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Fabrication of low-density carbon-bonded carbon fiber composites with an Hf-based coating for high temperature applications

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A novel Hf-based anti-oxidation coating has been prepared on the surface of low-density carbon-bonded carbon fiber composites (CBCFs). The coating exhibits a gradient transition structure, with mainly HfB₂, Hf₂Si and SiC ceramics. Oxyacetylene torch testing has been utilized to evaluate the ablation resistance under the condition ranging from 1.6 MW m⁻² to 2.2 MW m⁻² for 300 s. The experimental results show that the as-prepared Hf-based coating can effectively protect CBCFs under high-temperature oxidation conditions. The surface maximum temperature can reach 1616–2037 °C, and the mass ablation rates vary from $-3.5 \times 10^{-5} \text{ g s}^{-1} \text{ cm}^{-2}$ to $1.5 \times 10^{-5} \text{ g s}^{-1} \text{ cm}^{-2}$. The formation of a dense SiO₂ glass layer embedded with HfO₂ grains or particle accumulation in the HfO₂ layer is responsible for the good ablation resistance.

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1. Introduction

Thermal protection system (TPS) is one of the key technologies of aerospace vehicle design and development. A lot of manpower and financial resources have been invested in the development of high-performance and reliable thermal protection materials and structures for their use in space.^{1,2} In recent years, the development of a large number of new low-density materials has raised research interests in lightweight thermal protection materials such as phenolic impregnated carbon ablator (PICA),^{3,4} SIRCA,^{5,6} and toughened uni-piece fibrous reinforced oxidation-resistant composites (TUFROC).^{7–10} Specifically, TUFROC has become desirable due to its unique properties including lightweightness, low thermal conductivity, high temperature stability and low cost.^{9,10} TUFROC has a two-piece structure, with a treated carbonaceous cap, namely, refractory oxidation-resistant ceramic carbon insulation (ROCCI) and a fibrous insulation base, namely, toughened uni-piece fibrous insulation (TUFI)-treated alumina-enhanced thermal barrier (AETB).⁷ In this study, we focused on one kind of ROCCI, that is, carbon-bonded carbon fiber composites (CBCFs).

CBCFs are typical porous carbon-carbon (C/C) composites with low densities of 0.1–0.5 g cm⁻³ and high open porosities over 70%.^{11–13} They are thought to be desirable candidates for high-temperature heat insulation applications^{14,15} and thermal insulation applications in aerospace^{13,16,17} due to their unique

properties such as lightweightness, low thermal conductivity, and high temperature stability. However, low mechanical properties and poor oxidation resistance limit the wide applications of monolithic CBCFs. Recently, many research studies have been carried out to solve these problems.^{18–23} Carbon nanotubes (CNTs)¹⁹ and SiC nanowires (SiC_{NWs})²² have been used to improve the mechanical properties of CBCFs. Various Si-based coatings (including MoSi₂ and TaSi₂)²⁴ and Zr-based coatings (such as ZrB₂)^{19,25} have been widely investigated as an attractive way to ameliorate CBCFs' antioxidant properties. Unfortunately, up to now, the effective temperature of the anti-oxidation method has been limited to 1700 °C. To the best of our knowledge, reports on high or ultra-high temperature oxidation resistance of CBCFs are limited.

In this paper, a new type of Hf-based anti-oxidation coating was designed and prepared to protect CBCFs for use at high temperature. The microstructure and the oxidation behavior of the coated CBCF composites were analyzed and discussed in detail. The results showed that the as-prepared Hf-based anti-oxidation coating could protect CBCFs under aerobic conditions at a maximum temperature range of ~1616 °C to 2037 °C.

2. Experimental

2.1 Preparation of CBCFs

Rayon-based carbon fibers with 0.8 mm length were used to prepare CBCFs by dispersion and filtration technique. The details of the preparations were given in our previous study.¹⁸ In the present study, to improve the mechanical properties of CBCFs, pyrolytic carbon (PyC) was deposited on the surface of carbon fibers through chemical vapor infiltration (CVI) at

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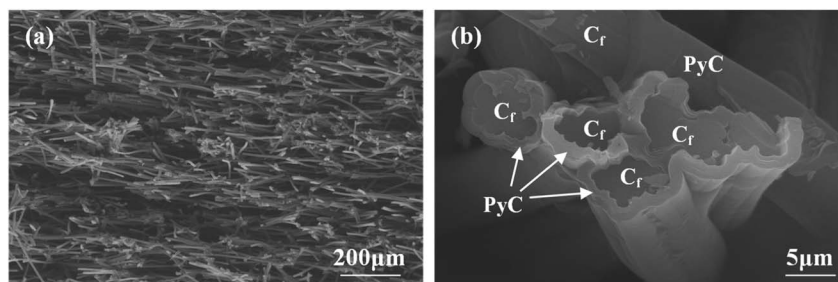


Fig. 1 SEM images of PyC-coated CBCFs after CVI: (a) low magnification; (b) high magnification in (a).

1000 °C using propane as the carbon source. After deposition for 200 h, the density of CBCFs increased from 0.25 g cm⁻³ to 0.36 g cm⁻³, and the open porosity decreased from 85.7% to 79.4%. Fig. 1 shows the microstructures of as-prepared CBCFs after the CVI process. The characteristics of the random distribution of fibers and the highly porous network did not change as compared to those before CVI (Fig. 1a). A uniform PyC layer with a thickness of about 1 μm was formed on the surface of the carbon fibers, as shown in Fig. 1b.

