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Short communication

Fabrication of a ZrC–SiC matrix for ceramic matrix composites and its properties

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Abstract

A ZrC–SiC matrix was fabricated by means of a liquid precursor conversion method, using an organic zirconium-containing polymeric precursor and polycarbosilane. The effects of the starting reagents and pyrolysis temperature on the fabrication of the ZrC–SiC matrix were studied. The ZrC–SiC matrix with different ZrC/SiC ratios could be formed using different starting reagents. The pyrolysis temperature also affected the pyrolyzed product. The reactions were substantially completed at a relatively low temperature (~1500 °C). The crystalline size and morphology of the synthesized matrix were characterized by scanning electron microscopy. Finally, the application of the ZrC–SiC matrix in ceramic matrix composites was investigated. The microstructures, as well as mechanical and ablative properties of three-dimensional C_f/ZrC–SiC composites were studied. The flexural strength of the composite was 324.9 MPa, and the elastic modulus was 27.8 GPa. The mass loss rate and linear recession rate of the composite during an oxyacetylene torch test were 0.01 g/s and–0.002 mm/s, respectively.

Keywords: B. Composites; E. Application; ZrC–SiC matrix; ZrC precursor

1. Introduction

Carbon fiber-reinforced silicon carbide (C_f/SiC) composites are promising candidates for many applications as a result of their excellent properties such as high strength and fracture toughness. These properties make these composites suitable for highly demanding engineering applications [1,2]. However, the applications of these composites are limited because of the active oxidation of silicon carbide (SiC) above 1650 °C. To improve the high-temperature performance of C_f/SiC composites, refractory carbides such as zirconium carbide (ZrC) need to be introduced into the SiC matrix in the composites. ZrC has gained much attention due to its exceptional properties, including a high melting point (up to 3540 °C), and the ability to form refractory oxide scales at high temperatures. ZrC also has a relatively low density (6.7 g/cm^3) that is half of that of HfC (12.2 g/cm^3) [3]. ZrC is one of the most promising ceramics for ultrahigh temperature applications due to the high melting point (2700 °C) of its protective zirconia (ZrO_2) layer. Ultra-high temperature ceramics based on the carbides, nitrides and borides of group IVB and VB transition metals have received a considerable attention, due to their unique combination of properties, such as high melting temperature, hardness, high electrical and thermal conductivities, as well as chemical inertness against molten metals.

C_f/SiC composites can be fabricated by chemical vapor infiltration (CVI) [4], vapor silicon infiltration [5], polymer impregnation and pyrolysis [6]. Each of these processing methods has disadvantages, such as difficult reproducibility, high cost, and poor performance of the composites. In the present study, a liquid precursor conversion method using ZrC precursor and polycarbosilane (PCS) was used to fabricate C_f/ZrC–SiC composites. Given that processing conditions are critical to the successful synthesis of ZrC–SiC mixed matrices,

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the selection of pyrolysis temperature and microstructures of the matrices were studied. The obtained matrices were then applied to the carbon fiber-reinforced silicon carbide (C_f/SiC) composites, and C_f/ZrC–SiC composites were successfully fabricated.

Generally, commercially available ZrC powders are directly introduced into carbon fiber reinforced ceramic matrix composites (CMCs) to improve their performances at high temperatures. Various techniques have been utilized to fabricate C_f/SiC–ZrC composites. The methods include chemical vapor infiltration (CVI) combined with modified polymer infiltration pyrolysis (PIP) [7], a soft-solution approach using inorganic precursors [8], hot-pressing and polymer infiltration pyrolysis (PIP) [9], as well as mold-pressing and polymer infiltration and pyrolysis (PIP) [10]. However, some of these processes have obvious disadvantages. Due to the particle size of commercially available ZrC powders, ZrC particles cannot be homogenously dispersed in the intra-bundle of composites. Therefore, the liquid precursor conversion method was used to fabricate C_f/SiC–ZrC composites.

So the purpose of this work is how to synthesize a ZrC–SiC matrix via a mixture of two precursors. The effects of pyrolysis temperature and time as well as the mixing ratio of the two polymers on the matrix microstructure were studied. The mechanical and ablation properties of the obtained C_f/ZrC–SiC composites were also investigated.

