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Short communication

Fabrication and comparison of 3D C_f/ZrC–SiC composites using ZrC particles/polycarbosilane and ZrC precursor/polycarbosilane

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Abstract

The fabrication of ZrC–SiC powders was studied and two kinds of ZrC–SiC powders were successfully obtained using ZrC particles/polycarbosilane and ZrC precursor/polycarbosilane. The reactions were substantially completed at a relatively low temperature (~1500 °C). The phase formation, crystallite size and morphology of the synthesized powders were characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. Two kinds of three-dimensional needled C_f/ZrC–SiC composites were successfully fabricated from ZrC particles/polycarbosilane and ZrC precursor/polycarbosilane by polymer infiltration and pyrolysis (PIP). The microstructure, mechanical and high-temperature properties were studied. The flexural strength of the ZrC precursor/polycarbosilane composite was 376 MPa and its elastic modulus was 138 GPa. The mass loss and linear recession rates of the composite obtained during an oxyacetylene torch test were 0.009 g/s and −0.003 mm/s, respectively.

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1. Introduction

The design and production of new materials suitable to withstand high temperature are currently stimulated by the increasing demand for their applications in thermal protection systems. The ability to withstand temperature of over 2000 °C is considered to be ideal for leading edge materials. At this temperature, the use of traditional silicon carbide matrix composites is limited because of the oxidation of silicon carbide (SiC), which is disadvantageous to ultra-high-temperature oxidation. The high-temperature resistance of SiC matrix composites and new materials is required in advanced thermal protection systems.

Ceramic carbides, such as zirconium carbide (ZrC), belong to a family of materials with extremely high melting temperatures and have been referred to as Ultra High Temperature Ceramics (UHTCs) [1–3]. UHTCs constitute a class of promising materials for use in high temperature applications, such as sharp leading edges on future generations of reentry vehicles, because of their high melting points and relatively good oxidation resistance in reentry environments [4]. ZrC has been given special attention because of its high melting points, relatively low density, good strength at high temperatures, high elastic modulus, low thermal conductivity, and ability to withstand temperatures in the range of 1900–2500 °C [5–8]. Thus, introduction of UHTC (ZrC) phases into the matrix of C_f/SiC composites can improve their ultra-high-temperature oxidation resistance.

At present, various techniques such as chemical vapor infiltration (CVI) combined with a modified polymer infiltration pyrolysis (PIP) [9], the soft-solution approach using inorganic precursors [10], hot-pressing and PIP [11], and mold-pressing and PIP [12], are utilized to fabricate C_f/ZrC–SiC

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composites. However, the microstructure of the resulting composites invariably feature UHTC particles, which are introduced by slurry impregnation, dispersed mainly in inter-bundle zones. Three-dimensional (3D) C_f/ZrC–SiC composites have been successfully manufactured using ZrC particles/PCS and ZrC precursor (PZC)/PCS as slurries by PIP.

The aim of the present work is to study pure ultra-high-temperature matrices (ZrC–SiC matrices). Two kinds of ZrC–SiC matrices were successfully fabricated using ZrC particles/PCS and PZC/PCS and their properties and microstructures were extensively studied. Initial studies have reported the preparation of 3D C_f/ZrC–SiC composites using ZrC particles/PCS and PZC/PCS via the PIP process. The mechanical and ablative properties of the 3D C_f/ZrC–SiC composites obtained were also determined.

2. Experimental procedure

Carbon fibers (T300SC, Toray, Tokyo, Japan) with an average diameter of 6 μm were used. The tensile strength and elastic modulus of them were about 3000 MPa and 210 GPa, respectively. The three-dimensional (3D) fabrics were fabricated by Nanjing Fiberglass Research and Design Institute (Nanjing, China) with four-step techniques. Fiber volume fraction in x, y, z directions of three-dimensional braided carbon fiber perform was 8:1:1. First, ZrC particles (Kaiér Nanometer Technology Development Co. Ltd., Hefei, China) and organic Zr-contained polymeric precursors (PZC, Institute of Process Engineering, Chinese Academy of Science) were separately mixed with PCS (National University of Defense Technology, Changsha, China) at a volume ratio of 3:1 and dispersed in xylene with ultrasonic agitation to form two kinds of homogenous mixtures. Recently Li et al. [13] reported the nature of the PZC precursor. The mixtures were cured using a rotating evaporator and then sieved through a metallic sieve (mesh size = 250 μm). Heat treatment of the powders was carried out in a graphite crucible using a high-temperature graphite resistance furnace at 1500 °C in an argon atmosphere at a rate of 10 °C/min. Sample A represents the matrix from ZrC particles/PCS and sample B represents that for PZC/PCS.

