R-curve behavior of laminated ZrB₂-SiC ceramic with strong interfaces

Peng Zhou ^{a,*}, Ping Hu ^b, Xinghong Zhang ^{a,b}, Wenbo Han ^b, Youhua Fan ^a

^a School of Natural Sciences and Humanities, Harbin Institute of Technology Shenzhen

Graduate School, Shenzhen 518055, China

^b Center for Composite Materials, Harbin Institute of Technology, Harbin 150001,

China

Abstract

The damage resistance and R-curve behavior of laminated ZrB₂-SiC ceramic fabricated by hot-pressing were investigated using indentation-strength technique. The difference in fracture resistance properties between the monolithic and laminated ZrB₂-SiC ceramics was also analyzed and results showed that obvious R-curve behavior was found in laminated ZrB₂-SiC ceramic, compared with monolithic ZrB₂-SiC ceramics. Moreover, the indentation strength values of laminated ZrB₂-SiC ceramic were observed to be insensitive to the increases in the indentation load, which indicated that laminated ZrB₂-SiC ceramic has excellent damage resistance. The improvement in damage tolerance and R-curve behavior of laminated ZrB₂-SiC ceramic was attributed to the macroscopical crack deflection due to the presence of residual compressive stresses.

Keywords: Laminated structure; ZrB₂-SiC ceramic; R-curve behavior; Residual stress; Fracture; Mechanical characterization

*Corresponding author: Peng Zhou

Tel/ Fax: +86 755 28159282

Email: zhoupeng85723@163.com;

1. Introduction

It is well known that ceramics as structural materials are commonly considered as inherently brittle. To increase the fracture toughness and improve the mechanical reliability of ceramic materials, new strategies that are significantly different from the conventional approach have emerged recently. The laminate is as new strategy to achieve “flaw tolerance” in opposition to the traditional “flaw elimination” approach of the dense ceramics [1, 2]. Up to now, the fracture toughness of multilayer ceramics has been enhanced by the two main methods over conventional ceramics, namely the introducing weak interfaces [3-5] or the introducing of residual compressive stresses in the laminated structures [6-8]. For the first case, the weak interlayers can introduce low-energy paths for crack propagation in laminated structures, which are usually obtained by utilizing different materials with respect to the main multilayer component to form layers not wholly sintered or introducing porous structures [9-12]. With respect to the other case, the residual compressive stresses in the laminated ceramics arising from a mismatch in the thermal coefficient of expansion between the different layers will enhance remarkably the fracture toughness and improve the fracture resistance and mechanical reliability [13, 14].

ZrB₂-based ceramics have attracted considerable attention due to excellent physicochemical properties, such as extremely high melting point and hardness, high thermal and electrical conductivity and chemical stability [15-17]. These properties make them a potential candidate for a variety of high-temperature structural applications [16, 18, 19]. Although ZrB₂-based ceramics have many excellent properties, like the

other ceramics, their low fracture toughness has long prevented them from being used in wide application. Therefore, mechanical reliability of ZrB₂-based ceramics must be improved before the potential applications can be fully realized.

Based on the superiority of laminated structure with strong interfaces in enhancing the toughness of ceramics and the disadvantage in fracture toughness of ZrB₂-based ceramics, according to above-mentioned facts, the laminated design of ZrB₂-based ceramics would obtain high mechanical performance and reliability materials. Unfortunately, few studies have been carried out on laminated ZrB₂-based ceramics composite reinforced and toughened by the residual compressive stress. In our previous works [20,21], the effect of residual stress on the mechanical properties of laminated ZrB₂-SiC ceramics with strong interfaces has been evaluated and results showed that the strength and toughness of laminated ZrB₂-SiC ceramics were enhanced significantly.

In this paper, *R*-curve behavior of laminated ZrB₂-SiC ceramic were investigated firstly by indentation-strength method in detail. The difference in fracture resistance properties between the monolithic and laminated ZrB₂-SiC ceramics was also analyzed.

