CARBONIZATION BEHAVIORS OF MESOPHASE PITCH BASED COMPOSITES REINFORCED WITH MULTI-WALL CARBON NANOTUBES

Song Yongzhong[a,b], Zhai Gengtai[a], Shi Jinli[a], Guo Quangui[a], Liu Lang[a]

[a]Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China

[b]Graduate School of Chinese Academy of Sciences, Beijing 100039, China

Abstract

The multi-wall carbon nanotubes (MWNTs) were mixed with naphthalene-derived synthetic mesophase pitch, and the pastes were oxidized at 200 ℃ for 2 hours. Then the oxidized pastes were molded into tapes, whose carbonization behaviors were studied using a dilatometer. The effects of the MWNTs content on the carbonization behaviors of the composites were investigated. Results indicated that the sintering of composites was in six stages: thermal swelling, liquid phase, coalescence, semi-coke, coke and carbon. The addition of MWNTs severely increases shrinkage in the liquid stage and reduces shrinkages in the coke and carbon stage. The sample shrinkage decreases with increase of concentration of MWNTs during the carbonization process. SEM micrograph of the fracture surface for the composites shows that the CNTs uniformly exit in the composites and well coalescent with the carbon derived mesophase pitches.

1. Introduction

Due to their nanometer-scale dimensions, high mechanical strength, and very high thermal and electrical conductivity, carbon nanotubes (CNTs) have attracted much attention to be recognized as an excellent material choice for nanocomposites, in which even a very small amount of CNTs can induce significant changes in the material's properties [1-4].

Because carbon and carbon-carbon composites have many advantages, such as excellent mechanical behavior at high temperatures, low reactivity, high heat capacity, and so on, modern advanced technologies make wide use of these materials in different fields, including nuclear reactor walls, rocket nozzles, battery electrodes, and seal and friction materials [5-7]. However, the conventional techniques to prepare

carbon and carbon-carbon composites are complicated and costly due to the time-consuming processing such as liquid phase impregnation and chemical vapor deposition which are indispensable to obtain high performance carbon and carbon-carbon composites. Much effort has been taken to develop new methods to simplify the processing and shorten the time of preparing carbon-carbon composite. Most significantly, Naphthalene-derived synthetic mesophase pitch (MP) have been recognized as excellent precursor to high-performance carbon and graphite due to their high carbon yield [8-11].

However, few researchers try to fabricate the MP based composites reinforced with CNTs because of the difficulties in homogeneously distributing CNTs in a MP matrix by traditional methods. In this paper，CNTs reinforced oxidized MP based composites were prepared by one-step self-sintering. The influence of concentration CNTs on the carbon behavior on obtained CNTs/Carbon derived from oxidized MP composites.

2. Experimental

2.1 Materials

The WNNTs (multi-walled carbon nanotubes, purity 99 wt%, diameter 20－40 nm) synthesized by chemical vapor deposition were supplied from Wuhan University of Science and Technology, China. Their FESEM and TEM images were shown in Fig. 1 and Fig. 2. Mesophase pitch (MP) was obtained by Mitsubishi Gas Chemical Co., Japan. Its typical properties were compiled in Table 1 and its SEM image was shown in Fig. 3.

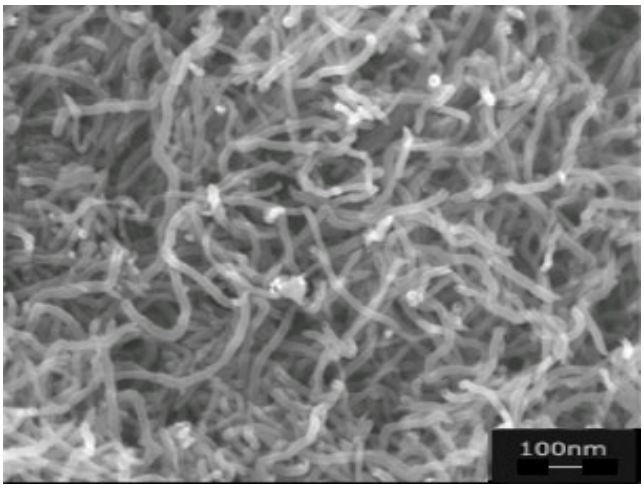


Fig. 1. FESEM image of MWNTs.

