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Ablation behavior of three-dimensional braided C/SiC composites by oxyacetylene torch under different environments

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Abstract

SiC ceramic matrix composites reinforced by three-dimensional braided carbon fibers were prepared via polycarbosilane infiltration pyrolysis (PIP). The ablation behavior of the composites was characterized by an oxyacetylene torch under different environments. The morphology and microstructure of the as-ablated composites were examined by scanning electron microscopy and the composition of the new phase was confirmed by energy dispersive spectroscopy. Two conditions showed different ablation mechanisms. The erosion mechanism of the high speed oxyacetylene torch was the main ablation behavior under oxygen free environment. Thermo-chemicals ablation was the main ablation behavior under abundant oxygen environment.

Keywords: C/SiC composites; Oxidation; Ablation

1. Introduction

Future engine components, in particular combustion chambers and expansion nozzles which were subjected to high thermal loads, need new materials which possessed outstanding thermo-mechanical and thermo-chemical properties [1]. In view of their low specific weight, excellent resistance to ablation as well as cost effective production, carbon fiber reinforced silicon carbide (C/SiC) composites represented an interesting material for high-temperature components of space propulsion systems [2].

Three-dimensional (3D) woven composites had been pursued in the aerospace industry primarily to improve the vulnerability of 2D composites under impact and subsequent local buckling failure under in-plane compression [3]. Before the practical application of C/SiC in these cases, investigation on the evolution of morphology and microstructure during ablation was required.

The main experimental methods were oxyacetylene flame ablation [4], plasma arc ablation [5,6], and wind tunnel tests [7]. The oxyacetylene flame ablation method was the simplest and easiest to conduct with the lowest cost. So, oxyacetylene flame testing was often used to simulate the rocket engine exhaust flame [8]. So far, the evolution of morphology and microstructure during ablation of 2D C/SiC composites [9] and 3D orthogonal C/SiC composites [10] and mechanical behavior of 3D braided C/SiC composites under simulated space environments [11] were reported. However, studies on ablation morphology and microstructure of three-dimensional braided C/SiC composites prepared via PIP process were rarely reported.

Ablation was 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 were mainly two kinds of ablation mechanism: chemical erosion and mechanical denudation. The chemical erosion referred to the reactions of the material with combustion gases (O_2, H_2O, etc.). The mechanical denudation meaned the peeling of the coating caused by the flame with high-temperature, high velocity and pressure [12].

The present paper is to investigate the effects of ablation at different regions in three-dimensional braided C/SiC

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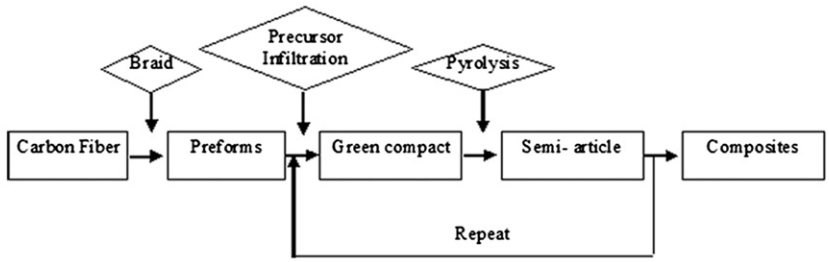

Fig. 1. Flow chart for preparation of 3D braided C/SiC composites via PIP route.

composites ablated by an oxyacetylene torch. Ablation researchers mainly concentrate on optimization of testing environment [9–11]. For better understanding of the ablation mechanism of 3D braided C/SiC composites, we designed different environment tests such as oxygen free environment and abundant oxygen environment. The ablation behavior and microstructure of the as-produced materials under oxygen free environment and abundant oxygen environment were discussed. The heterogeneous chemical reactions involved during the ablation tests were also studied.