2. Experimental Procedure

Commercially available ZrB₂ (mean particle size 2 μm, >99.5%, Northwest Institute for Non-ferrous Metal Research, China) and SiC (mean particle size 0.5μm, >99.5%, Weifang Kaihua Micro-powder Co. Ltd., China) were used in the present work. The manufacturing steps of the laminated ZrB₂-SiC ceramics included (a) ball milling of powders in certain proportions; (b) Stacking layers in sequence in graphite mold. Two compositions of layers were used: (1) ZrB₂+30vol%SiC, and (2) ZrB₂+20vol%SiC. The

mixtures of various compositions were ball-milled in a polytetrafluoroethylene bottle using ZrO_2 ball and ethanol as the grinding media at 220 rpm for 10 h, followed by rotating evaporation to remove the solvent. The obtained powders were put into graphite die according to a certain quality ratio. Both monolithic and laminated $\text{ZrB}_2\text{-SiC}$ disc-shaped samples ($\Phi=50$ mm, $h=4$ mm) were fabricated. The laminated $\text{ZrB}_2\text{-SiC}$ sample with a symmetrical multilayered architecture was prepared by alternately stacking thin $\text{ZrB}_2+30\text{vol\%SiC}$ layers and thick $\text{ZrB}_2+20\text{vol\%SiC}$ layers, with both of the surface layers being $\text{ZrB}_2+30\text{vol\%SiC}$. The monolithic $\text{ZrB}_2\text{-SiC}$ sample was fabricated from stacking layers with the same composition. The hot pressing was performed by the vacuum hot pressing furnace (ZYD-60, Jinzhou Hanxing, China) at 1950°C and 30 MPa for 60 min with a heating and cooling rate of 5°C/min in Ar atmosphere.

The specimens for mechanical tests were obtained by machining the hot pressed tiles. All flexural and fracture bars were cut with the tensile surface perpendicular to the hot-pressing direction. A minimum number of five specimens were tested for per experimental condition. The macroscopic cross-section and microstructures features of the composites were observed by optical microscope (ZEISS, MC80DX, Germany) and scanning electron microscope (SEM, FEI Sirion, Holland), respectively. The phase composition was determined by X-ray diffraction (XRD, Rigaku, Dmax-rb, $\text{CuK}\alpha=1.5418\text{\AA}$). According to ASTM-D790 standard, flexural strength (σ) was tested by the universal mechanical testing machine (Instron 5569, Instron, America) in three point bending on $3\text{mm}\times4\text{mm}\times36\text{mm}$ bars, using a 30-mm span and a crosshead speed of

0.5mm/min. Fracture toughness (K_{IC}) was evaluated by a single-edge notched beam (SENB) test, according to ASTM-C1421-01b standard, with a 16-mm span and a cross-head speed of 0.05 mm/min using 2 mm×4 mm×22mm bars, on the same jig used for the flexural strength. The elastic modulus was measured by three-points bending tests with a 30-mm span by using a calibrated strain gauge to measure the strain as a function of applied load and a cross-head speed of 0.5 mm/min using 3 mm×4 mm×36 mm bars. Hardness was determined by a Vickers pyramid diamond indenter (model HvS-5) through ASTM-E92 standard, using a indentation load of 5kg and a dwell time of 15s on polished surfaces.

Indentation strength bending technique (ISB) was used to further evaluate the fracture behavior [22]. The specimens were machined into the rectangular bars of 4mm (thickness)×2mm (width)×22mm (length), then polished using conventional polishing techniques. The test specimens were indented at the center of the polished tensile surface with a Vickers diamond pyramid indenter under loads ranging from 0.1 to 196 N. All indentations were made in air, and the indenter contacted the specimen surface for 15s before it was withdrawn to complete the load cycle. Care was taken to orient one set of the indentation cracks to be parallel to the longitudinal axis of the rectangular bars. After indentation, the specimens were tested in three point bending with a span of 16 mm and a crosshead speed of 0.5 mm/min. A minimum number of 3 tests were performed for each indentation load. R-curves of monolithic and laminated materials were obtained using indentation-strength method developed by Braun et al. [22], which considered a radial crack c produced by indentation at a load P and subjected to the

action of a tensile stress σ_a due to the applied stress load during three-point bending. During post-indentation bending, the crack is subjected to a total stress intensity, K_t , which is the sum of contributions from the residual stress intensity factor acting on the indentation crack resulted from the elastic mismatch associated with the indentation, K_r , and the stress intensity factor from the applied stress, K_a :

$$K_t(c) = K_a(c) + K_r(c) = \psi \sigma_a c^{0.5} + \xi \left(\frac{E}{H}\right)^{0.5} P c^{-3/2} = K_R(c) \quad (1)$$

