Surface & Coatings Technology 344 (2018) 250–258

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Effects of the second phase on the microstructure and ablation resistance of HfC coating on C/C composites

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ARTICLE INFO

Keywords:
HfC coating
Supersonic atmospheric plasma spraying
Second phase
Bonding strength
Ablation resistance

ABSTRACT

To improve the ablation resistance of HfC coating on carbon/carbon composites prepared by supersonic atmospheric plasma spraying, SiC, TaC and ZrC ceramics were added into HfC coating as the second phase. Effects of the second phase on the microstructure, interface bonding strength and ablation resistance of HfC coating were researched. The structure of HfC-SiC coating was denser and smoother than that of HfC-TaC and HfC-ZrC coatings. The dense structure, high interface bonding strength and formation of continuous Hf-Si-O glassy film resulted in the better ablation resistance of HfC-SiC coating. During ablation, the HfC-TaC coating was oxidized to a stable $Hf_6Ta_2O_{17}$ glassy film, which could restrain the oxygen penetration. A porous HfO_2-ZrO_2 layer was generated on the HfC-ZrC coating after ablation, some HfO_2 and ZrO_2 particles may be flown away by the high-speed flame. So, the ablation resistance of HfC-ZrC coating was worse than the other two coatings.

1. Introduction

Carbon/carbon (C/C) composites are noted for low density, low coefficient of thermal expansion (CTE) (1.0×10^{-6} °C^{-1}), high thermal conductivity and good high temperature mechanical properties [1–4]. These good properties make them to be promising high temperature structural materials in aerospace industry [5,6]. However, C/C composites are easily oxidized above 450 °C, resulting in the degradation of their mechanical properties [7]. Applying a ceramic coating is an effective method to protect C/C composites from oxidation [4–7]. Due to the good oxidation resistance and relatively low CTE of SiC ceramic, SiC-based coatings have showed outstanding oxidation and thermal shock resistance below 1700 °C [8,9]. While, the melting point of SiO_2 is 1600–1700 °C, in ultra-high temperature oxidizing environment with high-speed gas flow washout, the SiC-based coatings would be oxidized, melted and blown away. Refractory metal carbides and borides are suitable coating materials to improve the ablation resistance of C/C composites due to their high melting point, high hardness and high chemical stability [10–15]. It has been reported that the vapor pressure of carbides is lower than that of borides [16], so refractory metal carbides are more suitable to be used as the ablation resistance coating materials.

Among all of the refractory metal carbides, HfC is characterized by the highest melting temperature (3959 °C) [17], high mechanical properties, good resistance to chemical attack and ablation, and high temperature phase stability [12,18]. In addition, the melting point of HfO_2 is 2810 °C, which is higher than that of ZrO_2 (2667 °C) and Ta_2O_5 (1800 °C). So, from the perspective of thermal stability, HfC is a promising coating material to protect C/C composites from ablation in severe ablation environment. During ablation, HfC coating will be oxidized to porous HfO_2 layer. The pores in the oxide coating will provide penetration channels for oxygen. In addition, the chalked oxide coating will easily peel off from C/C substrate. Introducing carbides with lower melting point as the second phase could improve the oxidation resistance of HfC ceramic [19,20]. Xiong et al. [21] synthesized HfC/ZrC biphasic coating on C/C composites by chemical vapor deposition (CVD), results showed that ZrC could improve the ablation resistance of HfC coating. Wang et al. [22] synthesized Hf(Ta)C coating by CVD, which indicated that a dense and continuous $Hf_6Ta_6O_{17}$ glassy layer was generated during ablation, which could inhibit the oxygen infiltration and improve the ablation resistance of the coating. Yang et al. [20] prepared HfC-SiC coating by supersonic atmospheric plasma spraying (SAPS), results indicated that a Hf-Si-O compound oxide layer was formed during ablation, which could restrain the oxygen penetration. So, introducing carbide with lower melting point as the second phase could improve the ablation resistance of HfC coating.

