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Influence of fiber coating thickness on microstructure and mechanical properties of carbon fiber-reinforced zirconium diboride based composites

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Abstract

Unidirectional carbon fiber-reinforced zirconium diboride based composites were fabricated by hot pressing. The fiber–matrix interface was tailored by pre-coating the as-received carbon fibers with pyrolytic carbon (PyC) coatings of various thickness or silicon carbide (SiC) coating. The effects of the interfacial characteristics on mechanical properties and microstructure of the composites were studied. The results indicated that both the composites reinforced with as-received carbon fibers and SiC coated carbon fibers showed inferior flexural strength and fracture toughness. With optimized PyC coating thickness, the mechanical properties of the composites had been remarkably improved, i.e. a flexural strength of 309.6 MPa was achieved when the thickness of PyC coating was 0.1 μm, and a fracture toughness of 6.72 MPa $m^{1/2}$ was obtained when the PyC coating was 0.7 μm thick.

Keywords: B. Interfaces; C. Mechanical properties; Zirconium diboride; Ceramic composites

1. Introduction

Zirconium diboride (ZrB_2) based ultrahigh-temperature ceramics have been identified as the potential materials that are adequate for high-temperature uses in refractory industry, especially in aerospace field, as components in re-entry hypersonic aerospace vehicles, because of their low density, high strength, and high melting temperature, combined with excellent oxidation and thermal shock resistance [1–3]. However, the use of ZrB_2 based ceramic in refractory industry, even fully densified, is limited by its poor fracture resistance and damage tolerance. Many attempts have been made to improve the toughness of ZrB_2 based ceramic. Particulate-, whisker-, and fiber-reinforced ceramic composites are common ways to solve this problem [4–14].

The importance of fiber–matrix interface on mechanical properties of ceramic composites has long been recognized [15]. Two key functions may be assigned to fiber–matrix interfaces: strengthening and toughening of the composites. Strengthening results from load transfer whereas toughening is due to energy dissipation. It is often considered that toughening is the major issue. The major contribution to toughness involves crack deflection and sliding of the fibers along the debonded interfaces. Toughening thus requires extensive interface debonding which necessitates weak interfaces. In contrast, high strength results from efficient load transfer through strong interfaces, which requires strong fiber–matrix interactions, short debond and significant sliding friction [16–20]. In addition, in the carbon fibers reinforced ZrB_2 based ceramics, process corrosion between the carbon fibers and the matrix is unavoidable, which would arrested the perfect exhibition of the mechanical properties of the carbon fibers and the ceramic composites [5,6]. Hence, it is necessary for the deposition of a thin coating on the carbon fibers used to protect carbon fibers from the process corrosion and engineer the interfacial

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characteristics [21]. The most common coating materials adapted to improve the interface are pyrolytic carbon (PyC) [22,23] and boron nitride (BN) [24,25]. Silicon carbide (SiC) is also used to modify the interface of composites for high temperature applications [26,27].

The present study aims to optimize the fiber–matrix interface for enhanced mechanical properties of unidirectional carbon fibers reinforced ZrB_2 based composite. The as-received carbon fibers were coated with either the PyC coatings of different thicknesses or a SiC coating for the fabrication of unidirectional carbon fibers reinforced ZrB_2 based composite by CVD process. The mechanical properties and the fracture behavior of the composites were investigated and correlated to the fiber–matrix interfacial characteristics.

2. Experimental details

2.1. Sample preparation

The raw materials consisted of ZrB_2, SiC, silicon nitride (Si_3N_4) and mesophase pitch-based carbon fibers. ZrB_2 powders were supplied by Dandong Chemical Engineering Institute Co., Ltd, China, and the mean particle size and purity were 2 μm and 99%, respectively. SiC powders used in this work were provided by Weifang Kaihua silicon carbide micropowder Co., Ltd, China, and the mean particle size and purity were 1 μm and 99%, respectively. Si_3N_4 powders used in this work were provided by Hebei Shinuorui New Material Co., Ltd, China, and the mean particle size and purity were 1 μm and 99%, respectively. Mesophase pitch-based carbon fibers were offered by our lab, which were prepared through mesophase pitch spinning with a round nozzle, oxidation stabilization at 533 K and carbonization at 1173 K in nitrogen atmosphere [28].