2.2 Preparation of high temperature Hf-based anti-oxidation coating on CBCFs

Commercially available Hf powder (1–3 μm, purity 99.5%, Northwest Institute for Non-ferrous Metal Research, China), Si powder (1–2 μm, purity 99.9%, Weifang Kaihua Micro-powder Co. Ltd., China), B (1–2 μm, purity 99.5%, Alfa Aesar (China) Chemicals Co. Ltd.) were used in this study.

The cylindrical samples (Φ25.4 × 8 mm) used as substrates were cut from PyC-coated CBCFs. The samples were cleaned ultrasonically with ethanol and dried at 120 °C for 2 h. The Hf-based anti-oxidation coating was prepared by a simple SIR method, namely, slurry brushing, followed by infiltration processing and reactive sintering. The powdered mixtures of Hf (80 wt%), Si (15 wt%) and B (5 wt%) were ball-milled for 10 h. After mixing, the mixtures were added to a silicon resin to form a mixed slurry. Then, the Hf-based anti-oxidation coating was prepared by slurry brushing and infiltration processing using the above-mentioned mixed slurry. After drying at 200 °C for 2 h, the impregnated samples were sintered at 1550 °C for 120 min in a high-temperature vacuum furnace. The thickness of this infiltration layer was controlled by changing the brush and pyrolysis cycles, which was different to the processes used in vacuum slurry infiltration methods.²⁶

2.3 Ablation tests and characterization

The ablation behaviors of the as-prepared CBCFs with the Hf-based oxidation coating were evaluated under simulated atmospheric conditions using an oxyacetylene torch. Cylindrical-shaped samples with a size of Φ25.4 mm × 8 mm were used in this study. The as-prepared CBCFs with the Hf-based oxidation coating having these dimensions had a bulk density of 0.8 g cm⁻³. During the ablation test, a water-cooled Gardon gauge was used to calibrate the heat flux, and a two-

color pyrometer was used to record the surface temperature. Three typical ablation conditions were chosen by adjusting the ratio of acetylene to oxygen, *i.e.*, 0.6 : 0.4, 0.7 : 0.4 and 0.8 : 0.5, as shown in Table 1; the corresponding heat fluxes and testing samples were 1.6 MW m⁻² (S1), 1.8 MW m⁻² (S2) and 2.2 MW m⁻² (S3). The distance from the nozzle tip of the oxyacetylene gun to the samples was about 40 mm. The exposure time was 300 s. The mass ablation rates were calculated by the following formula:

$$R_m = \frac{m_0 - m_1}{st} \quad (1)$$

Here, R_m is the mass ablation rate; m_0 and m_1 are the masses of the samples before and after ablation, respectively; s is the ablation area of the surface and t is the ablation time.

The positive values of R_m represent weight losses, and negative values represent weight gains.

The phase composition was determined *via* X-ray diffraction using Cu K α radiation. Surface and cross-sectional morphologies of the coatings before and after the ablation tests were observed using scanning electron microscopy (SEM) with simultaneous chemical analysis by energy dispersive spectroscopy (EDS).

3. Results and discussion

3.1 Microstructure of the as-prepared Hf-based coated CBCFs

The morphology of the prepared Hf-based surface coating is displayed in Fig. 2. As shown in Fig. 2a, the surface coating exhibits a typical rough structure without the formation of macro-cracks, which demonstrates the physical compatibility of the coating with CBCFs. The details corresponding to elemental distribution maps are shown in Fig. 2b–e, which exhibit the uniform dispersions of Hf, Si, B and C. Fig. 3 shows the surface

Table 1 Ablation properties of CBCFs with the Hf-based oxidation coating for 300 s

Samples	O ₂ : C ₂ H ₂	H (MW m ⁻²)	t (s)	T _{max} (°C)	R _m (g cm ⁻² s ⁻¹)
S1	0.6 : 0.4	1.6	300	1616	-3.5 × 10 ⁻⁵
S2	0.7 : 0.4	1.8	300	1830	-1.7 × 10 ⁻⁵
S3	0.8 : 0.5	2.2	300	2037	1.5 × 10 ⁻⁵



