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Original Article

Floating catalyst chemical vapor infiltration of nanofilamentous carbon reinforced carbon/carbon composites – Integrative improvement on the mechanical and thermal properties

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ABSTRACT

Nanofilamentous carbon (NFC) reinforced carbon/carbon composites were produced by floating catalyst chemical vapor infiltration with ferrocene content ranging 0–2.0 wt%. The NFCs and increased graphitization degree led to an improvement on the mechanical and thermal properties. An excellent combination of high strength and thermal conductivity (TC), and low coefficient of thermal expansion (CTE) was reached by adding 0.5–0.8 wt% catalyst. When the content exceeded 0.8wt%, the strength and TC were decreased by the limited NFC growth and matrix transitioned from rough laminar to isotropic pyrocarbon. After the treatment of 2500 °C, the strength and CTE decreased whereas the TC was increased. With the catalyst contents at 0.5–0.8 wt%, the flexural and shear strength retention ratios achieved a high value of 73.1–74.5 and 79.1–79.4%, respectively, and the in-plane and out-of-plane TCs exhibited maxima of 339.1 and 72.5 W/(m K). Relatively low CTE was obtained at 2.0 wt% catalyst owing to the increased amount of cracks and pores.

1. Introduction

Carbon/carbon (C/C) composites are the integrative materials of thermo-structural and functional properties that are widely applied as aircraft brakes, rocket nozzles, heat shields of reentry vehicles, and turbine rotors. During the last decades, they are developed as the most promising candidates for thermal management systems, such as heat sinks and plasma facing components of fusion devices [1]. These strategic applications desire C/C composites to exhibit unique combination of good mechanical strength, high thermal conductivity (TC) and low coefficient of thermal expansion (CTE). The properties of C/C composites depend on the matrix microstructure and fiber/matrix interface besides fiber preform. Therefore many efforts have been made to improve the properties by controlling the matrix and interface, and the degree of graphitization [2–5]. However, it is difficult for the integrative improvement on the mechanical, thermal conduction and expansion properties due to their different mechanisms and sensitive factors [3–6].

Nanofilamentous carbon (NFC) involving carbon nanotube and nanofiber has advantages of superior mechanical and thermal properties.

Its large specific surface area can provide high interface percentage with matrix compared to carbon fiber, resulting in a more efficient transfer for the load and heat [7–9]. These exceptional properties give NFC superiority as secondary filler incorporated into the carbon matrix to reinforce C/C (NFC-C/C) composites. Several studies have confirmed that the NFCs grown on carbon fibers by fixed catalyst chemical vapor infiltration (CVI) can improve the fiber/matrix interface and induce a deposition of rough laminar (RL) pyrocarbon (PyC) [9–11]. The pull-out and bridging effects of NFCs enhance the mechanical strength, toughness, and TC of the composites. One issue of the fixed catalyst process is an insufficient bridging of NFCs on the porosity gaps of carbon fibers and the whole matrix especially in the interbundles and short fiber layers of large and complicated pores [11,12]. Another is that the NFCs can weaken the transfer of matrix precursor, leading to a low and nonuniform density of NFC-C/C composites [11,13]. These unfavor the further improvement of the mechanical and thermal properties. Subsequently, floating catalyst film boiling CVI is developed via dissolving the catalyst ferrocene in a liquid precursor. The benefit of this floating catalyst process is a fast and sufficient densification of NFC-C/C composites with a reinforcing network of NFCs and vapor grown

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carbon fibers (VGCFs) [14,15]. It is well known that the study on the mechanical and thermal properties is crucial for the application of NFC-C/C composites. Most efforts have focused on the composites produced by fixed catalyst method from gas precursors [8–13], while the researches on the properties of the composites produced by the floating catalyst process are insufficient and address the densification and matrix microstructure for understanding PyC deposition mechanism. Moreover, the thermal expansion behavior directly determines the dimensional stability and affects the thermal shock resistance of the composites. Unfortunately, few works have been reported on this aspect of NFC-C/C composites produced by the floating catalyst process.

Our previous works have studied the functions of the catalyst content and deposition temperature on the densification behavior and microstructure of NFC-C/C composites produced by floating catalyst film boiling CVI from xylene pyrolysis [15–17]. Two structural transitions are revealed as the catalyst content rises from 0 to 2.0 wt%: (i) the matrix transforms from RL to isotropic (ISO) PyCs; (ii) the NFC structure changes from nanotube to nanofiber. The structural transitions especially the matrix, with the variation of NFC amount and heat treatment, can vary the mechanical and thermal properties of the composites. In this work, the effects of the catalyst content and heat treatment on the mechanical and thermal properties were studied to establish the relationship between the structural transitions and properties thus controlling the sensitive factors. The mechanisms on the improvement of the mechanical properties, thermal conductivity and expansion were also discussed via analyzing the microstructure, fracture surface, and the degree of graphitization.

2. Experimental

2.1. Material preparation

Polyacrylonitrile based carbon fiber felts ($\phi 110$ mm \times 25 mm) with apparent density of 0.43 g/cm³ were used as the preforms, which were made of alternate lamination of long fiber layers and short fiber layers with a stepwise needle-punching. The long fiber layers were interlaced each other in a special orientation of 0°/90°. The purity and boiling point of the precursor xylene (C₈H₁₀) were 99.0% and 138.4–144.4 °C, respectively. Ferrocene ((C₅H₅)₂Fe) of the purity of 99.9% was dissolved in the precursor to form floating catalyst.

