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Effect of pre-oxidation on the ablation resistance of ZrB_2–SiC coating for SiC-coated carbon/carbon composites

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Abstract

To improve ablation resistance of carbon/carbon (C/C) composites at high temperature, ZrB_2–SiC coating was prepared on surface of SiC-coated C/C composites by supersonic atmosphere plasma spray. The coated C/C composites were pre-oxidized in air at 1373 K. In the present work, the influence of pre-oxidation treatment on the microstructure and ablation resistance of ZrB_2–SiC coating was investigated. Ablation resistance of coated C/C composites was tested in oxyacetylene torch environment with the heat flux of 2400 kW/m^2. Results show that the liquid glass phase seals defects in the as-sprayed coating after pre-oxidation for 15 min and a dense coating is obtained. The pre-oxidation coating can protect C/C composites for 90 s, which is due to the formation of a dense oxides layer and the molten ZrO_2 layer.

Keywords: Carbon/carbon composites; Coating; Supersonic atmosphere plasma spraying; Pre-oxidation; Ablation

1. Introduction

Carbon/carbon (C/C) composites are promising candidates for aerospace application (nose tips, leading edges, and nozzles of solid rocket motors) as high-temperature thermal field materials [1–3]. However, the oxidation of C/C composites above 723 K in air cannot meet the demand of practical application requirement, especially for high-temperature (higher than 2200 K) associated with high-speed combustion gas flow in oxidizing environment [4–6]. Hence, more efforts need to be made to improve the ablation resistance of C/C composites in such extreme environments.

It is well known that coating is an effective solution to protect C/C composites at high temperature. In recent years, many ultra-high temperature ceramics (UHTC), such as ZrC, HfC, and HfB_2, have been used as anti-ablation coatings for C/C composites [7–10]. As one of the UHTC, ZrB_2 has high melting point (3313 K), high thermal conductivity (65–135 W/m K), relative low density (6090 kg/m^3) and excellent thermal shock resistance, which is suitable for aerospace application [11–13]. However, it is not feasible for ZrB_2 as anti-ablation coating due to its rapid oxidation at high temperature [14,15]. In previous studies, ZrB_2 has been modified by SiC, where ZrB_2 provides mechanical resistance and SiC generates an oxidation protective scale on the material surface at high temperature [16–21]. In addition, ZrB_2 with an addition of 20–30 vol% SiC exhibits good property at high temperature [19,21,22].

Supersonic atmosphere plasma spraying (SAPS) has been applied to prepare the UHTC coatings [19,22]. The temperature of plasma arc is about 10,000 K and velocity of particle is up to 600 m/s. The deposition of melted particles on the substrate can generate great jet impact force, which is beneficial to the formation of dense coating with good bonding strength [23]. Yao et al. [24] prepared the ZrB_2–SiC coating by SAPS, which showed good ablation resistance after ablation for 60 s. While the microholes and microcracks on surface of the as-sprayed coating limited it for further ablation test. Previous results implied that thermal pre-treatment of ZrB_2–SiC in air at temperature between 1373 and 1473 K could be beneficial for its oxidation resistance [25]. Tului et al. [22] reported that ZrB_2–SiC coating had better property after pre-oxidation in air

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at 1373 K, which was attributed to formation of self-protection scale in oxidizing environment.

In present work, the ZrB_2–SiC coating was prepared by SAPS. The SiC inner layer was first prepared by pack cementation on surface of C/C composites to relive the mismatch of the coefficient of thermal expansion (CTE) between ZrB_2–SiC coating and C/C composites. The coated composites were pre-oxidized in air at 1373 K. The purpose of this study was to describe the influence of pre-oxidation on the microstructure and ablation resistance of the coating. The ablation mechanism of the coating under oxyacetylene torch environment was also discussed.

2. Experimental

2.1. Preparation of ZrB_2–SiC coating

The C/C composites were prepared by Thermal gradient chemical vapor infiltration (TCVI) with a density of about 1700 kg/m^3, and the samples (Φ30 × 10 mm) were cut from bulk 2D C/C composites. Then the samples were cleaned in an ultrasonic bath with ethanol and dried at 373–423 K for 2 h. The SiC inner layer was prepared by pack cementation with Si, C and Al_2O_3 powders in inert atmosphere at 1973–2173 K for 2 h [26].

