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Full Length Article

Microstructure and thermal shock performance of $Y_2Hf_2O_7$ coating deposited on SiC coated C/C composite

Shengyue Gu[a], Shouyang Zhang[a,*], Fei Liu[a,b], Yingguang Liang[a], Wei Li[a]

[a] State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, China
[b] College of Mechanical and Electrical Engineering, Xi'an Polytechnic University, Xi'an 710048, China

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ABSTRACT

$Y_2Hf_2O_7$ coating was prepared by SAPS on the surface of SiC coated C/C composites with distinct spraying power. The effect of spraying power on the microstructure, phase composition and bonding force was investigated. Meanwhile, thermal shock test has been conducted to evaluate the performance of the coating in extreme environments. Results show that $Y_2Hf_2O_7$ coating prepared under 50 kW possesses optimal microstructure and combination state. The bonding force of the interface between $Y_2Hf_2O_7$ and the SiC coating reaches up to 27.2 N. Compared with single SiC coating, composite coating shows a better protection of C/C composites from oxidation under thermal shock test. In addition, the coatings show excellent phase stability both in preparation and thermal cycles. Therefore, SAPS is an excellent method to prepare $Y_2Hf_2O_7$ coating and the coating can be used as a potential environmental barrier candidate for C/C composites.

1. Introduction

On account of poor performance in oxidation resistance, Carbon/Carbon (C/C) composites have been limited to apply in an oxygen-containing atmosphere at high temperature, though they have unique properties such as low density, high strength-to-weight ratio, high specific module, low coefficient of thermal expansion (CTE), high thermal shock resistance and good ablation resistance [1–4]. Numerous attempts have been made on improving the oxidation and ablation resistance of C/C composites and previously abundant works report that ultrahigh temperature ceramics (UHTCs) coated C/C composites perform good oxidation ablation resistance [5–10]. Moreover, preparing coating on the surface of C/C composites is a convenient and effective method, which is widely used in the field of oxidation ablative protection [7–10].

$A_2B_2O_7$ system (A is a rare earth cation, B is a transition element such as Ti, Si, Zr or Hf) is one of widely studied complex oxides in recent years due to their relatively high melting point, low thermal conductivities, excellent electrical, magnetic, optical properties and strong chemical stability [11–14]. Compared to zirconia, hafnia owns higher phase transition temperature and lower volume change caused by phase transition [15,16]. Promisingly, hafnate could be expected to become a new generation of environmental thermal barrier materials due to excellent thermophysical property [17–24]. As a typical material of $A_2B_2O_7$, $Y_2Hf_2O_7$ owing low thermal conductivity and high melting point, which make it promising for a new environmental barrier candidate for C/C composites [24]. In addition, supersonic atmospheric plasma spray (SAPS) has been proved to be an effective method to prepare ceramic coatings due to its precise control of the ceramic components and wide applicability for most ceramics [13,25,26]. In order to obtain excellent $Y_2Hf_2O_7$ coated C/C composites, SiC inner coating is prepared on the surface of C/C composites by pack cementation method [27,28].

In the present work, The effect of spraying power on the microstructure, phase composition and bonding strength of $Y_2Hf_2O_7$ coating were investigated. Meanwhile, thermal shock test has been carried out to evaluate the performance of the coating in extreme environments.

2. Experimental procedure

2.1. Powder synthesis

$Y_2Hf_2O_7$ powder was synthesized by solution combustion technique. CH_4N_2O (99%), $Y(NO_3)_3{\cdot}6H_2O$ (99.99%) and $HfCl_4$ (99%) were chosen as raw materials. $HfOCl_2$ solution was yield when $HfCl_4$ was dissolved in double distilled water. To obtain $HfO(NO_3)_2$, an appropriate amount of $NH_3{\cdot}H_2O$ was added into $HfOCl_2$ solution. The resulting white precipitant was washed with deionized water for several times to remove chloride ions and then dissolved in HNO_3 (A.R) solution. Subsequently, CH_4N_2O, whose amount was calculated based on total valence of the

* Corresponding author.
E-mail address: zhangshouyang@nwpu.edu.cn (S. Zhang).

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Table 1
The parameters of SAPS for the$Y_2Hf_2O_7$ coating.

Parameters	Values
Spraying power (kW)	40, 45, 50, 55
Main gas flow (Ar), L/min	75
Carrier gas (Ar), L/min	10
The second gas (H_2), L/min	5
Power feed rate (g/min)	20
Spraying distance (mm)	100
Nozzle diameter (mm)	5.5

oxidizing and the reducing agents for maximum release of energy during combustion, was added to the solution. The solution containing the precursor mixture was preheated to 550 °C. After vigorous combustion, fluffy powders were obtained. The prepared powders were calcined at 1200 °C for 2 h and then boiled and sieved for SAPS with the grain size about 50–100 μm.

2.2. Coating preparation

Cubical samples (10 × 10 × 5 mm) and cylindrical samples (Φ30 × 10 mm) utilized as substrates were cut from bulk 2 D C/C composites. They were ultrasonically cleaned with acetone and dried at 80 °C for 4 h. A SiC transition coating was first prepared on the specimens by pack cementation and the preparing details were reported in Ref. [25]. Supersonic atmospheric plasma spray (SAPS) was used for producing $Y_2Hf_2O_7$ coatings with distinct power. Detailed spraying parameters are summarized in Table 1.

