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Morphology and microstructure of 2.5 dimension C/SiC composites ablated by oxyacetylene torch

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Abstract

SiC ceramic matrix composites reinforced by 2.5 dimension carbon fibers were prepared by low-pressure chemical vapor infiltration. The ablation performance of the composites was characterized by an oxyacetylene torch. The morphology and microstructure of the as-ablated composite were examined by scanning electron microscopy. The composition of the new phase was confirmed by energy dispersive spectroscopy and X-ray diffraction. Three clear annular regions appeared on the surface of the as-ablated sample and each region had different ablation mechanism. Sublimation was the main ablation behavior in the centre region. Oxidation was the main ablation behavior in the middle region. Silica particles mainly resulted from the oxidation and deposition of Si and SiO gas from the centre to the outer region. The ablation mechanism of the C/SiC composites under oxyacetylene flame was a combined effect of thermo-physicals attack and thermo-chemicals ablation.

Keywords: Morphology; Microstructure; C/SiC composites; Oxyacetylene torch; Ablation mechanism

1. Introduction

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 [1]. Materials with outstanding thermo-mechanical and thermo-chemical properties are required for future engine components, in particular combustion chambers and expansion nozzles which are subjected to high thermal loads [2]. In view of their low specific weight, their excellent resistance to ablation as well as cost-effective production, SiC ceramic matrix composites reinforced by continuous carbon fibers (C/SiC) represent an interesting group of materials for high-temperature components for space propulsion systems [3–5]. Oxidation resistance and ablation resistance are very important properties in evaluating the usability of C/SiC composites. Cheng et al. intensively studied the oxidation resistance behavior of C/SiC composite prepared by low-pressure chemical vapor infiltration (LPCVI) [6–8]. Lee et al. studied the ablation characteristics of C/C composites in the presence of SiC coating [9,10]. Tang et al. studied the ablation behavior of C/C composites added with ZrB_2, SiC and HfC ceramic particles [11]; oxidation resistance and thermal shock resistance were improved. However, there are few reports about the ablation morphology and microstructure of SiC ceramic matrix composite reinforced by 2.5 dimension carbon fibers (2.5D C/SiC). The present paper is to investigate the ablation morphology and microstructure of 2.5D C/SiC prepared by LPCVI under oxyacetylene torch.

2. Experimental

2.1. Composite fabrication

M30 carbon fiber (from Toray, Japan), a type of mesophase pitch-based carbon fiber, was used as the reinforcement. The fiber preform was prepared using 2.5 dimensional braid methods and had an open porosity of 56%. Besides carbon fibers, the 2.5D C/SiC composite was composed of a pyrolytic carbon interfacial layer and silicon carbide matrix. The interfacial layer was prepared by LPCVI at 800 °C using

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C_3H_8 as precursor. SiC matrix was prepared by LPCVI at 1000 °C using CH_3SiCl_3 as precursor. Bubbling hydrogen was used as carrier gas to carry CH_3SiCl_3 vapor into reaction chamber. Argon was used as the dilute gas to slow down the deposition rate and hold the reaction chamber pressure at 5 kPa. The size of the C/SiC sample was Ø40 mm × 10 mm. In order to improve the thermal stability of the mechanical properties, the as-received samples were heat-treated in a vacuum at 1400 °C for 1 h.

2.2. Ablation experiment

The ablation performance of 2.5D C/SiC composite was characterized by oxyacetylene torch. The oxygen volume flow and acetylene volume flow were 1512 L/h and 1116 L/h, respectively. Oxygen pressure and acetylene pressure were 0.4 MPa and 0.095 MPa, respectively. The distance between the oxyacetylene torch and C/SiC specimen was approximately 10 mm. The nozzle tip diameter of the oxyacetylene torch was 2 mm. The heat flux of the combustion flame was 4186.8 ± 418.68 kW/m^2. The ablation time was 20 s.

2.3. Microscopic characterization

The morphology and microstructure of the as-ablated 2.5D C/SiC composites were examined by a scanning electron microscopy (SEM, FEI CO., Quanta200). The composition of the new phase was identified by an energy dispersive spectroscopy (EDS, FEI CO., Quanta200) and X-ray diffraction (XRD, Rigaku D/Max-B) using Ni-filtered Cu Kα radiation at a scanning rate of 0.5° s^{-1} and scanning from 15° to 80° of 2θ.

3. Results and discussion

Fig. 1 shows SEM photograph of the as-ablated 2.5D C/SiC composite. Three concentric annular regions can be observed on the surface of the ablated sample. The centre region was the core of oxyacetylene flame and its ablation was the severest in the three regions. Not only SiC matrix was sublimated or decomposed completely, but also some carbon fibers were sublimated. The sublimation temperatures of silicon carbide and carbon prepared by chemical vapor deposition are 2700 °C and 3550 °C, respectively [12]. It indicated that the temperature in the centre region was above 3550 °C. The middle region was covered by a white coating. The outer region was hardly ablated and still retained the as-received status.