2. Experimental procedure

Carbon fibers (T300SC, Toray, Tokyo, Japan) with an average diameter of 6 μm were used. The three-dimensional (3D) fabrics were fabricated by the Nanjing Fiberglass Research and Design Institute (Nanjing, China). The experimental procedure for the preparation of a ZrC–SiC matrix is described in Fig. 1. First, an organic zirconium-containing polymeric precursor (PZC, Institute of Process Engineering, Chinese Academy of Science) and polycarbosilane (PCS, National University of Defense Technology, Changsha, China) were mixed with a weight ratio of 1:1.The mixture was dispersed in xylene by ultrasonic agitation to form a homogenous mixture and cured using a rotating evaporator. The cured mixtures were pyrolyzed at 900 °C in an argon atmosphere at a rate of 10 °C/min. Afterwards, the pyrolytic products were ground into powder and sieved through a metallic sieve (mesh size = 250 μm). The pyrolytic products were heat treated in a graphite crucible using a high-temperature graphite resistance furnace in the range of 1400–1600 °C in an argon atmosphere at a rate of 10 °C/min.

The fiber perform was coated with PyC interphase (∼150 nm), as shown in Fig. 2, by forced pressure-pulsed chemical vapor infiltration (FP-CVI). To fabricate the 3D C_f/ZrC–SiC composites, the mixture of polymer and xylene was infiltrated into the fiber perform, cured and pyrolyzed under the same conditions. 3D C_f/ZrC–SiC composites were successfully fabricated by liquid polymer infiltration and pyrolysis (PIP) with mixture of PZC and PCS with a weight ratio of 1:1.

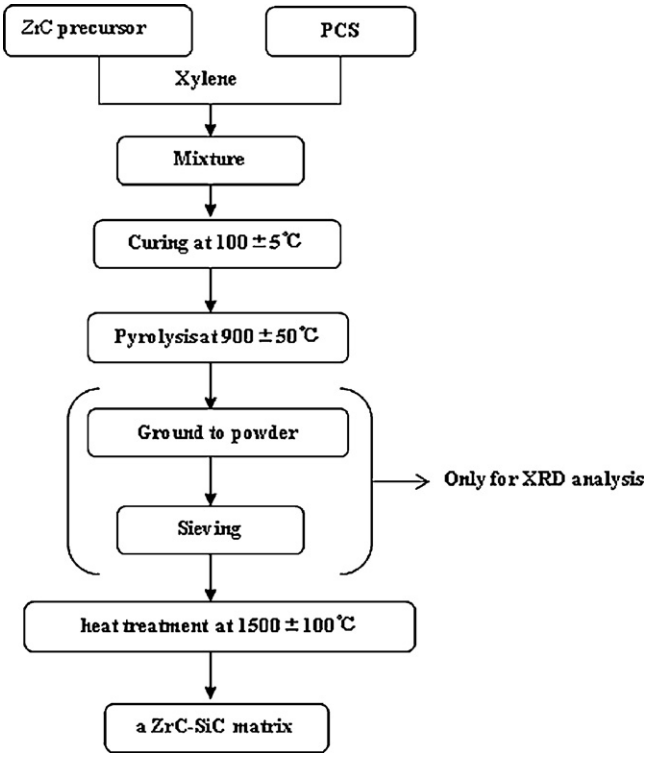

Fig. 1. Experimental procedure for preparation of a ZrC–SiC matrix.

Finally, another eight cycles of PIP process were performed again to get a desired density.

The phase compositions of the powdered pyrolytic product were characterized by X-ray diffraction (XRD) with Cu K_a radiation. The microstructures of the composites were studied by Electron Probe Micro-analyzer (EPMA, JXA-800, Jeol, Tokyo, Japan). The crystalline size and morphology of the synthesized matrix were characterized by scanning electron microscopy (SEM).

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, operated at a crosshead speed of 0.5 mm/min and a span of 48 mm. Both the polished

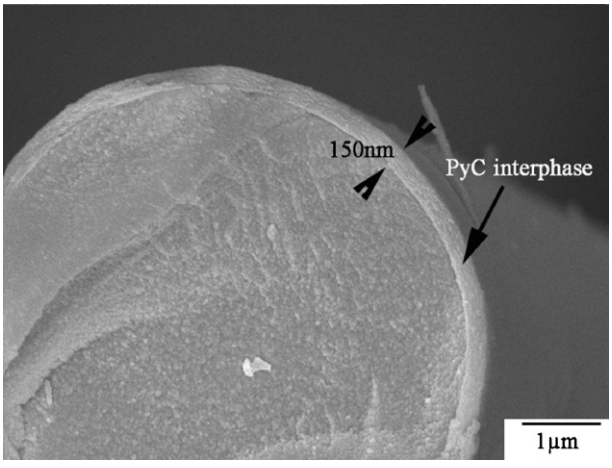

Fig. 2. Scanning electron microscope micrograph of PyC interphase on the fiber surface.