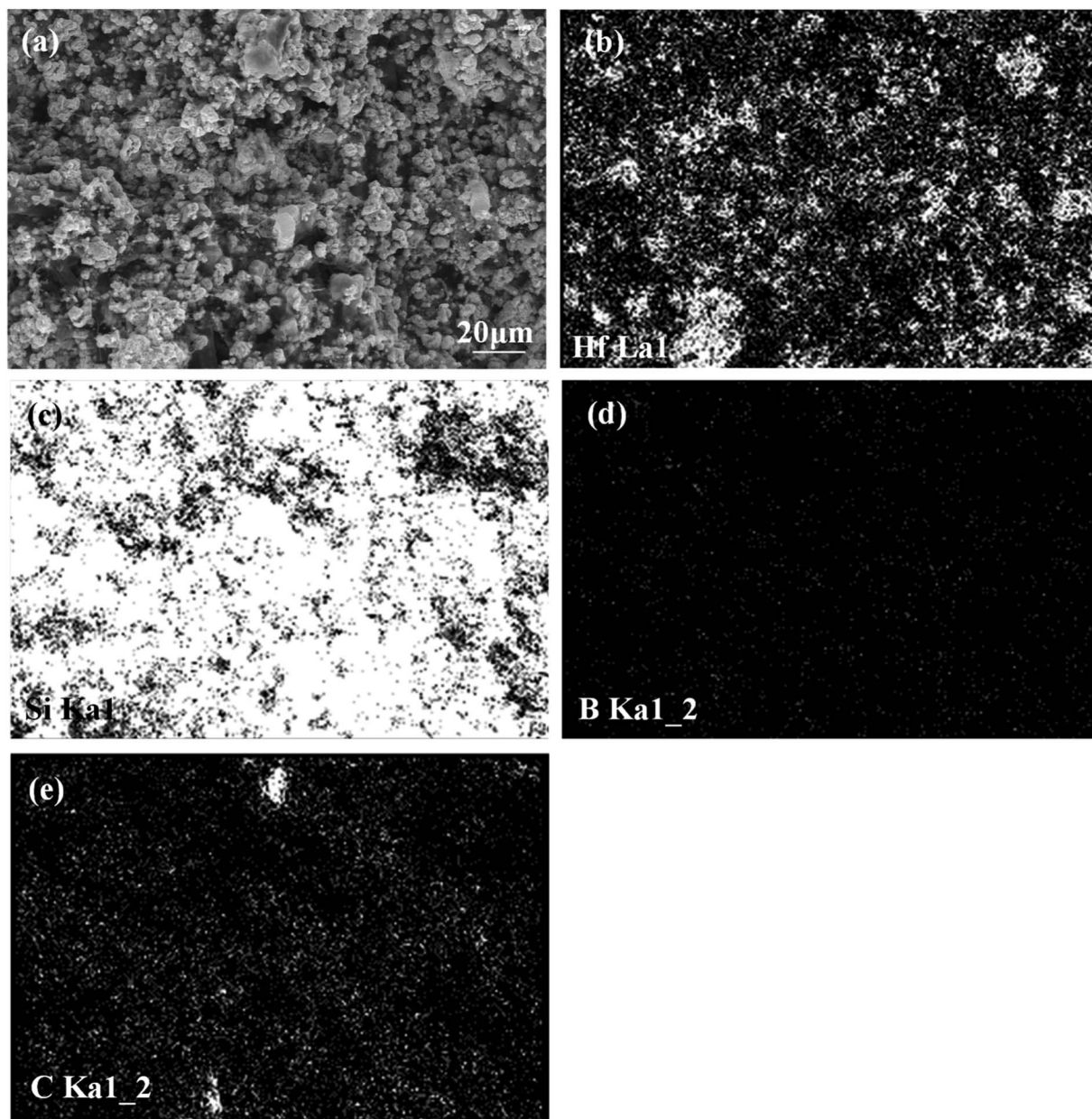


Fig. 2 SEM micrograph and the corresponding elemental distribution maps of Hf-based anti-oxidation coating: (a) SEM image; (b) Hf distribution; (c) Si distribution; (d) B distribution, (e) C distribution.

XRD results of the prepared Hf-based coating. Based on the diffraction peaks, the main phases in the coating are mainly HfB_2 , Hf_2Si and SiC . A small amount of residual Si is also detected by XRD. The results indicate that most of the impregnated ceramic powders have reacted *in situ* with each other or with carbon to form the HfB_2 - Hf_2Si - SiC coating, which can afford good oxidation protection under high temperature.^{27,28}

Fig. 4 displays the cross-sectional morphologies of the as-prepared Hf-based anti-oxidation coating. It can be found that the oxidation coating is about 300 μm in thickness, and there are no clear penetration cracks between the oxidation coating layer and CBCFs, revealing good compatibility between the

layers (Fig. 4a). Moreover, as shown in Fig. 4b and c, two oxidation layers can be found: an inner layer with a porous structure ($\sim 600 \mu\text{m}$ in thickness) and an outer layer with a more compact structure at the top of the coating layer ($\sim 100 \mu\text{m}$ in thickness). The main phases including white HfB_2 and Hf_2Si (marked as H) and gray SiC (marked as S) are dispersed homogeneously in the outer coating (Fig. 4b). The Hf-based anti-oxidation coating can penetrate into CBCFs to form an inner layer with porous carbon fiber embedded within the white Hf-based phase and gray SiC phase; the carbon fibers are marked as C_f and the pores are marked as P (Fig. 4c). Thus, the results clearly reveal that a gradient structure oxidation layer can be prepared using this SIR processing in the present study, which



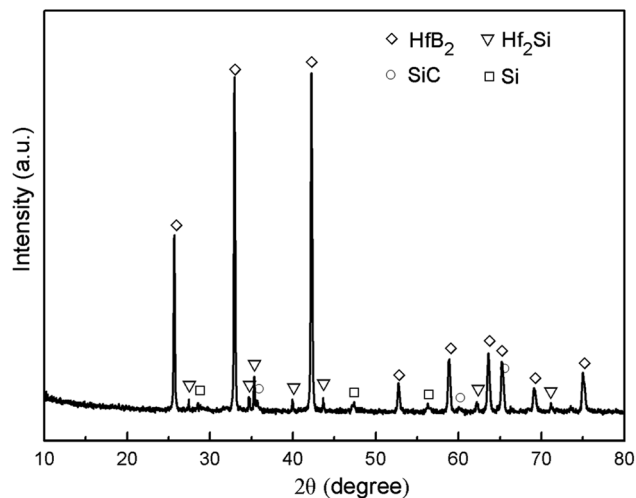


Fig. 3 XRD pattern of the prepared coating.

is beneficial to enhance the impact resistance and the thermal expansion matching between the coating and CBCFs, which is similar to the observations for the TUF1 coating of ROCCL.⁷⁹ Meanwhile, it is clear that the carbon fibers are covered with a thin layer of PyC, as shown in Fig. 4d, which is beneficial to improve the mechanical properties since it increases preform stiffness and prevents damage to the carbon fibers in the SIR processing.²⁰ In the present study, with the introduction of PyC interface, the compressive strength is improved from 0.22 MPa

to 0.97 MPa, with a 341% improvement as compared with that for the original CBCFs.