2.3. Thermal shock and adhesion test

Thermal shock test was performed in an electric furnace at 1200 °C in air. After oxidation at 1200 °C for 90 s, the specimens were taken out of the furnace and cooled down in water with room temperature for 3 s. Then, the specimens were put into the furnace for 90 s and then taken out for 10 min at room temperature. The specimens were weighted for the next cycle. The adhesive strength was measured through the scratch tester (WS-2005 multi-functional tester. China) equipped with a C diamond pinhead (cone apex angle 120, tip radius 0.2 mm) was employed to investigate the interface bonding strength between $Y_2Hf_2O_7$ coating and SiC coated C/C composites. Scratch test was carried out by applying a constantly changing load which ranged from 0 to 50 N during sliding on the 5 mm path at the loading rate of 50 $N{\cdot}min^{-1}$.

2.4. Characterizations

The morphologies of powder and coating were analyzed by a scanning electron microscopy (SEM, JSM-6460, JEOL Ltd., Mitaka, Japan) equipped with energy dispersive spectroscopy (EDS). The porosity of the powder was evaluated by volume density and Archimedes method. For high quality images, gold sputtering was used on each specimen for SEM investigation. The crystalline structures of powder and coating were analyzed by X-ray diffraction with Cu Kα radiation. (XRD, X Pert PRO, PANalytical, Almelo, The Netherlands). TEM was adopted to analysize the structure of $Y_2Hf_2O_7$ coating after thermal cycles (TEM, JEM3010, JEOLLtd., Tokyo, Japan). 3D morphologies and roughnesses (Ra) are obtained by a confocal laser scanning microscope (Optelics C130, Lasertec Corp., Yokohama, Japan).

3. Results and discussion

3.1. Microstructure and the phase of $Y_2Hf_2O_7$ powder

Fig. 1 reveals the microstructure and XRD pattern of $Y_2Hf_2O_7$ powder used for SAPS. According to the magnified image (Fig. 1(a)), it is obvious that the powders have typical porous characteristic of combustion synthesis with the porosity about 70%. The average size of prepared $Y_2Hf_2O_7$ powder is about 70–80 μm. In Fig. 1(b), the diffraction peaks at 2θ = 29.74°, 34.47°, 49.53°, 58.85°, 61.74°, 72.64°, 80.41°, and 82.94° correspond to the diffraction planes (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1), and (4 2 2), respectively, and they are characteristic for Yttrium Hafnium Oxide (00-024-1406) possessing defective fluorite structure. EDS of blue dashed frame area and elemental atomic ratio are shown in Fig. 1(a). Clearly, the atomic ratio of Y to Hf is close to 1:1, which can show that the elements do not deviate during the synthesis process.

3.2. Microstructure and the phase composition of the SiC inner coating

The surface morphology and 3D morphology of the SiC inner coating prepared by pack cementation are exhibited in Fig. 2. It reveals a rough surface with the roughness (Ra) about 28.67 μm, which is benefit for enhancing bonding force between SiC inner coating and $Y_2Hf_2O_7$ outer coating (Fig. 2(a) and (c)). As shown in Fig. 2(b), the inner coating is composed of α-SiC and diamond-Si. Silicon possesses a smaller thermal expansion coefficient. Therefore, as a buffer phase in SiC coating, the free silicon can relieve thermal mismatch, thereby weakening the stress between coatings.

3.3. Microstructure and the phase of $Y_2Hf_2O_7$ coating with different power.

Fig. 3 shows the XRD patterns of $Y_2Hf_2O_7$ outer coating prepared at distinct spraying powers. The spraying temperature increases along with the growth of spraying power and only the phase of $Y_2Hf_2O_7$ is observed in the Fig. 3(a)–(d), which show no evident decomposition occur of $Y_2Hf_2O_7$ with the high plasma arc temperature.

Fig. 4 displays the surface morphology of $Y_2Hf_2O_7$ coating prepared with distinct spraying powers. With the increase of spraying power, the surface becomes more compact with fewer microcracks (as seen in Fig. 4(b) and (c)). Individual lamellae are formed where some micropores exist, which is the typical feature of plasma-sprayed coating. However, as spraying power reaches to 55 kW (Fig. 4(d)), some pores are found in the coating, which might be caused by the large thermal stress during the cooling process. In addition, due to the high temperature of flame (about 3000 °C), the pores might also be caused by the internal residual stresses during the spraying process. Moreover, to clearly explain the distinction between the coatings, the roughnesses (Ra) and 3D morphologies are shown in Fig. 4(e). The surface roughnesses (Ra) of the $Y_2Hf_2O_7$ coating prepared at 40 kW, 45 kW, 50 kW, and 55 kW are 6.93 μm, 6.75 μm, 6.02 μm, and 6.53 μm, respectively. The data show that the coating has the lowest roughness at 50 kW, indicating that the coating possesses optimal microstructure. This result is consistent with the surface morphology of the coatings.

Fig. 5 reveals the cross-section micrographs of $Y_2Hf_2O_7$ coating prepared at distinct spraying powers. The thicknesses of each coating are measured in distinct positions and their average values are used as the thicknesses of the coatings. The marked positions in Fig. 5 are close to the average thicknesses of the coatings. Moreover, the thicknesses of $Y_2Hf_2O_7$ coatings prepared at 40 kW, 45 kW, 50 kW and 55 kW are about 98 μm, 73 μm, 71 μm and 76 μm, respectivily. Obviously, the coating prepared at 40 kW has numerous microcracks and loose structure (Fig. 5(a)), which can be explained why the coating has the maximum thickness. There is no obvious cracks in interfaces, indicating excellent bonding between the coatings. Irregular interface morphology is shown in Fig. 5. The outer coating fluctuates with the surface shape of the inner coating presenting a mechanical locking structure of the interface, which can enhance the bonding between the coatings. The line scan of the coating at spraying power of 45 kW (Fig. 5(b)) is shown in Fig. 5(e). O, C, Y, Si and Hf are the main elements of the coating. Along the test direction, SiC, $Y_2Hf_2O_7$ and resin are presented, respectively. The thickness of an element diffusion zone about 10 μm of Hf and Si is