Investigations of Micro- and Nano-structures of C/C Composite Fabricated by CVI

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Abstract

The morphology, microstructure and graphitization degree of C/C composites fabricated by chemical vapor infiltration were studied by scanning electron microscope (SEM), high-resolution transmission electron microscope (HRTEM). The pyrolytic carbon matrix consists of flakes with the thickness from several tens to several hundreds nanometer. These flakes are oriented parallel to the fiber surface. They are of rough laminar structures and are easily folded so as to form a lot of micro-cracks. A disorder zone with the thickness of about 15nm was also identified between the carbon fiber and pyrolytic carbon. Election diffraction analyses and HRTEM observations also revealed that the graphitization degree of pyrolytic carbon near the interface was lower than those in the outer of the pyrolytic carbon.

Introduction

C/C composites consisting of carbon fibers and pyrolytic carbon matrix are promising candidate materials for high-temperature applications, such as rocket nozzle, gas turbine engine and aircraft brakes, due to their high mechanical properties at enhanced temperature and excellent friction and wear performances together with light weight (Fitzer, Manocha, 1998 and Zou, Huang, *et al.*, 2001). However, many defects induced during manufacturing procedure hindered their applications in industry. The chemical vapor infiltration (CVI) is frequently applied for the C/C composite production since the density of the C/C composite can be increased and the processing period can also be shorten. Therefore, it is necessary to characterize their microstructure on both micron and nanometer scale thoroughly in order to establish a correlation between their microstructures and mechanical properties.

C/C composite is usually composed of carbon fibers with several microns in diameter and carbon matrix which usually refers to the pyrolytic carbon. Gray and Cathcart proposed first to divide the pyrolytic carbon matrix into three types according to their polarized light property (Gray, Cathcart, 1966). After that, Diefendorf and Tokarshy established a more-detailed classification with four types according to their angle extinctions: isotropic (ISO) structure ($Ae<4^o$), dark lamellar (DL) structure ($4^o \leq Ae<12^o$), smooth lamellar (SL) structure ($12^o \leq Ae<18^o$) and coarse lamellar (CL) structure ($Ae>18^o$) (Diefendorf, Tokarsky, 1971). Recent years, Reznik and Hüttinger gave a new classification on the base of the texture degree of the pyrolytic carbon matrix. According to the orientations angle (OA), pyrolytic carbon can be divided into four types also: Isotropic (OA =

180°), law-texture (180°≥OA ≥80°), middle-texture (80°≥OA ≥50°) and high-texture (OA≤5°) (Reznik, Hüttinger, 2002). It is important that these two kinds of classifications can correspond to each other although the former is based on the optical property (macro-structure) while the latter on the microstructure. However, the information on the microstructures of the C/C composite is still very limited, especially on the sub-micron scale, even on the nanometer scale. Therefore, it is very necessary to characterize microstructures of the C/C composite on the sub-micron and nanometer scale, including the interfacial structure between the carbon fiber and pyrolytic carbon matrix. In this present study, the morphology, microstructures and graphitization degree of the C/C composite fabricated by CVI were studied by using scanning electron microscope (SEM), high-resolution transmission electron microscope (HRTEM).

Experimental

The C/C composite, which was fabricated by CVI, was cut from the aircraft brake produced by the MESSIER Company of France. SEM investigations were carried out in a SUPRA 35 field emission scanning electron microscope. TEM observation was carried out in a JEM-2010(UHR) transmission electron microscope with a point resolution of 0.194nm. For the TEM specimen preparation, slices with the thickness of about 200μm were cut from the composite and cutting directions were selected to ensure the carbon fibers were almost normal to the cutting face. The slices were further thinned to 80μm by mechanical grinding. In order to minimize damages by an ion milling, the sample was carefully dimpled to less-than ten microns or even to perforation. The ion milling with the low incidence angle was employed only for the final cleaning.

Results and Discussions

Figure 1 is typical SEM images of the C/C composite. Figure 1a shows a low-magnification cross-sectional morphology. The carbon fibers are separately distributed in the pyrolytic carbon matrix and surrounded by matrix carbon. Their diameters are about 6 μm. Fig.1b is an enlarged SEM image which demonstrates a typical morphology of carbon matrix between the two carbon fibers located separately at top-right and bottom-lift corners. The pyrolytic carbons are flake-like and deposited parallel to the fiber surface in a lamellar structure. The thicknesses of the flakes range from several tens to several hundreds nanometer. These are typical

