materials adjusted according to Reaction (1) were used in this work. The detailed molar ratios of ZrSi₂:B₄C:C for the powder mixtures are shown in Table 1. One of the molar ratios was corresponded to the stoichiometric Reaction (1), and others contained excessive ZrSi₂. With these starting powders, the composition of the composites after sintering was calculated according to Reaction (1), which contained excessive ZrSi₂ of 0%, 10%, 15%, 20%, 25% in volume fraction, respectively. Hereafter, these five composites were referred as RZSZ-0, RZSZ-10, RZSZ-15, RZSZ-20, and RZSZ-25.

As we know, it is quite difficult to obtain highly dense ZrB₂–SiC ceramics below 1700 °C because of the covalent bonding characters of ZrB₂ and SiC. The excessive ZrSi₂ used as the sintering additive could reduce the process temperature of ZrB₂–SiC based composites [21]. The improved sintering ability could be attributed to the ductile deformation of ZrSi₂ particles and liquid phase formation on the grain boundaries at high temperature [22]. Furthermore, it was found that the formation of liquid phase was beneficial for the formation of platelet-shaped ZrB₂ grains [23]. Therefore, different content of excessive ZrSi₂ was also used to investigate its influence on the microstructure features and mechanical properties of the final composites.

The powder mixtures were ball-milled at 250 rpm for 12 h using WC balls and ethanol as the milling media. The mass ratio among powders, balls, and ethanol was 1:10:1. The ball-milled powder mixtures were dried in a rotary evaporator under vacuum condition, and then charged into the graphite die coated with a

Table 1 Composition of the powder mixtures and the composites after sintering

Label	Molar ratio of the composition of raw mixture			Calculated composition after reaction (vol%)		
	ZrSi ₂	B ₄ C	C	ZrB ₂	SiC	ZrSi ₂
RZSZ-0	2.00	1	3	42.5	57.5	0
RZSZ-10	2.32	1	3	38.3	51.7	10
RZSZ-15	2.51	1	3	36.1	48.9	15
RZSZ-20	2.72	1	3	34.0	46.0	20
RZSZ-25	2.96	1	3	31.9	43.1	25

BN coating. The in-situ reactive hot pressing was carried out at 1550 °C for 30 min under 40 MPa in vacuum with a heating rate of 10 °C/min. The obtained samples had dimensions of 30 mm diameter and 5 mm thickness.

After a fine grinding, the contaminated surface layer was removed. The bulk density of the samples was measured via Archimedes method. The theoretical density of the composites was calculated based on the composition shown in Table 1 according to the rule of mixtures. The consisting phase of the samples was determined by XRD. The Vickers hardness was measured under a load of 5 kg for 10 s on a polished surface. Flexural strength was tested in three-point bending on 2 mm × 2 mm × 25 mm bars using a 18 mm span and a crosshead speed of 0.5 mm/min. Fracture toughness was measured by means of the single edge notched-beam test on 2 mm × 4 mm × 25 mm bars using a 18 mm span and a crosshead speed of 0.05 mm/min. The depth and width of the notch were 1.5 and 0.3 mm, respectively. The surface morphology and fracture surface after mechanical test were observed by FE-SEM. Grain sizes were estimated from the scanning electron microscopy (SEM) micrographs of the fracture surfaces.

3 Results and discussion

3.1 XRD analysis

Figure 1 shows the XRD spectra of the milled powder mixtures and the fabricated RZSZ-0 sample. In the milled powder mixtures, the peaks of ZrSi₂ and B₄C were primarily identified. In addition, trace ZrO₂ and WC were detected simultaneously as shown in Fig. 1(a). The formation of trace ZrO₂ should be attributed to the surface oxidation of the ZrSi₂ powders, which may be occurred in the starting powder and handling after the ball-milling. The impurity of WC came from the WC balls which interacted with the B₄C during high-energy ball-milling because B₄C is a typical hard material in nature [24].

In the case of the RZSZ-0 composite, ZrB₂ and SiC were identified as the dominant crystalline phases and no obvious peaks from the starting materials were detected. The result indicated that Reaction (1) completely finished after the in-situ reactive hot pressing. Trace ZrO₂ phase was still present in the final composites. Furthermore, WSi₂ was identified as a new crystalline

Fig. 1 XRD spectra of raw powder mixtures and the final composite for RZSZ-0.

phase besides the products of Reaction (1). The formation of WSi₂ could be associated with the reaction between WC and ZrSi₂ as indicated in our previous work [25]. However, it has been outlined that the W-compounds are helpful for the improvement of the oxidation resistance of ZrB₂ and ZrB₂–SiC composites [26].

