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Short communication

Mechanical and thermal properties of C_f/SiC composites reinforced with carbon nanotube grown in situ

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Abstract

A hierarchical C_f/SiC composite was fabricated via in situ growth of carbon nanotubes (CNTs) directly on three-dimensional needle-punched carbon fabric following polymer impregnation and pyrolysis process. The mechanical and thermal properties of the composites reinforced with CNTs grown in situ were investigated. The results show that the flexure strength and fracture toughness were improved by 15% and 8.7%. Brittle fracture character of CNTs is observed due to strong interfacial bonding strength between CNTs and matrix. The parallel thermal conductivity and perpendicular thermal conductivity are improved by 24% and 57% respectively.

Keywords: B. Composites; B. Fibers; C. Thermal conductivity; Carbon nanotubes

1. Introduction

Continuous carbon fiber reinforced silicon carbide matrix (C_f/SiC) composites are promising candidates for advanced materials such as gas turbine engines, combustion chambers, thrusters, nozzles and the noses or leading edges of reentry vehicles because of their excellent toughness, good thermal shock resistance and good mechanical properties at high temperature [1,2]. Current modification of C_f/SiC are mainly focused on the fiber type, interface tailoring and matrix enhancement. Seldom multiscale enhancement is applied in ceramic matrix composites. Nanoscale reinforcements can be introduced into the space among fibers to improve the mechanical properties in micro-scale due to their own small scale. In situ SiC nanowires enhanced SiC_f/SiC composites have been studied and significant improvements in mechanical property are achieved [3–5], but the multiscale enhancement using carbon nanotubes (CNTs) grown on carbon fibers in situ have been less investigated.

CNTs have exhibited excellent mechanical properties [6], where the strength, modulus, and resilience are equal or superior to any current materials. CNTs also possess super electrical and thermal properties [6,7], making them attractive for enhancing a variety of matrix. The challenge of fully utilize the mechanical property of CNTs is to realize a homogeneous dispersion in matrix. The in situ growth of CNTs on fiber surface provides an optional method to solve the dispersion issue [8,9]. In this study, C_f/SiC composites with CNTs grown in situ as a second phase reinforcement were fabricated, and the mechanical and thermal properties are investigated.

2. Material and methods

Three dimensional (3D) needle-punched carbon fiber fabrics (T300) with pyrolytic carbin/silicon carbide (PyC/SiC) interphase were immersed into a catalyst solution to

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load catalysts. The aim of coating PyC/SiC is to prevent catalyst from diffusing into fibers and to protect fibers against damage. The catalyst solution for CNTs growth is a mixture of iron nitrate and aluminum nitrate in ethanol. After loading catalysts, the fabric was dried in oven at 80 °C and then located in a horizontal hot wall quartz tube furnace. When the fabric was heated up to 700 °C, a mixed gas of hydrogen and acetylene with flow ratio of 2:1 were introduced into the chamber for the growth of CNTs. The flow rate of acetylene is 25 sccm and the reaction time is 60 min. The obtained fabrics were densified by polymer impregnation and pyrolysis process. Firstly, the CNTs/CF performs were infiltrated with a mixture of polycarbosilane-Si_3N_4/xylene under vacuum and then xylene was vacuumed away using a vacuum pump. Afterwards, the samples were cured at 120 °C for 6 h under vacuum atmosphere and then pyrolyzed at 900 °C for 30 min under Ar atmosphere. Finally, polycarbosilane/xylene was used to densify these samples. The infiltration of polycarbosilane/xylene and pyrolysis of samples make up one cycle. In this study, 10 cycles were performed. The obtained hybrid composite is named as NF-C. Composites without CNTs were also prepared with the same process for comparison (named as F-C).

The bulk densities and open porosities were measured by the Archimedes' method. Morphology of CNTs and fracture surface of composites were characterized by JSM-6700F field emission scanning electron microscopy (FESEM). The bending strength was evaluated using 3-point bend test on a universal testing machine. The dimension of a test specimen was $4 \times 5 \times 60\ mm^3$, the span was 50 mm and cross-head speed was 0.1 mm/min. Elastic modulus (E) was measured from the elastic deformation region of load–displacement curves. Single edge notched beam was applied on specimens to determine the fracture toughness. The average bending strength, elastic modulus and fracture toughness were obtained from four test specimens.