3.2 Ablation properties of CBCFs with the Hf-based coating

The ablation test results are summarized in Table 1, illustrating the maximum surface temperatures of S1, S2 and S3 as 1616 °C, 1830 °C and 2037 °C, respectively. This indicates that the surface temperature increases monotonously with the heat flux from 1.6 MW m⁻² to 1.8 MW m⁻² and 2.2 MW m⁻². At the same total exposure time of 300 s, the mass ablation rates vary from -3.5×10^{-5} g s⁻¹ cm⁻² (S1) to -1.7×10^{-5} g s⁻¹ cm⁻² (S2) and then to 1.5×10^{-5} g s⁻¹ cm⁻² (S3), and they increase with the heat flux. Meanwhile, clearly, the thicknesses of all samples did not change.

Time-surface temperature data under different heat flux conditions are shown in Fig. 5. The macrographs of the coated samples after ablation are shown in Fig. 6. The un-ablated surface is compact and gray in color (Fig. 6a). After ablation at 1.6 MW m⁻², the coated surface turns black with many glassy oxidation products, as shown in Fig. 6b. During the whole ablation process of 300 s, the oxidizing reaction on the surface tends to be steady, and the temperature is also steady at around 1600 °C (Fig. 5). However, when the ablation heat flux increases to 1.8 MW m⁻², the surface temperature of the ablation center region rapidly reaches about 1700 °C and remains stable for about 250 s, followed by a slow increase to a maximum temperature of 1830 °C, as shown in Fig. 5. At this high temperature condition, an oxidation surface mixture with black

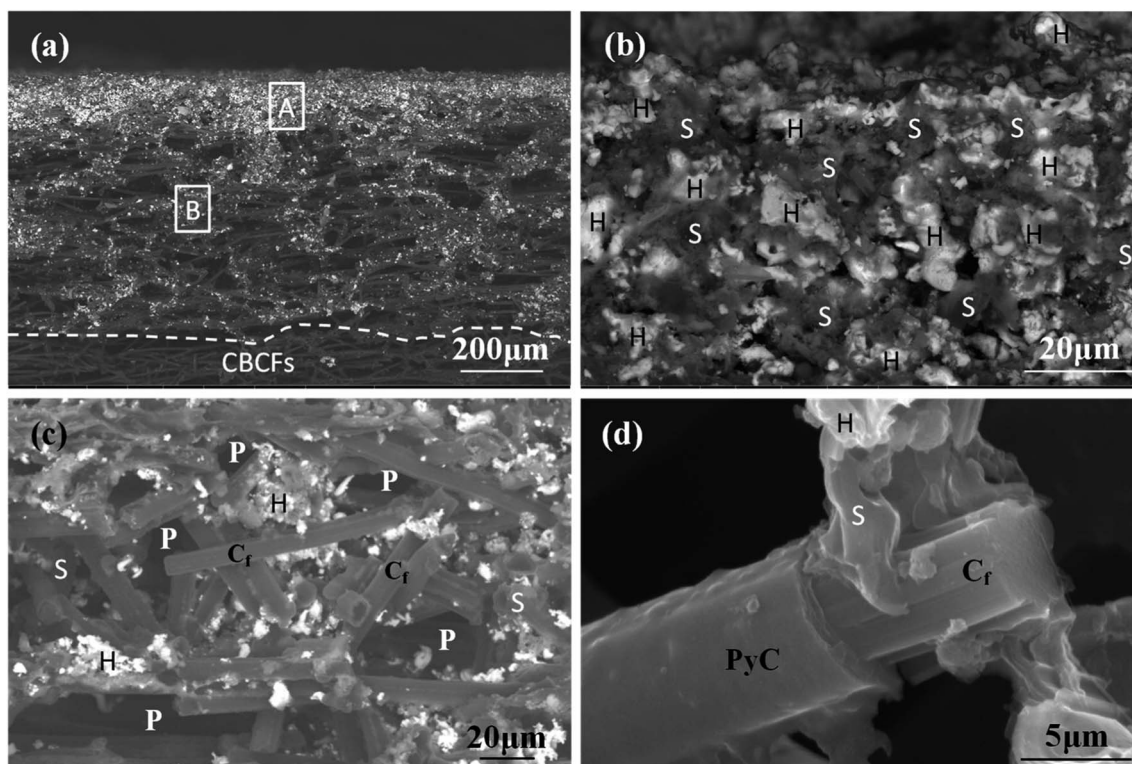


Fig. 4 Cross-sectional SEM images of the prepared coatings: (a) low magnification; (b) and (c) high magnification corresponding to regions A and B in (a), respectively; (d) high magnification of (c).



