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Electrophoretic deposition of carbon nanotubes for improved ablation resistance of carbon/carbon composites

Shen Qingliang, Li Hejun*, Zhao Fengling, Song Qiang*, Fu Qiangang

State Key Laboratory of Solidification Processing, Carbon/Carbon Composites Research Center, Northwestern Polytechnical University, Xi'an 710072, China

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ABSTRACT

CNTs have been introduced into C/C composites by electrophoretic deposition to improve their ablation performance. Mass ablation of C/C composites decreases by 64% with an optimized CNT content. Mechanical exfoliation is mainly responsible for the mass loss of C/C composites under oxyacetylene ablation as confirmed by SEM observations and static oxidation experiments. By applying CNTs with an optimized content, thermal conductance of the composites increases by 24.5% and the fiber-matrix interfacial strength increases by 74.6%. Local thermal damage is significantly relieved and matrix peeling off by high-velocity gas is inhibited, which lead to the significant decrease of mechanical ablation.

1. Introductions

C/C composites are important ultra-high temperature ablators for thermal protection systems [1,2]. They are generally applied in extreme working conditions where both excessive aerodynamic heating and surface friction exist [3,4]. C/C composites with lighter weight and higher strength but still capable of withstanding the high temperature environments are of great interests [5,6]. Unfortunately, the high ablation rate of C/C composites limits their service life and threatens the reliability of the thermal protection system [7,8].

Two main reasons are responsible for the high ablation rates of C/C composites [9]: (I) the oxidation of carbon matrix and fibers at high temperature (chemical ablation) [10]; (II) removal of both carbon fibers and matrix due to aerodynamic shear and particle impact (mechanical ablation) [3]. So far, coating [11,12] and matrix modification [13,14] using ultra-high temperature ceramics (UHTCs) are two primary methods to improve the ablation resistant ability of C/C composites. The coating technology mainly focuses on how to utilize UHTCs to prevent carbon fibers and matrix from oxidation. The matrix modification method mainly concerns with the decrease of ablation by replacing the carbon matrix with UHTCs. Both methods mainly focus on reducing the chemical ablation of C/C composites and have achieved remarkable improvements [15,16].

However, methods to reduce the mechanical ablation of C/C composites are still lacking. Improving the matrix cohesion and fiber-matrix bonding is the key to decrease the mechanical ablation [17,18]. Carbon nanotubes (CNTs) are suitable for enhancing both matrix cohesion and fiber-matrix interfaces due to their high specific strength and excellent thermal conductivity [19,20]. Applying CNTs as ablative materials has attracted intensive interests so far and the positive effects of CNTs on ablation-resistance performance are demonstrated by many researches. Zahra et al. introduced CNTs in CNT/ZrB_2/carbon/phenolic nanocomposite and excellent anti-ablation performance was realized [21]. Park et al. studied the effect of CNTs on the ablation properties of carbon/phenolic composites and found that the addition of CNTs enhanced the thermal conduction of the composites and minimized the local thermal damage [22].

However, in-situ growth of CNTs on carbon fiber directly [23,24] is not suitable for ultrahigh temperature ablation applications. It introduces a large amount of additional metal catalysts in the matrix, which will catalyze and further accelerate the oxidation process [25,26]. Thus, an alternative method for introducing CNTs without applying metal catalysts should be chosen to avoid the side-effects of in-situ growth for the ultra-high temperature ablation applications.

Electrophoretic deposition (EPD) is realized by the motion of charged particles in a suitable solvent under a DC electric filed [27], which has been proved to be a feasible method to prepare fiber-CNT hierarchical structures [28]. It avoids the utilizing of metal catalysts and offers a uniformly deposition of CNTs on complex fiber fabrics at a much lower cost compared with the in-situ growth of CNTs. EPD of CNTs on carbon fiber is an effect way to enhance both the matrix and fiber-matrix composites for C/C composites. Song et al. have demonstrated that by EPD of CNTs on carbon fiber, both the in-plane and out-of-plane strengths of C/C composites are significantly improved [29,30]. Based on the previous researches, it can be inferred that EPD of CNTs can help to decrease the mechanical ablation of C/C composites.

* Corresponding authors.
E-mail addresses: lihejun@nwpu.edu.cn (L. Hejun), plusring@163.com (S. Qiang).

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However, no researches have been reported in this topic so far and the ablation behaviors of EPD CNT reinforced C/C composites have not been systemically explored.

In the present work, it is demonstrated that for C/C composites, metal catalysts are avoided by introducing CNTs via EPD. Thermal conductivity and fiber-matrix interface are improved with the presence of CNTs. Subsequently, the mechanical ablation of C/C composites under oxyacetylene torch was significantly reduced.

2. Experiments and characterizations

2.1. Preparation of CNT-C/C composites

Carbon fiber cloth (T300, 1 K, obtained from Toray Inc.) were used as the starting materials. Detail descriptions for EPD of CNTs on carbon fibers are reported in our previous works [30,31]. To realize the EPD of CNTs on carbon fiber, multi-walled CNTs (97% purity, outer diameter in the range of 20–80 nm, ~10 μm in length, obtained from Timesnano Inc., China [32]) were dispersed in isopropyl alcohol with a concentration of 1.6 g/L to form CNT suspension. Carbon fiber cloth (140 mm × 140 mm) was fixed on the surface of the cathode plate and a steel plate was used as the anode. The working distance between the two electrodes was 20 mm and the working voltage was 50 V. Specially, the EPD time was kept for 2,4,6 and 8 min for obtaining different content of CNTs on carbon fibers (marked as fiber-CNT preform) and the average weight ration of CNTs for a 140 mm × 140 mm carbon fiber cloth is ~0.25%/min. The final composites with different EPD time (2, 4, 6 and 8 min) are marked as CNT-2-C/C, CNT-4-C/C, CNT-6-C/C and CNT-8-C/C.