cross sections and the fracture surfaces were observed by Electron Probe Micro-analyzer (EPMA, JXA-800, Jeol, Tokyo, Japan). The anti-ablation property test was carried out 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

Fig. 3 shows the XRD patterns of the matrix samples obtained by pyrolyzing the mixtures of ZrC precursor and PCS at 900 °C for 30 min, which confirms the formation of ZrO_2 and SiC phases. The precursor mixture converts into ZrO_2 and amorphous SiC. This finding implies that oxygen is already contained in the PZC.

The XRD patterns of the product after heat treated for different times at 1500 °C are shown in Fig. 4. The XRD patterns show significant differences, and they include ZrO_2 peaks at 1500 °C for 30 and 60 min. There is insufficient available time to reduce ZrO_2 into ZrC. However, after 90 and 120 min, the ZrO_2 peaks disappear, indicating the completion of ZrO_2 conversion into ZrC. After 120 min, the peak intensities of ZrC and SiC continue to increase. Thus, a pure ZrC–SiC matrix can be obtained at 1500 °C for 120 min.

The XRD patterns of the ZrC–SiC matrix with various molar ratios of PZC to PCS (1:1, 2:1, and 3:1) after heat treatment at 1500 °C for 120 min are plotted in Fig. 5. It can be concluded from the diffraction peaks that the main phases existing in the composite powders are ZrC, SiC, and ZrO_2. With increased PZC to PCS molar ratio, the diffraction peak intensities of ZrO_2 increases and those SiC decreases. It indicates that the precursor carbothermal reactions are not completed with increased PZC to PCS molar ratio. The carbon in the precursor also cannot completely convert ZrO_2 into ZrC. In order to transform the remaining ZrO_2 into ZrC, additional carbons from phenolic resin or a carbon-rich sintering environment should be supplied.

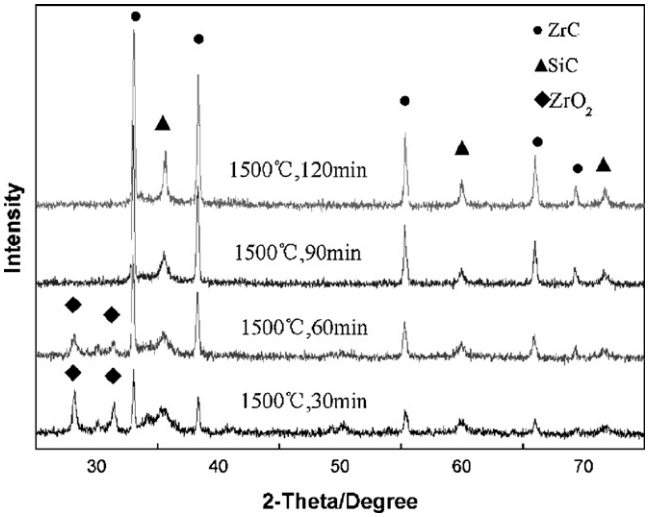

Fig. 4. XRD patterns of the ZrC–SiC matrix at 1500 °C for different heat treatment times.

The SEM images of the ZrC–SiC matrix with a PZC/PCS molar ratio of 1:1 heated at 1500 °C for 2 h are shown in Fig. 6. It is shown that the SiC phases (dark background in the backscattered electron micrograph) are regularly dispersed in the ZrC matrix (white background). From the images, the particle sizes of the matrix range between 100 and 200 nm, with a nearly spherical morphology. However, agglomeration still exists.

The SEM micrographs of the polished cross-section of the C_f/SiC–ZrC composites are shown in Fig. 7. It can be observed that application of the PZC and PCS mixture as precursor results in the filling of the CMCs with a ZrC–SiC nanocomposite matrix in an intra-bundle matrix. The ZrC

