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Study on the thermal expansion properties of C/C composites

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Abstract Two different woven (2D and 3D) carbon/carbon composites (C/C) and a block carbon have been prepared by chemical vapor infiltration (CVI). The effects of the density and porosity of composites, preform architectures and heat treatment on the thermal expansion properties of the C/C composites were investigated. It is revealed that the coefficient of thermal expansion (CTE) of C/C composites is negative below 100 °C, and the CTE values are inversely proportion to its porosity. Comparing with 2D C/C composites, 3D C/C composites have a better thermal stability. Heat treatment can increase the thermal stability of composites by changing interfacial thermal stress. The thermal expansion behavior of C/C composites is considered as the result of interaction between fibers and matrix.

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Introduction

Because C/C composites have excellent thermal properties of good heat transmission, low CTE and high mechanical strength at high temperature, they have been successfully used in the manufacture of aviation engine nozzle and thermal assemblies of the firebox as well as brake discs for airplane in the aeronautical, astronautical, military, and civil fields [1, 2]. In these applications, thermophysical properties of C/C composites are very important. Up to now, some dates on thermal expansion of C/C composites have been reported [3, 4], but these have not been systematically investigated, especially about 3D C/C composites, there are almost no reports about them.

The fibers, matrix and interlayer in C/C composites have different CTE, and thermal stress will be produced in these three microstructure constituents. Clearly, the expansion behavior of the C/C composites depends upon the thermal stress. Because the radial CTE of the fibers is much larger than the axial one, the thermal stress is complicated and different for 2D and 3D C/C composites [5]. It is necessary to relate the expansion behavior to the thermal stress to reveal failure mechanisms of the composites at different temperatures. When used at high temperatures, the thermal stress conditions will be changed and the composites will then exhibit a different expansion behavior. Therefore, it is very important to clarify the effect of heat treatment on the expansion behavior of different C/C composites.

For this purpose, in this paper, 2D and 3D C/C composites, as well as a block CVD C material, were prepared and the effects of the density and porosity of composites, preform architectures and heat treatment on the thermal expansion behavior of the composites from room temperature to 1,300 °C were investigated.

Experimental

Preparation of materials

In this study, three-dimensional (3D) preforms were braided into a rectangular shape by a four-step method using 1K T-300 carbon fibers. Two- dimensional (2D) preforms were cross-ply stacked by laying-up 1K T-300 carbon fabrics, the edges of preforms were stitched with 3K T300 carbon fibers. The C/C composites were fabricated by an isothermal chemical vapor infiltration (CVI) process at temperatures from 900 to 1,200 °C in low vacuum (10^4 Pa), using propylene (C_3H_6) as the organic feed gas and nitrogen (N_2) as the diluent, respectively. Ten densification cycles were carried out until the density reached 1.50–1.72 g/cm^3.

The deposition conditions for the CVD carbon were as follows: temperature 1,000 °C, time 200 h, the other fabrication conditions were similar with those of the PyC matrix, measuring its CTE is necessary to investigate the effect on thermal expansion behavior of the composites.

Macroporosity (P) of C/C composites is calculated from the relation:

$$P = 1 - V_f - \frac{\rho - V_f \rho_f}{\rho_m},$$

where ρ is the apparent density of composites, ρ_f and ρ_m are the densities of CF and PyC, respectively. The densities are measured according to the method reported by [4]. V_f is the volume fraction of CF in the preform.

Measurements of CTE

A Netzsch DIL 402C dilatometer was used for CTE measurements. The required specimens were cut off and machined into dimensions of 20 × 3.5 × 3.5 mm^3. All measurements were conducted on each sample in an Ar atmosphere from room temperature to 1,300 °C and at a heating rate of 3 °C per min. Tests are limited in the X–Y direction, and CTE is calculated by the formula

$$\alpha = \frac{\Delta L}{L(T_0) \cdot \Delta T},$$

where $L(T_0)$ is the length of the samples at the room temperature (25 °C), $\Delta L = L(T) - L(T_0)$ and $\Delta T = T - T_0$ are the changes of the length of the samples and the temperature, respectively. The accuracy of the measurements was ±4%.

Results and discussion

Effect of porosity and density

The C/C composites are made of the CF, PyC and pores, as showing in Fig. 1. The crystallites of PyC are arranged in the strip on the surface of the CF, in which carbon atom plane (002) are parallel to the direction of fiber axis [5]. In the process of chemical vapor infiltration (CVI), the small pores between the CF are filled by the PyC, but the larger pores between the fiber bundles are difficult to be densified, because of slow deposition or surface crust, so the remained pores in CVI C/C composites are unavoidable and result in the discontinuous distribution of PyC.

