Self-sinterability of mesocarbon microbeads (MCMB) for preparation of high-density isotropic carbon

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In this paper, self-sinterability of MCMB derived from a refined petroleum residue was studied in detail. Green pieces were prepared from the MCMB by hot pressing and further heat treatment in the range of 300°C to 1100°C under argon atmosphere. The properties of carbon blocks such as weight loss, volume shrinkage, conductivity during heat-treatment were measured after each step. Thermalgravimetric analysis (TGA) of green pieces with different β resin content as well as Scanning Electron Microscopy (SEM) morphology of fracture surfaces of carbon blocks were also determined. From the results above, it is indicated that below 1100°C the process of carbonization shows two distinct stages: plastic sintering below 550°C and solid carbonization at higher temperature than 550°C. Different reactions took place in the interior of the carbon blocks during the two different stages, of which the plastic sintering stage was more important to the properties of carbon blocks. Accordingly, the model of self-sinterability of MCMB during heat treatment was proposed.
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1. Introduction

High-density high-strength isotropic carbon and graphite materials are needed in various applications such as crucibles in semiconductors, electrodes in metallurgy and reactors in the nuclear industry. They were initially prepared from powdered coke as filler and pitch as binder through repeatedly mixing, grounding, kneading and impregnating. Another technique was developed using self-sintering green coke or mesophase pitch without any binder by cold isostatic pressing [1–3]. But it was not easy to obtain desirable properties indispensable to advanced technology due to the difficulty in controlling their self-sinterability. Mesocarbon microbeads (MCMB) have been recognized as an excellent precursor for high density and high strength artifacts since it was prepared in 1974 [4]. MCMB has been widely used in modern industry in the rechargeable Li-ion battery, high performance liquid chromatography [5–9] etc. due to its unique morphology and structure. Its application to high-density isotropic graphite (HDIG) was another important usage for its controllable self-sinterability, spherical shape and high compact density. It is easy to obtain the desirable properties for HDIG by simple techniques through molding, carbonization and graphitization if necessary.

MCMB mainly contains a PI fraction (Pyridine Insoluble, PI) which does not melt when heat-treated.

The self-sinterability of MCMB results from the β resin (Toluene Insoluble-Pyridine Soluble fraction, TI-PS fraction) which was called *in situ* binder [10] in this system. β resin resided on the surface of MCMB when mesophase pitch was extracted with pyridine, therefore the content of β resin in MCMB could be controlled by the times of solvent extraction [10, 11]. In general, β resin has some aliphatic substitutes and lower-molecular weight compounds which show good fluidity under pressure or heat treatment, and thus improve the whole fluidity of MCMB with β resin as the plasticizer. *In situ* high temperature ^{1}H NMR [12] showed some β resin becomes fluid at 475°C, illustrated by the introduction of a narrower line-shape in the middle spectrum while the PI showed no softening. So the presence of β resin was essential to the densification and self-sintering of MCMB.

MCMB with moderate β resin content presented good self-sinterability when was hot pressed and carbonized under inert gases. Much work [13–15] has been done to prepare high-density high-strength isotropic carbon materials, which showed excellent mechanical, thermal and electrical properties. But the mechanism of self-sinterability of MCMB during carbonization was rarely studied compared to the efforts exerted to discuss the influences of processing parameters on the properties of carbon blocks. W. R. Hoffmann [16, 17]

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studied the self-sinterability of mesophase powder in detail and proposed that the self-sintering processes were composed of a transient liquid-phase sintering step and a subsequent solid state carbonization step. It was concluded that higher pressure during carbonization could decrease the temperature of sintering because pressure as well as heat treatment promoted the fluidity of β resin. As MCMB was of unique structure and good self-sinterability, the carbon disc prepared from MCMB had excellent properties with compressive strength up to 420 Mpa [15], which was much higher than that of mesophase powder, and it seems to be significant to verify the self-sintering process of MCMB.

In this paper we present the results of heat treatment of green carbon pieces from self-sintering MCMB at various temperature ranging from 300°C to 1100°C. The properties and structural changes of carbon blocks during this processing were investigated thoroughly. It was concluded that the self-sinterability of MCMB was owing to β resin in the surface of MCMB; and the carbonization processing had two stages, the first one was a plastic sintering stage below 550°C and the second was solid carbonization stage at higher temperature. we also considered the structure changes during carbonization and its influences on the properties such as conductivity of carbon blocks. Finally, a model of self-sintering of MCMB were proposed.

