Effect of physical disturbance on the structure of needle coke*

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(Received 15 January 2010; revised manuscript received 6 April 2010)

Through different preparation technology, this paper reports that the needle coke is prepared with coal-tar pitch under the effect of magnetic field and ultrasonic cavitation. It studies the effect of physical disturbance on the structure of needle coke. The structure of needle coke is characterized by scanning electron microscope and x-ray diffractometer, and the influence mechanism is analysed. Results showed that the structure and property of needle coke could be effectively improved by magnetic field and ultrasonic cavitations, such as degree of order, degree of graphitization and crystallization. Comparatively speaking, the effect of magnetic field was greater. The graphitization degree of needle coke prepared under the effect of magnetic field is up to 45.35%.

Keywords: needle coke, magnetic field, ultrasonic, ordering, structure

PACC: 8100, 8140, 6150J, 6160

1. Introduction

Needle coke, a kind of important raw material in carbon industry, is mainly used to produce high-power electrodes and ultra-highpower electrodes.[1] The property of electrode is largely dependent on that of needle coke. Needle coke is divided into two types, petroleum-based and coal-based, according to different raw materials. Petroleum-based needle coke is manufactured by heavy oil and coal-based needle coke is manufactured by coal-tar pitch and its fractions. Needle coke used as electrode material[2] is required to have the properties of low coefficient of thermal expansion, low resistivity, good heat shock resistance, and high intensity.[3−5] The above properties can be improved by further ordering of the micro-structure of needle coke. Magnetic field effect[6] provides a new approach to chemical reaction since it can affect the rate of chemical reactions and processes.[7−11] The ultrasonic nature of liquids is closely related to the molecular structure.[12] Sonochemical,[13] as a new interdisciplinary, has the function of accelerating and controlling chemical reactions with its ultrasonic energy and improving the reaction yield and initiating some new chemical reactions.[14,15] At present, there exist vacancies for study on ordering of needle coke under the effect of physical disturbance. This paper mainly aims at structural change and mechanism of needle coke prepared under the effect of magnetic field and ultrasonic wave.

2. Experimental

2.1. Raw material

Raw medium coal-tar pitch, with quinoline insolubles removed, was supplied by Shanxi Hongte Coal Chemical Co. Ltd. The basic quality of coal-tar pitch is listed in Table 1.

Table 1. The basic quality of medium temperature coal pitch.

softening point/°C	toluene insolubles/%	ash/%	moisture/%	volatile/%
72	20	0.4	5.0	60

*Project supported by the National Natural Science Foundation of China (Grant No. 20843002) and the Scientific and Technological Foundation of Shanxi Province of China (Grant No. 20080321065).

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2.2. Sample preparation

The manufacturing process of coal-based needle coke includes pretreatment of raw material, delayed coking and calcination. Because the medium coal-tar pitch used as raw material in this experiment has been treated, needle coke was prepared with thermal polymerization and high-temperature calcination. Three groups of samples were prepared. The raw material coal tar was placed in a closed stainless steel reactor (self-made), as shown in Fig. 1. First, a certain amount of nitrogen was input into the reactor in order to eliminate the air in the reactor. Then coal tar was slowly heated up to 420 °C and cooled to room temperature after polymerization for 6 h at 420 °C. Finally, with a rapid heating rate from the room temperature to 940 °C, samples were calcined for 3 h in an anoxybiotic atmosphere. Thermal polymerization and calcination were accomplished in the same pit resistance furnace. The sample needle coke was obtained after cooling. Sample a was prepared without any special treatment; sample b with the induction of magnetic field during thermal polymerization (magnetic induction intensity: 22 mT; cumulative acting time: 30 min); and sample c with ultrasonic cavitation (excitation current of ultrasonic instrument: 10 A; ultrasonic processing time: 30 min). Needle coke was ground into powder for further test and analysis.

