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Short communication

Laminated ZrB_2–SiC/graphite ceramics with simultaneously improved flexural strength and fracture toughness

Chuncheng Wei[a,b,*], Xinghong Zhang[a], Shuang Li[a]

[a]Science and Technology on Advanced Composites in Special Environments Laboratory, Harbin Institute of Technology, Harbin 150001, PR China
[b]School of Materials Science and Engineering, Shandong University of Technology, Zibo 255049, PR China

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Abstract

Layered graphite was introduced into ZrB_2–SiC ceramics to prepare laminated composite by tape casting and hot pressing. Both fracture toughness and flexural strength were improved in the laminates, reaching the peak values of 12.4 MPa $m^{1/2}$ and 580 MPa, respectively. Cracks propagated in a step-like mode resulting from the layered, soft interface layer, so crack branch and interface delamination were considered as the main toughening mechanisms. The compressive stress in the ZrB_2–20 vol% SiC layer was the main strengthening mechanism.

Keywords: A. Tape casting; A. Hot pressing; C. Mechanical properties; Layered

1. Introduction

Ultra-high temperature ceramics (UHTCs) are identified as the next generation material for the high temperature aerospace application. Among UHTCs, ZrB_2–SiC ceramics have attracted significant attention recently due to their low density (6.08 g/cm^3), high melting point (>3000 °C), low cost and excellent oxidation resistance in the extreme environments [1–3]. The major problem with the use of ZrB_2–SiC ceramics is their brittleness. Even though many attempts have been made to improve mechanical properties of ZrB_2–SiC ceramics, the preparation of ZrB_2–SiC ceramics with improved reliability and high thermal shock resistance is still an obstacle for their application in severe environments. It seems that it is not impossible to solve the above problem with the conventional approaches [4–6].

Based on the structure of natural biomaterials, such as bamboos, trees and nacres, it is found that these biomaterials have fine and special structures rather than complicated compositions. Nacre consists of 99 vol% aragonite wafers and 1 vol% organic phase; however, the flexural strength and fracture toughness are one order of magnitude higher than those of the aragonite single crystal [7]. As a result, the special structure of natural biomaterials provides us profound insight on the design and fabrication of structural materials [8]. Nacre and turtle shell show excellent load bearing capacity and fracture resistance, resulting from the well-constructed laminated structure. Now, laminated structure is considered as an effective approach to reinforce ceramic matrix composite [9–11]. The essential point of laminates is that the interface between the layers is weak enough to deflect cracks and thus consume more fracture energy [12,13].

ZrB_2–SiC ceramic laminates have been considered as a possible route for improving the brittleness and thermal shock behaviors of monolithic ZrB_2–SiC ceramics. Lü et al. [14] manufactured laminated ZrB_2–20 vol% SiC/ZrB_2–30 vol% SiC/ZrB_2–20 vol% SiC ceramic with symmetric structure. The high compressive stress on the material surface resulted in a high flexural strength, showing that mechanical properties could be tailored by composition and structural design. Weak interface has been introduced into ZrB_2–SiC laminates. Wei et al. [15] selected BN as the soft layers, achieving a higher fracture toughness of 16.3 MPa $m^{1/2}$. Nevertheless, the flexural strength was reduced due to the introduction of a weak phase. Graphite is an attractive interfacial material for high

*Corresponding author at: Shandong University of Technology, School of Materials Science and Engineering, No. 12 Zhangzhou Road, Zhangdian District, Zibo 255049, China. Tel./fax: +86 451 86403871.
E-mail address: chun_cheng@sdut.edu.cn (C. Wei).

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temperature application because of the low strength, high modulus and good chemical stability in inter atmosphere [16,17]. Especially, graphite possesses a typical layered structure, which is beneficial to the crack deflection and thus can improve the fracture toughness [16,18]. To date, there are only a few papers focused on the strengthening and toughening of laminated ZrB_2 ceramics by layered graphite.

In the present work, laminated ZrB_2–SiC/graphite ceramics with uniform layer thickness were formed by tape casting. ZrB_2–20 vol% SiC (ZS) sheets and graphite–10 vol% ZrB_2–20 vol% SiC (GZS) sheets were used as the rigid layer and the soft layer, respectively. The rigid layer and the soft layer were alternately stacked and then hot pressed under a uniaxial load. By introducing layered graphite into the soft layer, the laminated ceramics showed a simultaneous improvement of the flexural strength and fracture toughness.

