

Graphitization of Anthracites with the Addition of Transition Metal Organic Compounds

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Introduction

Graphitization of anthracite has long been an interesting area in coal and carbon science[1-5]. It has been demonstrated that anthracites retain their non-graphitizing carbon structure at temperatures lower than 2000°C[2], while the graphitization of anthracite occurs by sudden phase changes[6]. Mineral impurities, formation of catalytic carbons[6], as well as high confining pressure[7] have been proposed as the factors that may enhance the structural conversion of anthracite into graphite.

Catalytic graphitization of various carbons has been extensively investigated[8,9]. Among many catalysts that have been studied, transition metals and their compounds seem to be promising in terms of catalytic graphitization, particularly those that do not form high melting point carbides[9].

Our interest in catalytic graphitization of anthracite is stimulated by two considerations: (i) the impurity (ash) in most powdered anthracite specimens can be very high[10]; and (ii) transition metal organic compounds are commercially available at reasonable cost, which gives the potential of good dispersion of the metals in coal, or making metal-containing carbons from these compounds[11]. Preliminary results on catalytic graphitization of anthracites are reported here, with the emphasis of structural changes of anthracites.

Experimental

Powdered anthracite specimens (-60 mesh) were used as precursors without any treatments. The ultimate analyses of these samples have been reported previously[10].

Heat treatment or graphitization of anthracite were performed as follows: (1) the calcination of anthracite (1000°C) was carried out in a quartz tube furnace under nitrogen gas flow with a soak period of 1 hour; (2) graphitizations (2500 and 2725°C) were performed in a graphite tube furnace (Centorr Vacuum, NH) under argon gas flow with 0.25-1 hour of soak time. No heating rate control was selected in either case. Graphitization at 2900°C was performed outside the university.

Iron and cobalt naphthenates were purchased from Alfa[®] Aesar[®] and Sigma Chemical, respectively. The metal contents in these

compounds are approximately Fe, 6% and Co, 8%. Anthracite was mixed with 30-35 wt.% of the naphthenates, which adds 2-3% metals into the anthracite. The slurry then was put into a 30 mL tubing bomb reactor. After purging with high-purity nitrogen, the reactor was heated to 500°C in a sand bath and held for 3 hours. The residue was further heated to 1000°C in a tube furnace under nitrogen gas flow.

Iron- or cobalt-containing carbons were made by mixing naphthenates with coal tar pitch in 1:1 weight ratio. Subsequent procedures were the same as those used for coal. The carbon powder thus prepared was mixed with calcined anthracite in a ratio of 1:1.

Graphitizations of mixtures of anthracite and metals were carried out at three different temperatures, 2000, 2200, and 2500°C, under argon gas flow with 2-3 hours of soak time

X-ray diffraction (XRD) and polarized-light microscopy were used to study the structural changes of anthracite during the graphitization. Crystalline data were calculated using a high-purity silicon powder (SRM 640b) as internal standard.

Results and Discussion

Graphitization of anthracite

Table 1 summarizes the crystalline data, *i. e.*, d-spacings, $d_{(00)}$ and crystalline domain sizes, L_c and L_a , of #1 anthracite graphitized at 2500 and 2700°C. Compared to the anthracites reported previously, which were graphitized at higher temperature of 2700 and 2900°C[12], anthracite #1 shows excellent graphitizability indicated by small d-spacings and larger L_c and L_a . Fig. 1 illustrates its X-ray diffractograms; the typical three-dimensional graphite structure indicated by hkl lines, (101) and (112), being observed after graphitization at the relatively low temperature of 2500°C. Micrograph 1 shows a very porous optical texture found in anthracite #1 graphitized at 2700°C. The needle-like particles, however, are fully anisotropic, suggesting that the graphitization of this anthracite may be achieved by removing the impurities which surround or are distributed in the particles.

The specimen of anthracite #1 has a very high volatile matter along with high hydrogen

content[10]. Because of its high carbon content, the chemical skeleton of this anthracite may be distinctly different from other specimens. Further study is necessary for understanding the graphitization mechanism in detail.

