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Preparation and properties of carbon fiber reinforced ZrC–ZrB_2 based composites via reactive melt infiltration

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ABSTRACT

Carbon fiber reinforced ZrC–ZrB_2 based (C/C–ZrC–ZrB_2) composites, which were prepared by reactive infiltration of zirconium into a porous C/C–B_4C preform, had the density of 3.07 g/cm^3, the open porosity of 9.1% and the flexural strength of 147 MPa. ZrB_2 matrix was surrounded by or adjoined to the ZrC one and Zr–ZrC eutectic including residual α-Zr dispersed among the reaction-formed ceramics. The amount of ZrC–ZrB_2 matrix in the composites was ~30.2 vol.%. The mass loss rate and the linear recession rate under an oxyacetylene torch were 0.0039 g/s and 0.01 mm/s, respectively.

1. Introduction

Ultra-high temperature ceramics (UHTCs) are attractive in aerospace applications owing to extremely high melting temperature, excellent strength, and outstanding ablation resistance [1–3]. Continuous carbon fiber reinforced ZrC- and ZrB_2-based composites, the most accessed UHTC materials, are mainly prepared by slurry infiltration (SI) combined with precursor infiltration and pyrolysis (PIP) [4,5], soft-solution method [6,7] and reactive metal infiltration (RMI) [8,9]. RMI outweighs others due to the time-saving preparation and relatively low cost. Johnson, Zhang and Woo prepared ZrB_2- or ZrB_2–ZrC-based composites by reacting boron or boron carbide preform with Zr–Cu alloy or Zr [10–13]. Application of bulk ceramics is hindered by fabrication difficulty of structural components and poor thermal shock resistance. Carbon fiber reinforced metal carbide composites can be fabricated through reacting molten metal with carbon matrix in porous C/C preform. Regardless, it is difficult to prepare continuous fiber reinforced ZrB_2-based composites via RMI because boron source cannot readily be introduced into the preform. Wang introduced B_4C–C matrix into porous C/SiC composites to yield C/SiC–B_4C–C preform that was then infiltrated with molten $ZrSi_2$ alloy to fabricate C/SiC–ZrB_2–ZrC composites [14]. The composites had the flexural strength of 380 ± 9 MPa and the line-ablation rate of 0.002 ± 0.001 mm/s, but they did not function well at high temperatures because of the low-amount UHTCs matrix and residual Si.

In this paper, B_4C powders were utilized to prepare C/C–B_4C preform by slurry infiltration and then C/C–ZrC–ZrB_2 composites were prepared via the RMI of zirconium into the preform. The microstructure, mechanical properties and ablation behaviors of the composites were also investigated.

2. Experimental procedure

Twenty-four pieces of plain weave carbon cloth (3 k, Toray T300) sized 100 mm × 180 mm were stacked in a mould after being infiltrated in a slurry of phenolic resin, boron carbide particles (~53 μm, over 90% purity) and ethanol with the weight ratio of 1:1.6:1. Then a 3D architecture was obtained by *Z*-stitching the stacked carbon cloth with carbon fiber (3 k Toray) in a 3 × 3 mm space. The green preform was cured at 180 °C and then pyrolyzed at 1000 °C in an inert atmosphere. Desirable C/C–B_4C preform was obtained by repeating several infiltration and pyrolysis cycles with a solution of phenolic resin and ethanol (50 wt%). The resultant preform was heat-treated at 2200 °C for 1 h in argon and then cut into 40 × 30 × 6 mm pieces. The cut preform was covered by zirconium powders (99.5% purity, JingRan Metal Materials Co., Ltd., Changsha, China) and placed in a graphite crucible. Then zirconium was molten at 2000 °C and infiltrated into the preform to react with the carbon and B_4C matrix, yielding C/C–ZrC–ZrB_2 composites.

Apparent density of the composites was measured by the Archimedes' method. Flexural strength (σ_f) was determined by a three-point-bending test on 3.0 × 4.0 × 40 mm specimens with the span

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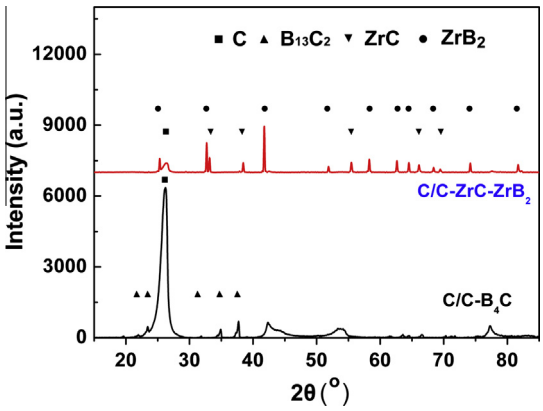

Fig. 1. XRD patterns of C/C–B_4C preform and C/C–ZrC–ZrB_2 composites.

of 30 mm and the crosshead speed of 0.5 mm/min using a universal machine (WDW-100, China). Microstructures of the composites were investigated by X-ray diffraction (Siemens D-500, Germany) and scanning electron microscopy (JEOL JSM-5600LV, Japan). Ablation test was carried out in a flowing oxyacetylene torch environment according to the Chinese National Standard GJB 323-96A. Flat-face specimens sized 30 mm × 30 mm × 4.5 mm were mounted in a concave graphite anvil. The nozzle tip (inner diameter: 2.0 mm) and the surface of the specimen was 10 mm distant. The surface temperature of the sample was ~2000 °C and the test lasted for 30 s.