The relations of longitudinal CTE to temperature for CVD C and 3D C/C composites with three different densities are shown on Fig. 2. All these tested specimens have very small CTE with values from -1.5412×10^{-6}/°C to 4.3211×10^{-6}/°C their CTE variation with temperature are approximately linear and the slope of CTE vs. T curves are the same roughly, which is probably owing to the restriction of the interfaces between CF and PyC when expansion or shrinkage occurs. In the same temperature range from room temperature to 100 °C, they present obviously negative expansion behaviors with values ranging from -0.60341 to -1.5435×10^{-6}/°C.

For these composites, a comparison of CTE values at 85 °C is listed in Table 1. From Table 1, their absolute calculated values are smaller than those of the

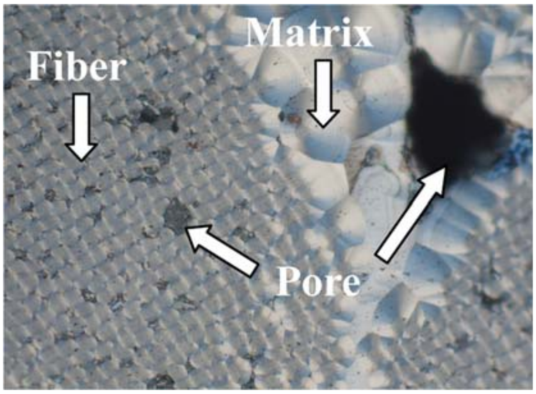

Fig. 1 The microstructure of C/C composites

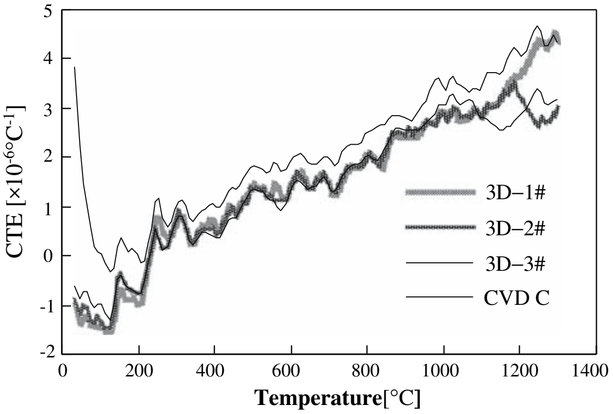

Fig. 2 Relations of longitudinal CTE to temperature of 3D C/C composites

measured negative expansion owing to the important contribution of the pores in the C/C composites, and under the present conditions, the values of CTE are inversely proportional to their porosity. The fewer the pores of the C/C composites are, the larger their CTE are usually, which agrees with the conclusion drawn by Baxter et al. [3]. When the C/C composites is heated in a condition of lower temperature, the volatilization of the absorbed water in them make the pores shrink, and the more porosity allows the composites to absorb more water, which results in more shrinkage. The composites possess different porosity, which explains their differences of the largest negative CTE. For example, the sample 3D-1# possesses the lowest density, the highest porosity, so it shows the largest negative CTE value.

Above room temperature –100 °C, their slopes of CTE vs. T curves with different densities have almost as same as that of CVD C. But above 1,000 °C, the expansion behaviors with different densities change with increasing temperature, the longitudinal CTE of sample 3D-3# and2# reach a peak value at about 1,000, 1,150 °C, respectively, but the sample 3D-1# not. The 3D-1# has a highest negative and positive CTE, that of 3D-3# is the lowest, and that of 3D-2# is in between that of them.

Table 1 Relationship between CTE and apparent density and porosity of the C/C composites under 85 °C

Samples ID	Fiber volume fraction (%)	Measured CTE (×10^{-6}/°C)	Apparent density (g/c m$^{3)}$	Porosity (%)
3D-1#	45	–1.4306	1.51	9.4
3D-2#	45	–1.3502	1.68	7.1
3D-3#	45	–1.0502	1.72	6.2
2D	45	–0.9821	1.72	6.2

It is well-known that the fibers, matrix in C/C composites have different CTE, the longitudinal, radial CTE of T300 carbon fiber were about –0.7–1 × 10^{-6}/°C and 7 × 10^{-6}/°C, respectively, and that of PyC matrix can reach about 8 × 10^{-6}/°C and 1.8 × 10^{-6}/°C, respectively, so there is mismatch between the fibers and the matrix, and the radial CTE of the fiber was much larger than that of C matrix. In a result, compressibility of the fibers and stretch of the matrix are responsible for the thermal expansion behavior of C/C composites above mentioned. The matrix carbon is encircled on the surface of the carbon fiber, which produces the intensive restriction for the carbon fiber expansion with the temperature. In consequence, under the same temperature range, C/C composites show the lower CTE than that of CVD C, as showing in Fig. 2.

