Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 2893–2897

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Ablative property of ZrC–SiC multilayer coating for PIP-C/SiC composites under oxy-acetylene torch

Xiang Yang *, Li Wei, Wang Song, Chen Zhao-hui

Key Laboratory of Advanced Ceramic Fibers & Composites, National University of Defense Technology, Changsha 410073, People's Republic of China

Received 12 November 2011; received in revised form 22 November 2011; accepted 22 November 2011
Available online 9 December 2011

Abstract

To improve ablation resistance of PIP-C/SiC composites, ZrC–SiC multilayer coating was prepared on surface of PIP-C/SiC composites by chemical vapor deposition and slurry. The coating shows dense surface and outstanding anti-ablation ability. Compare with uncoated PIP-C/SiC, the linear and mass ablation rates of the coated PIP-C/SiC decrease by 59.5% and 50.3%, respectively, after ablation for 30 s. Large amounts of heat can be taken away by the gas generated during ablation, which is also helpful for protection for the composites.

Keywords: PIP-C/SiC composites; Coating; ZrC; Ablation

1. Introduction

As one kind of the most popular methods to fabricate C/SiC composites, precursor infiltration and pyrolysis (PIP) route has been actively developed [1–5]. However, at higher temperatures (>1200 °C), oxidation of the fiber, interphase and matrix cooperatively influence the oxidation behavior of PIP-C/SiC composites in oxygen atmosphere [6].

Preparing coatings on surface of the PIP-C/SiC composites is an efficient way for protection at high temperature [7]. SiC is an effective coating for protecting carbon materials from oxidation at high temperature [7,8]. The oxidation protection ability of SiC coating was commonly tested at an invariable temperature. However, for supersonic vehicle use, the coating will not be competent. So materials with higher melting point such as HfC [9], TaC [10], NbC, ZrC [7,11] have been introduced into C/C composites to improve ablation resistance of C/C composites, however the materials have not been reported into PIP-C/SiC composites up to now.

Among these carbides, ZrC possesses high melting point (3803 K) and low vapor pressure, and become the optimal option for protection at the supersonic environment. While, the CTE (coefficient of thermal expansion, $7.2 \times 10^{-6}\ \mathrm{K}^{-1}$) of ZrC is much higher than that of PIP-C/SiC [11], which will lead to debonding of the coatings, when suffering large temperature gradient in service. To solve this problem, SiC is introduced as transition layer, the multi-layer coating is expected to better anti-ablative property and lower thermal stress of the coating. And up to now, no research about ablative property or ablative mechanism of ZrC–SiC multilayer coated PIP-C/SiC composites has been reported.

In this paper, ZrC–SiC multilayer coating was prepared on surface of PIP-C/SiC composites by chemical vapor deposition and slurry, then the ablation property was evaluated under an oxyacetylene torch flame.

2. Experimental

2.1. Fabrication of PIP-C/SiC composites

Three-dimensional braided carbon fibers (T-300, ex-PAN carbon fiber, Toray) were used as the reinforcement [3]. PCS with molecular weight ~1742 and soften point ~448 K was synthesized in our laboratory. Firstly, the polydimethylsilane was decomposed in an autoclave under N_2, when the temperature was during 633–773 K. Secondly, the products were dissolved in xylene, and then the impurities were filtrated. Finally, the PCS was fabricated from the solution by the reduced pressure distillation [12]. Xylene was used as solvent for PCS.

---

* Corresponding author. Tel.: +86 731 88576446; fax: +86 731 84573165.
E-mail address: shmily_0427@163.com (X. Yang).

0272-8842/$36.00. Crown Copyright © 2011 Published by Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2011.11.063