Prior to the fabrication process of the ceramics, carbon fibers were coated with PyC or SiC using CVD process [22,29], which was carried out in a hot-wall tube reactor. Before the deposition, the continuous carbon fibers were cut into short carbon fibers (5 cm). Mixture of methane and argon gases was used to deposit PyC at 1373 K and mixture of methyltrichlorosilane, hydrogen and argon was used to deposit SiC at 1373 K. The thickness of PyC and SiC coating was controlled by the deposition time. The resulting thicknesses were 0.1, 0.3, 0.7and 1 μm for PyC coatings and 0.3 μm for SiC coating.

The fabrication process of the unidirectional carbon fibers reinforced ZrB_2–SiC based composite (C_f/ZrB_2–SiC) is shown in Fig. 1. The volume fraction of ZrB_2 powders, SiC powders and carbon fibers in the composite was 64%, 16% and 20%, respectively. To fabricate the C_f/ZrB_2–SiC, Si_3N_4 (3 wt%) was used as a sintering aid. The matrix powders (ZrB_2 and SiC) and additive powders (Si_3N_4) were ball-mixed for 5 h in an agate bottle using agate balls and ethanol as the grinding media. Short carbon fibers were unidirectionally arranged on the same plane and then stacked alternately with the mixed slurry in a graphite die. The mixture was cold-pressing under a uniaxial load of 20 MPa to form a compact. Then, the compact was hot-pressing at a maximum temperature of 2173 K for 1 h under a uniaxial load of 30 MPa. The composite samples were denoted according to the composition and thickness of coatings as as-received, C0.1, C0.3, C0.7, C1.0 and SiC0.3.

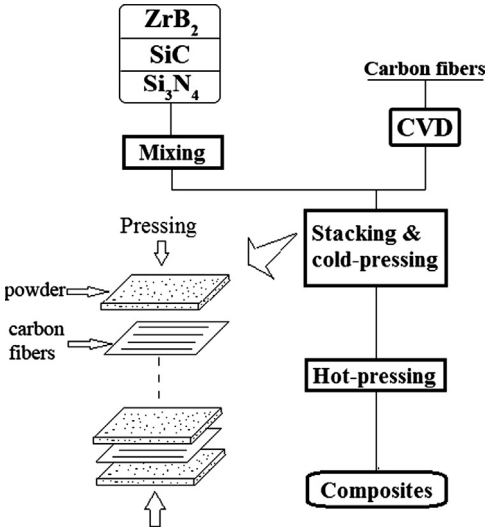

Fig. 1. Illustration of the preparation process of unidirectional carbon fibers reinforced ZrB_2–SiC based composite.

2.2. Mechanical evaluations

The test specimens were cut in parallel to the carbon fibers axis and then polished before ultrasonic cleaning. Flexural strength (σ) was evaluated by three-point bending test with a 30 mm span and a crosshead speed of 0.05 mm/min using 3 mm × 4 mm × 36 mm test bars. The test was conducted following the general guidelines of ASTM standard C1341. Fracture toughness (K_{IC}) was evaluated by a single-edge notched beam (SENB) test with a 16 mm span and a crosshead speed of 0.05 mm/min using 2 mm × 4 mm × 22 mm test bars. The test was conducted following the general guidelines of ASTM standard C1421. Field emission scanning electron microscopy (FESEM, model HITACHI S-4800) was employed to examine the fracture surfaces of the composites after the SENB test.

3. Results and discussion

3.1. Effect of interfacial layer on flexural behaviors of C_f/ZrB_2–SiC

Typical stress–strain curves of the C_f/ZrB_2–SiC composites reinforced with the as-received, PyC coated and SiC coated carbon fibers, which were recorded by the three-point bending test, are shown in Fig. 2. The typical stress–strain curves indicate that the failure behavior of the composites is significantly dependent on the characteristics of the interfacial layer. The composites reinforced with as-received carbon fibers gives a flexural strength of 272.6 MPa, a modulus of 306.5 GPA and the failure behavior (Fig. 2a) shows elastic response in the initial stage, followed by inelastic behavior as

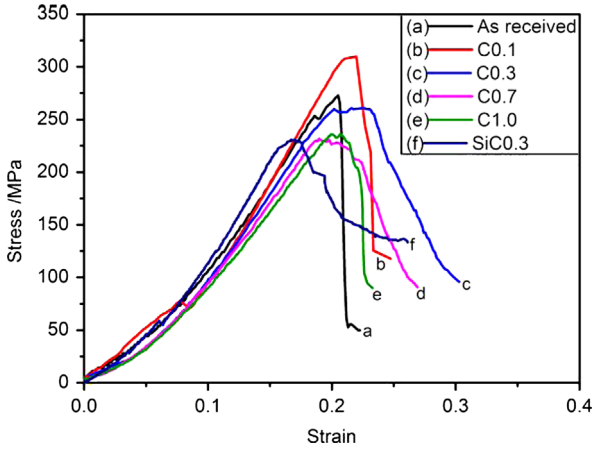

Fig. 2. Typical stress–strain curves recorded by the three-point bending test for the composites with various interfacial layers.