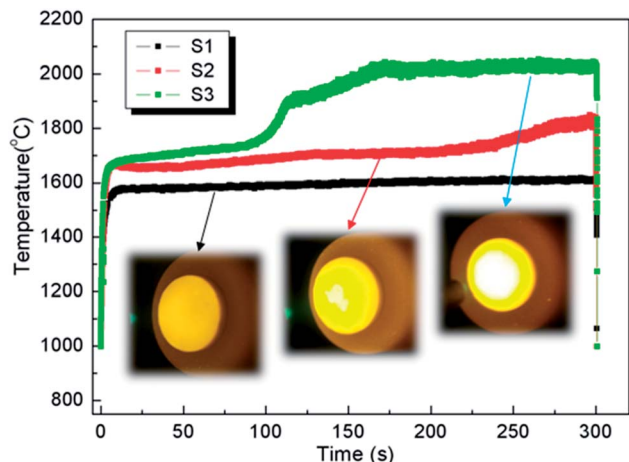


Fig. 5 Surface temperatures measured during ablation testing for different samples.

and white phases is formed on the surface of S2 (Fig. 6c). When the heat flux further increases to 2.2 MW m^{-2} , the temperature rapidly reaches around $1730 \text{ }^\circ\text{C}$ and then, it further increases to $2037 \text{ }^\circ\text{C}$ at 170 s and remains steady for the last 130 s. During this condition, more white oxidation products can be found on the surface of S3, as shown in Fig. 6d. All the CBCF samples with Hf-based coatings appear without cracks and spallation on the surface during the test. It should be pointed out that according to Fig. 5, temperature jump phenomena are detected for S2 and S3 probably due to the formation of white products, which is different from the observations for C/SiC and C/SiC-HfC composites.^{28,29} Additional experimental verification including theoretical analysis is needed to explain the temperature jump phenomenon of Hf-based CBCFs under an oxidation environment.

3.3 Microstructure evolution of CBCFs with the Hf-based coating after ablation

Fig. 7 exhibits the XRD patterns of CBCFs with the Hf-based coatings after ablation testing. Different phases were formed under different heat fluxes at the same exposure time. It was clear that the identified phases on the surface of S1 were composed of HfB_2 , Hf_2Si and SiC from the original coating as well as the new phase of SiO_2 , as shown in Fig. 7a. When the

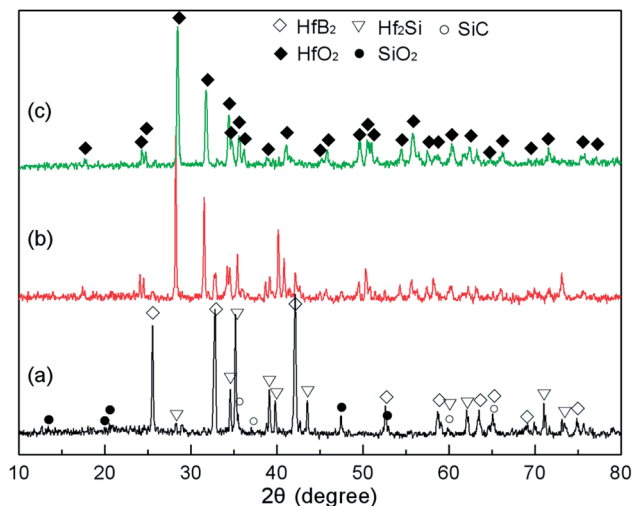


Fig. 7 XRD patterns of different CBCFs with the Hf-based oxidation coating after ablation for 300 s: (a) S1; (b) S2; (c) S3.

maximum surface temperature increased up to $1830 \text{ }^\circ\text{C}$, the peaks were mainly of HfO_2 and SiO_2 along with those corresponding to small amounts of HfB_2 and Hf_2Si , implying that the oxidation coating of S2 was partly oxidized (Fig. 7b). When the surface temperature further increased up to $2037 \text{ }^\circ\text{C}$, it was found that only HfO_2 was present, indicating that the surface of S3 was completely oxidized (Fig. 7c), and these results were in good accordance with the results of macrograph analysis (Fig. 6d).

To further understand the ablation behaviors of different samples, the evolution of surface microstructure has been investigated. As shown in Fig. 8, the oxidized surface of S1 was covered with a dense gray glassy layer embedded within a white phase. According to EDS and XRD analyses (Fig. 7 and 8), the gray glassy layer was SiO_2 , and the white phase was composed of Hf, O and Si, which might have been HfO_2 oxide grains covered with an amorphous silica layer. The element Ir was detected from the surface spray process of SEM analysis. In addition, no clear cracks were found on the surface due to the crack-sealing function of the glassy phase, which could prevent the oxygen diffusion and protect the layers beneath.

As indicated in Fig. 9, there are two typical ablation regions on the surface of S2: the brim ablation region and the ablation center region. The brim ablation region was covered with a gray

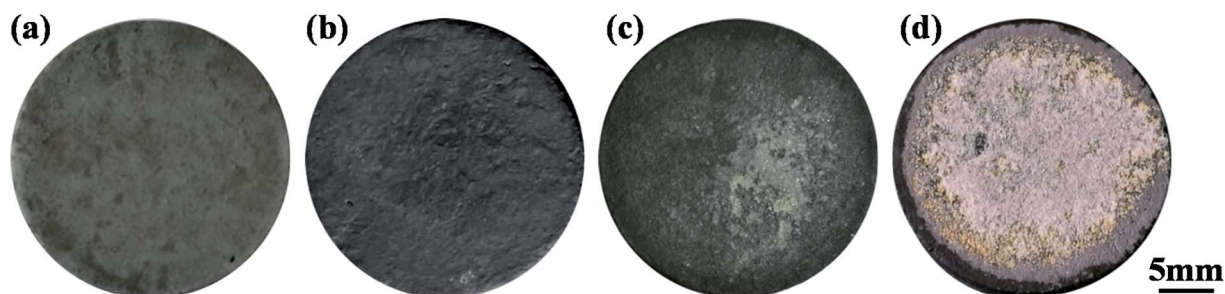


Fig. 6 Macro-photographs of CBCFs with the Hf-based oxidation coating before and after the ablation test for 300 s: (a) before ablation; (b) after ablation of S1; (c) after ablation of S2; (d) after ablation of S3.