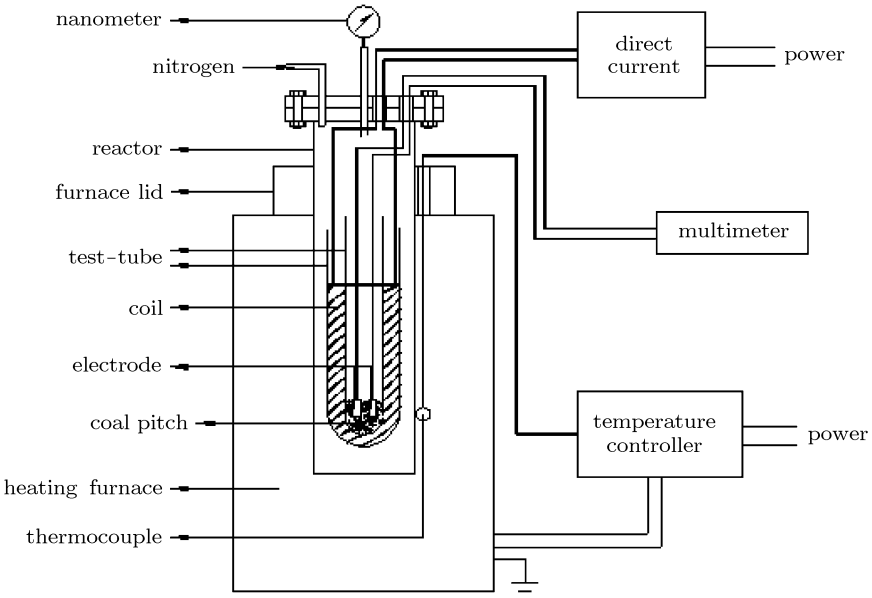


Fig. 1. Diagrammatic sketch of reactor equipment.

2.3. Characterization

To examine the microstructure of needle coke under scanning electron microscope (SEM, Jeol JSM-6700F) and x-ray diffractometer (XRD, Rigaku Geigerflex: CuKα, 0.154178 nm, 30 kV, 20 mA), all samples were ground into powder. The scans were made over a range of 2θ values of $10^\circ \sim 75^\circ$ with intervals of 0.05°. In the XRD result, the interlayer distances (d_{002}) and the crystallite sizes (L_c and L_a) were calculated by Bragg's law ($\lambda = 0.154178$ nm, Eq. (1)) and Scherrer's equation ($K = 1$, Eq. (2), and Eq. (3)), respectively. The degree of graphitization (g) was calculated by Mering and Maire's law (Eq. (4), 0.3440: the interlayer spacing of turbostratic carbon having not been graphitized; 0.3354: the crystal interlayer spacing of ideal graphite).[16]

$$d_{002} = \lambda/(2\sin\theta_{002}), \tag{1}$$

$$L_c = K\lambda/(\beta_{002}\cos\theta_{002}), \tag{2}$$

$$L_a = 1.84\lambda/(\beta_{100}\cos\theta_{100}), \tag{3}$$

$$g = \frac{0.3440 - d_{002}}{0.3440 - 0.3354}. \tag{4}$$

3. Results and discussion

3.1. Microstructure (SEM) analysis of the as-received needle coke

Figure 2 shows SEM micrographs of samples a, b and c respectively. It is illustrated that the cokes after

thermal polymerization and high-temperature calcinations present needle-like structure with layered and orderly fibre. The section layered structure of sample a was obvious but its degree of order was low and the impurity components without being volatilized were distributed immethodically. As for sample c, because of the ultrasonic cavitation, micro-bubbles in heated liquid coal-tar pitch experienced oscillation, growth, contraction and collapse, which made it favouring for the release of light components and volatiles during the processes of intense thermal decomposition and thermal polycondensation. In that case, needle coke was obtained as that in Fig. 2(c). It can be seen that morphology of the sample includes micro-layered structure and coarse needle-like fibers with fewer impurities. Sample b was prepared under the effect of magnetic field. It is illustrated in Fig. 2(b) that magnetic field played a more important role in the fibre orientation of needle coke. Because mesocarbon microbeads formatted during thermal polymerization of coal tar were arranged in order in the magnetic direction under the effect of magnetic field, degree of order of fibres was significantly increased and needle-like fibres were refined. Aromatic ring planar macromolecules were accumulated into lamellar structure so that they could be arranged sequentially under the effect of magnetic traction and stretching force of airflow coming from light volatile components of coal tar. As temperature rose, coke was gradually solidified. Since the volatile components or impurities could not completely escape in time, a certain amount of impurities was contained in the fibre surface of as-received needle coke.

