Carbon blocks from natural flake graphite and mesophase pitch: fabrication processing, microstructure, mechanical property, and electrical performance

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Abstract: Traditional preparation process of carbon blocks is relatively high-cost and time-consuming. Hence natural flake graphite (500nm) and mesophase pitch with high charyield were used as filler and binder respectively to solve this problem. In this research, by controlling the molding pressure, the highest temperature of calcination and the content of different additives separately, the properties of the obtained carbon blocks were investigated. SEM, mechanical and electrical tests were carried out to investigate the phase composition and microstructure of the samples. The results showed that the properties of carbon blocks could be improved.

1. Introduction
Carbon-graphite is believed to be a promising new materials due to its wide range of superior properties such as low density, high heat corrosion resistance, heat shock resistance, electric conductivity, good heat transfer performance, good high temperature strength and self-lubrication[1,2]. Conventional carbon graphite blocks have a rather low strength, electric and thermal conductivity and high porosity because of the decomposition and volumetric shrinkage of the binder during heat treatment. Repeated impregnation and calcination procedures were adopted to overcome this shortcoming [3,4]. However, it cannot solve the problem fundamentally and prolong the production period and raise the production cost greatly.

Recently, mesophase pitch has evoked tremendous interest due to its physical and chemical attributes, such as self-sintering function similar to that of clay and powder metallurgy materials, wide range of sources and its high char-yield. Although there have been many in-depth studies on the properties of mesophase pitch and the preparation for carbon blocks derived from mesophase pitch [3], however the preparation route is also complex and the high temperature graphitization happens in this method. Hence high-level equipment is required resulting in enormous energy consumption. Therefore, the current study publishes a simple and less-energy-consumption method to produce carbon blocks.

2. Experimental

2.1 Material preparation
This study proposed a promising route to produce carbon blocks that natural graphite (d=500nm, jiecheng Graphite Products co., LTD, Dongguan, China), mesophase pitch (Mingmeidi Chemical Co., Ltd, Weihai, China) were utilized as filler and binder respectively; silicon powder and Ti powder (Nitrogen compounds co., LTD, Liaoning, China) were used as additives. The first part of this experiment was to pulverize the bulky mesophase pitch by ball milling for 12 h by planet lapping machine (Kejing instrument plant, Jintan, China). In this step, anhydrous ethanol was used as the blending solvent. The as-acquired blended materials were desiccated by water bath at 50°C and sieved by a 60 mesh screen. The natural graphite flake, mesophase pitch powder, and the additive powder were mixed and ball-milled once again with pitch with contents of 25 % and alcohol for 3 h. Finally the mixtures were dried at 50°C by water bath and sieved.

The resultant materials were collected and processed by compaction in a rectangular steel mould of ~60 × 44 mm² and compression for 30 min under different pressure conditions (15, 30, 50 and 60MPa) by a hydraulic press (500KN, Pressure machinery co., LTD, Hefei, China). Subsequently these cubic samples were put into alumina crucible covered by graphite powder and alumina power acting as shielding layers. And the crucible was located at the center of a box resistor-furnace which was heated up to 1200, 1300, 1400 and 1500°C respectively and lasted for 30 minutes before cooling.

In this report, non-additive added samples prepared under the pressures of 15, 30, 50 and 60MPa at ultimate temperature of 1300°C were labeled as P15, P30, P50 and P60 respectively; T12, T13, T14 and T15 were used to define the non-additive added samples obtained at temperatures of 1200, 1300, 1400 and 1500°C respectively under pressure of 50MPa; Additionally, Si powder, Ti powder and the mixture powder of Si and Ti were used as additives to prepare the samples which were represented under pressure of 15MPa and temperature of 1300°C by C1, C2 and C3 respectively to investigate the influence of additive on the properties of the samples.

2.2. tests and characterization methods
Archimedes principle was applied to measure the volume density and the open porosity of the specimen. Universal-testing machine (Material Analysis and Test centre, Haerbin, China) was used to carry out three-point bending experiment to get the flexural strengths, which was in accordance with China standards JB/T8133.7-1999 (sample size: 4 mm×8 mm×32 mm, span between supports: 25.6 m, Time > 5 s). The tribological tests were carried out on an HT-1000 ball-on-disk tribometer (Zhong Ke Kai Hua Corp., China) with the steel ball of 3mm diameter at ambient temperature. Raw materials are machined at a processing speed of 560 r/ min with the applied load of 5 N for 10 min. The shore hardness was measured by HS-19GDV shore scleroscope (Aipeiyi Precision Instrument Co., Ltd, Chengdu, China) according to the equation (1),

\[ HSD = KT + W \]  

(1)

where HSD is shore hardness, T is the bounce time.

The phase composition and microstructure of the samples were characterized by X-ray powder diffraction (XRD, D/max-γB, Japan, X-ray diffractometer with Cu K radiation (λ=1.54056 Å)) and scanning electron microscope(SEM).