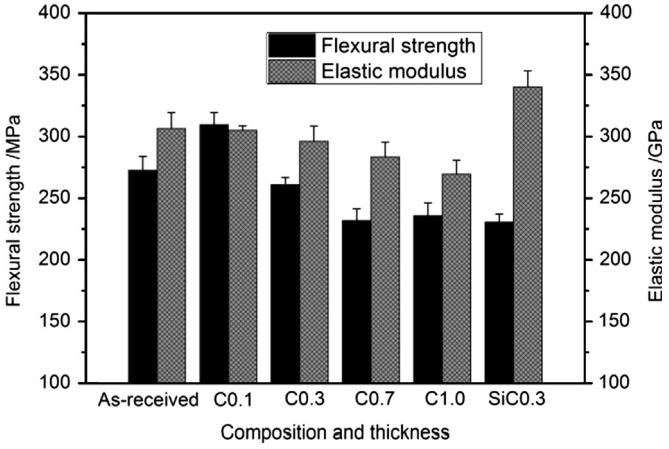

Fig. 3. Effect of the interface composition and thickness on the flexural strength and elastic modulus of the composites.

the stress increases. After the stress increases to its maximum value, the stress then decreases rapidly with step-failure, which is responsible for the brittle failure within the specimens. In contrast, the curves for the PyC coated fiber-reinforced composites, especially for sample (c), (d) and (e), indicate a standard toughened fracture behavior. When the load reaches its maximum value, it will drop off gradually. The areas under these curves are much larger compared with the composite reinforced with as-received carbon fibers. These indicate that abundant of fracture energy has been exhausted and the toughness has been improved prominently. The highest flexural strength of 420.6 MPa is achieved with the PyC coating thickness of 0.1 μm. However, the typical stress–strain curve of this sample (see Fig. 2b) shows an elastic response in the beginning, and then a non-linear behavior near the peak load, followed by a sudden decreasing after the maximum load. These demonstrate a catastrophic and early failure mode. As for the SiC layer, the curve for the composite presents a flexural strength of 216.4 MPa and an elastic modulus of 117.6 GPa. The sample failed in a brittle mode is likely due to a strong fiber–matrix interface bonding.

The flexural strength and elastic modulus of composites reinforced with the as-received, PyC coated or SiC coated carbon fibers are shown in Fig. 3. It can be seen that composite with a thin PyC interlayer, i.e. 0.1 μm thick, possesses a much higher flexural strength (420.6 MPa) than the composite with as-received carbon fibers. That is to say, the flexural behavior of C_f/ZrB_2–SiC composites in this study is improved by the tailored fiber–matrix interface. The flexural strength decreases with further increase of PyC layer thickness. This result is in good agreement with Miller′s work [18]. Whereas, the introduction of SiC interface coating led to a large degradation of the flexural strength of the composite.

It can also be seen from Fig. 3 that the C_f/ZrB_2–SiC composites containing PyC coated carbon fibers has a lower modulus than the composite reinforced with as-received carbon fibers. It is probably because of the presence of an easy slipping PyC layer, which can′t transfer stress from matrix to carbon fibers efficiently. While the composite

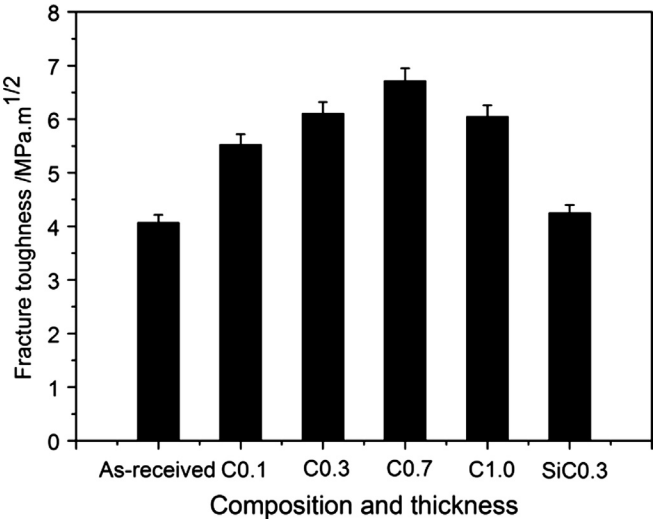

Fig. 4. Effect of the interface composition and thickness on the fracture toughness of the composites.

