Microstructure and elastic properties of individual components of C/C composites

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ABSTRACT

Carbon fiber reinforced carbon matrix (C/C) composites are often used for structural and frictional applications at a wide range of temperatures due to their excellent mechanical and thermal properties. Tailoring of mechanical properties through optimization of microstructure is critical for achieving maximum composite performance. This article addresses the evolution of the fiber and matrix microstructure and related nano-mechanical properties in two different C/C composites after being subjected to heat treatment at temperatures between 1800 and 2400 °C. Microstructure and corresponding nano-mechanical properties of C/C composites were studied using Polarized Light Microscopy (PLM), High-Resolution Transmission Electron Microscopy (HRTEM) and nanoindentation techniques. Increased heat treatment temperature (HTT) led to formation of a better-organized microstructure of fiber and matrix and also to formation of thermal cracks. The elastic modulus of rough laminar CVI pyrocarbon decreased from 18 to 12 GPa with increased HTT. In contrast, the isotropic CVI pyrocarbon and charred resin matrix displayed only a slight change of elastic modulus. The elastic modulus of PAN fiber increased from 18 to 34 GPa, indicating the development of a better-organized microstructure in the fiber-axial direction.

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1. Introduction

Carbon fiber reinforced composites are ideally suited for applications where high strength, stiffness, low density, and excellent fatigue resistance are critical requirements. In addition, they can be used in situations where high temperature, chemical inertness and high damping are important. Although carbon fibers were first produced a century ago [1], they only have been used as a fibrous reinforcement for composite materials since late 1970s [2]. High-performance carbon fibers were first introduced in the 1960s and the physical properties of these reinforcing fibers have improved dramatically over the past decades [3]. The aircraft brake industry is one of the largest markets for C/C composites.

The high cost has motivated designs with improved friction and wear properties. Microstructure–mechanical property relationships of carbon fiber reinforced composites have always been of interest to scientists addressing the composite performance [4–7].

The two major components of C/C composites are the carbon fiber and the carbonaceous matrix, whose microstructure and mechanical properties collectively determine the properties of the composite. The most commonly used carbon fibers are PAN, pitch and rayon based carbon fibers. Carbon fiber properties can show great variation depending on the precursor type, degree of graphitization, orientation and processing methods [1,3,8]. The carbon matrix is commonly produced either using chemical vapor deposition, or through the appli-
cation of a thermosetting resin. The structure of carbon matrix varies depending on the type and processing conditions. Heat treatment temperature of C/C composites has significant influence on developing of crystal structure and interplanar spacing of graphene sheets [9,10]. Mechanical and thermal properties and as well as frictional performance of C/C composites depend on the microstructure of both fiber and matrix [11–14].

Reliable assessment of composite performance requires a fundamental understanding of the compressive behavior of the individual components of the composite. Although standardized methods, such as ASTM test [15], provide information about the compressive properties of the composite as a whole, the deformation mechanisms involved in individual components are less understood. As opposed to tensile testing, direct measurement of compressive properties is very difficult, and requires alternative procedures that will relate a measured quantity to compressive strength and stiffness parameters. The anisotropy in both fiber and matrix prohibits the application of Hooke’s law, making the interpretation of the test results difficult. Characterization of compressive behavior is further complicated by the potential buckling instability, which limits the length of the specimens to be tested.

Several methods have been developed to measure the compressive strength and modulus of the components of composites [16–18]. The tensile recoil [16,19], the single fiber composite [20] and the bending beam [21] are some of the methods to determine compressive properties of single carbon fiber. Application of nanoindentation technique is a very common and useful method for characterization of near surface properties of the composite [22–24] as well as its individual components [11,18,25,26]. In this study, development of microstructure by heat treatment and related compressive elastic moduli of two different types of C/C composites have been investigated.

