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Anisotropic crystalline growth developed in Bangladeshi coking coal during mesophase transformation

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Abstract

The anisotropy of the mesophase spherules is developed during the carbonization of extracted coking coal in the temperature range 430 to 450°C. Mesophase transition is observed by the differential scanning calorimetric study. Enthalpy ΔH involved in the mesophase transformation is found to be 46.26 J/g. The growth of mesophase spherules, their coalesced structures, mosaic and flow type mosaic are observed by the polarized light technique as the evidence of graphitizing carbon. The solvent extraction of coking coal is carried out using benzene as a solvent at atmospheric pressure by Soxhlet apparatus.

Keywords: DSC; Enthalpy; Mesophase; Polarized-Light

1. Introduction

The broad division of carbons are classified [1] into two groups: graphitizing carbon (soft, coke) and non-graphitizing carbon (hard, char). The graphitizing carbons are generally formed from substances containing more hydrogen and less oxygen. Substances including the vitrinites of medium-volatile coking coal, high temperature coal tar pitch, petroleum bitumen, polyvinyl chloride and poly-nuclear aromatic compounds such as anthracene and phenanthrene belong to the group of graphitizing carbon [2, 3]. These substances pass through a plastic stage on heat treatment. The non-graphitizing carbons are produced from substances containing less hydrogen or more oxygen. All low rank coals yield typical non-graphitizing carbon. They do not show any significant improvement in crystalline growth even after heat treatment upto 3000°C. Synthetic

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manufacture of graphite is based on the initial formation of carbon during carbonization of aromatic organic substance. The formation of carbon structure and its ability to become graphite at high temperature have been observed in the early stages of carbonization (350 to 600°C).

In 1949, Mackowsky [4] stated that the fine anisotropic mosaic structure, observed in coke from coals, originated from continuous ordering of crystallites during the period of fluidity of the carbonization process. The coal becomes more plastic during carbonization between 350 and 550°C, where the larger anisotropic regions-mosaic units are observed. This aspect of the relationship of size of anisotropic unit in cokes with rank of coal was developed by Alpern [5] in 1956. Taylor [6] in 1961, recognized that this anisotropic sphere provided the clue to the development of graphitizing carbons. Brooks and Taylor [7–9] in 1968 subsequently developed a concept of the transformation of an anisotropic carbon from pitch like substances. This transformation is known as mesophase transformation that takes place in graphitizable carbon during pyrolysis in the temperature range 350 to 600°C. This transformation is a liquid state structural transition in which the large polymerizing aromatic molecules are aligned in a parallel array to form an anisotropic liquid crystal.

The structure of vitrinite was reviewed by Derbyshire [10] in 1991 and observed that the structure and properties of coal derived carbons are strongly dependent upon those of the precursor and the extent of cross-linking reactions during the process of transformation.

In view of the above discussion, it is clear that some rank of coals do not pass through a liquid or plastic phase transition on heat treatment but undergo structural changes in the solid phase. On the other hand, some pitches, bitumen, and certain polynuclear aromatic compounds etc. extracted from coal provides graphitizing carbons. The thermal behaviour and coking properties of Bangladeshi coal have been studied [11]. The objective of his research is to see whether the Bangladeshi coking coal are the graphitizing carbon or not.

2. Experimental

2.1. Sample preparation

Medium volatile coals having higher amount of carbon and low ash (i.e. coal of borehole GDH-45) have been chosen for solvent extraction. The solvent extraction of coal is carried out using benzene as a solvent at atmospheric pressure by Soxhlet apparatus. Coal samples were carefully ground and completely sieved to less than 200 mesh. The coal particles were then dried under vacuum. About 20 g of the sample was taken in a cellulose thimble. Extraction was carried out with 250 ml of fresh benzene. The experiments were performed by recycling the solvents 15 times in the Soxhlet apparatus. To avoid side reactions and agglomeration of extracts, the solvent was changed after 4 to 5 h.

