Effects of Preform and Pyrolytic Carbon Structure on Thermophysical Properties of 2D Carbon/Carbon Composites

LUO Rui ying, CHENG Yong hong
( College of Science, Beijing University of Aeronautics and Astronautics, Beijing 100083, China)

Abstract: Four kinds of carbon/carbon (C/C) composites, including the needle carbon fiber felt/the pyrolytic carbon (two different pyrolytic carbon microstructures), the chopped carbon fiber/resin + pyrolytic carbon (PyrC), and the carbon cloth/PyrC, named as the composites 1#, 4#, 2#, and 3#, are prepared respectively. Effects of the preform and pyrolytic carbon structure on the thermophysical properties of 2D C/C composites are studied. The C/C composites possess low coefficient of thermal expansion (CTE). In a range of some temperatures, the negative expansion emerges in x-y direction for four C/C composites. From 0 to 900°C, the CTE is small and almost linear with the temperatures. The C/C composites have high thermal conductivities (TCs). As a function of temperature, TCs of the C/C composites are varied with the structures of preform and pyrc as well as the direction of heat transfer. In x-y and z direction, TCs differ greatly and that in x-y direction (25.6–174 W/m°C) is several times larger than that in x direction (3–50 W/m°C).

Key words: carbon/carbon(C/C) composite; pyrolytic carbon; thermal expansion; thermal conductivity

C/C composites have been successfully used as materials for engine nozzle and thermal assemblies of firebox as well as brake discs of vehicles in the aeronautical, astronautical, military, and land transportation fields[1,2]. In these applications, their thermophysical properties are very important, but these properties are less reported. Preform structure, microstructure of PyrC, density and porosity of C/C composite have significant effects on its thermophysical properties. R. I. Baxter[3] reported that with temperature increasing from 1000 to 2000 °C, for the low density C/C composites (0.18 g/cm³) the TCs increased, and that for the high density C/C composites (1.25 g/cm³), the TCs decreased and CTEs increased. In this paper, the effects of the preform structure and the microstructure of the matrix carbon on the thermophysical properties of C/C composites are investigated. The mechanisms of thermal expansion and heat transfer for the C/C composites are discussed.
1 Experimental Investigation

1.1 Preparation of material samples

The PAN based fibres containing 12K filaments per tow obtained from Lanzhou Carbon Fiber Plant, China, are used to prepare preforms. The three kinds of preforms are fabricated according to the following steps: for the preforms 1# and 4#, the CF felts have been laminated (Fig. 1), of which two layers are oriented at an angle of 90°, and then needled progressively to the thickness of preforms, which have been described elsewhere\(^4\). Preform 2# is prepared at hot pressure of the chopped CF infiltrated by using the phenolic resin and following carbonization and graphitization. Plain type HS carbon cloth of 1K PAN based fiber fabricated in Jilin Carbon Co., China, is used as preform 3# by spreading layers of carbon cloth. The four composite samples (named as 1#, 2#, 3#, and 4# respectively) are prepared from the different preforms. The volume fractions of the four preforms are all 40%. The sizes of preforms are 400 and 150 mm in outer and inner diameters, 15-30 mm in thickness. The reactant and carrier gases are propylene and nitrogen respectively. After the densities of the four samples are up to 1.70-1.75 g/cm\(^3\), they are treated at 2500°C for 2 hours, and finally the required C/C composite samples are obtained.

1.2 Coefficient of thermal expansion (CTE)

The samples are placed in a dilatometer equipped with silica tube and push rods. Measurements are performed in a nitrogen atmosphere at a heating rate of 2°C per min. From 0-100°C up to 0-900°C nine different temperature segments are selected. Tests are limited in x-y direction, and \(\alpha = \frac{\Delta L}{L \times \Delta T}\). Sample dimensions are 65 mm × 10 mm × 5 mm.

