Summer 6-23-2014

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ABSTRACT

As a novel porous multi-functional carbon material, carbon foams have high bulk thermal conductivity and low density, making them as excellent materials for thermal management systems applications, such as heat exchangers, space radiators, and thermal protection systems. In this paper, the carbon foams with high thermal conductivity, derived from three kinds of mesophase pitches, were fabricated by the process of foaming, carbonization and graphitization. The microstructures of the foams were examined by scanning electron microscopy. It was found that the pores were uniformly distributed, and the pore wall thickened with increasing foams' density. The properties of the foams were studied, including compressive strength and thermal conductivity. The results showed that lower density and higher thermal conductivity were achieved for the foams using the two kinds of pitches with higher volatile components. The bulk thermal conductivity of carbon foams were up to 179 W/(m·K) and 201 W/(m·K), for the densities of 0.66 g/cm^3 and 0.83 g/cm^3, respectively. The foams' compressive strength was in the range of 1.6 MPa to 3.4 MPa.

Keywords: Carbon foam; Mesophase pitch; Microstructure; Thermal conductivity; Compressive strength

1   INTRODUCTION

Carbon foam is a new porous multi-functional carbon material with properties including low density, controllable electric and thermal conductivity, fire-resistance, erode-resistance, sound and impact energy absorption and so on [1-5]. There are many applications for carbon foam in commercial purposes as thermal management material, structural material, sound absorption material, catalyst support [6-11]. This material was different from the carbon and graphite foams produced previously. This material has a predominately spherical porosity with smaller openings between the cells. It is fabricated with the highly oriented sheets of the graphite parallel to the cell walls, yielding thermal conductivities in the ligaments as high as 1700 W/(m·K). The bulk thermal conductivity is more than 100 W/(m·K) at a bulk density of approximately 0.5 g/cm^3 [11].

The properties of the carbon foam are mainly determined by the natures of the precursor material and preparing parameters. Mesophase pitch is an important type of foaming precursor, which can be either optically anisotropic or isotropic in nature. It is known that pitch can develop large anisotropic domain yields highly graphitizable carbon, while pitch develops small anisotropic domains is less graphatizable [3,6]. In the present paper, three different mesophase pitches were introduced as precursors to prepare high thermal conductivity carbon foams. The properties of precursors and carbon foams were studied.

2   EXPERIMENTAL

2.1 Raw materials

Three different mesophase pitches power with different soften points were used as precursors of carbon foams, respectively. The properties of the three mesophase pitches are listed in Table 1.

Table 1 Properties of precursors

Precursors	Volatile component (Wt.%)	Quinoline insoluble (wt.%)	Toluene insoluble (Wt.%)	Softening point (℃)
A	23.08	35.76	68.19	275
B	30	17.5	40.1	219
C	16.11	35.64	67.60	305

2.2 Preparation of carbon foams

The processing of graphite foam takes three main steps: foaming, carbonization, and a graphitization heat treatment. The foaming process of carbon foams were carried out in a pressure vessel by heating the foaming precursors at the specified heating rate to 500 ℃in a nitrogen atmosphere and pressure up to 5-9 MPa, soaking for two hours, and then cooling to room temperature by natural cooling.

Following the foaming process, each sample was carbonized in an atmosphere of nitrogen at a heating rate of 0.2℃/min to 1000℃. The final processing step was graphitization, which occurred at 3000℃ in an atmosphere of argon.

2.3 Characterization of foams

The morphologies of porous carbon foams were examined by a field emission scanning electron microscopy (SEM; Hitachi S-3000N). Due to the high electrical conductivity of carbon foams, samples were not gold sputter coated at high magnificationgs. The average pore size, apparent porosity and pore size distribution of porous carbon foams were obtained using image analysis by sampling at least 10 random regions on samples.

The thermal conductivity of foams was determined using the thermal flash technique at room temperature with a xenon flash lamp source. The thermal diffusivity of the foam was measured on samples 10mm diameter by 8mm thicken (z direction: the foaming direction) on the JR-3 nanoflash machine. The sample density and specific heat capacity were then used to calculate the thermal conductivity from the following equation:

$$\kappa = \alpha \cdot \rho \cdot Cp \qquad \text{Equation 1}$$

where, κ = Thermal conductivity (W/(m·K)), α = Thermal diffusivity (cm^2/s), Cp =Specific heat (J/(g·K)), and ρ = Density (g/cm^3).