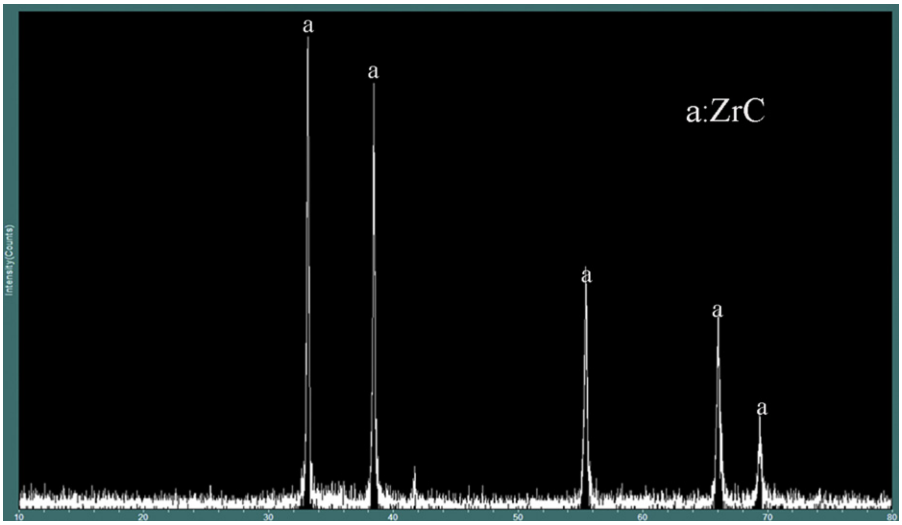

Fig. 1. XRD patterns of as-prepared ZrC–SiC multilayer coating.

The C/SiC composites denoted as raw sample were prepared using 9–12 cycles of infiltration of PCS-xylene solution and subsequently pyrolysis at 1473 K under an inert atmosphere [3].

2.2. Preparation of ZrC–SiC multilayer coating

A ZrC powder (1.25 μm, ChangSha Wing high-tech new materials Co., Ltd., China) layer was then pasted on the composite, followed by depositing a SiC coating. In this process, CVD SiC will penetrate in the gaps between ZrC powders and form a mixture of SiC–ZrC coating with a layer of dense SiC on the top.

As for the CVD SiC process, methyltrichlorosilane (MTS, CH_3SiCl_3) with a molar ratio of 10 between H_2 and MTS, the deposition temperature was controlled in the 1373 K for 5 h at reduced pressure of 3 kPa [13].

2.3. Ablation tests and microstructure analysis

Ablation behavior was tested under oxyacetylene torch. The coated samples were placed vertically to the flame for 30 s. The linear and mass ablation rates of the samples could be obtained according to the formulas below:

$$R_l = \frac{\Delta d}{t} \tag{1}$$

$$R_m = \frac{\Delta m}{t} \tag{2}$$

R_l is the linear ablation rate; Δd is the change of the sample's thickness at center region before and after ablation; R_m is the mass ablation rate; Δm is the sample's mass change before and after ablation; t is the ablation time.

The morphologies and crystalline structures of the samples were analyzed by scanning electron microscopy (SEM, JSM-5600LV) and X-ray diffraction (XRD) (D8 Advance, Cu-kα radiation, 5–75°, 2θ range, 0.01° wide scanning steps, 1 s/step acquisition time).

3. Results and discussion

3.1. Morphology and microstructures of coated PIP-C/SiC

XRD patterns of as-prepared coating are showed in Fig. 1. It can be seen that the inter coating is ZrC, which is infusible phase, with melting points of 3803 K. The oxide of ZrC has high melting point (3003 K), However, the oxide coating is porous and do not provide oxidation protection. Thus, the addition of SiC can improve the oxidation resistance of ZrC.

Fig. 2 shows surface and cross-section morphology of the ZrC–SiC multilayer coating. SEM image of ZrC–SiC multilayer coating surface is exhibited in Fig. 2(a). SiC grains connect each other compactly. It revealed the formation of dense coating surface and no crack can be found on surface of coating.

PIP-C/SiC composites with ZrC–SiC multilayer coating are mainly composed of carbon fibers, SiC, pores and cracks (Fig. 2(b)). PCS will shrink in pyrolysis, which may result in cracks. Pores result from incomplete densification by the PCS impregnation/pyrolysis steps.

The coating can be divided two layers: the first layer is ZrC, whereas the following layer is SiC successively. ZrC coating is not a dense layer (Fig. 2(b)), while, the deposition of SiC will penetrate in the gaps between ZrC powders and form a mixture of SiC–ZrC coating with a layer of dense SiC (Fig. 2(a)) on the top. The thickness of each coating is more or less 20 μm, respectively.

