© Applied Science Innovations Pvt. Ltd., India Carbon – Sci. Tech. 1 (2010) 139 - 143

Carbon – Science and Technology

ISSN 0974 – 0546

http://www.applied-science-innovations.com

ARTICLE

Received :29/03/2010, Accepted :02/09/2010

Ablation morphologies of different types of carbon in carbon/carbon composites

Jian Yin, Hongbo Zhang, Xiang Xiong, Jinlv Zuo

State Key Laboratory of Powder Metallurgy, Central South University, Lushan South Road, Changsha, China.

---

1. Introduction : Carbon/carbon (C/C) composites combine good mechanical properties and designable capabilities of composites and excellent ultrahigh temperature properties of carbon materials. They have low densities, high specific strength, good thermal stability, high thermal conductivity, low thermal expansion coefficient and excellent ablation properties [1]. As C/C composites show excellent characteristics in both structural design and functional application, they have become one of the most competitive high temperature materials widely used in aviation and spacecraft industry [2 - 4]. In particular, they are considered to be the most suitable materials for solid rocket motor nozzles.

C/C composites are composed of carbon fibers and carbon matrices. Carbon fibers are framework which determines the mechanical properties of C/C composites. Structural and mechanical properties of carbon matrices have great influences on properties of C/C composites, as well. Carbon matrices combine carbon fibers together, keep the arrangements of carbon fibers and fill in pores of C/C composites. As far as stress distribution is concerned, carbon matrices can transfer external force to carbon fibers.

Structures and types of carbon matrices are determined by the densification process of C/C composites. The main methods to manufacture C/C composites include chemical vapor deposition (CVD) and liquid impregnation-carbonization with resin or pitch. Based on its structural characteristics, pyrolytic carbon can be divided into smooth laminar pyrolytic carbon, rough laminar pyrolytic carbon and isotropy laminar pyrolytic carbon. Structures and types of carbon matrices and carbon fibers will affect ablation properties of C/C composites [5-8]. In order to select suitable preparation technique and explore ablation mechanism of C/C composites used as thermal-structural components, it is important to investigate the ablation morphology and formation mechanism of each types of carbon.

In this study, ablation morphologies of resin-based carbon, carbon fibers, pyrolytic carbon with smooth laminar structure and rough laminar structure has been investigated in detail and their formation mechanisms were discussed.

2 Experimental :

2.1 Preparation of C/C composites : Bulk needled polyacrylonitrile (PAN) carbon fiber felts were used as reinforcements. Three kinds of C/C composites, labeled as sample A, B and C, were prepared. Sample A is a C/C composite mainly with smooth laminar pyrolytic carbon, sample B is a C/C composite mainly with rough laminar pyrolytic carbon, and sample C is a C/C composite merely densified by impregnation-carbonization with furan resin. Both sample A and B were first densified by CVD with C_3H_6 and then by impregnation-carbonization. But, pyrolytic carbon structure of sample A was different from that of sample B because of different treat temperatures and temperature rising rates during CVD. Sample A, B and C had similar densities and they were all treated at high temperature of 2300 ^oC.

2.2 Ablation test : Ablation experiments of C/C composites were performed on a high-pressure arc heater (Figure 1). In the arc heater, with high voltage or strong electric current between its two electrodes, high pressurized cool air can be heated and ionized to form a high temperature air ionization channel. Through a taper nozzle, air plasma flame spurts out, and its temperature can be adjusted by controlling the electric current. The specimen to be tested is put at a place 6 mm from the exit of the nozzle which is located by a laser auto-check instrument. When the ablation process begins, the specimen will keep at the original place by a supplying control system.

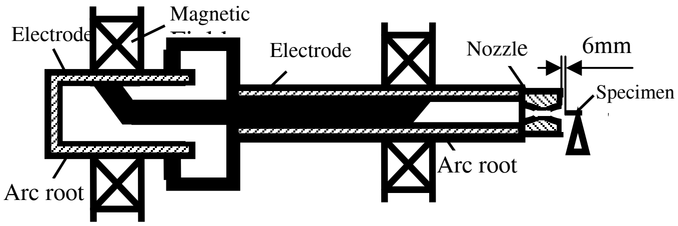

Figure (1) : Sketch of the arc heater

In the test, ablation specimens of C/C composites were cylinders of Φ 15×45 mm. The following parameters were chosen to test the ablation rates of C/C composites : Stagnated pressure (MPa) : 4.35, Thermal enthalpy (MJ/kg) : 4.96, Stagnated heat current (MW/m^2) : 22.1, Ablating time (s) : 3

2.3 Investigation of optical microstructures and ablation morphologies : The optical metallo-graphies of carbon fibers, pyrolytic carbon, resin-based carbon and the combination states between them in C/C composites were investigated by optical microscopy (OM). The ablation morphologies were investigated by JSM-5600LV scanning electron microscopy (SEM).