The preforms were firstly treated at 1600 °C holding for 2 h in a high temperature furnace filled with nitrogen gas. The treated preforms were densified with PyC matrix by floating catalyst film boiling CVI in a deposition temperature ranging from 1000 to 1100 °C. After 30–35 h densification, C/C and NFC-C/C composites were produced at the initial catalyst contents of 0, 0.2, 0.5, 0.8, 1.2, and 2.0 wt%. The details on the film boiling CVI furnace and deposition process were described in Refs. [15–17]. The composites were lastly cut in two parts, in which one part was used as the as-deposited state and the other was treated at 2500 °C for 2 h under Ar atmosphere.

2.2. Material characterization

The mean density of the composites was measured using Archimedes's method on several samples sliced in the both directions perpendicular (out-of-plane) and parallel (in-plane) to the long fibers. The sliced profiles of the samples were shown in Ref. [15]. The matrix microstructure was observed by a polarized light microscope (PLM, Leica DLMP) on polished cross-sections of the composites. The corresponding extinction angle (Ae) was captured via computer image analysis on a series of digital images with the light angle rotated from 0 to 24° in an interval of 1° for one fixed position. This measurement method had been reported elsewhere [18]. The mean Ae was achieved from 20 fixed positions on the polished cross-section. Powdered samples were obtained from the as-deposited and heat-treated composites to analyze the crystal parameter and phase by X-ray diffractometer (XRD, X'Pert

PRO MPD). The degree of graphitization (g) and apparent crystallite height (L_c) were calculated using Eqs. (1) [19] and (2), respectively. Raman spectroscopy was also employed to study the structural order of PyC on the polished cross-section. The analysis was performed on a Renishaw inVia Raman system with a 514.5 nm argon ion laser excitation. Raman spectra were recorded from 3 measurements in the ranging 1100–1800 cm⁻¹ to study the typical first-order features of PyC.

$$g = (0.3440 - d_{002})100\% / (0.3440 - 0.3354) \quad (1)$$

$$L_c = 0.89\lambda / (\beta \cos\theta) \quad (2)$$

where d_{002} was the interlayer distance of (002) plane (nm), 0.3440 and 0.3354 denoted the d_{002} values of turbostratic carbon and ideal graphite crystal (nm), respectively. λ was the wavelength of Cu K α radiation (0.1541 nm). β and θ corresponded to the half-height width (rad) and diffraction angle (°) of (002) diffraction peak.

Three-point flexural and interlaminar shear tests were performed under a universal testing machine (SANS CMT5304-30 kN) with a cross-head speed of 1.0 mm/min. The dimension of the flexural samples was 55 mm length \times 10 mm width \times 4 mm thickness. A span of 40 mm was provided to give a span-to-thickness ratio of 10. The interlaminar shear strength (ILSS) was measured by compression of the samples with two notches on their both sides. The size of the shear samples was 30 mm length \times 10 mm width \times 10 mm thickness and the load was applied in the length direction. The width and depth of the notches were 1 and 5 mm, respectively. The distance between the two notches was 10 mm. The scheme of interlaminar shear samples was depicted in Ref. [14]. The sample number tested in the both modes was 5 for each type of the composites. The fracture surfaces were studied by scanning electron microscope (SEM, JEOL JSM-6460 and FEI QUANTA-600F).

A MicroFlash instrument (NETZSCH LFA 457) was used to measure the thermal diffusivity and specific heat of the composites. The tested samples were disc-shaped of a dimension of $\phi 12.7$ mm \times 3 mm, whose cross-sections were taken in the out-of-plane and in-plane directions, respectively. Six test points were selected from room temperature (RT) to 1000 °C in an interval 200 °C. The thermal expansion tests were performed in a NETZSCH DIL 402 C dilatometer from RT to 1200 °C at 5 °C/min under argon atmosphere. The sample size was ϕ 6 mm \times 20 mm, and the tested directions were also in the out-of-plane and in-plane. The sample number used in these thermal measurements was 3 for each type of the composites, and the TC and CTE were calculated by following formula:

$$TC = \rho\alpha C_p \quad (3)$$

$$CTE = [L(T) - L(T_0)] / [L(T_0)(T - T_0)] \quad (4)$$

where ρ was the sample density (g/cm³), α was thermal diffusivity (mm²/s), C_p was the specific heat at constant pressure (J/(g·K)), $L(T)$ and $L(T_0)$ were the sample length (mm) at temperatures T and T_0 , T_0 denoted reference temperature (303 K). The C_p was determined by comparative method using graphite as the reference sample. The density and RT C_p of the reference sample were 1.75 g/cm³ and 0.709 J/(g K), respectively.

3. Results and discussion

3.1. Basic physical properties

The deposition parameters and corresponding results of the composites are listed in Table 1. The matrix of the composites is dominated by RL PyC for the catalyst contents at 0–0.8 wt% (Fig. 1a₁). The mean Ae of the PyC achieves a high value around 20.0° at 0.5 wt% catalyst content. ISO PyC layer is formed on the fiber surfaces and at the local positions of the matrix for the catalyst content at 1.2 wt% besides RL PyC. The thickness of the ISO layer is increased by adding 2.0 wt%

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