2. Experimental

2.1. Composites fabrication

Fig. 1 shows the experimental flow diagram for three-dimensional braided C/SiC composites prepared via PIP process. Three-dimensional braided carbon fibers (T-300, ex-PAN carbon fiber, Toray) were used as the reinforcement [2]. The fiber volume fraction was ~45%. Polycarbosilane (PCS) with molecular weight ~1742 and soften point ~448 K was synthesized in our laboratory. Xylene was used as a solvent for PCS. C/SiC composites denoted as raw sample were prepared using 9–12 cycles of infiltration of PCS–xylene solution (mass ratio 1:1) and subsequently pyrolysized at 1473 K under N_2 (purity: 99.99%) atmosphere [2].

2.2. Ablation experiment

Cylindrical samples (∅25 mm*x5 mm) for ablation tests were machined from the as-produced composites. The ablation properties of samples were tested under an oxyacetylene torch, and oxyacetylene flame was parallel to the axial orientation of the samples. The pressure and flux of O_2 and C_2H_2 are shown in Table 1. The inner diameter of the nozzle was 2 mm. The distance between the nozzle tip and the sample was 10 mm. The samples were fixed in a water-cooled copper concave fixture and the surface temperature of the samples was monitored with an optical pyrometer.

During the tests, the ablation gun was ignited first. After the flame was steady, the ablation gun was moved vertically to the sample surface. The ablation properties of the samples were tested with an oxyacetylene torch. The pressure and flux of O_2 and C_2H_2 are shown in Table 1. The samples were exposed to the flame for 30 s. The erosion direction of the flame was parallel to the *Z* direction of carbon felts. Both the linear and mass ablation rates were calculated by thickness and weight changes per unit time. The final ablation rates of the samples were the average ablation rates of three samples.

Table 1
Two ablation tests parameters in the flowing oxyacetylene torch environment.

Item	Test of standard	Surface temperature (K)	D_{nozzle} (mm)	Gas press (MPa)		Gas flux (L/h)	
				O_2	C_2H_2	O_2	C_2H_2
Oxygen free	GJB 323 A-96	2373	2.0	0.4	0.095	1512	1116
Abundant oxygen	Self	2323	2.0	0.4	0.095	800	400

The linear and mass ablation rates of samples could be obtained according to the formulas below:

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

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

where R_l is the linear ablation rate, Δd is the change in the samples thickness at center region before and after ablation, R_m is the mass ablation rate, Δm is the samples mass change before and after ablation, and t is the ablation time.

2.3. Samples characterization

The phase and composition of the samples before and after ablation were identified by X-ray diffraction (XRD, D8 Advance, Cu-kα radiation, 5–70°, 2θ range, 0.01° wide scanning steps, 1 s/step acquisition time).

The microstructure and morphology of the samples were analyzed by field emission scanning electron microscopy (SEM, JSM-5600LV) combined with energy dispersive spectroscopy (EDS).

