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Ceramics International 37 (2011) 2089–2093
CERAMICS INTERNATIONAL
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Preparation and characterization of three-dimensional carbon fiber reinforced zirconium carbide composite by precursor infiltration and pyrolysis process

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Received 11 October 2010; received in revised form 1 January 2011; accepted 26 February 2011

Abstract

Three-dimensional carbon fiber reinforced zirconium carbide composite (3D C/ZrC) was fabricated for ultra high temperature applications by precursor infiltration and pyrolysis (PIP) process using the mixture of zirconium butoxide ($Zr(OC_4H_9)_4$) and divinylbenzene (DVB) as precursor of zirconium carbide. The micro-structural, mechanical and ablative properties of the 3D C/ZrC composite were studied. The flexural strength of the composite was 107.6 MPa, the elastic modulus was 28.8 GPa, and the fracture toughness was 7.03 MPa $m^{1/2}$. The mass lose rate and linear recession rate of the 3D C/ZrC composite during oxyacetylene torch test was 0.012 g/s and -0.002 mm/s, respectively. The formation of ZrO_2 melt on the surface of the composite contributed mainly the excellent ablative property.

Keywords: B. composites; C. mechanical properties; C. ablation properties; D. ZrC

1. Introduction

Continuous fiber reinforced ceramic matrix composites (CFCMCs) have the advantages of excellent toughness, good thermal shock resistance and good mechanical properties at high temperatures, and thus have wide applications in aeronautic and astronautic fields. For example, carbon fiber reinforced silicon carbide composites (C/SiC) are widely used in rocket engines (such as combustion chambers, thrusters, nozzles) [1], as well as thermal protection systems of the vehicles (such as the nose and leading edges) [2], which may work at the temperatures up to 1750 °C. However, with ever increasing velocity the nose and leading edges of the vehicles, and with ever increasing chamber pressure the combustion chamber, are facing ever increasing working temperature (2000 °C or above). Since C/SiC will soften at high temperatures over 1750 °C, new kinds of composites are needed to satisfy these requirements.

Zirconium carbide (ZrC) ceramic is a material of great interest for ultra high temperature use because of its high melting point (3400 °C), good chemical inertness, low evaporation, high hardness and good ablation resistance [3]. In particular, introduction of carbon fiber into ZrC matrix (C/ZrC composite) will greatly improve fracture toughness and thermal shock resistance properties of bulk ZrC ceramics.

CFCMCs can be prepared by many methods, such as chemical vapor infiltration (CVI), reactive melting infiltration (RMI), precursor infiltration and pyrolysis (PIP), slurry infiltration followed by hot pressing (SI-HP), etc. However, C/ZrC composites are difficult to be prepared by CVI, RMI, PIP, SI-HP process because of the shortage of proper precursors and the high melting point of ZrC. Few papers were published about ZrC matrix composites and almost all of the papers concentrated on preparation of 1D or 2D composites. Dong et al. [4] reported unidirectional carbon fiber reinforced ZrC-SiC composites by slurry and hot pressing method. Zhang et al. [5] reported 2D C/ZrC-SiC composites by CVI process. Hu et al. [6] reported 2D carbon cloth reinforced SiC-ZrC composites by slurry and PIP process. Padmavathi et al. [7] prepared unidirectional carbon fiber reinforced (SiC + ZrC)

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doi:10.1016/j.ceramint.2011.02.024

mini-composites via soft-solution process using inorganic precursors. Recently Zou et al. reported C/ZrC preparation via RMI method by Ultramet [8]. These reports are limited to the composites of 1D and 2D carbon fiber reinforcement and these methods are not suitable to prepare the composites with 3D fiber reinforcement.

In this paper, three-dimensional carbon fiber reinforced zirconium carbide composite (3D C/ZrC) was prepared by precursor infiltration and pyrolysis process, and accordingly the mechanical and ablation properties were investigated.

2. Experimental procedure

Precursor of ZrC was prepared using zirconium butoxide ($Zr(OC_4H_9)_4$, ZTB) and divinylbenzene (DVB) as sources of zirconia and carbon, respectively [9]. The mixture of ZTB and DVB with a molar ratio of ZrO_2 (ZTB) / carbon (DVB) = 1 / 3 was stirred for 2 hours, and then used as precursor of ZrC. This precursor could be cured at 150 °C, and pyrolyzed at 1600 °C to obtain ZrC matrix according to the following equation.

$$ZrO_2 + 3C = ZrC + 2CO\uparrow \tag{1}$$

3D carbon fiber preforms were fabricated as follows. Firstly, plain weave carbon cloth (3k, Toray T300) was cut into pieces of size 60 mm × 180 mm and stacked to a thickness of 4 mm. Then the fiber preform was finished by stitching these pieces of carbon cloth with carbon fiber (3k Toray) in 3 mm × 3 mm space.