Addition of iron organic compound

Fig. 2 shows X-ray diffractograms of raw #1 anthracite, calcined anthracite and anthracite with addition of iron naphthenate, IN (after heating to 1000°C). It is clear from these results that calcination at 1000°C completely removed some material existing in raw anthracite which appear at low scattering angles ($2\theta=5-25^\circ$, diffractograms A and B). No detailed chemical structural identification about these materials is available at this point; they may be, however, attributed to its high ash content in powder specimens as discussed previously[10]. Mixing iron naphthenate with anthracite successfully introduced iron into coal, as illustrated in diffractogram C. Neither iron carbide nor iron oxide was found in the anthracite at this temperature. Such a procedure may provide a simple way to disperse metal in the coal. It is interesting, therefore, to investigate the graphitization of anthracite with the addition of metal-containing naphthenates.

Further investigations in terms of anthracite selection, impurity composition and role during graphitization, graphitization catalyzed both by impurities and additives, as well as structural changes of anthracite, will be performed.

Table 1. Crystalline data of graphitized anthracites

samp.	d (002) (nm)	d (004) (nm)	Lc (002) (nm)	Lc (004) (nm)	La (110) (nm)
1	0.3371	0.3366	42.5	24.0	26.0
2	0.3370	0.3367	40.2	23.6	22.2
3	nd	0.3364	nd	25.5	nd
4	nd	0.3362	nd	33.0	nd

Samples: 1 and 2—#1 anthracite graphitized at 2700 and 2500°C; 3 and 4—PSOC1468 anthracite graphitized at 2700 and 2900°C[12]; nd— not determined.



Microphotograph 1 Optical texture of #1 anthracite graphitized at 2700°C.

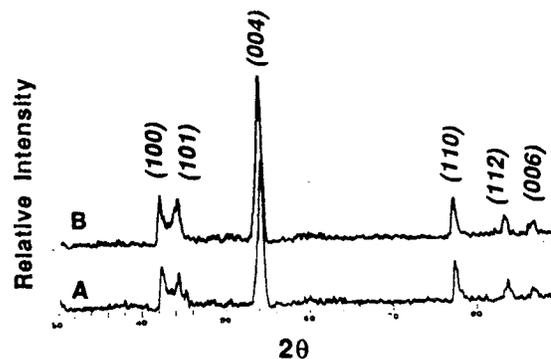


Fig. 1 XRD diffractograms of #1 anthracite graphitized at 2500 (A) and 2700°C (B).

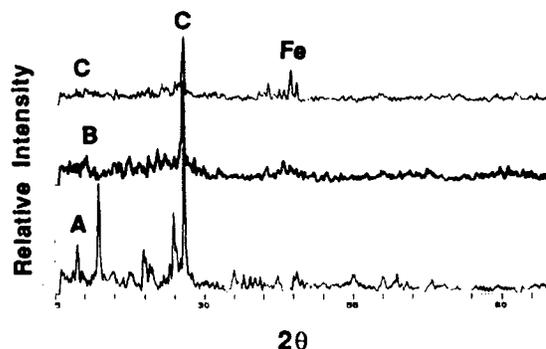


Fig. 2 XRD diffractograms of #1 anthracite raw coal (A), calcined anthracite (B), and anthracite mixed with IN (heating to 1000°C (C)).

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References

1. R. E. Franklin, *Proc. Roy. Soc.*, **209**, 196 (1951).
2. *Idem.*, *Acta Crystallogr.*, **4**, 253(1951).
3. E. L. Evans, J. L. Jenkins, and J. M. Thomas, *Carbon* **10**, 637(1972).
4. A. Oberlin and G. Thriere, *Carbon* **13**,367(1975).
5. M. Bonijoly, M. Oberlin, and A. Oberlin, *Inter. J. Coal Geol.* **1**, 283(1982).
6. A. Deurbergue, A. Oberlin, J. H. Oh, and J. N. Rouzaud, *ibid.* **8**, 375(1987).
7. J. V. Ross and R. M. Bustin, *Nature* **343**, 58(1990).
8. H. Marsh and A. P. Warburton, *J. Appl. Chem.* **20**, 133(1970).
9. A. Oya, *Tanso* (No. 102), 118(1980).
10. S. M. Zeng *et al.*, 22nd Conf. on Carbon(1995).
11. S. Miyanaga, H. Yasuda, A. Hiwara, and A. Nakumura, *J. Macromol. Sci.—Chem.*, **A27**(9-11), 1347(1990).
12. J. Atria *et al.*, 21st Conf. on Carbon, 342(1993).