The coefficient of temperature conductivity (α, cm^2/s) of specimens (10 mm diameter and 2 mm thickness) was measured at room temperature using a laser flash thermal diffusivity analyzer. Specific heat (Cp, J/(g K)) was measured using a differential scanning calorimeter (DSC-2C) under nitrogen, the sample had a cylindrical shape with 5.5 mm in diameter and 1 mm in thickness. The thermal conductivity (λ, W/(m K)) was calculated by

$$\lambda = 100 \times \rho \times \alpha \times Cp$$

where ρ (g/cm^3) is the sample density. Both the thermal conductivities parallel to and perpendicular to fiber axis are measured.

3. Results and discussion

3.1. Morphology of CNTs

CNTs can be easily grown on the outside surface of single fibers or fiber cloth [10–12], but the growth of CNTs in 3D architecture is different from 2-dimentional architecture due to the different atmosphere between the inner part and out surface. The current understanding of CNTs growth is based on a model proposed by Baker [13]. In this model, dissociation of carbon precursors on catalyst surface was followed by diffusion of carbon into the metal catalyst particle. Once the catalyst was saturated with carbon, the carbon would precipitate in the form of a fiber/nanotube that continues to grow as more carbon dissociated and precipitated from the catalyst particle. However, relative experiments have been shown that the carbon precursor chemistry affects the type and structure of products [14–16]. Therefore, apart from the heterogeneous reaction (the reaction between carbon source and catalyst), the homogeneous gas phase pyrolysis of carbon source will also play an important role in the growth of CNTs. Due to a 3D structure of carbon fiber preform, the transportation of gaseous species inside a fibrous preform should be considered. Carbon source can decompose and be converted into intermediate species in the presence or absence of catalyst. Large hydrocarbon species such as polycyclic aromatic hydrocarbons (PAHs) produced by the excess pyrolysis of C_2H_2 should be avoided. Excess PAHs can lead to premature poisoning of catalysts and formation of soot. In our process, low temperature (700 °C) and short resident time (0.3 s/cm) of C_2H_2 are adopted to avoid excess form of PAHs, and the homogenous growth of CNTs in inert part of 3D carbon fiber perform was realized. The morphology of CNTs grown in the inner part of 3D needle-punched carbon fiber fabric is shown in Fig. 1. It is found that CNTs can be grown into the inner part of the fabric during our growth process. The little space (1–2 μm) among fibers in inner fiber-bundles can also be filled with CNTs. A homogeneous percolating network of CNTs is formed through the fiber fabric, which benefit the homogeneity in composite properties.

3.2. Mechanical properties of composites

The physical and mechanical properties of samples F-C and NF-C are listed in Table 1. After the growth of CNTs, the thickness of fabric expanded to ~7.5 mm from original ~6.5 mm, which results in a decrease in fiber volume fraction (26%). The volume fraction of CNTs was estimated to be about 4% according the weight gain of fabric during the growth of CNTs with an assumed density of $1.4\ g/cm^3$ [17]. It is found that the density and porosity of NF-C are a little lower than that of F-C. The elastic modulus of NF-C (42.9 ± 0.4 Gpa) does not vary significantly comparing with that of F-C (43.0 ± 0.8 Gpa), but the fracture toughness was improved by 8.7%. Although with lower fiber volume fraction, the bending strength in NF-C is improved, about 15% higher than that of F–C.

Fig. 2 shows the fracture surface FESEM images of F-C and NF-C after 3-point bending tests. The two composites have different features at their fracture surface. The pull-out lengths of fibers in NF-C (Fig. 2b) are much shorter