1.3 Thermal diffusivity

Laser flash method is used in thermal diffusivity test. The equipment is composed of red gem laser (light beam diameter is less than 10 mm in sample), vacuum furnace (pressure is less than 1.3 Pa) and back face temperature collecting system. In this method the front face of the wafer shape sample is heated with a short laser pulse and in the condition of heat insulation and that one dimension heat flow comes into being in the back face. The process is monitored by the back face collecting system to record the temperature curves through which thermal diffusivity is calculated. Tests are carried out in a vacuum or an argon atmosphere from 0°C up to 900°C in x-y and z direction. Ten temperature points are measured in each direction. Sample is disc-shaped with a diameter of 10 mm and a thickness of 1-3 mm.

1.4 Specific heat capacity

Mixture method is used to measure specific heat capacity. The equipment is composed of furnace, calorimeter, heat insulation system and temperature measurement system. In the experiment, sample is suspended by a nickel thread with a diameter of 0.1 mm in the furnace and heated. When the temperature reaches the required stable value \(T_1\), the sample is put into heat insulation copper calorimeter with a temperature of thermal conductivity. The heat emitted makes the calorimeter temperature go up to the terminal value \(T_n\). By calculating the temperature change, the mean specific heat capacity is obtained and furthermore the real specific heat capacity can be achieved. The whole experiment process is performed in a vacuum or an argon atmosphere. Sample is column-shaped with a diameter of 14 mm and a height of 20-30 mm.

1.5 X-ray diffraction

Powder shaped X-ray diffraction test is taken on a diffractometer, operated at 20 kV and 100 mA, by using CuKα radiation. Two groups of data of diffraction peaks (002) and (1 1 0) are obtained. The interlayer spacing and crystallite size (\(L_a, L_c\))
are calculated from the Bragg formula $2d \sin \theta = \lambda$ and Scherrer equation $L = \frac{k \lambda}{I \cos \theta}$ respectively, where $\theta$ is angle of diffraction, $\lambda$ is incident ray wavelength, $L_a$ and $L_c$ are mean width and mean thickness of crystallite in intra layer and inter layer, $k$ is Scherrer constant, and $I$ is value of the area divided by the height of diffraction peak. Growth characteristics of PyrC are examined with polarized light microscope model Neophot 21.

2 Results and Discussion

2.1 Microstructure

The four C/C composites are made of CF, PyrC and pores. The CF is of skin-core structure [5]. Crystallites are arranged in strip in the surface of CF, in which carbon atom plane (002) is parallel to the fiber axis direction [6]. In the process of PyrC deposition, the small pores among fibers are closed by deposition, but the large pores among fiber bundles are difficult to be densified because of slow deposition or gas block. These remained pores make PyrC matrix discontinuous in the composites. For the four samples, there are large differences in PyrC growth characteristics such as crystallite size and orderliness degree (Table 1).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Interlayer spacing $d_{002}$ (nm)</th>
<th>Intra layer width of crystallite $L_a$ (nm)</th>
<th>Interlayer thickness of crystallite $L_c$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#</td>
<td>0.3379</td>
<td>35.3</td>
<td>18.9</td>
</tr>
<tr>
<td>2#</td>
<td>0.3422</td>
<td>15.2</td>
<td>8.56</td>
</tr>
<tr>
<td>3#</td>
<td>0.3409</td>
<td>19.7</td>
<td>9.78</td>
</tr>
<tr>
<td>4#</td>
<td>0.3396</td>
<td>28.7</td>
<td>15.1</td>
</tr>
</tbody>
</table>

The optical micrographs under polarized light conditions are shown in Fig. 2. For the sample 1#, PyrC is mainly composed of rough laminar tissue (RL), which grows with ringed multilayer around CF (Fig. 2(a)). PyrC in 4# is also of RL (Fig. 2(d)), but it has larger interlayer spacing and smaller $L_a$ and $L_c$ than in 1# (Table 1). In 3#, PyrC belongs to smooth laminar tissue (SL) (Fig. 2(c)), and is filled well in fiber bundles, however, among between the carbon cloth layers PyrC develop in cone side by side to grow like dendritications and make the pores form flat. As for 2#, PyrC is chiefly made up of isotropic tissue (ISO) that is weak in optical activity and loose in structure (Fig. 2(b)), leading to the largest discontinuities and make the pores form flat. As for 2#, PyrC is chiefly made up of isotropic tissue (ISO) that is weak in optical activity and loose in structure (Fig. 2(b)), leading to the largest discontinue.
ity of matrix. Preform architecture and PyrC microstructure result in differences of thermal properties for the C/C composites.