Figure 2 shows the XRD spectra of the fabricated composites with different ZrSi₂ contents. On the whole, the main consisting phase of the four composites presented no significant difference. The primary crystalline phases were still ZrB₂ and SiC, and trace WSi₂ and ZrO₂ were also observed. In addition, some weak peaks of ZrSi₂ were detected in the final composites attributed to the excessive ZrSi₂ introduced as the sintering additive. Among these four composites, the intensity of WSi₂ peak increased with increasing

Fig. 2 XRD spectra of the final composites with different compositions: (a) RZSZ-10, (b) RZSZ-15, (c) RZSZ-20, and (d) RZSZ-25.

quantity of ZrSi_2 . Furthermore, ZrC as a new phase was detected by XRD analysis when the ZrSi_2 content was above 20 vol%.

As mentioned above, ZrSi_2 would react with WC during the preparation process. The WSi_2 and ZrC were the products as shown in Reaction (2). If B_4C was present, ZrB_2 would be also probably formed via Reaction (3) [27].

Figure 3 shows the Gibbs free energy of reactions as a function of temperature. From the results of thermodynamic calculations, Reactions (1–3) are feasible at all temperatures. However, the Gibbs free energy of Reaction (1) is much lower than that of Reactions (2) and (3), resulting in the limited B_4C to react with ZrC . Therefore, the absence of ZrC was observed in the XRD spectra of RZSZ-10 and RZSZ-15, while the ZrC appeared and the WSi_2 intensity increased in XRD spectra of RZSZ-20 and RZSZ-25.

3.2 Densification and microstructure

Figure 4 shows the relative density of the ZrB_2 - SiC based composites fabricated by the in-situ reactive hot pressing. Without the excessive ZrSi_2 as the sintering additive, the final composite RZSZ-0 presented a low relative density of 91.8% due to the covalent bonding characters of ZrB_2 and SiC . In the case of RZSZ-10 and RZSZ-15, the relative density was 94.9% and 98.5%, respectively, indicating ZrSi_2 could effectively improve the sintering ability of composites during the in-situ reactive hot pressing process. Further increasing the ZrSi_2 content, the relative density was 97.6% for

Fig. 3 Gibbs free energy of different reactions as a function of temperature.

Fig. 4 Relative densities of the ZrB_2 - SiC based composites prepared by reactive hot pressing.

RZSZ-20 and 96.4% for RZSZ-25, respectively, which slightly decreased in comparison to RZSZ-15 as shown in Fig. 4. Similar result was also indicated in Ref. [28]. In the ZrB_2 - ZrSi_2 - SiC ternary system, it was found that the high ZrSi_2 content would be accompanied by an increase of porosity due to the interaction of ZrSi_2 with components of the ceramics [28].

Figure 5 shows the back-scattered electron (BSE) images on the polished surface, which were used to investigate the typical microstructural features of the in-situ reactive hot pressed composites. It can be observed that different phases with different colors dispersed homogeneously in the composites. The main phases were the grey and black phases identified as ZrB_2 and SiC , respectively. From the low magnification images of RZSZ-15 and RZSZ-20 shown in Figs. 5(a) and 5(b), a larger amount of elongated ZrB_2 grains were observed as the arrows indicated. In addition, some elongated ZrB_2 grains interconnected with each other and generated the interlocking microstructures as shown in Fig. 5(c). From the high magnification image of RZSZ-20, it also could be found that the grain size distribution of the ZrB_2 was non-uniform. During the sintering process, ductile deformation or even local melting of ZrSi_2 particles would occur as Reaction (1) was an exothermic reaction ($\Delta H < 0$). The elongated ZrB_2 with multimodal grain distribution would be much easier to slide and interlock under applied pressure thereby promoting the formation of interlocking microstructure. The interlocking microstructures were considered to improve the damage tolerance of the composites. Some insular elongate ZrB_2 grains were found in the dark phase which could be produced by the liquid ZrSi_2 phase. This eutectic-like microstructure also suggested that local melting occurred during the in-situ reaction process.

Fig. 5 BSE images of the ZrB₂-SiC based composites on the polished surface: (a) RZSZ-15, (b) RZSZ-20, (c) high magnification image of RZSZ-20, and (d) RZSZ-25. EDS analysis taken from (e) the zone A and (f) the zone B in (a).

The EDS analysis was performed on these samples. EDS analysis in zone A in Fig. 5(a) revealed that the white phase with irregular shape was mainly consisting of 59.53 at% Si, 21.38 at% W, 11.42 at% C, and 7.67 at% Zr (Fig. 5(e)). It indicated the white phase could be the coexistence of WSi₂ and ZrC, which were the products of Reaction (2). Furthermore, EDS analysis in zone B in Fig. 5(a) revealed that the dark phase was mainly consisting of 58.91 at% C, 34.51 at% Si, and 6.58 at% Zr (Fig. 5(f)), indicating zone B was the SiC-rich region. The small amount of element Zr might come from the ZrSi₂ and ZrC phases. Owing to the ductile deformation of ZrSi₂ at high temperature, some ZrC particles could be carried by ZrSi₂ to the SiC-rich region under the applied pressure during the reactive hot pressing.