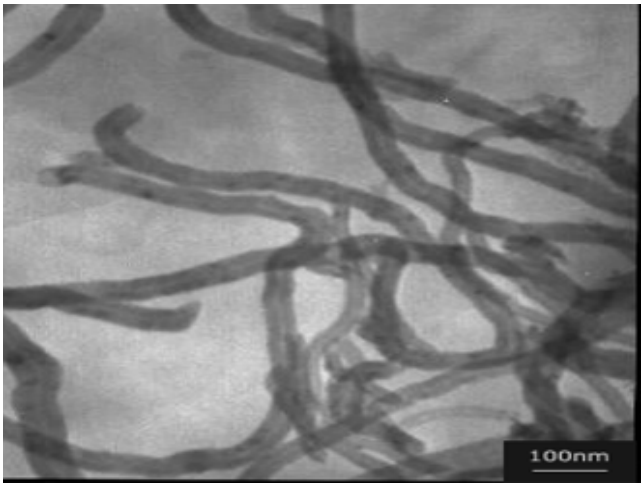


Fig. 2. TEM image of MWNTs.

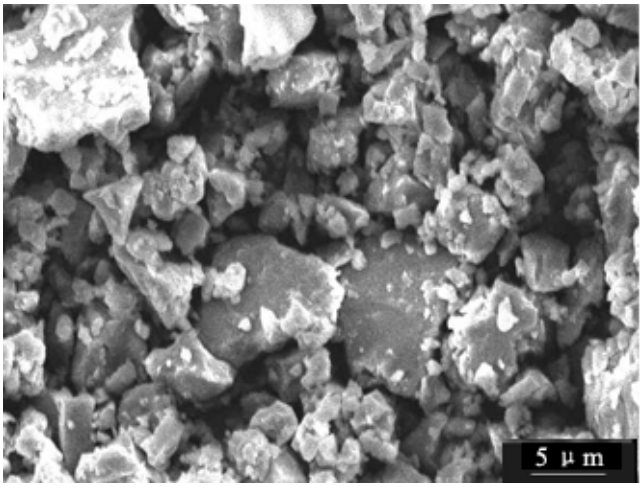


Fig. 3. SEM image of MP.

Table 1. Basic properties of MP

Softening point, ℃	260
Content of mesophase, %	100
H/C Atom ratio	0.64
Specific gravity (25℃), g/cm^3	1.23
Volatile constituent, wt.%	21.46
Carbon yield, wt.%	91.58
Solubility, wt.%	
Pyridine insoluble	61.98
Toluene insoluble- pyridine soluble	16.12
Toluene soluble	21.90

2.2 Fabrication and characterization of composite materials

MWNTs were sonicated in a bath containing toluene for 10 minutes to separate the aggregation and to form a suspension, and then the milled MP was added to the suspension and hot-mixed at 333 K in the other bath containing toluene under moderate stirring for 2 hours. Subsequently, the system was moved to a plate and dried at 373 K in a vacuum oven for 24 hours to get rid of the redundant solvent and moisture.

The dried compound was ground by a ball-mill into grains of particle size in the range of 2.8～8.2 μm. Then the grains were heated to 433 K at a rate of 3 K/min, and then heated to 473 K at the rate of 0.5 K/min, finally the temperature was kept for 60 minutes in air.

