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LETTER

Properties of multi-walled carbon nanotube reinforced carbon foam composites

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Introduction

Mesophase pitch (MP)-based carbon foam as a new class of structural and functional material has attracted attention owing to their peculiar properties such as high open porosity, light weight, high temperature tolerance, and adjustable thermal conductivity. It is one of the promising candidate materials for applications as heat exchangers, catalyst supports, electrodes for energy storage [1, 2]. However, the two main drawbacks of carbon foam, namely, the intrinsical brittleness and the relatively low thermal conductivity, make it impossible to meet the engineering demand. Much effort has been dedicated to improve the performance of carbon foam [3–7]. These modified carbon foams showed tailored properties and microstructure. Multi-walled carbon nanotubes (MWNTs)-based composites have been intensively studied owing to the nanometer-scale dimensions, high mechanical strength, and high thermal conductivity. However, few researchers try to fabricate the MP-based carbon foam reinforced with MWNTs because of the difficulty in efficient dispersion of MWNTs in MP matrix. In this study, carbon foam was prepared by the mixtures of MWNTs and MP. This article focused on the relationship between the MWNTs content and physical properties of carbon foams.

Experimental

In this research, the Mitsubishi naphthalene-based MP was used as the precursor of carbon foams. MP was obtained by Mitsubishi Gas Chemical Co., Japan. The MWNTs (purity 99 wt%, diameter 20–40 nm) synthesized by chemical vapor deposition were supplied from Wuhan University of Science and Technology, China. MP was pulverized into granules of 150 μm. In order to obtain a good dispersion of MWNTs in MP, MWNTs were first treated with concentrated nitric acid and sulfuric acid to get rid of amorphous carbon on the tube walls and to introduce carboxyl groups. Then the oxidized MWNTs were washed by distilled water and filtered with PTFE membranes multiple times. Finally, the oxidized MWNTs were dried at 373 K for 24 h to get rid of the redundant moisture. MWNTs were sonicated in a bath containing toluene to form the suspension, and then the milled MP was added to the suspension. The mixture was mixed at 343 K in the water bath under moderate stirring for 2 h. The mixture was filtered out with a PTFE membrane and dried in vacuum oven at 403 K.

Mixture of MP and MWNTs was put in a pressure vessel under an applied pressure of 4 MPa in nitrogen atmosphere. The foaming processes of carbon foams are the following: First, the temperature was increased from room temperature to 703 K at 2 K/min, and soaked for 2 h to obtain the green foams. Then the green foams were carbonized at 12 K/h to 1123 K in nitrogen flow and soaked for 2 h. Finally, they were graphitized at 2 K/min to 2573 K and soaked for 2 h to obtain graphitized foams.

The microstructure of foams was examined by scanning electron microscope (SEM) and Raman spectroscopy. The bulk density of the sample was determined on weight and geometry. The properties of carbon foams such as morphology (examined by using JEOL JSM-6360LV SEM),

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thermal conductivity, and compressive strength (measured by Instron3369 electronic universal testing machine and JR-1 type synthetical thermal tester) were determined. The graphitized foams were named as GF*X* (also called "the modified foams"), where *X* represented the addition amount of the MWNTs, such as GF2 meant carbon foam prepared from pitch with addition of MWNTs by 2 wt%.

Results and discussion

Figure 1 presented SEM photograph of fracture surface of GF1. The dispersion could be observed, which indicated that well dispersion could be achieved by using sonication and hot-mixing method for carbon foam containing suitable amount of MWNTs. The effect of MWNTs content on microstructure of carbon foams is shown in Fig. 2a–e. It showed the variation of MWNTs content obviously influenced the pore structure in terms of cell wall thickness, width of ligament, and open porosity. The MWNTs provided nucleation sites in pitch for heterogeneous nucleation of bubbles. Figure 2b showed that carbon foam without MWNTs addition presented narrow ligaments and thin cell walls. More and disordered cracks in GF0 while less cracks for modified foam were observed. The formation of bubble of molten pitch was influenced by several factors, such as viscosity, elasticity, and surface tension [8]. Addition of MWNTs would increase the viscosity. It was well established that the foaming process consists of the formation and bubbles growth [9]. The low viscosity leaded to larger extension of the cell walls. The thickening of the cell wall thickness with increasing viscosity can, thus, be well understood. When the foam without or with low content of MWNTs, the viscosity of the mixture was low. Thus the bubbles were free to move in molten pitch, which made the combination of bubble become easy. So the cell wall was thinner and the ligament was narrower compared with the modified foam.