The fiber perform was coated with a PyC/SiC interphase (~300 nm), as shown in Fig. 1, by forced pressure-pulsed chemical vapor infiltration (FP-CVI). To fabricate the 3D C_f/ZrC–SiC composites, a mixture of ZrC particles/PCS and xylene or PZC/PCS and xylene was infiltrated into the fiber perform and cured and pyrolyzed at 900 °C for 30 min. Two kinds of 3D C_f/ZrC–SiC composites were successfully fabricated from ZrC particles/PCS and PZC/PCS at a volume fraction of 3:1 by PIP. The composites were heat treated at 1500 °C for 90 min to increase the crystallinity. Eight cycles of PIP were performed at obtain the desired density.

The phase compositions of the powdered pyrolytic product were characterized by X-ray diffraction (XRD) with Cu Ka radiation. The microstructures of the two matrices were studied by Electron Probe Micro-analyzer (EPMA, JXA-800, Jeol, Tokyo, Japan). The crystallite size and morphology of the synthesized powders were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

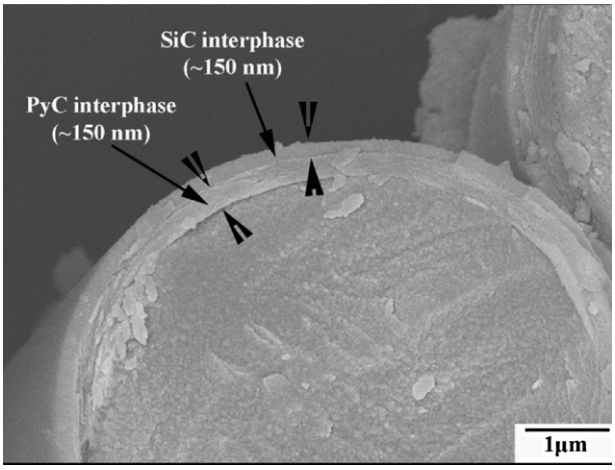

Fig. 1. Scanning electron microscope micrograph of PyC/SiC interphase on the fiber surface.

The 3D C_f/ZrC–SiC composites were cut and ground into 5 mm × 4 mm × 60 mm specimen for three-point-bending tests in an Instron-5566 machine, which was operated at a crosshead speed of 0.5 mm/min and a span of 48 mm. Both the polished cross-sections and the fracture surfaces were observed by the EPMA. Anti-ablation property tests were performed in a flowing oxyacetylene torch environment. During the test, a specimen with a size of 80 mm × 80 mm × 10 mm was vertically exposed to the flame for 600 s. The distance between the nozzle tip and the specimen surface was 10 mm, and the inner diameter of the nozzle tip was 2.0 mm.

3. Results and discussion

The XRD patterns of the two powders pyrolyzed at 900 °C for 30 min, as shown in Fig. 2, reveal noticeable differences that indicate the presence of three phases (i.e., ZrC, ZrO_2 and C) in sample A and only one phase (i.e., ZrO_2) in sample B. This suggests that the PZC and PCS products are amorphous and that the reaction is not complete.

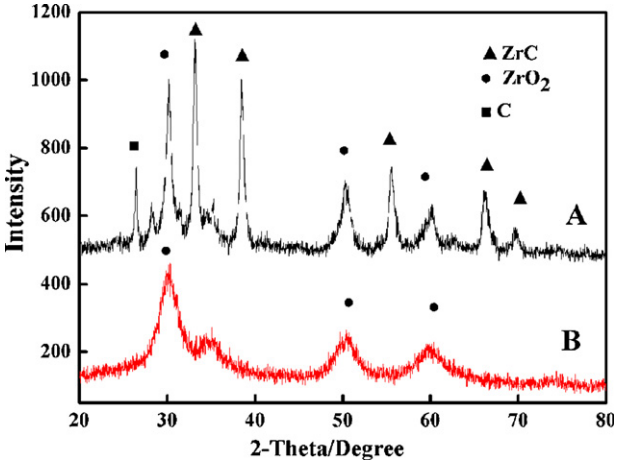

Fig. 2. XRD patterns of the matrices at 900 °C for 30 min.

