ABLATION PROPERTIES OF CARBON/CARBON COMPOSITES WITH TUNGSTEN CARBIDE THREADS

Jian Yin , Hongbo Zhang, Xiang Xiong, Boyun Huang, Jinlv Zuo

State Key Laboratory of Powder Metallurgy, Central South University, Changsha, China, 410083，

Abstract

The ablation rates of carbon/carbon (C/C) composites with tungsten carbide (WC) threads were investigated on an arc heater and their morphologies were observed by scanning electron microscopy (SEM). The ablation properties and morphologies between C/C composites with WC threads and the C/C composites using similar preforms and densification technology were compared. It shows that the ablation process of C/C composites with WC threads contains oxidation of carbon fibers, carbon matrices and WC, melting of WC and WO_3, together with denudation of WC, WO_3 and C/C composites. The ablation properties of C/C composites with WC threads are worse than that of C/C composites. Both the macroscopic and microscopic ablation morphologies of C/C composites with WC threads are different from those of C/C composites. The oxidation and melting of WC threads leading to formation of the holes in Z directional carbon fiber bundles promote the coarseness of the material and speed up the ablation process; In addition, the melted WC and WO_3 did not form a bed of continuous film on the ablation surfaces to prevent further ablation of the composites.

Keywords

carbon/carbon composites with WC threads， ablation property, ablation morphology

Introduction

Carbon/carbon (C/C) composites have superior characteristics of low density, high strength, excellent anti-friction and anti-wear, good thermal shock resistance, and extremely low ablation rate. These outstanding properties of C/C composites make them the essential candidate materials for high temperature applications, which is especially true for the ablation thermal-proof components in aerospace industry. With the development of new solid propellant, the conditions in rocket nozzles become even more severe. The requirements for nozzle materials are accordingly increased. In order to be used under the conditions with high load, high temperature and particle erosion for longer time, the properties of C/C composites have to be improved.

In order to sustain temperature higher than 3700K, refractory metal carbide must be added into C/C composites. For example, TaC, HfC and ZrC etc. have been added into C/C composites and their ablation properties were investigated.

Tungsten (W) has high melting point and good anti-erosion property. W and W based materials are widely used in high temperature fields. Adding W into C/C composites may exert the advantages of both C/C composites and W. Therefore, it may be a new approach to improve the ablation properties of C/C composites.

In this study, carbon fiber preforms with W threads in Z directional carbon fiber bundles were densified by chemical vapor deposition (CVD) and successive resin impregnation/carbonization process. After high temperature heat treatment, C/C composites with W threads would turn into C/C composites with WC threads. Then the properties of the new materials were investigated.

2 Experimental

Fine weaved preforms with W threads in the pierced carbon fiber bundles (Figure 1) were used as the reinforcements. The diameter of the W threads was about 100μm and the distance between pierced carbon fiber bundles was about 1.54mm. The preforms were firstly densified by chemical vapor deposition (CVD) process to about 1.30g/cm^3, followed by furan resin impregnation-carbonization process to final density of about 1.91 g/cm^3 prior to heat treatment at 2300℃. During the process of CVD and heat treatment process, W and carbon around it would react with each other to form WC, and consequently, W threads change into WC threads. As the result, the C/C composites with WC threads could be prepared (sample A). This process is mainly caused by the diffusion of carbon atoms into W threads since W is the slower diffuser here.

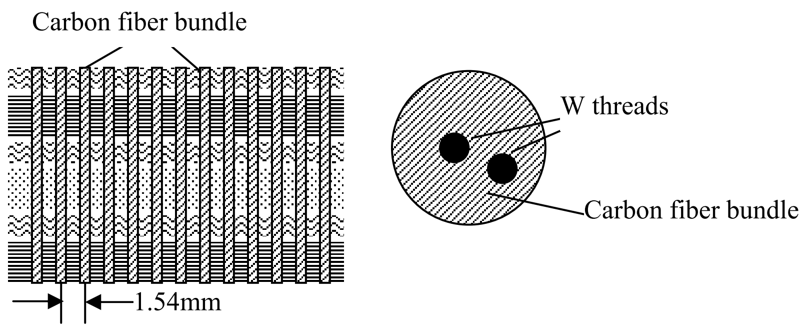

Figure1. Sketch of the prefrom

To further describe the ablation properties of C/C composites with WC threads, C/C composites (sample B) using similar preforms and treating process were prepared and the final density of sample B was about 1.80g/cm^3.