3D C/ZrC composite was obtained by 16 cycles of infiltration with precursor of ZrC into the preform, curing, pyrolysis at 1200 °C, and heat treatment at 1600 °C after the eighth and the sixteenth cycle, respectively.

The actual density of the ZrC matrix was measured by pycnometer using kerosene as medium. Before the measurement the ZrC matrix was crushed into powders using an agate mortar, and sifted by 200 mesh screen.

The apparent density and open porosity of the composite was measured by Archimedes's method. Flexural strength was determined using a three-point-bending test on specimens of 3.5 mm × 5 mm × 65 mm with 50 mm span and 0.5 mm/min crosshead speed. A single-edge-notched-beam (SENB) test was applied on notched specimen of 4.0 mm × 8.0 mm × 40 mm (notch with 0.3 mm in width and 4.0 mm in depth) with 0.2 mm/min crosshead speed and 30 mm span to determine fracture toughness.

Anti-ablative property test was carried out in a flowing oxyacetylene torch environment, with approximately 4187 $kW\cdot m^{-2}$ heat flux and ~3100 °C flame temperature. During the test, the specimen with a size of 30 mm × 30 mm × 5 mm was vertically exposed to the flame. The distance between the nozzle tip and the surface of the specimen was 10 mm and the inner diameter of the nozzle tip was 2.0 mm.

The microstructure and composition of the composites were examined by scanning electron microscopy (S4800 Hitachi), and X-ray Diffraction (Siemens D-500).

3. Results and discussion

3.1. Structure and composition

The longitudinal cross-section of the composite is shown in Fig. 1. In Fig. 1a it is clear that stitched fibers existed across the depth direction. The enlarged part in Fig. 1a square area was shown in Fig. 1b, and for clearance the stitched fibers were removed. The carbon cloths were uniformly embedded in the composite and due to the stitching, some carbon cloths deformed and large voids left behind. These voids were filled by ZrC matrix with size around 0.6 mm × 0.15 mm. The microstructure of the 3D C/ZrC composite in Fig. 1c showed that the matrix was dispersed uniformly around the single