3 Results and Discussion :

3.1 Metallo-graphies : Figure (2) shows the metallo-graphies of three types of C/C composites with different matrices. It is found that carbon fibres were not sensitive to polarized light. Figure (2a and b) show that pyrolytic carbon displayed different colours under polarized light. In figure (2a), sample A showed typical smooth laminar characteristics: Pyrolytic carbon has smooth surfaces, low optical sensitivity, big and regular + extinction stripes, and it looks just like compact discs. But it also has some concentric annular cracks which are homocentric as carbon fibers. In figure (2b), pyrolytic carbon around carbon fibres obviously showed same optical characters of anisotropy and had a typical structure of rough laminar: Pyrolytic carbon has + extinction stripes and rough surfaces. In addition, pyrolytic carbon is very sensitive to polarized light and looks colourful. There were few annular cracks in pyrolytic carbon. Combinations between pyrolytic carbon and resin-based carbon were good. In figure (2c), resin-based carbon mainly showed isotropy optical characteristic. But in some regions anisotropy optical characteristics appeared as a result of stress graphitization, which was caused by different thermal expansion between different types of carbon during heat treated process at high temperature.

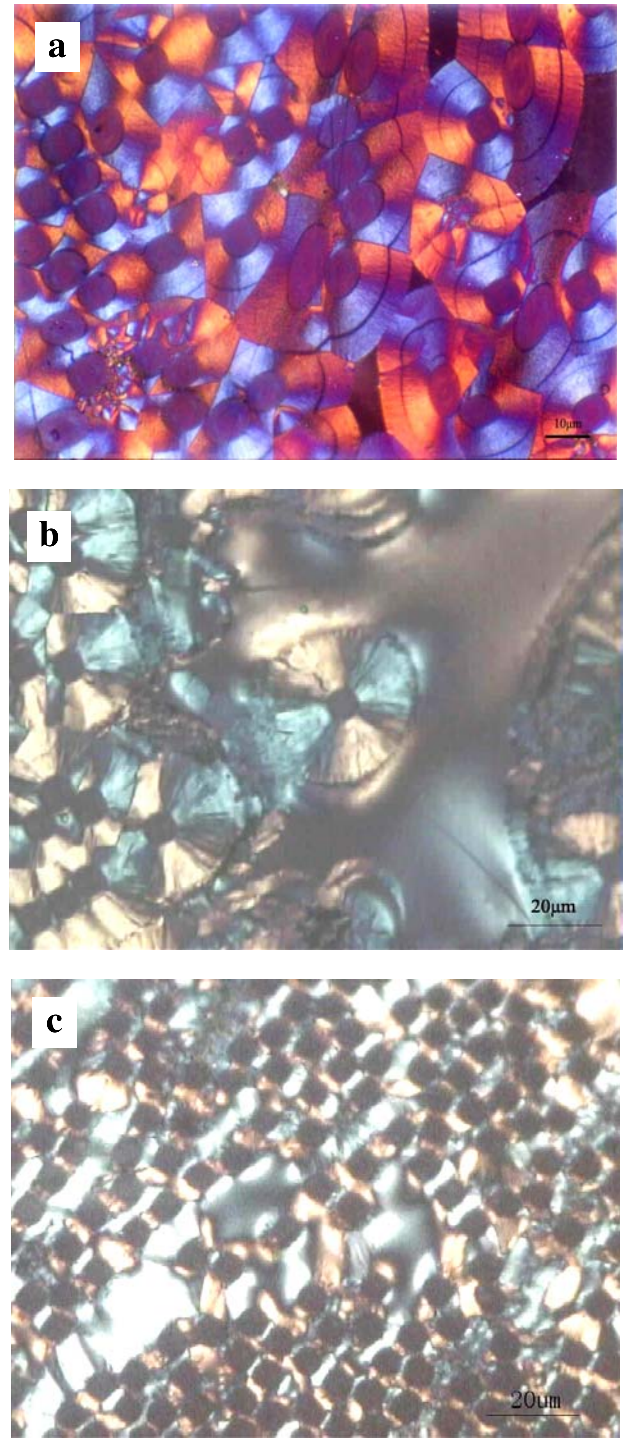

Figure (2) : Metallo-graphies of three kinds of C/C composites with different matrices (a) Smooth laminar pyrolytic carbon (b) Rough laminar pyrolytic carbon (c) Resin-based carbon.