2. Experimental procedures

Two types of commercial C/C composites were used in this study: a two directional randomly chopped pitch fiber reinforced composite with charred resin/CVI matrix (CC-A) and a three directional composite made by using needled felt PAN fibers and CVI matrix (CC-D). The C/C composites were kindly provided by Honeywell Aircraft Landing Systems. The as received densified C/C composite samples were first cut into discs with outside diameter 117.5 mm and thickness 25 mm, and heat treated at 1800, 2100 and 2400 °C in a graphitization furnace (Model: TP-4X10-G-G-D64A-A-27, Centorr Associates Inc.) with protective argon atmosphere. Table 1 shows the sample codes and the corresponding heat treatment temperatures.

After the heat treatment, specimens with dimensions approximately 15 mm × 15 mm × 15 mm were randomly cut from different discs, mounted into an epoxy resin, ground and then polished using diamond polishing slurries with a grain size ranging from 6 to 0.25 μm. The polishing was completed with a 0.05 μm grain size alumina suspension. The nanoindentation experiments were conducted at room temperature with a Nano IndenterTM XP system (MTS NanoInstruments, Knoxville, TN) using a Berkovich-type diamond tip. The indenter tip used in the tests is called AccuTip® and the radius of curvature at the end of the tip is about 40–50 nm. Before each test, the system was calibrated using a fused silica sample. The continuous stiffness mode (CSM) was used for the tests. Thirty randomly selected different fiber and thirty CVI carbon matrix locations were indented for each sample. The calculation method given by Oliver and Pharr [27] was employed for calculating the elastic modulus.

Microstructure of polished samples was examined using a polarized light microscope (Nikon Microphot-FX), and classified according to the extinction angle (Δn) of polarized light [28–30]. Correspondence between extinction angle (Δn) and the classification of the texture of pyrocarbon is given in Table 2.

The HRTEM studies were carried out using a JEOL 2010 EF transmission electron microscope operating at 200 kV. Thin foils for the HRTEM study were prepared from 300 μm thick sections using Linear Precision Diamond Saw, Isomet 4000. The 3 mm diameter disks were core-drilled from these sections (Core Drill, VCR Group, Model V 7110) and dimpled down to a thickness of about 5 μm (Dimpler, D 500i, VCR Group). The ion mill (Gatan, 691 Precision Ion Polishing System) was used for the final thinning and polishing stage with a beam at 4° angle at 3 keV.

3. Results and discussion

Representative micrographs of transverse sections of two different types of C/C composites examined by PLM are given in Fig. 1. Composite CC-A consists of chopped pitch-based carbon fiber embedded in a charred resin matrix, which was subsequently densified using a CVI process (Fig. 1a and b). The CVI matrix in composite CC-A (Fig. 1b) displayed a low extinction angle indicating isotropic microstructure. Pitch fibers exhibited a strong reflectance suggesting a highly graphitizeable microstructure (Fig. 1b). The charred resin matrix showed mostly homogenous contrast to the polarizer activity.
However different microstructure with a slightly lighter colors are visible near the pitch fiber and CVI matrix (Fig. 1a and b). Typical PLM micrographs of CC-D composite consisting of PAN-based carbon fiber and CVI matrix are shown in Fig. 1c and d. The CVI matrix displayed strong optical activity ($A_\varepsilon = 20$) indicating a rough laminar microstructure (Fig. 1d). Highly anisotropic pyrocarbon with a high extinction angle ($A_\varepsilon > 18^\circ$) has been defined recently by Bourrat et al. and called regenerative laminar [31]. This type of laminar structure can be easily identified under polarized light. Regenerative laminar pyrocarbon shows a smooth extinction of the Maltese-cross in polarized light in contrast to rough laminar [31]. In this study, the pyrocarbon in CC-D composite is rough laminar pyrocarbon and shows typical high optical activity. PAN fiber, having a isotropic microstructure, did not exhibit any distinct response to polarizer activity.

Examples of longitudinal and transverse sections (with respect to the fiber axis) of low magnification bright field HRTEM micrographs are shown in Fig. 2. Individual fibers and CVI matrix can be well distinguished. The detailed microstructure characterized by HRTEM, using lattice fringe observations, is presented in Figs. 3-10.