The compressive strength of carbon foams were measured on the samples 10mm diameter by 20mm thicken (z direction: the foaming direction) by SANS CMT5000.

3   RESULTS AND DISCUSSION

3.1 Structure of carbon foams

Table 2 shows the structural parameters of samples CF1-6. Samples CF1-3, CF4-5 and CF6 were drived from precursors A, B and C, respectively. Fig. 1-6 show the typical pitch-based carbon foams, derived from mesophase pitches A, B and C, respectively.   Some observations can be made directly from these images. It is clear that these foams are not reticulated networks of linear rods as seen in typical glassy carbon foams. They are exhibit a cellular morphology in which cell walls are made up of layers of graphite. Fig. 2-6 shows the cell structure of these graphitized samples is significantly less smooth and less uniform than that of foam that has been carbonized(Fig. 1), but not graphitized. This is expected because a carbonized specimen contains amorphous films and softer phase that get subsequently distorted and polygonized due to increased crystallization when graphitezed. SEM images (Fig. 2-6) clearly show that the cell walls have an open, interconnected pore structure. pore diameters vary, mostly in the vicinity of 100 μm. Pores in the graphitized sample appear to be larger than those in carbonized samples due to greater shrinkage of material in the former. The majority of the pore openings have cracks and irregular ruptured edges, indicating brittle fracture during carbonized and graphitized processes. These cracks mainly occur between the layers aligned parallel to the cell surface, especially in the junction area of the foam cell. It is very possible that this kind of cracks is due to the CTE mismatch between in-plane and out-of-plane graphitic layers developed from large anisotropic flow domains. Fig.2b,3b,4b,5b,6b show the pores with cracks of carbon foams. The morphology of these openings is expected to be important for the failure mechanisms of these structures. It appears that the cracks will decrease the mechanical strength of carbon foam. The pitch precursors that generate larger anisotropic domains will be more graphitizable, thus the resultant foam will have better thermal and electrical conductivity, but will be mechanically weaker.

Fig. 2c-d, Fig. 3c-d and Fig. 4d show that ligaments (lines along which two cell walls meet) and junctions

(corners of ligaments) consist of layered graphitic planes. In higher magnification images (Fig. 2d), these structures can be seen to consist of folded graphitic planes. It is obvious that carbon wall of CF5-6 is thicker than that of CF1-2. Most pores within CF1 and CF2,4 distribute in range of 350-450 μm and 300-400 μm, most pores within CF5-6 and CF3 fall in range of 250-350 μm and 200-300 μm. The pore size of samples is decrease ordered by CF1

(0.54 g/cm^3), CF2,4 (0.66 g/cm^3,0.65 g/cm^3), CF5 (0.73 g/cm^3), CF6 (0.77 g/cm^3), CF3 (0.83 g/cm^3) and the apparent porosity of them is 76.1%, 70.8%, 71.2%, 67.7%, 65.9% and 63.3%, respectively. The results indicate that the carbon wall thickened and pore size decreased with the increasing foams' density, although the foams derived from different precursors.

