Effect High Temperature Annealing on Graphitization of Anthracite

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Effect of high temperature anneal on the graphitizability of an anthracite coal is explored. A thermal anneal of Taixi Coal Mine anthracite at 1400, 1600 and 1800 °C in argon was investigated. The sample was investigated by XRD, FTIR and SEM. The result shows that after low temperature anneal, the anthracite is amorphous state carbon, high temperature benefit to graphitization of the sample. The anthracite contains chemical functional groups of COOH and C-H, which decomposed at high temperature; after high temperature anneal, vitrinite and fusinite separated from the anthracite base. The shape of vitrinite is round particles and the fusinite is rod like.

Keywords: Anthracite, High temperature annealing, Graphitization.

INTRODUCTION

Coal has a complex chemical structure system which plays an important role during pyrolysis[1,2]. Upon heating, the structure of coal changes dramatically. The configuration of the chemical structure of a char from softening coals is significantly different from that of the initial coal[3-5]. For softening coals, the original pore structure may be blocked due to the high fluidity during heat-treatment[6,7]. The char structure is therefore determined by the thermoplastic properties of the coal and heating conditions rather than by the original pore structure[8-11]. As in the case of coals, the process of physical adsorption of gases on the internal surface of cokes was found to be very complex. The data for cokes depend on rank of initial coals, the experimental conditions and strongly on the carbonization temperature[12,13]. Because of the high carbon content of anthracite coals, perhaps using anthracite to produce high-value carbon materials rather than as a fuel makes sense economically. researchers have been exploring modifying the structure of anthracite to produce value-added marketable products, including synthetic graphite production, filler for cathodes in aluminum smelting, anthracite-based pitch and activated carbons[14,15]. Anthracite has also been examined for use as a filler in the production of cathodes for aluminum smelting[16,17]. Before using anthracite as a cathode filler, it must be treated at temperatures far above 1000 °C. This can be achieved in two ways: (1) gas calcined anthracite where fuel gas is heated to 1300 °C or (2) electrically calcined anthracite, which uses electrical current to temperatures of 1600-2200 °C, the median temperature 1800 °C[18,19].

In this paper, we have ball milling anthracite and anneal the anthracite in the presence of argon, to investigate the relation of anneal temperature and graphitization of anthracite.

EXPERIMENTAL

Synthesis of samples-materials, ball milling and heat treatment: The coal used is anthracite from Taixi Coal Mine Ningxia province, China and the sample has a fairly low ash content coal (2.36 %, dry), with low volatile matter content (8.12 %, dry) and high fixed carbon content (89.52 %, dry). Proximate analysis was done on a Thermogravimetric Analyzer LECOMAC 400 to determine the ash and volatile content of the coal and products. The moisture temperature was set at 105 °C, the temperature for measurement of volatiles was set at 950 °C and the ash temperature was set at 750 °C. Maceral composition was determined using standard ASTM methods. Sample was milled both under dry conditions and in the presence of a argon (99 % purity), After milling, samples were heated in a tube furnace at 1400, 1600 and 1800 °C for 3 h under 1 L/min of argon. Milling in argon is expected to inhibit adsorption of any gases, such as O_2, CO_2, *etc*. The temperature ram prate was 2.5 °C/min. The annealing temperature was selected based on previous reports of annealing ball-milled graphite to form multi-walled carbon nanotubes.

Characterization of samples: A Hitachi S 3000-H at 20 eV was used for SEM, XRD was performed on a Phillips X'Pert MPD with CuK_α (1.54051 nm) radiation operated at 40 kV and 40 mA with a beammask of 10 mm and divergent slit of 2°. Scans were made from 10° to 80° with a scan rate of 0.020°/s

and the scan type used was continuous. To calculate the Lc (crystallite stacking height), La (crystallite size) and d-spacing (height between adjacent layers in the z direction), the JADE + Version 7.1was used.

RESULTS AND DISCUSSION

X-ray powder diffraction: Details of the ultimate and proximate analysis are included in Table-1. The maceral composition of sample was determined to be 85.9 %, vitrinite and 14.1 % inertinite, with no liptinite found in it. XRD of sample is typical for an anthracite coal, with broad peaks at 26°, 64° and 78° representing carbon (Fig. 1a).

