Ablative Property of C/C–SiC–HfC Composites Prepared via Precursor Infiltration and Pyrolysis under 3,000 °C Oxyacetylene Torch

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Received: 14 November 2013 / Revised: 28 February 2014 / Published online: 23 July 2014
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Abstract C/C–SiC–HfC composites were fabricated via precursor infiltration and pyrolysis using a mixture solution of organic hafnium-containing polymer and polycarbosilane as precursor. The microstructures and the phases of the composites were analyzed by scanning electron microscopy and X-ray diffraction. The ablation resistance of the composites was evaluated under 3,000 °C oxyacetylene torch. After ablation for 120 s, the composites exhibit good ablation properties with the linear and mass ablation rates of 9.1×10^{-4} mm/s and 1.30×10^{-3} g/s, which are far lower than those of the C/C–SiC composites. The excellent ablative property of the C/C–SiC–HfC composites is resulted from the formation of HfO₂ molten layer on the surface of the composites, which could play a positive role in reducing heat transfer and preventing oxygen transport to the underlying carbon substrate.

KEY WORDS: C/C–SiC–HfC composite; Ablation performance; Thermal behavior

1 Introduction

Carbon fiber-reinforced carbon and silicon carbide (C/C–SiC) composites are considered to be a promising candidate for thermal protection systems owing to their low density, high thermal shock resistance, excellent oxidation resistance, as well as cost-effective production [1–3]. However, the maximum working temperature of C/C–SiC composites is limited to about 1,650 °C, which would restrict their potential application in aerospace vehicles because of their rapid ablation in the harsh application environment with high-speed and high-pressure oxidizing gas flow, ultra-high temperature, and particle erosion with supersonic velocity [4]. Introduction of ultra-high

temperature ceramics (UHTCs) including transition metal borides and carbides is expected to improve the ablation resistance of C/C–SiC composites. Various approaches such as reactive melt infiltration [5], chemical vapor infiltration [6], hot pressing [7], slurry/powder infiltration [8], and precursor infiltration and pyrolysis (PIP) [9] have been used to introduce UHTCs. Researches show that both the content and the distribution homogeneity of UHTC phases in the composites could be improved via PIP method using organic precursor. Great efforts have been made to prepare C/C–SiC–UHTCs composites by PIP method [10–12].

Ablation is an erosive phenomenon which contains thermo-mechanical, thermo-chemical, and thermo-physical processes due to the high temperature, pressure, and velocity of the oxidative gases [13]. HfC possesses high melting point (3,890 °C), excellent chemical stability, and the resistance to thermal shock. In addition, HfO₂, as the oxide of HfC formed during the ablation, also has high melting point (2,900 °C), excellent chemical stability, and relatively low vapor pressure. In our present work [14, 15], HfC-based multilayer ablation resistance coatings for C/C composites were prepared by CVD. The results show that

Available online at <http://link.springer.com/journal/40195>

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Fig. 1 Schematic procedure for the preparation of C/C–SiC–HfC composites

both mass and linear ablation rates are much lower than those of uncoated C/C composites. So far, there are few research about the ablation property of C/C–SiC–HfC composites, and further investigation is of considerable importance for their application at ultra-high temperature.

In this work, the fabrication, the microstructure, and the ablation property of C/C–SiC–HfC composites were studied. Effect of HfC on the ablation behavior of C/C–SiC composites under 3,000 °C oxyacetylene torch was discussed as well.

2 Experimental

2.1 Fabrication of the Composites

2D needled carbon fiber felts with a density of 0.45 g/cm³ were used as the reinforcement for C/C composites, and they were densified to 1.1–1.3 g/cm³ by thermal gradient chemical vapor infiltration (TCVI). A mixture solution of organic hafnium-containing polymer (PHC) and polycarbosilane (PCS) was used as HfC–SiC precursors and dispersed in xylene to form a homogeneous solution. After 16 cycles of vacuum infiltration, drying between 100 and 120 °C in a drying oven, and heat treated at 1,400–1,600 °C for 2 h under an argon atmosphere, C/C–SiC–HfC composites were obtained. For comparison, C/C–SiC composites were fabricated via PIP method using PCS as precursor under the same condition. The density and open porosity of the prepared C/C–SiC–HfC composites were 2.41 g/cm³ and 11.52%, and those of C/C–SiC composites were 1.95 g/cm³ and 9.29%, respectively. The schematic preparation procedure of C/C–SiC–HfC composites is shown in Fig. 1.