Stagnation ablation experiments for the C/C specimens were performed on a high-pressure arc heater, who works in a similar way to the electric welding machine widely used in industry. High temperature cool air is heated up and ionized to form a high temperature air ionization channel between two electrodes in the arc heater under high voltage or strong current flow. Through a taper nozzle, the air plasma flame spurts out, with temperature adjustable. This method can be used to investigate ablation mechanisms and help to select thermal-structure materials.

The following parameters were chosen to test the ablation rates of both sample A and B:

Stagnated pressure (MPa): 4.35

Thermal enthalpy (MJ/kg): 4.96

Stagnated heat current (MW/m^2): 22.1

Ablating time (s): 3

Microstructures and ablation morphologies of sample A and B were investigated by scanning electron microscopy (JSM-5600LV).

3 Results and discussions

3.1 Microstructures of C/C composites with WC threads

Figure 2 presents the cross-section of one single W thread which had the same CVD process as that of C/C composites with W threads for comparison. It's found that a pyrolytic carbon layer was equally deposited on the surface of the W thread and diameter of the W thread still kept 100µm. The EDS figure (Figure 3) shows that carbon can be found at the centre of the W thread. After heat treatment, X-ray analysis verified that W thread had been turned into WC thread. In addition, the combination between pyrolytic carbon layer and WC thread was loose. It might be caused by the different shrinkage rate between WC and pyrolytic carbon during the cooling process because there are great differences of thermal expanding coefficients between them. Figure 4 presents SEM photo of the distribution of WC threads of C/C composites with WC threads. It was found that WC threads were in the pierced carbon fiber bundles. But there was just one WC thread left in some of the carbon fiber bundles because WC is crisp and WC threads was broken during the machining process.

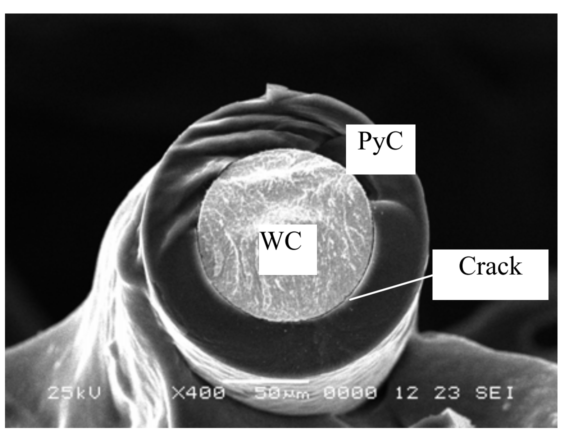

Figure 2. Cross-section of one single W thread after CVD

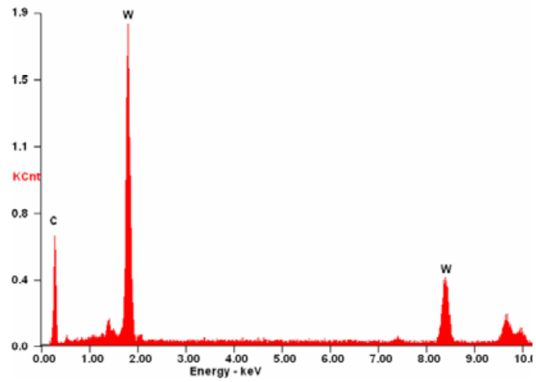

Figure 3. EDS analysis of W threads in sample A

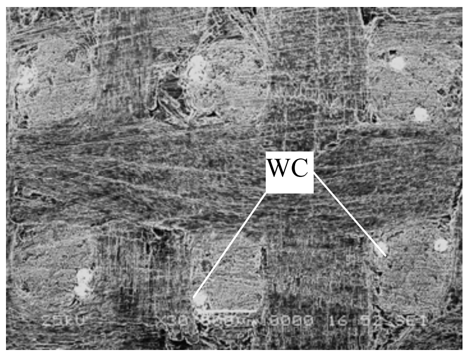

Figure 4. Distribution of WC threads in C/C composites

3.2 Properties of C/C composites with WC threads

Table 1. Properties of C/C composites with and without W

Index	A		B	
Direction	Z	XY	Z	XY
Density/g•cm^{-3}	1.91		1.78	
Graphitization degree/%	79.4		62.4	
Compressive strength /MPa	163.20	113.20	224.31	138.37
Shearing strength/Mpa	15.4	10.10	19.91	23.77
Linear ablation rate/(mm.s^{-1})	1.6		0.774	
Mass ablation rate/(g.s^{-1})	0.69		0.274	

