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Short communication

# Enhanced anti-ablation performance of carbon/carbon composites modified with ZrC-SiC

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ABSTRACT

The ZrC-SiC inhibited carbon/carbon composites (C/C-ZrC-SiC) were fabricated by combining precursor infiltration and pyrolysis (PIP) of ZrC and reactive melt infiltration (RMI) of $ZrSi_2$. The achieved C/C-ZrC-SiC composites exhibited an unusual microstructure. The dense ZrC-SiC matrix formed by RMI was distributed in the fiber webs. The ZrC-C matrix developed by PIP and isothermal chemical vapor infiltration (ICVI) was uniformly distributed in the non-woven layers. After ablation under oxyacetylene torch, C/C-ZrC-SiC composites exhibited a desirable ablation resistance. The formed $ZrO_2$ with a framework structure acted as the barrier to effectively shield the ablation heat and withstand mechanical denudation of high speed flame stream. In the brim region of the ablated surface, the $SiO_2$ layer was capable of further reducing ingress of oxygen into the materials below.

## 1. Introduction

Carbon/carbon (C/C) composites as an ideal candidate aerospace materials for application in thermal structure components such as leading edge and nose tip of hypersonic vehicles have been received much attention due to the uncommon combination of physical and chemical properties [1–3]. However, high aerothermal heating, high heat flux involved a reactive species will induce ablation of C/C composites during hypersonic flight [4,5]. The desirable anti-ablation performance of C/C composites is required for fulfilling advanced hypersonic vehicles.

It is a favored route to improve the ablation resistance of C/C composites by introducing ultra-high temperature ceramics (UHTCs) into carbon matrix. UHTCs have been used as candidate materials in thermal protect system (TPS) due to their high melting temperature and unique mechanical properties at high temperature [6]. However, the application of UHTCs in TPS is limited someway due to their poor fracture toughness and thermal shock resistance [7]. It has been reported that the fracture toughness of UHTCs such as $ZrB_2$-SiC could be improved using various carbon allotropes [8–10]. In addition, the efficiencies and formation of practical composites of the designed UHTCs can be realized by the incorporation of carbon [10]. Therefore, C/C composites doped with UHTCs could exhibit a good high temperature performance due to the rare combination of refractory properties of UHTCs and good thermal shock resistance of carbon.

C/C composites modified with ZrC-SiC have shown a good ablation resistance [11–14]. Among the preparation of C/C-ZrC-SiC composites, PIP and RMI exhibit different characteristics in regard to cost, cycle, requirement for the facility as well as performance of the composites. In the case of PIP, the even distribution of ZrC-SiC phases can be achieved due to the good fluidity of the liquid precursor which is beneficial to fully infiltrate the preform. However, only using PIP is a time-consuming process. The repeated infiltration and pyrolysis of the ZrC-SiC precursors (above 10 cycles) are necessitated for the preparation of C/C-ZrC-SiC by only using PIP [11–13]. Only one process cycle is needed for C/C-ZrC-SiC composites fabricated by RMI and the reaction-bonded ZrC-SiC matrix is mainly present in the region with large-sized pores in the preform [14] but the space and pores between the fibers of the fiber bundles are not readily infiltrated. However, the microstructure of C/C-ZrC-SiC composites prepared by a combined process of RMI and PIP and their anti-ablation performance are less explored. According to the advantages and disadvantages of PIP and RMI, the combined process not only offers a path towards achieving the distribution of ZrC-SiC in the whole composites, but shortens the preparation time. Additionally, compared with the single process, the combined process could be further extended to prepare the multiphase UHTCs inhibited C/C composites and the controllable distribution of UHTCs in the composites are expected to be achieved.

In the present study, in order to improve the ablation resistance of C/C composites, infiltration of ZrC-SiC into C/C composites was

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prepared by the combination of PIP and RMI. Microstructure and ablation behavior of the C/C-ZrC-SiC composites were investigated.

