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Short communication

Variation of thermal expansion of carbon/carbon composites from 850 to 2500 °C

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Abstract

Thermal expansion behaviors of carbon/carbon composites consisting of carbon fiber felts with high textured pyrolytic carbon matrix were investigated in a temperature range of 850–2500 °C. Coefficient of thermal expansion (CTE) of the composites without heat treatment decreased clearly in the two temperature ranges of 1300–1500 °C and 2100–2500 °C. Raman spectra and scanning electron microscope analyses of the composites heat treated at different temperatures showed that the reduction of structural defects in fibers, and the graphitization of carbon matrix were responsible for the decrease of CTE. Furthermore, fiber/matrix interfacial debonding and fiber pull-out during the CTE measurement occurred with the increase of heat treatment temperature up to 1500 °C, while at higher heat treatment temperature, circumferential cracks and layer bridging in the matrix were observed.

Keywords: C. Thermal expansion; Carbon/carbon composites; Microstructure; Heat treatment

1. Introduction

Carbon/carbon (C/C) composites are widely used in the fields of aeronautics and astronautics, such as brake discs of aircrafts, rocket nozzles, and wing leading edges of space shuttles. The thermophysical properties of C/C composites play important roles in all these applications [1,2]. Therefore, it is important to fully understand their thermophysical mechanism under various thermal conditions.

Coefficient of thermal expansion (CTE) is an important thermophysical property of C/C composites, which is critical for the study of stress analysis, stability of the interface and thermal shock resistance at high temperatures [2,3]. Baxter et al. [4] reported that the increase in bulk density of the C/C composites resulted in the increase of their CTEs. It was found that the C/C composites with high textured pyrocarbon, designated by a rough laminar had higher CTEs than those with other textured pyrocarbons (i.e., smooth laminar and isotropic) [5]. The CTEs of C/C composites were found to increase with the increasing temperature until 1200 °C, followed by a gradual decrease [6]. So far, many reports described the CTE measurements of C/C composites which were tested up to 1600 °C, and there are few reports on the variation in thermal expansion behaviors of C/C composites with increasing temperature up to 2500 °C. In this paper, the C/C composites heat treated at different temperatures were used to study the variation of CTEs with the increase of the heat treatment temperature (HTT). Meanwhile, Raman spectra and scanning electron microscope analyses of the same specimen heat treated at different temperatures were used to explain the variation in the thermal expansion behaviors of the C/C composites with the increase of temperature up to 2500 °C.

2. Experimental

2.1. Materials

Needle-punched integrated felts made up of 12 K T-700 PAN fibers were used as preforms. The preforms were densified to a density of 1.81–1.82 g/cm^3 by isothermal isobaric chemical vapor

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infiltration (ICVI) process. The C/C composites with high textured pyrocarbon were prepared and heat treated at various temperatures (i.e., 1300, 1500 and 2100 °C) for 2 h in order to study the variation of C/C composites. The samples without heat treatment were designated as UT, while the composites with different heat treatment temperatures (i.e., 1300, 1500 and 2100 °C) were designated as HT13, HT15 and HT21, respectively.

2.2. CTE measurements

DIL 402E dilatometer made by NETZSCH Company was employed for the CTE measurement. Cylinder specimens with a size of $\Phi 6\ \mathrm{mm} \times 11\ \mathrm{mm}$ were machined in parallel and perpendicular to the direction of the non-woven fabrics for measuring the CTEs of C/C composites in *XY* and *Z* directions, respectively. All the thermal expansion measurements were conducted in a high purity helium atmosphere at a heating rate of 5 °C/min from 850 to 2500 °C with accuracy of ± 3%.

2.3. Characterization

The same polished and cleaned sample without heat treatment was designated as SHT13, SHT15 and SHT21 as it was heat treated at 1300, 1500 and 2100 °C, respectively. The heat treatment process of the polished specimen was the same as the process of the CTE measurement in order to imitate the condition during the CTE measurement.

The microstructural changes of the same position on the polished surface were examined and observed before and after the heat treatments by Raman micro-spectroscope (Renishaw inVia) and scanning electron microscope (VEGA3 TESCAN) to investigate the mechanism involved in the CTE variation with temperature.

