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Disclinations in the Carbonaceous Mesophase

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When the organic precursors to coke and manufactured graphite (petroleum and coal-tar pitches) are carbonized, large, flat, polynuclear aromatic molecules are formed by the reactions of aromatic polymerization. As the molecular weights approach 1500, usually near 450 C, the molecules condense to form a liquid crystal which has been termed the carbonaceous mesophase. The distinctive feature of the carbonaceous mesophase is the plate-like molecule, in contrast to the rod-like molecule of nematic liquid crystals. The carbonaceous mesophase thus appears to be a lamellar liquid crystal in which space is filled by plate-like molecules which may vary in size and shape but tend to pack in parallel arrays. These arrays are free to bend and twist as they trace out a lamelliform or Möbius morphology with topological discontinuities which bear similarities to the disclination structures found in conventional liquid crystals. Two types of lamellar disclinations may be conceived: layer-stacking disclinations resulting from long-range discontinuities in parallel stacking, and layer disclinations that may exist within a given layer. Layer-stacking disclinations exist in profusion in most cokes and fabricated graphites and appear to play significant roles in determining such properties as graphitizability, thermal expansion, and fracture toughness.

1 INTRODUCTION

Disclinations are no longer academic curiosities. Frank[1] described disclinated crystals as topological oddities and named them Möbius crystals. Nabarro[2] sketched crystal disclinations, but stated that such highly strained configurations are unlikely to occur naturally. However, it is now apparent that the disclinations characteristic of a lamelliform or Möbius body, in which space is filled by lamellar molecules, exist in most cokes and fabricated graphites, and appear to play significant roles in determining the morphology, crystallinity, and structure-sensitive properties of these materials.

Harris[3] has offered a stimulating discussion of the geometry of disclinations in crystals. Emphasis in his report is on surface crystals, for which the structural unit is a single molecular layer, and on liquid crystals, in which space is

filled by rod-like molecules in nematic, smectic, or cholesteric arrays. The disclination structures in surface crystals, which abound in nature, appear to be involved in many basic biological processes.

Disclinations occur in cokes and manufactured graphites because in a brief, but critical, stage of carbonization there is formed a liquid crystal that has become known as the carbonaceous mesophase.[4] When the organic precursors to coke and graphite are subjected to severe thermal cracking, reactions of aromatic polymerization normally predominate to build large, flat, polynuclear aromatic molecules. When the molecular weights approach 1500, the molecules condense to form parallel arrays with the structural characteristics of a lamellar liquid crystal. The disclinations represent the structural discontinuities that result from the parallel packing of lamellae that retain some freedom to splay, bend, or twist as they trace out the layers of the lamelliform Möbius body.

The formation of carbonaceous mesophase is common to most industrial processes of coking and carbonization, and the present understanding of this unique material stems largely from studies of the pyrolysis behavior of such practical materials as coal, coal-tar pitch, and petroleum feedstocks.[4] The mesophase transformation usually occurs in the range of 400 to 500 C as the pyrolyzing liquid becomes more viscous and begins to congeal to semicoke. In the early stages of nucleation and growth, the mesophase appears as small spherules suspended in the optically isotropic matrix, as illustrated by the polarized-light reflection micrograph of Figure 1. The characteristic lamelliform structure of the spherules[5] consists of aromatic layer molecules that lie perpendicular to the polar diameter but splay outward to reach the interface with the matrix normally.

Under the usual conditions of pyrolysis, the carbonaceous mesophase retains its plasticity long enough to allow at least some of the structural mechanisms illustrated by the micrographs of Figure 1 to occur. As the pyrolysis reactions proceed, the spherules grow and tend to sink through the matrix, while gas bubbles stir the two-phase liquid mixture as they percolate to the surface. When spherules or larger bodies meet, coalescence can occur, producing bulk mesophase with various morphologies as indicated by the complex patterns of polarized-light extinction contours. Coarsening of the microstructure initially introduced by spherule coalescence is also evident. The lower micrograph of Figure 1 illustrates the deformation of some of the coarse mesophase constituents to a fibrous microstructure by the stresses applied by bubble percolation.[6]

Chemical studies indicate that the freshly formed mesophase consists of planar aromatic molecules ranging appreciably in molecular weight but with typical values near 2000.[7] If the typical mesophase molecule is assumed to be rather well-formed polynuclear aromatic molecule, it can be modeled as a

