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Microstructure and ablation mechanism of C/C-ZrC-SiC composites in a plasma flame

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ABSTRACT

Ablation behavior of C/C-ZrC-SiC composites was investigated using a plasma flame. The composites exhibited excellent ablation performance. After ablation for 180 s, three kinds of ablation behavior appeared from the border to the center on the surface, which were closely related to the temperature and denudation force. Additionally, the ablation behavior in the cross-sectional direction of the composites was mainly controlled by the temperature. During the ablation, ZrC and SiC were oxidized into ZrO_2 and SiO_2, respectively, resulting in the formation of a ZrO_2-SiO_2 binary eutectic system. The ablation mechanism was also discussed, which could provide strong illustration of the evolution processes of the eutectic system at different temperatures.

1. Introduction

Carbon/carbon (C/C) composites are considered as a promising candidate material for aerospace applications due to their excellent characteristics [1–3], such as low density, high strength, low thermal expansion coefficient, high thermal conductivity, outstanding thermal shock resistance and excellent ablation property at ultrahigh temperatures. However, C/C composites are vulnerable to ablation in oxidizing environments. This greatly restricts their potential applications [4,5]. Therefore, improving the anti-oxidation ablation ability of C/C composites has become an attractive new subject.

As widely proved, introducing ultrahigh temperature ceramics (UHTCs), such as SiC, HfC, TaC, ZrC, and ZrB_2 [6–10], into C/C composites is an effective method to improve the anti-oxidation ablation resistance. Among this UHTC family, ZrC possesses many merits, including a high melting point (3813 K), low evaporation, excellent chemical inertness, and resistance to thermal shock and ablation [11,12]. Meanwhile, SiC is also a fascinating ceramic with low density, high hardness and a thermal expansion coefficient close to that of carbon matrix (α_{SiC}: 3.8–5.12×10^{-6}/K; α_{PyC}: 1–2×10^{-6}/K). These properties enable the matrix to withstand thermal shocks during fabrication and service. In addition, SiC can be oxidized into SiO_2, with a melting point of 1996 K, under an oxidizing environment, while ZrC can be oxidized into ZrO_2, with a melting point of 2950 K [13,14]. The molten SiO_2 bonds with ZrO_2 to help seal defects such as cracks and pores during the ablation at ultrahigh temperature. Thus, there is an enormous advantage to improve the anti-oxidation ablation performance of C/C composites by introducing ZrC-SiC ceramic phases into the matrix.

Recently, many studies have investigated the anti-ablation properties of C/C-ZrC-SiC composites. The effects of porous C/C density [15,16], SiC/ZrC ratio [17–19] ceramic coating [20,21], and ablation variables [22–24] on the ablation performance of composites were studied. Most of these studies were focused on the ablation behavior of C/C-ZrC-SiC composites [25,26]. Actually, ZrC-SiC ceramic phases as modified constitutions play a significant role in improving the anti-oxidation ablation performance. However, the specific mechanism of ZrO_2 and SiO_2 oxidized from ZrC and SiC during ablation in the oxidizing environment is unclear.

In the present study, C/C-ZrC-SiC composites were fabricated by chemical vapor infiltration (CVI) combined with polymer infiltration and pyrolysis (PIP). The ablation properties were analyzed using a plasma flame for 180 s. The microstructure and ablation behavior of the composites were studied in detail. The purpose of this work was to elucidate the ablation mechanism of C/C-ZrC-SiC composites, based on a heterogeneous ablation reaction model and the phase diagram of ZrO_2- SiO_2 system.

2. Experimental procedures

2.1. Material preparation

The needled carbon fiber integer preforms (0.2 g/cm^3) were deposited through the chemical vapor infiltration process (CVI) by using propene (C_3H_6) as the precursor. A homogeneous solution containing zirconium-containing polymer (PNZ, Institute of

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Table 1
Basic parameters of C/C-ZrC-SiC composites.

Samples	Initial Density /g cm^{-3}	Final density /g cm^{-3}	Vol/%		
			PyC	ZrC	SiC
C/C-ZrC-SiC	1.27	1.98	53	7.28	4.88

Chemistry, Chinese Academy of Sciences, Beijing, China) and polycarbosilane (PCS, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China) was used as a ZrC-SiC precursor. The C/C skeleton was infiltrated by the precursor through vacuum impregnation equipment and then solidified in a drying oven and heat-treated at 1873 K for 2 h in an argon atmosphere. The C/C-ZrC-SiC composites were prepared by the PIP process for cycling 10 times until the mass increase percentage of the composites was no more than 1%. The basic parameters of the final C/C-ZrC-SiC composites are presented in Table 1.

2.2. Ablation testing

The ablation properties of the C/C-ZrC-SiC composites were determined using a plasma flame with cylindrical samples (Ø30 mm×10 mm). The ablation direction of the flame was parallel to the needle punching direction. The flux was 40 L/min for Ar and 10 L/s for H_2. The working current and voltage were 652 A and 62 V, respectively. The sample was exposed to the flame for 180 s, and the maximum temperature of the ablation center surface of the samples reached as high as 2615 K, measured by an optical pyrometer. The linear and mass ablation rates were calculated by the thickness and mass changes before and after ablation. The final ablation rates of the composites were the average results for three specimens.