For oxyacetylene ablation applications, C/C composites with rough layer matrix rather than smooth layer matrix are preferred. For the infiltration of rough layer pyrocarbon inside these preforms, the CVI process was carried out at 10 kPa and 1080 °C. CH_4 with a flow rate of 20 L/h was kept for 250 h without dilution gas. The final bulk densities of these obtained C/C composites were 1.70 ± 0.2 g/cm^3.

2.2. Ablation tests

Disk specimens (∅30 mm × 10 mm) were cut from the prepared composites and hand polished using 1200 grit abrasive paper. Then the specimens were ultrasonically cleaned for half an hour and dried at 80 °C for one hour before the ablation tests. The ablation tests were conducted according to GJB 323A-96 under oxyacetylene torch with a heat flux of 2.38 MW/m^2. The pressures of O_2 and C_2H_2 were 0.4 MPa and 0.095 MPa. The related fluxes of O_2 and C_2H_2 were 0.42 L/s and 0.18 L/s. The distance between the oxyacetylene torch nozzle and the tested sample was 10 mm and the inner diameter of the nozzle was 2 mm. The ablation angel was 90° and these ablation tests were carried out at room temperature and atmosphere pressure. The linear and mass ablation rates were calculated according to Eqs. (1) and (2):

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

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

where R_l is the linear ablation rate, μm/s; △d is the change of the sample thickness at center region before and after ablation, μm; R_m is the mass ablation rate, mg/s; △m is the mass change before and after ablation, mg; t is the ablation time, s.

2.3. Thermal conductivity tests

Thermal conductivity of the samples was measured by the laser flash method using a NETZSCH LFA427 system. Specimens with the dimension of Ø12.6 mm × 2.5 mm were used for the tests. To obtain the thermal conductivity of a specimen, the lower surface of the specimen was first heated by a laser pulse and the resulting temperature change on the upper surface was recorded using an infrared detector. Thermal conductivity λ of the composites was calculated by

$$\lambda = \alpha C_p \rho v \tag{3}$$

where α is the thermal diffusivity coefficient obtained by LFA427, C_p is the specific heat capacity at constant pressure, and ρ is the density of the composite.

2.4. Fiber bundle push-in tests

Fiber bundle push-in test is a method to evaluate the fiber-matrix bonding. The push-in test was carried out by loading a vertical fiber bundle with a flat-punch micro-indenter until the fiber-matrix interface between the bundle and the neighbor fibers fractured. The push-in tests were performed using a micro-hardness tester (NANOVEA MHT) with a flat-punch diamond micro-indenter (50 μm in diameter). The loading rate was 10 N/minute with a maximum load of 5 N. The applied load and the fiber bundle displacement, were recorded simultaneously until the final fracture.

2.5. Characterizations

The surface temperature of the specimen during the ablation was monitored by an infrared thermometer (Raytek MR1SCSF) in 2-color mode with an error of ± 0.75% during the ablation tests. The velocity field of the ablation process was simulated using Ansys Fluent software. Scanning electron microscopy (SEM, FEI NanoSEM450) equipped with energy dispersive spectroscopy (EDS) was used to characterize the surface morphology before and after ablation. High magnification microstructure of the matrix was characterized by a Tecanai F30 G^2 high-resolution TEM. The static oxidation behaviors of the samples were tested using a Thermogravimetric Analyzer (TGA, Mettler Toledo TGA/SDTA851) with an oxygen flow of 50 mL/min.

3. Results and discussions

3.1. Characterization of the CNT-pyrocarbon transition layer

Theoretically, the CNT content increases linearly with the EPD time. However, CNTs are of large specific surface area, which makes them easily agglomerate at a relatively large density. Fig. 1a shows the low magnification morphology of CNT film covered on carbon fiber with different EPD time. The density of CNTs increases with the EPD time and random distribution of the CNTs is observed. The CNT film covers the fiber surface homogenously when the EPD time increases from 2 min to 6 min while CNTs tend to agglomerate when the EPD time reaches 8 min.

Pyrocarbon can infiltrate into the CNT films and a dense CNT-pyrocarbon transition layer can be formed. Fig. 1b shows the typical cross-sectional morphology of the CNT-carbon fiber transition layer after the CVI process. The layered structure of the pyrocarbon is disturbed by the presence of CNTs. To better understand the microstructure of the transition layer, HRTEM image of the transition layer is provided (Fig. 1c). Amorphous carbon fills the gaps of the CNTs, which is consistent with our former research that CNTs can induce the presence of isotropic carbon [33].

3.2. Specification of the ablation environment

Fig. 2a shows the setups of the ablation process. The surface temperatures of the specimens were recorded by the infrared thermometer simultaneously. The thermometer data (Fig. 2b) show that surface temperatures of these composites increase sharply to 1950 ± 25 °C within ten seconds (Fig. 2b). Fig. 2c shows the simulated velocity filed