TABLE-1
ULTIMATE AND PROXIMATE ANALYSES OF SAMPLE

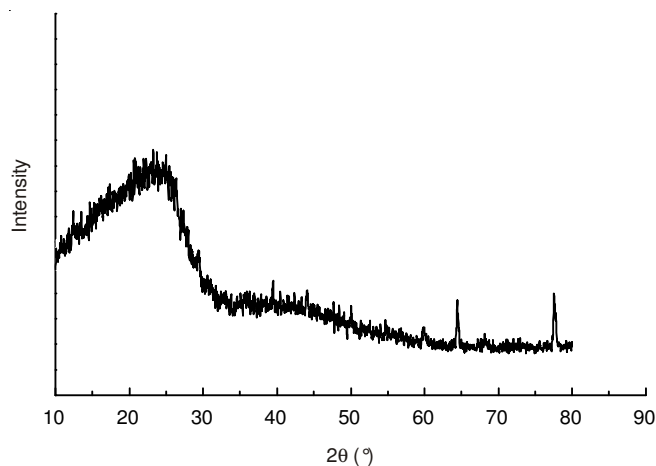| Analytical method	Value
Moisture, asreceived	6.53
Ash, wt. %, dry	2.36
Volatile matter, wt. %, dry	8.12
Fixed carbon, wt. %, dry	89.52
Carbon, wt. %, dmmf	88.85
Hydrogen, wt. %, dmmf	1.29
Nitrogen, wt. %, dmmf	0.78
Sulfur, wt. %, dmmf	0.49
Oxygen (by difference),wt. %, dmmf	1.76
Vitrinite reflectance, %	5.45
Inertinite reflectance, %	14.1

Fig. 1(a). XRD of anthracite coal

The [002] peak characteristic for graphite in XRD is broadened for coals and cokes and likely due to contributions from multiple carbon structures, as the carbon structure within coal and coke is in between a graphitic and amorphous state, or turbostratic in structure, so there are a clear amorphous peaks at 26°. Fig. 1(b) is the XRD pattern of anthracite after annealed. It is observed that with the increase of temperature the diffraction peak became narrow, at the same time hight of the peak increase with the increase of anneal temperature, indicated that high temperature is to the benefit of the graphitization of coal. The intensity of anthracite at 1800 °C is much higher than that of 1400 °C. We have calculated the crystalline index is 0.22 annealed at 1400 °C, whereas the crystalline index is 0.71 annealed at 1800 °C.
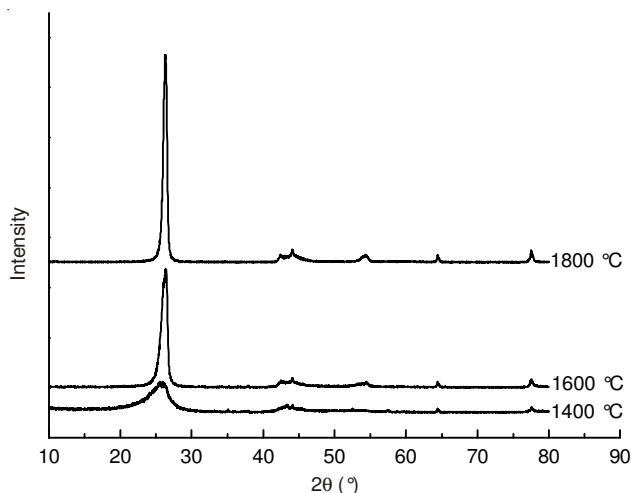

