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Microstructure and ablation mechanism of graphite/SiC composites under oxy-acetylene flame

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Abstract

Graphite/SiC composites were prepared by reactive metal infiltration (RMI). The microstructure and the ablation mechanism under oxy-acetylene flame were investigated. The ablation surface was composed of a central zone, an intermediate zone and an outer zone. The surface of the intermediate zone was covered by a SiO_2 layer due to the oxidation of Si and SiC. A particle layer, which consisted of SiC particles and graphite particles, was found beneath the SiO_2 layer due to the large inner stress. In the central zone, an extra SiO layer was detected owing to the high temperature and the few oxygen in the particle layer. Due to the good wettability with graphite, the SiO_2 layer exhibited excellent ablation resistance by inhibiting oxygen diffusion and lowering the mechanical erosion of the flame. Besides, the evolution of the gases formed inside the composite helped to improve the ablation resistance.

Keywords: B. Composites; D. SiC; E. Thermal applications; Ablation mechanism

1. Introduction

Carbon-based composites have attracted much attention in aerospace field for their outstanding high temperature strength, low coefficient of thermal expansion, high thermal conductivity, light weight and good thermal shock resistance [1–3]. They are considered to be one of the promising materials for high temperature structural parts, such as rocket nozzles, leading edges and re-entry heat shields. However, when carbon is exposed to oxygen, it will be easily oxidised above 773 K. The poor oxidation resistance turns to be the technical bottleneck of carbon-based materials [4–6].

The current research on carbon based materials for high temperature focuses on improving the oxidation resistance of C/C composites through the addition of various refractory carbides or borides such as SiC, ZrC, TaC, TiC, and HfC [7–12]. The carbides can withstand much higher temperature than carbon in oxidative atmosphere. Besides, C/C composites exhibit a much lower porosity after they are filled by carbides. Materials with a lower porosity have a smaller contact area with oxidation atmosphere. The reduction of the porosity hence improves the ablation resistance. Furthermore, during ablation, a liquid oxide layer can be formed on the surface to prevent heat transfer and oxygen diffusion. However, the liquid oxide layer will be easily blown off by the flame due to the poor wettability between carbon fibre and the liquid oxide layer [9,13].

Graphite has a good wettability with molten SiO_2. Using graphite to replace C/C may enhance the stability of the molten SiO_2 layer and further improves the ablation resistance. However, little work has been done on the ablation properties of graphite/SiC composites. In this paper, graphite/SiC composites were prepared by the RMI method. The microstructure and the ablation mechanism under oxy-acetylene flame were investigated.

2. Experimental

2.1. Preparation of the composites

The porous graphite XH-104 (manufactured by Nantong Xianghai Carbon Corporation, China) was used as the preform. Relevant properties of the graphite were described elsewhere

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[14]. Si particles (produced by Fujian Hongjing Chemical Industry Corporation, China) with an average diameter of 0.5 mm and a purity of 99.9% were chosen as the infiltrated penetrant.

The RMI method was utilised to fabricate graphite/SiC composites. After cleaning by ethanol in ultrasonic waves for 20 min, the graphite preform together with Si particles was heated up to 1873 K in a crucible in a vacuum furnace. Argon was then poured into the furnace to 0.2 MPa. After holding at 1873 K for 30 min, the graphite was pulled out from the crucible and cooled to room temperature. The residual Si and the thin SiC film on the surface of the composites were ground off by 400 grit SiC paper. And then the composites were ground by 2000 grit SiC paper.

2.2. Ablation tests

The ablation properties were tested by oxy-acetylene flame. The size of the specimens was ∅ 30 mm × 10 mm. The ablation surface was 15 mm from the copper nozzle. The inner diameter of the copper nozzle was 2.5 mm. The angle between the ablation surface and the nozzle was 90°. The flux and the pressure of the oxygen and the acetylene were 1512 L/h and 0.4 MPa, 1116 L/h and 0.095 MPa, respectively. The temperature of the ablation surface measured by an optical pyrometer was about 2173–2223 K. The ablation time was 180 s. Five samples were tested to get the linear ablation rate and the mass ablation rate according to the following formulae:

$$R_l = \Delta l/\Delta t \quad (1)$$

$$R_m = \Delta m/\Delta t, \quad (2)$$

where

R_l was the linear ablation rate,
Δl was the length change of the ablation centre,
R_m was the mass ablation rate,
Δm was the mass change of the specimen,
Δt was the ablation time.

