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To cite this article: S A Chen et al 2019 IOP Conf. Ser.: Mater. Sci. Eng. 479 012110

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Effects of pyrocarbon matrix type on the microstructure and properties of C/ZrC composites

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Abstract. Three porous C/C preforms with various carbon matrix type (deposited PyC, vitreous carbon and pitch derived carbon), and reinforced by three-dimensional needled felt, were used to prepare C/ZrC composites via reactive melt infiltration of zirconium. C/ZrC composites prepared from pitch derived C/C preform obtained the highest density of 3.31 g/cm³ and lowest porosity of 9.8%. The deposited carbon matrix can protect the carbon fiber from melt erosion at high temperatures, leading to the higher flexural strength and modulus of 203 MPa and 15.5 GPa. But the C/ZrC fabricated by the phenolic resin derived C/C exhibited the poorest mechanical properties because of the weak interface bonding strength and carbon fiber degradation. And the composites exhibited the poorest anti-ablation properties because the amorphous vitreous carbon was easier to be oxidized and eroded than the others. But pitch derived composites displayed the best anti-ablation properties, with linear recession rate of 0.0053 mm/s and mass loss rate of 0.0035 g/s, close to those of deposited carbon derived composites.

1. Introduction
The thermal-structural component in hypersonic craft, such as sharp leading edges, nose caps and rocket engine in propulsion system, endure severe service environment [1-5] where traditional C/C, C/SiC and oxides-based composites are invalid [6-9]. Continuous carbon fiber reinforced ultrahigh temperature ceramics (C/UHTCs) are attractive for aerospace applications because of their extremely high melting temperatures, high ablation resistance and enhanced fracture toughness compared with the sintering bulk ceramic [10, 11]. Therefore, C/ZrC composites have been highlighted and prepared by soft-solution method [12] or reactive melt infiltration (RMI) [13]. Hu et al. prepared 3D C/ZrC composites by precursor infiltration and pyrolysis process (PIP) [14]. Zou et al. reported the microstructure of C/ZrC composites supplied by Ultramet, Inc. [15]. RMI is fascinating for its short preparation time and relatively low cost. Wang et al. and Tong et al. studied the effects of process parameters on infiltration during the preparation of C/C-ZrC and investigated the ablation properties [16, 17]. The properties of C/C preform significantly affect the performance of C/C-SiC composites prepared by liquid silicon infiltration (LSI) [18, 19], so the microstructure and content of pyrocarbon matrix are bound to enormously affect the microstructure and properties of C/ZrC composites prepared by RMI. However, the effects of these factors of C/C preform on C/ZrC composites have
seldom been referred. Wang reported that resin derived C/C preform could prepare 3D C/ZrC composites by RMI of Zr\textsubscript{2}Cu with flexural strength of 285MPa, but the 3D C/ZrC composites fabricated from pitch derived C/C obtained higher ablation resistance. But the reactions between carbon and Zr or Zr\textsubscript{2}Cu were diverse, thus it is necessary to research the effects of pyrocabon matrix type on the properties of C/ZrC composites prepared by reactive melt infiltration of zirconium.

In this study, C/C preforms with various pyrocabon matrix type derived from propylene, phenolic resin and pitch, and then reactive melt infiltrated with zirconium to fabricate C/ZrC composites. The effects of pyrocabon matrix type in C/C preform on the composition, microstructure, mechanical properties and ablation resistance of C/ZrC composites were investigated.

2. Experimental procedure
The reinforcement of C/C porous prform used here was three-dimensional needled textile supplied by TianNiao Carbon Corporation in China. C/C preform derived from pitch is labeled as C\textsubscript{P}. C/C preform prepared by CVI process is labeled as C\textsubscript{C}. The C/C preform derived from phenolic resin is labeled as C\textsubscript{R}. And the properties of C/C preform were shown in Table 1. The C/C preforms were all heat-treated at 2200°C for 1h in flowing argon.

The C/C preforms, cut into pieces with dimensions of 40×30×5mm, were covered in zirconium powder (99.5% purity, JingRan, Changsha, China) and placed in graphite crucible. The zirconium melted at 2000°C and infiltrated into the preform by capillary forces, then reacted with the carbon to form C/C-ZrC composites. The resultant C/C-ZrC composites prepared from various C/C preform are labeled as CZ\textsubscript{P}, CZ\textsubscript{C} and CZ\textsubscript{R}, respectively.

