

THE EFFECT OF OXIDATIVE STABILIZATION ON THE SINTERING OF MESOCARBON MICROBEADS AND IN-SITU OBSERVATION OF THEIR CARBONIZATION PROCESS

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Introduction

High density isotropic graphite (HDIG) has been widely used in a wide field of industries. Such graphite materials have been prepared by two typical procedures. In the industrial process for manufacture HDIG, filler coke and binder pitch are used as raw materials. The other process involve the utility of self-sintering carbonaceous mesophase[1-3]. The self-sintering ability of MCMB is believed to derive from β -resin (toluene insoluble and quinoline soluble fraction), which transfer into liquid at 400~500 °C, adhering MCMB together by liquid-phase sintering mechanism. However, the thermoplasticity of mesophase is usually too high; as a result, the green artifacts deform and swell in the carbonization process. Oxidative pretreatment is an effective method to reduce the plasticity to an appropriate level, leading to an optimal mechanical property. It is of importance to elucidate how oxidative pretreatment affects the sintering mechanism and the subsequent mechanical properties. In the present work, two types of MCMB with different oxidative pretreatment extent were used and moulded without any addition binder by CIP, followed by carbonization and graphitization. The sintering process was observed by using in-situ Scanning Electron Microscopy (in-situ SEM).

Experimental

Two types of commercially available MCMB were provided by China Steel Chemical Corporation, Taiwan, China. The MCMB were oxidized in air at about 200 °C for different extent. One was lightly oxidized and thus had a better self-sintering ability. The other was over oxidized for comparison. The general characteristics of these materials are summarized in Table 1.

Table 1. Characteristics of lightly oxidized MCMB(M-LO) and excessively oxidized MCMB(M-EO)

	M-LO	M-EO
D10 (μm)	18.42	19.20
D50 (μm)	25.04	24.69
D90 (μm)	35.47	33.19
Ash Content (%)	0.10	0.13
Tap Density (g/cm ³)	0.744	0.748

The MCMB were compacted by cold isostatic pressing under 200 MPa into a cylinder-shaped green carbon artifact of ca. 70 mm in diameter and 70 mm in height. The green carbon artifact was sintered from ambient temperature to 1000 °C for 90 h and held at 1000 °C for 2 h. The graphitization of samples was performed in an Achison furnace. It took about 20 days for the whole graphitization process including heating, holding and cooling. The maximum graphitization temperature was about 2900 °C.

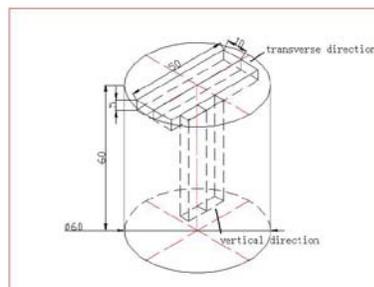


Figure 1. Sampling directions of the specimens from the carbon artifact and dimensions of 3-points bending test specimens (in mm)

The 3-point bend specimens were manufactured from both carbonized artifact and graphitized artifact. The cutting pattern is shown in Figure 1. The specimens had a width of 10 mm, a depth of 5 mm and a length of 50 mm, they were sectioned along two perpendicular directions, vertical(VE) direction and transverse(TR) direction. The pyrolysis behavior of both types of MCMB was investigated by characterizing the weight variation with Thermal Gravimetric Analysis (TGA) and evolved gas analysis with Thermogravimetry-Infrared Spectroscopy (TG-FTIR). The TG-FTIR system composed of the NETZSCH STA 409C thermal analysis instrument and a NICOLET NEXUS 670 fourier transform infrared spectrometer. The heating rate of the TG furnace was 20 K/min, and nitrogen gas of high purity (99.999%) with a flow rate of 100mL min⁻¹ was used as carrier gas. The sample was heated from ambient temperature to 1300 °C. The microstructure evolution during carbonization process was investigated using FEI Quanta 200FEG environmental scanning electron microscopy (SEM). In order to reduce the volatile content, the polished green artifact was preheated at 900 °C in N₂ flow for 30min.

Results and Discussion

Table 2. Physical properties of green, carbonized and graphitized artifacts.

Characteristic s	M-LO			M-EO		
	Green n	1000 °C	2900 °C	Green n	1000 °C	2900 °C
bulk density (g/cm ³)	1.36	1.70	1.82	1.33	1.61	1.68
Linear shrinkage (%)	-	89.4	86.7	-	90.1	88.3
d002 (nm)			0.3363			0.3361
Flexural strength (MPa)		55.88 (TR)	34.28 (TR)		17.48 (TR)	5.60 (TR)
		56.50 (VE)	34.06 (VE)		15.3 (VE)	5.48 (VE)

Table 3. CTE and isotropy ratio of graphitized artifact.