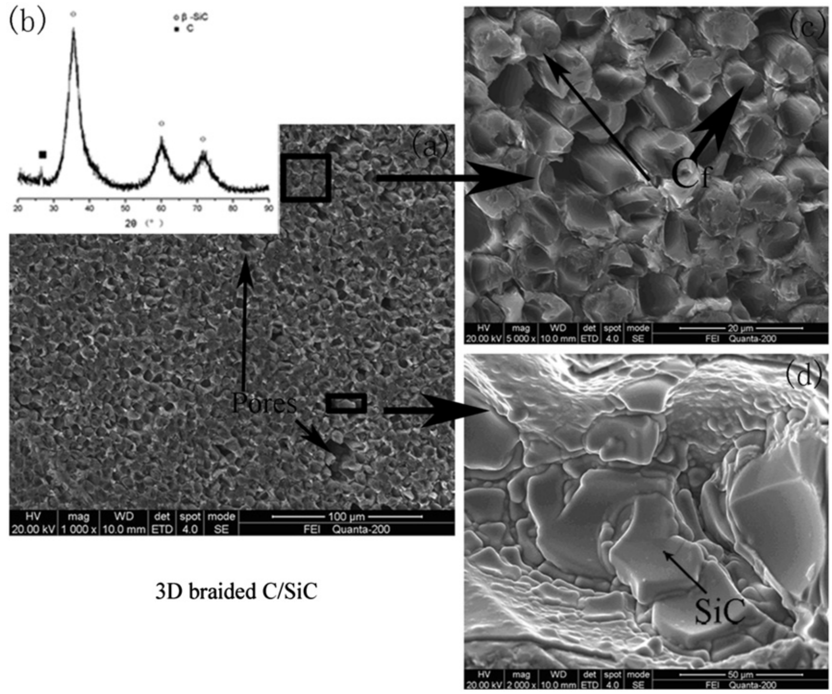

Fig. 2. SEM morphology and XRD of 3D braided C/SiC composites via PIP route: (a) cross-section of 3D braided C/SiC, (b) XRD of C/SiC, (c) carbon fibers of C/SiC and (d) SiC matrix of C/SiC.

3. Results and discussion

3.1. Ablation of 3D braided C/SiC composites under oxygen lack environment

According to the calculations by the Chemical Equilibrium with Applications Code from NASA, the equilibrium composition of oxyacetylene combustion products were O_2, CO_2, CO, O, OH and H_2O, which was a program calculating chemical thermodynamic equilibrium compositions by the principle of free energy minimum [13,14].

Fig. 2 shows the microstructure of 3D braided C/SiC composites before ablation test. Composites are mainly composed of carbon fibers, pores and SiC. It can be seen that there are visible denude regions and matrix cracks, which are caused by polymer precursor pyrolysis. PCS shrinks in pyrolysis, which may result pores in the composites. The open porosity is less than 11% [11], with a density of 1.93 g/cm^3.

Table 2 shows the ablation property of 3D braided C/SiC composites after ablation test under different environments. Fig. 3 shows SEM micrographs of composites after the ablation test under oxygen free environment. The center region is the core of an oxyacetylene flame and its ablation is the severest in the two regions. Not only the SiC matrix is sublimated or decomposed completely, but also some carbon fibers are sublimated. SiC matrix has been cleared away by the mechanism erosion of the high speed oxyacetylene torch. The sublimation temperatures of silicon carbide and carbon are 2700 °C and 3550 °C, respectively [15]. It indicates that the temperature in the center region is above 3550 °C. The transition region is hardly ablated too, while SiC matrix still exists in the composites, and carbon fibers are covered by some white grain.

Table 2
The ablation property of 3D braided C/SiC composites.

Item	Linear ablation rate (mm/s)	Mass ablation rate (g/s)
Oxygen free	0.0622	0.0425
Abundant oxygen	0.0466	0.0087

In the center region, the microstructure of the carbon fiber is changed. Fig. 3 (a) shows SEM photograph of the naked fibers in the center region. SiC matrix is sublimated completely and carbon fibers were ablated to break off in the center region.

In the transition region, oxyacetylene torch test annealed at comparatively lower temperature than center ablation region in atmosphere. SiC matrix is not sublimated completely and still some SiC exists in the samples (Fig. 3(b)).

In general, ablation phenomenon was a combination of oxidation and erosion factors from high temperature, pressure, and velocity of an oxyacetylene flame. Under oxygen free environment, the mechanical denudation was the main erosion mechanism. Under the ablation temperature above 3550 °C, all of the following reactions possibly proceeded [16–18]:

$$2SiC\ (s) + 3O_2(g) = 2SiO_2(l) + 2CO\ (g) \quad (1)$$

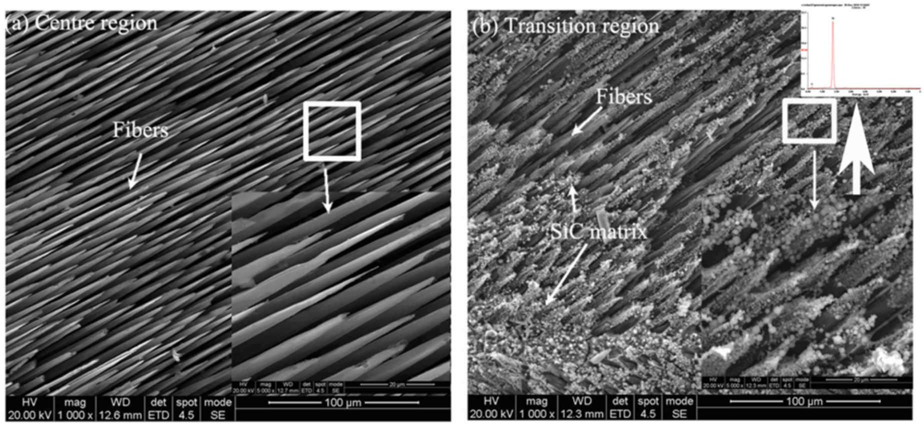

Fig. 3. Ablation morphology of samples: (a) center region and (b) transition region after ablation under oxygen free environment.

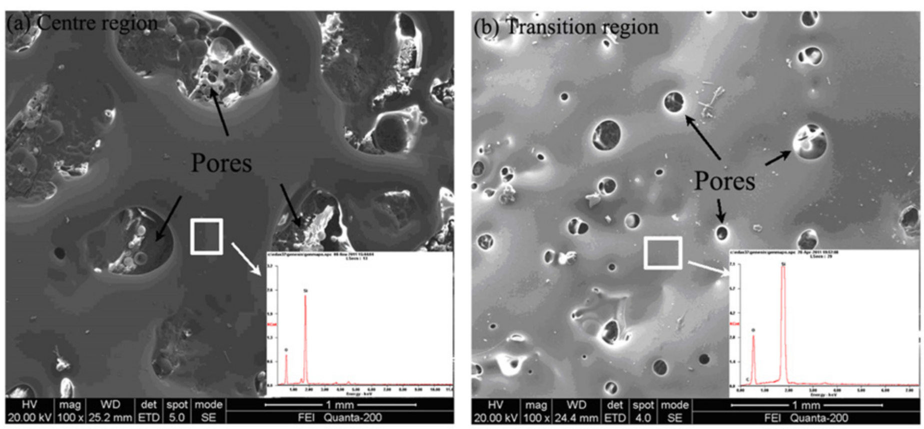

Fig. 4. Ablation morphology and EDS of samples: (a) center region and (b) transition region after ablation under abundant oxygen environment.

