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Binding natural graphite with mesophase pitch: A promising route to future carbon blocks

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ABSTRACT

Carbon blocks with relatively high graphitization degree (>92%) were prepared by simply binding natural graphite flakes with mesophase pitch at 1300–1500 °C without the traditionally used high-temperature graphitization process (~3000 °C). The influences of pitch content, molding pressure and heat-treatment temperature on the volume density and open porosity, mechanical property, and electrical resistivity of the carbon blocks were systematically investigated. The thermal conductivity and frictional property for typical carbon blocks were tested. The microstructure of the carbon blocks was characterized by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). Results showed that carbon blocks with excellent comprehensive properties could be manufactured. Carbon blocks with bending strength up to 41.98 MPa were obtained when the mesophase pitch content was 25 wt%, the molding pressure 40 MPa, and heat-treatment temperature 1300 °C. The electrical resistivity and thermal conductivity of the carbon blocks (parallel to the graphite layers) were in the range of 10–15 μΩ m and 50–60 W/(m K), respectively. The frictional coefficient of the carbon blocks was below 0.1.

1. Introduction

Carbon blocks have attracted continuous attention due to their wide practical applications, such as electrode materials for metallurgical industry [1,2], hearths for blast furnace [3,4], electric brushes and high-speed-train pantograph slide [5–7], heat exchangers and sinks for high-power electronic devices [8], moderator for nuclear reactors [9], seal materials for aero-engines and so on [10]. Such diverse applications are directly related to their unique physical and chemical attributes including good high-temperature mechanical performance, superior frictional property, high electrical and thermal conductivity, low thermal expansion and density, and high corrosion resistance [11–13]. Traditionally, carbon blocks are fabricated from the filler of coke and the binder of pitch via a series of complex processing steps involving mixing of raw materials, molding, many times of dipping and pyrolysis, and graphitization at elevated temperatures [14]. Though this route has been adopted for many years, it is rather time-consuming and energy intensive. Recently, fabrication of carbon blocks by direct sintering mesocarbon-microbeads (MCMBs) is considered a simple method [15–17], but the cost is relatively high and the high-temperature graphitization procedure cannot be avoided. Therefore, it is of great importance and practical significance to develop simpler, lower-cost, and energy-saving techniques for the fabrication of carbon blocks.

Natural graphite (NG) is widespread on this planet and is conventionally consumed as refractory material and mold lubricant [18]. Using NG as filler instead of coke to prepare carbon blocks can avoid high-temperature graphitization and repeated dipping owing to the high degree of graphitization and high thermal stability of NG; thus it can simplify the working process, save energy and reduce cost. Although the idea is straightforward, the preparation of NG-based carbon blocks has rarely been attempted. Starting from NG and mesophase pitch binder, Yuan et al. fabricated carbon blocks with electrical resistivity of 1.45 μΩ m, thermal conductivity of 522 W/m K and bending strength up to 10 MPa [8]. These carbon blocks can be potentially used as heat-sinks in aviation and electronic cooling devices. Also, Liu et al. fabricated carbon blocks from NG and mesophase pitch via a hot-pressing method. The thermal conductivity is as high as 704 W/m K, and the bending strength is up to 21 MPa [19]. Additionally, to improve the mechanical properties of the

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carbon blocks, Zhao et al. prepared short-fiber-reinforced carbon blocks by simply mixing NG, mesophase pitch and short carbon fibers, and subsequent hot-pressing procedure. The bending and compressive strength of the carbon blocks are improved to 39.6 MPa and 65.5 MPa, respectively [20]. Though the NG-based carbon blocks are prepared, the above-mentioned works mainly focus on the thermal conductive performance of the blocks, leaving other properties uninvestigated.

In the present contribution, fabrication of carbon blocks using natural graphite and mesophase pitch by a facile molding and sintering process is conducted in an attempt to develop a simple and low-cost technique to prepare carbon blocks. The dependence of electrical and mechanical properties of the carbon blocks on the process parameters including mesophase pitch content, molding pressure and heat treatment temperature is systematically investigated. The microstructure of the carbon blocks is characterized and correlated with the electrical and mechanical properties. The thermal conductivity and the friction performances of the carbon blocks are also briefly discussed.

2. Experimental

2.1. Material preparation

Natural graphite (NG) and mesophase pitch were used as filler and binder, respectively. The NG was supplied by Aoyu Graphite Co. Ltd., China, with $d_{50}=22.25$ μm. The mesophase pitch was commercially obtained from Weihai Mingmeidi Chemical Co. Ltd., China, with a softening point of 266 °C and carbon yield of about 60%. All other chemical reagents used in this study were analytical grade unless otherwise specified. The lumpy mesophase pitch was first ball-milled for 12 h using alcohol as the blending solvent, and then the as-obtained slurry was dried and sieved by a 60 mesh screen. After that, the NG powders and the milled mesophase pitch powders were added into a ball-milling machine with pitch contents of 10, 15, 20, 25 and 30 wt%, respectively. The mixtures were milled for 3 h employing alcohol as the blending solvent to achieve uniform multiphase powers. Finally, the mixtures were desiccated at 100 °C for 3 h to remove the solvent and sieved by a 60 mesh screen. The mixtures thus obtained were used for the subsequent treatments.

