DISCLINATION STRUCTURES IN COKE AND GRAPHITE[*]

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Introduction

The crystal defects known as rotational dis-clinations are rare in metals and ceramics because the strong curvatures of a disclinated crystal involve intolerable lattice strains [1, 2]. However, discli-nations are common in liquid crystals because the absence of crystalline registry between adjacent par-allel molecules allows local displacement and ample relaxation in lattice strain [2]. Disclination struc-tures are prominent features of coke and graphite because a lamellar liquid crystal, the carbonaceous mesophase, forms in the final stages of liquid-phase carbonization [3, 4].

Some basic aspects of disclinations in the car-bonaceous mesophase were discussed at the Baden-Baden Conference [5]. The distinctive feature of carbonaceous mesophase is the plate-like aromatic molecule, which serves as the basic building block of the lamellar liquid crystal in contrast to the rod-like molecules of nematic liquid crystals. Four types of line wedge disclinations commonly found in the mesophase as well as coke and graphite are sketched schematically in Fig. 1. The disclinations are topological discontinuities that result from the stacking of layer-molecules to form lamellae which retain some freedom to bend and twist as they trace out a lamelliform or Möbius morphology.

The Formation of Disclination Structures

In the pyrolysis of a graphitizable precursor, the mesophase appears initially as spherules with the morphology first defined by Brooks and Taylor [6]. See Fig. 2. The mesophase layers define doubly curved surfaces (except for the equatorial plane) which intersect the spherical phase boundary at or
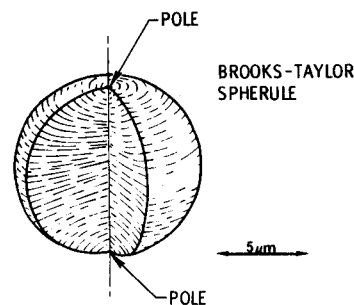

Fig. 2. Layer orientation in mesophase spherule

near 90°. As pyrolysis proceeds, these spherules grow and coalesce to form bulk mesophase with its characteristic lamelliform morphology. The dis-clinations found in fresh undeformed mesophase are thus complex three-dimensional structures that re-sult from the repeated formation of multiple con-nections between coalescing spherules.

Many mesophases are sufficiently fluid, at least in the early stages after precipitation and co-alescence, to be readily deformed by the percolation of gas bubbles or by mechanical deformation [7]. Such deformations produce the fine fibrous or lamel-lar microconstituents which are the hallmark of the needle cokes. These microconstituents offer good subjects for detailed study of disclination structures because knowledge of the preferred orientation of mesophase lamellae relative to a selected cross-section can markedly simplify interpretation of the polarized-light response on the polished section.

Disclinations in the Lamellar Microconstituent

The disclination structures in the deformed microconstituents generally occur at a scale just resolvable by polarized-light microscopy. The carbonaceous mesophase as well as its heat-treated fossils, coke and graphite, are uniaxial negative crystals demonstrating maximum reflectivities when the line of polarization is parallel to the lamellae and minimum reflectivities when this line is perpendicular to the lamellae [8]. By varying the polarizing con-ditions, information can be obtained on the details of disclination structure.

The fine lamellar morphology [7] occurs in the walls of bubbles formed by the escape of volatile gases. The lamellar microconstituent in such a bubble wall is illustrated in Fig. 3 for three con-ditions of polarization: (a) crossed polars, with the lamellae at 45° relative to the line of polarization to obtain maximum contrast; (b) polarizer only, with the line of polarization perpendicular to the lamellae; and (c) polarizer only, with the line of polarization
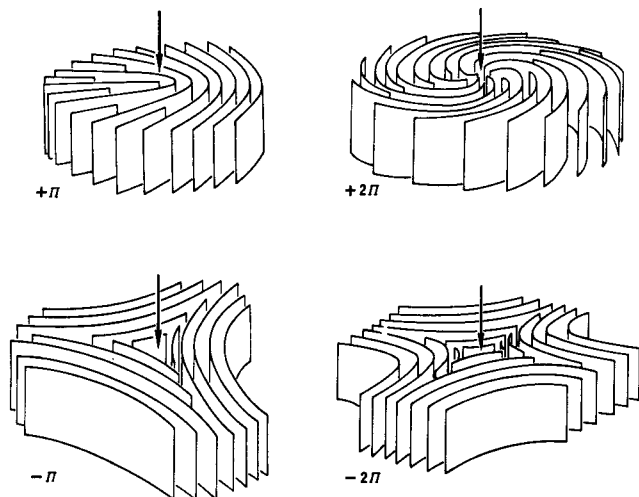

