A PHASE-CONTRAST ELECTRON MICROSCOPE AND OPTICAL MICROSCOPE STUDY OF ANISOTROPIC CARBONS OF DIFFERENT OPTICAL TEXTURE

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Introduction

It is an interesting aspect of formation of synthetic graphites that their structure is closely dependent upon the chemical composition of the parent pitch substance and the conditions of carbonization. Graphites with a wide range of physical properties can thus be fabricated, possessing optical textures ranging from large domains of needle-cokes to the small fine mozaics (<5 μm) of the so-called isotropic graphites. Metallurgical and foundry cokes contain anisotropic components, usually mozaic (<1 μm) and some flow-type (Ref. 1). Those differences, chemical, structural or physical, in the formation of nematic liquid crystals and the properties of subsequent mesophase, which influence the size and coalescence behaviour of mesophase require further investigation. Once the mesophase is recognizable it is not susceptible to chemical analysis (being an aromatic polymeric substance) and structural analyses may be more rewarding. Two experimental approaches have therefore been adopted, i.e. quantitative reflectance microscopy and phase-contrast electron microscopy to image molecular constituents.

The Experimental Approach

Carbons have been prepared from A200 Ashland petroleum pitch, D112 coal-extract, Orgreave coal-tar pitch, Gilsonite pitch and polyvinyl chloride by carbonizing at 5 K min^{-1} to 1100 K under nitrogen, and then under argon to 1300, 1500, 1700, 2000 and 2300 K. Resultant carbons were mounted in resin and polished surfaces prepared. Carbons from the petroleum and coal-tar pitch possessed optical textures of isochromatic domains, with the carbons from the D112 coal-extract possessing large mozaics (10 μm) and from the Gilsonite pitch small mozaics (<5 μm). There was, accordingly, available a series of carbons, of increasing size of optical texture, prepared by identical methods.

Quantitative reflectance microscopy: The percentage of light (of given wavelength) reflected from polished surfaces of carbon is a function of the refractive index 'n', density, and the orientation, size and perfection of the constituent anisotropic units or molecules. Cornford and Marsh (Ref. 2) discuss the use of quantitative reflection measurements from surfaces of carbons. This method may therefore be capable of distinguishing aspects of lamellar molecular composition and perfection of stacking within the carbons of different optical textures.

High-resolution electron microscopy: This technique is capable of resolving the lamellar structure of these carbons by fringe-imaging. The magnification involved are so high and the sample examined so small that a criticism of the method is that a non-representative portion of the sample may have been examined. To overcome this criticism, use is made of a micro-manipulator whereby a micro-cutting tool is operated in conjunction with an optical microscope and carbon from a characterized region of the optical texture is removed for microscopic investigation, using a JEOL 100C electron microscope.

Objectives

The overall purpose of this study is to further our understanding of these factors which influence the viscosity of the mesophase. This is because viscosity influences the ability of the mesophase to coalesce (formation of disclinations) or to form small mozaics without coalescence (unless restricted to boundary situations), the mozaics being fused growth units of mesophase. In the carbons of higher HTT it may be possible to image some of the disclinations predicted by White and Zimmer (Ref. 3) from analyses of optical micrographs.

Differences in viscosity may be associated with chemical bonding between (across) the lamellar molecules, or to non-lamellar molecules. Direct imaging of the molecules and a reflectance analysis should give relevant information. An analysis of X-ray diffraction studies of Mochida et al. (Ref. 4) indicates no close correlation of $C_o(\overline{002})$, $L_c(002)$ with size of optical texture.

Discussion

In quantitative reflectivity studies, interest is with maximum and minimum reflectivities from selected areas of the surface. Using both air and oil objectives one is then in a position to calculate other optical parameters such as bireflectance and absorptive index. To obtain the maximum reflectivities one has to scan the specimen diligently. Maximum reflectivities occur either from basal plane surfaces (these are essentially isotropic, exhibiting no minimum on rotation of the specimen stage of the microscope) or when the polarized light is parallel to the basal planes (rotation through 90° will then reveal the minimum reflectivity).

It is found that maximum reflectivites in air continue to rise with increasing HTT to about 1500 K. The reflectivity from the A200 Ashland petroleum cokes appears to level off with HTT at about 30-31%. The reflectivity of cokes from D112 coal-extract is still rising at 33.5% (HTT 2000 K), with the Gilsonite cokes showing reflectivities which fall from about 33% (HTT 1500 K) to about 28% (HTT 2000 K). The reflectivities of carbons from polyvinylchloride (PVC) also show this maximum. This maximum may have several origins. It could be due to the development of micro-fizzures whereby the amount of carbon under the spot of light of the reflectance

microscope diminishes as the micro-cracks widen. A second explanation is that, at a certain stage of the graphitization process, the lamellar constituent molecules become strained and deformed by cross-linkage and bond-shortening mechanisms. This zig-zag structure of molecules has actually been recognized in phase-contrast fringe-imaging in the electron microscope (Ref. 5). A third explanation is that an adsorption edge is moving into the cokes of increasing HTT and reflectivities will be modified by significant changes in electronic absorption processes within the lattice of the graphite. A fourth explanation is essentially an experimental artefact , namely that some form of preferential alignment is occurring in the resin blocks so that true maximum values are not being located.

However, on the evidence so far available it would appear that reflectivities from polished surfaces of carbons are not closely dependent upon the optical texture. This implies that optical texture is essentially a macro phenomenon and that the structure of individual constituent lamellar molecules is a function of the chemistry of pyrolysis and growth of the lamellae with its inclusion of heteroatoms, single and multiple vacancies etc.

The high-resolution electron micrographs show the transition from the small lamellae, approximately in parallel stacking and characteristic perhaps of structure in mesophase, to the graphitic crystallites of the samples of highest HTT. The detail can best be assessed by inspection of the many available micrographs which will be available at the Conference.

References

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