After extraction, one hundred ml of the solvent extract was taken and the solvent was distilled off according to ASTM standards [12]. The extraction yield is 4.04%. The extracted materials contain hydrogen-rich structure and mainly condensed aromatic organic compounds.

2.2. *Differential scanning calorimetry apparatus and procedure:*

Mettler DSC 20 standard cell, microprocessor TA-3000 system were used. Coal sample was ground to <65 µm size. 16.42 mg of the sample was placed in aluminium pan, lightly packed and sealed with aluminium cover. While same wt. of Al_2O_3 was similarly treated and placed in the reference pan. The cells were then purged with argon flow at ambient pressure. The DSC. curve was then recorded at the heating rate of 20°C/min. After substracting the baseline signal (blank), the normalized heat flow curve was obtained. The calorimetric calibration was performed by measuring heats of fusion of pure metals using the following equation $\Delta H = \Delta_{fus}H \cdot m/E$ and the specific heat of an alumina standard [13, 14] was calculated using following equation $Cp = 60\,E.(dh/dt)/(\beta.\,m)$, where: E the calorimetric sensitivity (dimensionless), $\Delta_{fus}H$ fusion enthalpy of the pure metal standard (in Jg^{-1}); Cp the heat capacity of the alumina standard (in $Jg^{-1}K^{-1}$); dh/dt instantaneous heat flow at a prescribed temperature in mW; β the heating rate (in °C/ min); and m the sample mass (in mg). E is essentially unity over the entire temperature range.

2.3. *FT–IR Spectroscopy*

Absorption infrared spectra of the parent raw coal samples were obtained using a Nicolet FT–IR, 20 DXB, having 4000 to 400 cm^{-1} wave number, made by Nicolet Instrument Corporation, U.S.A. KBr pellets of coal were prepared by mixing 1 mg of dry finely powdered extracted coal with 300 mg of KBr. Pellets (13 mm in diameter) were pressed in an evacuated die under 1290 bar pressure for 1 min and then dried over night at 105°C to remove water.

2.4. *Low temperature carbonization*

The extracted organic material was carbonized by sealed tube technique in the temperature range 430 to 450°C. Carbonization was carried out using pyrex glass tubes in a solenoidal electric furnace having temperature limit up to 800°C. The pyrex glass tube of 25 cm in length, 16 mm in internal diameter and 1.5 mm in wall thickness along with the sample inside was sealed at both the ends and again placed inside a steel bomb fitted with screw caps at both the ends, to avoid blast or blow, if any due to heavy pressure inside.

2.5. *Micrographic Preparation*

The mounted specimens were ground by silicon carbide papers, using tap water as lubricant and progressing from 120 to 600 grit. Final polishing of the sample was carried out by high purity linde Alpha Alumina powder. Reichert metavert polarizing microscope equipped with 35 mm Remica III photomicrographic camera was used for optical study of the mesophase.

3. Results and discussion

3.1. FT–IR analysis

Figure 1 shows the FT–IR spectra of extracted coal sample. Infrared spectroscopic study suggests that the strong absorption band at 2922 cm^{-1} is due to the presence of higher aromatic hydrogen bond, which is stronger than aliphatic hydrogen bond at 2850 cm^{-1}. The strong absorptions at 1611 cm^{-1} and 1459 cm^{-1} suggest that these may be due to aromatic $C=C$ stretching and CH_2 (methylene) bridges between aromatic rings. The band at 880 cm^{-1} also indicates the existence of condensed aromatic benzene rings.