| Samples | Density (g/cm\textsuperscript{3}) | Porosity (%) | G (%) | \(\sigma_{3f}\) (MPa) | \(E_f\) (GPa) |
|---------|---------------------------------|--------------|-------|----------------|-------------|
| \(C_P\) | 1.20                            | 21.43        | 0     | 202±11         | 21.7±4.4    |
| \(C_C\) | 1.40                            | 22.05        | 16.05 | 300±15         | 28.3±0.8    |
| \(C_P\) | 1.42                            | 28.15        | 31.16 | 60±8.5         | 9.6±1.0     |

The apparent density was measured by Archimedes’ method. Flexural strength (\(\sigma_f\)) was determined using a three-point-bending test on specimens of 4.0×4.5×60 mm with 50 mm span and 0.5 mm/min crosshead speed. Over five samples were measured for the flexural tests. A single-edge-notched-beam (SENB) test was applied on notched specimen of 4.0×8.0×40 mm (notch with 0.3 mm in width and 4.0 mm in depth) with 0.05 mm/min crosshead speed and 30 mm span to determine fracture toughness (\(K_{IC}\)).

Ablative resistance property test was carried out in a flowing oxyacetylene torch environment for 30s, with approximately 4187 kW·m\textsuperscript{-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. Over three samples were measured for oxidation and ablation tests.

The microstructure and composition of the samples were examined by scanning electron microscopy and energy dispersive spectroscopy (S4800, Hitachi; JSM-5600LV, JEOL), and X-ray diffraction (Siemens D-500).

3. Results and discussion
3.1. Microstructure of C/ZrC composites
The XRD patterns of C/ZrC composites were similar to those of C/C preforms (Figure 1). The diffraction intensity of carbon in CZ\textsubscript{R} was higher after high-temperature treatment, but that of ZrC was the lowest of the three samples. The narrow and sharp-pointed diffraction peaks of carbon in CZ\textsubscript{P} resulted into the high diffraction intensity of ZrC because of the high graphitization degree and
reactivity of the pitch derived carbon matrix. Thus the diffraction intensity of carbon and ZrC in CZ\textsubscript{C} were between those of CZ\textsubscript{R} and CZ\textsubscript{P}.

![XRD patterns on the cross-section of C/ZrC composites.][1]

**Figure 1.** XRD patterns on the cross-section of C/ZrC composites.

![Microstructure of C/ZrC composites.][2]

**Figure 2.** Microstructure of C/ZrC composites.

The microstructure of C/ZrC composites prepared from different preforms were shown in Figure 2. A plenty of residual pores were observed in CZ\textsubscript{R}, including macro-pores between fiber bundles and in
ZrC matrix and micro-pores in fiber bundles (Figure 2a). A few α-Zr were surrounded by massive reaction formed ZrC matrix (Figure 2b), but a small amount of isolated ZrC particles were distributed in the α-Zr, forming Zr-ZrC eutectic after cooling down. ZrC matrix was more well-distributed in CZC than in CZR, but a plenty of cracks were observed in the ZrC matrix, which were caused by CTE mismatch during cooling (Figure 2c). Rarely residual α-Zr was detected in ZrC matrix in CZC because of the less variation of pore size in C/C preform. Obvious ZrC grain boundary and the formation of big grain by combination of smaller grain can be observed in Figure 2d. The cracks in CP were infiltrated and filled up by ZrC matrix, but residual cracks and pores also existed in ZrC matrix (Figure 2e). Residual Zr-ZrC eutectic was included in ZrC matrix, and some impurity concentrated after reaction in the eutectic and at the interface of the eutectic and ZrC (Figure 2f).

3.2. Mechanical properties of C/ZrC composites

The densities and mechanical properties of C/ZrC composites were shown in Table 2. The density and open porosity of CZR were 3.00 g/cm$^3$ and 12.7% respectively, whose low density and high open porosity must be caused by the poor wettability between vitreous carbon and melt zirconium and volume shrinkage of carbon matrix during high temperature preparation process. CZP obtained the highest density (3.31 g/cm$^3$) and the lowest open porosity (9.83%) because the higher graphitezization degree of pitch derived carbon benifited the wettability, infiltration and reaction between melt zirconium and porous C/C preform.

The flexural strength and modulus of CZR were 88 MPa and 10.4 GPa, respectively, much lower than those of CZC. The reason of substantially decrease of mechanical properties after reactive infiltration must be as following: 1) the volume shrinkage of low density resin derived vitrous carbon (1.37 g/cm$^3$) and the unfolding of closed pores would weaken the interface bonding strength between fiber and carbon matrix, then leading to the fracture of composites at low stress; 2) the porous carbon matrix prepared by PIP process could not effectively protect the carbon fiber from erosion of melt zirconium, resulting into decrease of the mechanical properties after reactive infiltration.