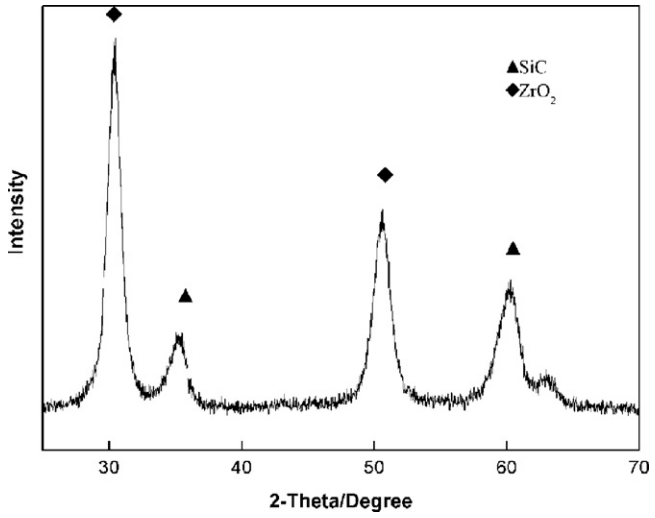

Fig. 3. XRD pattern of the ZrC–SiC matrix at 900 °C for 30 min.

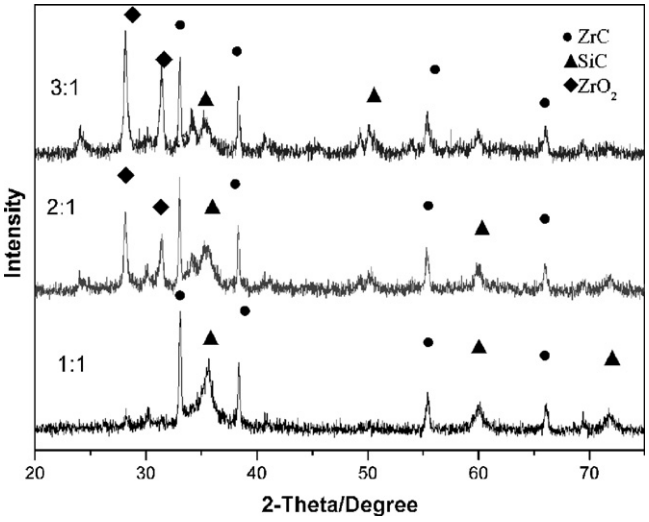

Fig. 5. XRD patterns of the ZrC–SiC matrix with various molar ratios of PZC to PCS.

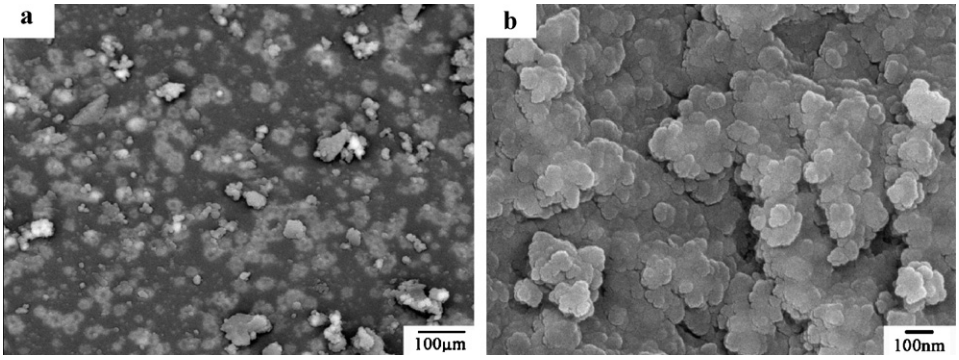

Fig. 6. Scanning electron microscopy images of the ZrC–SiC matrix at 1500 °C for 2 h: (a) back-scattered electron image, (b) larger magnification.

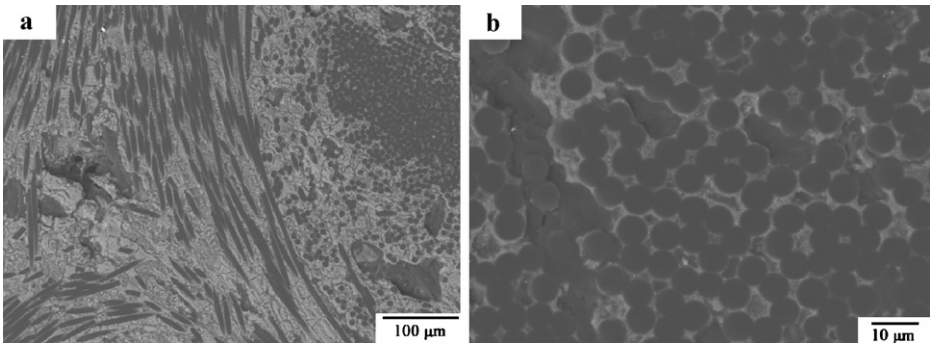

Fig. 7. Back-scattered electron images for the polished cross sections of 3D C_f/ZrC–SiC composites: (a) back-scattered electron image, (b) larger magnification.

phases almost homogeneously disperse in composite matrix.