Fig. 1. Line wedge disclinations found in coke and graphite [3, 5]

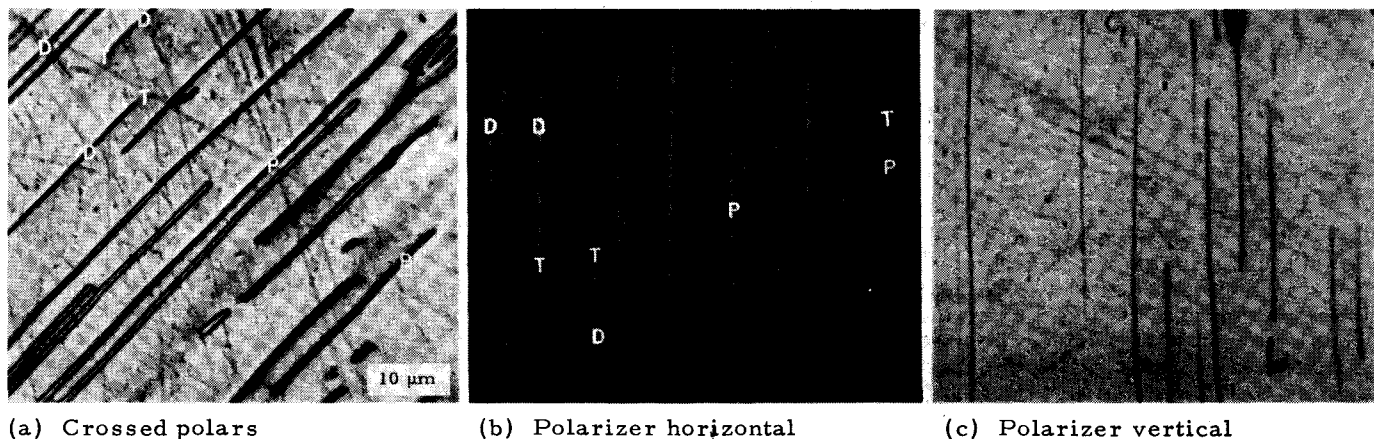| (a) Crossed polars | (b) Polarizer horizontal | (c) Polarizer vertical |

Fig. 3. Lamellar microconstituent of a bubble wall in a decant oil pyrolyzed to 500°C

parallel to the lamellae. Inspection of these micrographs will show that some lines of Fig. 3b, marked D, disappear when the polarizer is rotated by 90° and that most of the remaining non-disappearing lines can be resolved as doublets by crossed polarizers.

These observations are consistent with the structure sketched in Fig. 4. Each line of Fig. 3b corresponds to a fold. If the plane of section is nearly parallel with the top of the fold, the line will disappear when the polarizer is parallel to the fold and the line observed by crossed polars will not be resolvable to a doublet. In this case, the fold terminates in a twist disclination (indicated by T in Fig. 3); the disclination core is sketched as a ribbon rather than a line to account for the apparent radii of most folds (of the order of 0.5 micron). If the plane of section intersects the fold at a higher angle, the line will not disappear upon rotation of the polarizer and can usually be resolved to a doublet under crossed polars. In this case, the line is terminated by line wedge disclinations of strength $\pm\pi$ (cf. Fig. 1), and the specific type of wedge disclination can be resolved by noting the direction of movement of an extinction contour when the line of polarization is rotated.

It may be noted that two lines, marked P, of Fig. 3 are partially disappearing, i.e., one segment disappears when the polarizer is rotated while the remaining segments can be resolved to doublets under crossed polars. This response implies that the rotation vector of the fold varies, i.e., the edge of the fold is not straight but curved with only a limited segment running nearly parallel to the plane of section. Thus the double curvature of mesophase layers, which may be regarded as normal for coarse undeformed mesophase, can be retained to some degree in highly deformed microconstituents. From the viewpoint of graphitizability, the process of de-wrinkling such doubly curved layers to attain graphitic interlayer registry must necessarily involve mass transfer by diffusion within the layers.
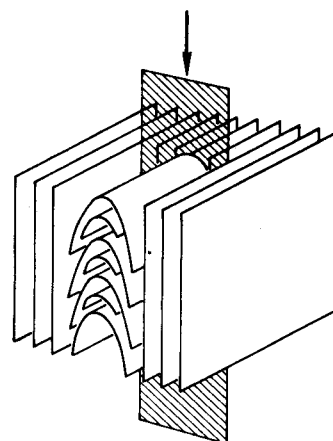
Acknowledgments

Fig. 4. Twist disclination of rotation π normal to disclination line

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