reinforced with SiC coated fibers, the higher modulus may be due to the addition of SiC layer, which not only is an anti-slipping layer, but also protects the carbon fibers from the process corrosion during the hot pressing process.

3.2. *Effect of interfacial layer on the fracture toughness of C_f/ZrB_2–SiC*

The SENB test data is given in Fig. 4. The presence of PyC or SiC interfacial layer always led to the increase of fracture toughness. The fracture toughness increases at first and then decreases with the increase of PyC coating thickness. A peak value of 6.72 MPa $m^{1/2}$ is obtained when the PyC coating is 0.7 μm thick. The fracture toughness of the composite reinforced by SiC coated carbon fibers is higher than that of the composite reinforced by as-received carbon fibers, but lower than that of the composite reinforced by PyC coated carbon fibers. In order to improve fracture toughness, a desirable fiber–matrix interface would be the one which is not only

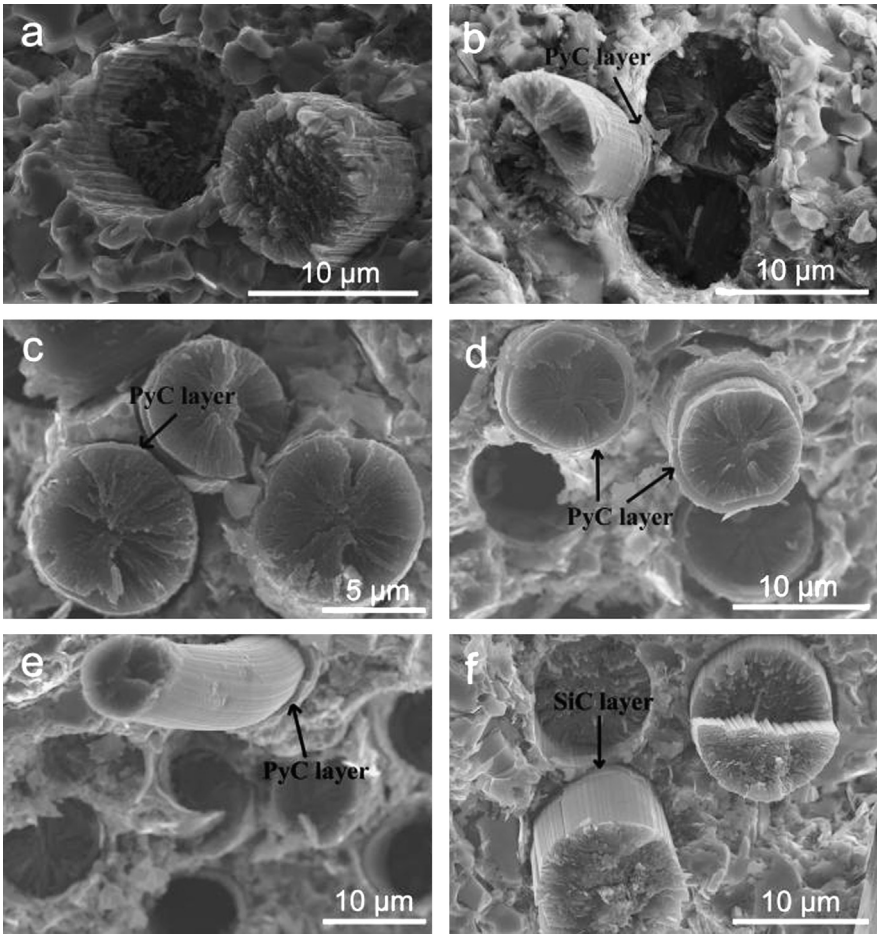

Fig. 5. SEM micrographs showing fracture surfaces of $C_f/ZrB_2/SiC$ after the SENB test: (a) as-received, (b) 0.1 μm PyC coating, (c) 0.3 μm PyC coating, (d) 0.7 μm PyC coating, (e) 1.0 μm PyC coating and (f) SiC coating.