In the centre region, the microstructure of the carbon fiber was changed. Fig. 2 shows SEM photograph of the naked fibers in the centre region. In general, ablation phenomenon was a combination of oxidation and erosion factors from high temperature, pressure, and velocity of oxyacetylene flame. Under the ablation temperature above 3550 °C, all of the following reactions possibly proceeded [10,13,14]:

$$SiC \rightarrow Si + C \quad (1)$$

$$SiC(s) \rightarrow SiC(v) \quad (2)$$

$$SiC + O_2 \rightarrow SiO_2 + CO \quad (3)$$

$$SiC + O_2 \rightarrow SiO + CO \quad (4)$$

$$SiO_2 + CO \rightarrow SiO + CO_2 \quad (5)$$

$$SiO_2 + SiC \rightarrow SiO + CO \quad (6)$$

$$C(s) \rightarrow C(v) \quad (7)$$

$$C + O_2 \rightarrow CO_2 \quad (8)$$

$$C + O_2 \rightarrow CO \quad (9)$$

$$C + H_2O \rightarrow CO + H_2 \quad (10)$$

The ablation mechanism of carbon fiber and SiC matrix in C/SiC composites was clearly different with oxidation behavior. When ablating, the end parts of the carbon fibers were tapered [15]. When oxidizing, the end parts of the carbon fibers were flat-bottomed [16]. 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 [17].

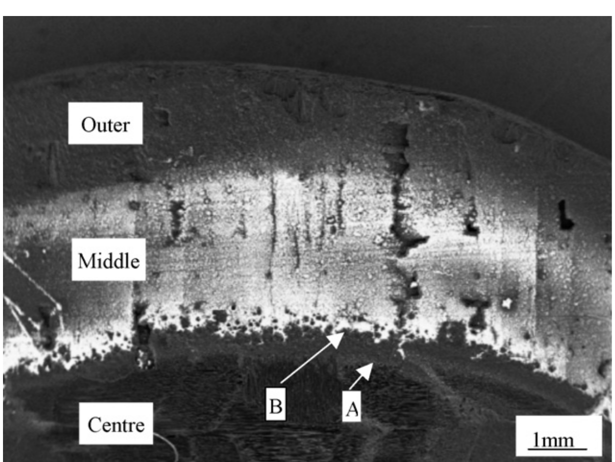

Fig. 1. SEM photograph of the as-ablated 2.5D C/SiC composites.

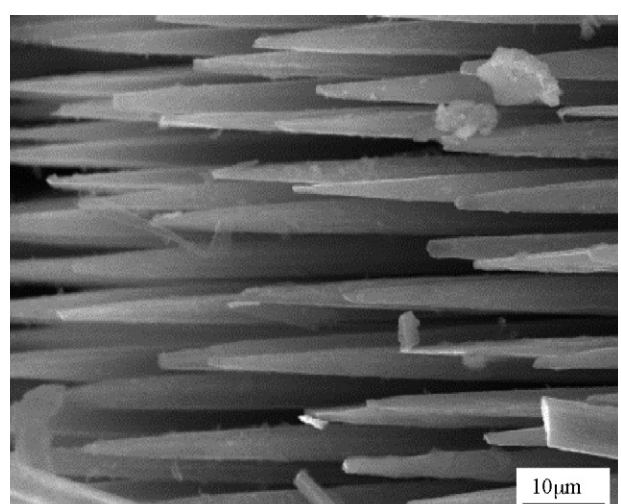

Fig. 2. SEM photograph of the naked fibers in the centre region.

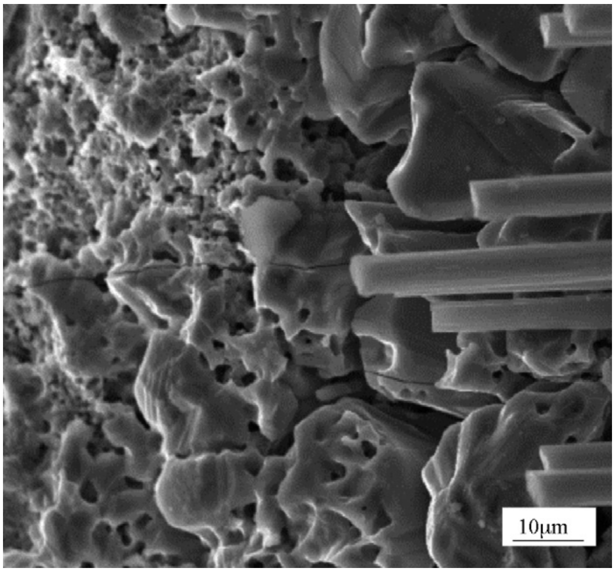

Fig. 3. SEM photograph of the area "A" in Fig. 1.