2. Experimental procedure

Commercially available ZrB_2 powder (2 μm, > 99.5% purity, Northwest Institute for Non-ferrous Metal Research, China), SiC powder (0.5 μm, > 99.5% purity, Weifang Kaihua Micro-powder Co., Ltd., China) and graphite flake (mean diameter and thickness are 15 μm and 1.5 μm, respectively, > 99% purity, Qingdao Tiansheng Graphite Co., Ltd., China) were used as starting materials. The preparation process of the laminated ceramics consisted of (1) forming the ZrB_2–20 vol% SiC (ZS) and the graphite–10 vol% ZrB_2–20 vol% SiC (GZS) green sheets, (2) heating of the laminated material to remove organics and (3) sintering of the laminated ceramics.

The starting mixture of ZrB_2 and SiC was first ball-milled for 10 h in a polyethylene bottle with ZrO_2 balls and ethanol as the grinding media. Then adhesive and plasticizer were added to the slurry and a further ball-milling for 4 h was carried out to obtain a uniform slurry. Here polyvinyl butyral resin and polyethylene glycol-6000 were chosen as the adhesive and plasticizer, respectively. The mass ratio of ethanol, polyvinyl butyral resin and polyethylene glycol-6000 to ZrB_2–SiC mixtures in the slurry was 15:1:1:10. The ZS green sheets were subsequently formed by tape casting from the as-prepared ZrB_2–SiC slurry and then dried in air. By the same route the GZS green sheets were formed. After drying, the ZS sheets and GZS sheets were alternately stacked until the desired height. The laminated material was then heated at 700 °C for 1 h in a vacuum furnace to remove the organics; finally, the laminated material was hot pressed at 1900 °C for 1 h to obtain laminated ZrB_2–SiC/graphite ceramics. For comparison, monolithic ZrB_2–20 vol% SiC ceramics were prepared by ball-milling and hot pressing.

Microstructures of the ceramics were observed by scanning electron microscopy (SEM, FEI Sirion, Holand). Flexural strength (σ) was tested in three-point bending on 3 mm × 4 mm × 36 mm bars, using a span of 30 mm and a crosshead speed of 0.5 mm/min. Each specimen was ground and polished with diamond slurries to 1 μm finish. Fracture toughness (K_{IC}) was evaluated by a single edge notched beam (SENB) test with a span of 16 mm and a crosshead speed of 0.05 mm/min, using 2 mm × 4 mm × 22 mm bars. Before the test, a notch of 0.02 mm in width and 2 mm in depth was introduced on the surface. When loading, the laminated surface was perpendicular to the pressing force direction. A minimum of 10 specimens were tested for each experimental condition. Vickers' indentation was introduced with a 49 N load for 15 s on the polished surface.

3. Results and discussion

The macro- and microstructures of polished cross-section of the laminated ZrB_2–SiC/graphite ceramics are shown in Fig. 1. The dark and thick layers correspond to the ZS layers, whereas the gray and thin layers are the GZS layers (Fig. 1a). From the SEM images, the thicknesses of the ZS layer and the GZS layer are 300 μm and 30 μm, respectively. It reveals that both the ZS and the GZS layers have a uniform thickness. The slots in Fig. 1b are from the significant pullout of graphite that occurred during the polishing process, implying a weaker bonding strength within in the ZrB_2–SiC–graphite layers due to the presence of the soft graphite. The ZS layer consists of gray ZrB_2 and dark SiC phases, as shown in Fig. 1c, demonstrating a uniform dispersion of SiC particles into the ZrB_2 matrix. The gray ZrB_2 phase and the dark SiC phase were confirmed by EDS analysis, as shown in Fig. 1e and f. This SiC phase is confirmed to enhance both mechanical properties and oxidation resistance of ZrB_2 ceramics by the formation of silicate based glasses [1,10]. From the magnified image in Fig. 1d, the graphite retains the original layered structure after hot pressing, revealing an excellent thermal stability. Some particles of 2 μm are the ZrB_2 phases, which are indicated by white arrows. The introduction of layered graphite converts GZS layer into a weak layer. When cracks enter this layer, the layered graphite shields the stress at the crack tip. For this reason, crack deflection arises and crack path increases, and thus the fracture toughness is enhanced.