3.2 Ablation morphologies :

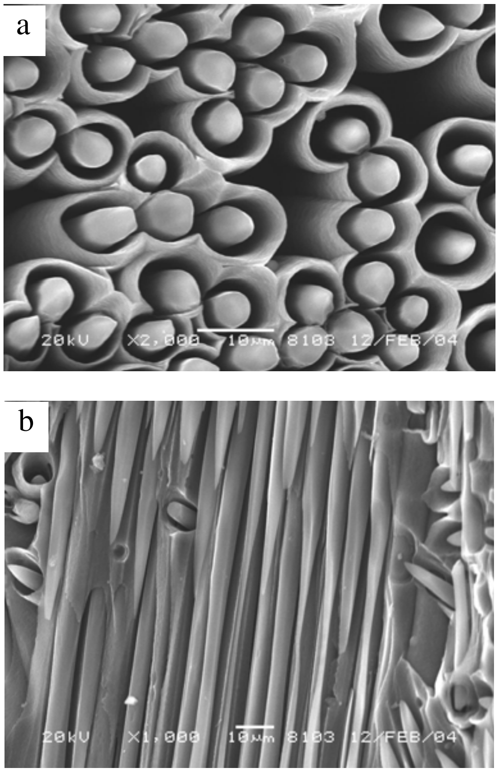

Figure (3) : Ablation morphologies of sample A.

Figure (3) shows the micro-ablation morphologies of sample A. When carbon fibers were parallel to ablation flame (Figure 3a), ablated pyrolytic carbon took on ring-like structure around carbon fibers. This structure is always described as the POG (Parallelly Oriented Graphite) structure [9] which further verifies that ablation always tends to start at interfaces between carbon fibers and carbon matrices. Furthermore, smooth laminar pyrolytic carbon looks very smooth and carbon fibers tend to become needled. However, for those carbon fibers, which are vertical to the ablation flame (Figure 3b), there were less carbon matrices left and carbon fibers became needled under strong erosion of the ablation flame. But some of the carbon fibers would turn into blunt shape after a new blow-off.

Figure (4) shows SEM images of micro-ablation morphologies of sample B. Ablation tended to start at open pores and interfaces between carbon fibers, pyrolytic carbon and resin-based carbon, and grows, which made the gaps between them wider and deeper. Heads of carbon fibers has a needle-like shape as reported in Ref [10,11] (Figure 4a and b). During the ablation process, carbon fibers were ablated in the form of surface denudation. With further ablation, carbon fibers became thinner. Pyrolytic carbon was very coarse and showed ring like shape around carbon fibers, which was mainly caused by chemical erosions. Resin-based carbon was easy to be burnt off, because it was filled in C/C composites and had small volumes and large interfacial areas. For those big blocks of resin-based carbon, they exhibited good ablation property with few ablation traces (Figure 4a).

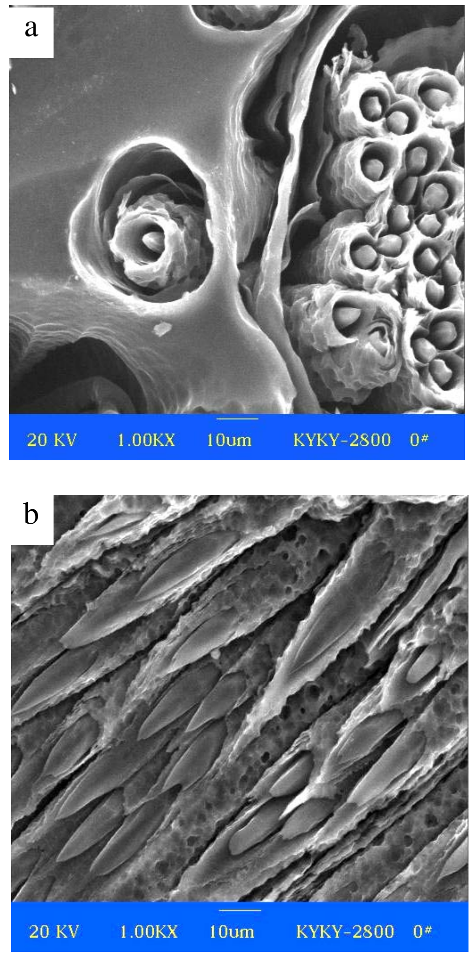

Figure (4) : Ablation morphologies of sample B.