As shown in Fig. 3, effects of the MWNTs content on the crystalline structure of resultant graphitized foam were analyzed by XRD. The crystalline parameters of these samples are summarized in Table 1. It showed that an increase in *La* was observed with increasing MWNTs content in the foams. However, as the MWNTs content was further increased and approached 2 wt%, the *La* exhibited an abrupt decrease. It indicated that suitable addition of MWNTs promoted graphitization degree of MP due to carbon atoms can orderly grow along MWNTs [10]. Yet more MWNTs addition clearly had a detrimental effect on the degree of graphitization, the *d*-spacing, and the crystallite size of the graphitized foams. More MWNTs may prevent the carbon atoms forming graphite crystal lattice, which resulted in the disordering of carbon atoms in the graphitized foam with 2 wt% MWNTs.

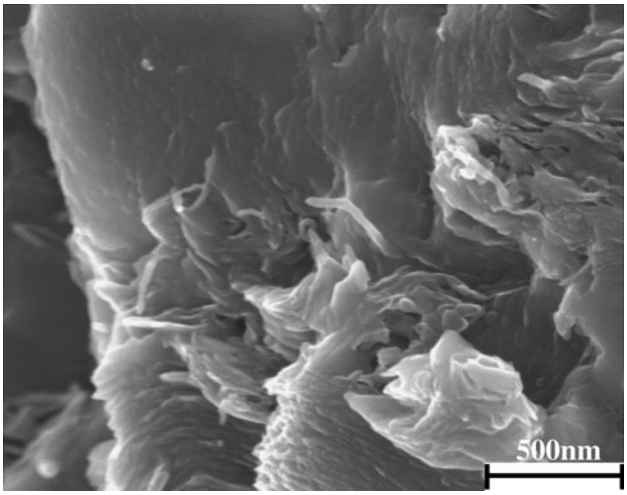

Fig. 1 SEM micrograph of fracture surface of GF1

For further understanding of the effect of MWNTs on carbon crystallite, Raman spectra were introduced. Two main bands can be seen. One was about 1335 cm^{-1} and the other was about 1584 cm^{-1}. The ratio of intensities of 1335–1584 cm^{-1} band, *R*, was inversely proportional to the microcrystalline planar size *La* [11], so $1/R$ was proportional to *La* [12]. Figure 4 showed the Raman spectrum of graphitized foam at ligament. The $1/R$ values of GF0, GF1, and GF2 were 1.25, 1.85, and 1.59, respectively. It could be seen that $1/R$ value of GF1 was higher than that of other foams. It further confirmed that the carbon foam with suitable amount of MWNTs had higher microcrystal order, compared with other samples.

Table 1 displayed the thermal conductivities of graphitized foam. It could be seen that carbon foam with MWNTs presented higher thermal conductivity than that of pure foam. It was obvious that MWNTs could greatly enhance thermal conductivity of carbon foam. The increase in thermal conductivity might be attributed to following reasons. First, most of heat was transferred by the ligament and cell wall. As can be seen from Fig. 2, the modified foam possessed wider ligament compared with the pure foam. Moreover, the modified foam had less microcracks. This structure allowed the heat transfer throughout the graphitic foam efficiently. Second, thermal conductivity of graphite material was mainly influenced by phonon transport in crystalline lattice. In graphite material, thermal conductivity (λ) is represented by the following relationship (Debye equation):

$$\lambda = cvL/3,$$

where c is the specific heat per unit volume of the crystal, v is the velocity of heat-transporting wave (phonon group

