

# Preparation, ablation behavior and mechanism of C/C-ZrC-SiC and C/C-SiC composites



Zhigang Zhao, Kezhi Li\*, Wei Li, Qing Liu, Gang Kou, Yulei Zhang\*

State Key Laboratory of Solidification Processing, Carbon/Carbon Composites Research Center, Northwestern Polytechnical University, Xi'an 710072, PR China

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## ABSTRACT

ZrC precursor was synthesized by a solution approach using  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ , acetylacetonate, glycerol and boron-modified phenolic resin. A ZrC yield of  $\sim 40.56$  wt% was obtained at  $1500^\circ\text{C}$  in the C/Zr molar ratio of 1:1. C/C-ZrC-SiC composites were fabricated by a combined processes of chemical vapor infiltration (CVI) and precursor infiltration and pyrolysis (PIP) using the synthesized ZrC precursor. For comparison, C/C-SiC composites were prepared by CVI. Thermogravimetric analysis showed that C/C-ZrC-SiC composites exhibited better oxidation resistance than C/C-SiC composites. After oxyacetylene torch ablation, the mass ablation rate of C/C-ZrC-SiC composites was 9.23% lower than that of C/C-SiC composites. The porous  $\text{ZrO}_2$  skeleton in the ablation center was prone to be peeled off by the flame flow, resulting in the higher linear ablation rate of C/C-ZrC-SiC composites. The oxide layers of  $\text{ZrO}_2$  and  $\text{SiO}_2$  were formed on the transition and brim region of C/C-ZrC-SiC composites and acted as effective heat and oxygen barriers. For C/C-SiC composites, the C-SiC matrix was severely depleted in the ablation center and the formed  $\text{SiO}_2$  layer in the brim region could protect the matrix against further ablation.

## 1. Introduction

Carbon/carbon (C/C) composites as an excellent thermal structural materials have been widely used in aerospace components such as leading edges, nose tips and heat shields for reentry vehicles for advanced aircraft [1,2]. These components operate in severe conditions including higher temperatures, faster speeds, higher stresses, hostile environments and more [3]. Therefore, the improved ablation resistance of C/C composites are required to withstand the severe thermal conditions.

Introducing ultra-refractory materials into C/C composites is an effective route to improve their ablation resistance. Ultra-high temperature ceramics (UHTCs), including the carbides, nitrides, and borides of some transition metals (TMs) such as Zr, Hf, Ti, Nb, and Ta, have received much attention in aerospace field [4]. These materials have the high melting points ( $> 3000^\circ\text{C}$ ), good thermal-shock resistance, excellent ablation resistance and chemical erosion resistance [5]. Among the UHTCs, zirconium carbide (ZrC) exhibits unique properties such as high melting temperature [6], relatively low density [6] and excellent ablation resistance at high temperatures [7]. Moreover, the refractory  $\text{ZrO}_2$  with a melting point of  $2770^\circ\text{C}$  which allows them to endure temperatures as high as  $2500^\circ\text{C}$  [8]. Generally, ZrC-SiC ceramics have better high temperature performance due to the combination

of the passivating character of SiC and the high melting temperature of ZrC [9]. In addition, the molten  $\text{SiO}_2$ - $\text{ZrO}_2$  under ultrahigh temperature can seal the defects such as pores and cracks. Therefore, the anti-ablation performance of C/C composites can be improved by modifying the matrix with ZrC-SiC ceramics.

Various methods, such as precursor infiltration and pyrolysis (PIP) [10–15], reactive melt infiltration (RMI) [16–20] or a combined processes [21,22] have been used to fabricate C/C-ZrC-SiC composites. PIP is a solution-based processing which can make ZrC and SiC homogeneous distribution into C/C composites. In this process, the low density C/C composites are selected as preform and pyrolytic carbon is commonly used as interphase layer to protect the carbon fiber from the chemical erosion by ZrC and SiC precursor during pyrolysis [14,15]. However, the significant difference of coefficient of thermal expansion (CTE) between carbon fibers and ZrC-SiC matrix will induce stress in the composites, which results in fiber-matrix interface cracking after heat treatment. SiC has a thermal expansion coefficient close to that of carbon matrix ( $\text{SiC}: 3.8\text{--}5.12 \times 10^{-6}/\text{K}$ ;  $\text{PyC}: 1\text{--}2 \times 10^{-6}/\text{K}$ ) [11] and has the capacity to generate  $\text{SiO}_2$  layer under the oxidative conditions which acts as a diffusion barrier between oxygen and carbon surface [23,24]. Moreover, SiC layer can alleviate the CET difference existing between the fiber and matrix to a certain degree. So far, most literatures are focused on the ablation behavior of C/C composites only by

\* Corresponding authors.