ZrB_2–SiC coating was prepared on the SiC-coated C/C composites by SAPS in air. The ZrB_2 and SiC particles were selected as the raw material. Commercially available ZrB_2 powders (purity > 99.9%, 800 mesh) was supplied by Dan-Dong Research Insitute of Chemical Industry. SiC powder (purity > 99.9%, 800 mesh) was supplied by Linyi Jin meng Carborundum Co. Ltd. The mixture particles containing 80 vol % ZrB_2 and 20 vol% SiC were preliminary prepared by attrition milling with ZrO_2 milling media for 2 h. However, the mixture powders cannot be used as spraying powders, because they are lack of flowability when transported from powder feeder to nozzle. In order to increase flowability of particles, spraying powders were obtained by agglomerating a kind of slurry through a spray drier. This slurry was composed of distilled water (49 wt%), polymeric binder (2 wt%), and mixture particles (49 wt%). The polymeric binder was used as an additive to agglomerate the powders. Fig. 1 shows SEM morphology of the agglomerated powders. The average size of the powders was about 50 μm. The spraying system consists of plasma torch, powder feeder, gas supply system, water-cooling circulator, control unit with PC interface and power supply unit. The samples were perpendicular to plasma arc and injector, and the inner diameter of injector was 5.5 mm. The argon (Ar) was used as both the primary gas and carrier gas, and the hydrogen (H_2) as the secondary gas. More details of spraying parameters are summarized in Table 1.

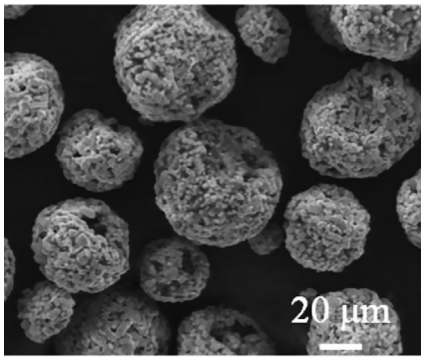

Fig. 1. SEM image of agglomerated powders.

Table 1
Details of the spraying parameters for ZrB_2–SiC multilayer coating.

Content	Parameters
Spraying current (A)	380–415
Spraying voltage (V)	130–150
Primary gas Ar (L/min)	75
Carrier gas Ar (L/min)	10
Second gas H_2 (L/min)	5
Powder feed rate (g/min)	20
Spraying distance (mm)	100
Injector internal diameter (mm)	5.5
Injector position	Perpendicular to samples

2.2. Pre-oxidation and ablation test

The pre-oxidation test concentrated on exposing coated C/C composites in ambient air at 1373 K in an electrical furnace. The as-sprayed composites were cleaned in an ultrasonic bath with ethanol and dried at 373–423 K for 2 h, and then put into isothermal region of the furnace. The oxidation time was 10, 15 and 20 min.

The ablation resistance of the pre-treatment samples was carried out in oxyacetylene torch system according to the National Standard of Ablation Test method of ablative materials (GJB 323A-96) with heat flux of 2400 kW/m^2 [27]. The pressure and flux of oxygen were 0.4 MPa and 0.244 L/s, and they were 0.095 MPa and 0.167 L/s for acetylene. The inner diameter of the oxyacetylene gun tip was 2 mm and the distance between the gun tip and the sample was 10 mm. In this study, all of the as-sprayed and pre-treatment samples were tested in the same condition. The ablation gun was primarily ignited. As the flame was stable, the sample was vertically placed to the flame and exposed to the flame for 60 s, 90 s and 120 s, respectively. The surface temperature of the sample was detected by an infrared thermometer.

2.3. Characterization

The crystalline structure of the coating before and after ablation was measured by X-ray diffraction (XRD, X'Pert Pro MPD) with a Cu $K\alpha$ radiation of wavelength 0.154 nm. The morphology and chemical composition of the coated composites were investigated by scanning electron microscopy (SEM, JSM 6460) equipped with energy dispersion spectroscopy (EDS).