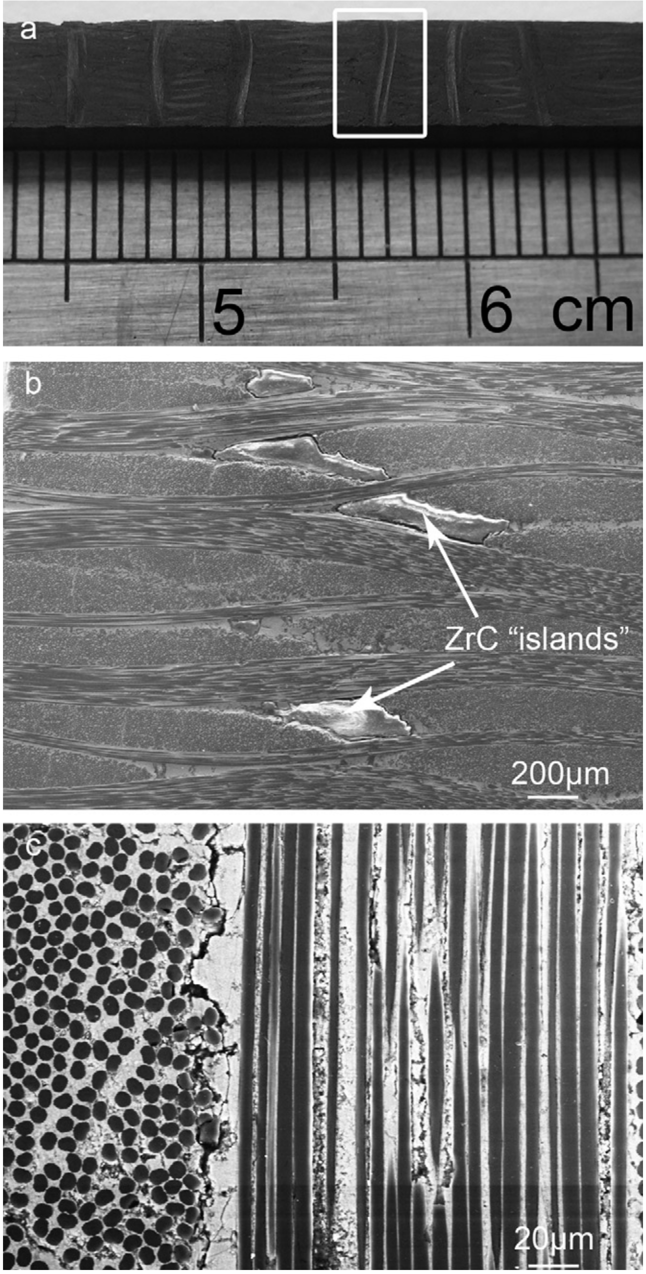

Fig. 1. Longitudinal cross-section of the 3D C/ZrC composite.

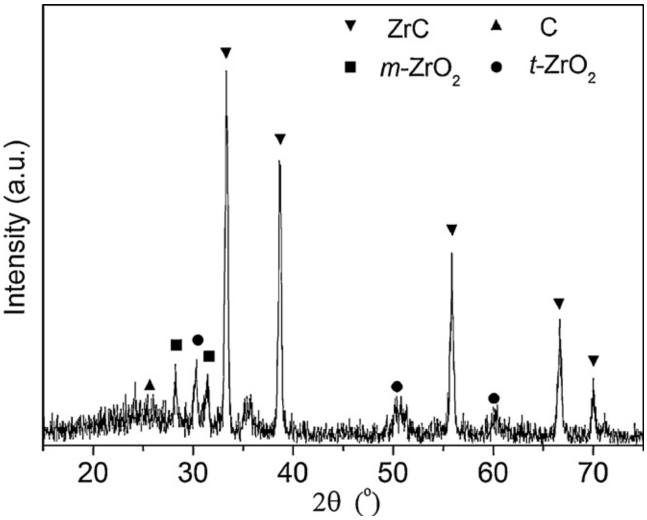

Fig. 2. XRD pattern of the 3D C/ZrC composite.

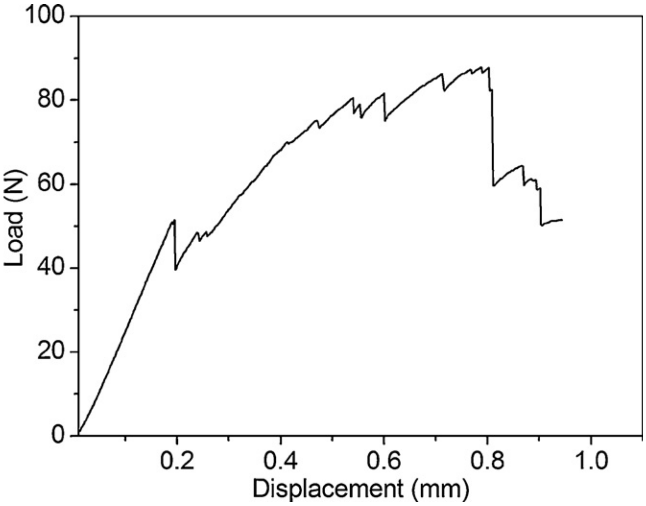

Fig. 3. Load-displacement curve of 3D C/ZrC composite.

fibers, and also long, zigzag micro-cracks between the fiber bundles were obvious.

The XRD pattern of the 3D C/ZrC composite is shown in Fig. 2. The dominant phase in the composite matrix was ZrC, while small amount of monoclinic zirconia (*m*-ZrO_2) and tetragonal zirconia (*t*-ZrO_2) were also present due to the existence of much weaker peak intensities. Carbon was observed as the broad and weak peak at about $2\theta = 26.6^\circ$, which may come from carbon fiber and/or pyrolytic carbon (PyC). The existence of ZrC matrix proved that carbo-thermal reduction happened between ZrO_2 and PyC during heat treatment up to 1600 °C, while small amount of ZrO_2, and perhaps some PyC, still remained in the matrix. Thus the feasibility to prepare 3D C/ZrC composite by PIP process was fully proved.