where ψ is a material independent constant that depends on crack geometry and is usually estimated to 1.24 for a semi-elliptical surface crack [23], ξ a non-dimensional geometry constant that is estimated as 0.016 and dependent on the indenter geometry and the Poisson's ratio of the indented material [24], E the Young's modulus, H the hardness and K_R the toughness of the material. For a given indentation load, P , failure is assumed to occur at the stress where the applied stress, σ_a , is equal to the fracture stress, σ_f , which is given by the condition of the common-tangent intersection for the $K_t(c)$ and $K_R(c)$ curves. This required that:

$$K_t(c) = K_R(c) \quad (2)$$

$$\frac{dK_t(c)}{dc} = \frac{dK_R(c)}{dc} \quad (3)$$

The R-curve is estimated by solving Eqs. (2) and (3) for each beam simultaneously. In other words, the R-curve is determined as the common envelope of the tangency points of the family of $K_t(c)$ curves from the $\sigma_f(P)$ data sets.

3. Results and Discussion

Fig. 1a shows the XRD results of the ZrB₂+20vol%SiC and ZrB₂+30vol%SiC mixtures obtained by ball-milling. From the XRD patterns, characteristic peaks of ZrB₂

and SiC were identified and no characteristic peaks of ZrO_2 were detected. This suggests that the amount of ZrO_2 impurity in ZrB_2 -SiC mixtures due to ball milling process is very small. So, the effect of ZrO_2 on the mechanical properties of monolithic and laminated ZrB_2 -SiC ceramics can be ignored in the present work. Fig.1b and Fig.1c shows the macro- and micro-structures of symmetrical 9-layer laminated ZrB_2 -SiC ceramic. As it can be seen, the ZrB_2 +30vol%SiC layers (bright regions) and ZrB_2 +20vol%SiC (dark regions) are reasonably uniform and the interfaces are straight and well-distinguishable (see Fig.1b). The thickness of ZrB_2 +30vol%SiC layers is about 250 μm , and the thickness of the ZrB_2 +20vol%SiC layers is about 650 μm . In addition, the SiC grains have been homogeneously dispersed in the layers (see Fig.1c).

The mechanical properties of laminated ZrB_2 -SiC ceramic (hereafter denoted by LZS) and monolithic ZrB_2 +30vol%SiC ceramic (hereafter denoted by ZS30) are given in Table 1. It should be noted that for SENB tests of laminated ZrB_2 -SiC ceramic the notch tips were located in the compressive layer of the tested samples. The flexural strength of the laminated ZrB_2 -SiC ceramic is 750 ± 67 MPa, which is much higher than 520 ± 63 MPa of monolithic ZrB_2 -SiC ceramic. It is believed that the fracture toughness of specimens with crack tips in layers under compression is higher than that of specimens with crack tips in layers under tension. When crack tips are in layers under compression, the fracture toughness of the laminated ZrB_2 -SiC ceramic can reach to 7.4 ± 0.4 $\text{MPa m}^{1/2}$, which increased by approximately 32.1% in ZrB_2 +30vol%SiC ceramic (5.6 ± 0.5 $\text{MPa m}^{1/2}$). What is more, the hardness (21.5 ± 0.8 GPa) and elastic modulus (484 ± 12 GPa) of laminated ZrB_2 -SiC ceramic are higher than those of the monolithic

ZrB₂-SiC ceramic. Compared with the monolithic ZrB₂-SiC ceramics, the remarkable improvement in mechanical performance of laminated ZrB₂-SiC ceramic is attributed to the presence of residual compressive stresses on the surfaces of the tested specimens.

Fig. 2 shows the indentation fracture strength values against indentation load for both LZS and ZS30. The surface damage produced at different indentation loads demonstrates the differences in flexural strength losses for the laminated and monolithic ZrB₂-SiC ceramics. As developed previously, the damage tolerance represented the resistance to damage of materials, especially the ability of resistance to strength degradation under external loads [26]. For a given indentation flaw, ceramic with compressive stresses at the surface always provides higher value of retained strength, which means that such ceramic presents higher damage tolerance. As can be seen in Fig. 2, the strength values for LZS were higher than for ZS30, in the high-indentation-load region the strength values for the two materials decreased linearly with indentation load, but the slope being much steeper for ZS30 than for LZS. This means that LZS has a higher retained strength than ZS30 for an equivalent indentation load, hence an improved damage tolerance in comparison with ZS30. It also suggested that LZS might have a higher fracture resistance than that of ZS30. Linear regression was used to obtain the best fit for the experimental data in Fig. 2. It showed that the slopes of ZS30 and LZS were 0.425 and 0.262, respectively. According to the reported work, Griffith materials, which show no rising *R*-curve behavior, present a slope of 1/3, and materials with slopes lower than 1/3 are expected to have *R*-curve behavior [25].