HRTEM micrographs of the CC-Dnt sample (Fig. 3a) show relatively less organized microstructure of the CVI matrix. Smaller crystallites were observed in CC-Dnt samples as compared to that in CC-D24 samples. Fig. 4 shows medium and high magnification HRTEM micrographs of the CVI as seen in the CC-D24 sample heat treated at 2400 °C. It can be seen that the highly crystalline structure dominates the microstructure. A detail from the encircled area within crystallite is shown the Fig. 4b. However, almost the entire volume of CVI has been totally rearranged towards graphite-like carbon. In well-organized carbon, the graphene sheets are parallel to each other in crystallites with considerably lower content of defects as shown in Fig. 4b. The rearrangement of carbon atoms during heat treatment at 2400 °C leads to more or less highly oriented three-dimensional hexagonal crystalline microstructure. A higher heat treatment temperature or a longer holding time is necessary for further conversion of CVI matrix into highly organized carbon.

Fig. 5 presents characteristic bright field HRTEM micrographs of isotropic CVI carbon matrix as observed in the CC-A24 sample. It is clear that, the applied heat treatment at 2400 °C only slightly altered the microstructure of isotropic CVI carbon matrix. The turbostratic graphene layers and relatively small crystallites are visible in Fig. 5. As seen in Fig. 6, the charred resin matrix of CC-A24 sample also consists of relatively small crystallites (less than 5 nm) and exhibits turbostratic isotropic microstructure with curved and bent...
graphene sheets. It was found that heat treatment up to 2400 °C does not have significant impact on further development of this isotropic microstructure as reported in literature [32–36].

Fig. 2 – Low magnification TEM micrographs of longitudinal (a) and transverse sections (b) of CC-Dnt and CC-D18 composites.

Fig. 3 – Medium (a) and high magnification (b) HRTEM micrographs of CVI matrix in CC-Dnt sample.

Fig. 4 – Medium (a) and high magnification (b) HRTEM micrographs of rough laminar CVI carbon matrix in CC-D24 sample.
The HRTEM micrographs of longitudinal sections of PAN fibers in CC-Dnt and CC-D24 are shown in Fig. 7. As seen in Fig. 7a and b, the PAN fiber in the CC-Dnt sample consists of small crystallites with thicknesses less than 3 nm. The less organized carbon is present between the better-organized crystalline regions. Typically, crystallites are attached to each other (Fig. 7b) forming the dominant ribbon-like microstructure in the longitudinal direction [37]. Similar to the observation of Guigon et al.[37], the crystallites are intertwined and the preferred orientation of ribbon-like microstructure is parallel to the longitudinal fiber axis (Fig. 7b).

The HRTEM micrographs of longitudinal PAN fiber sections of CC-D24 are shown in Fig. 7c and d. Comparison of the bright field images shows that increased HTT led to a higher degree of preferred orientation in the CC-D24 samples compared to the CC-Dnt material shown in Fig. 7a and b. As can be seen in Fig. 7c and d, the extended graphene sheets in the CC-D24 sample consist of larger crystallites compared to the CC-Dnt samples. On the other hand, crystalline and less organized phases always coexist in PAN carbon fiber even after heat treatment at 2400 °C.

Fig. 8 shows the HRTEM 002 lattice fringe micrographs of transverse sections of CC-Dnt and CC-D24 PAN fibers. The turbostratic graphene sheets in CC-Dnt samples (Fig. 8a) and heat treated samples (Fig. 8b) have similar morphology and size. The relatively small crystallites (~4 nm) and turbostratic graphene sheets are typical for transverse microstructure of PAN fiber in CC-D composites for all heat treated and non-heat treated samples. As opposed to the longitudinal cross sections, where the microstructure development in heat treated samples was easily detected by HRTEM (see Fig. 7), there was no appreciable microstructure change in transverse cross sections of the fiber.