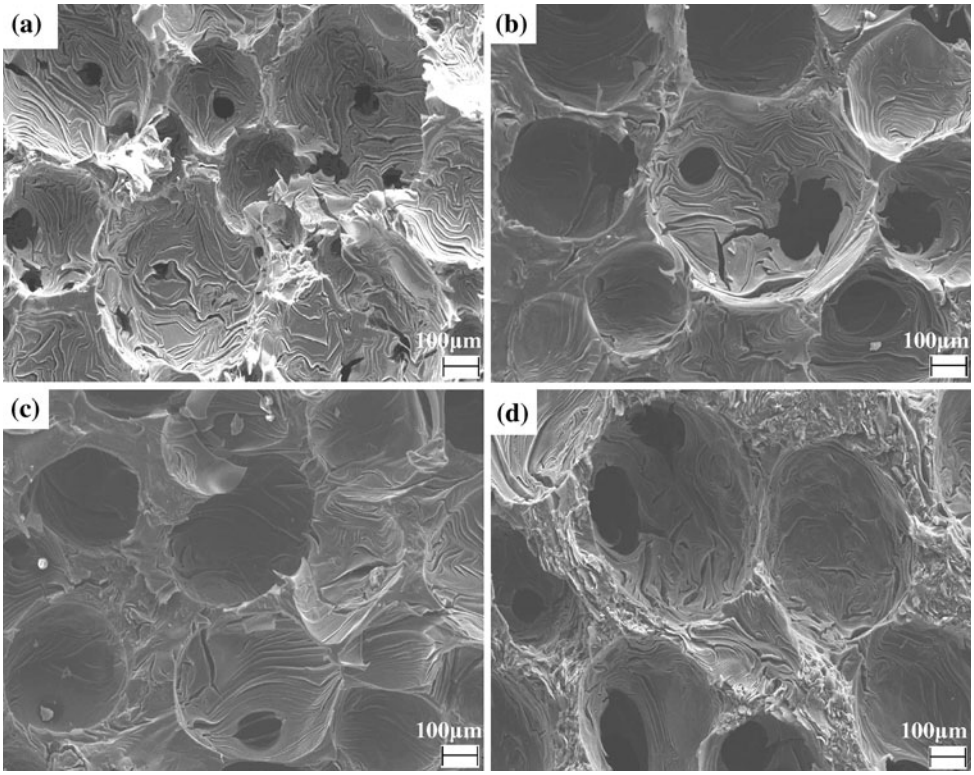

Fig. 2 SEM micrographs of graphitized foams: **a** GF0, **b** GF0.5, **c** GF1, and **d** GF2

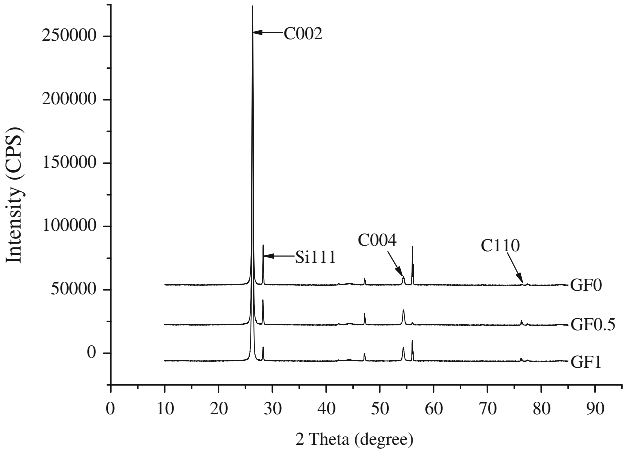

Fig. 3 XRD patterns of graphite foams with different amount of MWNTs

Table 1 Performance of graphite foams

Samples	CF0	CF0.5	CF1	CF2
MWNTS content (wt%)	0	0.5	1	2
Density (g/cm^3)	0.75	0.76	0.77	0.79
Compressive strength (MPa)	4.1	4.7	5.1	6.8
Thermal conductivity (W/m k)	39.2	53.0	66.8	58.4
Inter-layer spacing of d_{002} (nm)	0.3373	0.3370	0.3365	0.3368
La (nm)	34.25	39.82	48.85	37.65