CVD has been applied to fabricate HfC single-phase coating and HfC-based composite coating [6,12,21–23]. While, the deposition process is usually time-consuming and high-cost. SAPS technology is characterized by high deposition rate and low cost, which has been

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https://doi.org/10.1016/j.surfcoat.2018.03.023
Received 2 November 2017; Received in revised form 24 January 2018; Accepted 11 March 2018
Available online 12 March 2018
0257-8972/

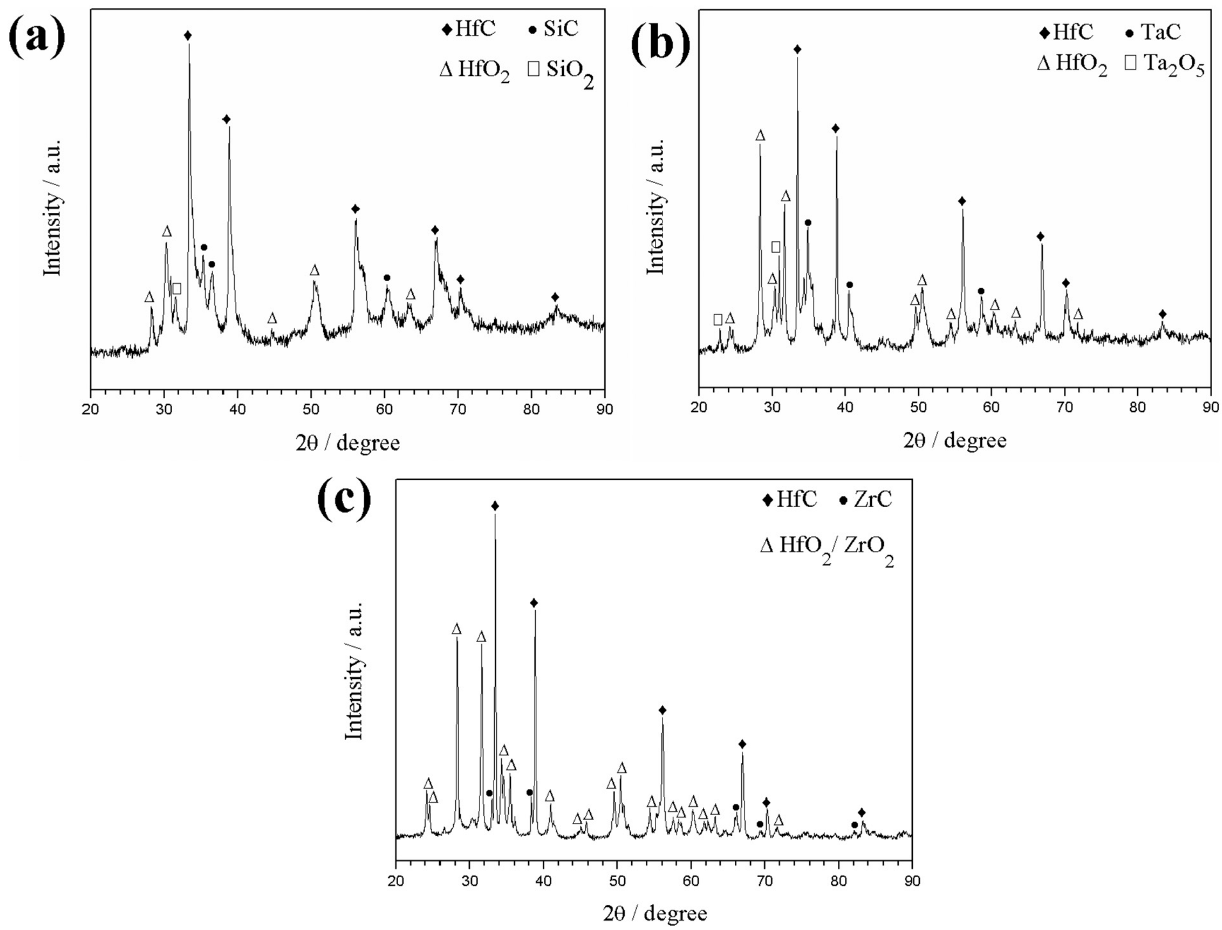

Fig. 1. XRD patterns of the as-prepared HfC-based biphasic coatings: (a) HfC-SiC coating; (b) HfC-TaC coating; (c) HfC-ZrC coating.

widely applied to synthesize coatings. During SAPS process, the temperature of plasma arc is very high (above 10,000 °C) and the velocity of spraying particle is supersonic [21,24–26]. The composition, microstructure and thickness of the coatings could be designed by adjusting the spraying parameters. So, SAPS is a promising method to prepare refractory metal carbides coatings.

In this work, HfC-SiC, HfC-TaC and HfC-ZrC coatings were prepared on SiC-coated C/C composites by SAPS. Effects of the second phase on the microstructure, bonding strength and ablation resistance of HfC coating were investigated.

2. Experimental procedure

2.1. Synthesize of HfC-based coatings on SiC-coated C/C composites

Two-dimensional (2D) C/C composites with a density of 1.65 g/cm^3 were used as substrates. The bulk C/C composites were cut into two kinds of small specimens: 10 × 10 × 10 mm^3 for morphology characterization and bonding strength test; φ30 × 10 mm^3 for ablation test. The specimens were polished using 400 grit SiC paper, ultrasonically cleaned by distilled water and dried at 85 °C for 2 h. SiC inner coating was prepared on C/C substrates by pack cementation. The mixture powders composed of 60–80 wt% Si, 15–25 wt% C and 5–10 wt% Al_2O_3 were used as raw materials. C/C specimens were embedded in the mixture powders and then heated to 1800–2100 °C for 2 h. The detailed preparation process has been reported in Ref. [27].