HRTEM micrographs of transverse and longitudinal sections of pitch fiber in CCA samples subjected to heat treatment at 2100 °C are given in Figs. 9 and 10, respectively.
opposed to the PAN fiber, pitch fiber consists of highly oriented graphene sheets and larger crystallites. The highly oriented graphene sheets were observed in both longitudinal and transverse sections of pitch fiber, indicating that this fiber type readily alters microstructure during heat treatment. The changing order of carbonaceous microstructure was detected after heat treatment at elevated temperatures of 2100 and 2400 °C. Pitch fibers consist of extended graphene sheets preferentially oriented parallel to the fiber axis (Fig. 10).

The mean and standard deviation of the elastic moduli are shown in Fig. 11. The highest elastic modulus (33.85 GPa) was measured for PAN fiber heat treated at 2400 °C when load is applied in the axial fiber direction, while the lowest elastic modulus (11.73 GPa) was measured for rough laminar CVI matrix of sample CC-D24. The elastic modulus for fiber-axial loading of PAN fiber in composite CC-D24 (33.85 GPa) is almost twice that in CC-Dnt samples (17.80 GPa). The elastic modulus of pitch fiber changed from 24.75 GPa after heat treatment at 2100 °C to 24.11 GPa with heat treatment at 2400 °C for fiber-axial loading.

For all matrix types in both composites, the elastic modulus decreased with increase in heat treatment temperatures. This is expected, since heat treatment changes the microstructure towards the better-ordered carbon in the matrices. Compressive loading causes shearing of graphene sheets, since the weak van der Waals bonds fail at low debonding energies. Consequently, the shearing of graphene sheets and crystallites causes significant plasticity.

The rough laminar matrix causes lower elastic moduli due to its highly anisotropic microstructure. Microstructure analysis of longitudinal sections of PAN fibers revealed that heat treatment improves both the preferred orientation and the degree of crystallinity (Fig. 7). Consequently, the PAN fiber became more resistant to compressive loading in the axial direction.

The effect of heat treatment on the elastic moduli is explained by the nanostructural changes. Two main deformation modes can be expected under axial compressive loading of the carbon fiber: shearing and kinking of graphene sheets in the crystallites. Schematics of these modes are
Kinking of graphene sheets occurs in the crystallite and crystallite boundaries where lamellae recoil and form steps when loaded. During kinking, in plane covalent bonds in the graphene sheets stay intact to some extent, leading to a continuous strain distribution. Consequently, in the absence of debonding, the deformation due to kinking is expected to be mostly elastic, at least during the initial part of the loading. On the other hand, shearing of crystallites or graphene sheets is associated with debonding of van der Waals bonds. Since debonding is irreversible, deformation due to shearing is plastic in nature.

It has been noticed that the elastic modulus of fiber in compression measured by nanoindentation is considerably lower than the elastic modulus measured in tensile loading conditions, typically ranging between 300 and 1000 GPa [1,2,18,25,38,39]. This can be attributed to the different deformation mechanisms of fibers in compression and tension. This difference is schematically shown in Fig. 12. The elastic deformation mechanism of PAN fiber in tension involves straightening and stretching of the ribbon shape crystallites until their movement is limited by disclination in the microstructure. However, the elastic deformation mechanism in compression is associated with buckling and kinking (Fig. 12b). The values reported here are the compressive elastic moduli measured by nanoindenter and are in good agreement with the published data [18,25,40]. Characteristic loading vs. displacement curves obtained from indentation tests of composites heat treated at 2100 °C are shown in Figs. 13–17. The inserts show the enlarged view of the beginning of loading and the end of unloading. The experiment was controlled in such a way that unloading started when the preset force of 4.1 mN was reached. The
corresponding maximum displacement depends on the tested microstructure. The elastic moduli were calculated from the initial slope of the unloading curve.