3. Results and discussion
1. Effect of the molding pressure on the microstructure and properties of carbon graphite
Cold moulding pressing adopted in this study is a pressure process method taking advantage of external force to make the materials reach a certain shape and size. The density is closely related to the packing level of the graphite particles inside carbon blocks and this means that the molding pressure exerts a huge influence on the dispersion of particles and performances of the carbon blocks. Hence, the samples prepared under different molding pressures with 25vol% mesophase pitch at 1300°C without additives required to be investigated.

Figure 1(a) shows the variation of the open porosity and volume density under different pressures. It can be easily found that the volume density increases as the pressure increases. However, the open porosity decreases with the increase of pressure. Proper increase of the applied pressure can contribute
to the defect reduction and the block densification, while over-pressurised processes leads to permanent damage to the blocks and then causes the mechanical property deterioration. Hence the pressure should be carefully selected. And it is found that the optimum molding pressure is 60MPa, under which the volume density increases notably without obvious defects. This inferred mechanism can be furnished by evidence obtained from the bending strength data as shown in Fig. 1(b).

The bending strength of the samples increases with pressure when the pressure is low. However, it decreases when pressure is above a critical pressure, 60MPa. The bending strength of the carbon blocks prepared under the optimum molding pressure is 28.5 ± 0.16MPa, which is much smaller than that of the carbon blocks (42MPa) prepared from coarse grain graphite under the same pressure [6].

As shown in Fig. 1(c), the resistivity of carbon graphite blocks decreases gradually as the pressure increases. The resistivity of the carbon blocks is ranging from 4.7 to 7.2mΩ·cm, which is much lower than that of carbon products (X-78) suggesting that the final products using mesophase pitch as binder have excellent conductive properties. The reason why the resistivity is improved might be that the increase of molding pressure leads to the close integration of graphite and mesophase pitch particles, improving the volume density, which results in increase of the number of carbon atoms per unit volume at the micro level. Hence the carrier density of carbon blocks is enhanced that contributes to the better conductive properties.

The relationship between the shore hardness of carbon blocks and molding pressure is demonstrated in Fig.1 (d). It can be noted that the shore hardness rises gradually to 33.4 under the pressure of 60MPa. The increase of molding pressure reduces the distance between particles that results in the increase of binding force between two particles. Hence, the particles are tightly bound to each other and the macroscopical shore hardness increases.

![Fig.1.--(a) Volume density and open porosity (b) Bending Strength (c) Resistivity (d) HS at 1300°C with 25 wt.% mesophase pitch content under different molding pressures](image)

The microstructure evolution of the samples prepared under different molding pressures (15MPa, 30MPa, 50MPa and 60MPa) with 25 wt. % mesophase pitch at 1300 °C is shown in Fig.2, which is represented by P30, P60 respectively. It can be seen that the pores on the surface of carbon blocks at 30MPa distribute in a relatively uniform way with apparent gap between graphite layers.

Fig.2 (f) shows the microstructure of the carbon block prepared under pressure of 60MPa. It can be seen that the pores of the sample decrease remarkably and the graphite layers are bound tightly together. The loose places shown in this picture are speculated to be the exhaust outlet with the size up to 20μm. It can be inferred from these facts that the increase of the density is related to the internal defects, the electrical conductivity and flexural strength of carbon blocks.
Fig. 2—SEM images of typical fracture morphology of carbon graphite blocks prepared under different molding pressures: (a) low magnification SEM image of samples prepared under 30MPa; (b) high magnification SEM image of samples prepared under 30MPa; (c) low magnification SEM image of samples prepared under 50MPa; (d) high magnification SEM image of samples prepared under 50MPa; (e) low magnification SEM image of samples prepared under 60MPa and (f) high magnification SEM image of samples prepared under 60MPa.

2 Effect of the heat-treatment temperature on the microstructure and properties of carbon graphite

In order to understand how heat-treatment temperature affects the mechanical and electrical parameters of final products, carbon block samples were prepared at different temperatures of 1200°C, 1300°C, 1400°C, and 1500°C under the pressure of 50MPa with mesophase pitch content of 25 wt.%, corresponding to samples T12, T13, T14, and T15 respectively.

![Fig. 3](image)

Fig. 3—(a) Volume density and open porosity. (b) Bending strength. (c) Resistivity and (d) HS under 50MPa with 25 wt.% mesophase pitch content at different heat treatment temperatures.
Fig. 3(a) provides information about the changes of the volume density and the open porosity with heat-treatment temperature. It can be seen that the open porosity increases at the elevated temperature, while the volume density decreases.

Fig. 3(b) shows that there is a dramatic increase of the bending strength after a slight reduction with the increase of the temperature. Compared with low temperature at which the molten mesophase pitch has relatively low viscosity and high flowability, higher temperature converts it into liquid more thoroughly, improving the mechanical property.

