Differences in structure of mesophase spheres prepared through homogeneous and heterogeneous nucleation

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Abstract

Mesophase spheres were prepared through homogeneous and heterogeneous nucleation from two coal tar pitches with some and nearly without quinoline insolubles. The pitches suffered thermal condensation in a stainless steel reactor at 440 and 410℃ for 1 or 7h, respectively. SEM was introduced as a useful tool to detect the structures of the two kinds of mesophase spheres. As a result of the paper, it was found that the structure of mesophase spheres prepared through homogeneous nucleation was Brooks-Taylor type, which is consistent with the analysis result of optical microscopy. Whereas, the structures of the heterogeneous nucleation mesophase spheres were complex, which were parallel in parts of the structure.

Keywords: A. Coal tar pith, Carbon microbeads, Mesophase; C. Scanning electron microscopy, Optical microscopy

1. Introduction

Carbonaceous mesophase as a promising carbon product has gained much attention from not only researchers in institutes but also producers in factories all over the world. In some special applications of carbonaceous mesophase, for example as the anode of rechargeable lithium ion batteries, its structure exerts an important influence on the electrochemical performance, say charge/discharge capacity, cycle life, etc. Generally, it is regarded that the initial spherical carbonaceous mesophase, i.e. mesophase sphere, has Brooks-Taylor type structure with the carbon layers parallel to each other and perpendicular to the surface of the sphere, which is deduced from the extinction contours of mesophase spheres when they are still in the isotropic pitch matrix by the aid of polarized light microscope [1-2]. For mesophase spheres with complex structures their exact structures were very difficult or even impossible to be determined by optical microscopy. Therefore, the further studies on the relation between the structures of these mesophase spheres and their electrochemical performance are consequently restricted.

The scanning electron microscopy (SEM) method developed by the present authors could be applied to detect the structures of mesophase spheres, which are either Brooks-Taylor type or others [3-5]. The present paper would employ this method to detect the structures of mesophase spheres prepared through homogeneous or heterogeneous nucleation and discuss the differences in morphology and optical characteristics between the two kinds of mesophase spheres. To fulfill the objective, two coal tar pitches with different concentrations of quinoline insolubles (QI) were used as raw materials and the structures of the as-received mesophase spheres were focused with the aid of SEM.

2. Experimental

2.1 Parent pitches

Two coal tar pitches with different quinoline insolubles (QI) concentrations were selected to produce homogeneous/heterogeneous nucleation mesophase spheres. Some properties of the parent pitches are summarized in Table 1.

Table 1 Some properties of the parent pitches

Pitch	SP (℃)	Solubility (*wt %*)			
		HS	HI-TS	TI-QS	QI
CTP1	27	20.6	67.0	12.1	0.3
CTP2	78	19.6	58.8	16.9	4.7

SP, Softening Point;
HS, Hexane Solubles;
HI-TS, Hexane Insolubles-Toluene Solubles;
TI-QS, Toluene Insolubles-Quinoline Solubles;
QI, Quinoline Insolubles

2.2 Preparation of mesophase spheres

About 300g parent pitches (CTP1 and CTP2) were enclosed in a 2L stainless steel reactor and then heated up to desired temperatures (440℃ for CTP1 and 410℃ for CTP2) under the protection of purified nitrogen. At the above temperatures, CTP1 and CTP2 were thermally treated for 1 and 7 h, respectively, before the reactor was naturally cooled to room temperature. The preparation conditions and nomenclature were listed in Table 2.

Table 2 Preparation conditions of mesophase spheres

Mesophase sphere	Parent Pitch	HTT [a]	HT [b]
MCB1	CTP1	440	1
MCB2	CTP2	410	7

a, Heat treatment temperature (℃);
b, Holding time (h);

2.3 Analysis methods

Mesophase pitch samples were embedded in sulphur and then ground and polished. The obtained carbon/sulphur bulk was observed on Nikon E600 POL optical microscope with polarized light system fitted and results were recorded using in situ Nikon DXM1200 digital camera.

Mesophase spheres were separated from isotropic matrix in Soxlet extractor with toluene as the solvent. The isolated spheres were carbonized in a horizontal tube furnace at 1000℃ for 1h. To observe the structures of the carbonized mesophase spheres (also called mesocarbon microbeads, MCMB), they were fixed with thermosetting resin and then opened according to the method developed by the present authors [3-5]. The uncarbonized and opened MCMB were analyzed on Philip XL30 scanning electron microscope (SEM) after being gilded in vacuum.

3. Results and discussions

3.1 Optical characteristics of MCMB

The optical micrographs of MCB1 and MCB2, which are still in the matrix of heat-treated pitch, are shown in Fig.1 (a) and (b).

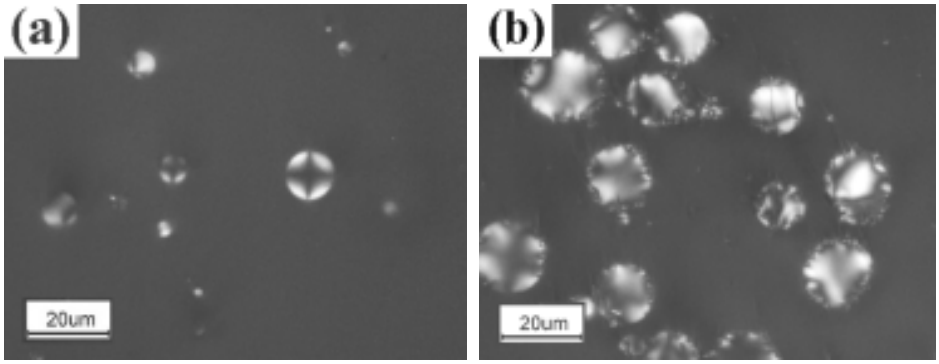

Fig.1 Optical micrographs of MCB1 and MCB2 under polarized light, which are still in the matrix of the isotropic pitch

It could be seen that the mesophase spheres generated from CTP1, i.e. MCB1, have a wide size distribution and regular extinction contours, implying that they followed homogeneous nucleation formation and the formed structure of them is Brooks-Taylor type [1-2]. From the uniform size and small particles at the edges of MCB2, we know that the mesophase spheres generated from CTP2 belong to heterogeneous nucleation formation. The irregular extinction contours of MCB2 indicate that their structures are different from MCB1. In fact, we could not or could not easily deduce their exact structures from these complex extinction contours.