Isotropic CVI matrix of CC-A21 exhibited the largest displacement (over 400 nm) at the maximum load (Fig. 13). The PAN fiber with isotropic microstructure exhibited the maximum deformation of only 275 nm (Fig. 16). Comparison of pitch fiber (Fig. 15) and PAN fiber (Fig. 16) shows that pitch fiber has higher plasticity than PAN fiber. The difference in plasticity can be attributed to the low shear resistance be-

Fig. 10 – Medium (a) and high (b) magnification lattice fringe HRTEM micrographs of longitudinal section of pitch fiber in CC-A21.

Fig. 11 – Measured elastic modulus of CC-A (a,b) and CC-D (c,d) composites. The error bars represent 2 standard deviations. Indentation in parallel direction (with respect to the fiber axis) was performed on transverse sections, and indentation in normal direction was performed on longitudinal sections of fibers (see Fig. 2a).
tween the preferentially oriented graphene sheets in the pitch fiber. The smaller value of the peak displacement and the absence of plastic behavior in the PAN fiber are caused by the basket weave arrangement of the ribbon shaped crystallites in the fiber microstructure. All three matrix types had a permanent deformation of around 20 nm after complete unloading (Figs. 13, 14 and 17), as opposed to the much smaller values measured from the PAN and pitch fibers.

The influence of heat treatment in the elastic modulus of PAN fibers is substantial when loading in fiber-axial direction. In PAN fiber, the lamellae shaped crystallites are associated edge-to-edge in an undulated form (Fig. 7). With increasing heat treatment temperature, the better oriented graphene sheets form much larger crystallites in longitudinal direction of PAN fibers (Fig. 7). However, only a very small change in crystallite size was detected in direction perpendicular to the carbon fiber axis. As a result, minimal changes in the elastic moduli of PAN fiber were observed when loaded normal to the fiber axis.

Fig. 12 – Schematic of indenter tip and the longitudinal section of PAN fiber (a). Possible deformation mechanisms of PAN fiber: kinking and shearing of crystallites under loading condition (b). Schematic representation of possible indentation-related compressive deformation of highly oriented pitch fiber in fiber-axial direction (c). deformation under tensile loading (d) [18].

Fig. 13 – Load vs. displacement graph detected in nanoindentation experiment with CVI carbon matrix in CCA-21. Sample loaded in fiber-axial direction.
Although the elastic modulus of the CVI matrix of the CC-A composite exhibited a slight, gradual decrease with increasing heat treatment temperatures; a significant decrease in the elastic modulus was observed in the CVI matrix of the CC-D composite. While no dramatic structural changes were detected for CC-A composite matrix, the better oriented structure of CVI carbon develops and crystallite size increases at higher heat treatment temperatures. This shows that the more highly oriented soft CVI carbon is plastically deformed from the beginning of indentation.

4. Conclusions

Heat treatment of C/C composites between 1800 and 2400 °C strongly influences the carbon microstructure and corresponding elastic moduli. Individual structural components (fiber and matrix) respond differently to heat treatment. The pitch fiber exhibited the largest capacity to form well-ordered graphite-like microstructure while the isotropic CVI pyrocarbons showed a very limited development of crystallinity. The rough laminar CVI pyrocarbon crystallite size increased and formed better-organized carbon microstructures with increased heat treatment temperatures. Structural re-arrangement in PAN-type carbon fiber was detected only in longitudinal direction, parallel to the fiber axis. However, stacks distribution in PAN fiber remains turbostratic isotropic with numerous amorphous elements in parallel and perpendicular directions with respect to carbon fiber axis when compared to a better-organized graphite-like carbon. The development of microstructure is well reflected by detected elastic modulus measured by nanoindentation of individual composite elements. For all matrix types in both composites, the elastic modulus decreased with increase in heat treatment temperatures. Better-organized carbon microstructures with increased heat treatment temperatures are formed. Compressive loading causes shearing of graphene sheets since the weak van der Waals bonds fail at low debonding energies. The deformation of pitch fiber is more plastic than PAN fiber. The difference in plasticity can be attributed to the low shear resistance between the well-organized graphene sheets in the pitch fiber.
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