The oxidized powders were uniaxially pressed under 100 MPa in two 3.5×25 mm and 9.5×50 mm quadrate dies for the measurement of shrinkage behavior and other physical properties, respectively. The behavior during sintering was studied using a NETZCH dilatometer (DIL 420 PC) under the following sintering conditions: flowing argon atmosphere, temperatures up to T_m=1273 or 1823 K and heating rates

in the range Ω=1 K/min. The dilatometer was calibrated using an alumina reference. The molded tapes of 3.5×25 mm were carbonized at different temperature from 600 ℃ to 1500 ℃ for 1 hour with a heating rate of 1 ℃/min in a nitrogen atmosphere. Further the graphitization treatment was performed in argon at temperature up to 2200 ℃ with a heating rate of 10～20 ℃/min. In order to make comparisons, oxidized MP powders were also molded into tapes with size of 3.5×3.5×25 mm and 9.5×9.5 ×50 mm for the measurement of shrinkage behavior and other physical properties, respectively.

The bulk densities of tapes after molding, carbonization, and graphitization were calculated by measuring their dimension and weight. The flexural strength and modulus were determined according to ASTM D 790-92. The tapes were sectioned into a test piece for the measurement of the compressive strength. The fractured surfaces of the test pieces were observed with a JEOL field emission scanning electron microscope (FESEM, model JSM-6700F).

3. Results and discussion

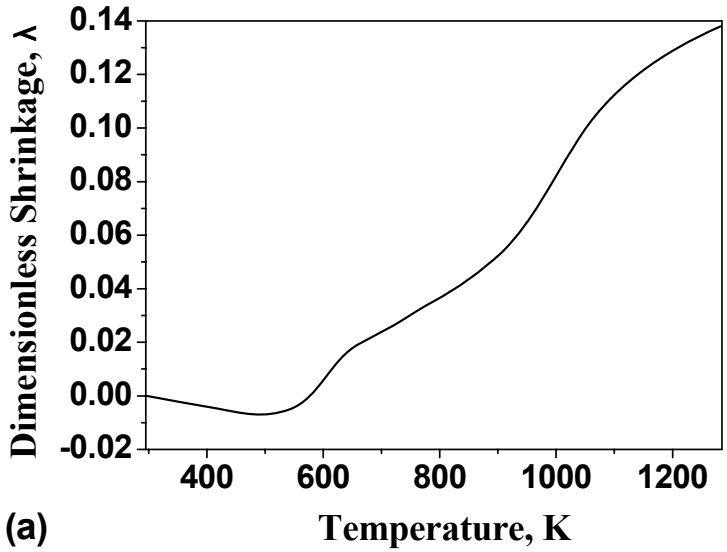
The influence of MWNTs concentration on the sintering behavior of composite was investigated. In these experiments, the maximum sintering temperature T_m was maintained at 1273 K and 1823 K. Dynamic experiments were conducted to obtain sample length-time during sintering.

The dynamics of sample's length changes were investigated using a dilatometer. A typical experimental length-temperature profile is shown in Fig. 4(a). The process can be divided into different regions based on differential of length changes (Fig. 3(b)). The first region is swelling stage. Shrinkage begins in the next region. Distinctive shrinkage take place in region Ⅱ, Ⅴ, and Ⅵ, which reaches a maximum at ～1000 K.

Different MWNTs concentration on the sintering behavior of composite was investigated. And their experimental length-temperature profiles are shown in Fig. 5. In region Ⅰ, the composites reveal lower swellings than that of tape derived from pure oxidized MP, which indicates that MWNTs reduce the swelling of samples.

Further, the shrinkage in region Ⅱ is due to the pitch powder begin to soft, and the liquid phase rapidly infiltrate through pores inside the tape as a result of capillary force [12]. The composite containing 5 % MWNTs exhibits higher shrinkage rate than that of tape from pure oxidized MP. It might because that suitable MWNTs form some pores which absorb a few softening pitch due to capillary effect. It could be the same reason which leads to lower initial sintering characteristic temperature (T_1) and higher final characteristic temperature (T_2) (as shown in Table 2) in this region. However, excessive MWNTs decrease the shrinkage, which might because that quantity of softening pitch can not fill in the pores formed by MWNTs. In the next two regions of coalescence and semi-coke, a mass of evolved gases greatly restrain shrinkage of the composites [12]. In the next two stages of coke and carbon the composites exhibit lower shrinkage rate than that of tape from pure oxidized MP, which indicates that MWNTs restrain the shrinkage of samples. Its reason is as follow: the shrinkage of sample comes from the consolidation of the molecular association and further improvement of the lamellar structure of MP through cyclization and aromatization reactions in coke stage. Formation and decrease of graphite interlayer spacing and increase of graphite crystallite size are the reasons of the shrinkage of sample in the carbon stage [12]. However, the MWNTs do not produce these changes.