	M-LO		M-EO	
	TR	VE	TR	VE
Mean CTE ($\times 10^{-6}/K, 20\sim 400\text{ }^{\circ}C$)	4.48	4.48	3.17	3.77
Isotropy ratio	1.00		1.19	

The oxidative pretreatment significantly changed the pyrolysis behavior of mesophase. The thermogravimetric curves (TG/DTG) of MCMB-LO and MCMB-EO in Figures 2 shows that, in the case of higher oxidization extent, the mesophase begin to lose weight at lower temperature but gives a higher carbonaceous residue at 1300 $^{\circ}C$ [4]. Both samples lose weight continuously but in different manner. For MCMB-LO oxidized under milder conditions the DTG curve shows a major peak around 500 $^{\circ}C$ and a minor peak between 700~800 $^{\circ}C$. By further oxidization, the minor peak remains but the large peak around 500 $^{\circ}C$ disappeared. Thus, we may infer that the pyrolysis behavior of oxidized mesophase would change significantly with the variation of oxidization extent.

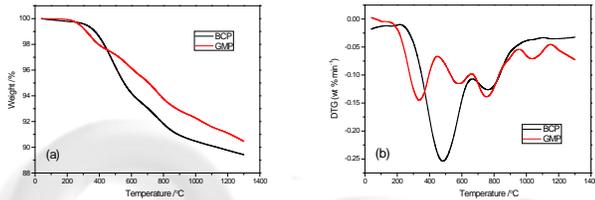


Figure 2. TG (a) and DTG (b) curves of oxidized MCMB.

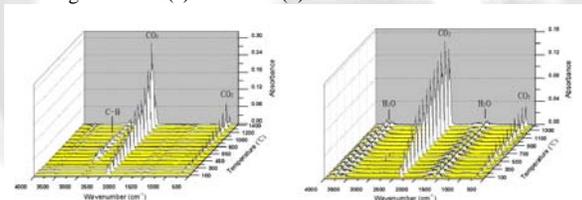


Figure 3 evolution gas analysis by FTIR

The coupling of thermogravimetric analysis and Fourier transform infrared spectroscopy provides not only a quantitative assessment of the pyrolysis process, but also an identification of the decomposition products from the IR spectra of the evolved gases. The 3D FTIR spectra of the evolved gases of both MCMB in Figure 3 reveal that CO₂, H₂O were existed in both cases. For M-LO, peaks between 2850~3000 cm⁻¹ was detected from 400 $^{\circ}C$. These region is related to aliphatic C-H stretching[5], indicating the low-molecular-weight hydrocarbon components may existed. It should be noted that CH₄ or CO was not detected in our experiments.

Figure 4 displays the microstructure evolution during sintering process. As we discussed above, M-LO is able to self-sinter due to β -resin, the particle boundary formed by liquid-phase sintering mechanism is strong enough to keep itself when subjected to shrinkage. In the situation when boundary is stronger than particle matrix, cracks will form inside particles. On the contrary, in poorly sintered M-EO

artifact, boundary is much weaker than particle matrix, so it is the particle boundary where cracks prefer to develop.

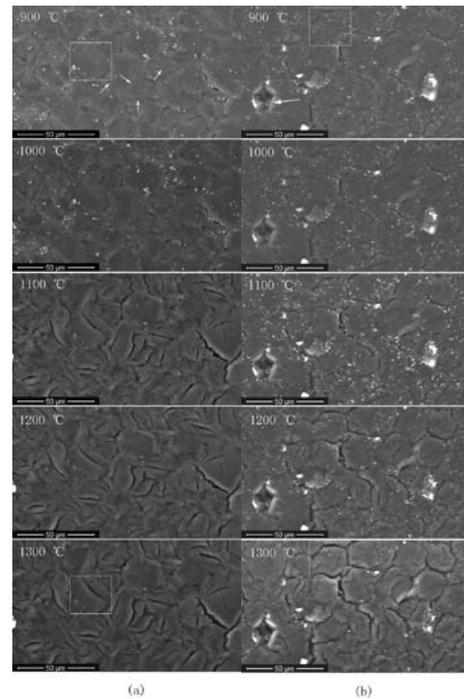


Figure 4 microstructure evolution of M-LO (a) and M-EO (b) artifacts during 900~1300 $^{\circ}C$

Conclusions

The High density isotropic graphite artifact with excellent physical properties and isotropic ratio can be obtained on the condition that the MCMB is oxidized to an appropriate extent. This is because oxidation pretreatment greatly influences the pyrolysis behavior and sintering ability of MCMB. If the MCMB is well sintered during liquid-phase sintering, cracks will not generate on the particle boundary due to shrinkage, so that a continuous microstructure could be preserved, which is very essential to optimize the mechanical property.

References

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