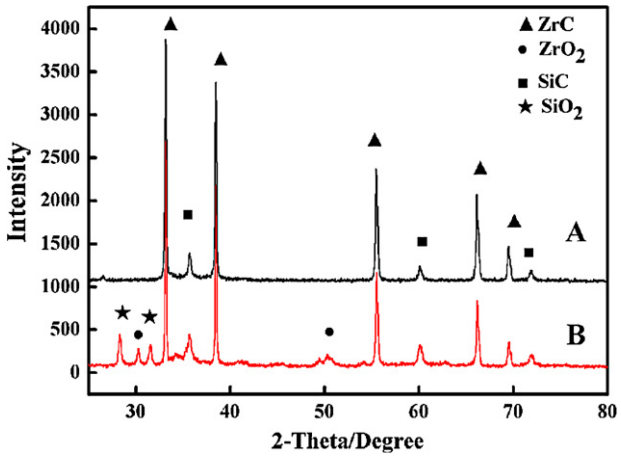

Fig. 3. XRD patterns of the matrices at 1500 °C for 90 min.

Fig. 3 shows the XRD patterns of the two powders after firing at 1500 °C in Ar for 90 min. The final products of sample A contain only ZrC and SiC while those of sample B contain residual levels of ZrO_2 and SiO_2, indicating that the reaction cannot be completed at this temperature and that the carbon in PZC is not enough. More carbons from phenolic resins or the carbon-rich sintering environment must be applied to transform the remaining ZrO_2 and SiO_2 into ZrC and SiC, respectively.

SEM micrographs of the two samples are shown together in Fig. 4. The figure displays a two-phase material consisting of ZrC and SiC but a significant difference between particle sizes is evident. The grain size of sample A (∼100 nm) is larger than that of sample B (<30 nm).

SEM micrographs of the polished cross-section of the 3D C_f/ZrC–SiC composites are shown in Fig. 5. ZrC particles are difficult to insert into intra-bundle areas when ZrC particles/PCS is used. In contrast, PZC/PCS materials are easily inserted into the intra-bundle matrix, and the ZrC phases disperse almost homogeneously into the composite matrices. Densities, open porosities and ZrC fractions of the fabricated composites are summarized in Table 1. The results obtained are consistent with Fig. 5. Compared with the 3D C_f/ZrC–SiC composite obtained from ZrC particles and PCS, the 3D C_f/ZrC–SiC composite obtained from PZC/PCS has a relatively high density of 2.20 g/cm^3, almost double that of the ZrC fraction (25 vol% versus 14 vol%) and a relatively open porosity (8%).

The mechanical tests were performed along the longitudinal fiber direction. Fig. 6 shows the bending stress–displacement curves of two 3D C_f/ZrC–SiC composites with PyC/SiC interphase. Typical non-brittle fracture behaviors are observed, and the composites show an elastic deformation at the beginning of the test, exhibiting a zigzagging rise until the maximum stress is reached. A gradual decline then follows. As

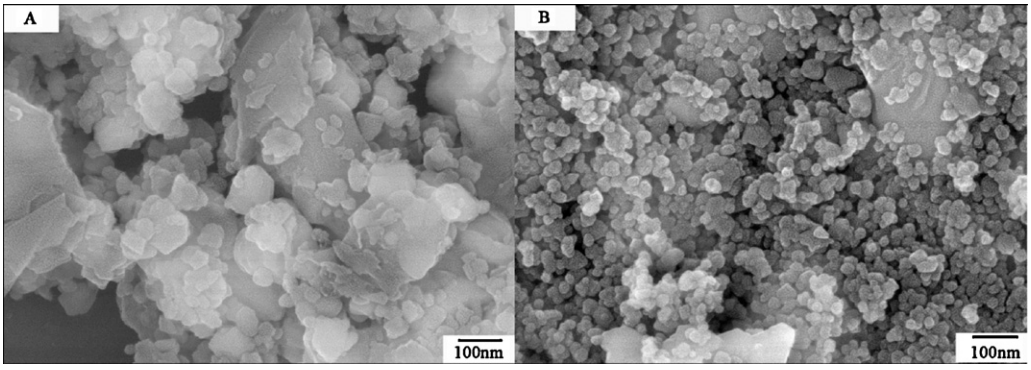

Fig. 4. Scanning electron microscopy images of sample A and sample B after heat treatment in argon atmosphere at 1500 °C for 90 min.