strong enough for effective load transfer between the matrix and the carbon fibers, but also sufficiently weak to allow the interface debonding and cracks deflection and branching [15,30]. The brittle fracture behavior of composite reinforced with the as-received carbon fibers is likely due to the corrosion of the carbon fibers during hot-pressing process as well as the extreme weak bond between the carbon fibers and the matrix, which reduces the load transfer at the interface. In contrast, the brittle fracture behavior of the composite with SiC interfacial layers can be attributed to the strong interfacial bond, which suppressed the possible interface debonding, cracks deflection, cracks branching, fiber bridging and fiber pull-out. With the increase of the thickness of PyC coating, more and more PyC remains after the process corrosion during the hot-pressing process, and then continuous and further thicker PyC layers are formed between the carbon fibers and the matrix. Because the PyC interfacial layer is a low interfacial shear strength and easy slipping interfacial layer, a huge amount of interface debonding and cracks deflection and branching would occur in the interface zone but the efficiency of the load transfer through the interfacial layer would reduce. When the thickness of the PyC coating is 0.7 μm, the fiber–matrix interface is appropriate, which is not only strong enough for effective load transfer between the matrix and the carbon fibers, but also sufficiently weak to allow the interface debonding and cracks deflection and branching.

3.3. Microstructure of fracture surfaces of C_f/ZrB_2–SiC

In order to investigate the interfacial conditions, SEM micrographs of fracture surfaces of the ZrB_2 based composites after the SENB test are shown in Fig. 5. It should be noted that the interfacial conditions of the composites are corresponding to that of the mechanical properties and fracture behavior of the composites. Serious damage on the carbon fibers surface in the sample of the composite reinforced by as-received carbon fibers is shown in Fig. 5a, which is possibly caused by the process corrosion during hot-pressing process. This would lead to poor mechanical properties of the carbon fibers and the composites. It can be seen from Fig. 5b that most of the PyC in the interfacial layer has been consumed by protecting the carbon fibers from process corrosion during the fabrication process and continuous interfacial PyC layers had not been formed between the carbon fibers and the matrix. As a result, the sample has a high flexural strength but a brittle failure behavior. For the composites reinforced with carbon fibers with PyC coatings of the thickness from 0.3 to 1.0 μm, PyC coating residues are found adhered to the surfaces of the

pullout fibers (Fig. 5c–e), which indicate that rich crack deflection and crack branching occurred in interfacial zone and a large amount of energy had been consumed during the failure process. Whereas, Fig. 5f shows the strong interface bonding in the SiC coated fiber-reinforced composite. The potential large near-crack tip stress field could not be effectively dissipated and buffered by means of these strong interfaces, and subsequently the cracks passed through the carbon fibers, leading to typical unstable catastrophic failure characteristic, such as the flat fracture surface with short fiber pullout, and ultimately resulting in a lower flexural strength and toughness.

4. Conclusions

ZrB_2–SiC based composites reinforced with unidirectional carbon fibers have been fabricated by hot-pressing process. The interfacial zone between the carbon fibers and the matrix has been engineered by pre-coating carbon fibers with PyC of different thickness or SiC. The effects of the interfacial characteristics on the mechanical properties of the composites have been studied. Results show that, for the composite reinforced by the as-received carbon fibers, the weak interfacial bond between the carbon fibers and the matrix and the inevitable corrosion to the carbon fibers during manufacturing process led to relatively poor flexural strength and fracture toughness. The composite reinforced with the SiC coated carbon fibers resulted in a very strong interface between the carbon fibers and matrix. However, the strong interface was not propitious to the occurring of toughening mechanism. The composites reinforced with PyC coated carbon fibers had obviously improved mechanical properties compared to the composite containing the as-received fibers. These composites have a peak value of 309.6 MPa for flexural strength and 6.72 MPa $m^{1/2}$ for fracture toughness occurred when the PyC layer is 0.1 μm and 0.7 μm thick respectively. This is due to the appropriate characteristics of the fiber–matrix interfaces. Thus, it is clear that neither a weak nor a strong fiber–matrix interface bond is beneficial to the flexural strength and fracture toughness of composites, only an interface coating with suitable thickness and proper level of bond between fibers and matrix can lead to an optimal combination of mechanical properties.

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