As shown in Fig. 3(c), the resistivity of carbon graphite blocks decreases moderately from 5.6mΩ·cm to 4.0mΩ·cm with temperature, distinctly contrary to that of pure graphite (6.87mΩ·cm), indicating that carbon graphite materials possess high conductivity.

Fig. 4 -- Typical fracture morphology of carbon graphite blocks prepared at different heat treatment temperatures under 50MPa with 25 wt.% mesophase pitch content by SEM: a (1200°C); (1400°C)

Typical SEM images of the fractured surfaces of samples T12 and T14 are shown in Fig. 4. The size of pores at 1200 °C is 10μm, while at 1400 °C (Fig. 4 (b)), the dimension of pores is about 5μm within the sintered graphite layers. It can be explained by the fact that high temperature makes the decomposition and transformation of mesophase pitch more completed and leads to the closer combination of graphite interfaces, lower porosity and higher density of carbon blocks. It also provides a basis for further study of the bending strength.

3 Effect of the additive on the microstructure and properties of carbon graphite

In order to develop an effective approach to enhance the performances of carbon blocks, the introduction of Si powder and Ti powder as additives to react with graphite directly was adopted. Noticeably, the corresponding angle of all the graphite peaks is 26.52 ° and the calculated graphitization degree is 95.07 %, showing that the graphitization degree of carbon blocks remains the same with additives.

Fig. 5 — (a) HS and (b) bending strength of samples prepared with different additives
Fig. 5(a) shows that all the shore hardness of carbon graphite with different additives increase gradually with pressure and there is a significant increase when Si powder is used, indicating that the addition of Si powder can have a significant positive influence on the improvement of the hardness of materials.

Fig. 5(b) shows that the bending strength of carbon graphite with different additives increase with pressure. Through using Si/Ti powder as additives, relative chemical reaction products including silicon carbon and titanium carbide are generated and the corresponding chemical bonds are introduced into carbon blocks. The bond energy of these bonds is higher than that of carbon-carbon bond and contributes to the stability of block structure. As a result, the shore hardness and the bending strength of carbon blocks increase.

Fig. 6-- SEM images of typical fracture morphology of carbon graphite blocks prepared with different additives: (a) low magnification SEM image of samples prepared with 10 wt.% Si; (b) high magnification SEM image of samples prepared with 10 wt.% Si; (c) low magnification SEM image of samples prepared with 10 wt.% Ti; (d) high magnification SEM image of samples prepared with 10 wt.% Ti; (e) low magnification SEM image of samples prepared with 5 wt.% Si and 5 wt.% Ti, and (f) high magnification SEM image of samples prepared with 5 wt.% Si and 5 wt.% Ti

Fig. 6 shows typical SEM images of the carbon blocks prepared with 10 wt.% Si powder and 10 wt.% Ti powder as additive. Compared with the coarse mosaic texture of the blocks prepared without additives, the carbon blocks prepared with additives have a finer mosaic texture and the combination of graphite layers are more close-knit without obvious gap.

4. Conclusions
In this study, carbon graphite products with superior performances have been prepared by using flake natural graphite (500 nm) and mesophase pitch as aggregate and binder respectively. The key conclusion is listed below.

(1) The molding pressure is a crucial factor that affects the performances of final products such as the volume density, open porosity, mechanical and electrical properties.
(2) High-temperature heat treatment impacts the graphitization degree of carbon graphite. Using mesophase pitch as the binder, the graphitization degree increases with the calcination temperature, enhancing the mechanical and electrical properties.

(3) The introduction of Si powder and Ti powder as the additives can contribute to the enhancement of the performances of carbon graphite materials significantly.

Overall, the carbon blocks fabricated under 60MPa with a mesophase pitch content of 25 wt.% at 1400°C have relatively superior performances. The comprehensive performances of carbon blocks are improved notably. The bending strength of the carbon blocks is up to 33.1±0.46MPa, with the graphitization degree of 95.07 % and the electrical resistivity of 4.0mΩ·cm. Additionally, higher shore hardness of 30.2 can be obtained.

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References
[1] Fitzer, E., Future of carbon-carbon composites. Carbon, 1987, 25(2), 163–190.
[2] P. R. Wallace, The band theory of graphite. Physical Review 71(1947) 622.
[3] Yurkov, A.A., Khramenko, S.A. & Borisov, V.I. Refract Ind Ceram (2008) 49: 90.
[4] L.-j. Guo, H.-j.Li,K.-z.Li,C.Wang,NewCarbonMater.23(2008)51–57.
[5] LIU Zhan jun, SHI Jing li, LIU Nai zhi, SONG Jin ren, LIU Lang, Preparation of impregnant pitch with high fixing carbon[J]; Carbon Techniques;2000-05
[6] Chen W, Zhang H, Liu X, et al. Study of factors affecting electric performance of carbon black-graphite electric coating[J]. Carbon Techniques, 2003 (2; ISSU 125): 25-27.