2. Experimental

The mesophase pitch containing MCMB was synthesized from a Refined Petroleum Residue (RPR) in the presence of 1 wt% carbon black under nitrogen atmosphere at 420°C for 6 h. MCMB was extracted from parent pitch first with an industrial oil and then with pyridine for several times, washed with acetone and dried under vacuum at 120°C. The as-prepared MCMB weas hot pressed at 150°C under 250 MPa into carbon block with size of 60 mm × 20 mm × 3 mm. The details of the experiment were described elsewhere [11]. The green pieces of MCMB were heat treated at various temperatures ranging from 300°C to 1100°C for 1 h under flowing argon at the heating rate of 1°C/min below 700°C and 3°C/min at higher temperature.

The morphology of MCMB and fractured surface were observed under Scanning Electron Microscopy (Cambridge S-250MK3). TGA was conducted on the green pieces from 110°C to 800°C at the heating rate of 10°C/min under nitrogen atmosphere using Pekin-Elmer Instrument. The conductivity was determined with GM-II multifunction Automatic Testing Instrument of Resistivity.

3. Results and discussion
3.1. The morphology of MCMB powder

Fig. 1 shows the morphologies of MCMB extracted for different times with pyridine. It is seen that with the increase of extraction times, MCMB is dispersed gradually. When mesophase pitch was extracted with pyridine four times, most microbeads congregate together and there is a lot of β resin on the surfaces of the MCMB. From the pictures of Fig. 1b and c, it seems that there is not much difference when mesophase was extracted seven times and eight times respectively. But their β resin contents are different, in the former it is 8.9 wt% and the latter it is 6.7 wt%, and their self-sinterability differs distinctively. When hot-pressed and carbonized at 1000°C for 1 h, the bending strength of MCMB with 8.9 wt% β resin is much higher than that with 6.7 wt% β resin content [11]. This indicates that β resin content is very important to the properties of MCMB and can be controlled by the solvent extraction times. Therefore we choose the MCMB with β resin content of 8.9 wt% to carry out the following experiments.

3.2. Physical properties of carbon blocks

Fig. 2 shows the physical properties of carbon blocks heat treated in the range of 300°C to 1100°C. It is seen from the curves that the properties of carbon blocks during heat treatment shows two distinct steps, one is below 600°C and the other is above 600°C. The rate of weight loss below 600°C is higher than that of above 600°C, and the amounts of weight loss below 600°C accounts for 80% of the total weight loss between 300°C and 1100°C, which indicates that the weight loss of the carbon block from MCMB is mostly attributed to the
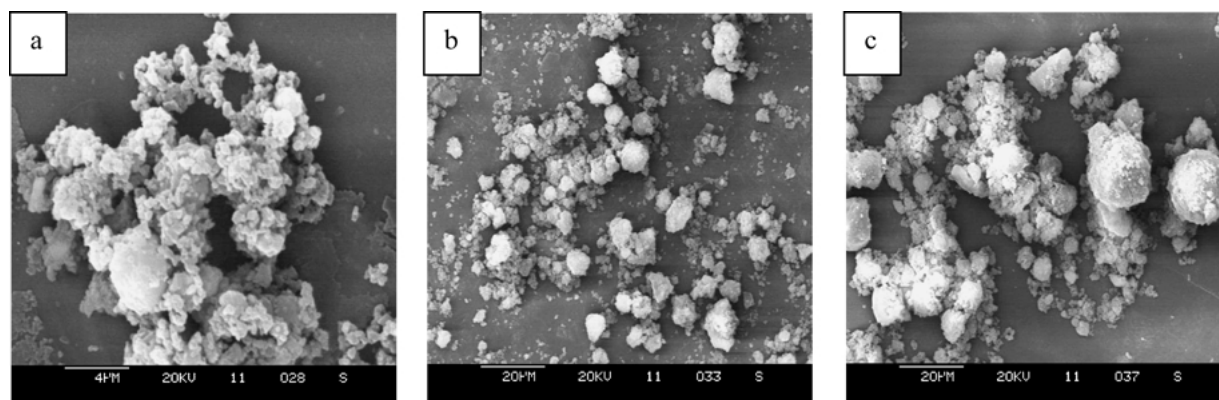