2.2 Coefficient of thermal expansion (CTE)

2.2.1 Effects of CF and PyrC

For PAN-based CF, CTE is about $1 \times 10^{-6}$ /K[^7] in the axis direction. PyrC belongs to disordered layer, which is similar to the layered structure of graphite. However, the interlayer spacing is larger and the crystallite is less developed than those of graphite. With rising of the temperature, the graphite crystal shrinks in a direction and CTE is always negative at $0-400 ^\circ C$, as shown in Fig. 3[^8]. Therefore, as a function of temperature, the expansion performance of PyrC in C/C composite is similar to that of graphite. CTE of C/C composite closely connected with CTE of each element and abided by mixture regulation,

$$\alpha = V_f \alpha_f + V_m \alpha_m$$

where $f$ and $m$ denote the fiber and PyrC respectively, $V$ and $\alpha$ stands for the volume and CTE respectively, and the value of exponent $c$ determined by experiment is between $-1$ and $1$. In this paper, $c \approx 1$, so the above expression becomes

$$\alpha = V_f \alpha_f + V_m \alpha_m$$

A comparison between theoretical and actual CTE values at $0-100 ^\circ C$ is listed in Table 2. The result shows that the theoretical value is larger, namely, the actual negative expansion values are smaller mainly owing to the important contribution of the pores in C/C composite.

### Table 2 Relationship between CTE and apparent density as well as porosity at $0$ $100 ^\circ C$

<table>
<thead>
<tr>
<th>Samples</th>
<th>Fiber volume fraction $V_f$</th>
<th>Actual CTE $\alpha_f$</th>
<th>Theoretical CTE $\alpha_f$</th>
<th>Apparent density $\rho$</th>
<th>Porosity $%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1#</td>
<td>0.4</td>
<td>-0.29</td>
<td>-0.19</td>
<td>1.75</td>
<td>6.3</td>
</tr>
<tr>
<td>2#</td>
<td>0.4</td>
<td>-0.85</td>
<td>-0.39</td>
<td>1.70</td>
<td>9.1</td>
</tr>
<tr>
<td>3#</td>
<td>0.4</td>
<td>-0.56</td>
<td>-0.37</td>
<td>1.72</td>
<td>7.5</td>
</tr>
<tr>
<td>4#</td>
<td>0.4</td>
<td>-0.38</td>
<td>-0.31</td>
<td>1.74</td>
<td>6.9</td>
</tr>
</tbody>
</table>

2.2.2 Effects of pore and density on CTE

Porosity can be expressed as

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

where $\rho$ is apparent density, $\rho_f$ and $\rho_m$ are densities of CF and PyrC respectively. Table 2 shows that the density and pore of the composites have effects on the thermal expansion of C/C composite. CTE is directly proportional to the density and inversely proportional to the porosity. Higher densified materials and fewer pores usually lead to small absolute values of the negative expansion and the large positive expansion values for the C/C composites, which agrees with the conclusion drawn by R. I. Baxter[^3]. Except the macroscopical pores among PyrCs, PyrCs themselves contain the various microscopic pores leading to the different densities so that they have different effects on the thermal expansion of C/C composite. Generally PyrC can be divided into three types: RL, SL and ISO, and their density sequence is RL $>$ SL $>$ ISO[^9]. As a result, the sequence of their ability inducing the negative expansion is RL $<$ SL $<$ ISO. In sample 1# and 4#, PyrC is mainly composed of RL, in 2# of ISO, and in 3# of SL. Their different PyrC microstructures and porosities prove the contribution to the negative expansion of the C/C composites.