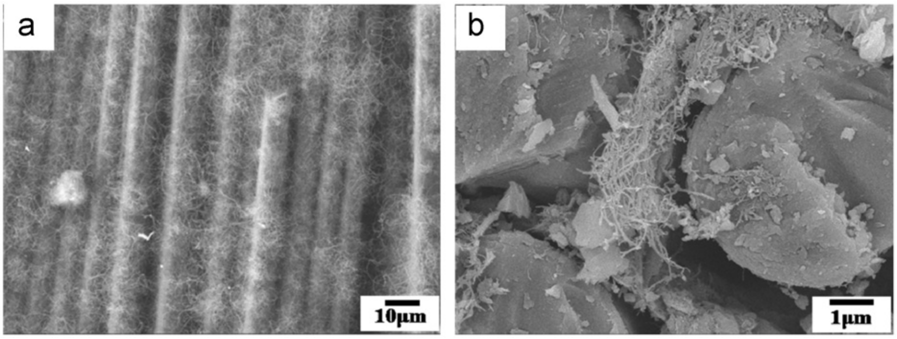

Fig. 1. Morphology of CNTs in the inner parts of 3D carbon fiber fabric: (a) inner plane (b) inner intra-bundle.

Table 1
Physical and mechanical properties of F-C and NF-C.

Composites	CNTs volume fraction (%)	Fiber volume fraction (%)	Density (g/cm^3)	Porosity (%)	Bending strength (Mpa)	*E* (Gpa)	Fracture toughness (Mpa m$^{1/2}$)
F-C	0	30	1.90 ± 0.01	11.2	293 ± 41	43.0 ± 0.8	11.5 ± 0.1
NF-C	4	26	1.89 ± 0.01	11.0	336 ± 16	42.9 ± 0.4	12.4 ± 0.2

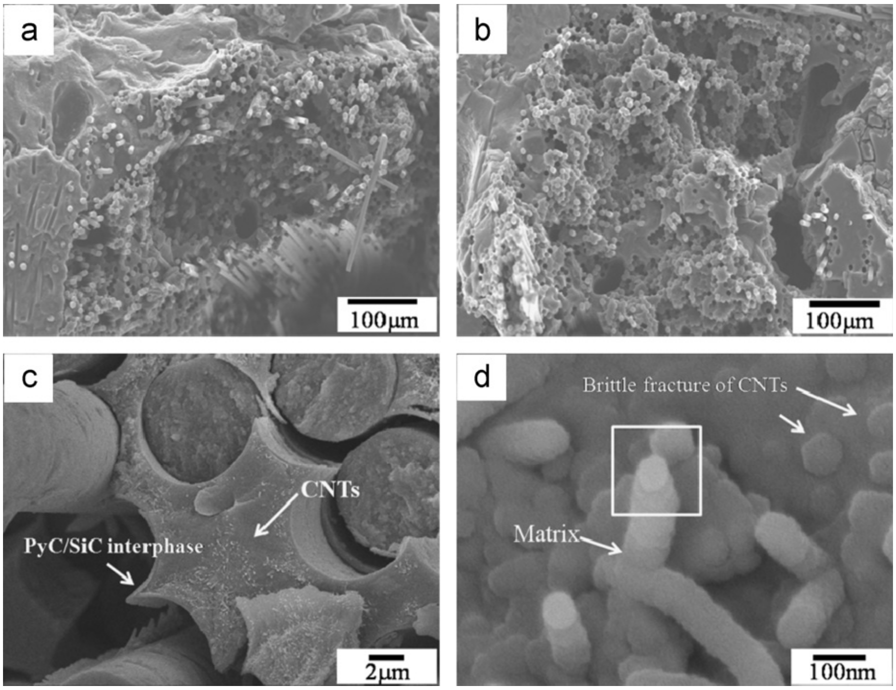

Fig. 2. FESEM images of fracture surfaces for F-C (a) and NF-C (b–d).

than that in F-C (Fig. 2b), which indicates that the interfacial bond strength between fiber and matrix is improved by CNTs grown in situ. The high magnification FESEM images of fracture surface in NF-C are shown in Fig. 2c and d. It can be found from Fig. 2c that CNTs were pulled out during the fracture process. The deflection of cracks at the interface between PyC interphase and SiC interphase and within the PyC interphase is observed. No debonding cracks can be found at the interface between CNTs and SiC interphase, which indicates a firm adhesion between CNTs and SiC interphase (Fig. 2c). The close-up view of CNTs present in fracture surface is shown in Fig. 2d. CNTs perpendicular to failure surface direction exhibit a brittle fracture character, as shown in top right corner of Fig. 2d. The surfaces of parallel direction CNTs are covered with thick matrix and cracks are deflected