To compare fracture behaviors of the laminated ZrB_2–SiC/graphite ceramics with the monolithic ZrB_2–SiC ceramics, a series of mechanical tests were carried out. Crack propagation of the laminated ZrB_2–SiC/graphite ceramics under SENB test is shown in Fig. 2a. The crack initiated at the notch tip, propagated through the ZS layer, and then changed the direction at the GZS layer. After propagating in the soft GZS layer for some distance, the crack turned back to the load direction again. The horizontal distance of the crack was determined by the strength of the soft layer. With such a cyclic process, the crack propagated in a brick shape. Especially, from the magnified image in Fig. 2b, when the main crack changed direction, the branched crack propagated in two opposite directions in the GZS layer, which increased the crack length in the horizontal direction. From the simulation study of Zhang et al. [19], extremely high or low strength of the soft layer was not good for the toughness improvement of the laminated ceramics. Here, the crack branch reveals the GZS layer having a proper strength. Compared with the straight crack path in the monolithic ZrB_2–SiC ceramics (Fig. 2e), the main fracture modes of the laminated ZrB_2–

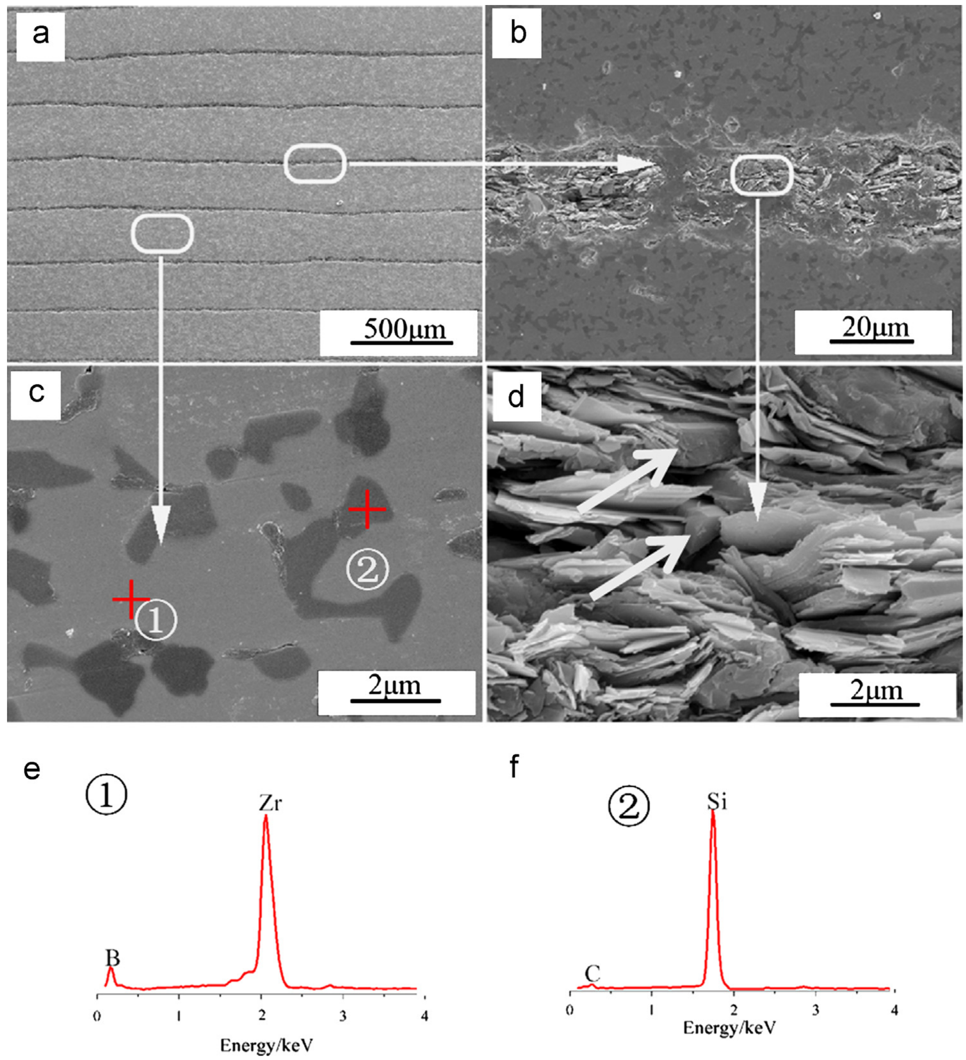

Fig. 1. SEM images of polished cross-section of the laminated ZrB_2–SiC/graphite ceramics: (a) uniform thickness of the layers, (b) GZS layer, (c) ZS layer, (d) layered structure of the graphite, (e) EDS pattern of ZrB_2 phase and (f) EDS pattern of SiC phase.

SiC/graphite ceramics are crack deflection, crack branch and interface delamination.

Fig. 2c shows crack propagation of the laminated ZrB_2–SiC/graphite ceramics in the three-point bending test. The crack passed straightly through the ZS layer until the crack tip reached the GZS layer; then a crack deflection occurred at the soft layer. In the magnified image (Fig. 2d), the