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Effect of Cu on the ablation properties of C_f/ZrC composites fabricated by infiltrating C_f/C preforms with Zr-Cu alloys

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Abstract

C_f/ZrC composites were fabricated by reactive melt infiltration at 1200 °C, Low melting Zr_7Cu_{10}, ZrCu and Zr_2Cu alloys were used as infiltrators and the effect of Cu on ablation properties of the composites was investigated. The results show that the C_f/ZrC composites exhibit excellent anti-ablative properties affected apparently by the Cu contents. With the increase of Cu in infiltrators, the linear recession rates decrease from 0.0019 ± 0.0006 to -0.0006 ± 0.0002 mm s^{-1}, whereas the mass loss rates increase from 0.0006 ± 0.0003 to 0.0047 ± 0.0009 g s^{-1}. The formation of a dense ZrO_2 protective layer and the evaporation of residual Cu are in favor of their ablation resistance.

Keywords: B. Composites; D. Carbides; Ablation; Reactive melt infiltration

1. Introduction

Carbon/carbon (C/C) composites own unique properties including low density, good high-temperature strength, high thermal conductivity and resistance to thermal shock and ablation [1–5], which enable them to be used as components in hypersonic reentry vehicles and solid rocket motors [6–8], etc. However, C/C composites are liable to failure because of erosion in oxygen-containing environment at ultra-high temperature (over 2000 °C), which remains an obstacle to their more widespread utilization [9–12]. As an effective approach to improve their ablation resistance, introducing ultra-high temperature ceramics (UHTCs) into C/C composites has attracted increasing interest [13–16]. Among the UHTCs, zirconium carbide (ZrC) is used most widely for its outstanding properties including extremely high melting point (3540 °C) [5], great hardness (25.5 GPa) [17], relatively low density (6.64 g cm^{-3}) and excellent ablation resistance [9,18,19]. As reported in literature [14,17], C/C composites doped with ZrC exhibit the superiority in improvement of the anti-ablative properties at 3000 °C.

In the last few years, numerous approaches such as precursor infiltration and pyrolysis (PIP), chemical vapor infiltration (CVI) and reactive melt infiltration (RMI) have been applied to fabricate C/C-UHTC composites. For example, Shen et al. [14] and Zhao et al. [20] prepared the ZrC modified C/C composites by the PIP process. Chen et al. [21] prepared the C/ZrC composites by the CVI method. Zou et al. [22,23] and Wang et al. [24] investigated the mechanical and anti-ablative properties of C_f/ZrC composite obtained by RMI. Compared to PIP and CVI methods, RMI has obvious advantages including short process period, low cost, near net shape and high yield of UHTC. Up to now, pure Zr [22–24], Zr-Si alloy [25] and Zr-Ti alloy [10] have been adopted to prepare the C_f/ZrC composites. But due to the high melting points of these infiltrators, the infiltration step had to be operated at temperature above 1900 °C, usually leading to a poor mechanical property of the obtained composites. In our previous studies [26–29], we used a novel, simple and low cost molten Zr-Cu infiltration process to prepare the C_f/ZrC composites. The fabricating procedure could be carried out at 1200 °C, and both mechanical properties and ablation resistance of the composites were improved. However, little attention has been paid to the effects of Cu on ablation

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resistance of the obtained composites, and the ablation behavior and mechanism of the C_f/ZrC composites are still unclear. The aim of the present work is to make clear above problems.

2. Experimental procedure

2.1. Materials preparation

Porous C_f/C preform with an open porosity of 40% and a fiber (T300, carbon content of 93% (impurities of $O+H+N+S \leq 7\%$), Toray, Japan) fraction of about 32 vol. % was fabricated by PIP method, using a solution of ethanol/phenolic resin with a weight ratio 1:1 as the carbon precursor. The details were described elsewhere [26]. Three Zr-Cu alloys with Zr/Cu molar ratios of 7:10, 1:1 and 2:1 were used as reactive infiltrators for this study. The alloy ingots were received from Hunan Rare Earth Metal & Material Institute, prepared with spongy Zr pieces (99.6% purity) and electrolytic Cu plate (99.99% purity) by arc melting.

The C_f/ZrC composites were fabricated through following steps: Zr-Cu alloys were placed in a graphite crucible and heated up to 1200 °C in a vacuum of 0.5 Pa. After the alloys melted completely, the porous C_f/C preforms were mechanically driven into the melts and kept there for 1–3 h, and then separated from the liquid Zr-Cu baths and cooled spontaneously to room temperature.