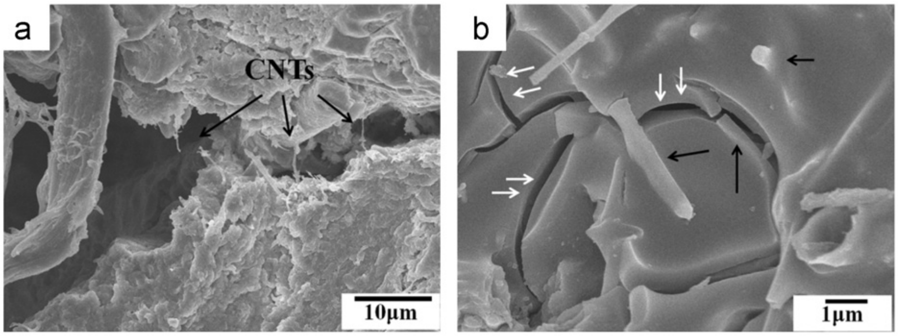

Fig. 3. Bridging (a) and deflection effect (b) of crack caused by CNTs.

at the interface between CNTs and matrix (named as $I_{CNT/M}$), which have been marked by a rectangle in Fig. 2d. The failure mode of CNTs reveals strong interface bond of $I_{CNT/M}$, which results in a contribution of the increase of flexural strength to some extent. The matrix among micro-scale fibers always exhibits brittle behavior because there are no reinforcements in these areas. However, CNTs are filled in these areas in NF-C. The crack bridging caused by CNTs can be found during the surface crack propagation as shown in Fig. 3a. It can be also seen that the matrix cracks (marked with white arrows in Fig. 3b) are deflected while encountering CNTs (marked with black arrows in Fig. 3b). The matrix among micro-scale fibers are toughed by CNTs and more energy would be consumed when these areas were damaged compared with those in F-C. Although the fracture toughness decreases when a shorter length of fibers are pulled out, the pull-out of CNTs, crack bridging and crack deflection by CNTs will improve the final fracture toughness. However, considering the super high strength of carbon nanotube, the reinforcement effects of CNTs in the current composites are not significant. The interfacial bonding strength between reinforcement and matrix should be neither too strong nor too weak. The efficiency of CNTs might be largely decreased by the strong interfacial bonding strength of $I_{CNT/M}$. Therefore the interfacial bonding strength of $I_{CNT/M}$ should be further optimized.

3.3. Thermal properties

The room temperature thermal properties of F-C and NF-C are shown in Table 2. It is found that the coefficient of temperature conductivity increases while the specific heat decreases after the introduction of CNTs. The parallel thermal conductivity and perpendicular thermal conductivity are improved by 24% and 57% respectively. As shown in Fig. 1, a percolating network of CNTs can go through the carbon fiber fabric, which provides another heat conduction path. Although significant improvement in thermal conductivity can be achieved, the increase is disappointed compared with the super thermal conductivity of CNTs. A great number of interfaces are introduced due to the high specific surface area of CNTs, the presence of interface thermal resistance (Kapitza resistance) [18–20] will play an important role in heat conduction. The interface thermal resistance between CNTs and matrix due to difference in phonon spectra of the two phases may be responsible for lower thermal conductivity than expected.

Table 2
Thermal properties of F-C and NF-C composites.

Composites	Direction	α, (cm^2/s)	Cp, J/(g K)	λ, W/(m K)
F-C	$\parallel$	0.0436	0.796	6.59
	$\perp$	0.0142	0.805	2.10
NF-C	$\parallel$	0.0564	0.768	8.18
	$\perp$	0.0225	0.777	3.30

4. Conclusion

C_f/SiC composites with and without carbon nanotubes grown in situ were fabricated by the PIP process. The mechanical and thermal properties are improved. The interfacial bond strength between fiber and matrix are improved by CNTs grown in situ, causing a shorter pulled-out length of fibers. The pull-out of CNTs and crack deflection at interface between CNTs and matrix improved the ultimate fracture toughness of composites. The $I_{CNT/M}$ should be further tailored to optimize the interfacial bonding strength of $I_{CNT/M}$. The percolating network of CNTs provides a new path for heat conduction and improved the thermal conductivity. The interface thermal resistance between CNTs and matrix due to difference in phonon spectra of two phases may be responsible for lower thermal conductivity than expected.

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