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MICROSTRUCTURES FORMED IN THE CARBONIZATION OF COAL-TAR PITCH*

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ABSTRACT

Recent investigations by several groups⁽¹⁻³⁾ on the structural conditions for graphitizability have demonstrated the significance of the mesophase transformation which takes place in graphitizable organic materials during pyrolysis at temperatures in the neighborhood of 425°C. This transformation is a two-phase liquid-state transition in which the aromatic sheet-like molecules are aligned in a parallel array to form a liquid crystal. The mesophase is readily distinguished from the isotropic matrix phase by its optical anisotropy.

In the initial stages of nucleation and growth the mesophase appears as spherules with the simple structure noted by Brooks and Taylor.⁽¹⁾ The molecular layers are stacked parallel to a polar diameter and curve to meet the pitch-mesophase interface normally. However as carbonization progresses the growing spherules coalesce and deform to form relatively complex structures which are the precursors to the structures observed in fully graphitized materials. In the present work, polarized-light micrography has been employed to define some structural features of the coalesced mesophase which have also been found in electron micrographic studies of graphitized materials.

The starting material was a conventional coal-tar binder pitch from which the insolubles were removed by solvent extraction with tetrahydrofuran. Since the mesophase transition is very sensitive to temperature, a temperature-gradient heat-treatment technique was employed to obtain a series of specimens representative of slightly varying degrees of carbonization.

When a micrographic section of the transformed pitch is examined under polarized light with crossed polarizers, a relatively complex array of extinction contours is observed. The nodal points at which the extinction contours pinch down sharply are prominent features of the coalesced mesophase. If the plane of polarization of the incident light is rotated, the extinction contours are observed to move across the face of the specimen, but the nodal points remain fixed. In many cases, the extinction contours are observed to bow out between pairs of nodes as the plane of polarization is rotated. Thus both co-rotating and counter-rotating nodes are observed, with the extinction contours rotating either with or counter to the direction of rotation of the plane of polarization.

By applying an overlay technique to a series of polarized-light micrographs taken at various angles of rotation of the metallograph stage, the microstructure may be sketched in terms of the intersections of the mesophase layer planes with the micrographic plane of section. The co-rotating nodal regions possess a simple arch structure, with the curved layer planes lying either concave or radial relative to the position of the node. The counter-rotating nodal regions are found to have a delta structure, with three-fold symmetry in the idealized case, and the curved layer planes lie convex relative to the position of the node.

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Both nodal structures involve discontinuities in the stacking of the mesophase layer planes. On following an extinction contour through a node, the layer planes are found to lie perpendicular to one another at the node. Analogous to crystal dislocations, the co-rotating and counter-rotating nodal structures are essentially linear stacking defects of opposite sign.

When pyrolysis is continued beyond the temperature range of the mesophase transformation, gas bubbles nucleate and grow in the mesophase. As the bubbles percolate through the viscous mesophase, various regions are subjected to large plastic strains leading to an increasingly fine texture of extinction contours. Two types of fine texture may be distinguished: a fibrous texture, and a more equiaxed, mosaic texture. The fibrous texture is usually found in the vicinity of a bubble and is comprised of tightly folded mesophase layers. Examination of these fine textures at the highest magnifications reveals that the nodes in the extinction contours possess essentially the same character as found in the mesophase in the initial stages of coalescence.

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 2. Innatowicz, Maria, Chiche, P., Dednit, J., Pregermain, S., and Tournant, R., Carbon 4 (1966).
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