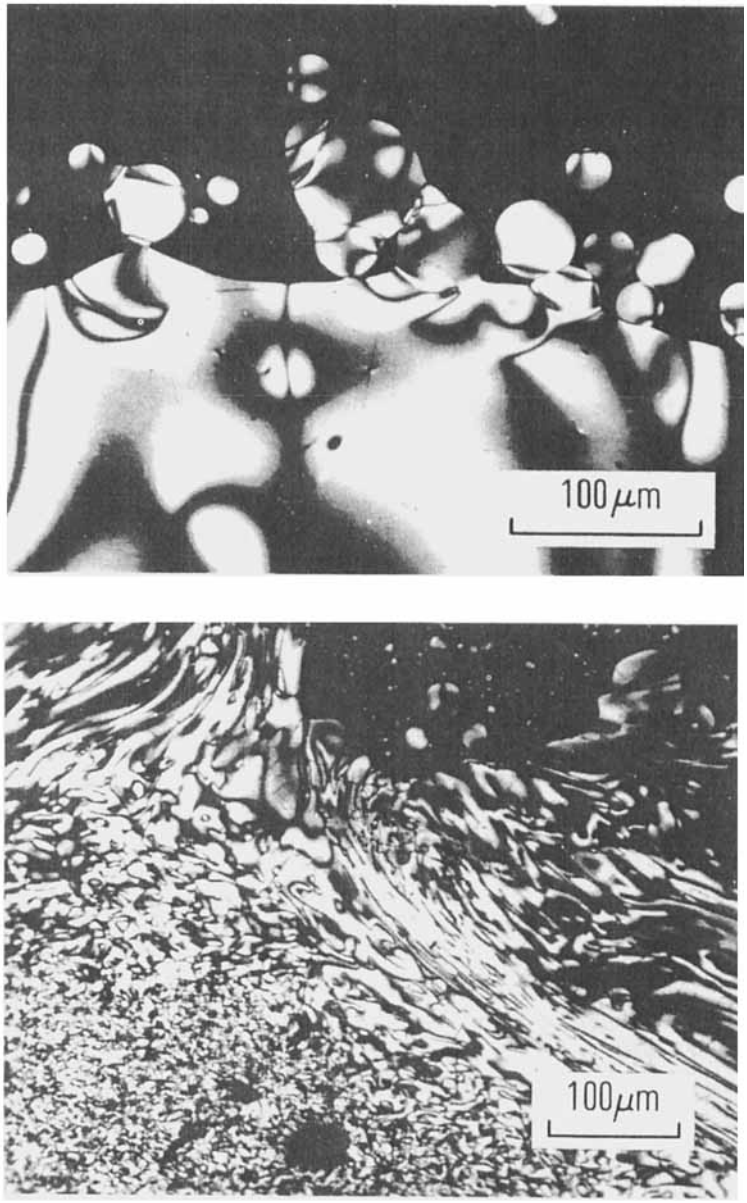


FIGURE 1 Formation of mesophase microstructures in pyrolysis of typical carbon precursors, as observed by crossed polarizers. Upper view illustrates coalescence and coarsening processes in extracted coal-tar pitch. Reproduced by permission from *J. Chim. Phys.*, special number 33, April 1969. Lower view illustrates several microconstituents formed in petroleum coker feedstock; the fine randomized constituent coexists with coarser mesophase, which is deformable by the stresses of bubble percolation. Reproduced by permission from *Carbon*, **12**, 321 (1974).

plate of the order of 25 Å in diameter with a ring of hydrogens at the edge. The H/C atom-ratio is dependent on the precursor but tends to 0.4 as a minimum value.[4] This ratio requires that an appreciable fraction of the edge sites be occupied by methyl groups. Measurements of electron-spin resonance indicate that many mesophase molecules are free radicals with at least one unoccupied edge site.[8]

The carbonaceous mesophase displays conventional characteristics of liquid crystals such as the alignment of the molecular layers with a substrate surface[4] or with a magnetic field.[8] However, the ability to deform or flow at low stress to produce drastic changes in the lamelliform morphology is probably the most striking as well as useful liquid-crystalline property of this precursor to graphite.

The carbonaceous mesophase has only a transient existence in the temperature range in which its plastic properties are evident. As temperature is increased, the viscosity steadily rises as the reactions of aromatic polymerization continue between the molecules in the layered configuration, eventually producing a hardened coke with the mesophase microstructure frozen in place. Thus this mesophase transformation is an irreversible reaction that proceeds from the isotropic phase to the liquid crystal phase with increasing temperature.