The as-obtained mixtures were compacted in a steel die and pressed uniaxially for 30 min at relevant pressures (20, 40, 60 and 80 MPa, respectively) with a hydraulic machine to produce green blocks of $\sim 60 \times 44 \times 15$ mm^3. The green blocks were subsequently placed into a heat treatment furnace with shielding gas. The furnace temperature was raised at a heating rate of 5 °C/min to 300 °C, and further raised to 600 °C at a heating rate of 1 °C/min. The heating rate was retained at 3 °C/min between 600 °C and the ultimate temperatures of 1300, 1400 and 1500 °C. The dwelling time is 1 h for all samples. After that the samples were cooled inside the furnace to room temperature. The samples obtained on the basis of the above procedures were directly used for characterization.

The sample names used in this study were defined as follows: C10, C15, C20, C25 and C30 referred to samples prepared with mesophase pitch contents set at 10, 15, 20, 25 and 30 wt%, respectively. The corresponding molding pressure was 40 MPa and final furnace temperature was 1300 °C; P20, P40, P60 and P80 referred to samples prepared with molding pressures set at 20, 40, 60 and 80 MPa, respectively. The corresponding mesophase pitch content was 20 wt% and final furnace temperature was 1300 °C; T13, T14, and T15 referred to samples prepared with final furnace temperatures set at 1300, 1400 and 1500 °C, respectively. The corresponding mesophase pitch content was 25 wt% and molding pressure was 40 MPa.

2.2. Characterization techniques

The open porosity and density of the carbon blocks were measured by the Archimedes principle. Both the three-point bending strength (sample size: 4 mm × 8 mm × 32 mm^3, span between supports: 25.6 mm) and the compressive strength (sample size: 10 mm × 10 mm × 10 mm^3) tests were carried out on an Instron 1186 universal testing machine (Instron Crop., USA) with a crosshead moving speed of 0.5 mm/min at ambient temperature. The mechanical properties were measured from the direction parallel to the pressing direction and that vertical to the pressing direction. The electrical resistivity of the samples was tested by an RTS-8 Four-Point Probes meter (Four Probes Tech. Guangzhou, China). Thermal conductivity (sample size: 10 mm × 10 mm × 2 mm^3) of the carbon blocks was measured by LFA 447 NanoFlash analyzer (NETZSCH, Germany) at room temperature. The thermal conductivity was measured from the direction parallel to the graphite layers and that vertical to the graphite layers. The tribological tests were performed on an HT-1000 ball-on-disk tribometer (Zhong Ke Kai Hua Corp., China) at room temperature. The counterpart ball was steel ball with a diameter of 4 mm. The sliding speed was 560 r/min, the applied load was 5 N, and the testing time was 10 min. The morphology and crystal structure of the carbon blocks were characterized by field emission scanning electron microscopy (FESEM, FEI Quanta 200) and X-ray powder diffraction (XRD, Rigaku D/max-γB X-ray diffractometer with Cu K radiation ($\lambda=0.154178$ nm)).

3. Results and discussion

3.1. Effect of the mesophase pitch content on the microstructure and properties of carbon blocks

It is essential to control the content of the mesophase pitch for the realization of compact carbon blocks with relatively low porosity and high mechanical properties. Fig. 1(a) shows the variations of volume density and open porosity as functions of pitch content in the range of 10–30 wt%. It can be seen that the volume density decreases with pitch content. This is because the pitch is lighter than the filler graphite and also because the pitch decomposition at high temperatures generates gaseous species, which leads to porous structures in the carbon blocks. The value of open porosity first increases with pitch content, and then reduces to a minimum value of 17.07% at 25 wt%, and finally reaches a maximum value of 23.81% at 30 wt%. This result appears to be abnormal since a rule-of-thumb presumes that the open porosity behaves in the opposite way to the volume density. In the present study, the micropores in the carbon blocks are generated from two sources: one is the original voids among graphite particles, the other is the pores in the pitch residue formed by pitch decomposition at high temperatures. The former decreases with pitch addition, while the latter increases with pitch addition. When the two factors work together, the porosity tends to fluctuate, which explains the sudden reduction of open porosity at 25 wt% pitch content.

As shown in Fig. 1(b) and (c), both bending strength and compressive strength measured from the two principal directions increase with pitch content, reach their maxima at 25 wt% pitch content, and then decrease. This indicates that 25 wt% pitch is the proper quantity with which the graphite powders can be well bonded together and form compact blocks with relatively high mechanical properties. Lesser pitch content results in the reduction of the mechanical properties due to the lack of adequate binding