3.2. Differential scanning calorimetry

Differential scanning calorimetry (DSC) curve for the extracted coking coal of borehole DGH-45 of Khalaspir is shown in Fig. 2(a). The total enthalpy (ΔH) involved in this mesophase transformation of extracted coking coal is calculated from the second endothermic peak area of the DSC trace. The specific heats of the extracted coals lie in the range (4.18 to 5.48 $Jg^{-1}K^{-1}$). The endothermic heat flow from 440 to 560°C has been associated with the development of the plastic state or mesophase transition, and the onset of secondary gasification, which is responsible for semi-coke formation. ΔH is

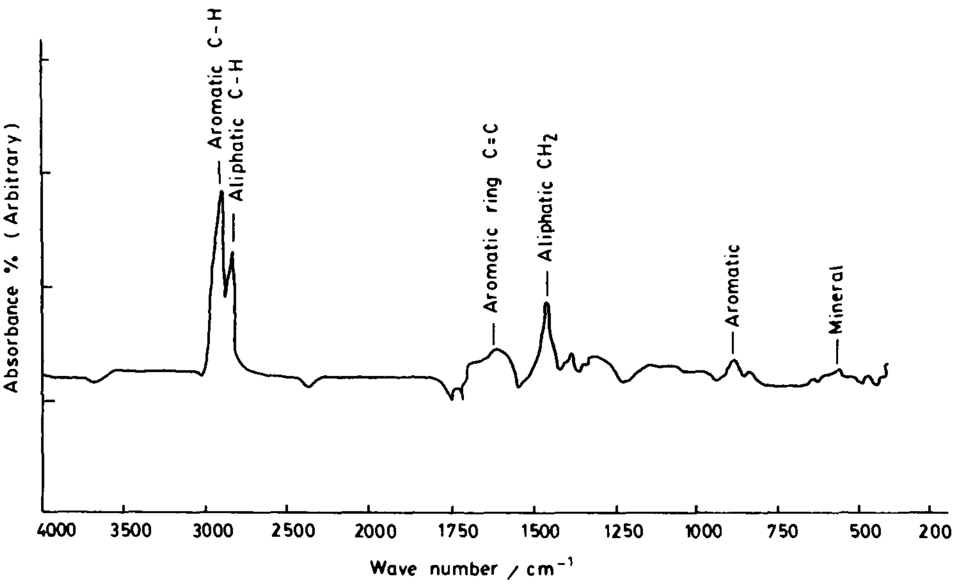

Fig. 1. Fourier transform infrared spectra (FT–IR) of extracted coal sample of borehole DGH-45 of Khalaspir.

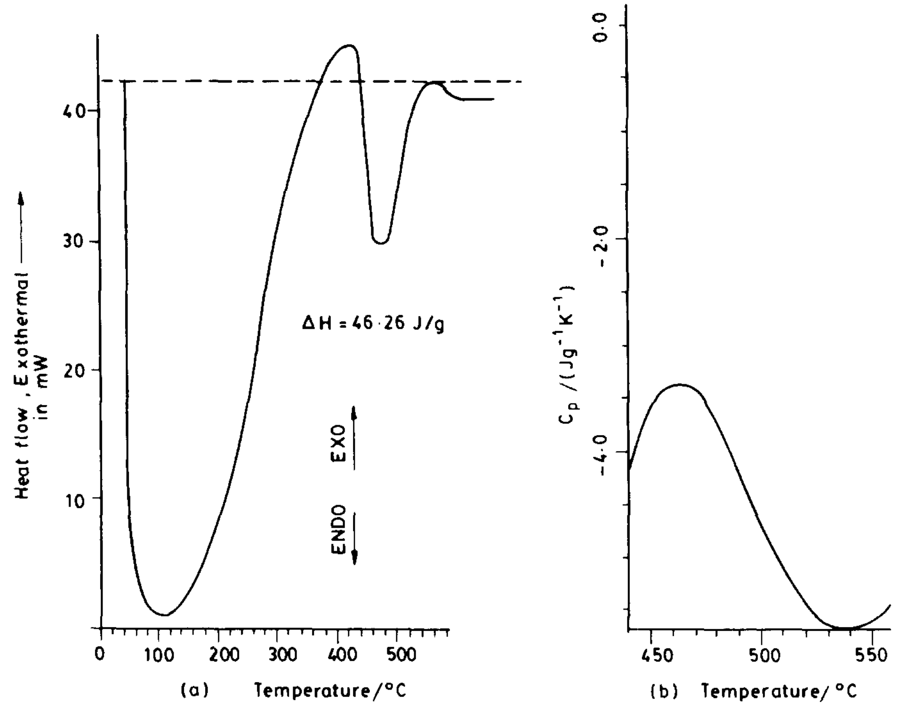

Fig. 2. (a) Differential scanning calorimetry curve for the extracted coking coal of borehole GDH-45 of Khalaspir. (b) Specific heat vs temperature curve (negative sign in C_p is an indication of the heat absorption by the sample).