As shown in Fig. 4, Table 2 and 3, the composite containing 5 % MWNTs severely increases shrinkage in the liquid stage and reduces shrinkages in the coke and carbon stage. Suitable MWNTs concentration slightly increases the shrinkage of sample. However, excessive MWNTs concentration moves the shrinkage to higher temperature and reduces the shrinkage of sample.



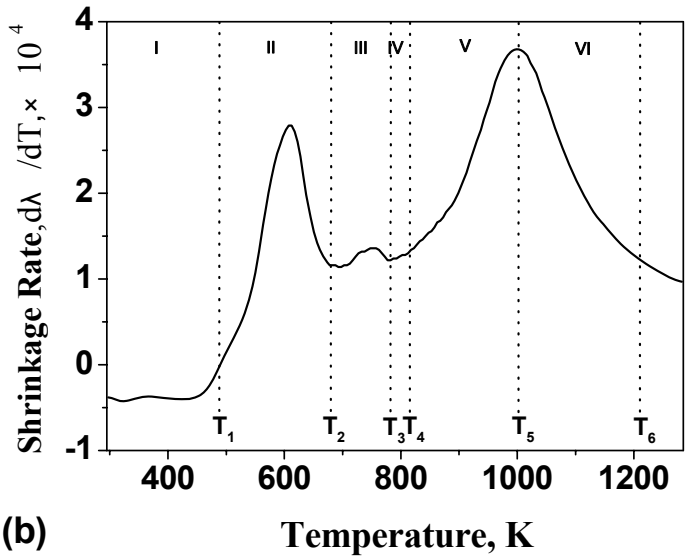


Fig. 4. Typical sample shrinkage during sintering: (a) dimensionless shrinkage λ, as a function of temperature, (b) dλ/dT; MWNTs concentration: 5 %, heating rate: 1 K/min in argon.

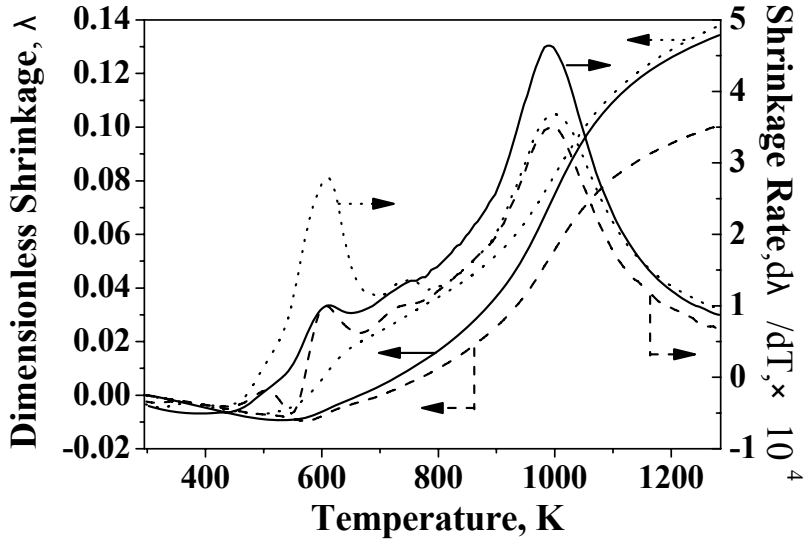


Fig. 5. Comparison of typical dilatometric results. — pure oxidized MP, ····· MWNTs concentration: 5 %, - - - - MWNTs concentration: 20 %; Heating rate: 1 K/min in argon.