## 2. Experimental

2D needle-punching carbon felt with a initial density of ~0.45 g/cm$^3$ was firstly deposited with pyrolytic carbon (PyC) using ICVI in order to protect the carbon fiber from the chemical erosion of ZrC precursor during pyrolysis. The synthesized ZrC precursor solution was used as the source of ZrC and the preparation of the precursor can be found elsewhere [15]. After deposition of PyC, the carbon/carbon preforms (0.7 g/cm$^3$) were used for infiltration of the ZrC precursor. Firstly, the preform was infiltrated with the ZrC precursor solution under vacuum. The infiltrated preform was processed by orderly drying at 60 °C for 10 h and at 180 °C for 3 h. The dried preform was held at 1500 °C for 2 h at Ar atmosphere, resulting in the formation of C/C-ZrC composites. These steps were repeated for several times and the content of ZrC in the preform was about 45 wt %. Then the as prepared C/C-ZrC composites were densified again with PyC using ICVI. The apparent density was calculated by dividing mass by volume. The open porosity of the composites was measured by Archimedes method. The apparent density and open porosity of the ICVI-fabricated C/C-ZrC composites were 1.37 g/cm$^3$ and 19.5%, respectively. In order to further increase the density and the content of ZrC and SiC in the C/C-ZrC composites, commercial $ZrSi_2$ powder (purity ≥ 99.5%, size ~ 200 mesh, Jinzhou Haixin Metal Materials CO., LTD, Liaoning, China) was used as the source of ZrC and SiC. The ICVI-fabricated C/C-ZrC composites were machined into the plate-shaped sample of 30 mm in diameter and 10 mm in thickness. The samples were placed in graphite crucible and wrapped with $ZrSi_2$ powder. This system was processed at 2100 °C under Ar atmosphere for 2 h, resulting in formation of C/C-ZrC-SiC composites. After RMI, the residual melt on the sample surface was removed by using sand paper. The density and open porosity of C/C-ZrC-SiC composites were 2.97 g/cm$^3$ and 4.8%, respectively. The content of ZrC and SiC in the C/C-ZrC-SiC composites were about 53.3 wt% and 30.7 wt%, respectively.

Ablation testing was performed on an oxyacetylene torch operating at the heat flux of 4.18 MW/m$^2$. The high temperature flame flow was generated with acetylene (pressure of 0.095 MPa and flow rate of 0.31 L/s) and oxygen (pressure of 0.4 MPa and flow rate of 0.42 L/s) based on GJB323A-96 [16]. The sample was fixed in a water-cooled steel concave. The inner diameter of the oxyacetylene torch gun was 2 mm and the distance of the gun tip from the exposed surface of the sample was 10 mm. The sample was exposed to the flame for 60 s. During ablation, a two-color infrared thermometer (Raytek MR1SCSF) was used to measure the temperature of the exposed surface. The change of ablation center thickness as per unit time pre- and post ablation was used to calculate the linear ablation rate. The ablation property was of the average value of linear ablation rates of the three tested samples.

The phase compositions of the as-prepared composites were analyzed using X-ray diffraction (XRD, X'Pert Pro MPD). The microstructure and compositions of the composites were studied using scanning electron microscopy (SEM, TESCANVEGA3) equipped with energy dispersive spectroscopy (EDS).

## 3. Results and discussion

In the process of the initial PIP and subsequent ICVI, the pores of fiber bundles are prone to be completely infiltrated by ZrC and PyC because of the pore size in the fiber bundles of non-woven layer of 2D carbon fiber felt is smaller than the size in the webs of the felt. Much larger pores are still present in the fiber webs after PIP and ICVI (Fig. 1a). The infiltration of PyC is contributed to densify ZrC matrix in the bundles and simultaneously offers the carbon source for the formation of ZrC-SiC by RMI of $ZrSi_2$ melt. The microstructure of C/C-ZrC-SiC composites after RMI is shown in Fig. 1b. No obvious pits can be observed in the composites and the ceramics are nearly distributed in the whole composites. Fig. 1c shows the morphology of non-woven layer of the composites. The corresponding EDS elemental maps of C/C-ZrC-SiC composites cross-section show that ZrC-C formed by PIP and ICVI is distributed in the gaps between the fibers of the bundles of non-woven layers, as shown in Fig. 1f and g which is consistent with that of spectrum 1 (Fig. 1h). The PyC layer is maintained well on the carbon fiber and not chemically eroded by ZrC precursor and $ZrSi_2$ melt after