found to be 46.26 J/g. Specific heat capacity (C_p) vs temperature graph is shown in Fig. 2(b).

3.3. Polarized-light photomicrographic analysis of mesophase

The importance of the formation of carbonaceous mesophase as a precursor to graphitization has been discussed earlier [6–9]. The polarized-light photomicrographs of the solvent extracted coal samples during mesophase formation have been examined in order to study the nucleation, growth and coalescence processes of the mesophase spherules developed at different heat-treatment temperatures.

Photomicrographs of selected mesophase spheres of subsequent heat-treated samples are presented in Figs. 3–6. Mesophase spherules start to appear at 430°C (Fig. 3). There after they start to coalesce forming larger spherules at higher temperature. Fig. 4 shows the picture of such a coalescence at 435°C. Complete coalescence takes place to form mosaic pattern at 445°C (Fig. 5). Finally, flow type mosaic and semi-coke formations are observed at 450°C (Fig. 6). All mesophase features and semi-coke formations are seen optically within the temperature range of the second endothermic peak area.

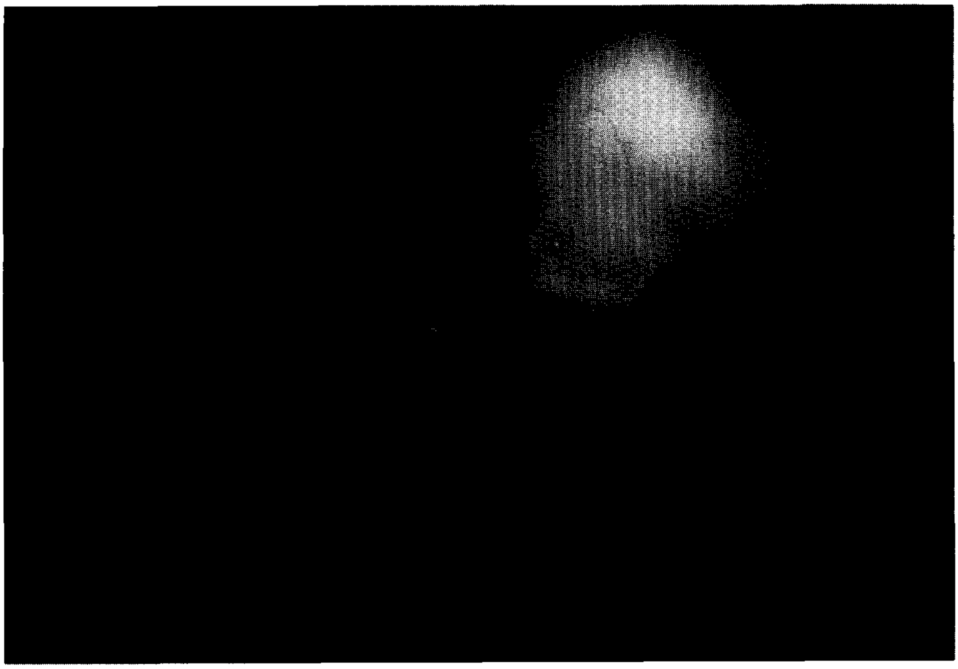

Fig. 3. Photomicrograph of mesophase spherules developed in benzene extracted coal on heat-treatment at 430°C for 4 hrs. Crossed nicols, 250X.

