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LETTER

The thermal expansion of carbon/carbon composites from room temperature to 1400 °C

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The coefficient of thermal expansion (CTE) is one of the most important properties for materials used under variable temperatures. Carbon/carbon composites must be capable of high geometric stability and low thermal expansion when they are used in engine turbine blades, rocket nozzles and seal rings in a liquid propellant rocket engine [1]. The thermal expansion of C/SiC composites and pyrocarbon films has been studied by Cheng et al. [2] and Taylor et al. [3], respectively. Carbon/carbon composites were developed using high-pressure impregnation/carbonization techniques and their thermophysical properties studied by Manocha et al. [4]. The thermophysical properties of five different carbon/carbon composites were discussed by Luo et al. [5]. Baxter et al. studied the effect of density on thermal expansion [6]. Piat and Schnack [7] studied pyrocarbon with different texture degrees and attempted to model the influence of microstructure on the coefficients of thermal expansion by collecting experimental data from the real physical structure using SAED and HRTEM. A material with a specific thermal expansion can be designed by adjusting the microstructure. Here we report the influence of heat treatment, preform architecture and the microstructure of the matrix carbon on the thermal expansion of carbon/carbon composites.

A layer of carbon fiber cloth without a weft thread and a random short fiber layer were laminated alternately to prepare porous carbon fiber preform felt with an apparent density around 0.6 g/cm^3. The carbon cloth layer was stacked in such a way that each layer was oriented at 90° to the adjacent layer. Carbon/carbon composites with a density of 1.75 g/cm^3 were prepared by a thermal gradient CVI process using natural gas (98%CH_4, 0.3%C_3H_8, 0.3%C_4H_{10}, 0.4% other hydrocarbons) as precursor. Specimens were subjected to heat treatment at different temperatures in an argon atmosphere. The detailed description of the preparation had been reported elsewhere [8].

The coefficient of thermal expansion of the densified composites was measured parallel and perpendicular to the carbon fiber cloth layer, or the random short fiber layer, from room temperature to 1400 °C in an argon atmosphere by using a Netzsch DIL 402C dilatometer. The specimen size was $3.5 \times 3.5 \times 20$ mm^3. The microstructures were analyzed using an X'Pert X-ray diffraction analyzer. Data for diffraction peaks (002) was obtained. The microstructures were examined by a Olympus PMG3 polarized light microscope.

The thermal expansion of graphite materials is anisotropic and is higher perpendicular to the graphite layers than parallel. In carbon/carbon composites, the graphitic flat-layered structure crystallites of pyrocarbon are arranged on the surface of the carbon fiber, and grow around the carbon fiber in the form of a ringed multilayer structure, in which the graphitic layers are parallel to the fiber axis. Therefore, the thermal expansion is anisotropic as well if the preform

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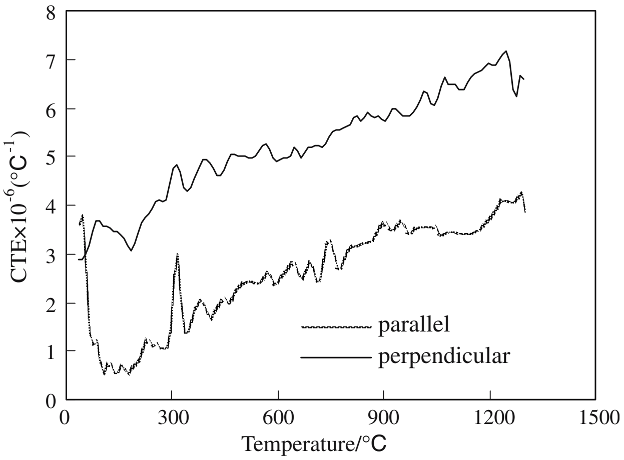

Fig. 1 The anisotropic thermal expansion of carbon/carbon composites

is anisotropic. Figure 1 shows that the coefficient of thermal expansion is higher perpendicular than parallel to the fiber direction.