2.2. Characterization

The volume fractions of solid phases were measured by inductively coupled plasma (ICP) and chemolysis, based on the theoretical densities of $6.63\ g \cdot cm^{-3}$ for ZrC, $1.55\ g \cdot cm^{-3}$ for deposited C, $8.96\ g \cdot cm^{-3}$ for Cu, $6.49\ g \cdot cm^{-3}$ for Zr and $1.76\ g \cdot cm^{-3}$ for T300 fiber, which were described in details elsewhere [26]. The open porosities were measured using the Archimedes method, and five samples were tested. The phases were analyzed by X-ray diffraction, using a Bruker D8 Advance instrument with Cu Kα radiation ($\lambda = 1.5405$ Å) operated at a voltage of 40 kV and a current of 30 mA. The 2-theta was in the range of 20–85° and the scanning rate was 4 ° min^{-1}. The peak positions of phases were identified from the Inorganic Crystal Structure Database (ICSD). The microstructure was observed by scanning electronic microscopy (SEM, Quanta-200) with accessorial energy-dispersive spectroscopy (EDS).

2.3. Anti-ablative properties tests

The ablation properties were tested in a flowing oxyacetylene torch environment with approximately 4187 kW m^{-2} heat flux and 3100 °C flame temperature, according to GJB323A-96 Ablation Standard (China). The pressures of acetylene and oxygen were 0.095 and 0.4 MPa, respectively; while the gas fluxes were 1.116 and 1.512 $m^3\ h^{-1}$. The distance between the tip of gun (gunpoint diameter: 2.0 mm) and the sample surface was 10 mm. The test lasted for 60 s and the surface temperature of the sample was monitored with an optical pyrometer. At least three samples with a dimension of 30 mm × 30 mm × 3.5 mm were examined in each test. The mass loss rate (R_m) and linear recession rates (R_l) were calculated by following formulas:

$$R_m = (m_0 - m_1)/t$$

$$R_l = (l_0 - l_1)/t$$

Where, R_m and R_l mean the mass loss rate and linear recession rate, respectively; m_0 and l_0 represent the weight and thickness before ablation, respectively; m_1 and l_1 represent the weight and thickness after ablation, respectively; and t is the ablation time. In detail, l_1 is the average thickness of seven equidistant points along the longest chord of the ablated region with an approximately circular shape. The ultimate ablation rates were taken from three specimens on average.

3. Results and discussion

3.1. Composition

The XRD patterns of the C_f/ZrC composites are shown in Fig. 1. It is found that all the specimens have the same constituent phases of ZrC (ICSD 043370), C (ICSD 031829) and Cu (ICSD 064699). Determined by ICP and chemolysis, the volume percentages of ZrC in composites fabricated by Zr_2Cu, ZrCu and Zr_7Cu_{10} are 43.3, 40.2 and 28.3 vol. %, respectively. That is, Cu exhibits a negative impact on ZrC yields. The basic reason is that the increase of Cu would accordingly reduce the portion of Zr, and then the production of ZrC is inhibited due to lack of Zr supply. Additionally, Cu instead of Zr_xCu_y as the by-product indicates a complete consumption of Zr, regardless of Cu contents in the infiltrators. The residual Cu contents in the final composites derived from Zr_2Cu, ZrCu and Zr_7Cu_{10} are 6.7, 11.6 and 16.2 vol. %, respectively. Therefore, the use of alloy with higher Cu content resulted in more Cu in the final composites.

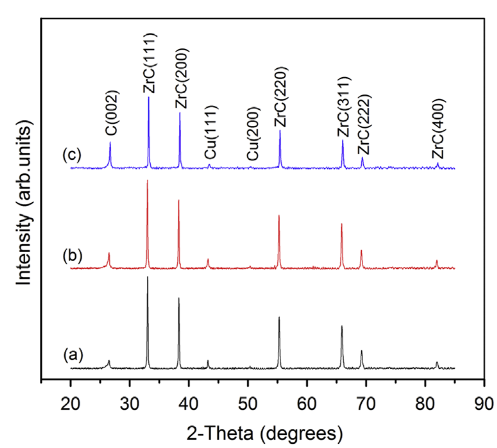

Fig. 1. XRD patterns of the C_f/ZrC composites fabricated by (a) Zr_2Cu, (b) ZrCu and (c) Zr_7Cu_{10}.