The evidence for disclination structures in the carbonaceous mesophase has been largely confined to the literature on carbon[4-9]; the purpose here is to present some aspects that may be of interest to the liquid crystal community.

2 GEOMETRICAL ASPECTS

The carbonaceous mesophase is a liquid crystal consisting of plate-like molecules that display long-range orientational order in the sense that the molecules tend to lie, parallel to each other and equidistant. Point-to-point registry between the molecules in adjacent layers is not required. The crystal symmetry elements of the mesophase are (1) any translation in the plane of the molecules, (2) any translation perpendicular to the molecules of magnitude d, where d is the interlayer spacing of 3.47 Å,[5] (3) any rotation about the axis normal to the molecules, and (4) a rotation of π about any axis in the plane of the molecules or in the plane midway between the molecules—a two-fold symmetry axis. A schematic model of the carbonaceous mesophase is shown in Figure 2. This representation offers an estimate of the spacing, size, and shape of the polynuclear aromatic molecules that form the mesophase. The density of the carbonaceous mesophase is much less than that for crystalline graphite (1.46 g/cm^2 compared to 2.25 g/cm^3), and, thus, there

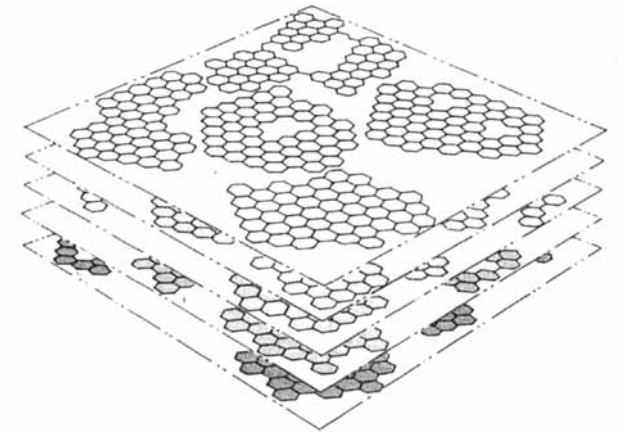


FIGURE 2 Model of the carbonaceous mesophase—a lamellar liquid crystal.

must be open spaces in the plane of the molecules. Each molecule sketched has a molecular weight of about 1500 including edge methyl groups. The molecules may have various shapes and probably do not have to be perfect in that they may contain vacant sites or holes. Also, the molecules may be rotated in the plane with respect to the neighboring molecule. Although the perfectly ordered carbonaceous mesophase has symmetry elements similar to smectic A liquid crystals[10] only, there is a discrete difference in the shape of the molecules (plate-like versus rod-like in smectics) and in the local stacking arrangement (parallel to the layers versus perpendicular to the layers in smectics). Thus the carbonaceous mesophase may be described simply as a lamellar liquid crystal.

This lamellar liquid crystal contains both rotational disclinations and translational dislocations. It is convenient to classify two types of disclination structure in the carbonaceous mesophase—layer-stacking disclinations that result from the long-range discontinuities in the parallel stacking of the molecular layers, and disclinations that exist within a single layer. The layer-stacking disclinations in the carbonaceous mesophase correspond to the rotational distortions as proposed by Volterra.[11] Consider a cut on a plane parallel and midway between two layers of molecules, as illustrated in Figure 3. The two cut surfaces are then displaced by a rotation. The edge of the cut is the disclination line, and its sense is defined by its tangent at any point. A rotation of the cut surfaces about an axis parallel to the tangent to the disclination line results in a wedge disclination, and a rotation perpendicular to the tangent results in a twist disclination.[2] The wedge disclinations are of two types: (1) positive if the rotation vector has the same sense as the tangent and (2) negative if the rotation is antiparallel to the tangent.[2] The symmetry