Figures 5(a)–5(d) show that the quantity of excessive ZrSi₂ had a significant influence on the grain size

evolution of ZrB₂. For RZSZ-15 and RZSZ-20, these elongated ZrB₂ grains presented a length of 0.5–2 μm approximately with a submicron width. While, ZrB₂ grain coarsening was observed and some large ZrB₂ grains appeared as shown in zone C in Fig. 5(d). It was concluded that increasing the quantity of excessive ZrSi₂ would result in grain growth of ZrB₂. The grain coarsening could be attributed to the high atom diffusion ability along the grain boundaries due to the occurrence of more liquid phase. However, significant anisotropy growth of ZrB₂ grains occurred in all the fabricated composites.

Figure 6 shows the SEM image of the fracture surface of RZSZ-15. It could be seen that the anisotropic growth of ZrB₂ grains was evident and nearly all the ZrB₂ grains developed into the platelet morphology. Moreover, a large number of nano-sized SiC particles were formed among the ZrB₂ grains. The grain size of

Fig. 6 SEM image of the sample RZSZ-15 on the fracture surface.

SiC has a strong influence on the mechanical properties of ZrB_2 -SiC composites. Fine grain size of SiC would result in high mechanical properties, while huge SiC grains in the composites acted as the critical flaws for the failure of ZrB_2 -SiC composites [29].

It is known that ZrB_2 has a hexagonal crystal structure which could be promoted to present the anisotropic grain growth similar as Si_3N_4 . The fastest growing planes of ZrB_2 are the $\{010\}$, $\{110\}$ families. The low-activation energy diffusion path is along $\langle 210 \rangle$ and $\langle 110 \rangle$ directions, that lead to the ZrB_2 grains tending to grow along c -axis perpendicular to the basal plane [30]. It was also indicated that the formation of ZrB_2 platelets was strongly related to the liquid phase and plastic flow mechanism [20,31]. In the present work, the liquid phases might be from two sources. One was the oxide impurities such as SiO_2 and B_2O_3 appeared on the surface of the raw powders. The other was the melt of ZrSi_2 at the local region due to the exothermic Reaction (1). Under the applied pressure, the Zr and B atoms in the liquid phase would

easily transport to the low surface energy planes of ZrB_2 grains, which favored in the anisotropic growth of ZrB_2 grains resulting to the platelet morphology.

3.3 Mechanical properties and toughening mechanisms

Figure 7 shows the mechanical properties of the composites. It indicated that the quantity of excessive ZrSi_2 had great influence on the mechanical properties of the ZrB_2 -SiC based composites. With an increase of the ZrSi_2 content, the Vickers hardness, flexural strength, and fracture toughness of the composites first increased and then decreased. The relationship of the mechanical properties and the ZrSi_2 content is similar to that of the relative densities. However, the RZSZ-20 sample presented the highest Vickers hardness, flexural strength, and fracture toughness, which was 17.1 ± 0.7 GPa, 655 ± 21 MPa, and 6.08 ± 0.17 $\text{MPa} \cdot \text{m}^{1/2}$, respectively. Furthermore, comparing with RZSZ-20, the Vickers hardness and the flexural strength of RZSZ-25 decreased more obviously, while the fracture toughness of RZSZ-25 decreased slightly.

The typical fracture surfaces and the path of crack propagation of the composites after mechanical tests were observed by SEM as shown in Fig. 8. It can be seen that the fracture surfaces of all the samples are rugged. For the RZSZ-0 composite without excessive ZrSi_2 , several obvious pores were found on the fracture surface (Fig. 8(a)), in agreement with the relative density data given in Fig. 4. In addition, the formed SiC grains were submicron sized. However, the nano-sized SiC grains were formed in the composites with excessive ZrSi_2 . This indicated that the excessive ZrSi_2 could refine the SiC grains formed during the in-situ reactive hot pressing. Therefore, in the RZSZ-0,

Fig. 7 Vickers hardness, flexural strength, and fracture toughness of the ZrB_2 -SiC based composites prepared by reactive hot pressing.