Carbon/carbon composites possess turbostratic graphite structure, which can be transformed from turbostratic graphite into hexagonal crystal, with increase in the heat treatment temperature. The bond between adjacent graphite layers is weak van der Waals forces, so the layers are liable to sliding as a result of the thermal stress, causing a transformation from a turbostratic to a more ordered structure at high temperature. As a result of the interlayer spacing decreasing and stronger van der Waals forces between the layers the coefficient of thermal expansion of the carbon/carbon composites decreases. Figure 2 shows that the coefficient of thermal expansion decreases with increasing heat treatment temperature. The deposition temperature of the pyrocarbon is 1200 °C, so the heat treatment temperature for the untreated carbon/carbon composites is also 1200 °C. Figure 3 shows that the d_{002} values for untreated samples are larger than those of samples heat-treated at 2500 °C from room temperature to 1400 °C. The d_{002} values of both samples increase with the increasing temperature. The spacing of the graphite layers also increases with increasing temperature, which is the essential reason why the coefficient of thermal expansion increases.

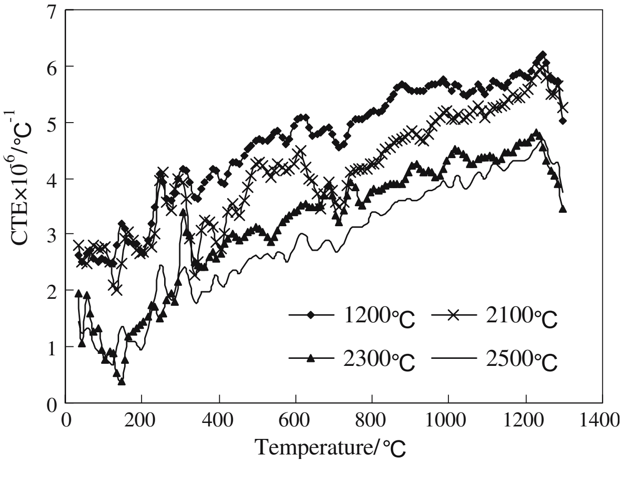

Fig. 2 Effects of heat treatment temperature on the thermal expansion of carbon/carbon composites

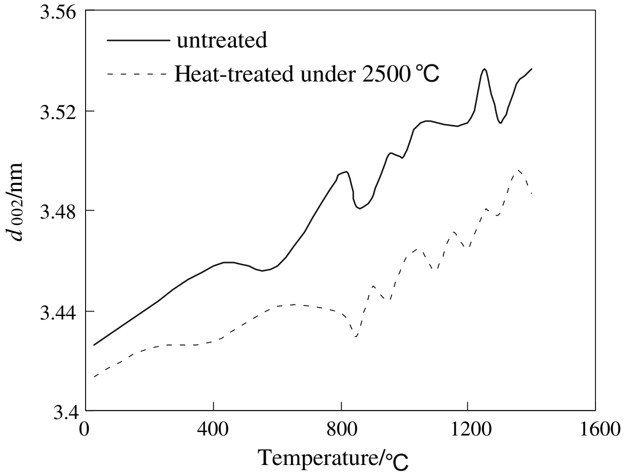

Fig. 3 The variation of interlayer spacing of the matrix carbon with temperature

The macroscopic property of a material is determined by its microstructure, so the thermal expansion of carbon/carbon composites depends on their microstructures. For composites with the same preform, the main reason that leads to different density is the macroscopical pores and the various microscopical pores in the pyrocarbon themselves, which exert different effects on the thermal expansion. Generally, smooth laminar texture pyrocarbon possesses lower density than rough laminar texture pyrocarbon [9]. As a result, the former is more capable of inducing a negative expansion than the later. Therefore, the coefficient of thermal expansion of pyrocarbon with a smooth laminar texture is smaller than that of pyrocarbon with a rough laminar texture under the same conditions as shown in Fig. 4. The above mentioned explanation is similar to that in the literature [5], but it still requires further investigation. In this study, the interlayer spacing d_{002} for pyrocarbon with a rough laminar texture is smaller than that of pyrocarbon with a smooth laminar texture from room temperature to 1400 °C as shown in Fig. 5.