2.2.3 Effects of temperature on CTE

Temperature can be explained by atom or molecular vibration in solid material. Different temperatures induce different atom vibration breadths to make solid volume change, which means expansion or shrinkage effect. For the C/C composites their curves of CTE-temperature are shown in Fig. 4. They all have low CTE. Within the range of some temperatures all samples have negative expansions, and the negative expansion effect is the most obvious one at $0$-$100 ^\circ C$. Above $0$-$100 ^\circ C$ the CTE is approximately linear with the temperature and the slope is roughly the same. These phenomena can be explained through the atom vibration and porosity. In the C/C composites, CTEs of CF is small in $x$-$y$ direction, and the
CF volume fractions in four preforms are all 40%. The fiber surface is encircled by PyrC and the interface combination is fine, which produces the restriction on the fiber expansion. Consequently CTE is predominated by the thermal expansion of PyrC. The performance of thermal expansion of PyrC in fiber axis direction is similar to that shown in Fig. 3, in which the trend of CTE of C/C composite trend with temperature is determined.

When the C/C composite is heated at low temperature, due to the carbon atom vibrating, atom spacing decreases in $x$-$y$ direction, thus making the pores shrink. The more pores result in the more shrinkage (Table 2, Fig. 4), which explains the differences among the largest negative expansions in different samples. In the range of low temperatures, the CTE of CF is small. The comprehension of the large negative expansion and small positive expansion leads to the apparent negative CTE of C/C composite. In spite of diverse preform and microstructure, two ingredients are both made up of carbon atoms and their atom spacings are similar, so that their thermal expansions have the same trend with the temperature. This is the main reason responsible for the almost same slope for the four composites. Compared with the changing ratio of graphite CTE with the temperature, a smaller ratio occurs in the C/C composite, which probably owes to the restriction of the interface between CF and PyrC on the expansion or shrinkage. In Fig. 4, the segment of CTE increasing linearly with temperature can be expressed by formula

$$a = b_0 + b_1 T$$  \hspace{1cm} (1)

where $b_0$ and $b_1$ are shown in Table 3, $b_0$ reflects preform architecture, PyrC microstructure, and porosity in the composite; $b_1$ value is $10^{-13} \times 10^{-10}/K^2$, which reflects the same trend of CTE with temperature.

<p>| Table 3 Values of $b_0$ and $b_1$ by formula (1) |</p>
<table>
<thead>
<tr>
<th>Samples</th>
<th>1#</th>
<th>2#</th>
<th>3#</th>
<th>4#</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b_0/(10^{-6}K^{-1})$</td>
<td>-0.43</td>
<td>-1.10</td>
<td>-0.74</td>
<td>-0.57</td>
</tr>
<tr>
<td>$b_1/(10^{-8}K^{-2})$</td>
<td>10.1</td>
<td>13.0</td>
<td>12.2</td>
<td>12.8</td>
</tr>
</tbody>
</table>

2.3 Thermal conductivity (TC)

2.3.1 TC in the same direction

For four C/C composites, TC in $x$-$y$ direction is shown in Fig. 5 (a). For sample 1#, TC decreases with the increase of the test temperature. In other three samples TCs go up and subsequently decline with the temperature increase. In 2# and 3#, the change trend of TC are small. Considering the same temperature for TC, the result is 1# > 4# > 3# > 2#. TC value is the highest for sample 1#, more than 110 W/ m$\cdot$K; but for 2#, the lowest, less than 30 W/ m$\cdot$K. From Fig. 5 (b), in $z$ direction, TC is much smaller than that in $x$-$y$ direction, and from Table 2 and Fig. 5, it is found that TC varies in inverse ratio with the porosity (2# > 3# > 4# > 1#). Obviously the higher the porosity is, the more discontinuous the PyrC matrix is, which brings more obstacle to heat transfer. In addition, a large heat transfer difference exists in three kinds of PyrC tissues (RL, SL, ISO) and the heat transfer performance sequence is: RL> SL> ISO. From Fig. 2, it is seen that more RL is contained in sample 1#, which is one of the reasons for its higher TC. Although their PyrCs are all the RLs, the completeness of PyrC in sample 1# is higher than that in 4#, and consequently TC of 4# is lower in the same condition.