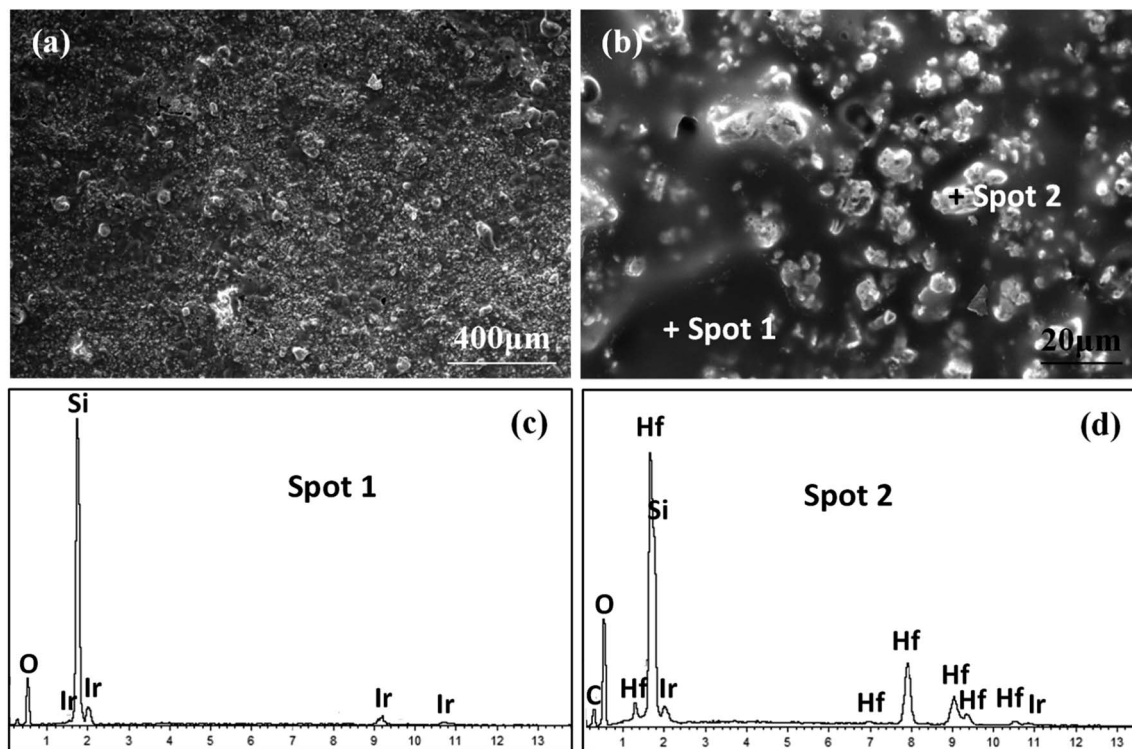


Fig. 8 Surface morphologies of S1 after ablation for 300 s: (a) low magnification; (b) high magnification of (a); (c) and (d) EDS patterns corresponding to spot 1 and spot 2 in (b), respectively.

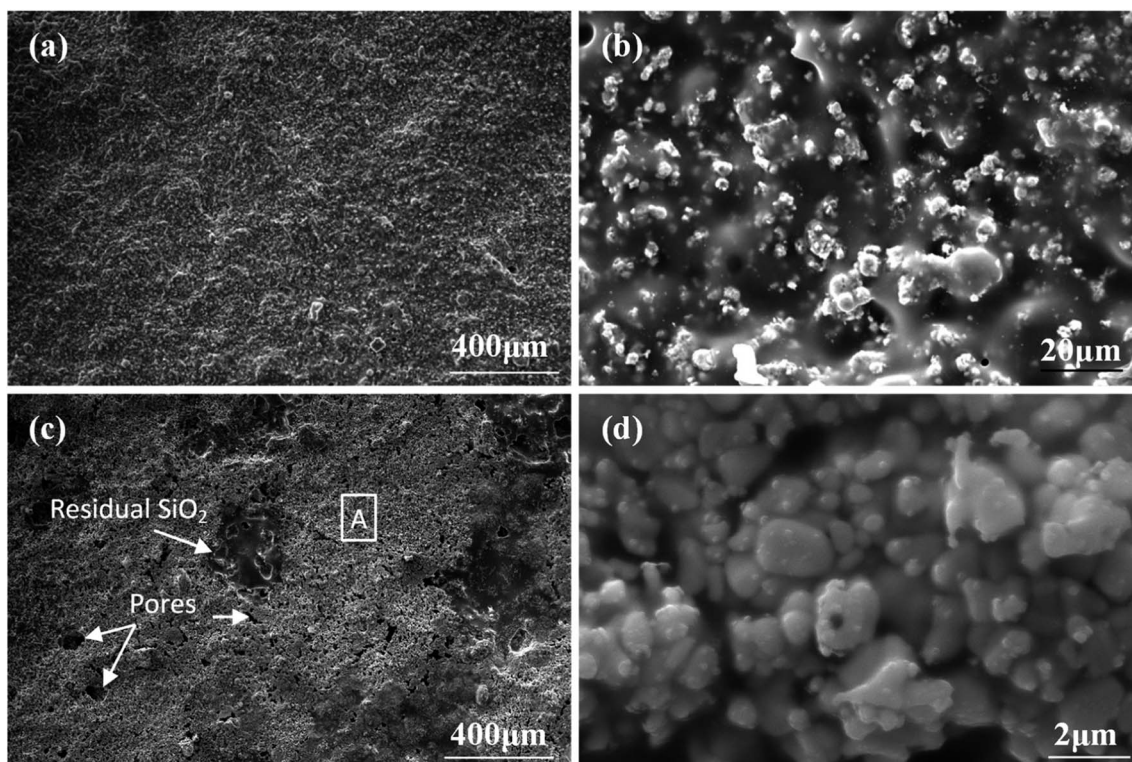


Fig. 9 Surface morphologies of S2 after oxyacetylene test for 300 s: (a) low magnification of the brim region; (b) high magnification of (a); (c) low magnification of the ablation center region; (d) high magnification corresponding to region A in (c).