During the preparation or heat treatment for carbon/carbon composites, strong thermal stress will be produced due to the anisotropic thermal expansion

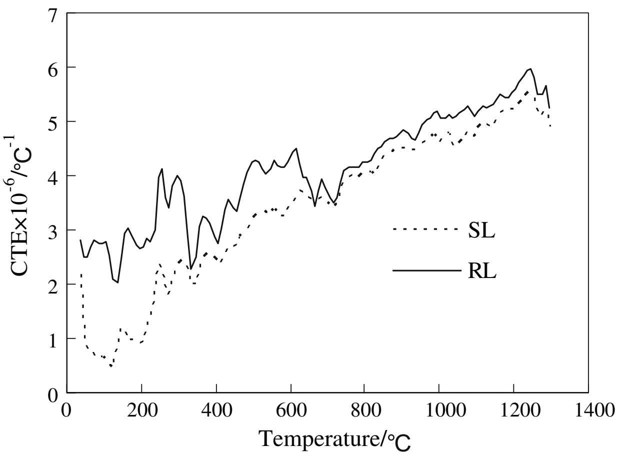

Fig. 4 The variation of thermal expansion coefficient of different pyrocarbon microstructures with temperature

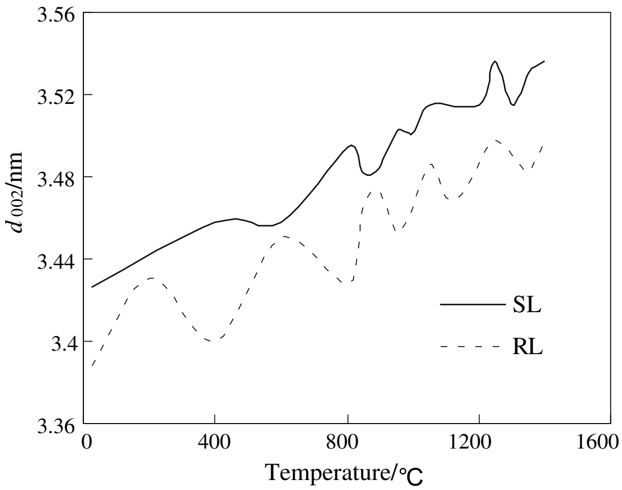

Fig. 5 The variation of interlayer spacing of different pyrocarbon microstructures with temperature

in these materials and the thermal expansion mismatch between carbon fiber and pyrocarbon. Therefore, pyrocarbon is liable to fracture when the heat treatment temperature or temperature gradient is changed. Figure 2 shows that with increasing temperature the coefficient of thermal expansion increases to a peak value at 1200 °C and then decreases. Since pyrocarbon is deposited from natural gas between 850 °C and 1200 °C, lots of microcracks are generated before 1200 °C. Those microcracks provide space for thermal expansion and begin to heal when the temperature is above 1200 °C. This is one explanation that the thermal expansion reaches to a peak value at 1200 °C with increasing temperature. Of course, this explanation remains to be proved in further investigations. Moreover, the negative longitudinal expansion of the fibers at high temperature restricts the expansion of the pyrocarbon matrix with increasing temperature, which also results in the decreasing of thermal expansion [2]. Therefore, the coefficient of thermal expansion decreases with increasing temperature when the temperature goes beyond 1200 °C. The thermal expansion is the result of interaction between carbon fibers, matrix pyrocarbon and their interface.

In conclusions, the thermal expansion of carbon/carbon composites is anisotropic and is higher perpendicular than parallel to the fiber direction. The coefficient of thermal expansion decreases with the heat treatment temperature increasing. The thermal expansion of pyrocarbon with a smooth laminar texture is smaller than that of pyrocarbon with a rough laminar texture under the same conditions. With the temperature increasing, the coefficient of thermal expansion increases first and then decreases with a peak value at 1200 °C.

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