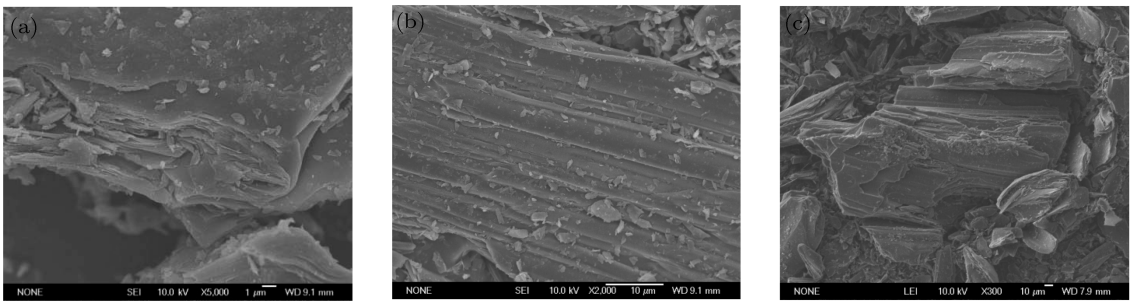


Fig. 2. The SEM micrographs of the as-received needle cokes.

3.2. The XRD analysis

The XRD patterns of needle coke samples are shown in Fig. 3. As can be seen, the diffraction intensity of needle cokes was significantly improved near 26° (plane 002), which illustrated the increased crystallinity, because mesocarbon microbeads formed during thermal polymerization of coal tar tended to arrange in order under the effect of external physical disturbance. Some disorderly textures were changed to be ordering so that the degree of crystallinity of the obtained needle coke was increased. Among the three samples, the crystallinity of sample b which was prepared under magnetic field was highest. Whereas that of sample c prepared under the effect of ultrasonic cavitation was higher. Moreover, a weak peak round 43° appeared in the diffraction curve of sample c, which was the diffraction peak in plane (100).

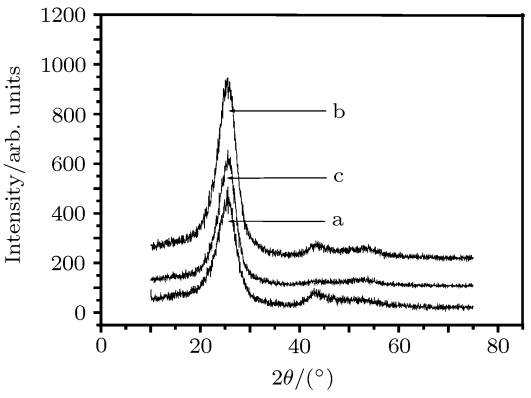


Fig. 3. XRD photographs of needle coke samples.

The x-ray d (002) diffraction parameters of the samples are listed in Table 2. It shows that the 002 peak tends to shift to the right, L_a sharply decreases and performance of graphitization (g) increases after external physical disturbance. Especially, the degree of graphitization is up to 45.35% when the magnetic induction intensity is 22 mT.

Table 2. Structural parameters of needle coke samples.

sample	$2\theta_{002}/(^\circ)$	d_{002}	L_c/nm	L_a/nm	g/%
sample a	26.00	0.3425	2.27	7.28	17.44
sample b	26.20	0.3401	2.09	5.39	45.35
sample c	26.10	0.3414	2.22	5.02	30.23

More than three-ring polycyclic aromatic hydrocarbons largely exist in coal-tar pitch. Non-polar polycyclic aromatic planar molecules are close to each other due to thermal diffusion in the process of heat polymerization. Planar molecules enable to orientate naturally with van der Waals force (dispersion force) among planar molecules.[17] Since the ultrasonic wavelength ranges approximately between 10 cm and 10^{-3} cm,[15] which is much larger than the molecular size, ultrasonic wave cannot directly act with other substances to provoke chemical reactions under the action of ultrasonic vibration. The collapse of bubbles in the cavitation process can generate instantaneous pressure and high-intensity local heating, whose energy density is much bigger than that of sound field. Therefore, high-energy chemical reactions are induced, which is equivalent to an instantaneous high temperature and pressure micro-reactor.[15] In that case, mesocarbon microbeads generated in molten pitch merge much easier so as to large form planar molecular structure; as a result, crystallinity is limited to rise and reduction amplitude of crystallite size is decreased. Mosophase polycyclic aromatic planar molecules are oriented and arranged directionally with the magnetic moment generated in molecular circulation under the effect of magnetic field. When the magnetic orientation force is stronger than the surface tension of the sphere, macromolecules with greater flatness are formatted, which creates a better environmental condition for the formation of anisotropy graphite-like planar layered structure. With the gradual rise of calcination temperature, layered macromolecules are solidified in the nematic order arrangement, so needle coke with higher degree of order, cystallinity and gaphitization degree is obtained.