3.2. Ablation resistance of coated PIP-C/SiC

The uncoated PIP-C/SiC samples exhibits severe ablation under oxy-acetylene torch (Table 1), without protection, composites can be consumed rapidly, for 30 s ablation, the linear and mass ablation rates reach 0.0622 mm/s and 0.0425 g/

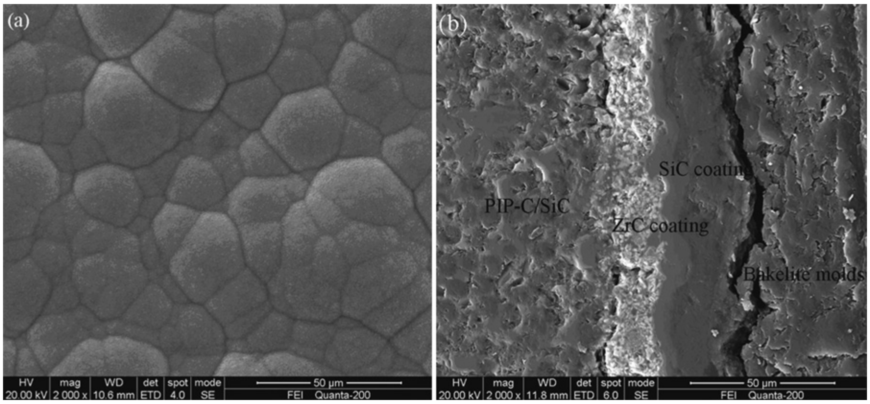

Fig. 2. Surface (a) and cross-section (b) morphology of coating.

Table 1
The ablation property of the ZrC–SiC multilayer coated samples.

Samples	Linear ablation rate (mm/s)	Mass ablation rate (g/s)
PIP-C/SiC composites	0.0622	0.0425
Coated PIP-C/SiC composites	0.0252	0.0211

s. While, compare with the uncoated PIP-C/SiC, the multilayer coating prevents matrix from ablation efficiently, the linear and mass ablation rates of the coated samples reach 0.0252 mm/s and 0.0211 g/s and decrease by 59.5% and 50.3%, respectively, which is attributed to the penetration of SiC in the ZrC to intermediate CTE of the coating and the high melting point of the coating. Meanwhile, the ZrC and SiC are high melted point materials, the oxidation of the coating and melting of the coating oxides may consume large amount of heat, which is also beneficial to the protection for PIP-C/SiC composites.

Ablation is an erosive phenomenon with a removal of material by a combination of thermo-mechanical, thermo-chemical, and thermo-physical factors from high temperature, pressure, and velocity of combustion flame. There are mainly two kinds of ablation mechanism: chemical erosion and mechanical denudation. The chemical erosion refers to the reactions of the material with combustion gases (O_2, H_2O, etc.). The mechanical denudation means the peeling of the coating caused by the flame with high-temperature, high velocity and pressure [14].

The surface morphologies of PIP-C/SiC composites with ZrC–SiC multilayer coating after ablation for 30 s are shown in Fig. 3, a great change in morphology occurs on the surface of the composites. From the SEM images of the center and transition zone, the ablation behavior can be inferred. The central region is the core of oxyacetylene flame and its ablation is the more severe of the two regions. The coating is oxidized in priority and becomes loosen and porous, which provide more channels for oxygen diffusing into composites. With the ablation going on, the oxides are washed away by the shearing action of the oxyacetylene flame. While, for 30 s ablation, the coating is consumed out, little of the oxides remain at the surface. As a result, C/SiC is oxidized. The SiC matrix is oxidation and its oxides sublimate completely, leaving naked needle-shaped carbon fibers in the central region. In the transition zone, the mechanical denudation becomes weakened; the chemical erosion becomes the leading mechanism. The matrix cannot be washed out during ablation. So there is more fiber and matrix in this region.

To reveal the ablation behavior further, the EDS of the center region are listed in Fig. 4. There are large amounts of white phase generated in the center region. EDS results show that there are Zr, C, O and Si, which indicated that the white phase is composed of carbides and oxides of Zr and Si, the white and

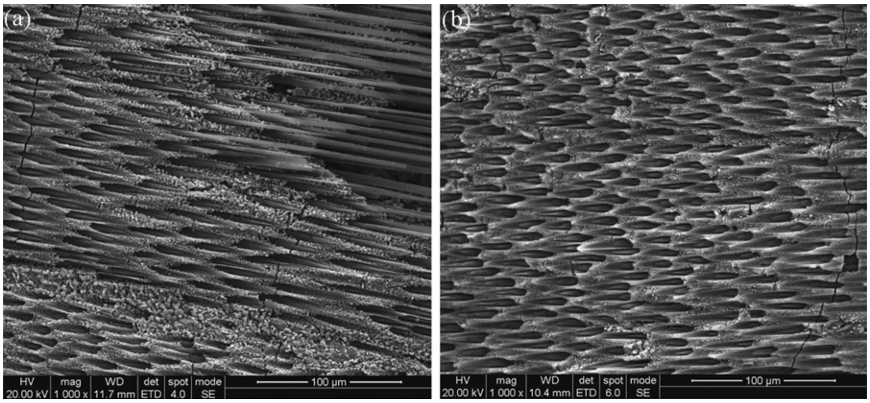

Fig. 3. Ablation morphology of the coated samples (a) center region and (b) outer region.