The flexural strength and modulus of CZC were 203 MPa and 15.5 GPa, respectively, the highest of the three composites. The PyC amount was enough to transmit the load effectively and protect the fiber from reactive erosion. But fiber degradation of T300 fiber at high temperature led to the decrease of mechanical properties after reactive infiltration.

The mechanical properties of CZP increased after high temperature infiltration because of the increased density and the filling up of massive cracks in the matrix by formation of ZrC matrix. The low fracture toughness of CZP must be caused by the low fraction of fiber, especially long fiber.

| Samples | Densities (g/cm$^3$) | Porosity (%) | $\sigma_f$ (MPa) | $E_f$ (GPa) | $K_{IC}$ (MPa$\cdot$m$^{1/2}$) |
|---------|---------------------|--------------|-----------------|-----------|--------------------------|
| CZR     | 3.00±0.22           | 12.7±0.4     | 88.3±12.5       | 10.4±1.1  | 6.3±0.2                 |
| CZC     | 3.07±0.01           | 10.0±0.1     | 203±8           | 15.5±1.4  | 8.5±2.0                 |
| CZP     | 3.31±0.10           | 9.8±0.1      | 95±17           | 17.2±2.3  | 3.5±0.1                 |

The fracture surface of C/ZrC composites were shown in Figure 3. The large amount and long pulled-out fiber of CZR verified the pseudo plastic fracture mode (Figure 3a). The original grooves of carbon fiber can be observed on the pulled-out fiber obviously and a plenty of carbon matrix particles adhered on the pulled-out fiber, indicating the weak interface bonding strength between fiber and carbon matrix and the low strength of carbon matrix (Figure 3b). Large amount of fiber pulled-out were observed on the fracture surface of CZC, indicating the non-brittle fracture mode (Figure 3c). Figure 3d exhibited the fiber pulled-out, fiber-PyC matrix interface debonding and carcks propagation in PyC matrix through axial direction of fiber. The clear trenches on the pulled-out fiber suggested that the deposited PyC around the fiber protected it effectively from the melt erosion and ensured the appropriate interface strength, resulting into the excellent mechanical properties. The flat fracture
surface of CZ\textsubscript{P} led to rarely pulled-out fiber (Figure 3e). The fractured fiber and the PyC matrix particles adhered on the pulled-out fibers both suggested that the fracture mode was developing to a brittle fracture mode (Figure 3f).

Figure 3. Fracture surface of C/ZrC composites after three-point bending test.

3.3. Ablation properties of C/ZrC composites

The ablation properties of C/ZrC composites were displayed in Table 3. CZ\textsubscript{R} exhibited the poorest anti-ablation properties of the three samples, with linear recession rate of 0.014 mm/s and mass loss rate of 0.0063 g/s. But CZ\textsubscript{P} displayed the best anti-ablation properties, with linear recession rate of 0.0053 mm/s and mass loss rate of 0.0035 g/s. The amorphous vitreous carbon was easier to be oxidized and eroded than graphite carbon, thus leading to its high ablation rate. The ablation properties of CZC were close to those of CZ\textsubscript{P}. The contents of ZrC matrix in the three samples were all 24–27 vol%, thus the difference of ablation properties must be caused by the carbon matrix types.

| Samples | Linear recession rate (mm/s) | Mass loss rate (g/s) |
|---------|-----------------------------|---------------------|
| CZ\textsubscript{R} | 0.014 | 0.0063 |
| CZ\textsubscript{C} | 0.0047 | 0.0052 |
| CZ\textsubscript{P} | 0.0053 | 0.0035 |
4. Conclusions
Three porous C/C preforms, reinforced by three-dimensional needled felt and various carbon matrix type (deposited PyC, vitreous carbon and pitch derived carbon), were used to prepare C/ZrC composites via reactive melt infiltration of zirconium. The C/ZrC composites prepared from pitch derived C/C preform obtained the highest density of 3.31 g/cm³ and lowest porosity of 9.8%. The deposited carbon matrix can protect the carbon fiber from melt erosion at high temperatures, leading to the higher flexural strength and modulus of 203 MPa and 15.5 GPa. But the C/ZrC fabricated by the phenolic resin derived C/C exhibited the poorest mechanical properties because of the weak interface bonding strength and carbon fiber degradation. And the composites exhibited the poorest anti-ablation properties because the amorphous vitreous carbon was easier to be oxidized and eroded than the others. But pitch derived composites displayed the best anti-ablation properties, with linear recession rate of 0.0053 mm/s and mass loss rate of 0.0035 g/s, close to those of deposited carbon derived composites.

Acknowledgement
The authors are grateful for the financial support provided by The National Natural Science Foundation of China (Grant No. 51602346) and The National Programme for Key Basic Research Projects (Grant no. 2015CB655200).

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