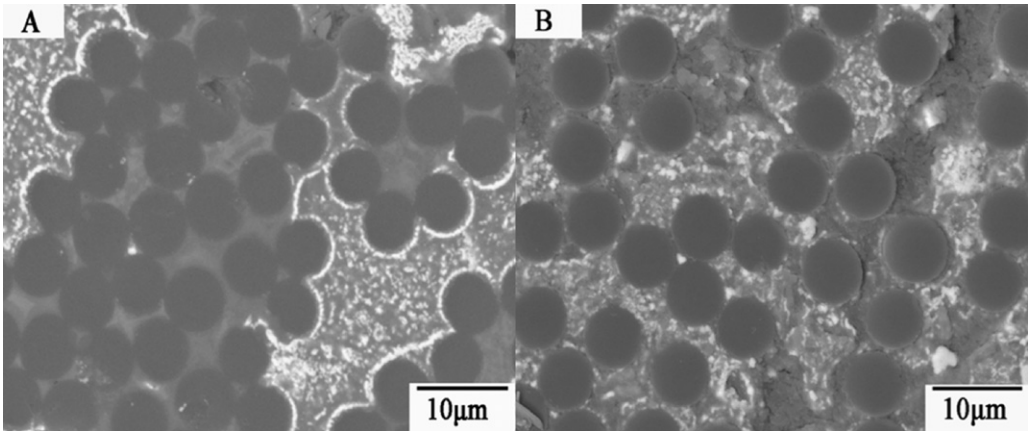

Fig. 5. SEM micrographs on the polished cross-section of 3D C_f/ZrC–SiC composites (A: using ZrC particles/polycarbosilane; B: using ZrC precursor/polycarbosilane).

Table 1
Properties of two kinds of 3D C_f/ZrC–SiC composites.

No.	Fiber fraction	ZrC fraction	SiC fraction	Density (g/cm^3)	Open porosity	Bending strength (N)	Elastic modulus(GPa)	Grain size (nm)
A	25 vol%	14 vol%	7 vol%	2.06	13%	308 ± 35	106 ± 4.0	~100 nm
B	27 vol%	25 vol%	11 vol%	2.20	8%	376 ± 43	138 ± 3.0	<30 nm

Grain size: the grain size of the SiC–ZrC powder.

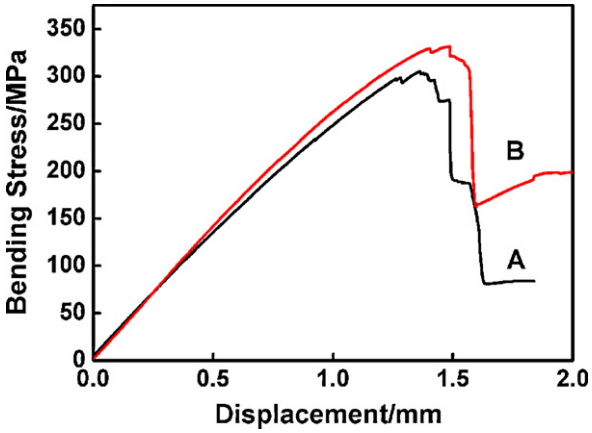

Fig. 6. Bending stress/displacement curves of 3D C_f/ZrC–SiC composites.

shown in Table 1, the 3D C_f/ZrC–SiC composite with PZC/PCS has a bending strength of 376 MPa and an elastic modulus of 138 GPa.

The morphologies of the fracture surfaces are shown in Fig. 7. All composites show typical non-brittle fracture behaviors, and fiber pullouts accompany the fracture process. This phenomenon can be explained by the bonding strength between the fibers and the matrix. When PyC/SiC or PyC interphases are deposited, weak bonding between the fibers and the matrix occurs [14–16], and deflection and pulling-out of the fiber, which improve the toughness of the fracture are facilitated.