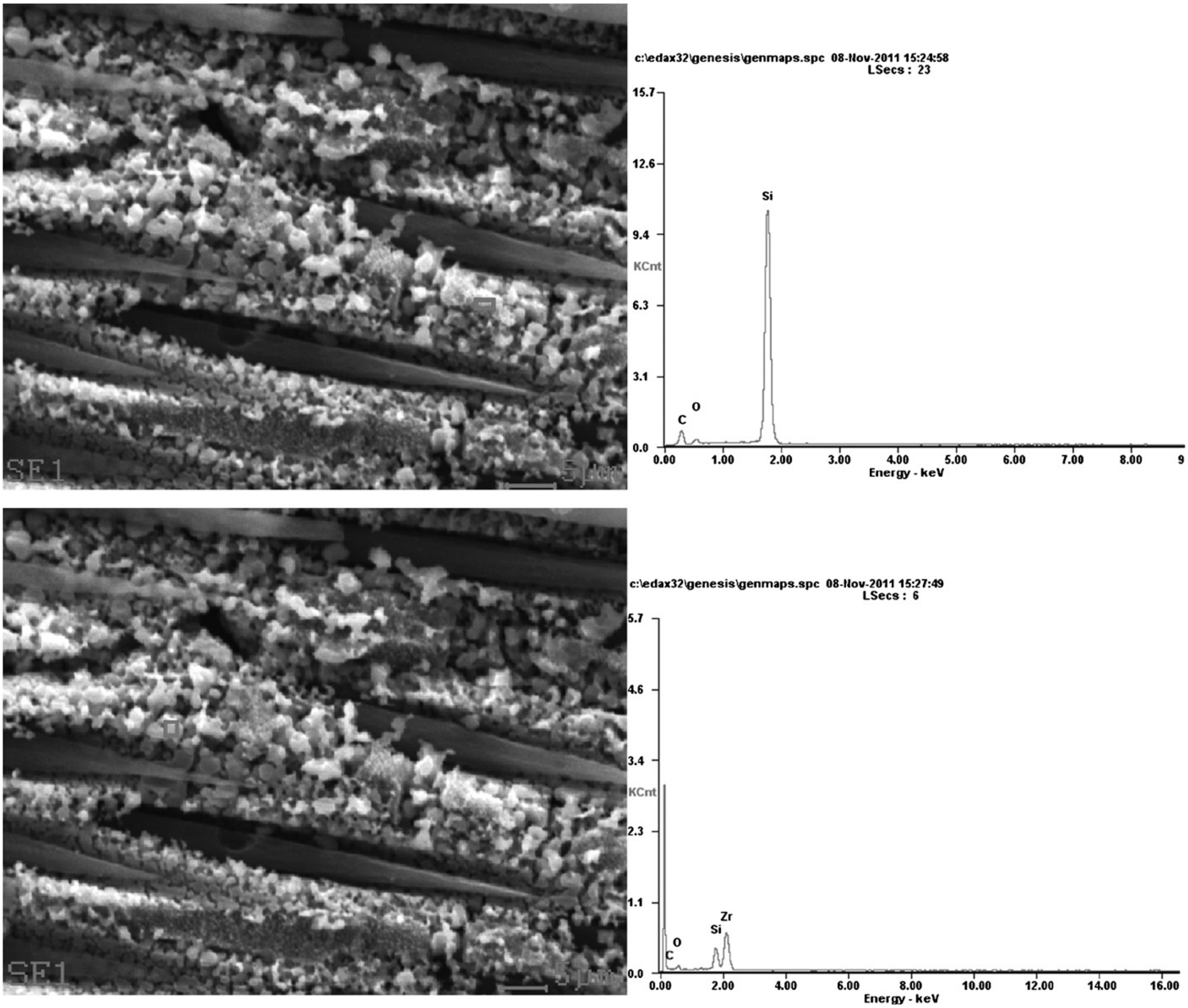

Fig. 4. EDS and center region SEM images of the coated samples after ablation.

gray phases could be distinguished as SiC and SiO_2, respectively. So it can be inferred that the coating was almost consumed out in the center region. The residual ZrO_2 combined with SiC grains because of the adhesive effect of glassy phase SiO_2.