2.2 Ablation Tests

Disk samples with a size of Φ 30 mm $\times$ 10 mm were cut from the prepared composites and slightly abraded with 80 and 400 grit SiC paper. The ablation tests were carried out

Table 1 Ablation test parameters of the oxyacetylene torch

Flux (L/s)		Pressure (MPa)		Heat flux (MW/m ²)	Ablation angle (°)
O ₂	C ₂ H ₂	O ₂	C ₂ H ₂		
0.42	0.31	0.4	0.095	4.2	90

according to GJB323A-96 under 3,000 °C in oxyacetylene torch. The parameters of the ablation test are shown in Table 1. The inner diameter of the oxyacetylene gun tip was 2 mm, and the distance between the gun tip and the specimen was 10 mm. The samples were fixed in a water-cooled copper concave, and exposed directly to the flame for 120 s. The surface temperature was measured by an infrared thermometer (Raytek MR1SCSF). The linear and mass ablation rates were calculated by thickness and mass changes before and after ablation test of each sample. The ultimate ablation rates were the mean value of three samples.

2.3 Characterization

Phase analysis of the composites was conducted by X-ray diffraction (XRD, Philips X'Pert Pro MPD) using Cu as anode material. The microstructures of the composites before and after ablation were analyzed by scanning electron microscopy (SEM, JSM-6460) equipped with an energy-dispersive spectroscopy (EDS). Thermal conductivity of the composites was measured by a laser flash on NETZSCH DIL 402 E thermal properties analyzer. The sample dimensions for the thermal conductivity measurement were Φ 12.6 mm $\times$ 3 mm. The temperature range of the measurement was from 100 to 2,300 °C.

3 Results and Discussion

3.1 Microstructure of the C/C–SiC–HfC Composites

Figure 2 shows the backscattered electron images of the C/C–SiC–HfC composites, from which the SiC and HfC–SiC ceramics are mainly concentrated in the fiber webs between the non-woven layers. The uniform distribution of the ceramics in the fiber webs could be attributed to the pore distribution of the C/C preform. It can be observed from Fig. 2b that a pyrolytic carbon layer was deposited around the carbon fiber during the TCVI process, protecting the fibers from damaging in the subsequent infiltration processes. From Fig. 2c, it can be seen that the bright-white HfC particles have a uniform distribution in the dark-gray SiC matrix around pyrolytic carbon, illustrating that a multiphase HfC–SiC ceramic has been introduced into carbon matrix. Some micropores can be observed in Fig. 2c, which were resulted from a volume shrinkage and

Fig. 2 Backscattered electron images and XRD pattern of the cross sections of C/C–SiC composites: **a** low magnification; **b**, **c** high magnification; **d** XRD pattern

gas evolution of the polymer precursor during the pyrolysis process [7]. Figure 2d shows the XRD patterns of the C/C–SiC–HfC composites. It can be seen that the main phases in the composite are carbon, HfC, and SiC, indicating that the PHC and PCS are completely transformed into HfC and SiC during PIP process, without other phases.

3.2 Ablative Property of the C/C–SiC–HfC Composites

Ablative property of the prepared C/C–SiC and C/C–SiC–HfC composites under 3,000 °C oxyacetylene torch is listed in Table 2. It can be concluded that the C/C–SiC–HfC composites exhibit good ablation properties with the linear and mass ablation rates of 9.1×10^{-4} mm/s and 1.30×10^{-3} g/s after ablation for 120 s, which are far lower than those of the C/C–SiC composites. Figure 3 shows the surface morphology of C/C–SiC and C/C–SiC–HfC composites after ablation, exhibiting different morphologies on the ablated surface of C/C–SiC and C/C–SiC–HfC composites. An ablation crater about 5 mm in diameter corresponding to the center of the flame was formed

Table 2 Ablation properties of the prepared composites

Material	Mass ablation rate (10^{-3} g/s)	Linear ablation rate (10^{-3} mm/s)
C/C–SiC	22.00	5.70
C/C–SiC–HfC	1.30	0.91

near the center area of C/C–SiC composites, in which carbon fibers can be observed. While a white dense layer was formed on the surface of the center ablation region after HfC was doped in.