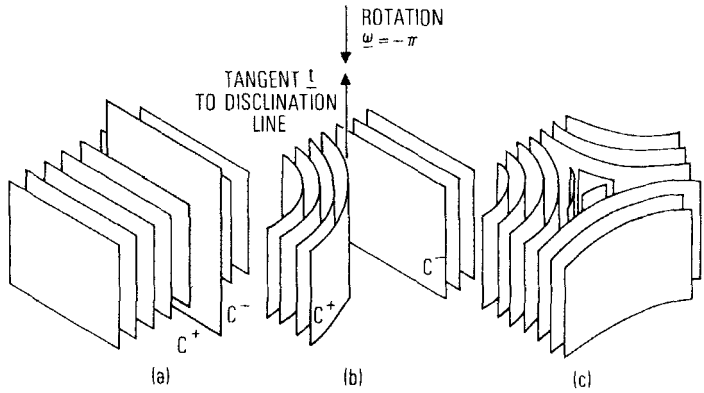


FIGURE 3 Formation of negative wedge disclination in a lamellar liquid crystal by the Volterra process. (a) A cut is made on a plane midway between two adjacent layers. (b) Face C^+ is rotated about one edge of the cut relative to face C^-. The axis of rotation is the disclination line. (c) Layers are added to heal the cut, retaining the parallel stacking away from the disclination core.

of the carbonaceous mesophase restricts the rotations to integral multiples of π. The disclination of Figure 3 is a negative wedge disclination with a rotation of π. Several wedge disclinations in this lamellar liquid crystal are shown schematically in Figure 4. For each, the rotation vector is parallel to the disclination line.

The structure of the layer-stacking disclinations in the carbonaceous mesophase can be described quantitatively by the curvature-elasticity theory

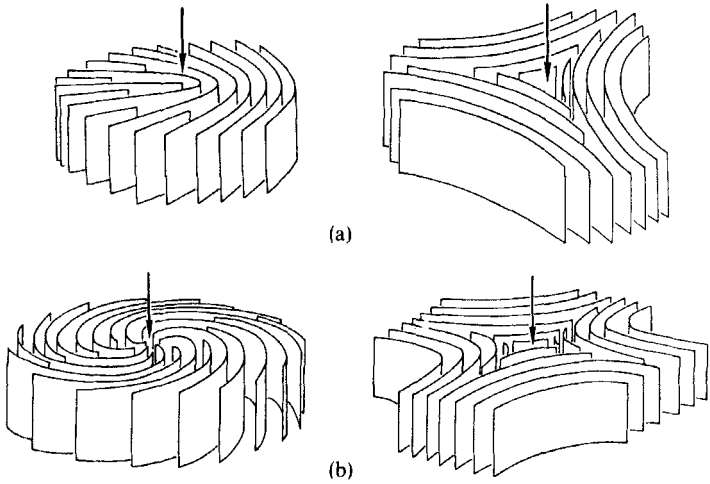


FIGURE 4 Layer-stacking wedge disclinations of rotation (a) $+\pi$ and $-\pi$ and (b) $+2\pi$ and -2π.

derived first by Oseen[12] and later revised by Frank.[13] The orientations of the plate-like molecules of this lamellar liquid crystal are uniquely defined by their normals. The direction of the normals can be described in a manner similar to that for conventional liquid crystals—the normal to the plate-like molecules is set parallel to the vector defining the length of the rod-like molecules of the conventional liquid crystals. The three basic modes of curvature strains are splay, twist, and bend. However, the equations for splay as defined by Frank[13] for nematic liquid crystals describe bend in the lamellar liquid crystal, and the equations for bend describe splay. The equations for twist apply directly. Splay (Figure 5) in the lamellar liquid crystal must necessarily contain edge dislocations (extra molecules must be inserted between adjacent splayed layers to retain the parallel stacking of the plate-like molecules). These are referred to as nonbasal edge dislocations.

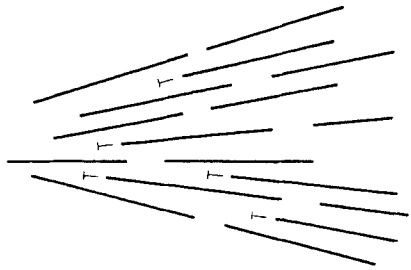


FIGURE 5 Splay in the carbonaceous mesophase. The extra layers are nonbasal edge dislocations. The normals to the plate-like molecules lie in the plane of the figure.