The SEM micrographs of the polished cross-section of the C_f/SiC–ZrC composites as published by other authors are shown in Fig. 8. It can be observed that ZrC particles are difficult to place into the intra-bundle areas using ZrC particles/PCS. However, the application of PZC and PCS mixture as precursor can fill CMCs with ZrC–SiC nanocomposite matrix

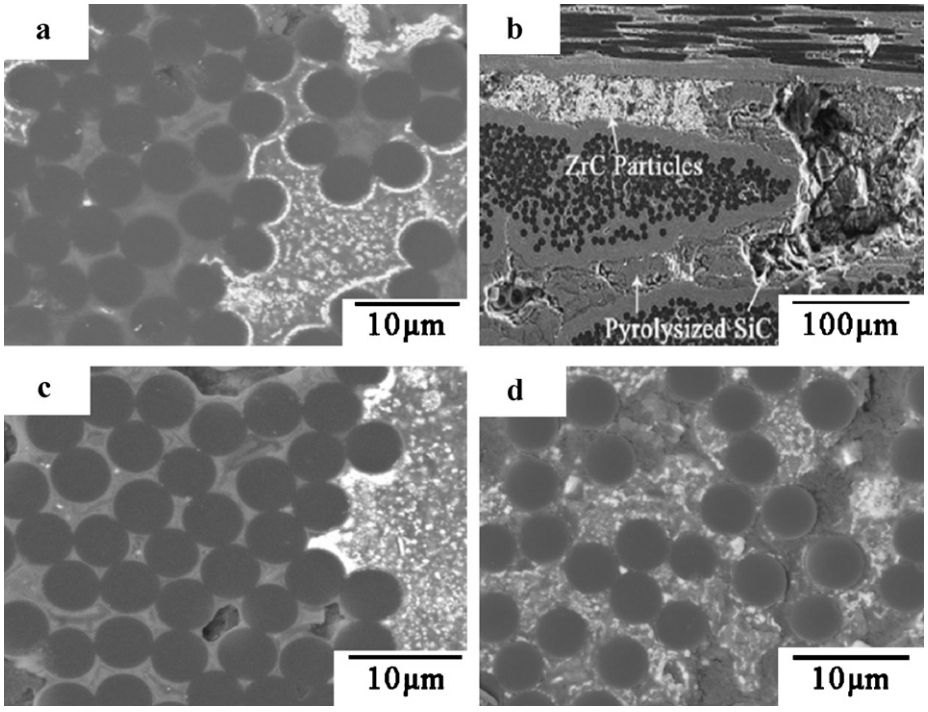

Fig. 8. SEM micrographs on the polished cross-section of C_f/SiC–ZrC composites: (a) [8], (b) [6], (c) [9]: using ZrC particles/PCS, (d) using ZrC precursor/PCS).

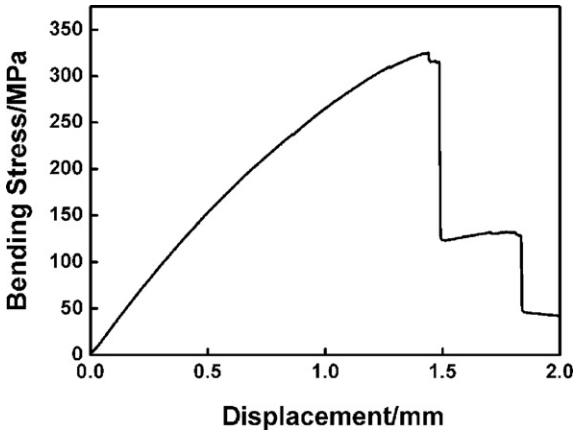

Fig. 9. Bending stress/displacement curves of 3D C_f/SiC–ZrC composite.

in an intra-bundle matrix. The ZrC phases almost homogeneously disperse in the matrix of composites.

Fig. 9 shows the bending stress–displacement curves of the C_f/SiC–ZrC composite with PyC interphase deposited. It can be concluded from the curve that the sample shows a typical non-brittle fracture behavior and the composite shows an elastic deformation at the beginning of the test, exhibiting a zigzagging rise untill the maximum stress is reached, and then a gradual decline follows. The 3D C_f/SiC–ZrC composite has a bending strength of 324.9 MPa, and the elastic modulus was of 27.8 GPa.

