Improving the self-sintering of mesocarbon-microbeads for the manufacture of high performance graphite-parts

Ming-Dar Fang, Wen-Liang Tseng, Jiin-Jiang Jow, Chien-Ming Lee, Ho-Rei Chen, Mao-Sung Wu, Tzong-Rong Ling

Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung 80782, Taiwan
China Steel Chemical Corporation, Kaohsiung 80245, Taiwan
Department of Chemical Engineering, I-Shou University, Kaohsiung 84001, Taiwan

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ABSTRACT

Fine spherical mesocarbon-microbeads (MCMBs), having average particle sizes of 24.57, 11.69 and 10.74 μm, were mixed with various amounts of solid-resins (with high β-resin contents) to prepare graphite-matrixes in self-sintering reactions. The results indicate that the self-sintering reactions of the MCMBs can be significantly improved by enhancing the contacting-pattern of the mixture. MCMBs with smaller particle sizes favor self-sintering reactions and can be used to form high-quality graphite-matrixes. In addition, the self-sintering reactions are strongly dependent on the β-resin content of the raw materials. The bending strength of the graphite-matrixes increases, while the density of the graphite-matrixes decreases, with an increase of the β-resin content in the raw materials. The optimum β-resin content in the mixtures needed to obtain high density graphite-matrixes is approximately 5.0 wt.%.

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1. Introduction

High-density isotropic graphites (HDIGs) are widely used for the fabrication of high performance graphite-parts in various applications in e.g. the electric, metallurgical, nuclear and chemical industries. The graphite-parts are conventionally manufactured using mechanical machining techniques, such as grinding, milling and sawing. The production of graphite-parts by the self-sintering of modeled mesocarbon-microbeads (MCMBs) has been recognized as a potentially useful method involving relatively simple procedures [1–5]. A lot of research has been devoted to developing new techniques and products from the sintering of MCMBs [1,2,5–12]. Altering the mechanical properties of the products by adding various auxiliary compounds, such as: TiB2 [5], TiC [6] and ZrB2 [7], has attracted significant attention due to the increasing demand for these materials in various applications. In addition, the need to improve the production process and the product quality of the resulting high-density crack-free graphite-parts has also received attention. Derfuss and co-workers investigated the injection molding method, as an alternative to the more generally used pressing method, for producing more complex parts – an approach that has the additional benefit of shortening the mechanical post-processing time [12]. They employed a water-soluble binder, to replace the conventionally used β-resin binder (i.e. the quinoline-soluble but toluene-insoluble (TI) part), to avoid cracking of the graphite-matrixes, which is caused by the evaporation of enclosed gases resulting from degradation of the β-resin during the self-sintering process. The β-resin content in the raw materials is essential because it promotes the fluidity and sinterability of the clumpy mixtures and improves the properties of the products. The β-resin content residing on the surface of the
MCMBs is generally controlled by altering the stages/times of the solvent extraction procedures [3].

The self-sintering reactions of MCMB raw materials containing the β-resin as the binder have been studied by several scholars and institutions [13–18]. Martínez-Escandell et al., investigated the self-sintering of MCMB containing 14–16 wt.% β-resin and found that the reaction is significantly dependent on the extraction and washing processes used for the preparation of the MCMBs due to differences in the composition of the raw materials [14]. Gao et al., studied the influence of the β-resin content of the MCMB on the properties of graphite products, and suggested that the β-resin content in the raw materials plays an important role in the sintering reaction [15]. The results correspond to those of Martínez-Escandell et al., because the β-resin contents residing on the surface of the MCMBs are related to the stages/times of the solvent extraction procedures. In addition, Norfokl et al., investigated the mechanism and kinetics of MCMB self-sintering with a 4 wt.% β-resin content, and reported the activation energy for graphitization as being 100 kcal mol$^{-1}$ [10].

