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Effect of SiC/ZrC ratio on the mechanical and ablation properties of C/C–SiC–ZrC composites

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ABSTRACT

The effect of SiC/ZrC weight ratio on the mechanical and ablation properties of carbon/carbon composites modified by SiC nanowires reinforced SiC–ZrC ceramics (C/C–SiC–ZrC) was studied. Results showed that C/C–SiC–ZrC composites with a SiC/ZrC ratio of 1:1.5 exhibited good mechanical and ablation properties. The flexural strength and modulus were 201 ± 20 MPa and 18 ± 1 GPa, respectively. After ablation for 120 s, the linear and the mass ablation rate were 0.012 mm/s and 0.0019 g/s. The good performance is attributed to a higher density, the reinforcing effect of SiC nanowires and the proper SiC/ZrC ratio.

1. Introduction

Due to the extraordinary mechanical and physicochemical properties, carbon/carbon (C/C) composites are one of the most available materials as structural components and thermal protection systems in high temperature environment, such as aircraft brakes, nose tips, sharp leading edges and rocket nozzles [1,2]. However, the oxidation and ablation resistance of C/C composites need to be further improved to satisfy demands for the new generation of hypersonic vehicles operated in the extreme environment with high heat flux, high-pressure airflow and high-speed erosion of particles [3,4].

An alternative solution is introduction of ultra-high-temperature ceramics (UHTCs) into C/C, preparing C/C–UHTCs composites. UHTCs based on several carbides, nitrides, and borides of group IV_B and V_B transition metals possess an excellent combination of high melting points, good thermal shock resistance and superior ablation/oxidation resistance [5]. In particular, zirconium carbide (ZrC) with high melting temperature (3540 °C), relatively low density (6.7 g/cm^3), and good chemical inertness [6] has been regarded as one of the most promising UHTCs. Meanwhile, its refractory oxide (ZrO_2) whose melting point is up to 2677 °C can effectively reduce the diffusion rate of oxidizing species toward the composite matrix [7]. Generally, high brittleness and poor thermal shock resistance make it unfeasible for ZrC to be used alone and the form of SiC–ZrC ceramics is widely applied to get a better high-temperature performance [8–10]. Thus C/C composites modified by SiC–ZrC ceramics have attracted much attention.

Recently carbon fiber reinforced SiC–ZrC composites have been fabricated by precursor infiltration and pyrolysis (PIP) method using a hybrid precursor containing polycarbosilane (PCS) and organic zirconium-containing polymer (PZC) [8,11–15], which can obtain continuous double-ceramic matrix, improve the distribution of ceramic phases and increase the content of them in the composites. These researches mainly focused on fabrication [8,11], densification [12] and ablation performance [13–15]. For multiphase ceramic composites, different phases in matrix play different roles in final performance and the relative content of them has a great effect on properties of the composites [16–19]. As an example, the flexural strength and fracture toughness of ZrB_2-based UHTCs increase as SiC content (0–30 vol% SiC particulates) increases [18]. Compared with pure ZrB_2 ceramics, the oxidation resistance of ZrB_2–30 vol% SiC is improved by the formation of SiO_2-based glassy layer at 1500 °C [19]. For C/C–SiC–ZrC composites, Li et al. [12] studied the effects of porous C/C density on their densification behavior and ablation property and concluded that composites with an initial C/C density of 1.21 g/cm^3 exhibited the best ablation resistance under an oxyacetylene torch. Wu et al. [14] reported that with the increasing content of ZrC, the ablation rates of C/C–SiC–ZrC composites under the plasma torch firstly decreased and then increased. The sample with 17.45 vol% ZrC had optimum ablation resistance. However, the specific effects of SiC, ZrC and their relative content on ablation properties were not explained in detail. Additionally, in our previous work modified C/C composites exhibited a low flexural strength [12,15] and their

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detailed mechanical behavior which is necessarily considered during practical application was paid little attention to. SiC nanowires are regarded as favorable reinforcing and toughing materials due to their large yield strength, good oxidation resistance and compatibility with SiC ceramics [20,21]. Chu et al. [22–24] concluded that SiC nanowires could suppress crack propagation in C/C coatings via various toughening and strengthening mechanisms including nanowire pullout, bridging, and micro-crack deflection. Thus the oxidation protection and mechanical performance of composite coating were efficiently improved. So it may be feasible to incorporate UHTCs reinforced by SiC nanowires into the carbon matrix in order to improve the mechanical property of composites.

The aim of our work is to evaluate effects of the relative content of SiC and ZrC in matrix on mechanical and ablation properties of C/C–SiC–ZrC composites which are prepared by PIP process using the mixed solution of PCS and PZC as precursor for SiC–ZrC ceramics. The reinforcement effect of SiC nanowires on the SiC–ZrC ceramic matrix is also discussed.

2. Experimental procedure

2.5-D carbon fiber felts (Yixing Tianniao High Technology Co., Ltd., Jiangsu, China) with a density of 0.40 g/cm^3 were fabricated by alternatively stacked non-woven layers and carbon fiber webs by a needle-punching technique, which were employed as reinforcement for C/C–SiC–ZrC composites. The volume content of the felts was about 24.5%. PCS (National University of Defense Technology, Changsha, China) and PZC (Institute of Process Engineering, Chinese Academy of Sciences, Beijing, China) were used as SiC and ZrC precursor, respectively. Dimethylbenzene was chosen as solvent of the precursors. Four groups of mixed precursors with different SiC/ZrC weight ratios of 1:0.5, 1:1, 1:1.5 and 1:2 according to the ceramic yield ratios of PCS and PZC were designed.