E-mail addresses: [likezhi@nwpu.edu.cn](mailto:likezhi@nwpu.edu.cn) (K. Li), [zhangyulei@nwpu.edu.cn](mailto:zhangyulei@nwpu.edu.cn) (Y. Zhang).

modifying the matrix with ZrC and SiC. There are few reports on the ablation behavior and mechanism of C/C composites fabricated by modifying the matrix with ZrC and meanwhile protecting the carbon fiber using SiC transition interphase layer.

In the present work, a low cost route was used to synthesize the liquid ZrC precursor for PIP. A combined processes of CVI and PIP were used to fabricate C/C-ZrC-SiC composites, in which the carbon fibers were protected by SiC coating and the matrix was modified using ZrC. C/C-SiC composites were fabricated by CVI for comparison. The phase and structure of ZrC precursor were characterized. Microstructure, oxidation resistance, ablation behavior and mechanism of the prepared composites were studied.

## 2. Experimental

### 2.1. Synthesis of ZrC precursor

Polyzirconoxane with a high stability and good reproducibility was chosen as the zirconium-containing precursor for the preparation of ZrC. Boron-modified phenolic resin was used as the major source of carbon due to its good solubility in polyzirconoxane and ethanol. The ZrC precursor was synthesized through a modified method similar to [25], and the schematic diagram is shown in Fig. 1.  $ZrOCl_2 \cdot 8H_2O$ , acetylacetonate, glycerol and boron-modified phenolic resin were used as the starting materials in the synthesis of ZrC. The mass % yield of  $ZrOCl_2 \cdot 8H_2O$  and boron-modified phenolic resin was determined using thermogravimetric analysis at the heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  to  $1500\text{ }^\circ\text{C}$  under Ar atmosphere. The mass % yield for  $ZrO_2$  and C at  $1500\text{ }^\circ\text{C}$  was 41.71% and 8.86%, respectively.  $ZrOCl_2 \cdot 8H_2O$  used as zirconium source was first dried at  $60\text{ }^\circ\text{C}$  for 3–5 h and then mixed with acetylacetonate (acacH) using molar ratio of 1 (acacH to Zr) and ethanol was used as a mutual diluent. Glycerol was added to the solution with the molar ratios in the range of 0.15–0.5 for glycerol/Zr under magnetic stirring. The resulting solution was refluxed at  $140\text{--}180\text{ }^\circ\text{C}$  for 2 h for the purpose of converting to polyzirconoxane-based solution. Appropriate amounts of the bulk boron-modified phenolic resin were added to the polyzirconoxane-based solution to give different C/Zr molar ratios (1:1, 1.2:1).

The as-prepared ZrC precursors were dried at  $60\text{ }^\circ\text{C}$  for 10 h and cured at  $180\text{ }^\circ\text{C}$  for 3 h under air atmosphere for the purpose of evaporation of solvent and cross-linking of the precursors, respectively. The cured precursors were crushed to powder. Pyrolysis was performed in a graphite furnace for 2 h at  $1500\text{ }^\circ\text{C}$  at a heating rate of  $2.5\text{ }^\circ\text{C}/\text{min}$  under flowing argon. The ceramics yield was determined by the mass ratio of the pyrolyzed product at  $1500\text{ }^\circ\text{C}$  to the cross-linked precursor at  $180\text{ }^\circ\text{C}$ .