The resulting toughness curve diagrams obtained for both LZS and ZS30 are plotted

in Fig. 3. Evidently, monolithic $\text{ZrB}_2\text{-SiC}$ ceramic almost does not have R-curve behavior. According to the reported work, such none or very soft R-curve behavior implies that there is almost absence of extrinsic toughening mechanisms that are operating in the wake of a propagating crack [26-29]. The slope of 0.425 in Fig. 2, higher than 1/3, further confirms the soft R-curve behavior for monolithic ceramic. It can be seen from Fig. 3 that laminated $\text{ZrB}_2\text{-SiC}$ ceramic exhibits obvious R-curve behavior compared with monolithic $\text{ZrB}_2\text{+30vol.\% SiC}$ ceramic, which is attributed to the presence of residual compressive stresses arising from a mismatch in the thermal coefficient of expansion between the adjacent layers.

The above-mentioned results showed that LZS possessed excellent damage tolerance and R-curve behavior in comparison with ZS30. This was related to their different toughening mechanisms. For the ZS30, the main toughening mechanism is crack deflection due to the second phase particles. However, the toughening mechanism to LZS contains two aspects as follows. The first aspect is at the scale of the microstructure due to the second phases, leading to flaw-tolerant materials. The second aspect is at a macroscale due to the interfaces between the layers[1]. The aim is to improve both the toughness and the strength. Fig. 4 showed the crack propagation paths in SENB tested ZS30 and LZS specimens, and in LZS indentation-fracture specimens under different Vickers indentation loads, which corresponds to polished sections of indentation-fracture specimens subjected to biaxial bending. It can be seen that the crack propagation (deflection) in LZS ceramic is readily observed in comparison with ZS30 ceramic. The occurrence of cracks deflection is due to

encountering high intensity biaxial residual compressive stresses, which improved the fracture resistance remarkably.

4. Conclusions

The laminated $\text{ZrB}_2\text{-SiC}$ ceramic was successfully prepared by hot-pressing. The damage resistance and R-curve behavior of laminated $\text{ZrB}_2\text{-SiC}$ ceramic were investigated using the indentation-strength method. Because of the shielding effect of residual compressive stress, the indentation strength values of laminated $\text{ZrB}_2\text{-SiC}$ ceramic were observed to be insensitive to the increases in the indentation load, which indicated excellent damage resistance. Moreover, obvious R-curve behavior was further found in laminated $\text{ZrB}_2\text{-SiC}$ ceramic compared with monolithic $\text{ZrB}_2\text{-SiC}$ ceramic. The improvement in damage tolerance and R-curve behavior was attributed to the macroscopical crack deflection due to the presence of residual compressive stresses arising from a mismatch in the thermal coefficient of expansion between the adjacent layers.

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Table Caption

Table 1 Mechanical properties of laminated ZrB₂-SiC and monolithic ceramics

Figure Captions

Fig. 1 XRD patterns of ZrB_2 +20vol%SiC and ZrB_2 +30vol%SiC mixtures obtained by ball-milling (a), optical micrograph of cross-section (b) and SEM image (c) of the laminated ZrB_2 -SiC ceramic.

Fig. 2 Strength plotted against indentation load for LZS and ZS30.

Fig. 3 Toughness curve diagrams for ZS30 (a) and LZS (b).

Fig. 4 Crack propagation in SENB tested ZS30 (a) and LZS (b) specimens, and in LZS indentation-fracture specimens under different Vickers indentation loads: (c)-0 N, (d)-9.8 N, (e)-19.6 N, (f)-29.4 N, (g)-49 N and (h)-98 N.

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Samples	σ (MPa)	K_{IC} (MPam ^{1/2})	E (GPa)	H (GPa)
LZS	750 $\pm$ 67	7.4 $\pm$ 0.4	484 $\pm$ 12	21.5 $\pm$ 0.8
ZS30	520 $\pm$ 63	5.6 $\pm$ 0.5	440 $\pm$ 18	19.6 $\pm$ 0.9