3.2. Mechanical properties

The 3D C/ZrC composite has a flexural strength of 107.6 MPa, an elastic modulus of 28.8 GPa, and a fracture toughness of 7.03 MPa $m^{1/2}$. The load-displacement curve of the flexural strength test was plotted in Fig. 3. The composite showed typical non-catastrophic fracture behavior that the composite showed an elastic deformation at the beginning of the loading, zigzag rise till the maximum load reached and then afterward fell off gradually.

With the introduction of carbon fiber, the 3D C/ZrC composite showed a much higher fracture toughness than bulk ZrC ceramic (~2 MPa $m^{1/2}$) [10]. However, the flexural strength, elastic modulus and fracture toughness of the 3D C/ZrC composite were relatively low compared with those of other composite [11]. This may be ascribed as the following two reasons.

Firstly, the 3D C/ZrC composite had rather low relative density and high porosity. The density of the 3D C/ZrC composite was 1.98 g/cm^3, and open porosity was 12.4%. The actual density of the matrix was 4.38 g/cm^3, much lower than that of dense ZrC (6.9 g/cm^3) by simple calculation from Equ. (1) (supposing that ZTB was totally transformed into ZrO_2 and DVB into carbon in 30% weight yield). The deviation may be from the existence of ZrO_2 (5.8 g/cm^3) and PyC, which was partially proven from XRD pattern of the composite, and the inevitable existence of close pores in ZrC powder.

The density of the composite can be calculated from the mixed rule as shown in Equ. 2, where ρ_c, ρ_f, ρ_m mean density of the composite, carbon fiber, and matrix, respectively, and V_f, V_m mean volume percentage of fiber and matrix in the composite, respectively.

$$\rho_c = \rho_f V_f + \rho_m V_m \quad (2)$$

Considering that $\rho_c = 1.98$ g/cm^3, $\rho_f = 1.76$ g/cm^3, $V_f = 34.3\%$, $\rho_m = 4.38$ g/cm^3, V_m can be calculated as 31.4%, so accordingly the total porosity of the composite was determined as 34.3%, in which closed porosity was 21.9%.

It is difficult to further densify the 3D C/ZrC composite by this method, because (1) the ceramic yield of the precursor for ZrC is rather low (18wt%), thus 16 cycles of infiltration, curing, and pyrolysis is not enough to fully densify the composite, yet more cycles are time-consuming and lack feasibility; (2) ZrC matrix was formed from carbo-thermal reduction of ZrO_2 and PyC, and this reaction inevitably left behind much porosity.

Secondly, carbo-thermal reduction between ZrO_2 and carbon fibers also might occur, causing fiber degradation, and thus composite degradation. So carbon fiber coating might be needed to avoid the reaction between ZrO_2 and carbon fiber, as well as adjust the interface between fiber and matrix.

More detailed observations of the 3D C/ZrC composite were shown in Fig. 4. From Fig. 4a large, long, narrow voids between fiber bundles were common, with size around 0.7 mm × 0.1 mm, indicating the matrix was loose and load transfer between fiber and matrix was not effective. As a comparison, the matrix around the single fibers (Fig. 4b) was dense and uniformly dispersed, meaning the bonding between fiber and matrix was strong, and the matrix formed preferentially around the single fibers. This is rather different from PIP processing of C/SiC and C/Si-C-N, in which SiC (Si-C-N) matrix filled preferentially the large voids