$$SiC\ (s) + 3O\ (g) = SiO_2(l) + CO\ (g) \quad (2)$$

$$2SiC\ (s) + 6OH\ (l) = 2SiO_2(l) + 2CO\ (g) + 3H_2(g) \quad (3)$$

$$SiC\ (s) + 5H_2O\ (g) = Si(OH)_4(g) + CO\ (g) + 3H_2(g) \quad (4)$$

$$SiC\ (s) + 4H_2O\ (g) = SiO(OH)_2(g) + CO\ (g) + 3H_2(g) \quad (5)$$

$$SiC\ (s) + 2H_2O\ (g) = SiO\ (g) + CO\ (g) + 2H_2(g) \quad (6)$$

$$SiC\ (s) = SiC\ (g) \quad (7)$$

$$SiO_2(l) = SiO_2(g) \quad (8)$$

$$SiC\ (s) + 3SiO_2(l) = 4SiO\ (g) + CO_2(g) \quad (9)$$

$$2C\ (s) + O_2(g) = 2CO\ (g) \quad (10)$$

$$C\ (s) + O\ (g) = CO\ (g) \quad (11)$$

$$CO_2(g) + C\ (s) = 2CO\ (g) \quad (12)$$

$$C\ (s) + H_2O\ (g) = CO\ (g) + H_2(g) \quad (13)$$

$$2C\ (s) + 2OH\ (g) = 2CO\ (g) + H_2(g) \quad (14)$$

$$C\ (s) + O_2(g) = CO_2(g) \quad (15)$$

$$2H_2O\ (g) + SiO_2(l) = Si(OH)_4(g) \quad (16)$$

$$H_2O\ (g) + SiO_2(l) = SiO(OH)_2(g) \quad (17)$$

When ablating, the end parts of the carbon fibers are tapered. When oxidizing, the end parts of the carbon fibers are flat-bottomed [19]. Under oxygen free environment, the needle-like microstructures are formed (Fig. (3)). Although a thermo-chemical reaction is one of the ablation reactions, thermo-physical and thermo-mechanical that attacks from the flame seems to be more important during ablation under oxygen free environment [20].

3.2. Ablation of 3D braided C/SiC composites under abundant oxygen environment

Fig. 4 shows SEM micrographs and EDS patterns of composites after ablation test under abundant oxygen environment. It indicates that the ablation surface is covered by SiO_2 film. Pores are also observed on the surface of film. EDS patterns of composites show that the film is composed of Si and O.

Due to its poor oxidation resistance at higher temperature, SiC matrix was oxidized after ablation (Eqs. (1)–(9)).

Since the temperature at junction area could be 3550 °C, SiO_2 resulting from the oxidation reactions could sequentially react to form a gas according to reactions (16) and (17), and also directly gasify (SiO_2 boiling point 2230 °C) (Eq. (8)). Then the surface of the composites is completely covered by SiO_2 with pores (Fig. 4). The higher temperature caused decomposition of the SiC matrix. Decomposition of the SiC matrix would consume the thermal energy, which was beneficial to reduce ablation. Meanwhile, compared with the different regions, more pores are observed in the center region (Fig. 4(a)). Pores were the diffusion passages of oxidizing gases at high temperature. Doubtlessly, the presence of pores would debase the oxidation resistance of composite. Carbon fibers were more easily oxidized due to their extensive contact with thermal oxidizing atmosphere, and they obeyed the oxidation reactions (Eqs. (10)–(15)).

Fig. 4(b) shows SEM micrograph of transition ablation region of three-dimensional braided C/SiC composites after ablation. There are fewer pores in this region. The parts of SiC are oxidized forming SiO_2 that not only shielded the inter-bundle pores on the erosion surface from the further attack by the thermal oxidizing atmosphere, but also acted as a barrier to oxygen diffusion due to its low oxygen permeability. In the transition ablation region, the degree of oxidation of carbon fibers and decomposition of SiC were less severe.

In the ablation tests, ablation mechanisms under different environments were discussed and compared. Under oxygen free environment, ablation mechanisms mainly were the mechanism erosion of the high speed oxyacetylene torch, while under abundant oxygen environment, ablation mechanisms mainly were oxidation erosion. Because the samples were suffered high speed oxyacetylene torch, after ablation tests, the samples were taken out of the furnace directly to air within several seconds, the cooling rate of the samples from high temperature to room temperature was very quick. Owing to the quick cooling, the composites would suffer pull-stress because of thermal expansion coefficient, which induced the formation of some pores and cracks. From Figs. 2 to 4, these meaned that 3D braided C/SiC composites showed worse ablative property under oxy-acetylene torch. After 30 s ablation, the composites were both ablated severely and the samples′ shape were destroyed completely. Thus, the protection coating was needed further research.

4. Conclusions

3D braided C/SiC composites were prepared via PIP process. Ablation morphology and microstructure evaluation were carried out by an oxyacetylene torch test under different environments:

(1) Under oxygen lack environment, the needle-like microstructures were formed. Although a thermo-chemical reaction was one of the ablation reactions, thermo-physical and thermo-mechanical attacks from flame seemed to be more important during ablation.
(2) There were a lot of pores on the surface of the ablation region under abundant oxygen environment, which resulted from the release of gas produced by the oxidation of SiC and carbon fibers with sufficiently abundant oxygen in the composites.
(3) Under oxygen free environment, ablation mechanisms mainly were the mechanism erosion of the high speed oxyacetylene torch, and while under abundant oxygen environment, ablation mechanisms mainly were oxidation erosion.