However, the techniques for the self-sintering of MCMBs are not fully developed and the factors affecting the production of high-quality graphite-parts are not totally clear due to the complexity of the reactions. For example, the reactions are not homogeneous and the shape and particle sizes of the MCMBs, which varies with the preparation procedures, tends to affect the contacting-pattern and the fluidity of the clumpy mixtures during the sintering reactions. Nevertheless, studies focused on the dependence of self-sintering on the contacting-patterns of the MCMB raw materials have been scarce. In addition, the composition of the β-resin, which resides on the surface of the MCMBs, also varied when the β-resin content was controlled by changing the stages/times of the solvent extraction. This was because the solubility of the various β-resin components in the extraction-solvent was different and the composition of the β-resin residue on the MCMBs varied with the extent of extraction.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Solid resin</th>
<th>GM</th>
<th>FGM</th>
<th>SGM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{av}$ (µm)</td>
<td>4.87</td>
<td>24.57</td>
<td>11.69</td>
<td>10.74</td>
</tr>
<tr>
<td>TI$^a$ (%)</td>
<td>77.4</td>
<td>99.5</td>
<td>99.1</td>
<td>99.1</td>
</tr>
<tr>
<td>QI$^b$ (%)</td>
<td>14.6</td>
<td>98.9</td>
<td>98.5</td>
<td>98.8</td>
</tr>
<tr>
<td>VM$^c$ (%)</td>
<td>–</td>
<td>7.93</td>
<td>8.99</td>
<td>8.88</td>
</tr>
<tr>
<td>β-resin$^d$ (%)</td>
<td>62.8</td>
<td>0.6</td>
<td>0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>0.03</td>
<td>0.15</td>
<td>0.28</td>
<td>0.312</td>
</tr>
</tbody>
</table>

$^a$ Toluene insoluble.
$^b$ Quinoline insoluble.
$^c$ Volatile materials.
$^d$ The difference between TI and QI.
2. Experimental

2.1. Characteristics of the MCMBs, the solid resins and the carbon-blocks

The various MCMBs and the solid-resin were provided by the China Steel Chemical Corp. (Taiwan). The characteristics and compositions of these raw materials are shown in Table 1. The MCMBs have a high quinoline insoluble (QI) content (ca. 99 wt.%) and a low β-resin content (0.3–0.6 wt.%). On the other hand, the solid-resin contains a high β-resin content (62.8 wt.%) and a low QI content (14.6 wt.%). The average particle sizes of the various MCMBs, i.e. GM, FGM, and SGM, (where GM, FGM and SGM are designations of MCMB whose characteristics are summarized in Table 1), are 24.57, 11.69 and 10.74 μm, respectively, and that of the solid resin is relatively small (4.87 μm). Scanning electron microscopy (SEM) images of the various MCMBs, the solid-resin and the carbon-blocks were obtained using a JEOL-JSM 6300 SEM. The appearance of the MCMBs shows very fine spherical grains of approximately equal size (Fig. 1).

The thermal behavior of the solid-resin and the raw material mixture was measured by thermogravimetry (TGA) using a Perkin-Elmer SDT-Q600 Thermogravimetric Analyzer/Differential Thermal Analyzer (DTA). Fig. 2 shows the TGA curve of the solid-resin, indicating that the main weight loss takes place at 300–550 °C and a small amount of weight loss due to volatile vaporization (ca. 2%) occurs at temperatures lower than 200 °C. The total weight loss of the solid resin below 1000 °C was 37%. The flexural strength of the products was measured using a three-point fixture on an MTS Sintech 10/GL testing machine based on ASTM C 1161-02, and the density was measured by the Archimedes drainage method.

2.2. Carbonization and graphitization of carbon-blocks

The various MCMBs were completely blended with the solid-resin using a high-speed mixer (HSM-25, She-Hui Machinery Co., Taiwan) in dry form at 200 rpm mixing rate for 15 min, and then submitted for modeling by cold isotropic compres-
REFERENCES