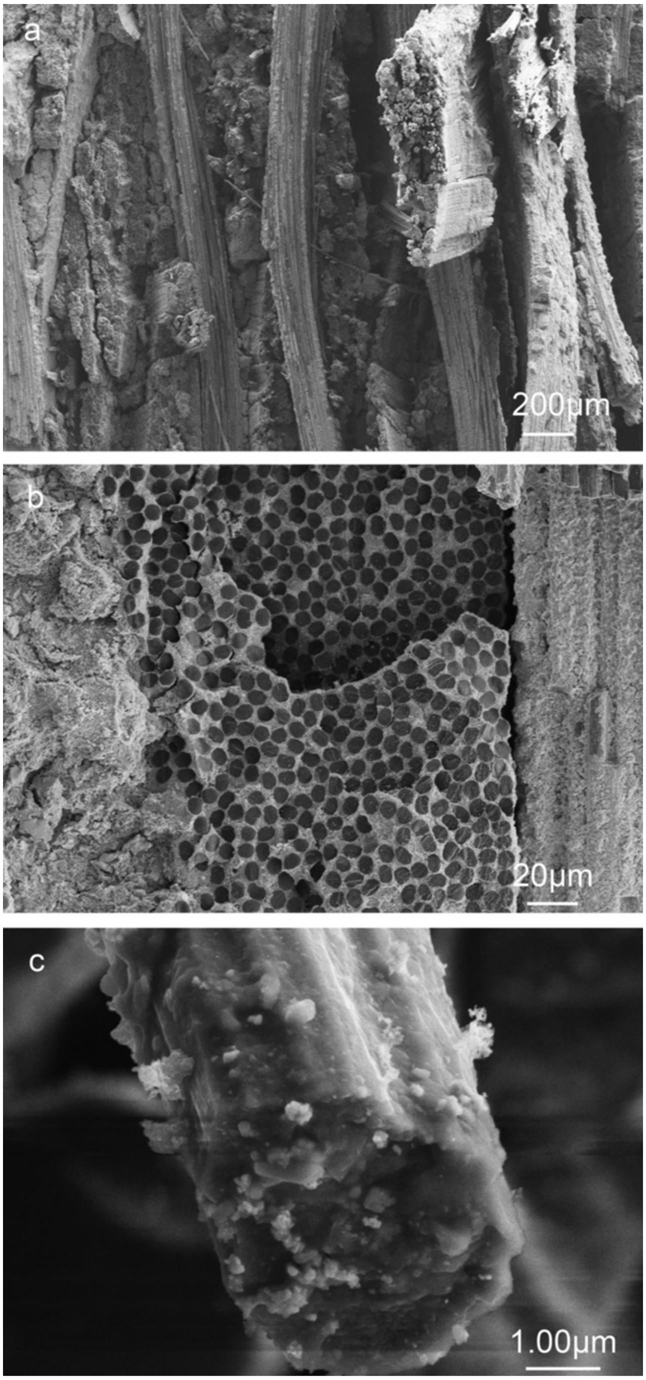

Fig. 4. SEM photos of fracture surfaces of the 3D C/ZrC composite.

between the fiber bundles [12]. The difference between the two material systems was mainly caused by the different viscosities and wettability of the two precursors. The precursor of ZrC shows lower viscosity (5 mPa s), and because of the existence of O-H bonding, better wettability than PCS. The ZrC precursor was easier to infiltrate into the confined space around the single fibers and stayed here because of capillary action, while it may flow away form the space between the fiber bundles. As a comparison, the SiC precursor was was hard to infiltrate narrow space and tended to stay between fiber bundles. The pulled-out of single fiber (Fig. 4c) showed the appearance of some matrix residue due to matrix peeling off during fracture process, which proved the strong fiber/matrix bonding.

3.3. Ablation properties

The ultra-high temperature ablation resistance property of the composite is an important aspect, so the 3D C/ZrC composite was exposed to oxyacetylene torch, and the mass lose rate and linear recession rate were 0.012 g/s and -0.002 mm/s, respectively. The negative recession rate was because white, loose shell formed on the surface, and apparent measurement found thickness increase after torch test. During the test, the surface temperature of the composite reached 2028 °C after about 10 s, and the surface changed from black to white, showing the oxidation of ZrC to ZrO_2. Above 2000 °C, following reactions might occur:

$$\mathrm{ZrC} + 3/2\mathrm{O_2} = \mathrm{ZrO_2} + \mathrm{CO} \tag{3}$$

$$\mathrm{C} + 1/2\mathrm{O_2} = \mathrm{CO} \tag{4}$$

During the test, viscous ZrO_2 melt formed at over > 3000 °C, higher than the melting point of ZrO_2 (2800 °C). ZrO_2 melt had rather high viscosity and strong adhesion to the composite, and could not be blown away by the gas flow, thus prevented the composite from further oxidation, so the composite had excellent anti-ablative properties.

4. Conclusion

3D C/ZrC composite was prepared by PIP process. The flexural strength of the 3D C/ZrC composite was 107.6 MPa. The low mechanical properties might be caused by the low density of the composite and the strong fiber/matrix bonding strength. The matrix around the single fibers was dense than that between the fiber bundles. During oxyacetylene torch test the mass lose rate of the composite was 0.012 g/s, and the linear recession rate was -0.002 mm/s. The formation of ZrO_2 melt on the surface contributes mainly the excellent ablative property.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No.90816020 and 90916019).

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