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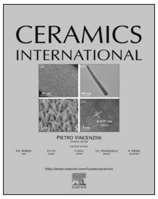

Effect of LaB_6 content on the gas evolution and structure of ZrC coating for carbon/carbon composites during ablation

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ABSTRACT

ZrC coatings with different contents of LaB_6 for SiC-coated carbon/carbon composites were fabricated by supersonic atmosphere plasma spraying. The mechanism of gas evolution during oxidation at ultra-high temperatures and the oxide scale structure evolution of the coating after addition of LaB_6 with different contents were studied. Results showed that rare earth borate rather than rare earth oxide mainly reduced the melting resistance of the oxide scale. The oxide scale for ZrC coating with 10% LaB_6 was unfavorable to the gas escape. After addition of 20% LaB_6, the oxide scale was favorable to the gas escape but disadvantageous to the coating applied in the environment containing scouring because of the reduced melting resistance. High content of LaB_6 also could cause evident boiling of B_2O_3, leading to producing big pores in the oxide scale during ablation. Appropriate content of LaB_6 for ZrC coating was found to be 15%.

1. Introduction

Oxidation or ablation is always considered to be a key problem that limits the aerospace applications of carbon/carbon (C/C) composites [1,2]. Among the methods of improving the oxidation/ablation resistance of C/C composites, coating is an effective method [3–9]. In general, ultra-high temperature ceramics (UHTCs), such as carbides (HfC, ZrC and TaC) and borides (HfB_2, ZrB_2), are ideal coating materials for the protection of C/C composites at ultra-high temperatures for a limited time because their extremely high melting points of over 3000 °C and the sufficiently high melting points of the corresponding oxides (2758 °C for HfO_2 and 2680 °C for ZrO_2) [10–18]. However, the UHTCs especially the carbides have poor oxidation resistance because of the pesting oxidation [11]. Although the oxidation resistance can be improved by addition of silicon phases, the protection temperature is limited to below 1800 °C.

Some rare earth compounds (oxides or borides) are promising additives to improve the oxidation/ablation resistance of carbide or boride coating under ultra-high temperatures below the melting point of ZrO_2 [19–22] Compared with the additives of silicon compounds, the oxide scale formed on the surface of rare earth modified coatings have higher viscosity, which therefore possess lower volatilization rate at elevated temperatures. This superiority make the rare earth modified carbide or UHTC coatings be the prospective coating systems owning long time oxidation resistance at ultra-high temperatures [23]. Rare earth borides not only contain rare earth element but also B element. The oxidation of rare earth borides results in the production of rare earth oxides and B_2O_3, the liquid B_2O_3 is also advantageous to the improvement in oxidation resistance (below 1200 °C) [24]. In our previous works on LaB_6 modified coatings [19,21], the attention was mainly focused on the ablation resistance of the coatings and the stability of the oxide scales after addition of La.

Nevertheless, because of the introduction of element B together with C from the carbide, the formation of gases (such as B_2O_3 (g) (at high temperatures), CO, and CO_2) is inevitable during oxidation. These gases often have great impacts on the integrity of the coating (such as collapse of the coating systems) if there are no enough paths for their escape [25]. The gas evolution therefore must be considered in the application of the coating. Since the oxide scale is the barrier impeding the gas escape, the structure of the oxide scale, which is closely related to the content of LaB_6 in the ZrC coating, has a strong influence on the gas release. However, few researchers investigate the effect of LaB_6 content on the gas evolution of coatings and structure of oxide scale during oxidation. Meanwhile, although LaB_6 as a compound has been added to ZrC coating, the mechanism of the effect of different element in LaB_6 on the ablation structure is also not investigated.

In this work, LaB_6 with different contents was doped into ZrC coating by supersonic atmosphere plasma spraying (SAPS), the mechanism of gas evolution during oxidation and structure variation of the oxide scale for ZrC coating were studied. Ultimately, an appropriate content of LaB_6 for ZrC coating was proposed for the application of this coating system. To alleviate the mismatch of the coefficient of thermal

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expansion, a SiC bonding layer was prepared between the sprayed coating and C/C composites.

2. Experimental

2.1. Coating preparation

The 2D C/C composites with a density of 1.75 g/cm^3 were shaped into cylindrical specimens 15 mm in diameter and 10 mm thickness. These specimens were then cleaned with acetone and dried at 80 °C for 3 h and used as substrates for coating. The SiC inner layer was deposited on the processed substrates by pack cementation. The precursor powders for this SiC coating were Si, graphite and Al_2O_3. Al_2O_3 in the pack powders was used to increase the rate of diffusing reaction. The details for preparing this transition layer were described elsewhere [26].

Three fractions of LaB_6, i.e. 10 vol%, 15 vol%, and 20 vol% were added to ZrC coating. The coatings were prepared on the SiC-coated C/C composites by SAPS and marked as ZLB10, ZLB15 and ZLB20 (ZLB represented LaB_6-doped ZrC coating), respectively, to simplify the discussion. The composition of La_2O_3-doped ZrC coating (named ZLO) was ZrC+26 vol% La_2O_3. ZrC (400 mesh, > 98% purity), LaB_6 (325 mesh, 99.5% purity), and La_2O_3 (325 mesh, 99.5% purity) powders were selected as the starting spraying material. The powders with different compositions were mixed homogeneously and agglomerated by a spray dryer to improve their flow ability for SAPS. The slurry for agglomerating the powder mixture contained 49 wt% distilled water, 2 wt% polymeric binder and 49 wt% powder mixture [18]. The SAPS parameters follow those of Ref. [19].

