PREPARATION OF GRAPHITIZABLE COKE FROM ANTHRACENE OIL

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Introduction

Anthracene oil (AO) is a heavy distillate fraction from coal-tar distillation. The boiling range typically ranges from 250 °C and 370 °C. AO is mainly composed of polycyclic aromatic hydrocarbons (PAHs) containing 3-5 aromatic rings [1, 2]. Major constituent compounds are phenanthrene, anthracene, fluoranthene and pyrene. Anthracene oil is primarily used for the production of carbon black.

Anthracene oil is virtually metal and QI free owing to the fact that it is produced via a distillation process. AO can be polymerized into anisotropic carbons with characteristics similar to those of commercial pitches [1, 3, 4]. This can be done at moderate temperatures in the presence of reagents such as sulfur, $AlCl_3$, etc. However, air-blowing transforms anthracene oil into pitches suitable as precursors for graphite. Careful control of oxidation conditions (temperature, reaction time and air-flow rate) is essential to avoid the formation of isotropic residues on pyrolysis [5]. The main aim of this study was to prepare graphitizable cokes from ArcelorMittal anthracene oil.

Experimental

Pitch samples were prepared from anthracene oil in a pressure vessel. The procedure entailed the following steps:

$$\text{Anthracene Oil} \xrightarrow{250\,^{\circ}C,\,N_2} \text{Pitch} \xrightarrow{300\,^{\circ}C,\,air} \text{Pitch} \xrightarrow{350\,^{\circ}C,\,N_2} \text{Pitch} \xrightarrow{1000\,^{\circ}C,\,N_2} \text{Coke} \xrightarrow{1800\,^{\circ}C,\,He} \text{Annealed Coke} \xrightarrow{2400\,^{\circ}C,\,He} \text{Graphite}$$

The pitches were carbonized by heating to 1000 °C in N_2 at a rate of 3 °C/min and then maintained at this temperature for 1h. Thereafter the atmosphere was changed to helium gas and temperature raised at 30 °C/min. The coke was annealed at 1800 °C for 1 h and finally graphitized at 2400 °C for 1h under.

Raman Spectroscopy

The Raman spectra for the graphitizable cokes and graphite samples were recorded on a T64000 series II triple spectrometer system from HORIBA Scientific, Jobin Yvon Technology using the 514.3 nm laser line of a coherent Innova® Ar^+ laser with a resolution of 2 cm^{-1} in the range 1200 to 1750 cm^{-1}. The spectra were recorded in a backscattering configuration with an Olympus microscope attached to the instrument (using a LD 50x objective). A liquid nitrogen cooled CCD detector was used with a laser power 6 mW at the sample surface. The spectra were baseline corrected using the Lab Spec software program.

Optical Microscopy

The carbon samples were embedded in an epoxy resin, ground, polished and viewed with an optical microscopy LEICA DM 2500M. The microscope is equipped with a polarizer and one wave-retarder plate that generates interference colors. The micrographs of the carbon samples were taken using an oil immersion lens with 50x magnification.

Table 1. Raman Parameters of Graphitizable Cokes and Graphite.

Sample ID	D-peak (cm^{-1})	G-peak (cm^{-1})	Intensity (I_D/I_G)
Coke 1000 °C	1346	1579	0.92
Annealed 1800 °C	1362	1586	0.21
Graphitized 2400 °C	1355	1583	0.12

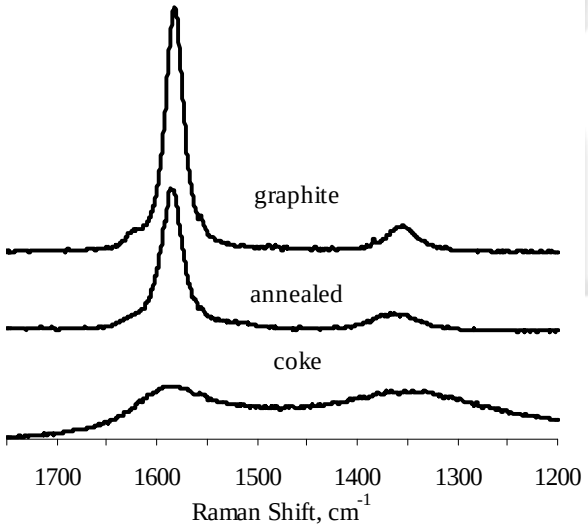

Fig. 1 Raman spectrum of the anthracene oil coke, annealed coke and graphite.

Results and Discussion

Fig. 1 shows the Raman spectra of the heat treated carbons. The coke features broad G- and D-peaks. The G-peak becomes narrower and more intense with increase in heat treatment temperature. At the same time the D-peak decreases in relative intensity. These trends indicate a progressive improvement in crystallinity. The graphitized samples featured a narrow intense G-band and a small broad D-band indicating a more graphitic nature. The I_D/I_G intensity ratios decreased from 0.92 for coke to 0.12 for the graphite (Table 1).

Fig. 2 shows the optical micrograph of the annealed coke. The interference colors were not visible when the material was viewed under normal light (Fig. 2a). However, they were observed when the material was viewed under polarized light with insertion a 1λ-retarder plate inserted (Fig. 2b). A purple color indicates that the basal planes are perpendicular to the polarizer while blue and yellow colors are observed when the planes are at an angle to the polarizer [6].

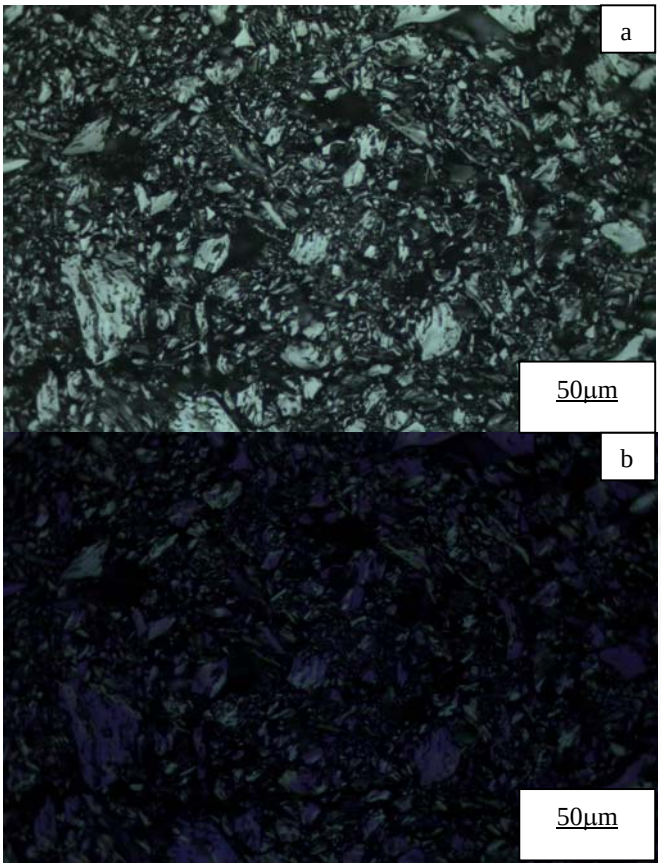

Fig. 2 Optical micrograph of the annealed coke (a) normal light, (b) polarizer and 1λ-retarder plate.

Conclusions

Optical microscopy proved that graphitizable cokes were obtained from anthracene oil by pyrolysis at 350 °C. Raman spectra indicated that further heat treatment at higher temperatures (2400 °C) yielded graphite-like materials.

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