### 2.2. Preparation of materials

The preparation process of the C/C-ZrC-SiC and C/C-SiC composites is illustrated in Fig. 1. The density of the 2D needle-punched carbon felt was increased from  $0.45$  to  $0.7\text{ g}/\text{cm}^3$  by depositing the pyrolytic carbon using isothermal chemical vapor infiltration (ICVI) at  $900\text{--}1200\text{ }^\circ\text{C}$  for 20 h, for the purpose of protecting the carbon fiber against the chemical erosion from the oxidative species produced by the ceramics precursor. The methane was used as carbon source. Then SiC was introduced into the preform of  $0.7\text{ g}/\text{cm}^3$  by chemical vapor infiltration. The details of the process were described elsewhere [26]. The as-fabricated C/C-SiC composites were infiltrated with the liquid ZrC precursor by vacuum impregnation and pyrolysis for several times. Finally, the obtained C/C-ZrC-SiC composites were further densified with pyrolytic carbon using thermal gradient chemical vapor infiltration (TCVI) for 130 h. The same process was also employed to prepare the C/C-SiC composites. It should be noted that the final composites were not further processed at higher temperature.

Mass changes of the composites before and after CVI (SiC) or PIP (ZrC) were recorded for evaluation of SiC or ZrC composition. The porosity of the composites was determined by Archimedes method. The bulk density of the composites was measured by dividing mass by volume. The phase compositions, density and open porosity of the as-prepared composites are listed in Table 1.

### 2.3. Oxidation tests

#### 2.3.1. Non-isothermal thermogravimetric analysis (TGA)

The oxidation behavior of C/C-ZrC-SiC and C/C-SiC composites was studied by thermogravimetric analysis using a TA Q600 synchronous thermogravimetric analyzer. The bulk specimens with average weight of 32 mg were heated from room temperature up to  $1400\text{ }^\circ\text{C}$  at the heating rate of  $20\text{ }^\circ\text{C}/\text{min}$  in dry air with a flow rate of  $30\text{ mL}/\text{min}$ .

#### 2.3.2. Oxyacetylene torch testing

The high temperature oxyacetylene torch tests were used to investigate the ablation resistance of the composites. The pressures and flow rates of  $C_2H_2$  and  $O_2$  used to produce the torch with a heat flux of  $4.18\text{ MW}/\text{m}^2$  were  $0.095\text{ MPa}$  and  $0.31\text{ L}/\text{s}$ ,  $0.4\text{ MPa}$  and  $0.42\text{ L}/\text{s}$ , respectively. The inner diameter of the oxyacetylene gun tip was 2 mm. Plate-shaped specimen had a diameter of 30 mm and a thickness of 10 mm. The distance and angle between the specimen and the tip were 10 mm and  $90^\circ$ , respectively. The specimens were exposed to the torch for 60 s. Both the mass and linear ablation rates were calculated by the changes in mass and ablation center thickness as per unit time before and after test, respectively. The surface temperature of the specimen

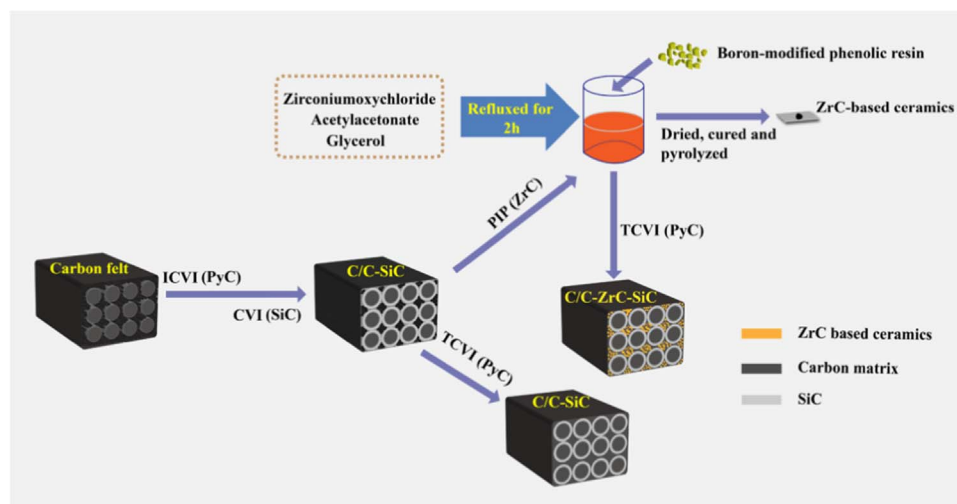


Fig. 1. The schematic diagram for the preparation of ZrC precursor, C/C-ZrC-SiC and C/C-SiC composites.

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