Figure 1 Morphology of MCMB extracted with pyridine: (a) 4 times, (b) 7 times, and (c) 8 times.
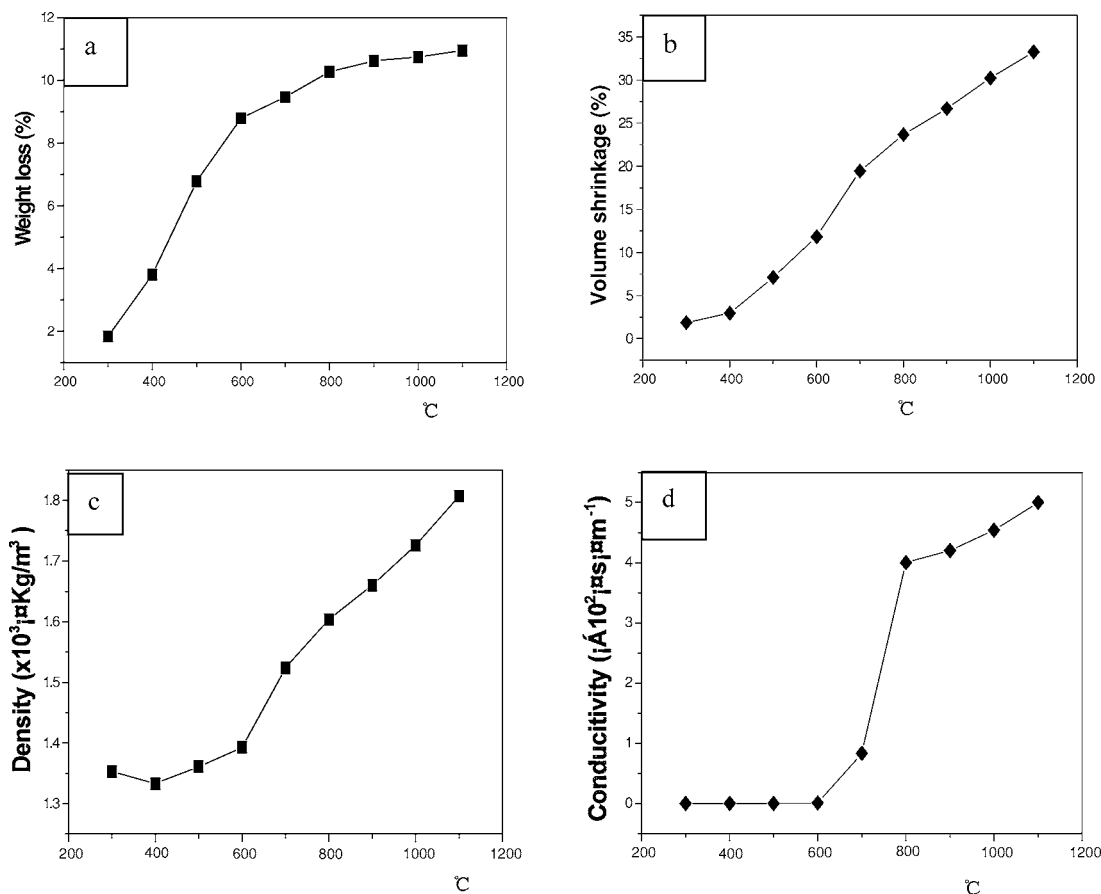
Figure 2 The physical properties of carbon blocks heat treated at different temperature: (a) weight loss, (b) volume shrinkage, (c) density, and (d) conductivity.

dehydrogenation and polycondensation of the β resin and PI fraction, which occurred at relatively low temperature. The volume shrinkage shown in Fig. 2b, increases gradually below 600°C and increases rapidly between 600°C and 700°C, and then slows down above 700°C. The amount of volume shrinkage between 600°C and 700°C accounts for 23% of the total volume shrinkage between 300°C and 1100°C. It is implied from the volume shrinkage curve that important changes occurred during 600°C and 700°C heat treatment. The density changes a little below 600°C because the rate of weight loss and the volume shrinkage is similar, and then increases quickly up to 1810 kg/m^3 when heat treated at 1100°C. From Fig. 2d, it is shown that when heat treated below 600°C, the conductivity of carbon blocks is near to zero and almost insulating, and increases promptly above 700°C. This can be explained that below 600°C, the size of molecules of polycondensed aromatic hydrocarbon (PAH) is very small due to the high H/C ratio and its disordered structure, and the π electron is localized and cannot move freely. When most dehydrogenation and polycondensation reactions are over and the molecular plane of carbon is larger, the π electrons are delocalized in the larger area of the whole system which contributes to the conductivity of the carbon blocks. When chemical reactions are nearly finished at about 700°C, the structure of carbon block changes gradually through structure rearrangement which is very slow below 1100°C and the carbon

micro-crystalline domains grow very slowly. And thus the conductivity between 700°C and 1100°C increases slowly.