SiC matrix sublimated completely and carbon fibers were ablated to break off in the centre region. The temperature at the ends of the broken carbon fibers was the highest, so that the sublimation velocity of carbon element at the ends was the fastest down the longitudinal direction of the fibers. For the high thermal conductivity of carbon fibers [18], the heat quantity at the ends of the fibers quickly transferred down the longitudinal direction of the fibers. Besides the effect of the temperature field of the oxyacetylene flame, the part of the adjacency ends also sublimated. Because of the high thermal conductivity of carbon fiber and the difference of the sublimation velocity, the needle-like microstructures were formed. Sublimating ablation, a kind of thermo-physical attack, was the main ablation behavior in the centre region.

Fig. 3 shows SEM photograph of the area "A" in Fig. 1. Both of these circular holes and smooth edges of the particles were all resulted from the sublimating ablation of SiC matrix. Sublimation and decomposition of the deficient spot and the irregular edges always were faster than others, so that circular holes and smooth edges appeared. The flat-bottomed ends of carbon fibers indicated that oxidation was the main erosion behavior for carbon fibers. Except reaction (7), all of the others reaction could occur in the junction area. Because SiC matrix was sublimated and decomposed, the temperature at junction area could be above 2700 °C. SiO_2 resulted from reaction (3) could sequentially react to form SiO gas according to reaction (5) and (6), also directly gasify (SiO_2 boiling point 2230 °C).

Fig. 4 shows XRD pattern of the surface of the middle region. It indicated the white ring in Fig. 1 was silica coating. Temperature, pressure, and velocity of oxyacetylene flame in the middle region were lower than the centre region, so that the silica glass layer was not cleared away by the combusting airflow. Fig. 5 shows SEM photograph of the surface of the middle region. The temperature in the middle region must have been above the boiling point of silica, hence the silica film on the surface of SiC matrix bubbled up. So that, a lot of cicatrices of silica bubbles which had an uncertain morphology like a cross-section of lotus root overlaid the surface of the middle region. Each big cicatrix was composed of a lot of small hexagonal cicatrices. A large number of black spots located on the surface among or in the hexagonal cicatrices, were consistent with the small bubbles. The presence of melting and boiling silica could be confirmed by the microstructure. With regard to solidification theory, the typical and stable morphology of the solidified mass from liquid is an equiaxed structure in hexagonal form [19].

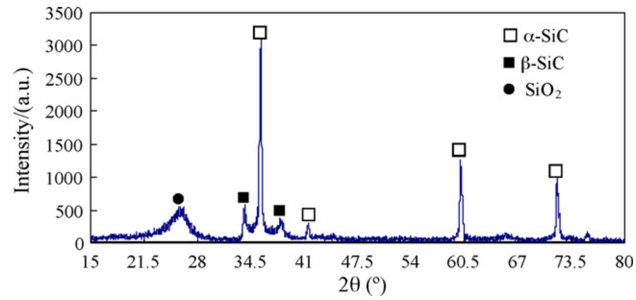

Fig. 4. XRD pattern of the surface of the middle region.

Fig. 6 shows SEM photograph of the area "B" in Fig. 1. There were some spherical particles and naked fibers in this region. For the poor wettability between liquid SiO_2 and carbon fibers, the liquid droplets of SiO_2 shrank into spherical particles during cooling process. SiC matrix was heavily eroded, then the fibers were naked.

Fig. 7 shows SEM photograph of the outer region. There were some white and spherical particles on the surface of the aggregates of SiC. Fig. 8 shows EDS pattern of the white particles in the outer region. It indicated the spherical particles were composed of SiO_2. Because there were not big SiC particles on the surface of C/SiC composites, the big SiO_2 particles must have been from the oxidation of Si and SiO steams which were from the centre region according to reactions (1), (4), (5) and (6). Si and SiO steams in the centre region were blown away by the oxyacetylene flame and floating

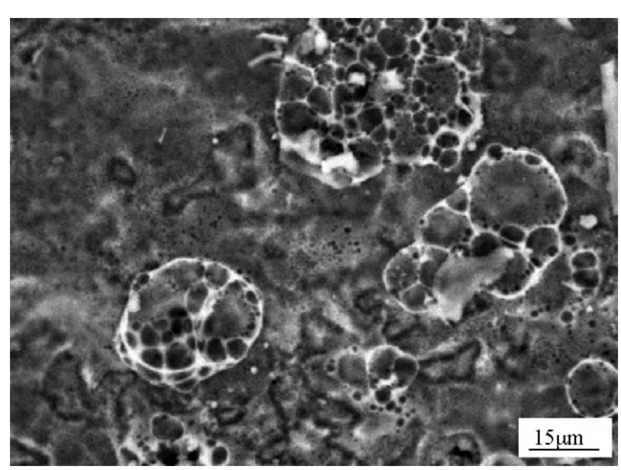

Fig. 5. SEM photograph of the surface of the middle region.