3.3 Ablation Mechanism of the Composites

3.3.1 Ablation Mechanism of the Composites near the Center Ablation Region

In the most severe ablated area of C/C–SiC composites, carbon fibers were ablated into needled shapes as shown in Fig. 4a, which are similar to those of the ablated fibers displayed in carbon-based composites during ablation by oxidation [16–18] or both oxidation and sublimation [19,

Fig. 3 Surface morphologies of C/C-SiC **a** and C/C-SiC-HfC **b** composites ablated by oxyacetylene torch for 120 s

Fig. 4 SEM micrographs of center ablation region of C/C-SiC **a** and C/C-SiC-HfC **b** composites ablated by oxyacetylene torch for 120 s; **c** high magnification of area A in **b**; **d** XRD pattern of C/C-SiC-HfC

20]. C-SiC matrix was ablated severely, and SiO_2 was not detected at the ablation crater of C/C-SiC composites via EDS analysis. This could be attributed to the following reasons. Firstly, SiO_2 vaporized heavily during the 3,000 °C oxyacetylene ablation, which led to the formation of micropores and grooves on the surface for further oxygen diffusion. Secondly, the formation of water molecules

as a result of the burning of the acetylene gas reduced the stability of SiO_2 by generating gaseous $\text{Si}(\text{OH})_4$, $\text{SiO}(\text{OH})_2$, and/or $\text{SiO}(\text{OH})$ [21].

Since high heat flux, rich oxidizing species, and rigorous gas scouring happened in this region, the ablation rate of the composites was controlled by the rate of chemical reactions. According to the standard Gibbs free energies

calculated by Fact-Sage software between 1,700 and 2,010 °C, the reactions could easily proceed as follows:

The gas escape of CO and SiO, and the evaporation of SiO₂ could decrease the surface temperature of C/C–SiC composites.

It can be seen in Fig. 4b that a glass-like layer with micropores covers on the center ablated area of C/C–HfC–SiC composite. Figure 4c shows the high-magnification image of area A in Fig. 4b, from which continuous layer containing good crystallization HfO₂ grains can be observed. The formation of this molten HfO₂ layer might be attributed to the rapid cooling of the samples after ablation test, which led to a poor crystalline state of HfO₂. Besides, the solution of SiO₂ in HfO₂ could result in a lower melting point of oxide layer. Thus, the molten HfO₂ would be formed when it was exposed at about 3,000 °C. The ablation rate of C/C–SiC–HfC composites was also controlled by rapid chemical reactions in this region. Together with reactions (1)–(8), more reactions would occur with HfC addition between 1,800 and 2,610 °C as follows:

Thus, due to the protective HfO₂ mol7ten layer which can reduce heat transfer and oxygen transport to the underlying carbon matrix, the linear and mass ablation rates of C/C–SiC composite are dramatically decreased after adding HfC.

3.3.2 Ablation Mechanism of the Composites near the Ablation Fringe Region

The temperature at the center of the flame is about 3,000 °C, while the temperature in the ablation fringe region is less than 1,800 °C. SEM micrographs of C/C–SiC and C/C–SiC–HfC composites near fringe ablation region by oxyacetylene torch for 120 s are shown in Fig. 5. As shown in Fig. 5a, b, discontinuous glass-like SiO₂ film

filled the interstices of the ablated C/C–SiC composites. This discontinuous film was formed as a result of the accumulation of the spherical ablation products observed on the residual carbon matrix. Oxidized gases could easily diffuse through the space between the discontinuous glass-like SiO₂ films, and thus it could only provide a certain extent of protection for the carbon substrate. The ablation rate of C/C–SiC composites in the fringe region was controlled by the diffusion rate of oxygen through this discontinuous protective film.

Morphology of fringe ablation region of C/C–SiC–HfC composites is shown in Fig. 5c. Combined with EDS analysis, it can be observed that a SiO₂ outer layer covers an inner oxide layer which was consisted of HfO₂ and SiO₂. This SiO₂ outer layer was partly damaged during the ablation process, and the inner oxidized layer was appeared. This phenomenon could be attributed to the following reasons. As the ablation process going, an oxidized layer consisted of HfO₂ and SiO₂ was formed on the surface of the composites. Gases such as CO and CO₂ were also produced below this oxidized layer and the vapor pressure increased till exceeding the sum of the ambient pressure of this layer. At the fringe ablation region, the ablation temperature is still higher than the melting point of SiO₂ (1,670 °C), and the molten SiO₂ was extruded from the oxidized layer to the surface as a result of the vapor pressure. Thus, a SiO₂ outer layer was formed. Because porous and loose HfO₂ layer was formed when HfC was oxidized at intermediate temperatures, and the pores generated in the oxidized layer provided the diffusion channels for oxygen. The SiO₂ outer layer could fill those pores and make up this drawback. Thus, the layered structure which consisted of SiO₂ outer layer and HfO₂–SiO₂ inner layer could provide an effective protection. Ablation rate controlled by diffusion rate of oxygen at this region was dramatically decreased, comparing with C/C–SiC composite. Differently from the molten HfO₂ structure formed in the center ablation region, HfO₂ particles were kept in crystalline state with the grain size around 1 μm in the fringe region. Obvious boundaries among HfO₂ grains could be observed in this region because of the mild oxidization phenomenon of HfC grains. The oxidation of HfC could absorb heat from the ablation flame, and the formation of the HfO₂–SiO₂ multiphase oxidized layer could also contribute to a better ablation resistance than C/C–SiC composites.

