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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.

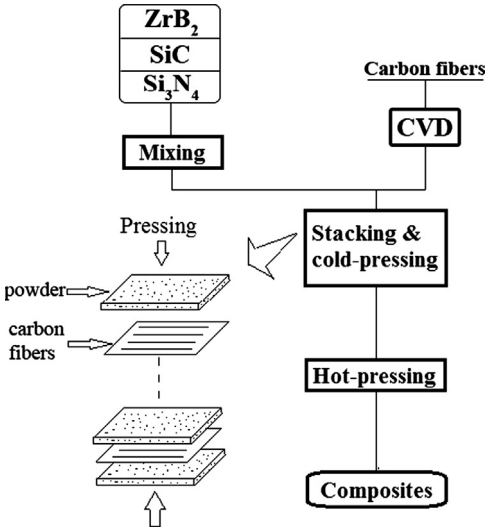

Fig. 1. Illustration of the preparation process of unidirectional carbon fibers reinforced ZrB_2–SiC based composite.

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