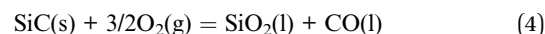
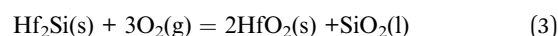
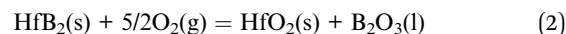
coating embedded within the white phase similar to the observations for the surface of S1 (Fig. 9a and b), which meant that both samples experienced equivalent environments. According to literature,³⁰ the temperature of the ablation center region is much higher than that of the brim ablation region under the vertically jetted flowing oxyacetylene torch testing environment. When the maximum temperature was increased to 1830 °C in the ablation center region, the vapor pressure of SiO₂ increased substantially,³¹ leading to its evaporation; also, SiO₂ was blown away due to the impact of oxyacetylene torch. Traces of gas volatilization were easily observed, and the ablation center zone was coated by a large number of fine HfO₂ grains (about 0.5–2 μm in size) with no exposed substrate, as shown in Fig. 9c and d.

SEM images of oxidized surfaces of S3 are presented in Fig. 10. The surface appeared similar to that of the ablation region of S2 but with a higher amount of HfO₂ phase, which was confirmed by EDS. It should be noted that at such a high temperature (maximum being 2037 °C), in addition to the significant evaporation of SiO₂ due to its low viscosity, the problem of the active oxidation of SiC was taken into consideration in the present study. The thermal stability of refractory carbide/boride composites in an oxidizing environment has been studied by Wang *et al.*³² The results confirmed that at a high temperature or a low oxygen partial pressure, SiC underwent a transition from passive to active oxidation, and the protective SiO₂ layer was removed as SiO (g). Furthermore, two kinds of HfO₂ phases were detected on the surface of ablated S3, as shown in Fig. 10. One

consisted of fine HfO₂ grains with an average size larger than that of the ablation region of S2, which was about ~5 μm (Fig. 10c). The other was similar to molten HfO₂ with a much larger size of over 10 μm (Fig. 10b). Additionally, no carbon fibers were detected, indicating that the HfO₂ layer could withstand the high-speed oxyacetylene torch flame and serve as an effective insulator to resist the high-temperature ablation.

3.4 Ablation mechanism

As shown in Fig. 11, a schematic diagram is used to explain the ablation mechanism of CBCFs with the Hf-based coating under different testing environments. During the ablation testing process, the coated CBCFs react with oxygen as follows:^{33–35}



When the ablation was started, the outer coating was exposed to the flame in the oxygen-rich environment. The surface temperature rose rapidly to the testing temperature

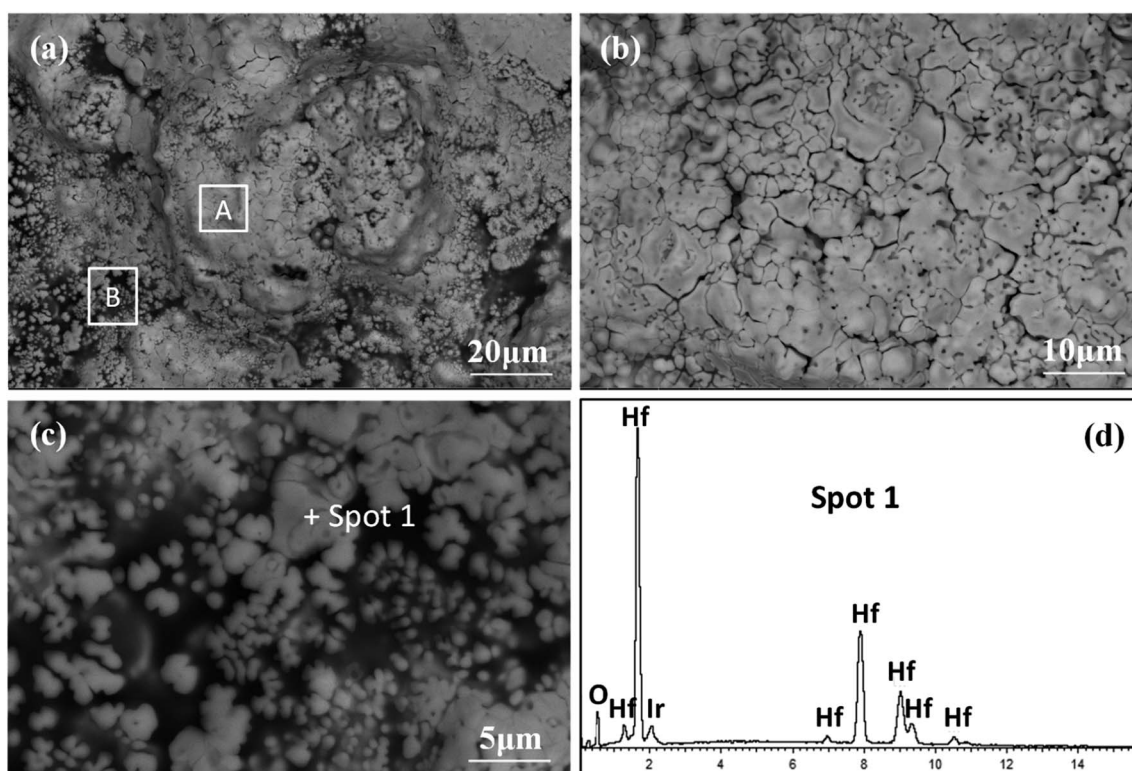


Fig. 10 Surface morphologies of S3 after oxyacetylene test for 300 s: (a) low magnification; (b) and (c) high magnification corresponding to regions A and B in (a), respectively; (d) EDS pattern corresponding to spot 1 in (c).