The morphologies of the fracture surfaces are shown in Fig. 10. It can be seen that the composite shows a typical non-brittle fracture behavior and there are fiber pullouts accompanying the fracture process. It can also be observed that the pulled-out fibers are longer and their surfaces are smoother. 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 [11–13], Consequently, deflection and fiber pulling-out, which benefit to the improvement of fracture toughness, are facilitated.

The high temperature ablation resistance property of the composite is important. Thus, the 3D C_f/SiC–ZrC composite was exposed to an oxyacetylene torch. The mass loss and linear recession rates are 0.01 g/s and–0.002 mm/s, respectively. Fig. 11 shows the thermal evaluation process. Using the obtained morphologies on the composite surface before and after thermal evaluation, it can be seen that the shape and surface of the composite remain intact. As a result, the 3D C_f/SiC–ZrC composites have anti-ablation properties.

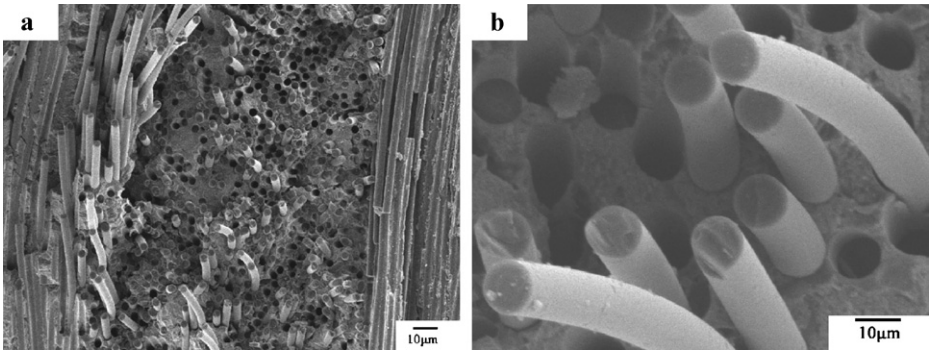

Fig. 10. SEM micrographs on the fracture surfaces of 3D C_f/SiC–ZrC composite.

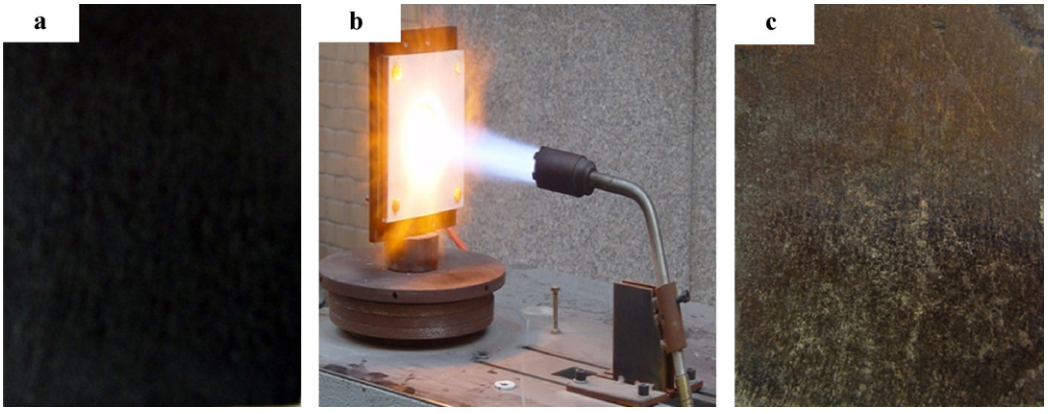

Fig. 11. The anti-ablation property test of 3D C_f/SiC–ZrC composite: (a) before ablation, (b) in the middle of ablation, (c) after ablation.

4. Conclusions

In conclusion, a ZrC–SiC matrix was fabricated by means of liquid precursor conversion method, using a 1:1 ZrC precursor and polycarbosilane mixture and their pyrolysis at 1500 °C for 120 min. The ZrC–SiC matrix had a small average crystalline size (<200 nm), and the SiC phase was regularly dispersed in the ZrC phase. Finally, 3D C_f/SiC–ZrC composites were successfully fabricated by the liquid precursor conversion method. The ZrC–SiC nanocomposite matrix was evenly dispersed not only in the inter-bundle matrix, but also in the intra-bundle matrix. During the oxy-propane torch test the mass loss rate of the composite was 0.01 g/s, and the liner recession rate was −0.002 mm/s. The fabricated 3D C_f/SiC–ZrC composites had anti-ablative properties.

Acknowledgments

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