3. Results and discussion

The XRD patterns of C/C–B_4C preform are shown in Fig. 1. The diffraction peaks indicate that boron carbide existed as $B_{13}C_2$, and the intense ones corresponding to carbon suggest high amount of carbon in the preform and high graphitization degree (~65.35%). The absence of boron carbide in the XRD patterns of C/C–ZrC–ZrB_2 composites suggests that boron carbide had been exhausted by the reaction with zirconium during infiltration. ZrC and ZrB_2 were yielded and no free zirconium was detected by XRD.

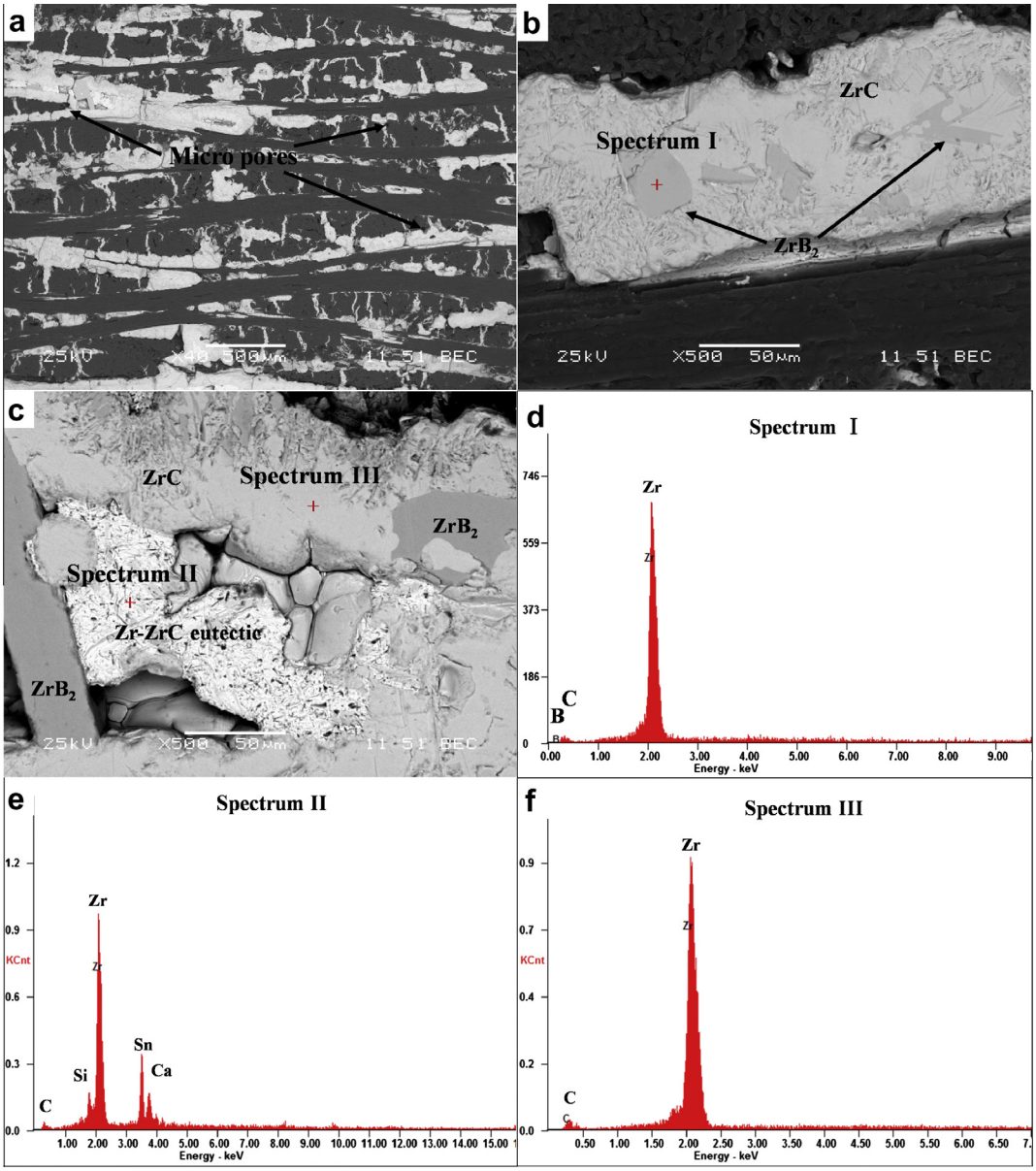

Fig. 2. Microstructure of C/C–ZrC–ZrB_2 composites.