Table 1 presents the properties of C/C composites with and without WC. Although the density of sample A was higher than that of B, the mechanical properties including compressive strength, shearing strength were worse. For sample A, W would react with the carbon matrices and carbon fibers nearby, thus weaken the mechanical properties of the material. In addition, By analyzing the structure of sample A, the connection between the WC threads and C/C composites were weak, which couldn't transfer the load to WC threads. Moreover, WC is crisp and it is easy to be broken under the outside force. Furthermore, because the linear expanding coefficient of WC（$3.7\times10^{-6}K^{-1}$） is much larger than that of carbon fibers, during the processes of CVD, carbonization and heat treatment, stress mismatch occurs between the WC threads, carbon fibers and matrices thus leading to the failure of the carbon fibers and cracks in the composites. All those factors would cause the descent of the mechanical properties. With regard to the ablation properties, no matter linear ablation rate or mass ablation rate, sample A was much better than sample B. Therefore, the ablation properties of C/C composites with WC were worse than that of C/C composites without WC threads, which indicated that the method of adding WC into C/C composites has to be improved.

3.3 Ablation Morphologies

Figure 5 shows the macro-morphologies of sample A and B. The ablation morphologies of sample A were quite different from that of sample B. On the ablation surface of sample B, there was a big platform retained, and around it the surface became rugged. It was obvious that the ablation process was mainly determined by block denudation. However, on the surface of sample A, there were disciplinary distributed holes at the locations of Z directional carbon fiber bundles and remnants caused by oxidation of WC in the holes.

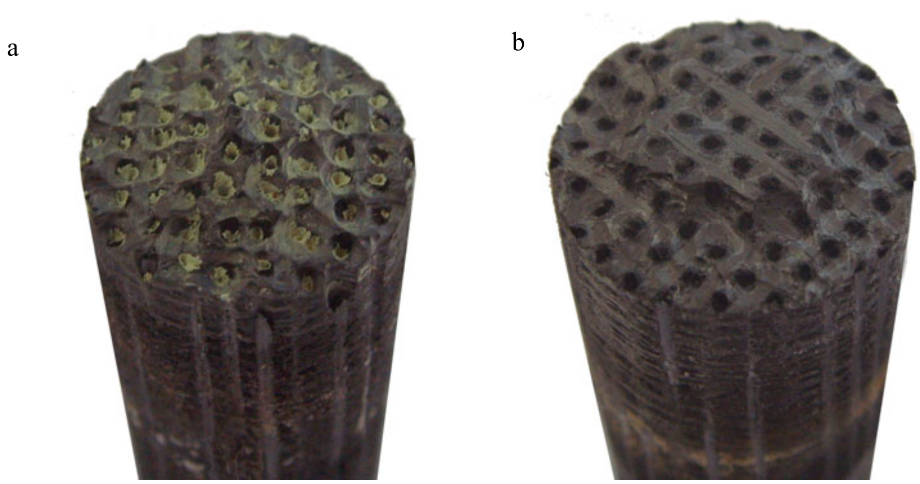

Figure 5. Macro-ablation morphologies of sample A and B

a- sample A   b- sample B

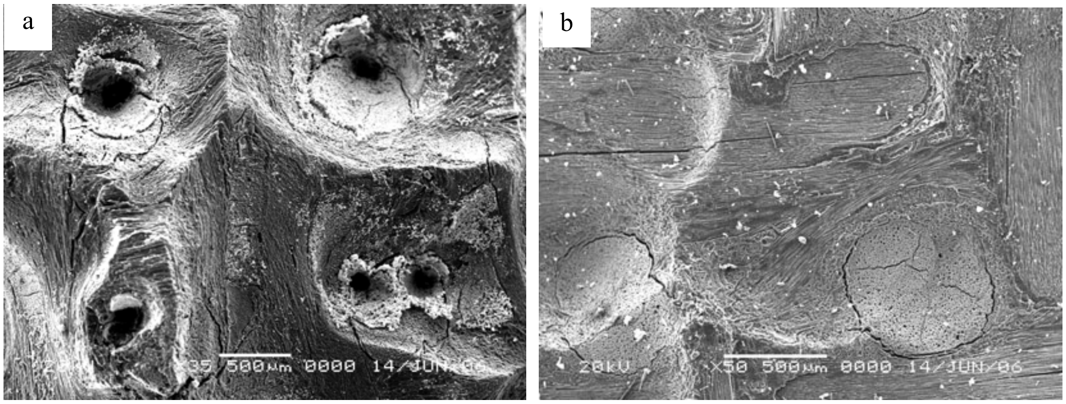

Figure 6. Macro-ablation morphologies of sample A and B

a- sample A b- sample B

Figure 6 presents the SEM images of macro-ablation morphologies of C/C composites with and without WC threads, from which it can be seen that the surface of sample B is much smoother than sample A. There were a lot of cracks were formed at the boundaries of the Z directional carbon fiber bundles, in the unidirectional carbon fiber layers and the disordered carbon fiber layers and the interior of each layer. Different from sample B, a lot of holes in sample A were formed right at the original locations of WC threads before the ablation process. Furthermore, the diameters of most holes were bigger than those of the WC threads (100μm). Those holes caused the rough surface of the material.