3. Results and discussion

CTE-temperature curves of all the composites are shown in Fig. 1. CTEs of all the composites in *Z* direction are apparently higher than those in *XY* direction due to the special fiber orientation in the preform and the specific orientation of high textured pyrocarbon on the surface of fibers [5]. Similar thermal expansion behaviors of the C/C composites as a function of temperature in both directions are also displayed in Fig. 1. Initially, CTEs of UT increase gradually with the increase of temperature up to 1300 °C and decrease from 1300 to 1500 °C. Beyond 1500 °C, there is a sharp increase in CTEs of the materials until 2100 °C, followed by an obvious decrease from 2100 °C afterwards. However, the decrease of CTEs of UT in *XY* direction is more significant than that in *Z* direction from 1300 to 1500 °C, and the sharper decrease of CTEs of UT in *Z* direction from 2100 °C afterwards. Because the performances of carbon fiber and matrix depend on CTEs of C/C composites in *XY* and *Z* directions [3], it implies the structures of carbon fiber and matrix may change in the temperature range of 1300–1500 °C and 2100–2500 °C, respectively. The shapes of CTE-temperature curve of HT13 are close to those of UT in *XY* direction. However, CTE of HT13 is obviously lower than those of UT and similar to CTE of HT15 in *Z* direction. It may result from the difference of carbon fibers and matrices, such fiber orientation, porosity, and defects of matrix [5]. CTEs of HT15 are lower than those of UT and HT13, which are higher than those of HT21 in both directions. There is an obvious change in the shape of the CTE-temperature curves of the C/C composites with the increase of heat treatment temperature (HTT). The variations in the CTEs of the C/C composites with increasing temperature gradually diminish as HTT increases.

Raman spectra of the heat-treated composites are shown in Fig. 2. For carbon materials, the ratio of *D* to *G* bands (I_D/I_G) is inversely related to the degree of graphitization [7]. As shown in Fig. 2, I_D/I_G of the carbon fibers in SHT13, SHT15 and SHT21 were calculated as 1.792, 1.356 and 1.011, respectively, while those of matrices are 1.065, 1.054 and 0.487, respectively. It is found that the influence of HTT on fibers from 1300 to 1500 °C is greater than that on matrices; but from 1500 to 2100 °C, HTT influenced more heavily on the matrices. Furthermore, the appearance of a weak *D′* band and the narrowing of the *D* band in Raman spectra of fibers in Fig. 2a also indicate the decrease of amorphous carbon and the formation of highly organized structure of the fiber in the

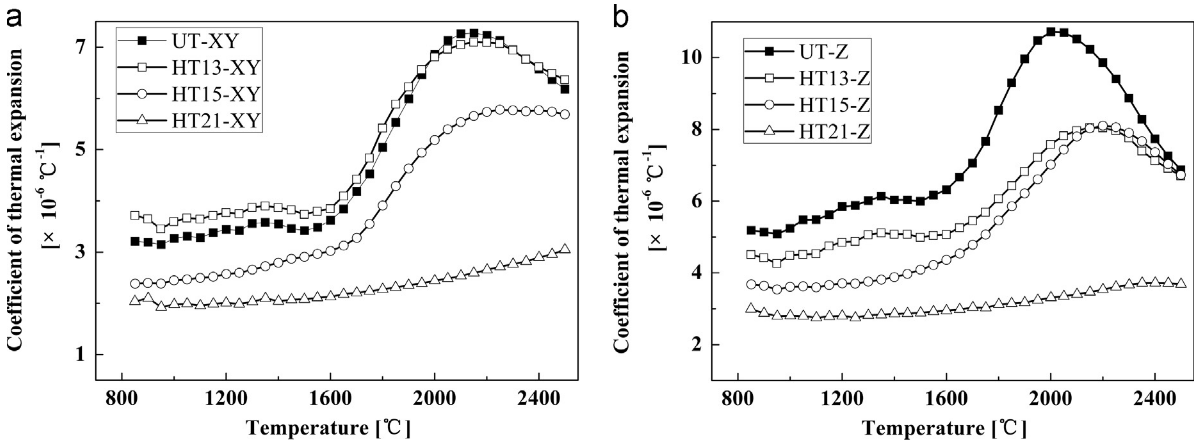

Fig. 1. Effect of heat treatment on the CTEs of the C/C composites in *XY* and *Z* directions: (a) *XY* direction and (b) *Z* direction.