3.3. Thermal properties of green pieces from MCMB

From Fig. 3, it is indicated that the weight loss of green pieces with β resin content of 8.9 wt% during heat treatment shows two distinct steps; the step between 180°C and 500°C and the step between 500°C and 800°C.
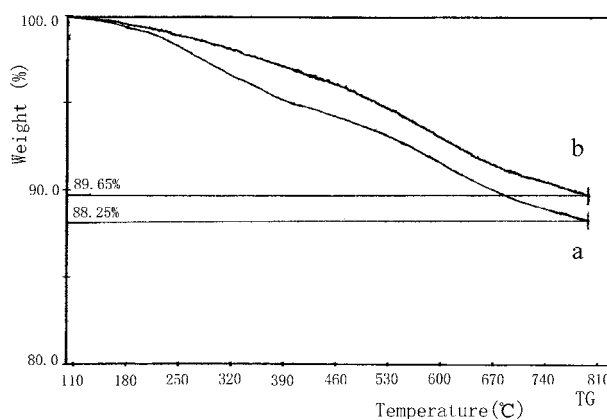

Figure 3 The curves of thermogravimetric analysis of green pieces with different β resin content: (a) 8.9 wt% and (b) 6.7 wt%.

2211

The weight loss of green pieces with β resin content of 6.7 wt% does not shows this tendency. The first step is called plastic-sintering which mainly consists of the interfacial reactions of β resin, and the MCMB aggregates and binds together through chemical bonding. The volume shrinkage is mainly composed of the shrinkage of interfaces and disappearance of the micro-pores and the green pieces become an integral solid through liquid sintering. The second step is the further dehydrogenation and main structure rearrangement, which results in uniform shrinkage of whole carbon blocks. From Fig. 3, it is seen that the second step of curves of (a) and (b) shows a similar and parallel tendency, which indicates that extraction time may only changes the surface of MCMB and has no influences to the inner composition and structure of MCMB.

3.4. The morphology of carbon blocks heat-treated at various temperatures

Fig. 4 shows the fractured surfaces of green pieces and carbon blocks heat-treated at different temperatures. It is seen that the surface of green piece hot pressed at 150°C under 250 MPa is basically smooth, and it tends to flow at some local areas at 500°C as shown in Fig. 4b, indicating the plastic sintering due to moderate β resin content of MCMB. The tendency of flowing is spreading to the whole area when carbonized at higher temperature and becomes distinct at the temperature of 1000°C. So, on the basis of controlling the appropriate β resin content in MCMB, the heating rate should be as low as possible, or else the carbon blocks

would be break up due to the excessive emission of gases.