crack propagated in two directions: the vertical crack passed the ZS layer; the horizontal crack propagated in the GZS layer initially and then deflected to the ZS layer. Crack branch caused energy dissipation, which consumed more fracture energy than that of the straight crack propagation in the monolithic ceramics (Fig. 2f).

The volume fraction of layered graphite in the GZS layer is 70 vol%, so the GZS layer can be considered as a porous structure. The propagation speed of crack in the porous layer is slower than that in the dense layer. In this study, the crosshead speeds of the three-point bending test and the SENB test were 0.5 mm/min and 0.05 mm/min, respectively. Such a speed difference leads to different fracture modes in the same laminated ceramics. Although effective crack deflection occurred in the two tests, more horizontal propagation was observed in the SEBN test. Further, this speed difference leads to different load–displacement curves, which will be discussed in the following part.

Fig. 3 shows typical load–displacement curves of the laminated and monolithic ceramics in the mechanical test. As described above, the crack that extended from the ZS layer during the SENB test was deflected by the thin, weak and layered GZS layer. Under increased applied loading, the crack propagated into the next ZS layer from the inherent processing defects. As a result, the laminated ceramic shows a step-like fracture with several pop-in events (Fig. 3a). In contrast to the catastrophic fracture of the monolithic ceramic at the maximum load, the laminated ceramic exhibits a layer-by-layer fracture after the maximum load. The later fracture mode can effectively consume fracture energy, and thus enhance reliability of the laminated ceramics as the structural components. The work of fracture was calculated as the area that the load–displacement curve envelopes divided by twice of the cross