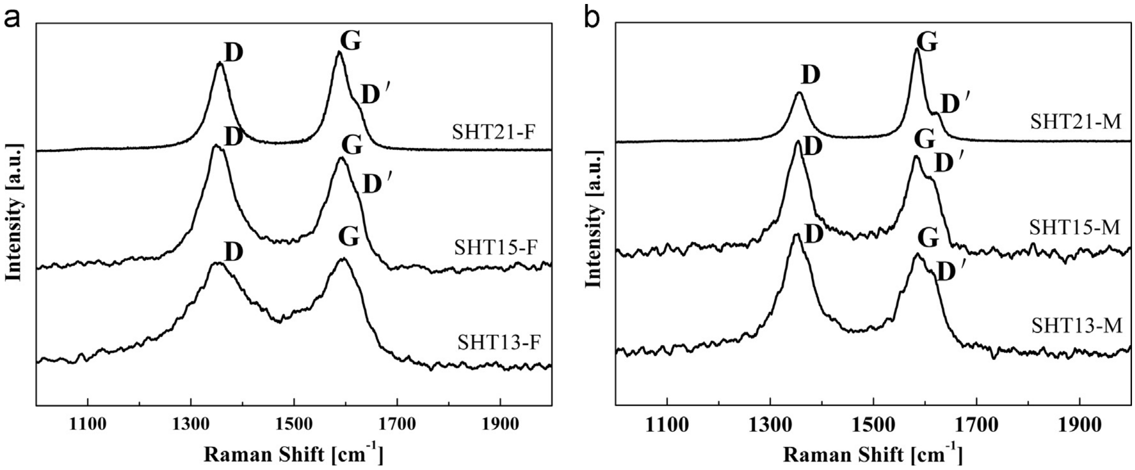

Fig. 2. Raman spectra of the C/C composites heat treated at different temperatures: (a) fibers and (b) matrices.