2.3. Microstructure analysis

HITACHI S-4800 and HELIOS NanoLab 600i scanning electron microscope (SEM) were used to examine the micromorphology and the composition of the composites before and after ablation. The phase constitution of the composites was identified by X-ray diffraction (XRD, Rigaku D/max-2400) at a rate of 4°/minute. A Fourier transform infrared spectroscope (FT-IR, Varian 3100) was utilised to analysis the constitution of the protective coating formed during ablation.

3. Results and discussion

3.1. Microstructure of the composites

Fig. 1 presents the surface morphology of the graphite and the graphite/SiC composites, as well as the XRD pattern of the graphite/SiC composites. Pores with irregular shape can be clearly observed in the graphite from Fig. 1a. After the infiltration process, most pores have been filled (Fig. 1b). Some residual pores are still visible, which may be related to the closed areas that could not be infiltrated or to inhomogeneous infiltration [15–17]. Fig. 1c shows that the phase constitution of the graphite/SiC composites is graphite, SiC and a little unreacted Si. Therefore, the bright areas in Fig. 1b correspond to SiC and unreacted Si. Unreacted Si is brittle and low-strength. The existence of unreacted Si deteriorates the mechanical properties of the composites [18].

3.2. Ablation behaviour

Oxy-acetylene flame is utilised to evaluate the ablation properties of the graphite/SiC composites. After ablating for 180 s, the graphite specimen has been burnt through, while the linear ablation rate of the graphite/SiC composites is only 8.3 ± 0.6 μm/s. The mass ablation rate of the graphite is 53.0 ± 0.8 mg/s, whereas that of the graphite/SiC composites is only 4.1 ± 0.5 mg/s. Both the linear ablation rate result and the mass ablation rate result show that the ablation resistance of the graphite gets remarkably increased after the addition of SiC. Fig. 2 is the optical image of the graphite/SiC composites after ablation. It can be seen that the ablation surface can be divided into a central zone, an intermediate zone and an outer zone.

The central zone directly contacts with the oxy-acetylene flame and is seriously ablated. Many ablation pits with a diameter of about 0.5–1 mm distribute on the surface of the central zone. The ablation pits increase the chemically active area of the surface and make the surface more sensitive to mechanical erosion [19]. Therefore, the ablation pits lead to the acceleration of surface recession. The intermediate zone withstands a lower temperature and a slighter gas flow. Fewer ablation pits can be observed and their size is much smaller. In the outer zone, the temperature further decreases and no ablation pits can be observed. The ablation conditions in the outer zone are much slighter than those in the central zone and the intermediate zone. Therefore, the research of the outer zone is not important. This paper emphasises on the microstructure and the ablation mechanism of the central zone and the intermediate zone.

Fig. 3 presents the SEM images, the energy dispersive spectrometer (EDS) results and the XRD pattern of the surface of the central zone. As shown in Fig. 3a, the surface of the central zone is covered by one kind of glassy substance. EDS result of Fig. 3a shows that the glassy substance is composed of Si and O (Fig. 3b). The atom ratio of Si/O is very close to 1/2. Further XRD result (Fig. 3c) shows that amorphous diffraction peaks in 20–30° are visible. Yang et al. [20] find that the amorphous diffraction peaks in 20–30° correspond to SiO_2. Therefore, the glassy substance coated on the ablation surface is identified to be amorphous SiO_2. The ablation surface is an oxygen-rich environment with ultrahigh temperature. The following reactions are highly possible to take place:

$$Si(l) + O_2(g) \rightarrow SiO_2(l) \quad (3)$$