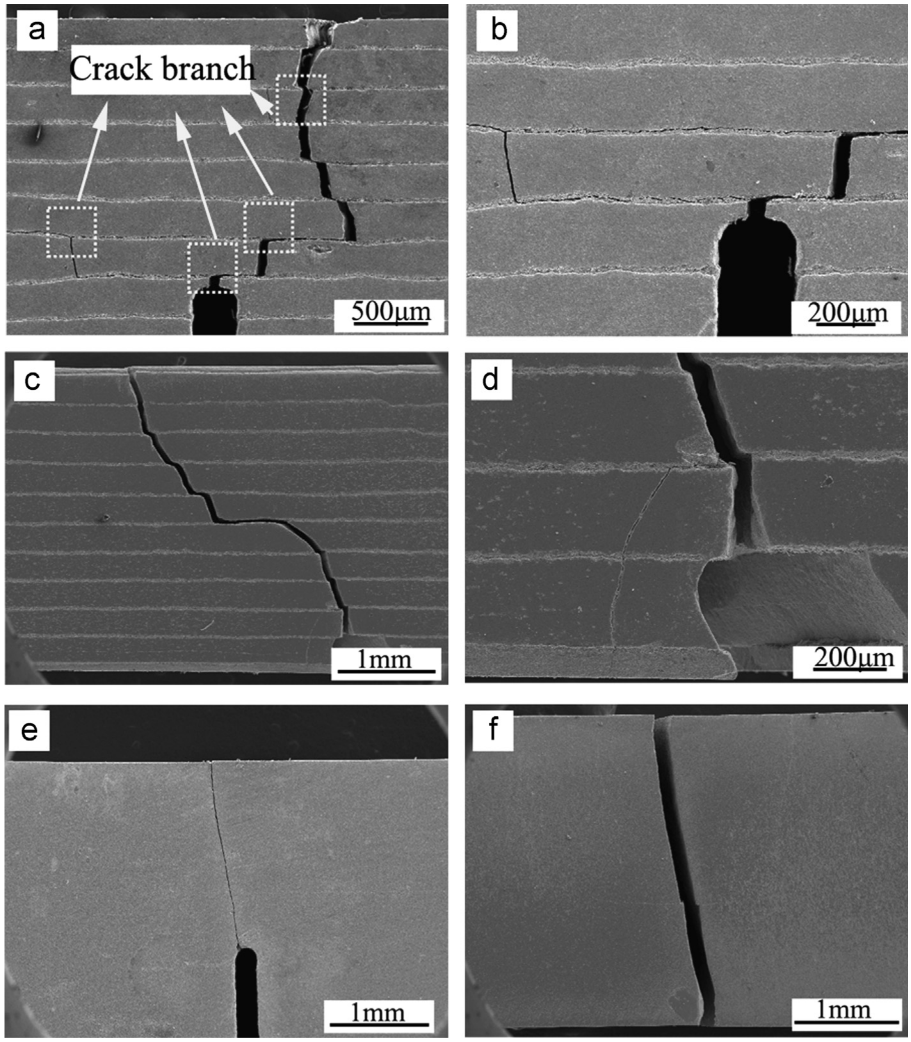

Fig. 2. SEM images of crack propagation in the ceramics: (a, b) laminated ZrB_2–SiC/graphite ceramics in the SENB test; (c, d) laminated ZrB_2–SiC/graphite ceramics in the three-point bending test; (e) monolithic ZrB_2–SiC ceramics in the SENB test; and (f) monolithic ZrB_2–SiC ceramics in the three-point bending test.

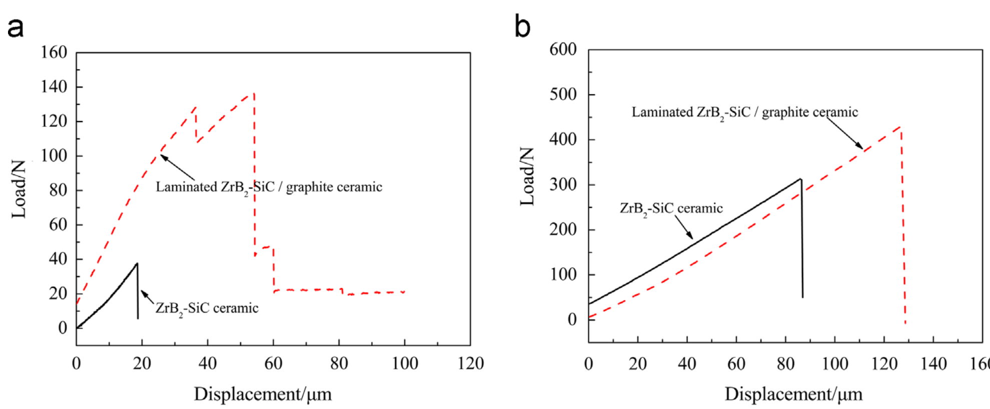

Fig. 3. Typical load–displacement curves of the laminated ZrB_2–SiC/graphite ceramics and the monolithic ZrB_2–SiC ceramics: (a) SENB test, and (b) three-point bending test.

sectional area of the specimen [20,21]:

$$\gamma = \frac{1}{2A}\int \mathrm{P}d\delta$$

where A is cross sectional area of the specimens; P is the load and δ is the displacement. By calculation, the fracture work of the laminated ceramic and the monolithic ceramic are 849 J/m^2 and 44 J/m^2, respectively. In other words, the fracture

Table 1
Mechanical properties of the laminated ZrB_2-SiC/graphite and the monolithic ZrB_2–SiC ceramics.