The strength of a disclination can be determined by considering the change in the direction of the normals to the layers of molecules about a circuit that encloses the disclination line. This method was devised by Nabarro[2,14] and is similar to constructing a Burgers circuit about a dislocation. Instead of counting steps along a Burgers circuit, one observes the change in local orientation of the lattice along the closed curve, or Nabarro circuit. The disclination strength is then defined as the number of complete rotations of the direction of the normals with respect to 1 rev (2π) about the Nabarro circuit. If the material has n-fold symmetry, disclinations of strength $S = p/n$, with p any integer, are possible. For the carbonaceous mesophase, layer-stacking disclinations of strength $S = \pm 1/2$ and $S = \pm 1$ have been observed.

The layer-stacking twist disclinations involve rotations that are perpendicular to the tangent to the disclination line. Several possible configurations of the cores of these twist disclinations are sketched in Figure 6. The disclination line must actually be ribbon-like since the region of bend and splay accompanying the rotation has a finite width. Each of these twist disclinations

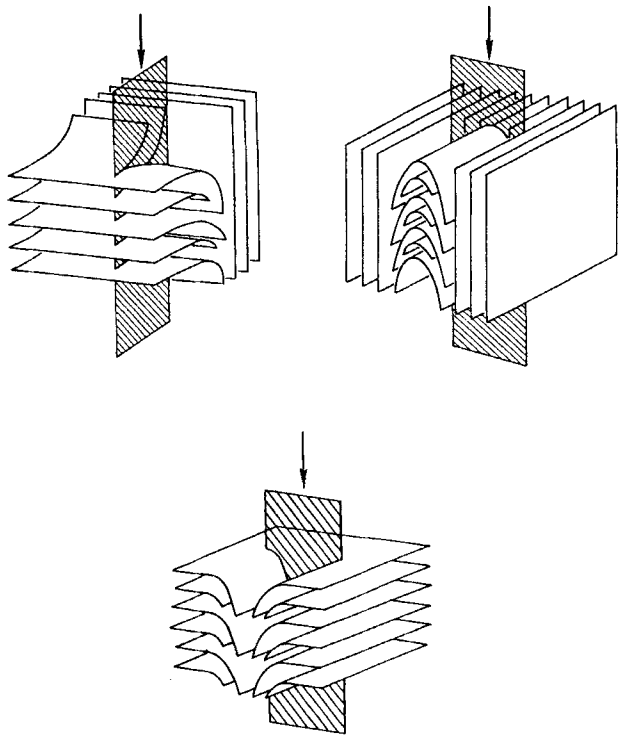


FIGURE 6 Layer-stacking twist disclinations in the carbonaceous mesophase. The rotation vector is perpendicular to the disclination core ribbon. All are of strength $S = \frac{1}{2}$.

has a strength of $S = \frac{1}{2}$. Traversing a Nabarro circuit about the twist disclination line results in a π rotation of the normal to the layers; the normals are not restricted to lie in the plane of the circuit.

If the disclination line encloses the Volterra cut, it is then a disclination loop. Such a loop is sketched in Figure 7. The character of the disclination around the loop varies depending on whether the rotation vector is parallel (wedge) or perpendicular (twist) to the tangent to the disclination line.

Layer disclinations are also theoretically possible. The coplanar molecules in a mesophase layer polymerize edgewise during pyrolysis and subsequent heat treatment to form an extensive sheet. Within the lamelliform Möbius morphology of the hardened mesophase, many of the layers may be doubly curved surfaces. As the flat, plate-like molecules within such a layer polymerize, defects will be created to account for the nonplanarity. The symmetry conditions change from no symmetry restrictions for the plate-like molecules within a layer in the lamellar liquid crystal to sixfold rotational

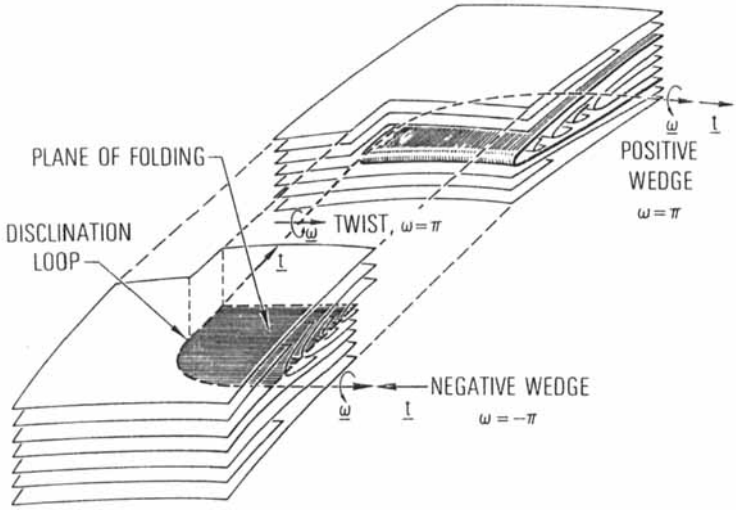


FIGURE 7 A disclination loop surrounding a folded region in the carbonaceous mesophase. These loops occur in the walls of gas bubbles blown in the plastic mesophase.

