THE EFFECT OF INTERCALATION ON MICROSTRUCTURE OF C/C COMPOSITES[*]

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Abstract

In order to improve the interface bonding stage, the pyrolytic carbon deposited on carbon fiber surface was intercalated to be used as transition layer between fiber and matrix. The microstructure of the as-received C/C composites were studied by polarized light microscopy (PLM), field emission scanning electron microscopy (FESEM), conventional and high resolution transmission electron microscopy (TEM, HRTEM) techniques respectively. The results show that the microstructure of the C/C composites has a big change after intercalation. Under PLM the grow cones of C/C composites with intercalation are smaller in size but more in quantity than C/C composites with no intercalation. Intercalation results in many defects which further affect the boundary of grow cones so that the texture is a little different. The texture is a mixture of rough and smooth laminar in intercalated C/Cs and smooth laminar in free-intercalated C/Cs. The results from FESEM show that the intercalated layer is characteristic of many pores, which is recognized to change the bonding stage between fiber and pyrolytic carbon so as to improve mechanical properties of C/C composites, especially toughness. The intercalated pyrolytic carbon take on laminar structure under TEM and the lattice fringes are the preferrally orientated under HRTEM. For the pyrolytic carbon of C/C with no intercalation the lattice fringes are turbostratic.

Keywords: Carbon/carbon composites; Microstructure; Intercalation; Interface.

Introduction

Carbon fiber reinforced carbon composite (C/C composite) has been the most expected material to be used for high temperature structures such as aerospace structures, utilizing its high mechanical properties and superior heat resistance. However, there can be large variations in the properties of C/C composites because of the type of carbon fiber reinforcement, the type of carbon matrix and the interfacial bonding strength between fiber and matrix. And at the same time it was reported that the desired mechanical properties could be attained by controlling the microstructure of the carbon matrix and/or by controlling the fiber matrix bonding through the proper choice of carbon fibers and their surface treatment. In order to get C/C composites with high mechanical properties the fiber of high strength and/or high modulus should be chosen. The different carbon fibers mean the different mechanical properties contributed to C/C composites. Many works in literature report the study of making the surface of the reinforcing fibers more or less active by surface treatment using many methods. The results show that the surface treatment is very efficient to improve the mechanical properties of C/C composites. Whereas these methods are mainly used in resin matrix C/C composites, because the active function group will decompose under the high temperature of 1173–1273 K used in chemical vapor deposition (CVD) process. Actually the action of fiber on pyrolytic carbon is

mostly of joggle function other than chemical action in CVD process. The topology of fiber surface mainly dominates the bonding stress of fiber and matrix. Therefore, in this study we consider adding transition layer between carbon fiber and pyrolytic carbon in order that the bonding stage may be changed and the fracture resistance of C/C composites may be improved. Based on the result of intercalation made in our work, we think that the intercalated pyrolytic carbon layer offers a flexile structure which may absorb external energy to keep C/C composites from destroying abruptly. In this paper the effect of intercalation on microstructure of C/C composites will be discussed.

Experimental

Preparation of C/C composites

The preforms used in this experiment were prepared by lamination technique with 1K high-strength PAN carbon woven cloth (Jilin Carbon Company, China). The fiber volume fraction of preforms was controlled to about 40%. The whole manufacture is divided into four steps. Firstly, the preforms were put into the deposition furnace to progress pre- deposition for 150h. The chemical vapor deposition (CVD) process was operated under negative gas pressure with propylene as precursor and nitrogen as carrier. The deposition temperature was controlled in the range of 1173–1273 K. Secondly, the pre-deposited preforms were graphitized in 2873K for 2 h. Thirdly, the pre-deposited preforms were dipped into liquid bromine in sealed equipment for 48h at room temperature. This step is called intercalation. After the reaction finished, the preforms were taken out and placed in a ventilation chamber for volatilization of absorbed bromine, and then they were washed and dried at 393K for 2 h. Finally, preforms were further densified using CVD process for several hundred hours to obtain the C/C composites for the further mechanical testing. The reference C/C composites was deposited in same parameters but free-intercalated.

Characterization of C/C Composites

Optical microscopy under cross-polars was used to characterize the texture of the C/C sample. A piece of the sample is cut, mounted in epoxy and polished parallel to the needle direction (perpendicular to the fabrics) and then observed under OLYMPUS PM-T3 optical metallographic microscope.

JSM-6700F FESEM (field emission scanning electron microscopy) were applied to observe the fracture surface and the interface morphology of the sample after mechanical test.