Materials	σ (MPa)	K_{IC} (MPa $m^{1/2}$)
Laminated ZrB_2–SiC/graphite ceramics	580 ± 21	12.4 ± 0.3
Monolithic ZrB_2–SiC ceramics	380 ± 35	4.8 ± 0.4

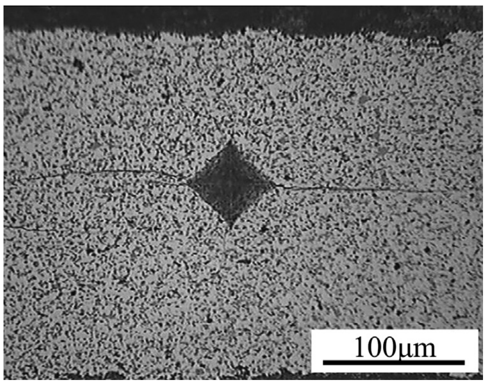

Fig. 4. Vickers' indentation and crack propagation in the ZS layer.

toughness of the laminated ZrB_2–SiC/graphite ceramics is notably improved by the layer-by-layer fracture, as listed in Table 1.

For the introduction of weak interface, the strength of the laminated ceramics is generally reduced. Many weakening factors, such as weaker bonding strength between the rigid–soft layers, lower load transfer of the soft layer and more defects in the soft layer, are negative issues for the mechanical behavior of the laminated material [7,9,13,22]. However, in this study, the fracture load of the laminated ZrB_2–SiC/graphite ceramics was much higher than that of the monolithic ZrB_2–SiC ceramics, as shown in Fig. 3b. With respect to flexural strength, an increase by 53% is achieved for the laminated ceramics (Table 1). In contrast to the step-like fracture in the SENB tests, the load–displacement curve in the three-point bending test followed a straight line (see Fig. 3b). This can be associated with the higher crosshead speed in the latter.

As the fracture of ceramics takes place mainly from the flaws on the surface, the flexural strength of laminated ceramics should be equal to the sum of the surface compressive stress and the strength of the outer layer [13]. The increase of surface compressive stress on the polished surface is speculated to yield higher flexural strength. For the laminated structure, the differences of coefficient of thermal expansion between different layers are evidenced to generate residual stress. This stress has been shown to enhance both mechanical and tribological properties of the composite. The thermal expansion coefficients of monolithic ZrB_2–SiC and graphite are 7.02×10^{-6}/K and 30×10^{-6}/K, respectively [16]. As a result, the ZS layer shows a compressive stress while the GZS layer undergoes a tensile stress in the laminated ZrB_2–SiC/graphite material.

To confirm the existence of compressive stress in the ZS layer, Vickers' indentation was introduced with a 49 N load for 15 s on the polished surface of the laminates. From Fig. 4, the cracks emanating from the corners of the Vickers' indentation were shorter when they propagate perpendicular to the interface than parallel to the interface. This is a direct evidence of compressive stresses in the ZS layers. On the contrary, tensile stress were generated in the ZSG layers, which enhanced crack deflection in the ZSG layers, as observed in Fig. 2.

4. Conclusion

In summary, laminated ZrB_2–SiC/graphite ceramics were prepared by tape casting and hot pressing according to the structure of natural biomaterials. The rigid ZrB_2–20 vol% SiC sheets and the soft graphite–10 vol% ZrB_2–20 vol% SiC sheets were alternately stacked to produce the laminated structure. Both flexural strength and fracture toughness were improved by the introduction of layered graphite, reaching the peak values of 580 MPa and 12.4 MPa $m^{1/2}$, respectively. Compared with the monolithic ZrB_2–SiC ceramics, a higher work of fracture was gained in the laminated ZrB_2–SiC/graphite material for the step-like fracture. The differences of coefficient of thermal expansion yielded residual comprehensive stress in the ZS layer but residual tensile stress in the GZS layer. Thus, crack propagation perpendicular to the interface in the ZS layer was restrained. In conclusion, crack branch and interface delamination were considered as the main toughening mechanisms; surface residual stress was responsible for the strengthening of the laminated ZrB_2–SiC/graphite material.

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