Table 2 Structural parameters of CF1-6

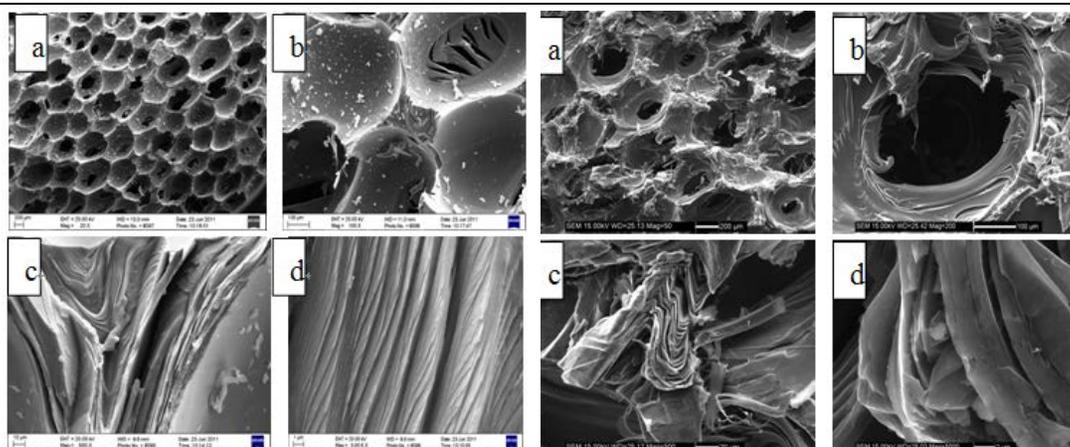| Sample	Precursor	Density （g/cm^3）	Range of pore size（μm）	Porosity （%）
CF1	A	0.54	350-450	76.1
CF2	A	0.66	300-400	70.8
CF3	A	0.83	200-300	63.3
CF4	B	0.65	300-400	71.2
CF5	B	0.73	250-350	67.7
CF6	C	0.77	250-350	65.9

Fig.1 SEM images of carbonized foam of CF-1 prepared from precursor A

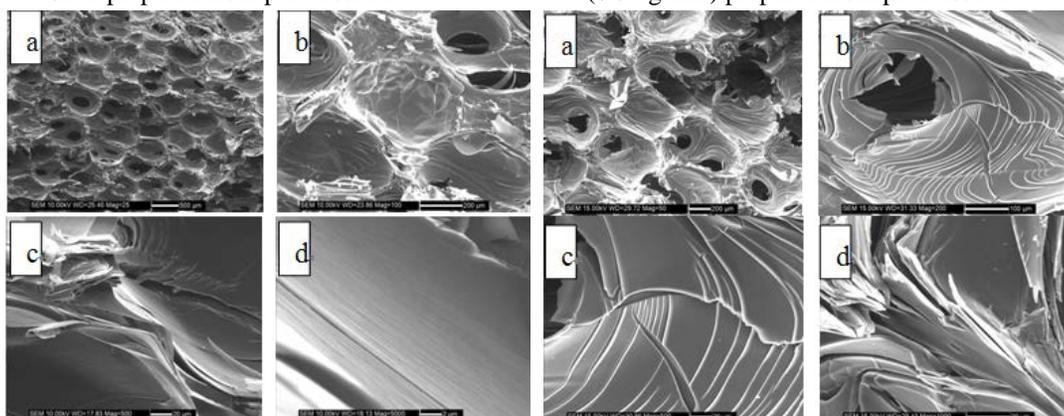Fig.2 SEM images of graphitized foam of CF-1 (0.54 g/cm^3) prepared from precursor A

Fig.3 SEM images of graphitized foam of CF-2 (0.66g/cm^3) prepared from precursor A

Fig.4 SEM images of graphitized foam of CF-3 (0.65 g/cm^3) prepared from precursor B
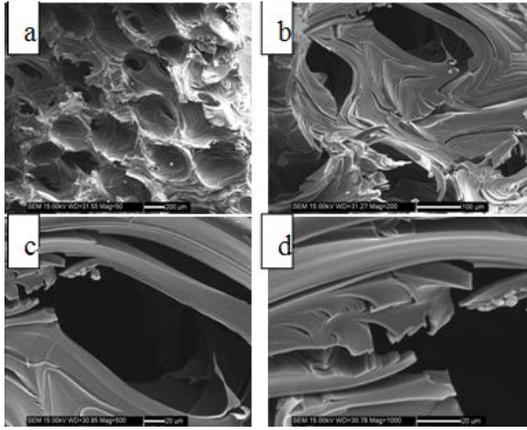
Fig.5 SEM images of graphitized foam of CF-4 (0.73 g/cm^3) prepared from precursor B
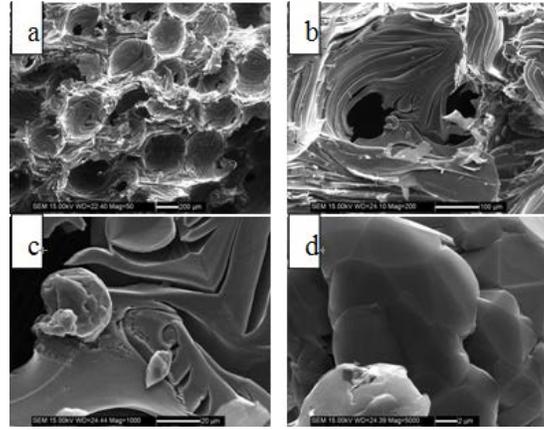
Fig.6 SEM images of graphitized foam of CF-5 (0.77 g/cm^3) prepared from precursor C