2.2. Ablation experiment

Ablation resistance of the coatings was evaluated by means of the oxyacetylene torch according to GJB323A-96 [27]. The heat flux of the test was 2.4 MW/m^2. The test parameters were the same as Ref. [19] Surface temperature of the coatings was determined by means of an infrared thermometer (Raytek MR1SCSF) in two-color mode with an error of ± 0.75%. The ZLB coatings were exposed to the oxyacetylene flame for 120 s. In order to assist exploring the mechanism on the structural evolution of the coatings, two groups of comparative tests, ZrC and ZLB20 for 30 s as well as ZLO and ZLB20 for 60 s, were additionally conducted. The specific weight variation rate (mg/s) and line ablation rate (μm/s) were calculated according to the following equation:

$$R_l = (l_0 - l_1)/t \quad (1)$$

$$R_m = (m_1 - m_0)/t \quad (2)$$

where R_l and R_m is the line ablation rate and mass variation rate, respectively. The definition of other terms follows those of Ref. [19]. The ultimate result was the average of three samples.

2.3. Coating characterization

The phase composition of the coatings before and after ablation was analyzed by X-ray diffraction (XRD, X′Pert Pro MPD). The microstructure and chemical composition of the coated specimens were analyzed by scanning electron microscopy (SEM, JSM6460) equipped with energy dispersion spectroscopy (EDS).

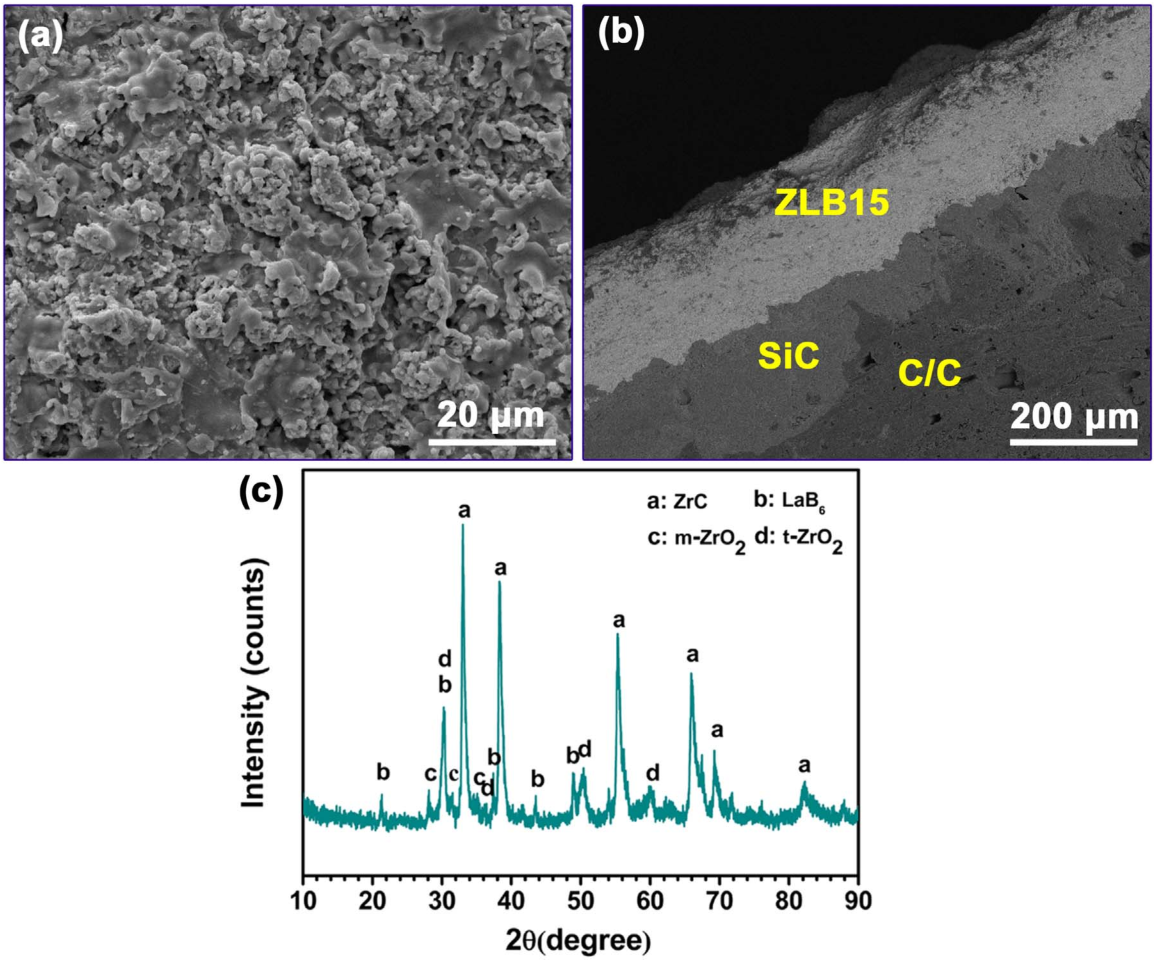

Fig. 1. Surface SEM, cross section BSE images and XRD pattern of the prepared ZLB15 coating surface. (a) SEM, (b) BSE, and (c) XRD.