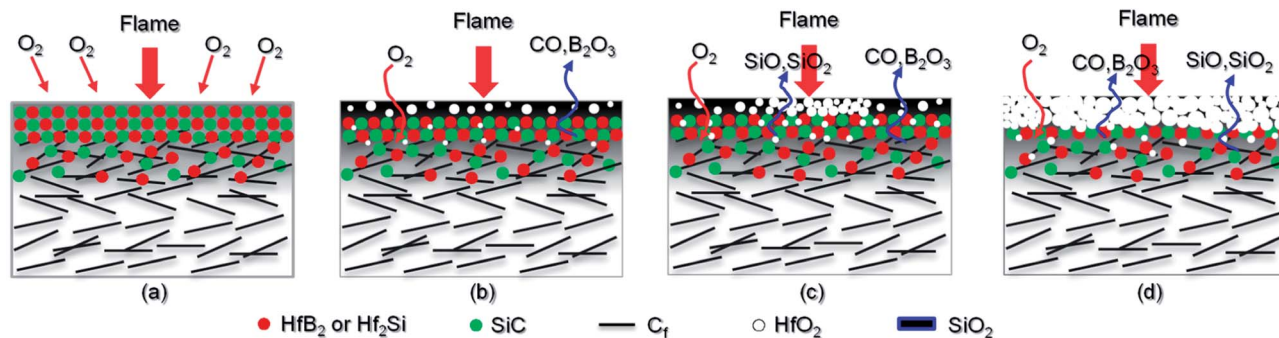


Fig. 11 Schematic diagram for the ablation of CBCFs with the Hf-based coating: (a) initial stage of ablation; (b) S1; (c) S2; (d) S3.

within 10 s (Fig. 5). When the temperature approached 1600 °C for S1, HfB₂, Hf₂Si and SiC were quickly oxidized to form an oxidation layer on the surface of the coated CBCFs, according to Reactions (2)–(4). A gray glassy layer of SiO₂ embedded within HfO₂ was formed on the surface, as shown in Fig. 11b. No B₂O₃ was detected through XRD or EDS analysis; it must have vaporized in the testing environment due to its low melting point and high vapor pressure.³⁶ In addition, there was no clear crack on the surface, which may be attributed to the possibility that the glassy phase effectively sealed the microcracks during ablation, and this could prevent the oxygen diffusion and protect the matrix beneath.

When the heat flux increase to 1.8 MW m⁻² for S2, the Hf-based anti-oxidation coating underwent different ablation environments due to the different temperature distribution on the surface. At the low temperature condition in the brim zone, a protective glass layer was formed, and it acted as a barrier to prevent further diffusion of oxygen (Fig. 11c). However, at the high temperature condition in the ablation region, the efficiency of SiC significantly decreased due to its rapid evaporation and active oxidation, according to Reaction (6). Residual SiO₂ and micropores were left after the evaporation of different gases such as SiO, SiO₂, CO and B₂O₃, as shown in Fig. 11c.

With the further increase of heat flux to 2.2 MW m⁻² for S3, the coating was gradually oxidized, and the glass phases on the surface were completely evaporated leaving only HfO₂, as shown in Fig. 11d. Therefore, a mass loss occurred in S3, which was different to the observations for S1 and S2 (Table 1). However, the surfaces of the composites were almost integrated, and they were fully covered with HfO₂ grains. In addition, there were no bare fibers, which indicated the excellent oxidation protection of the as-prepared CBCFs with the Hf-based coating at 2.2 MW m⁻² with the maximum temperature approaching 2037 °C for 300 s. Due to the complexity of the high temperature reaction and phase evolution, new fine detection techniques such as Raman spectroscopy, FESEM and TEM EDAX might be used in our future research.^{37,38}

4. Conclusions

In this study, a new type of Hf-based coating was designed and prepared to prevent the oxidation of CBCFs at high temperature. The as-prepared coating had a gradient transition

structure, and it was about 300 μm in thickness. No visible macrocracks were detected during the fabrication process and the high-temperature testing/cooling process, owing to the good performance of CBCFs with the Hf-based coating. The mass ablation rates of S1 and S2 were only $-3.5 \times 10^{-5} \text{ g s}^{-1} \text{ cm}^{-2}$ and $-1.7 \times 10^{-5} \text{ g s}^{-1} \text{ cm}^{-2}$ after 300 s, with the maximum surface temperatures being 1616 °C and 1830 °C, respectively. Meanwhile, the mass ablation rate of S3 was $1.5 \times 10^{-5} \text{ g s}^{-1} \text{ cm}^{-2}$ after ablation for 300 s, with the maximum temperature approaching 2037 °C. Overall, the as-prepared Hf-based coating exhibited excellent ablation resistance to protect CBCFs. The results presented in this paper suggest that CBCFs with the Hf-based coating are important considerations for potential applications in future TPS, which requires lightweight, high performance and low cost materials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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