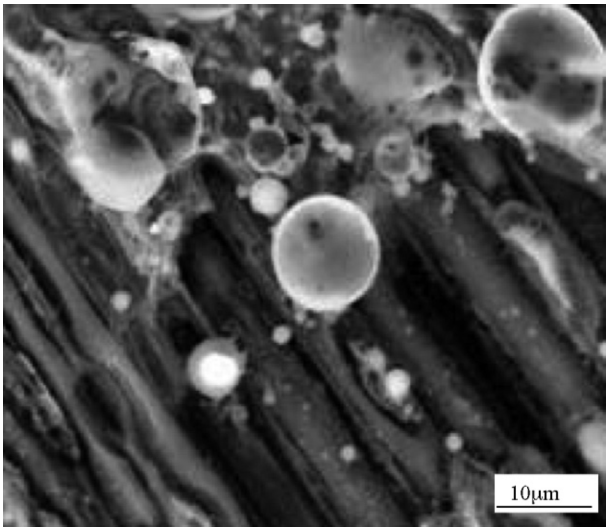

Fig. 6. SEM photograph of the area "B" in Fig. 1.

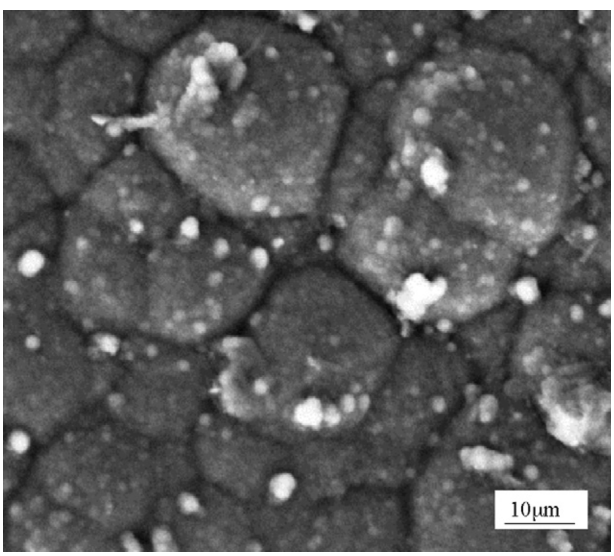

Fig. 7. SEM photograph of the outer region.

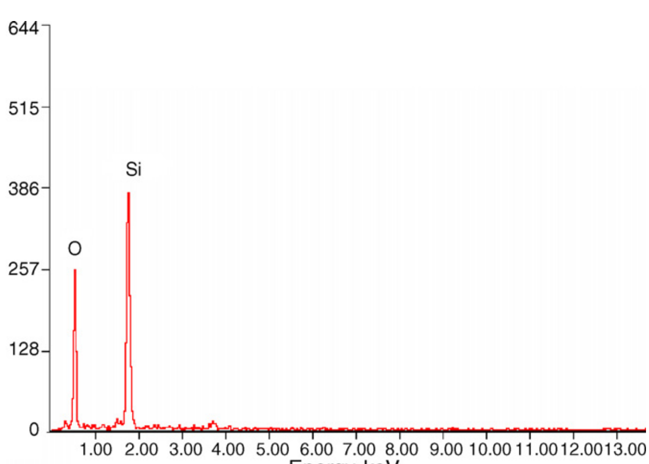

Fig. 8. EDS pattern of the white particles in the outer region.

in the combustion gas. When Si and SiO steams were oxidized, high-melting-point silica would be adsorbed by the outer region which had a relative low temperature. According to the gas dynamics [20], the condensation of the vapor would occur when the supersaturation degree reached the critical values. The condensation in the outer region would lead to the formation of liquid droplets which deposited on the surface of the composite and solidified to form silica particles.

4. Conclusions

(1) 2.5D C/SiC composites were prepared by LPCVI. Ablation morphology and microstructure evaluation was carried out by an oxyacetylene torch test. There were three clear regions on the surface of the as-ablated sample. Sublimation was the main ablation behavior in the centre region; oxidation was the main ablation behavior in the middle region. Silica particles in the outer region mainly resulted from the oxidation and deposition of Si and SiO gas. The ablation mechanism of C/SiC composites under the oxyacetylene flame was a combined effect of thermo-physical attack and thermo-chemical ablation.

(2) The ablated fibers had needle-like ends after SiC matrix sublimating in the centre region. Because of the high thermal conductivity of carbon fiber and the difference of the sublimation velocity in adjacency ends, a needle-like microstructure was formed.

Acknowledgement

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