HfC-based coatings were prepared on SiC-coated C/C specimens by SAPS using a HEPJ-II SAPS equipment (Beijing Armored Force Engineering College). Commercial HfC, SiC, TaC and ZrC powders were used as raw materials (400 mesh; 99 wt% purity; Jinzhou Metal Material Research Institute, China). HfC-15 vol% SiC, HfC-15 vol% TaC and HfC-15 vol% ZrC powders were mixed by a blender for 3 h. To improve the flowability of the powders, a slurry consisting of 48 wt% distilled water, 2 wt% polymeric binder and 50 wt% mixture powders was agglomerated and pelleted using a spray drier, then sifted by 200 mesh sieve. During spraying, the specimens were placed perpendicularly to the plasma torch. The spraying distance was 100 mm. Ar was used as the primary gas and carrier gas. H_2 was used as the secondary gas. The flow rate of Ar and H_2 was 80 and 5 L/min, respectively. The spraying current and voltage was 400 A and 125 V, respectively. The feed rate of the spraying powders was 25 g/min.

2.2. Phase composition and microstructure characterization of the coatings

The phase composition and morphology of the coatings were analyzed by X-ray diffraction (XRD, X'Pert Pro, PANalytical, Almelo, the Netherlands) and field emission scanning electron microscopy (SEM, TESCAN VEGA3, Czech), respectively. The phase distribution of the coatings were analyzed through back scattered electron (BSE) image of the coatings.

2.3. Bonding strength and ablation tests for the coatings

Scratch test was performed using WS-2015multi-functional tester to measure the interface bonding strength between SiC coating and HfC-based coatings. A load increasing from 0 to 20 N was applied on the coating surface with a sliding distance of 5 mm. The acoustic emission (AE) signal-load curve was recorded by computer. The final bonding strength was the average value of five samples.

The ablation test was performed under oxyacetylene flame. During