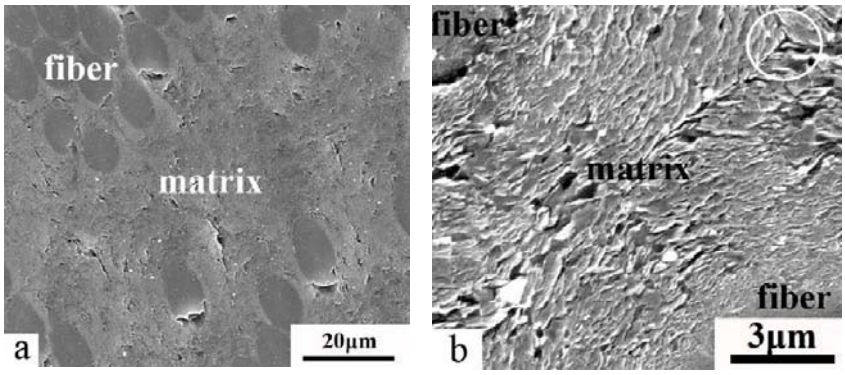

Figure 1 Cross-sectional SEM micrographs of the C/C composite. (a) A bird view image; (b) a high magnification image showing lamellar structure in the carbon matrix

morphologies of the C/C composite manufactured by CVI as reported elsewhere (Reznik, Gerthsen, 2003and Reznik, Gerthsen, Hüttinger, 2001). There is a clear boundary formed between the two pyrolytic carbon deposited separately on the two fibers. The distance between the two fibers is about 12 μm and the thicknesses of every pyrolytic carbon are about 6 μm. This implied that the deposition velocity is almost same from the two fibers.

In order to obtain more information about the microstructures of the composite in detail, the fibers, matrix and their interface were also studied by using HRTEM. Figure 2a is a TEM image which shows a typical morphology of the pyrolytic carbon matrix around a carbon fiber. The center part of the fiber was already ion-milled out and the left part was only 0.5 μm thick from the interface between the fiber and matrix. Although contrast of the matrix does not change greatly, the selected area electron diffraction (SAED) analyses along the radial direction from the fiber/matrix interfere revealed that the orientations angles were almost no change and 002, 004… diffraction spots were almost sharp, see the insets in Figure 2b and 2c. This implies that the matrix is of rough laminar structures with relatively high degree of graphitization. Figure 2b and 2c are HRTEM images of the inner pyrolytic carbon and outer one (near and far the fiber/matrix interface), respectively. The strings represent (002) sp^2 atomic planes and the planar distance between the adjacent strings is about 0.34 nm. It could be identified: near the fiber/matrix interface, the (002) strings were carving and the (*00l*) spots also stretched in

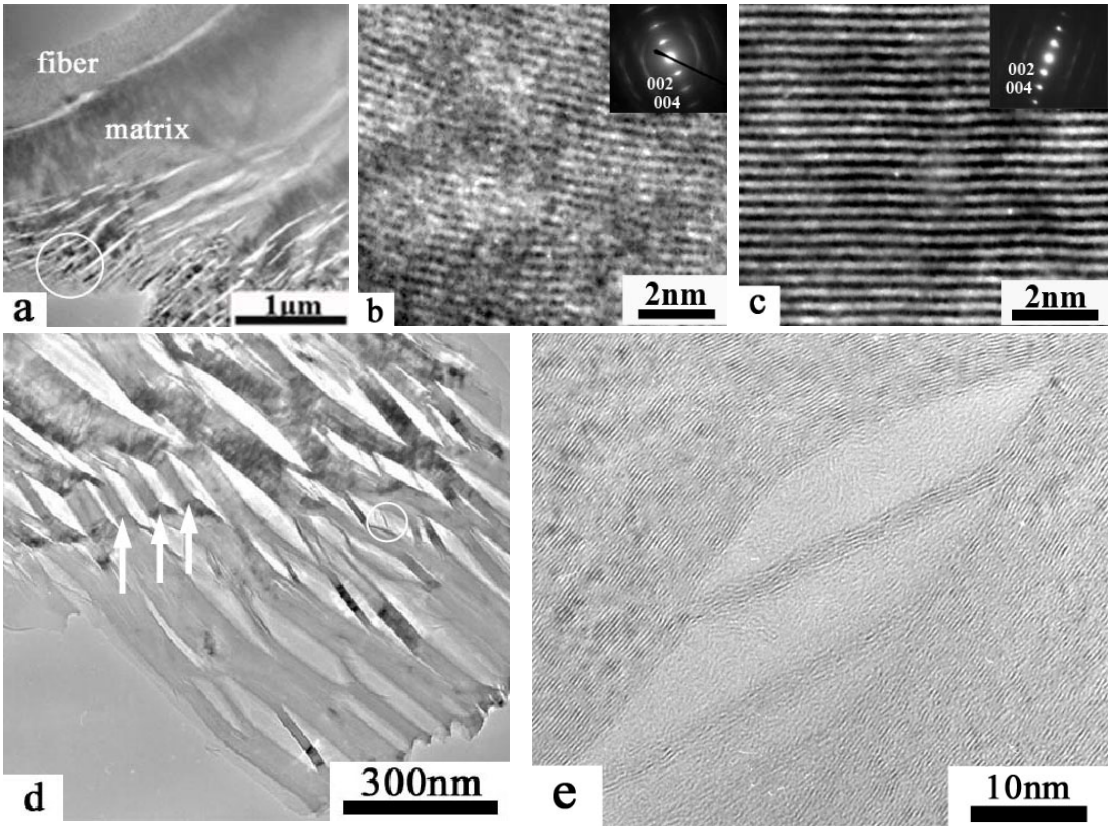

Figure 2 HRTEM observations and SAED analyses of the pyrolytic carbon matrix. (a) A bird-view morphology near the fiber/Matrix interface; (b) A HRTEM image and its corresponding SAED pattern of the pyrolytic carbon near the fiber/matrix interface; (c) A HRTEM image and a corresponding SAED pattern of the outer of pyrolytic carbon; (d) An enlarged image of the local area marked by white circle in Figure 2b. (e) A HRTEM image of a micro-crack showing that the folds of (002) sp^2 atomic planes cause the micro-cracks formed along the sp^2 plane.