Firstly, the primary felts were deposited with pyrolytic carbon (PyC) through thermal gradient chemical vapor infiltration (TCVI) process using methane gas as carbon source. Then the porous C/C preforms with a density of 0.80 g/cm^3 were infiltrated into the mixed precursors homogenously dispersed in dimethylbenzene for 1.5 h under vacuum. After dried at 60 °C in a drying oven, the samples were pyrolyzed within 1300–1600 °C in a graphite furnace under flowing argon atmosphere. To further densify the samples, repetition of infiltration, drying and pyrolysis was operated with the same PIP cycles until desired densities of C/C–SiC–ZrC composites were obtained.

The apparent densities and open porosities of the fabricated composites were measured by the Archimedes method. Samples with a size of 55 mm × 10 mm × 4 mm were used for three-point-bending tests in an electronic universal testing machine (CMT 5304, Suns Co., China) performed at a load speed of 0.5 mm/min and a span of 40 mm.

An oxyacetylene torch test was carried out to evaluate high-temperature ablation resistance of the composites according to GJB323A-96. The cylindrical-shaped specimens with a size of Φ30 mm × 10 mm were vertically exposed to the flame up to 3000 °C for 120 s. Their surface temperatures were over 2400 °C, which were measured by an optical pyrometer in 2-color mode. The pressure and flux of oxygen were 0.4 MPa and 1.512 m^3/h, and for acetylene 0.095 MPa and 1.116 m^3/h, respectively. The distance between the gun tip and the surface of the specimen was 10 mm and the inner diameter of the oxyacetylene gun tip was 2 mm. After the test, both the linear and mass ablation rates calculated by thickness and mass change of the specimen before and after ablation test were used to specifically characterize the ability of ablation resistance.

The phase compositions of the composites before and after ablation were characterized by X-ray diffraction (XRD, X'Pert MPD, Holland) with CuKα radiation. The microstructure and morphology of the materials were studied by scanning electron microscopy (SEM, VEGA TS5136XM), equipped with energy dispersive spectroscopy (EDS).

3. Results and discussion

3.1. Microstructure and composition

Based on the ceramic yield (about 60% for PCS and 28% for PZC) ratios of the precursors, four groups of samples marked as S1, S2, S3 and S4 are designed. The weight percentages of SiC and ZrC in the final composites have been calculated according to the following equations:

$$m_{\mathrm{SiC}} = \frac{(m_1 - m_0)[\omega_{\mathrm{PCS}}\eta_{\mathrm{PCS}}/(\omega_{\mathrm{Zr}}\eta_{\mathrm{Zr}} + \omega_{\mathrm{PCS}}\eta_{\mathrm{PCS}})]}{m_1} \times 100\% \tag{1}$$

$$m_{\mathrm{ZrC}} = \frac{(m_1 - m_0)[\omega_{\mathrm{Zr}}\eta_{\mathrm{Zr}}/(\omega_{\mathrm{Zr}}\eta_{\mathrm{Zr}} + \omega_{\mathrm{PCS}}\eta_{\mathrm{PCS}})]}{m_1} \times 100\% \tag{2}$$

in which m_0, m_1, ω_{PCS}, ω_{Zr}, η_{PCS}, η_{Zr}, means mass of felts without PIP process, mass of the final samples, mass fraction of PCS in the mixed precursors, mass fraction of PZC in the mixed precursors, ceramic yield of PCS, ceramic yield of PZC, respectively.

As a result, the contents of SiC and ZrC as well as densities and open porosities of four groups of samples are listed in Table 1. It can be seen that the weight percentage of SiC decreases while that of ZrC increases in the composites and their relative ratio is obvious. Meanwhile, the density of the composites increases with the raise of ZrC fraction until the value reaches 2.24 g/cm^3. When ZrC fraction continues to grow, e.g., over 38.16 wt.%, the density begins to decline. During the immersion process, since the viscosity of the mixed precursor distinctly reduces with the decreasing content of PCS which has a high viscosity, the infiltration efficiency of S4 must be faded after the same number of PIP recycles. Most importantly, when there is more content of PZC, there are more pores produced by the pyrolysis of big organic molecules containing zirconium because of their serious weight loss and volume shrinkage [25]. That is also the reason why the open porosity in the composites increases with the increasing content of ZrC. Thus it is inferred that higher ZrC fraction which will cause higher porosity is not beneficial for densification of the double-matrix composites.

The XRD pattern in Fig. 1 indicates that there are four kinds of phases, C, SiC, ZrC and ZrO_2 including in the obtained composites. From the diffraction peaks, main phases are SiC and ZrC produced from their respective precursors. The characterized peaks of ZrC are sharp, which implies its good crystallization during heat treatment at high temperature. The weak presence of ZrO_2 comes from the pyrolysis of PZC precursor. The precursor which contains zirconium and oxygen atoms can be reduced to amorphous carbon and ZrO_2, etc. As the temperature further increases, ZrO_2 reacts with amorphous carbon or PyC matrix and finally converts into ZrC. However, a small quantity of ZrO_2 is wrapped by ZrC and is difficult to be carbonized completely.

Fig. 2 shows the micrographs of cross sections for 2.5-D C/C–SiC–ZrC composites. From the back-scattered electron (BSE) images in Fig. 2(a) and (b), ceramic phases mainly fill the carbon fiber webs between non-woven layers where large gaps exist. Only a small part of those inhabit the pores in the intra-bundle areas. The generated SiC and ZrC displaying bright backgrounds in the images seem generally dense but some closed pores can be found as a result of gas escape during the conversion of precursors to double-phase ceramic. Additionally, the crystallization of ceramic phases at high temperature also leads to a part of pores retained. Although the following PIP cycles may fill most of the open pores,