Fig. 1(b). XRD of high temperature annealed anthracite coal

FT-IR spectra: To figure out the relationship of anneal temperature and chemical structure of the sample, we used FTIR. As shown in Fig. 2, we can see from the chart there are many peaks, the 3473 cm^{-1} peak related with the O-H stretching vibration, while 1632 cm^{-1} is the C=O bond stretching vibration peak, 1075 cm^{-1} is C-C vibration, 963 cm^{-1} and 852 cm^{-1} are C-H bending vibration peaks, all the peaks imply that at low temperature, the anthracite contain the groups of COOH and C-H. With increase of anneal temperature the intensity of infrared absorption peaks decreased, indicated that the chemical function groups of the sample decomposed at high temperature.
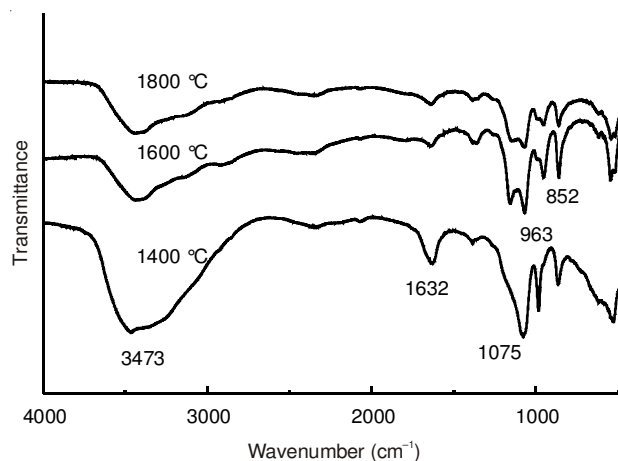

Fig 2. FTIR of the annealed anthracite coal

SEM indicated that the nominal particle size of the sample was on the order of 100-200 μm. The surface appears to have several 1-5 μm particles that appear to have agglomerated or accreted. Upon high temperature (1600 °C and 1800 °C) thermal annealing, unusual structures were observed in SEM, including amorphous, round particles and rod-shaped particles. The rod-shaped particles appear to be attached to the round particles and vary in width from 50-500 nm (Fig. 3). Energy dispersive X-ray spectroscopy (EDS) (data not shown) of the sample indicated the round particles are vitrinite, the rods are fusinite. So we believe the vitrinite and fusinite separated from the anthracite base at high temperature.
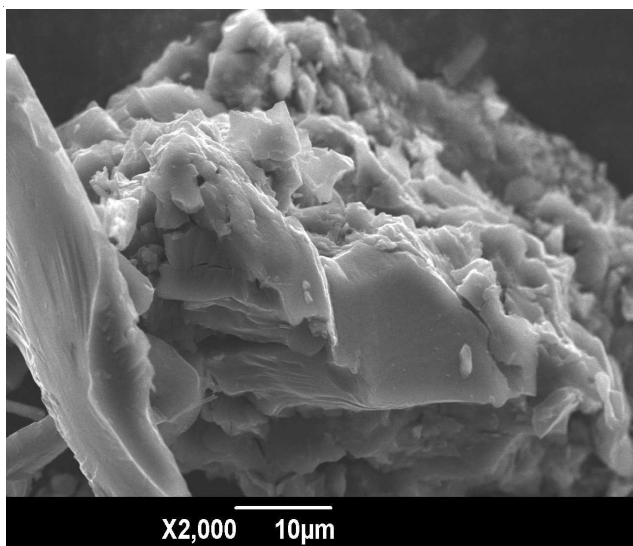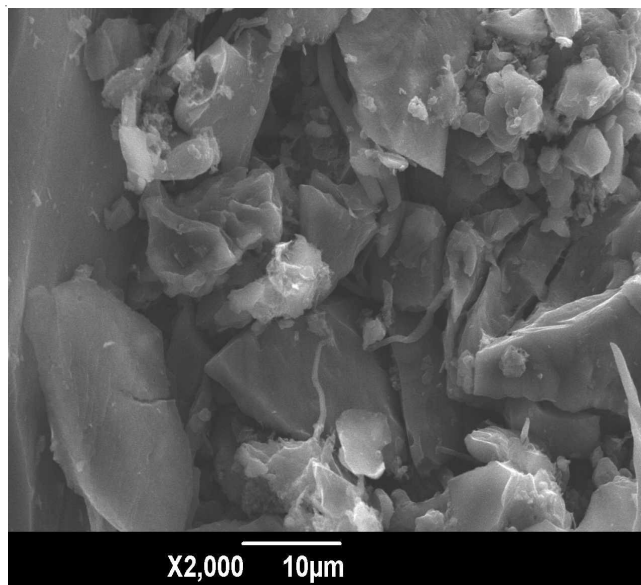
Fig. 3. (a) SEM of anthracite coal