2.3. Characterizations

The bulk density and open porosity of C/C-ZrC-SiC composites were obtained by the Archimedes method. The phase compositions and morphology of the composites were investigated by X-ray diffraction (XRD, Rigaku D/MAX) using Cu K_α radiation and scanning electron microscopy (SEM, HITACHI SU-1500), along with energy dispersive spectroscopy (EDS) for elemental analysis.

3. Result and discussion

3.1. Ablation properties of C/C-ZrC-SiC composites

The ablation properties of C/C-ZrC-SiC composites and C/C-UHTCs composites reported in other studies are listed in Table 2, which were calculated by the changes in the mass of the sample and depth at the center due to ablation. It can be seen that the as-produced composites show low average linear and mass ablation rates, which indicate that the C/C composites modified by ZrC-SiC ceramic phase exhibit excellent ablation performance.

Fig. 1 shows the macro-morphologies and XRD analysis of C/C-ZrC-SiC composites before and after ablation. A clear oxide layer on the ablated surface can be observed in Fig. 1(a), which includes three annular areas: a central region (region I), a transition region (region II), and a border region (region III). According to the XRD analysis in Fig. 1(b), the as-prepared samples consist of C, SiC and ZrC, while the analysis results from region I indicate that ZrO_2 and $ZrSiO_4$ are formed. As reported previously [25], ZrC and SiC phases can be oxidized into SiO_2 and ZrO_2, and then, SiO_2 (whose boiling point is 2507 K) will readily evaporate as the ablation temperature reaches 2615 K. In addition, rapid cooling after ablation prior to the crystallization of SiO_2 means that no detectable SiO_2 can be discovered by XRD. The $ZrSiO_4$ phase crystallizes from the eutectic SiO_2-ZrO_2 when the ablated sample cools down.

3.2. Ablation morphology and behavior of C/C-ZrC-SiC composites

3.2.1. The surface micro-morphology of the ablated sample

Fig. 2 shows a quite different micro-morphology for regions I_III of the ablated surface. As shown in Fig. 2(a), the structure of the surface on region III remained intact except for a few ditches, which resulted from the burnt-out carbon (including the carbon fibers and pyrolytic carbon matrix) at the beginning of ablation. Fig. 2(b) indicates that the surface is actually covered by a layer with low liquidity, which is a mixture of a few glass-like phases and solid particles, and both of them are composed of SiO_2 and ZrO_2 based on EDS analysis. In region III, there are few glass-like phases sealing the defects due to the low temperature. Fortunately, the erosive force of the plasm flame is too weak to destroy the surface.

As shown in Fig. 2(c), the appearance of the ablated surface in region II proves that a more continuous oxide layer is formed, with the oxidized ditches being sealed effectively. Fig. 2(d) demonstrates that the surface is actually covered by a great deal of glass-like phases and solid particles, which are mainly the eutectic SiO_2-ZrO_2 and solid-state ZrO_2 based on the EDS result. The molten eutectic SiO_2-ZrO_2 can seal the defects (including the cracks and holes) effectively and then retard infiltration of the oxidation atmosphere. However, a synergistic effect can be produced between the molten eutectic SiO_2-ZrO_2 and solid-state ZrO_2, where the solid-state ZrO_2 can help protect the molten eutectic SiO_2-ZrO_2 from being blown away; meanwhile, the molten eutectic can also cover up the defects of isolated ZrO_2 particles or clusters to avoid the exposure of flame denudation directly. In addition, it is worth noting that the zirconium content in the molten eutectic has increased relatively, which illustrates that ZrO_2 can be dissolved into the molten eutectic gradually with increasing temperature. In region II, many more glass-like phases are generated to fill the defects as the ablation temperature increases, which has a positive effect on withstanding the strong erosion.

As observed in Fig. 2(e), a coarse oxide layer with more obvious oxidized ditches is generated, which is closely related to the higher temperature and stronger erosion in region I. According to Fig. 2(f), there are many ZrO_2 particles or clusters and few molten eutectic SiO_2-ZrO_2 based on the EDS result. What's more, it is interesting that solid-state ZrO_2 particles have the largest diameter among regions I_III, which results from the sintering of ZrO_2 in the highest-temperature environment. The molten eutectic also features the highest content of zirconium due to the significant evaporation of SiO_2. Furthermore, the concentrated ZrO_2 particles on the surface, which pin into the molten eutectic, are not only resistant to being blown away but also contribute

Table 2
Ablation properties of C/C-ZrC-SiC composites and C/C-UHTCs composites reported in other studies.

Materials	Ablation time (s)	Surface or flame temperature (K)	Linear ablation rate (mm/s)	Mass ablation rate (g/s)
C/C-ZrC-SiC in this study	180	2615	1.94×10^{-4}	1.73×10^{-3}
C/C-ZrC-SiC [27]	60	2573	-1.88×10^{-3}	-3.51×10^{-3}
C/C-SiC [13]	20	3300	2.00×10^{-3}	7.3×10^{-3}
C/C-ZrC [28]	20	3300	2.00×10^{-3}	4.00×10^{-3}