For the TEM studies (JEOL-2010 transmission electron microscope at a voltage of 200KV with a point resolution of 0.194nm and lattice resolution of 0.14nm), the composites were mechanically ground and polished. Specimens about 500μm thick were sliced from blocks of the composites using a diamond saw. Three millimeter diameter discs were cut from such slices using a drill press. These discs were mechanically dimpled (Gatan 656 mechanical dimpler) to a thickness of roughly 10μm (a 3μm diamond pastes was used for the final stage of dimpling). The dimpled discs were then atom milled using a Gatan 691 ion miller. A beam current of 24μA at 5.0kV and an initial incident angle of 8-6° were used. With the increasing time of milling the atom bombarding angle were lowed to 4-2° until perforation occurred. The duration of the ion thinning process was 10-30h according to different samples.

Results and discussion

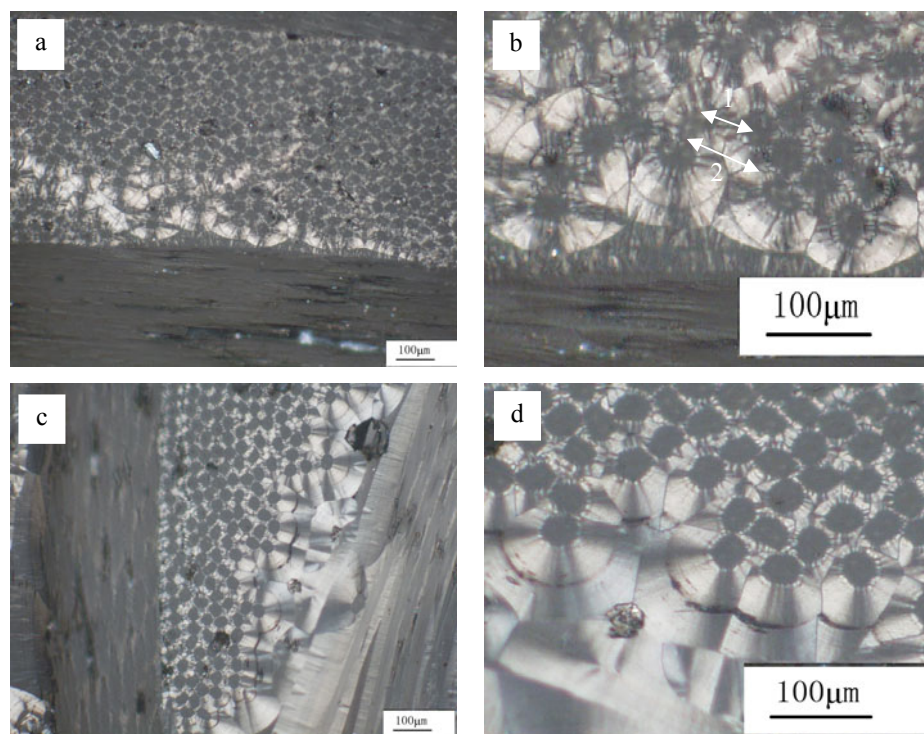*Polarized light microscopy*

Fig.1 PLM photographs of C/C composites

(a) (b) intercalated C/Cs   (c)(d) free-intercalated C/Cs

Optical observation under polarized light is classically the first characterization performed on the matrix. Fig.1 (a) and (c) showed the texture photographs of intercalated C/C and free-intercalated C/C composites using polarized light microscope. Fig.1 (b) and (d) are the partial magnification of Fig.1 (a) and (c) respectively. Cross-sectioned fibers are observed which are surrounded by concentric pyrolytic carbon layers. The black rings, which are observed between layers, may result from the deposition interruption during long time deposition. According to the conventional classification of different texture presented by Pierson and Liberman, the texture of the intercalated C/C composites (Fig.1a,b) is a mixture of rough laminar(layer 1, showed in white arrow) and smooth laminar(layer 2, showed in white arrow). While in the fig.1(c) and (d) the texture is mainly consisted of smooth laminar (layer 2). Meanwhile, when compared with the morphology of growth cone around the fibers an interesting phenomenon was found. The growth cones of C/C composites with intercalation are smaller in size but more in quantity than C/C composites with no intercalation at a glance. As we known that the growth cones are composed of sub-small cones. Many sub-small cones diffuse and grow slowly during deposition so that sub-small cones become a small cone. As a result, sub-small cones in large quantity appear 'smooth' with the boundary between sub-small cones disappearing, and contrariwise in small quantity appear 'rough' with the boundary broad.