3.2 Properties of carbon foams

Thermal conductivity is a property used to describe its ability to transfer steady state conditions. The thermal conductivity of carbon foam is typically calculated by measuring the thermal diffusivity and density of the sample, and then using Equation 1 in section 2.3. Table 3 shows the thermal conductivity of CF1-6, and is 153 W/(m·K), 179 W/(m·K), 201 W/(m·K), 171 W/(m·K), 169 W/(m·K), 151 W/(m·K), respectively. It is clear that the thermal diffusivity of CF1 (3.91 cm^2/s) and CF2 (3.78 cm^2/s) foaming from precursor A is higher than CF4 (3.65 cm^2/s) and CF5 (3.24 cm^2/s) foaming from precursor B, and CF4-5 is higher than CF6 (2.72 cm^2/s) foaming from precursor C. The alterative rule of specific thermal conductivity of samples is the same with their thermal diffusivity.

The high thermal conductivity reported for mesophase based carbon foams mainly results from the strongly oriented mesophase layers within the bubble walls. One process for preparing mesophase foams is confined carbonization, where the release of the volatile products in the pyrolysis process creates the open cell network of the foam. The thermal diffusivity of the graphite material was related to the graphite ligaments, crystal parameters, the bridge of micro-graphite structures, and the arrangement of micro-graphite structures. The thermal diffusivity and bulk density of carbon foam strongly influences the resulting thermal conductivity. As showing in Table 3, the thermal conductivity of CF3 is higher than CF2, and CF2 is higher than CF1. Usually, thermal conductivity increases with increasing density for the samples foaming from same precursor. There may be some micro-cracks with the test sample of CF5 for the reason of lower thermal conductivity than CF4.

The precursor is an important factor which determined the properties of carbon foams. According to Table 1 and Table 3, the results showed that lower density and higher thermal conductivity were achieved for the carbon foams using the two kinds of pitches A and B with higher volatile components.

Table 3 also summarizes the compressive strength of carbon foam derived from the various precursors. The compressive strength of the carbon foams ranges from 1.6 to 3.4 MPa. The compressive strength increases with increasing density for the samples foaming from the same precursor. Such as CF1-3 foaming from precursor A, its density is 0.54 g/cm^3, 0.66 g/cm^3, 0.83 g/cm^3, and compressive strength is 1.60 MPa, 2.48 MPa, 3.40 MPa, respectively. The mechanical property of cellular materials is complicated, which depend on both the kind of precursor and the material's microstructural arrangement. The mechanical strength of carbon foam depended on the length and quantity of cracks in samples, basing on the brittle materials fracture rule.

Table 3　Properties of CF1-6

Sample	Precursor	Density (g/cm^3)	Thermal diffusivity (cm^2/s)	Thermal conductivity (W/(m·K))	Specific thermal conductivity (W/(m·K))/(g/cm^3)	compressive strength (MPa)
CF1	A	0.54	3.91	153	283	1.60
CF2	A	0.66	3.78	179	271	2.48
CF3	A	0.83	3.36	201	242	3.40
CF4	B	0.65	3.65	171	261	1.81
CF5	B	0.73	3.24	169	232	3.31
CF6	C	0.77	2.72	151	196	3.35

4　CONCLUSION

Three different mesophase pitches are the suitable foaming precursors. They generate high thermal conductivity and certain compressive strength carbon foams, which is a good candidate for structural and energy absorption applications. Mesophase pitch mainly generates anisotropic carbon foam. Compared to precursor C, precursor A and B with higher volatile components generate lower density and higher thermal conductivity carbon foams. The properties of carbon foams could be adjusted by precursors and controlling the processes of heating procedure and foaming pressure. The thermal conductivity and strength of carbon foam is determined by the foam cell structure, and the pore wall thickened with increasing foams' density.

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