3.4 Thermal Conductivity of the Composites

High thermal conductivity has a positive role in improving thermal shock resistance and decreasing ablation temperature because the thermal gradients can be minimized. As shown in Fig. 6, the thermal conductivity of the C/C–SiC–

Fig. 5 SEM micrographs of fringe ablation region of C/C-SiC **a**; C/C-SiC-HfC **c** composites ablated by oxyacetylene torch for 120 s; **b** high magnification of **a**; **d**, **e** high magnification of area A and B in **c**, respectively; **f**, **g**, **h** EDS analysis of Spectrum 1, 2 and 3

HfC composites is higher than that of the C/C-SiC composites. As known to all, phonon interaction including phonon-phonon, phonon-defect, and phonon-interface interactions is responsible for the heat conduction. The

phonon scattering phenomenon of the composite can be increased with doping of HfC. This is because the introduction of HfC could increase the defects such as the formation of interface, which could increase phonon

Fig. 6 Thermal conductivity of the C/C–SiC and C/C–SiC–HfC composites from 100 to 2,300 °C

scattering. Moreover, graphitization of carbon could be restricted because of the addition of HfC [22]. These will lead to a decrease of the thermal conductivity. However, the results shown in Fig. 6 indicate that the introduction of HfC could increase the thermal conductivity. Thus, it could be determined that it is the phonon–defect interaction rather than the phonon scattering is the main reason of the improved thermal conductivity of C/C–SiC–HfC composites.

Indeed, the introduction of HfC has both positive and negative effects on the thermal conductivity of the composites. Phonon scattering could decrease the thermal conductivity. But it has little effects on the thermal conductivity. That is, though the phonon scattering could decrease the thermal conductivity, the phonon–defect interaction plays a key role in increasing the thermal conductivity.

Phonon–defect interaction of the C/C–SiC–HfC composites can be explained as follows. During the pyrolysis process, gases such as CO and CO₂ [7], which act as the thermal diffusion media, would be released from the polymer precursor. After repeated PIP process, gases accumulated in pores and microcracks caused by the mismatch of coefficient of thermal expansion between multi-phase ceramics. Because the ceramic productivity of PHC is lower than that of PCS, the generation of the gases and the probability of a molecular collision increase as HfC being added. The phonon–defect interaction in the composites increases as the accumulation of CO and CO₂, thus the thermal conductivity of the composites being improved. High thermal conductivity could improve the heat diffusion, which will lead to a decrease of the ablation surface temperature. Improved the thermal conductivity is benefit to enhance the ablation resistance of the composites.

4 Conclusions

C/C–SiC–HfC composites were fabricated via PIP method using a mixture solution of organic hafnium-containing polymer and polycarbosilane. After ablation for 120 s, the composites exhibit good ablation resistance with linear and mass ablation rates of 9.1×10^{-4} mm/s and 1.30×10^{-3} g/s, respectively. The improved ablation resistance could be attributed to the formation of the HfO₂ molten layer, which plays an important role in reducing heat transfer and oxygen transport to the underlying carbon matrix. Thermal conductivity was increased with the addition of HfC due to the CO and CO₂ generated from the precursor of HfC, which could act as the thermal diffusion media. The increased thermal conductivity of the composites could also contribute to the excellent ablative property.

Acknowledgments This work was financially supported by the National Natural Science Foundation of China (Nos. 51221001 and 51272213), the Author of National Excellent Doctoral Dissertation of China (No. 201036), the “111” project of China (No. B08040) and National Basic Research program of China (No. 2011CB605806).

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