4. Conclusions

Green carbon pieces from MCMB were heat treated under flowing argon at various temperatures in the range 300°C–1100°C. The weight loss, volume shrinkage, density and conductivity during carbonization were studied in detail, which shows two distinct stages: the plastic sintering below 600°C due to the fluidity of β resin below this temperature and the solid carbonization above 600°C, showing good and uniform shrinkage. TG analysis and SEM observation of fractured surfaces are consistent with the results above, verifying the self-sintering mechanism of MCMB that consists of plastic sintering and solid carbonization. Finally, we also considered the structure changes during carbonization and its influences on the properties such as conductivity of carbon blocks. A model of self-sintering process is illustrated in Fig. 5. When MCMB was hot pressed, there was some pores and cavities left in the green pieces. During plastic sintering at about 500°C, β resin on the surfaces of MCMB flowed, and the interfaces as well as cavities diminished gradually. At higher temperature, green pieces subsequently turned into substantial carbon blocks, which is called solid carbonization. The structure rearrangement of carbon blocks resulted in the increase of crystal size of carbon, but the disordered aggregate of mrico-crystals led to the isotropic properties of carbon blocks.
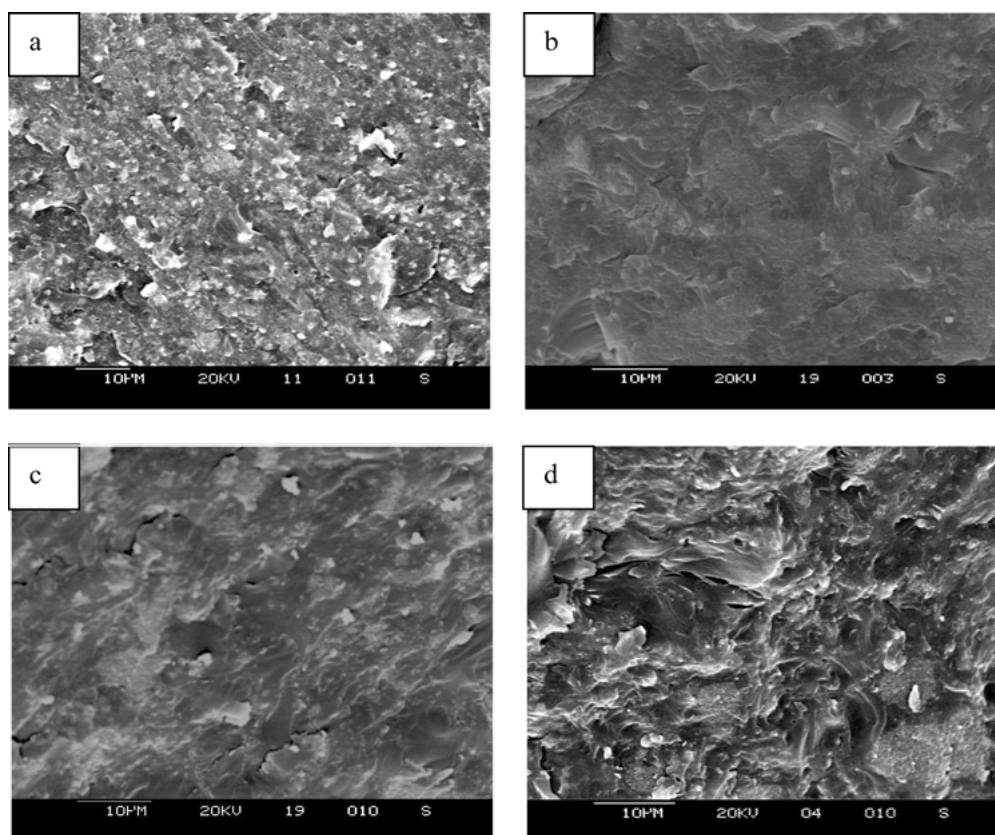

Figure 4 The fractured surfaces of: (a) green piece and carbon blocks heat treated at, (b) 500°C, (c) 700°C, and (d) 1000°C.
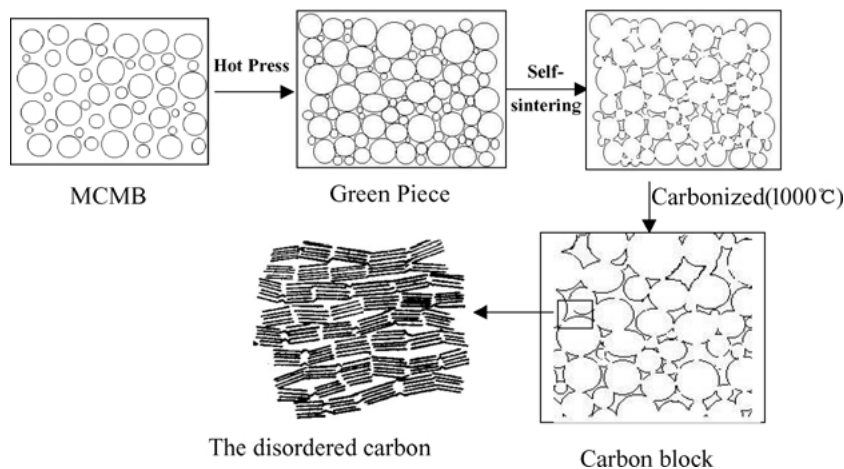
Figure 5 The model of self-sinterability of MCMB.

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