During ablation, the center region suffered the highest temperature (>2000 °C) and pressure, the main ablation behaviors are the chemical erosion related to oxidation and erosion. In the transition erosion region, the temperature and pressure decrease significantly. The oxyacetylene flame flowed from the center of sample to the border along the composite surface.

There are severe reactions between reactive gases and PIP-C/SiC composites with ZrC–SiC multilayer coating. In the present case, the main expected reactions during the oxidation process are as follows [15,16]:

$$\mathrm{SiC(s)} \rightarrow \mathrm{SiC(l)} \tag{3}$$

$$\mathrm{SiC(l)} + \mathrm{O_2(g)} \rightarrow \mathrm{SiO_2(l)} + \mathrm{CO_2(g)} \tag{4}$$

$$\mathrm{SiC(l)} + \mathrm{O_2(g)} \rightarrow \mathrm{SiO_2(l)} + \mathrm{CO(g)} \tag{5}$$

$$\mathrm{SiC(l)} + \mathrm{SiO_2(l)} \rightarrow \mathrm{SiO(g)} + \mathrm{CO(g)} \tag{6}$$

$$\mathrm{ZrC(s)} + \mathrm{O_2(g)} \rightarrow \mathrm{ZrO_2(s)} + \mathrm{CO_2(g)} \tag{7}$$

$$\mathrm{ZrC(s)} + \mathrm{O_2(g)} \rightarrow \mathrm{ZrO_2(s)} + \mathrm{CO(g)} \tag{8}$$

$$\mathrm{C(s)} + \mathrm{O_2(g)} \rightarrow \; + \mathrm{CO_2(g)} \tag{9}$$

$$\mathrm{C(s)} + \mathrm{O_2(g)} \rightarrow \; + \mathrm{CO(g)} \tag{10}$$

During ablation, as the ablation temperature reaches 2000 °C, the reactions about SiC based coating ((3)–(6)) happened firstly, and then are the reactions (7) and (8). After the coating being consumed out, SiC matrix ((3)–(6)) happened, and then are the reactions (9) and (10). It can be found that:

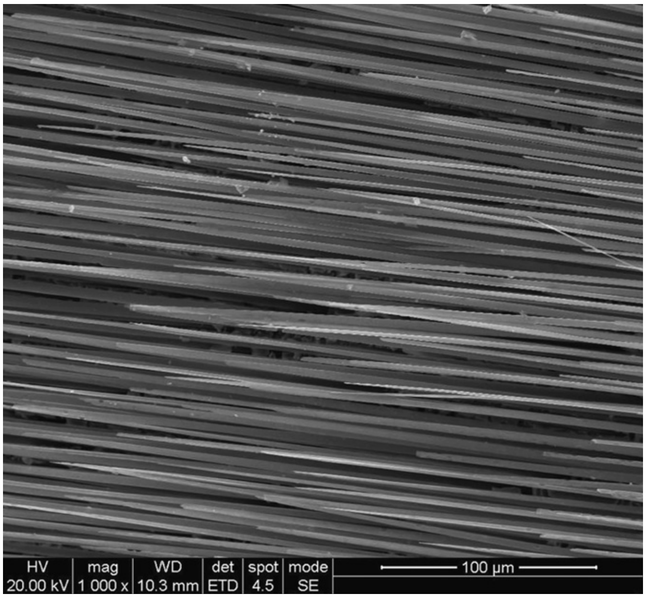

Fig. 5. Ablation morphology of the uncoated samples.

reactions (3) is melting process and could consume lots of heat during ablation; there are large amounts of gas generated, which could also take heat away from the coating surface. The temperature of the central region could be lowered according to the reactions, which is the reason of well anti-ablative property of ZrC–SiC multilayer coating.

Additionally, reactions (4)–(6) and (8) were all weight-gain process, which is the reason why the coated samples have low mass ablation rate.

Concerning the surface of uncoated PIP-C/SiC, as shows in Fig. 5, evident discrepancy can be found in comparison with coated PIP-C/SiC composites. After ablation for 30 s, obvious pores are observed on the surface of uncoated PIP-C/SiC. It was more serious that the matrix is almost consumed out after ablation with the time reaches 30 s and the fiber is oxidized. That means the uncoated PIP-C/SiC composites show worse ablative property under oxy-acetylene torch. After 30 s ablation, the composites are ablated severely and the sample shape is destroyed completely. Thus, the multi-layer coating exhibits better ablation resistance.