Fig. 8 shows the morphologies of the composite surface after the thermal evaluation test. The shape and surface of the composite with PZC/PCS remain intact, while those of the

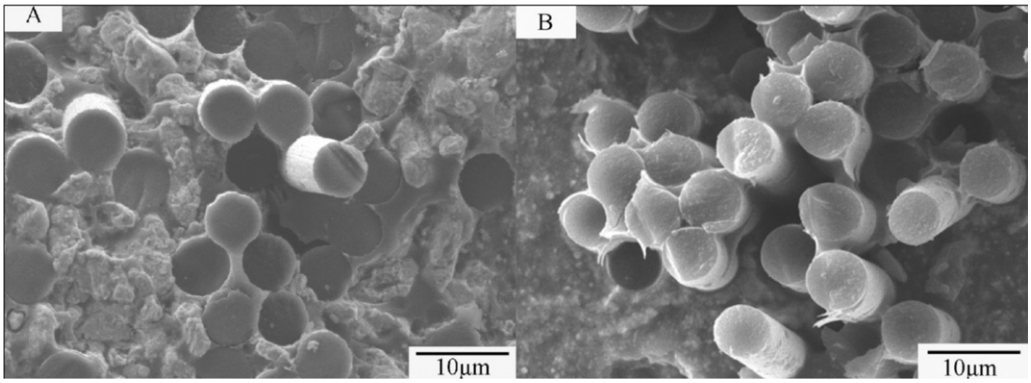

Fig. 7. SEM micrographs on the fracture surfaces of 3D C_f/ZrC–SiC composites.

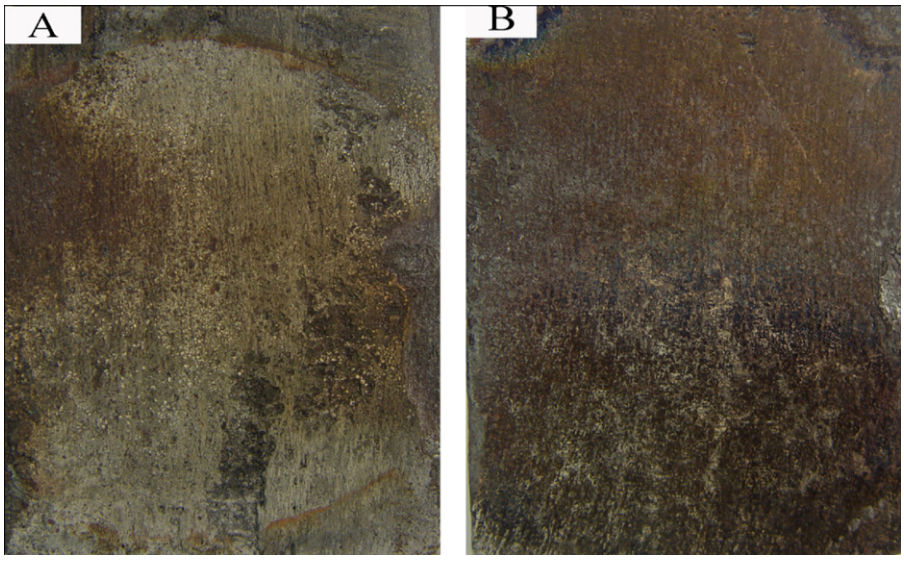

Fig. 8. The anti-ablation property test of 3D C_f/ZrC–SiC composite.

composite with ZrC particles and PCS show pitting. The mass loss and linear recession rates of the composite with PZC/PCS are 0.009 g/s and −0.003 mm/s, respectively, while those of the composite with ZrC particles and PCS are 0.03 g/s and 0.002 mm/s, respectively. Based on these results, the 3D C_f/ZrC–SiC composite with PZC and PCS has better anti-ablation properties.

4. Conclusions

Two kinds of ZrC–SiC powders were successfully fabricated using ZrC particles/PCS (sample A) and PZC/PCS (sample B). Sample B is superior to sample A in terms of performance and application in ceramic composites. Modification of the intra-bundle matrix may be undertaken by PIP using PZC/PCS as a slurry. The homogeneity of the composites can be further improved by developing novel ZrC precursor that can co-dissolve with SiC precursors through ZrC·SiC nano-composite matrix formation. 3D C_f/SiC–ZrC composite with PZC/PCS have good anti-ablation properties.

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