X. Bourrat analyzed Coffin's model and then brought forward that cones are not the result of "crystal growth", but the amplification layer after layer of a defect, because of the 'ever-increasing size' with the continuing deposition of this simple process. So it can be deduced that small cones are related to small defects of the growing graphene layers themselves in the case of growing laminar.

Thereby this may educe that the intercalation may cause the defect of grapheme layer.

On the other hand, intercalation means that a kind of foreign matter was introduced into the graphite lattices using chemical and/or physical method so that graphite lattices gave birth to defect and the property of graphite was changed effectively. The intercalated compounds are called graphite intercalated compounds, in short, GIC. GIC can maintain the structure of their parent graphite, but the interlayer crystal space d(002) increases because of the external substance inserted in the interlayer. In this work bromine was used as intercalater and the pre-deposited pyrocarbon was intercalated by bromine. In our former result, intercalation was affirmed in graphitized pyrolytic carbon. So it is reasonable to consider that intercalation results in the defects which were prone to induce the formation of growth cones. So compared with free-intercalated C/C composites, more defects were brought for intercalated C/C composites. The defects grow into the sub-smaller cones up to many small cones. The boundary between small cones didn't diffuse during the deposition process so that they appears rough lamellar. For the free-intercalated C/C composites the deposited pyrolytic carbon coating has fewer defects so that sub-small cones grow into a big cone in size which appears smooth lamellar. The sub-small boundaries between sub-small cones disappear during the diffusion and grow progress.