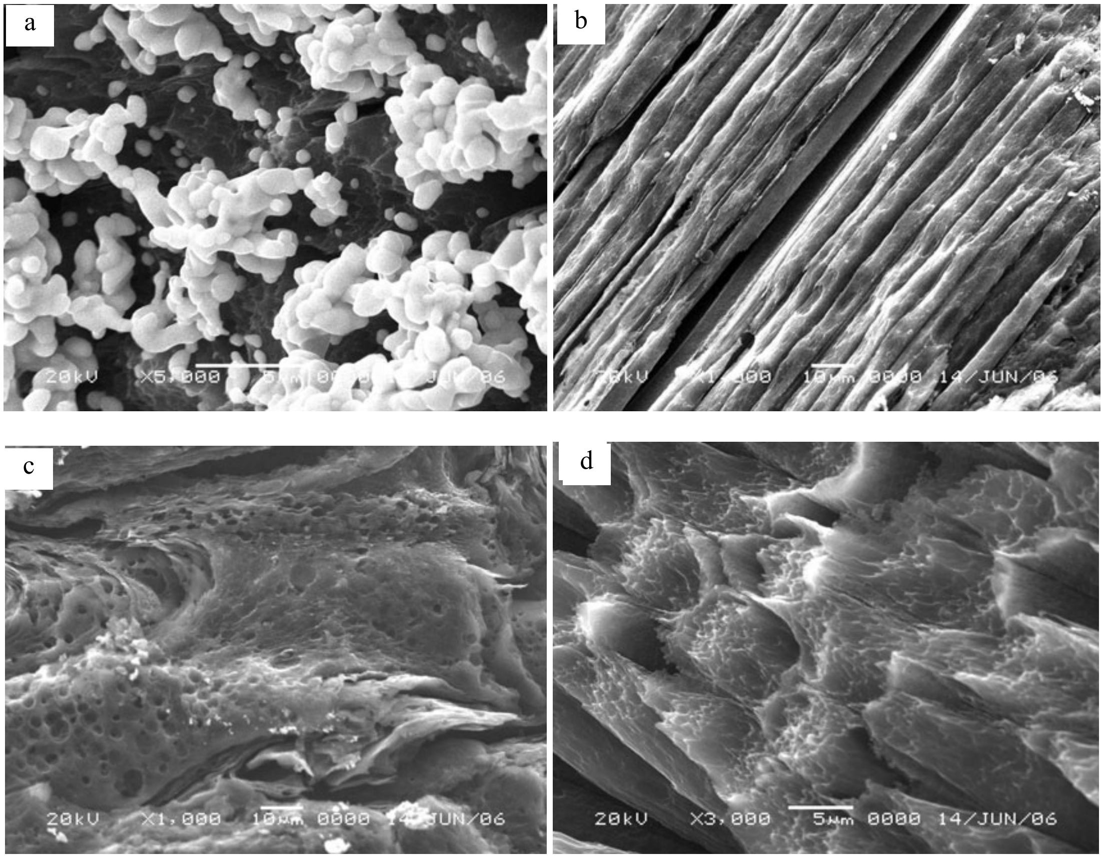

Figure 7. Micro-ablation morphologies of sample A

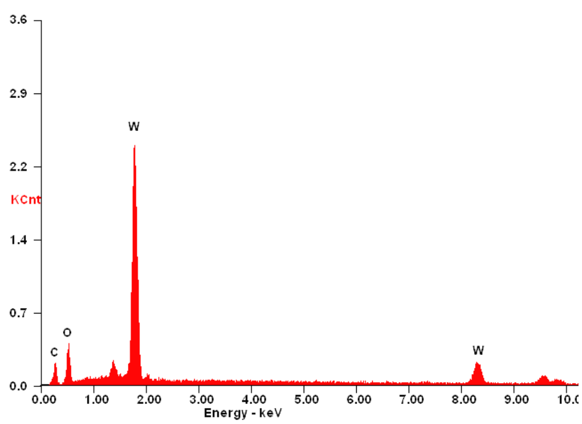

Figure 8. EDS analysis of ablation surface of sample A

Figure 7 presents the micro-ablation morphologies of sample A. The micro-ablation morphologies were also different from those of C/C composites. From Figure 6, it can be seen that there were a bed of matters covered on the wall of the holes. Magnified in figure 7a, it's found that the matters were dispersed and didn't form a continuous film on the ablation surface. From figure 8, it can be seen that the matters were composed of C, O and W. They might be WO_3 and WC. Underneath these matters, the ablation mode of C/C composites with WC threads was also different from the C/C composites without WC threads. Ablation wouldn't spread along the cracks and interfaces into the deep of the sample A because WO_3 and WC had efficiently prevented oxygen diffusing to the material. The carbon fibers besides the holes (figure 7b) were seriously eroded. Within the area with big block of matrices, ablation characteristic of start at the interfaces in priority can be easily observed, but on the surfaces of the matrices there were a lot of pits (figure 7c). There were also a lot of pits on the heads of carbon fibers (Figure 7d) which were quite different from that of C/C composites without WC threads. Obviously, the ablation morphologies of carbon fiber heads and matrices were related to W. Because WO_3 would react with carbon around it, which led to the change of the surface morphology and surface energy, thus part of the surface would be ablated.

3.3 Ablation process

The ablation process and mechanism of C/C composites with WC threads were very complex. When the ablation gases reached the surfaces of the material, the temperature of the material would rapidly rise. With the elevating of temperature, the oxidation gases would react not only with carbon in fibers and matrices but also with WC. Because the reacting velocity was much less than the diffusion speeds of the gases, the oxidation process was controlled by chemical dynamics process. In addition, the bonding energy of WC is very high thus it requires a lot of energy to break W-C bonding, therefore the increasing speed of temperature and the ablation process of the material would slow down. With further increase of the temperature, the oxidation velocity rapidly increased and the ablation process would be controlled by both chemical dynamics process and diffusing process of the gases. At higher temperature, the diffusion speed of the gases would be less than the oxidation velocity, so, the ablation process would be controlled by diffusion process of the gases.