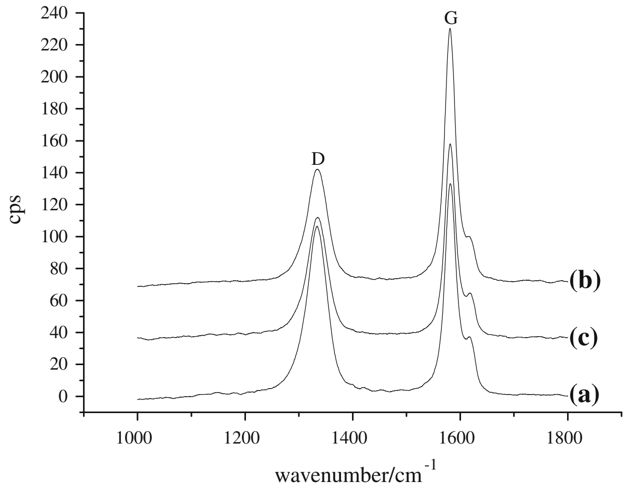

Fig. 4 Raman spectrum of the ligaments (*a*: GF0; *b*: GF1; *c*: GF2)

velocity), which depends on the lattice vibration; and *L* is the mean free path for phonon scattering, which is closely related to the size of the crystals. The larger crystal parameters (*La*) increase the phonon mean free path, which attributed to higher thermal conductivity [13]. Finally, the increase in bulk density of modified foam also plays an important role in enhancing bulk thermal conductivity.

The mechanical properties of carbon foams mainly depended on both their microstructure arrangement and bulk density. The microstructure mainly included the width of ligament and quantity of microcracks. Compressive strength tests were conducted to evaluate the effect of MWNTs content on the mechanical properties of foams. The results of mechanical properties are presented in Table 1. For specimens with 0–2 wt% of MWNTs, the compressive strength of MWNTs/carbon foam composites increased from 4.1 to 6.8 MPa, an increase of 65% in the mean compressive. However, for specimens with 4 wt% MWNTs, an abrupt decrease of compressive strength was observed when compared to the specimen with 2 wt% MWNTs.

The strength increase was due to the following factors, an increase in the foam density, less microcracks and the reinforcement of the foam with the strong MWNTs. It could be seen that the surfaces of MWNTs are covered by the carbon matrix. This indicated good interfacial properties between the reinforcement and carbon matrix. When outside force was loaded on carbon foams, MWNTs deflected and carried most of the applied load. For higher MWNTs fraction, the aggregation of MWNTs might restrain the enhancement of the mechanical properties of carbon foam.

Conclusions

In this study, the effects of different MWNTs content on the structure and properties of carbon foam were investigated experimentally. From the "Discussion" above, the following conclusions can be drawn. The MWNTs content could significantly affect the structure of carbon foams such as pore size, the thickness of cell wall, and the width of ligament. A high thermal conductivity of 66.8 W/m K for the carbon foam with MWNTs concentration of 1 wt% was obtained at temperature of 2573 K. The compressive strength of graphitized foam increased 65% for 2 wt% of MWNTs additive.

References

1. Lafdi K, Mesalhy O, Elgafy A (2008) Carbon 46:159
2. Yu QJ, Straatman AG, Thompson BE (2006) Appl Therm Eng 26:131
3. Beechem T, Lafdi K (2006) Carbon 44:1548
4. Wang M-X, Wang C-Y, Li T-Q, Hu Z-J (2008) Compos Sci Technol 68:2220
5. Li W-Q, Zhang H-B, Xiong X (2010) Mater Sci Eng A 527:2993
6. Li S-Z, Song Y-Z, Song Y, Shi J-L et al (2007) Carbon 47:2092
7. Eksilioglu A, Gencay N, Yardim MF, Ekinci E (2006) J Mater Sci 41:2743. doi:10.1007/s10853-006-7079-5
8. Neethling SJ, Lee HT, Grassia P (2005) Coll Surf A 263:184
9. Klett JW, Mcmillan AD, Gallego NC, Walls CA (2004) J Mater Sci 39:3659. doi:10.1023/B:JMSC.0000030719.80262.f8
10. Song Y-Z, Zhai G-T, Shi J-L et al (2007) J Mater Sci 42:9498. doi:10.1007/s10853-007-2049-0
11. Jones LE, Thrower PA (1991) Carbon 29:251
12. Leszek N, Paul WJ (1993) Carbon 31:1313
13. Adams PM, Katzman HA, Rellick GS, Stupian GW (1998) Carbon 36:233