2.3.2 TC comparison in both directions

Anisotropy of TC for the densified C/C com
The TC of C/C composites is mainly due to the anisotropy of the preform. In the condition of the same temperature TC in z direction (The maximum 50 W/m*K, minimum 3.5 W/m*K) is much lower than those in x-y direction (maximum 175 W/m*K, minimum 25.6 W/m*K). TC difference between both directions is primarily caused by different volume fractions of CF. CF is the channel of heat transfer, so the direction containing a greater amount of CF is more advantageous to TC for the C/C composites. There are CFs in z direction for samples 1#, 2# and 4#, but their CE volume fractions are much less than those in x-y direction, so the TCs in z direction are lower. In case of 4#, laminated carbon cloth sample, because of no any fiber in z direction, its TC is very low in this direction and a large TC difference between both directions comes into being (approximately as 5 times large in x direction as in z direction).

2.3.3 Effects of density, specific heat capacity and thermal diffusivity on TC

Theoretically speaking, TC of C/C composite is only dominated by three factors including density \( \rho \), specific heat capacity \( c \) and heat diffusivity \( \gamma \). Their product means TC, \( \lambda = \gamma \rho c \). Density, an important parameter, and specific heat capacity are shown as volume effects. From Fig. 5 (a), 5(b) and Table 2, a conclusion is drawn that TC increases with the density of the composite, which agrees with the result tested by Zhao J. X. \[7\]. Specific heat capacity of C/C composite increases with the temperature, as shown in Fig. 6, which gives a positive contribution to the TC. The specific heat capacity almost making no difference in the same temperature implies that the preform architectures and the microstructure of the matrix carbon have little effect on it. Actually two ingredients in the C/C composites are both composed of carbon element. As long as the material density does not differ too much, the specific heat capacity will not make much discrepancy. Here thermal diffusivity is worth to emphasize. The above formula shows that if \( \gamma \) becomes smaller, the more heat will be transferred to other parts of the materials. Therefore thermal diffusivity presents the performance of making the temperature uniform in the composites \[10\]. In x-y and z direction their thermal diffusivity is shown as in Fig. 7, and their values decrease with the increasing the temperature. TC is anisotropic due to the anisotropy of thermal diffusivity. In a large extent TC is dominated by thermal diffusivity.
In short, the preform and PyrC structure have the significant effects on TC of C/C composite, increasing the volume fraction of continuous long CF and content of PyrC of RL in the composite will raise the TC in this direction.

4 Conclusions

(1) Thermophysical properties of C/C composites are mainly dominated by preform and PyrC structure. The four C/C composites possess low CTE. In a range of some temperatures, the negative expansion emerge in x-y direction for four C/C composites and their CTEs reach their minimum at 0-100°C, values varying between -0.29 × 10⁻⁶/K and -0.85 × 10⁻⁶/K. From 0 to 900°C, CTE is almost linear with the temperatures. The sample having high density and RL possesses the larger CTE under the same condition.

(2) The C/C composites have high TCs. As a function of temperature, their TCs firstly increase and subsequently decrease for the sample 2#, 3# , 4#, whereas a continual decrease is found for sample 1#. In x-y and z direction, TC differed greatly and that in x-y direction (25.6 174 W/m·K) are several times higher than that in z direction (3.5-50 W/m·K). The sample 1# has the highest TC in x-y direction under the same condition owing to its PyrC of RL and the needled carbon fiber preform structure, but 3# the lowest TC in z direction due to no any CF in this direction. Increasing the volume fraction of continuous long CF and content of PyrC of RL in the composites will raise their TC in this direction.

References


Biographies:

LUO Rui ying  Professor of Materials Physics & Chemistry, College of Science, Beijing University of Aeronautics and Astronautics. Ph.D, College of Materials Science and Engineering, Northwestern Polytechnical University.

CHENG Yong hong  M. Sc., Materials Physics & Chemistry Research Center, College of Science, Beijing University of Aeronautics and Astronautics.