4. Conclusions

By studying the ablation behaviors of PIP-C/SiC composites with ZrC–SiC multilayer coating in the oxyacetylene flame conditions, the following conclusions can be made: The as-prepared coating exhibits dense surface, and protects the samples efficiently. The mass ablation and linear rates are much lower than that of uncoated samples. The gases released during ablation could take away a lot of heat, which is also helpful to the protection for the composites.

Acknowledgement

The authors are grateful to National Natural Science Foundation of China (90916002) for financial support.

References

[1] G.B. Zheng, H. Sano, Y. Uchiyama, et al., The properties of carbon fibre/SiC composites fabricated through impregnation and pyrolysis of polycarbosilanes, J. Mater. Sci. 34 (1999) 827–834.

[2] G.B. Zheng, H. Sano, K. Suzuki, et al., A TEM study of microstructure of carbon fibre/polycarbosilane-derived SiC composites, Carbon 37 (1999) 2057–2062.

[3] K. Jian, Z.H. Chen, Q.S. Ma, et al., Effects of pyrolysis processes on the microstructures and mechanical properties of Cf/SiC composites using polycarbosilane, Mater. Sci. Eng. A 390 (2005) 154–158.

[4] K. Jian, Z.H. Chen, Q.S. Ma, et al., Effects of polycarbosilane infiltration processes on the microstructures and mechanical properties of 3D-Cf/SiC composites, Ceram. Int. 33 (2007) 905–909.

[5] H.Q. Ly, R. Taylor, R.J. Day, Carbon fibre-reinforced CMCs by PCS infiltration, J. Mater. Sci. 36 (2001) 4027–4035.

[6] W.H. Glime, J.D. Cawley, Oxidation of carbon fibers and films in ceramic matrix composites: a weak link process, Carbon 33 (8) (1995) 1053–1060.

[7] D. Zhao, C.R. Zhang, H.F. Hu, Y.D. Zhang, Effects of SiC on the oxidation resistance performance of C/ZrC composite prepared by polymer infiltration and pyrolysis process, Mater. Sci. Forum 675–677 (2011) 415–418.

[8] S. Zhao, X.G. Zhou, H.J. Yu, H.L. Wang, et al., Compatibility of PIP SiCf/SiC with LiPb at 700 °C, Fusion Eng. Des. 85 (2010) 1624–1626.

[9] C.Y. Li, K.Z. Li, H.B. Ouyang, H.J. Li, Ablation behavior of HfC modified carbon/carbon composites, Rare Metal Mater. Eng. 35 (2006) 365–368.

[10] H. Xiang, Y.D. Xu, L.F. Cheng, L.T. Zhang, Preparation of TaC anti-ablation material by liquid precursor, J. Inorg. Mater. 21 (2005) 893–898.

[11] Q.F. Tong, J.L. Shi, Y.Z. Song, Q.G. Guo, L. Liu, Resistance to ablation of pitch derived ZrC/C composites, Carbon 42 (2004) 2495–2500.

[12] X.Z. Cheng, Z.F. Xie, Y.C. Song, J. Xiao, Influence of reaction temperature on the properties of polycarbosilane synthesized from polydimethylsilane under high pressure, Acta Polym. Sin. 6 (2005) 851–855.

[13] Y. Xiang, W. Li, S. Wang, Z.H. Chen, Oxidation behavior of oxidation protective coatings for PIP–C/SiC composites at 1500 °C, Ceram. Int. (2011), doi:10.1016/j.ceramint.2011.06.063.

[14] J.Yin, X. Xiong, H.B. Zhang, B.Y. Huang, Microstructure and ablation performances of dual-matrix carbon/carbon composites, Carbon 44 (2006) 1690–1694.

[15] D. Zhao, H.F. Hu, C.R. Zhang, Y.D. Zhang, J. Wang, A simply way to prepare precursors for zirconium carbide, J. Mater. Sci. 45 (2010) 6401–6405.

[16] Wang, H.J. Li, G.Q. Fu, H. Wu, D.J. Yao, Ablative property of HfC-based multilayer coating for C/C composites under oxy-acetylene torch, Appl. Surf. Sci. 257 (2011) 4760–4763.