Figure (5) is SEM images that show the ablation morphologies of sample C. Carbon fibers exhibited similar morphologies as those of the other two composites. Though ablation tends to begin at the interfaces between carbon fibers and carbon matrices, ablation morphologies of resin-based carbon were quite different from those of pyrolytic carbon. Because resin-based carbon was filled into carbon fiber felt and not deposited on the carbon fibers with layers, resin-based carbon after ablation was in slice but not as regular as the ablated pyrolytic carbon around carbon fibers. However, in net-like carbon fiber felts, there were less carbon fibers, the resin-based carbon was in big blocks and continuously distributed in C/C composites. Thus, it was hard to ablate off (in Figure 4b). In addition, the ablation surface of resin-based carbon was very smooth.

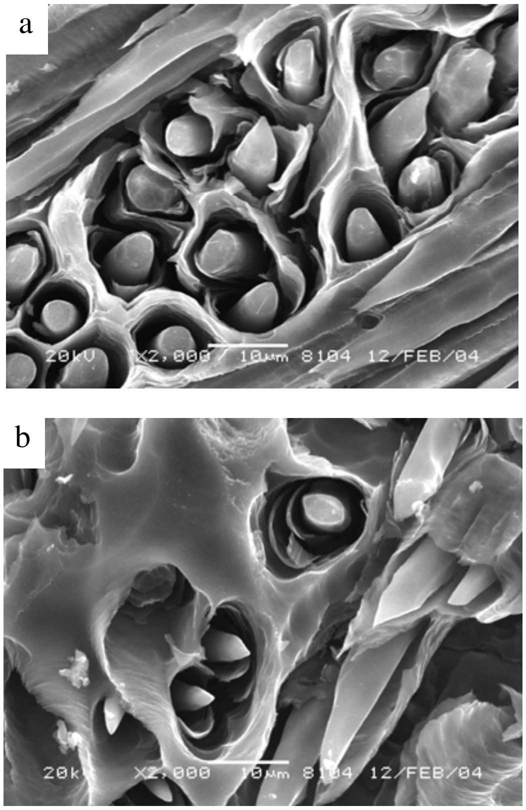

Figure (5) : Ablation morphologies of sample C.

3.3 Discussion : In the ablation test, ablation properties of C/C composites are controlled by two mechanisms including chemical erosion and mechanical denudation. On one hand, carbon in C/C composites and oxygen gases in the ablation flame will react with each other at high temperature; On the other hand, C/C composites will be considerably denudated by high pressure and high speed ablation flame which causes particle denudation and block denudation. Furthermore, during the ablation process, chemical erosion and mechanical denudation occur simultaneously and enhance the process mutually.

Chemical erosion mainly refers to oxidation reactions between the ablation flame and the surfaces of C/C composites. These oxidation reactions consume some carbon of C/C composites and weaken their mechanical properties. The pores, defects and interfaces are oxidation active spots with low surface energy and will be oxidized first and extended further. Chemical erosion will not only lead to the ablation of the surface but also make the interior surface looser. Mechanical denudation refers to particle and block denudations of C/C composites caused by high pressure and shearing forces of the ablation flame. Therefore, micro-ablation morphology of different types of carbon in C/C composites may be mainly caused by chemical erosion.

Different types of carbon in C/C composites exhibit various ablation morphologies which may be relate to the preparation techniques and the ablation conditions. Research shows that PAN carbon fibers have the "onion-like spheres and crystallites' structure **[12]**. Affected by the preparation technique, most of the hexagon layers in graphite crystallite at the exterior of carbon fibers are parallel to the axis of carbon fibers; however, those at the interior are in a more random orientation. As it is well known, carbon atoms in each hexagon layer are combined by covalent bonds, but those in the hexagon layers themselves are combined by weaker attractive bonds (Van der Waals type).Therefore, during the ablation process, carbon fibers will be peeled off from the exterior surfaces which enlarge the gaps between carbon fibers and matrix, thus the carbon fibers become needled. When the ablation flame arrives at the ablation surface, it will turn around, thus, carbon fibers will become peaked along the direction of the turning around ablation flame.