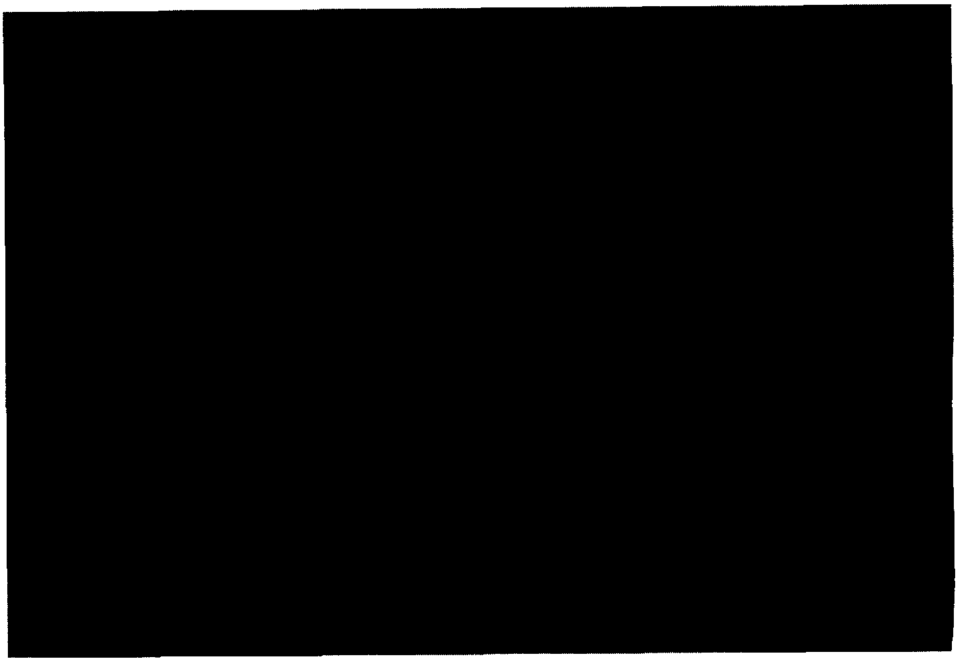

Fig. 4. Photomicrograph of mesophase spherules developed in coalesence on heat-treatment at 435°C for 4 hrs. Crossed nicols, 250X.

Fig. 5. Photomicrograph of mesophase formation developed on heat-treatment at 445°C for 4 hrs. Crossed nicols. 250X.

The degree of anisotropy of the mesophase or semi-coke formation depends exclusively on the carbonization temperature. The change from isotropic matrix to anisotropy are observed in the polished surfaces of the coke product. In a polished surface, the anisotropic areas represent a "variety of orientation". The highest degree of anisotropy can only be found if the plane of section is parallel to the c-axis of the graphite-like assemblege of crystallites in the coke. Photomicrographs presented in the Figs. 4 and 6 show highest degree of anisotropy with distinct maltese crosses. It reveals that graphite-like layer orientation along the growth axis-c is more ordered. The growth of spherical unit bodies with nodal structures, their coalesced structures, mosaic and flow type mosaic are the essential features for the evidence of graphitizing carbon. The Khalaspir coals show the anisotropic features, which are the indications of precursor states to graphitization.

4. Conclusion

The Bangladeshi coal is found to pass through a fluid phase during low temperature carbonization in the range of 430 to 450°C, where fluid phase converts slowly to an optically anisotropic carbonaceous material via a transient nematic crystal phase. Temperature interval for mesophase transformation could be identified from the DSC

Fig. 6. Photomicrograph of flow type mosaic and semi-coke formation on heat-treatment at 450°C for 4 hrs. Crossed nicols, 250X.

traces. In the mesophase formation, large planar aromatic molecules become aligned in a parallel array to form an anisotropic liquid crystal. The growth of spherical unit bodies, their coalescence and formation of mosaic pattern with maltese crosses and nodes under reflected polarized-light using cross polarizers are the basic characteristic features of the graphite microstructures. The Bangladeshi coal forms anisotropic structure in the mesophase transformation and proved its graphitizability.

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