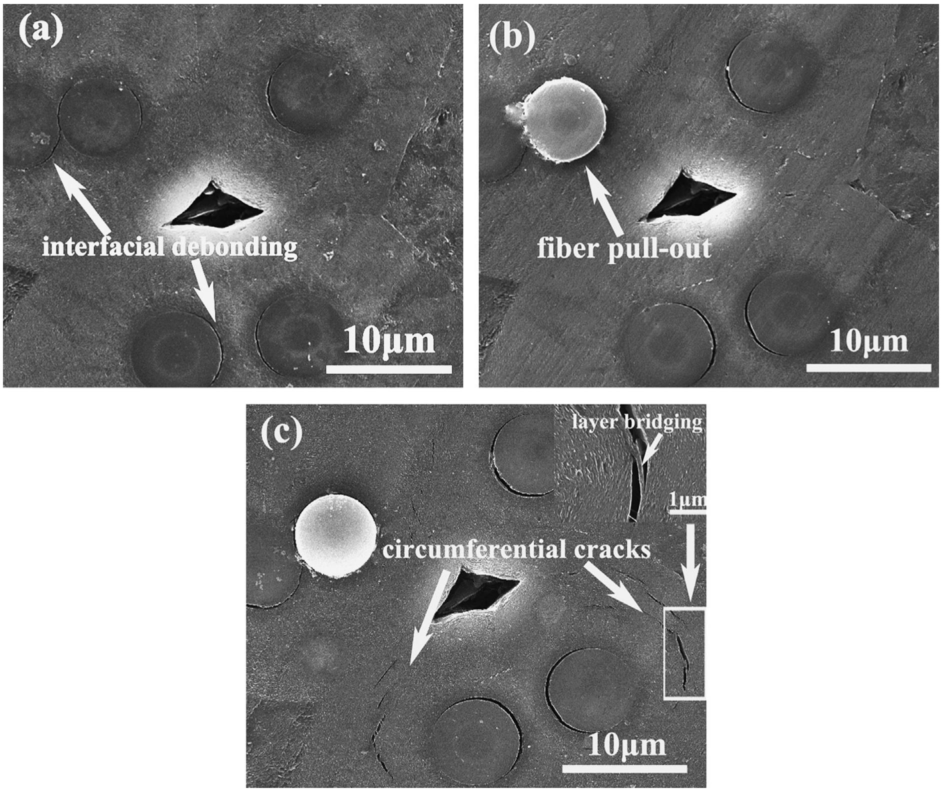

Fig. 3. Microstructure of the C/C composites heat treated at different temperatures: (a) 1300 °C; (b) 1500 °C and (c) 2100 °C.

temperature range of 1300–1500 °C [8]. These obvious changes in the structure of fibers resulted from the volatilization of non-carbon elements mainly nitrogen and oxygen, but the phenomenon did not take place in matrix [9–11]. It is suggested that the structural change of fiber is the main reason for the decrease of the CTEs at temperature below 1500 °C, which results in the smoothening of the CTE-temperature curves in the temperature range of 1300–1500 °C.

For many carbon materials without heat treatment, many distorted columns of layers and structural defects, defined as turbostratic features, were observed in carbon structure by transmission electron microscopy. After HTT at 2100 °C, the turbostratic features disappear and crystallites grow rapidly to reduce the crystal defects; in addition, the in-plane defects are virtually wiped out and the layers become perfect during the graphitization of carbon [11]. For these reasons, SHT21 has a higher degree of preferred orientation, and exhibits the lower thermal expansion due to the rapid graphitization of carbon [3]. As shown in Fig. 2b, the change in I_D/I_G of the matrix with the increasing HTT from 1500 to 2100 °C is greater than that of the fibers. It indicates that the high textured pyrocarbons are more easily to be graphitized than PAN fibers. Therefore, graphitization of the matrix is the main reason for the decrease of the CTEs above 1500 °C.

The microstructural changes of the same specimen are shown in Fig. 3. The fiber/matrix interfacial debonding takes place in SHT-13 (as shown in Fig. 3a). It results from CTE mismatch between fibers and matrices. Thus, the fiber/matrix interfacial debonding provides a channel which permits the relative movement between fibers and matrix. With the increase of heat treatment temperature up to 1500 °C, the fiber of SHT-15 is observed to protrude out of the surface through that channel (Fig. 3b). It mainly results from a higher CTE of the matrix than the fiber that leads to more thermal contraction of matrix than fibers during the cooling period. Meanwhile the fiber/matrix interfacial debonding also becomes significant due to less structural defects in the fibers after the release of non-carbon elements. As shown in Fig. 3c, the matrices are more easily to be graphitized which enlarges the CTE mismatch resulting in more serious fiber pulling-out and fiber/matrix interfacial debonding. Furthermore, circumferential cracks and layer bridging in the matrix of SHT-21 are observed clearly. These features both result from the structural stresses coming from the wrinkling of high textured pyrocarbon layers and the disappearance of turbostratic structure during the graphitization [11,12].

4. Conclusions

The variation of CTE with temperature and the effect of heat treatment temperature on the CTEs of C/C composites with high textured pyrolytic carbon matrix were investigated in the temperature range of 850–2500 °C. It was found that CTEs of the composites without heat treatment decreased clearly during the CTE measurement in the temperature ranges of 1300–1500 °C and 2100–2500 °C, and the heat treatment resulted in the decrease of CTEs. Raman spectra analyses showed that the orderly rearrangement of the fiber structure was the main reason for the decrease of the CTEs below 1500 °C. However, at higher temperatures (2100–2500 °C), graphitization of carbon matrix was the main reason for the decrease of the CTEs. In addition, fiber/matrix interfacial debonding and fiber pulling-out were observed with the increase of heat treatment temperature up to 1500 °C, while circumferential cracks around fibers and layer bridging in the matrix were observed with the increasing temperature up to 2100 °C.

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