Table 2. Sintering characteristic temperature for different MWNTs concentration

MWNTs concentration, %	Heating rate, K/min	Characteristic temperature, K					
		T_1	T_2	T_3	T_4	T_5	T_6
0	1	532	647	772	777	990	1174
	5	544	714	774	804	1030	1247
5	1	490	682	778	813	1000	1188
20	1	571	663	738	753	998	1188

Table 3. Sintering parameters for different MWNTs concentration

MWNTs concentration, %	Heating rate, K/min	Maximum shrinkage rate ×10^4, 1/K					Ratio of dimensionless shrinkage, %				
		Ⅰ	Ⅱ	Ⅲ	Ⅳ	Ⅴ	Ⅱ	Ⅲ	Ⅳ	Ⅴ	Ⅵ
0	1	-0.51	1.0	1.4	1.4	4.6	-----	9.3	0.52	42.6	38.8

	5	-0.46	2.6	1.3	1.3	4.3	10.7	5.1	2.8	39.1	39.3
5	1	-0.42	2.8	1.4	1.3	3.7	15.9	8.6	3.2	32.5	32.0
20	1	-0.51	1.0	1.0	1.0	3.5	-----	3.3	1.5	45.1	42.6

4. Conclusions

Different content MWNTs were added into MP, and then the compounds were oxidized at a suitable temperature. Then the tapes were prepared from oxidized grains and the carbonization behaviors were studied. Based on the obtained results, the sintering process of the tape was in six stages: thermal swelling, liquid phase, coalescence, semi-coke, coke and carbon. And different MWNTs concentrations on the sintering behavior of composite were investigated. Results show that suitable addition of CNTs significant increases the shrinkage during liquid phase stage. In contrast, excessive addition of CNTs significant decreases the sample shrinkage and shifts the shrinkage to higher temperature during sintering.

References

[1] Iijima S, Helical microtubules of graphitic carbon. Nature 1991; 354:56-8.

[2]Ajayan PM. Nanotubes from Carbon. Chem. Rev. 1999; 99:1787-99.

[3] Sreekumar TV, Liu T, Min BG, Guo H, Kumar S, Hauge RH, Smalley RE. Polyacrylonitrile Single-Walled Carbon Nanotube Composite Fibers. Adv. Mater. 2004; 16:58-61.

[4] Shaffer MSP, Windle AH, Fabrication and Characterization of Carbon Nanotube/Poly(vinyl alcohol) Composites. Adv. Mater. 1999; 11: 937-41.

[5] Schmidt J, Moergenthaler KD, Brehler KP, Arndt J. High-strength graphites for carbon piston applications Carbon 1998; 36:1079-84.

[6] Chen MH, Wu GT, Zhu GM, You JK, Lin ZG. Characterization and electrochemical investigation of boron-doped meocarbon microbeads anode materials for lithium batteries. J Solid State Electrochem 2002; 6: 420-7.

[7] Blanco C, Santamaria R, Bermejo J, Menendez R. Pitch-based carbon composites

with granular reinforcements for frictional applications. Carbon 2000; 38: 1043-51.

[8] Mochida I, Fujiura R, Kojima T, Sakamoto H, et al. Carbon disc of high density and strength prepared from heat-treated mesophase pitch grains. Carbon 1995;33(3):265 -74.

[9] Dumont M, Chollon G., Dourges MA, Pailler R, Bourrat X, Naslain R, et al. Chemical, microstructural and thermal analyses of a naphthalene-derived mesophase pitch. Carbon 2002; 40:1475-86.

[10] Drbohlav J, Stevenson WTK. The oxidative stabilization and carbonization of a synthetic mesophase pitch, Part Ⅱ: The carbonization process. Carbon 1995; 33(5):713-31.

[11] Hoffmann WR, Hüttinger KJ. Demonstration of spontaneous liquid-phase sintering of mesophase powders. Carbon 1993; 31(2):259-62.

[12] Song Y, Li S, Zhai G, Shi J, Fan Y, Guo Q, Liu L. Sintering mechanism of tape derived from oxidized mesophase pitch. Carbon, under review.