Ablation morphologies of rough laminar pyrolytic carbon are different from that of smooth laminar pyrolytic carbon, it may relate to the different deposition processes of pyrolytic carbon **[13]**. Smooth laminar carbon is mainly deposited with small molecules randomly, and the graphite crystallites in smooth laminar carbon are small, thus pyrolytic carbon exhibits isotropic characteristic. In C/C composites, areas of pores, interfaces and flaws have low surface energy and are easy to absorb oxygen. They will be firstly ablated, and then ablation behavior will expand along them. For smooth laminar pyrolytic carbon, graphite crystallites are small and have more flaws, thus oxidation reactions will take place at those flaws and expand along the hexagon layers. Therefore, the ablation morphologies become slick. However, rough laminar pyrolytic carbon is deposited mainly by large molecules in cone shape and display high orient. Furthermore, combination states in rough laminar pyrolytic carbon include strong, weak, and even fake combinations **[14]**. Therefore, free energies and chemical activities in the carbon matrix are different. These places with lower free energies are more likely to react with oxygen and thus create many ablation pits.

Unlike pyrolytic carbon's regular deposition on carbon fibers, resin-based carbon just fills in the carbon felts and shows isotropic characteristic. Since ablation tends to start at interfaces between carbon fibers and carbon matrices, pores and defects, the gaps between carbon fibers and resin-based carbon are enlarged and some areas on the ablation surface of resin-based carbon will not be homogenous.

4 Conclusions : Different carbon in C/C composites shows various ablation morphologies after the stagnation ablation test which is mainly caused by chemical erosion. Carbon fibers are mainly ablated into needle-like shape and blunt shape. Pyrolytic carbon has the ring-like structure, but the ablation morphology of smooth laminar pyrolytic carbon is slick and that of rough laminar pyrolytic carbon is coarse with many ablation pits in it. Resin-based carbon around carbon fibers is ablated into slices. However, the ablation surface of block resin-based carbon filled in the carbon fiber felts is smooth and has good ablation property.

Acknowledgement : This work was supported by national basic research program of China under the contact NO. 2006CB600908 and the Fundamental research funds for the Central Universities.

References :

[1] E. Fitzer, Carbon, 25 (1987) 163.
[2] T. Paulmier, M. Balat-pichelin, D. L. Quéau, Appl. Surf. Sci. 243 (2005) 376.
[3] J. C. Han, S. D. He, S. Y. Du, Carbon 33 (1995) 473.
[4] J. M. Su., Carbon Sci. Technol. (2001) 6.
[5] J. Lavenac, F. Langlais, O. FeÂron, R. Naslain, Compos. Sci. Technol. 61 (2001) 339.
[6] S. J. Zhou, J. M. Su, Z. A .Su, R. Z. Li, H. Cui, New Carbon Mat. 16 (2001) 49.
[7] J. J. Liu, J. M. Su, C. L. Chen, Carbon (2003) 15.
[8] J. Rodrı′guez-Mirasol, P. A. Thrower, L. R. Radovic, Carbon 33 (1995) 545.
[9] F. Dillon, K. M. Thomas, H. Marsh, Carbon, 31 (1993) 1337.
[10] H. X. Ran, H. Cui, Z. B. Hao, R. Z. Li, S. J. Zhou, Y. Zhang, Carbon (2002) 20.
[11] J. Yin, X. Xiong, H. B. Zhang, B. Y. Huang, Carbon 44 (2006) 1690.
[12] Y. J. Lee, H. J. Joo, Compo. Part A 35 (2004) 1285.
[13] Y. J. Bai, C. G. Wang, N. Lun, Y. X .Wang, M. J. Yu, B. Zhu, Carbon 44 (2005) 1773.
[14] F. Q. Zhang, B. Y. Huang, Q. Z. Huang, T. F Chen, Q. M. Gong, X. Xiong, Mining Metal. Eng. 22 (2002) 93.
[15] T. F. Chen, W. P. Gong, G. S. Liu, Mining Metal. Eng. 24 (2004) 77.