Fig. 8 Typical fracture surfaces of the ZrB_2 -SiC based composites prepared by reactive hot pressing: (a) RZSZ-0, (b) RZSZ-10, (c) RZSZ-15, (d) RZSZ-20, (e) RZSZ-25, and (f) SEM image of indentation crack propagation on the polished surface of RZSZ-20.

the porous microstructure and the coarse SiC grains might be responsible for the lowest mechanical properties. When excessive ZrSi_2 was introduced, only some tiny pores could be observed on the fracture surface of RZSZ-10 (Fig. 8(b)). Typical mixture mode of intergranular and transgranular fracture of ZrB_2 platelets presented as the arrows indicated. For the composite RZSZ-15, an obvious self-toughening microstructure of ZrB_2 platelets was observed (Fig. 8 (c)). Both intergranular and transgranular fractures were evidenced on the fracture surface, where the larger ZrB_2 platelets fractured mainly in a transgranular mode

which might be caused by the local stress concentration, whereas the smaller ZrB_2 platelets fractured predominantly in the intergranular manner. Particularly, on the fracture surface of RZSZ-20 (Fig. 8(d)), the unique interlocking microstructure formed by amounts of ZrB_2 platelets with multimodal grain sizes could be observed. Benefiting from the unique interlocking microstructure, the mechanical properties of RZSZ-20 did not deteriorate with its decreased density. On the contrary, this composite possessed the highest mechanical properties. Figure 8(e) shows the SEM images of RZSZ-25. Significant coarsening of ZrB_2 platelets appeared on

the fracture surface. Commonly, the coarse grains in ceramics easily become the defect source due to the stress concentration and therefore reduce the flexural strength of the ZrB_2 –SiC based composites. Due to the coarsening of ZrB_2 platelets, the fracture of RZSZ-25 presented in the transgranular mode. Furthermore, some secondary cracks propagated across the nano-sized SiC-rich region or along the interface of ZrB_2 and SiC grains as shown in Fig. 8(e). The secondary cracks caused by crack branching were shown to be beneficial to the enhancement of fracture toughness of ceramic materials [32]. Therefore, the fracture toughness of RZSZ-25 was as high as $5.96 \pm 0.23 \text{ MPa} \cdot \text{m}^{1/2}$. The improved fracture toughness might be attributed to the self-toughened interlocking microstructure. The in-situ formed interlocking microstructure of ZrB_2 platelets provided definite self-toughening effect on the ZrB_2 –SiC based composites. To achieve a deeper understanding of the toughening mechanism, the path of crack propagation on the polished surface of RZSZ-20 was further inspected by SEM as shown in Fig. 8(f). Benefiting from the effective self-toughening microstructure of the ZrB_2 platelets and the nano-sized SiC, it is easy to trigger various toughening mechanisms such as grain pull-out, crack bridging, crack deflection, and crack branching, resulting in the tortuous path and provided additional fracture energy dissipation, thereby resulting in an enhanced fracture toughness.

The self-toughening mechanism is schematically illustrated in Fig. 9. On the crack propagation path, when the initial cracks encountered the inter-locked ZrB_2 platelets, they would be stopped by the interlocking structure. With continuously increasing the applied force, the fracture energy would be high enough to break the inter-locked ZrB_2 platelets. The collapse of inter-locked structure could significantly reduce the stress intensity on the crack tips.

Simultaneously, the cracks with reduced stress intensity would hardly break the ZrB_2 platelets and be preferred to propagate along the grain interface with lower bonding strength. The ZrB_2 platelets pull-out was promoted and crack bridging occurred, which gave rise to the longer crack propagation path. When the crack-tip furtherly met the other ZrB_2 platelets, the stress intensity was reduced or even blocked. Furthermore, the crack branching caused by SiC rich region was also observed. For ZrB_2 –SiC composites, because of the mismatch of the coefficient of thermal expansion of ZrB_2 and SiC, tension residual stress would be generated in a tangential direction to the ZrB_2 matrix around the SiC grains during the cooling down [33]. Hence, the cracks propagated to the SiC-rich region resulting in the crack branching.

4 Conclusions

Self-toughening ZrB_2 –SiC based composites were fabricated via in-situ reactive hot pressing using ZrSi_2 , B_4C , and C as the raw materials. The effect of ZrSi_2 content on the microstructure and mechanical properties of the composites was investigated. The following results could be drawn from the current work:

(1) In-situ reactive hot pressing could promote the anisotropic growth of ZrB_2 grains resulting in the ZrB_2 platelets, and the nano-sized SiC grains were also formed in the fabricated composites.

(2) The anisotropic growth of ZrB_2 grains led to a unique interlocking microstructure when the excessive ZrSi_2 was used. The interlocking microstructure was more obvious in the case of composites with excessive ZrSi_2 higher than 20 vol%. Such microstructure could improve the mechanical properties, especially, for the fracture toughness.

Fig. 9 Schematic of the self-toughening mechanism for the ZrB_2 –SiC composites prepared by reactive hot pressing.

(3) The ZrB_2 platelets and the formed interlocking microstructure played an important role on the self-toughening mechanism of composites, which were activated by various toughening mechanisms such as grain pull-out, crack bridging, crack deflection, and crack branching, providing the main contribution to the high fracture toughness.

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