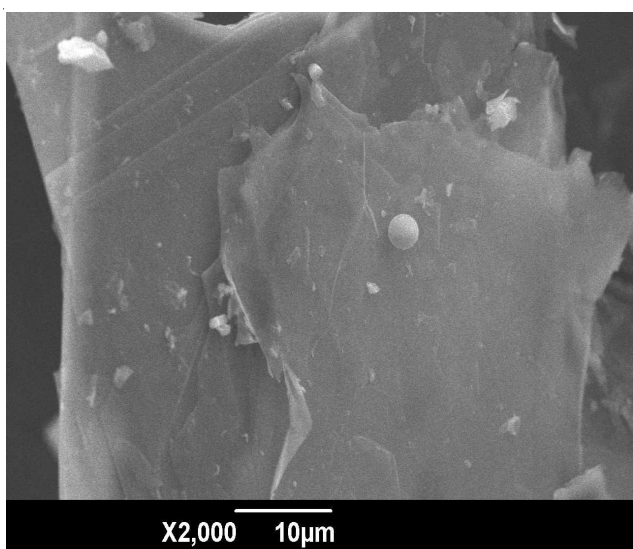Fig. 3. (d) SEM of fusinite (anthracite coal annealed at 1800 °C)

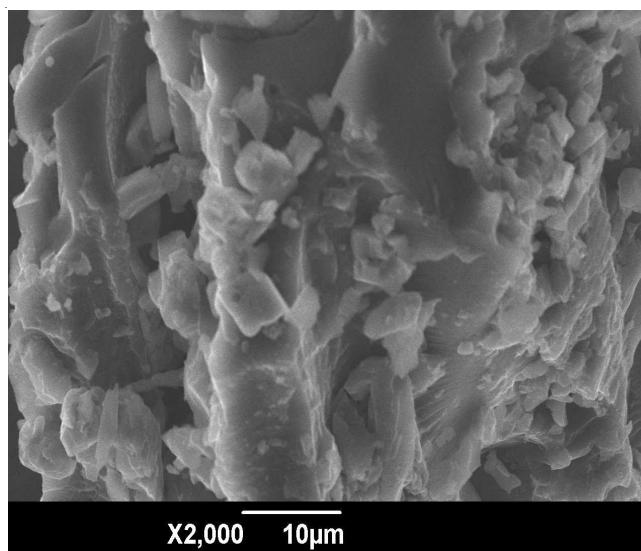Fig. 3. (b) SEM of anthracite coal annealed at 1400 °C

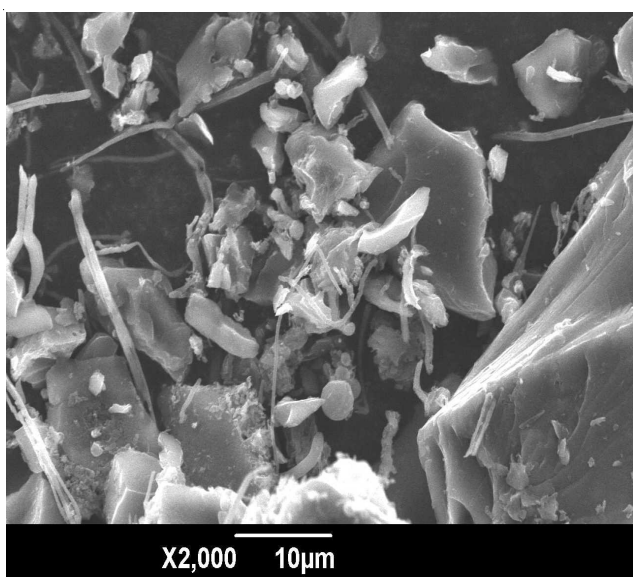Fig. 3. (e) SEM of vitrinite (anthracite coal annealed at 1800 °C)

Conclusion

The anthracite did not graphitize with a temperature lower than 1400 °C thermal anneal. After 1400 °C, The graphitization increased with the increase of anneal temperature. The sample contain the chemical groups of COOH and C-H, which doesn't decompose in low temperature, but at high temperature these chemical groups decompose quickly, at high temperature the vitrinite and fusinite will separate from the anthracite base, the shape of vitrinite is round particles and the fusinite is rod like.

Fig. 3. (c) SEM of fusinite (anthracite coal annealed at 1600 °C

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