3.2 Morphologies of the isolated mesophase spheres

Fig.2 shows the SEM micrographs of the isolated mesophase spheres of MCB1 and MCB2. From these micrographs, it could be seen the wide size distribution and smooth surfaces for MCB1 and uniform size and rough surfaces for MCB2 in accordance with the results of optical microscopy, which means that the mesophase spheres from homogeneous nucleation have very different morphologies from the heterogeneous ones.

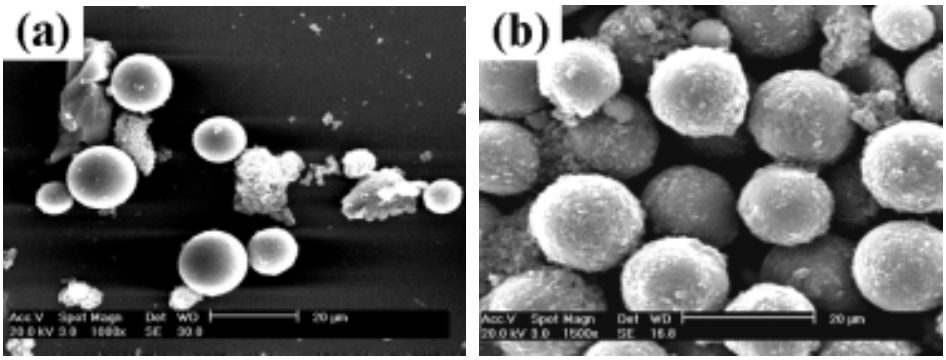

Fig.2 Morphologies of MCB1 and MCB2 under SEM

3.3 Structures of the carbonized MCMB

As mentioned above, people could not infer the complex structure of MCB2 according to the irregular extinction contours shown in Fig.1 (b). However, by the aid of the SEM method, we could easily analyze them after the spheres are opened. Fig.3 gives the obtained SEM micrographs of the cross-sections of MCB1 and MCB2 samples.

From Fig.3 (a), we can see that the structure of MCB1 is just the Brooks-Taylor type as deduced from their optical characteristics. The structures of MCB2 are very complex and most of them are different from

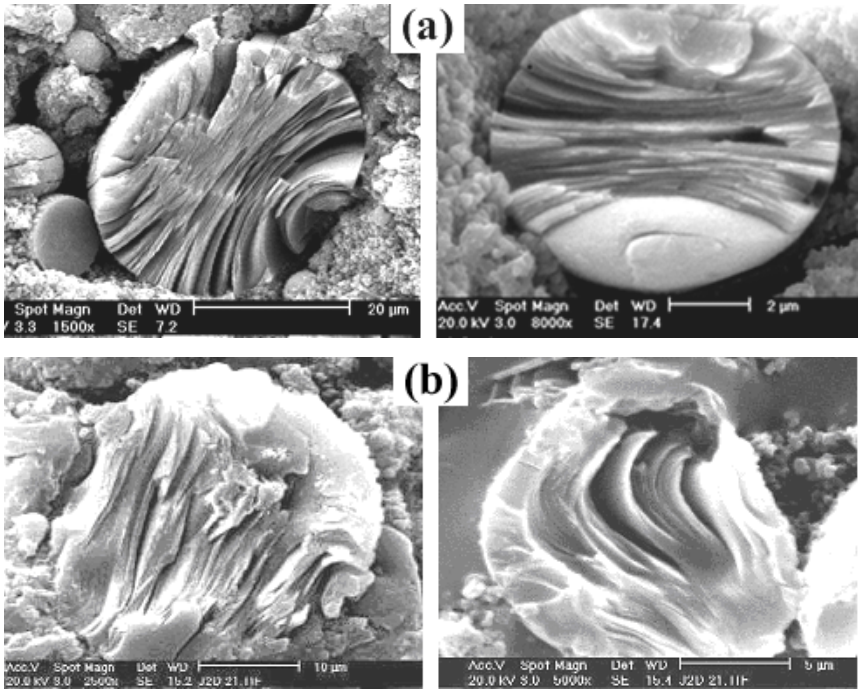

Fig.3 SEM micrographs of MCB1 and MCB2 with their cross-sections shown

Brooks-Taylor type. As examples, Fig.3 (b) gives two typical structures of them. The microtextural carbon layers of the left sphere in Fig.3 (b) are almost parallel, which could be regarded as near Brooks-Taylor type structure, whereas those of the right one in Fig.3 (b) are deformed into scoop shape and are very different from Brooks-Taylor type structure.

4. Conclusions

From two coal tar pitches homogeneous and heterogeneous nucleation mesophase spheres were prepared by heat-treatment at different temperatures. By analyzing the structures of the two kinds of mesophase spheres with SEM method, it was found that the mesophase spheres from homogeneous nucleation have Brooks-Taylor type structure, while those from heterogeneous nucleation have complex structures with their microtextural carbon layers parallel or distorted.

Acknowledgement

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