its corresponding SAED pattern (the inset); in the outer pyrolytic carbon, however, the (002) strings were rather straight and the (*00l*) spots were very sharp. From these compared observations, it could be concluded that the graphitizing degree in the outer layers are higher than that in the inter layers. In addition, no mater how to tilt the sample in the case of keeping (*00l*) diffractions spots unchanged, we could never obtain a two-directional SAED pattern. This implied that the matrix did not have the characterization of crystalline graphite structure. That means, although sp^2 (002) atomic planes were almost flat, their stacking along the [001] direction was still disordered, the twists among the sp^2 (002) atomic planes existed. It was so-called turbostrutic structure.

Besides, there were a lot of cracks formed in the pyrolytic carbon matrix. Fig.2d is an enlarged image of the local area marked by white circle in Figure 2b. In addition to micro-cracks, local folds of graphite layers, which usually contain several tens of (002) atomic planes, occurred and these folds caused their splits so that the micro-cracks formed between the graphite layers. Figure 2e is a HRTEM image of a typical micro-crack. From this image, it is clear that the folds of (002) sp^2 atomic planes caused the micro-cracks formed along the sp^2 atomic plane. The smallest cracks were only 2-3 nm.

Carbon fibers play the role of load-bearing while the carbon matrix protects the carbon fibers and keeps the shape of C/C composite; the interfaces between the fibers and matrix has a function of delivering the loading on the matrix to the fibers. Therefore, the interfaces play an important role in improving the mechanical properties of the C/C composite. Figure 3 demonstrates typical morphologies of the interface between the carbon fiber and matrix carbon. Figure 3a is a low-magnification image of an interface between a carbon fiber and the matrix. The interface (a white line) is almost slick, which reveals that this carbon fiber is round-like and its surface is almost smooth. Figure 3b is a high-magnification image of the interface. There is a disorder zone with the thickness of about 15 nm between the fiber and matrix. This disorder zone had a weak contrast and imaged as a white line along the fiber/matrix interface in the lower-magnification observation. The formations of the disorder zone should have been related with deposition parameters. Such a disorder zone may be induced by the surface structure of carbon fiber.

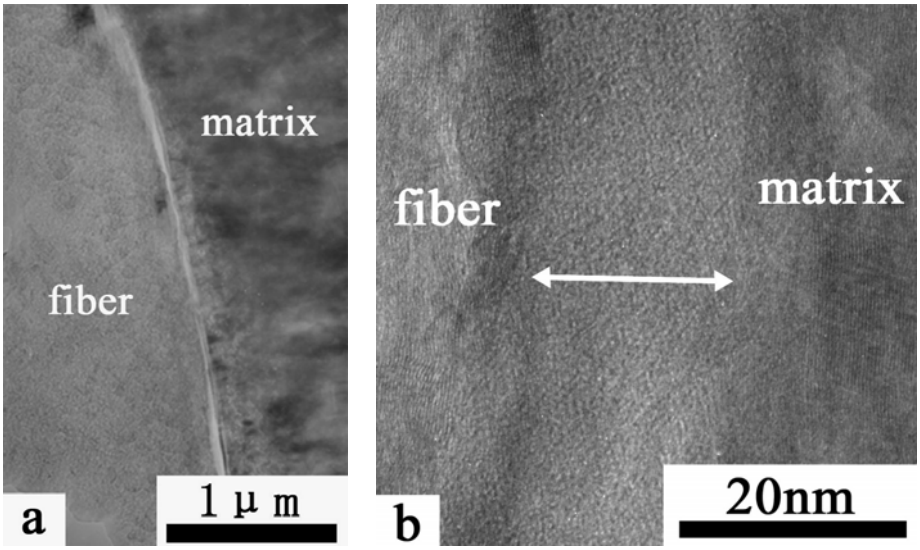

Figure 3 A typical TEM images of the fiber-matrix interface. (a) A low-magnification image of an interface between a carbon fiber and the matrix. (b) A high-magnification image of the interface showing a disorder zone with the thickness of about 15 nm.

Conclusion

Pyrolytic carbon matrix grew around the carbon fibers. They were flake-like and their thicknesses ranged from several tens to several hundreds nanometer. There were a lot of micro-cracks and folds in the pyrolytic carbon. The graphitization degree in outer pyrolytic carbon was higher than that near the fiber/matrix interface. There is a disorder zone with thickness of about 15nm along the interface between the carbon fiber and matrix.

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