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References

[1] S. Beyer, S. Schmidt, P. Peres, et al., Advanced ceramic matrix composite materials for current and future propulsion system applications, Proceedings of the American Institute of Aeronautics and Astronautics (2005) 3644.
[2] 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, Ceramics International 33 (2007) 905–909.
[3] C.H. Chiu, C.C. Cheng, Weaving method of 3D woven performs for advanced composite materials, Textile Research Journal 73 (2003) 37–41.
[4] D. Zhao, C.R. Zhang, H.F. Hu, et al., Ablation behavior and mechanism of 3D C/ZrC composite in oxyacetylene torch environment, Composites Science and Technology 71 (2011) 1392–1396.
[5] X. Zhang, P. Hu, J. Han, et al., Ablation behavior of ZrB_2–SiC ultra high temperature ceramics under simulated atmospheric re-entry conditions, Composites Science and Technology 68 (2008) 1718–1726.
[6] J. Yin, H. Zhang, X. Xiong, et al., Ablation properties of carbon/carbon composites with tungsten carbide, Applied Surface Science 255 (2009) 5036–5040.
[7] F. Monteverde, R. Savino., Plasma wind tunnel testing of ultra-high temperature ZrB_2–SiC composites under hypersonic re-entry conditions, Journal of the European Ceramic Society 30 (2010) 2313–2321.
[8] G.M. Song, Y. Zhou, Y.J. Wang, Effect of carbide particles on the ablation properties of tungsten composites, Materials Characterization 50 (2003) 293–303.
[9] S.F. Tang, J.Y. Deng, W.C. Liu, et al., Mechanical and ablation properties of 2D-carbon/carbon composites pre-infiltrated with a SiC filler, Carbon 44 (2006) 2877–2882.
[10] B. Yan, Z.F. Chen, J.X. Zhua, et al., Effects of ablation at different regions in three-dimensional orthogonal C/SiC composites ablated by oxyacetylene torch at 1800 °C, Journal of Materials Processing Technology 209 (2009) 3438–3443.
[11] B.F. Zhang, S. Wang, W. Li, et al., Mechanical behavior of C/SiC composites under simulated space environments, Materials Science and Engineering A 534 (2012) 408–412.
[12] J. Yin, X. Xiong, H.B. Zhang, et al., Microstructure and ablation performances of dual-matrix carbon/carbon composites, Carbon 44 (2006) 1690–1694.
[13] S. Gordon, B.J. McBride, Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications I:

Analysis, NASA Reference Publication, NASA Lewis Research Center, 1994, pp. 25–32.
[14] S. Gordon, B.J. McBride, Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications II: Users Manual and Program Description, NASA Reference Publication, NASA Lewis Research Center, 1996, pp. 65–71.
[15] Ceramics, 〈http://www.ultramet.com/materials101.html〉.
[16] J. Han, P. Hu, X. Zhang, et al., Oxidation-resistant ZrB_2–SiC composites at 2200 °C, Composites Science and Technology 68 (2008) 799–806.
[17] P. Lespade, N. Richet, P. Goursat, Oxidation resistance of HfB_2–SiC composites for protection of carbon-based materials, Acta Astronautica 60 (2007) 858–864.
[18] X. Yang, L. Wei, W. Song, et al., Ablative property of ZrC–SiC multilayer coating for PIP-C/SiC composites under oxy-acetylene torch, Ceramics International 38 (2012) 2893–2897.
[19] H. Mei, L. Cheng, L. Zhang, X. Luan, J. Zhang, Behavior of two dimensional C/SiC composites subjected to thermal cycling in controlled environments, Carbon 44 (2006) 121–127.
[20] Y.J. Lee, H.J. Joo, Investigation on ablation behavior of CFRC composites prepared at different pressure, Composites Part A: Applied Science and Manufacturing 35 (2004) 1285–1290.