Correspondingly, the longitudinal CTE reached a peak value at the sealing of crack temperature [6]. The compressive stress in the fibers is released as the matrix expanded, and then the negative longitudinal CTE of the fibers have little effect on the expansion of the composite. Therefore, the longitudinal CTE is controlled by expansion of the matrix and increase linearly below this sealing of the cracks temperature. Above the sealing of pores temperature, the CTE of the composites are controlled by a combination of expansion of the carbon matrix and shrinking of carbon fiber due to the negative longitudinal CTE at high temperature. The fiber restricts the expansion of the carbon matrix, and decreases the longitudinal CTE of the composites above the sealing of cracks temperature.

At the same time, a small quantity of fibers can be fractured by the stress concentration of the tip of cracks, and the expansion of the C matrix is slowly released, so the CTE values increase again, and appear a trough on the CTE vs. T curves, such as the sample 3D-2# and 3D-3#. Therefore, the longitudinal CTE remain lower than that of CVD C due to restriction of the fibers, and reach a peak value due to the sealing of cracks and the fiber fracture. In fact, the thermal expansion behavior of C/C composites can be regarded as the result of interaction of fibers and matrix.

For sample 3D-2# and 3#, the temperature 1,150, 1,000 °C are their sealing of cracks temperature of matrix, respectively, and there were different sealing temperature due to the different densities. Because the number of pores in the matrix is directly correlated to the density, the lower density, the higher porosity, and these implies higher sealing of pores temperature. The CTE of sample 3D-1# was no peak value owing to its lower density, but it was sure that the CTE of sample 3D-1# could reach a peak value at higher temperature, which may be above 1,300 °C.

Effect of preform architecture

Figure 3 shows the relations of longitudinal CTE to temperature of 3D and 2D C/C composites. It can be seen that the CET of 2D C/C composites is ranging between -0.4×10^{-6}/°C and 7.0×10^{-6}/°C, but the changing area of 3D C/C composites is from –0.8 to 3.0×10^{-6}/°C. It can be concluded that the CET of 2D C/C composites is much larger than that of 3D C/C composites, which indicated that the later have better thermal stability than the former. In addition, It was also noticed from Fig. 3 that the CTE of 3D and 2D C/C composites reached a same peak value at 1,000 °C, although the perform architecture were different, the sealing of cracks temperature was not changed owing to the same densities of matrix. Comparing Fig. 3 with Fig. 2, we can find that the curves variation tendency of three kinds of 3D C/C composites are similar in Fig. 1, though they have much difference in density, from the Fig. 3, though their density and porosity are much the same as each other, it was obvious that the CTE of 2D C/C composites are much larger than 3D C/C composites. The difference between 3D and 2D composites were made from the preform architecture. The 2D C/C composites was sandwich, there are no fibers among each layers. But the 3D C/C composites had fibers in the direction of thickness, and its fibers transfix the matrix in three directions, so they form an integral meshwork structure [4]. In this reasons, the longitudinal thermal expansion of 3D C/C composites are restricted with the meshwork structure of fibers. As a result, it is inevitable that the CTE of 3D C/C composites were lower than that of 2D C/C composites. Furthermore, all the fibers were laid at a small angle (22°) to the longitudinal axis of the 3D C/C, and the radial expansion of the fibers did not obviously increase the longitudinal CTE. But in 2D C/C, one half of the fibers were laid longitudinally and the other halves were laid transversely. The radial expansion of the transverse fibers increased the axial expansion of the longitudinal fibers, so that the longitudinal CTE of 2D C/C increased more rapidly than that of 3D C/C at the same temperature. It implies that the thermal stability of 3D C/C composites is better than 2D C/C composites under the same condition.

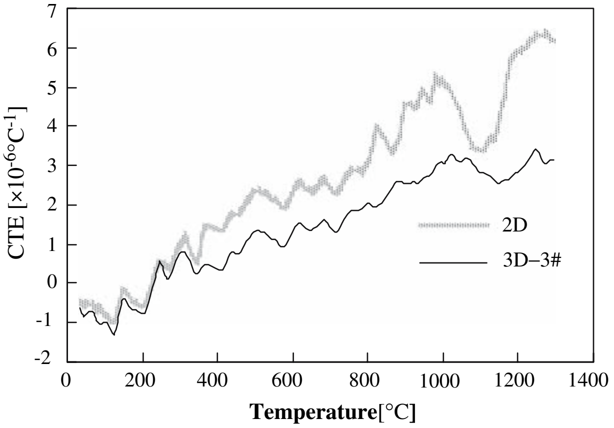

Fig. 3 Relations of longitudinal CTE to temperature of 3D and 2D C/C composites

Effect of heat treatment

Because there is mismatch between the fibers and the matrix in C/C composites, thermal stress will be produced in the interface between fibers and matrix. Clearly, the expansion behavior of composites depends upon not only the physics constant (CTE, E, et al.) of each component in the material, but also the thermal stress in the interface. When C/C composites used at high temperatures, the thermal stress conditions will be changed and the composites will then exhibit a different expansion behavior. Therefore, as high structure material, it is very important to clarify the effect of heat treatment on the thermal expansion behavior of 3D C/C composites. For this purpose, the samples were heated treatment at 2,100 °C for 2 h in a vacuum.