3.3. Analysis of influence mechanism of physical disturbance

3.3.1. Analysis of influence mechanism of ultrasonic cavitation

When high-intensity ultrasound propagates in the mediator, a series of effects will be caused including mechanical, thermal, chemical and biological effects. Apparently, there are mixing, dispersion, degassing, atomization, coacervation, impact grinding and fatigue damage in the mechanical effects. While in the chemical effects, it can promote the occurrences of oxidization, reduction, polymerization and degradation of polymers, etc. From the microscopic perspective, some unique physical effects and mechanical effects are generated in cavitation process, such as temperature gradients, pressure gradients and potential gradients of field strength in the interface of cavitation bubbles. Liquid movements in the vicinity of the above gradients also generate great shear and stress gradients. It can also cause a rapid evapouration of the solvent molecules around the bubbles during cavitation. In addition, a strong shock wave will appear when the bubbles are collapsed.[13−15] Since ultrasonic cavitation can form a micro-environment system with the advantages of high temperature, high pressure, flash heating or cooling, a variety of specific physical and chemical effects can be caused and a specific micro-reactor may be produced. When thermal coal-tar pitch is acted by ultrasonic cavitation, microbubbles generated in the liquid interface can provide the mesophase pitch with a passage for escaping light components, which can create a favourable environment for the formation of mesocarbon microbeads. As the temperature rises, the number of mesocarbon microbeads gradually increases and the opportunities for mutual mergence are increased. Therefore, larger planar molecular structures are formed, as shown in Fig. 2(c), which is solidified to be needle coke with large lamellar structure through high-temperature calcination.

3.3.2. Analysis of influence mechanism of magnetic field

Polymers usually arrange in disorder without external magnetic field. L. Stupp[10] from USA had discovered that the orientation stretching in magnetic field could significantly change the properties of polymers, especially their directivities. With the induction of external magnetic field, liquid polymer molecules can be stretched into a column so as to form a kind of induced structure. When the liquid polymers are solidified, the induced structure will be fixed.

Magnetic field can also refine the grains and fibrous structures. Paramagnetic molecules can arrange in magnetic direction so that the structures and properties of the products can be improved by effectively controlling the chemical reaction rate. During the thermal polymerization of coal-tar pitch, multi-core planar aromatic molecules are parallelly laminated under the effect of van der Waals force. Additionally,

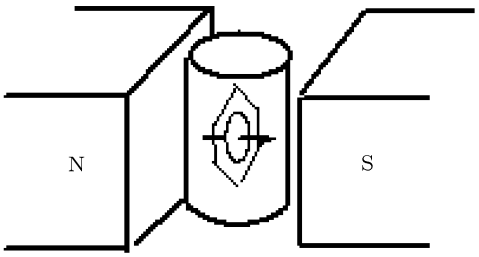


Fig. 4. Orientation of lamina in magnetic field.

magnetic moment generated by the ring current of multi-ring system is orientated in the magnetic direction. Mesophase macromolecules are laminated to form lamellar accumulations under the effect of magnetic force in the vertical direction of magnetic field, as shown in Fig. 4.[18] Lamellar accumulations are gradually solidified under the effect of magnetic force and air drawing of escaped light fractions and impurities after high-temperature calcination. Finally, as shown in Fig. 2(b), needle coke is formed with better ordered fibre and obvious needle-like structure.

4. Conclusions

(i) Ultrasonic wave and magnetic field can increase the degree of order of needle coke effectively. Needle-like structure was obviously refined. Ultrasonic wave is more effective in removing impurities and fractions generated during polymerization. Magnetic field can make the needle-like fibre dramatically ordered and the degree of order is greatly increased.

(ii) The average crystallite size $L_{\rm a}$ of needle coke prepared under ultrasonic wave and magnetic field was decreased while the crystallinity and graphitization degree were both increased. Comparatively speaking, effect of magnetic field is greater, because the graphitization degree is up to 45.35%. Comprehensively, magnetic field plays a more effective role in promoting the ordering and graphitizing of needle coke, which has a positive impact on producing high-power electrode and ultra-high-power electrode.

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