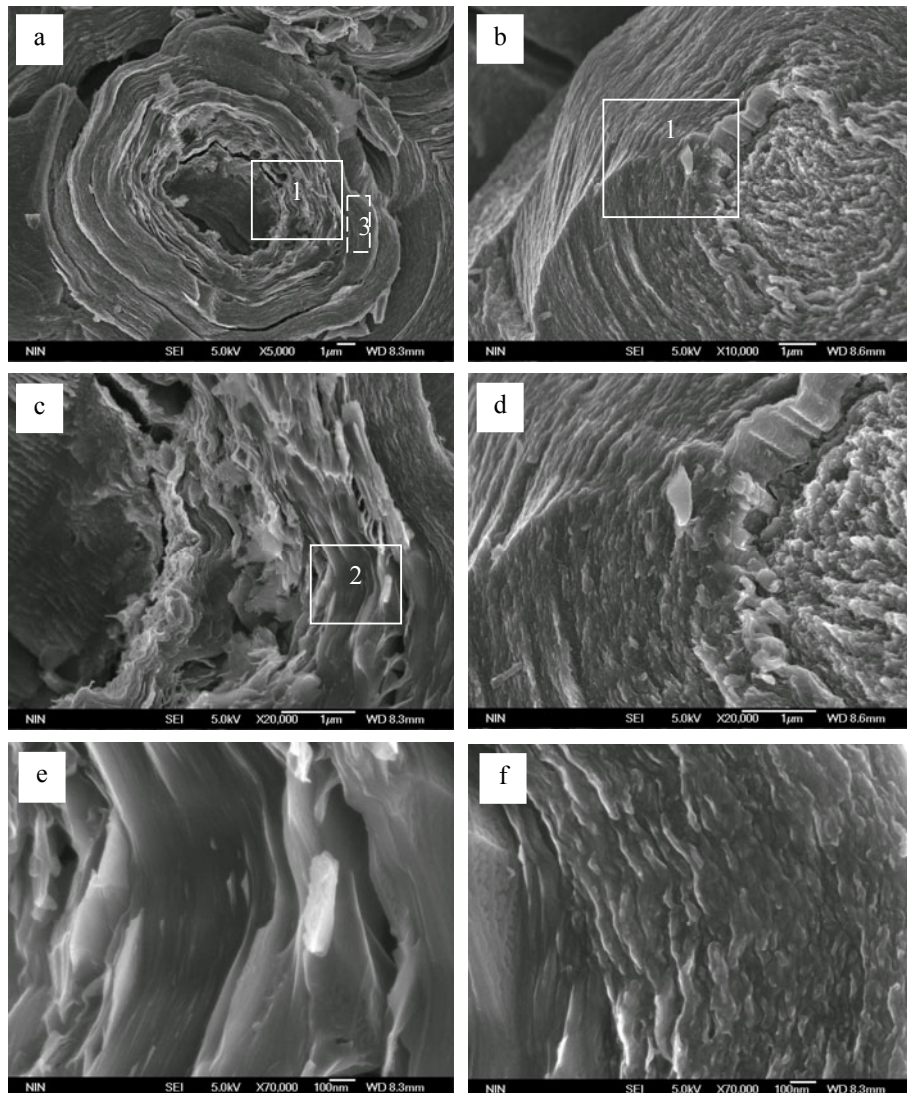### Scanning electron microscopy

Fig.2 SEM photographs of C/C composites

(a,c,e,f) intercalated C/Cs (b,d) free-intercalated C/Cs

Fig.2 is the fracture surface photographs of C/C composites, Fig.2 (a) is for the intercalated C/C composites and (b) for the free-intercalated C/C composites, (c) and (d) are the further magnification of the contact area-marked by the white rectangle 1 of Fig.2 (a) and (b) respectively, (e) and (f) are the magnification of the contact area-marked by the white rectangle 2 in Fig2(c) and 3 in Fig.2(a). The pyrolytic carbon coating next to the fiber was coated under same deposition parameters for two kinds of C/C composites. According to the description from Reznik about the morphology of pyrolytic carbon of the smooth and rough laminar, the texture of Fig.2(e), (f) and (d) are belong to rough laminar, smooth laminar and smooth laminar respectively which are consistent with that of Fig.1. For the intercalated C/C composites, the pyrolytic carbon coating looked like porous and crack appeared at the interface partially after intercalation. So we can deduce that the porous structure are caused by intercalation. Bromine was intercalated into the graphite microcrystals of pyrolytic carbon coating, then was deintercalated at high temperature. The graphite microcrystals of pyrolytic carbon coating expanded after deintercalation and the porous structure came into being. According to the relationship of property and structure of materials, the porous structure may affect the mechanical property of C/C composites. From our former results about mechanical property of C/C composites, the porous structure was in favor of improving the toughness. On one hand, the porous structure may absorb external energy by its deflection on a certain extent. On the other hand, the pores may slowered the speed of crack propagation and deflexed the path of crack propagation so that more energy were consumed.
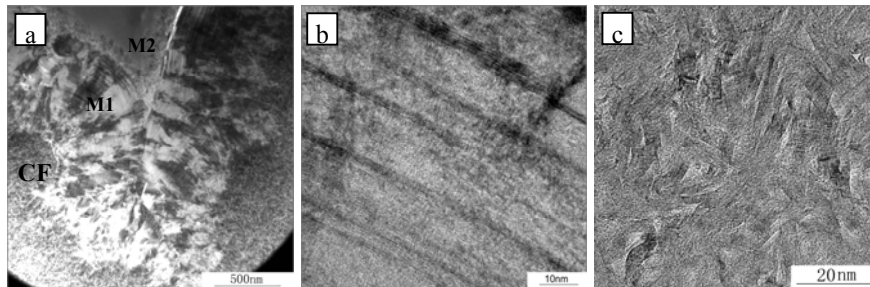
Transmission electron microscopy

Fig.3 TEM images of intercalated C/C composites

(a) Low magnification TEM image (b) HRTEM image of M1 (C) HRTEM image of M2

Fig.3 is a representative TEM image of the intercalated C/C composites. Fig.3 (b) is the HRTEM image of M1, the intercalated pyrolytic carbon matrix. Fig.3 (c) is the HRTEM image(c) of M2, the free-intercalated pyrolytic carbon matrix. There are big difference between Fig.3 (b) and Fig.3(c). Fig.3(c) is the same to the free-intercalated C/C composites. From the Fig.3 (b), the intercalated pyrolytic carbon take on laminar structure and the lattice fringes looked preferentially orientation, which was considered as the phenomenon of crystal dislocation. While the lattice fringes looked tortuous for the Fig. (c), which was considered as the phenomenon of turbostratic structure of pyrolytic carbon. Why did the intercalation change the microstructure of pyrolytic carbon? High resolution does not give any straightforward response. This point is still open and need be discussed later.

Conclusion

(1) Pyrolytic carbon deposited on the surface of carbon fiber was intercalated by bromine.

(2) Under PLM the grow cones of C/C composites with intercalation are smaller in size but more in quantity than that of free-intercalated C/C composites. Intercalation results in many defects which further affect the boundary of grow cones so that the texture is a little different.

(3) The results from FESEM show that the intercalated layer is characteristic of many pores, which is recognized to change the bonding stage between fiber and pyrolytic carbon so as to improve mechanical properties of C/C composites, especially toughness.

(4) The intercalated pyrolytic carbon take on laminar structure under TEM and the lattice fringes are the preferrally orientated under HRTEM. For the pyrolytic carbon of C/C with no intercalation the lattice fringes are turbostratic.

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