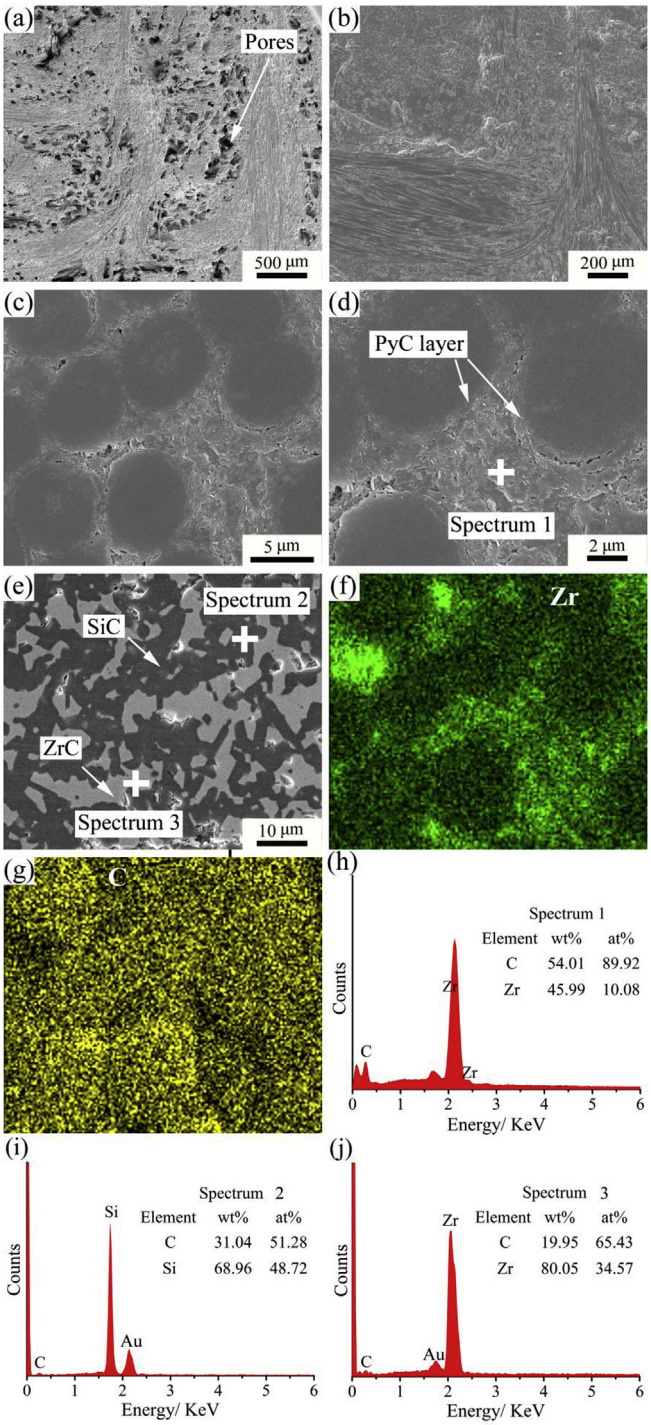


**Fig. 1.** Microstructures of (a) C/C-ZrC, (b) C/C-ZrC-SiC composites, (c) ZrC-C in the non-woven layer, (d) magnification view of carbon fiber in (c), (e) ZrC-SiC in the fiber web, (f) and (g) the EDS elemental maps of Zr and C in the non-woven layer, (h), (i) and (j) EDS analysis of the marked 1, 2 and 3, respectively.