During the ablation process, WC (Melting point: 2780K) and WO_3 (Melting point: 1746K) would melt and more complex ablation phenomenon would appear. the melted WO_3 and WC would flow on the ablation surface and fill in the interfaces, cracks and pores of the material. The liquid matters filled in the interspaces, cracks and pores would effectively obstruct the diffusing channels of the oxidation gases, thus, it would obviously intercept the priority ablation in interfaces, cracks and pores in C/C composites and made the Z directional carbon fibers not be ablated into needled shape or blunt shape like C/C composites without WC threads. In addition, part of the liquid matters would be blown off under the strong ablation gases. Part of the melted WC and WO_3 would splash about, and holes would be formed at those original locations of WC threads, which greatly increased roughness of the ablation surface. Therefore, the melted WC and WO_3 couldn't flow over the bulges and cover the ablation surface. The coarse ablation surface would change the state of the ablation gases and arouse separated vortex effect and heating area increasing effect. Thus, the ablation speed of C/C composites with WC threads would be speed up. In summary, the melted WC and WO_3 provided small areas of fluent surface, but on a whole, WC increased the roughness of the ablation surface and didn't protect C/C composites well.

Furthermore, , the mechanical properties of C/C composites with WC threads were worse than those of C/C composites without WC threads. In addition, during the ablating process, melting of WC and formation of the holes would further weaken the mechanical properties. With weaker mechanical properties, C/C composites with WC threads couldn't endure the strong erosion of the ablation gases. During the rapid increase process of the temperature, C/C composites and W threads would expand, but the expansion coefficient of carbon and WC are quite different, thus, some residual stress would be formed in C/C composites with WC threads and the composites were easier to fail.

Seen from the above analysis, the ablation process of C/C composites with WC threads included: Oxidation of carbon fibers and carbon matrices; Oxidation of WC; Melting of WC and WO_3; Denudation of WC and WO_3; Denudation of C/C composites and coupling of the above. And these processes were cycled, stimulated and coupled with each other.

4 Conclusions

The ablation properties of C/C composites with WC threads were worse than those of C/C composites.

The ablation process of C/C composites with WC threads includes: oxidation of carbon fibers, carbon matrices and WC, melting of WC and WO_3, together with denudation of WC, WO_3 and C/C composites. And these procedure was cycled, stimulated and coupled with each other.

The oxidation and melting of WC threads can cause the holes in Z directional carbon fiber bundles, which increase the roughness of the material and speed up the ablation process. In addition, the melted WC and WO_3 will not form a bed of continuous film on the ablation surfaces to prevent ablation of the material.

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