The relations of longitudinal CTE to temperature of 3D C/C before and after heat treatment are compared in Fig. 4a. Because some fibers were fractured after the treatment, the longitudinal thermal expansions of matrix are restricted by the fractured fibers. In a result, as the Fig. 4a shows, the longitudinal CTE after heat treatment remains lower than that of composites before heat treatment over all temperature range. Furthermore, the number of matrix cracks was increased by the treatment and thus the negative longitudinal CTE was decreased at low temperatures and no peak value at this sealing of the cracks temperature appeared below 1,300 °C.

Figure 4b shows the longitudinal CTE to temperature of 3D C/C composites with different densities after the treatment. It can be seen that the density had no obvious effect on the longitudinal CTE after heat treatment. There were some thermal stress cracks in the interface between fibers and matrix after the heat treatment, so less radial stress was produced in both the fibers and the matrix. As a result, the longitudinal CTE of the composite were dominated by the expansion of matrix after the treatment, so their thermal expansion behavior changed similarly comparing with that of the CVD C, although the former was lower than the latter in the whole temperature range due to the restriction of fibers.

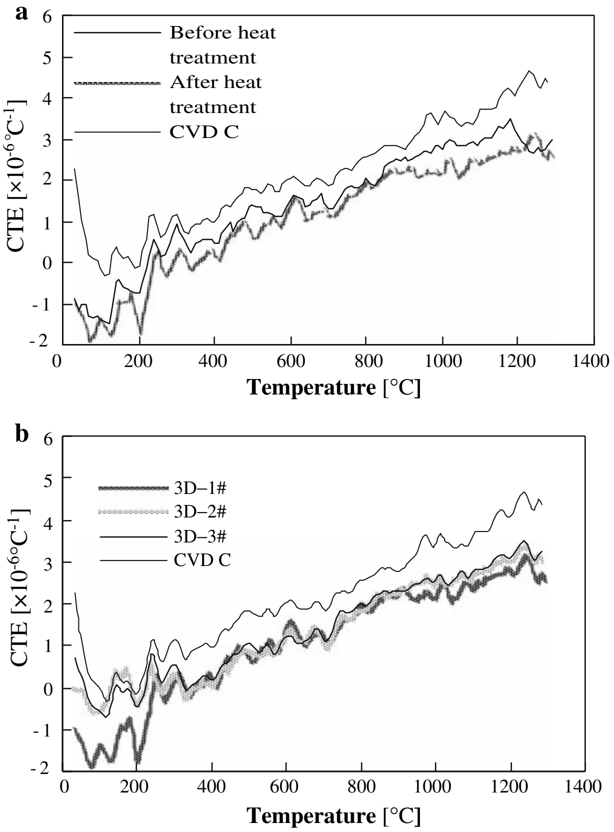

Fig. 4 Effect of heat treatment on the longitudinal CTE of 3D C/C composites

Conclusion

As a result of these studies the following conclusions may be made:

1. The coefficients of thermal expansion (CTE) of C/C composites are negative in the range room temperate to 100 °C due to the pores shrink, and inversely proportion to their porosity. Above 100 °C, the CTE vs. T curves have almost the same slope with different densities and reached a peak value at this sealing of the pores temperature, and then the compressibility stress of the fibers restricts the expansion of the C matrix, and decrease the longitudinal CTE of the composites above the sealing of pores temperature.
2. Comparing with 2D C/C composites, 3D C/C composites have a better thermal stability, in which the braided structure plays an important role, the longitudinal thermal expansion of 3D C/C composites are restricted with the meshwork structure of fibers. Furthermore, the radial expansion of the transverse fibers increased the axial expansion of the longitudinal fibers in 2D C/C composites.
3. The heat treatment can increase thermal stability of the composites by changing interfacial thermal stress of the materials, and the number of matrix cracks was increased by the treatment and thus the negative longitudinal CTE was decreased at low temperatures. In fact, the thermal expansion behavior of C/C composites can be regarded as the result of interaction of fibers and matrix.

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