(hexagonal) symmetry for the graphite sheet—a surface crystal. A complete description of both wedge and twist disclinations in surface crystals is given by Harris.[3,15] The rotation vector of a wedge layer disclination is parallel to the disclination line and normal to the layer. Wedge layer disclinations of strength $S = p/6$, with p any integer, are allowed. Wedge layer disclinations of strength $S = \pm 1/6$ are shown in Fig. 8. Twist layer disclinations can have complex configurations that resemble Möbius strips. An individual layer can bend and twist as it meanders through the lamelliform morphology and upon connecting with itself may produce a twist layer disclination.

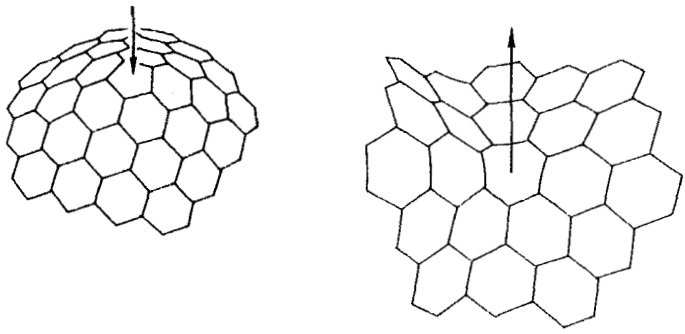


FIGURE 8 Wedge layer disclinations of rotation $\pi/3$ and $-\pi/3$.

3 OPTICAL MICROSCOPY

The utility of polarized-light microscopy for the study of disclination structures in the carbonaceous mesophase stems from the birefringence characteristic of crystalline graphite that commences from the parallel alignment of the mesophase molecules. Under the condition of crossed polarizers, the polarized-light extinction contours define the loci of mesophase layers that lie either parallel or perpendicular to the line of polarization of the incident light, and observations made by parallel polarizers or the sensitive-tint plate at various angles of stage rotation afford a means of resolving between the three possible layer orientations underlying each region or band of extinction. The structural sketches in Figs. 9 and 10 were prepared by applying overlays successively to a series of polarized-light micrographs taken at increasing angles of stage rotation and are thus representations of the layer morphologies authentic within the limits of precision of the optical micrographs.

The polarized-light response of polished cross sections was employed to map the lamellar arrays in bulk mesophase.[9,16] The response characteristics are similar to those of nematic liquid crystals.[17] Prominent features of the

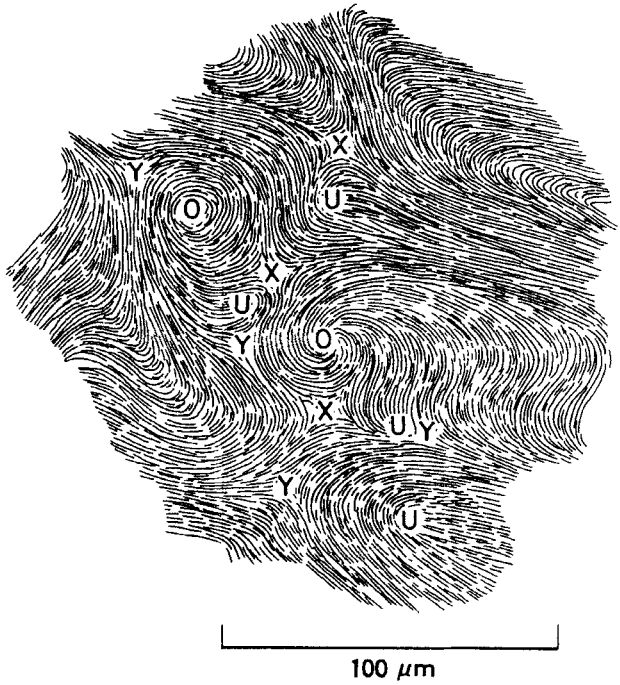
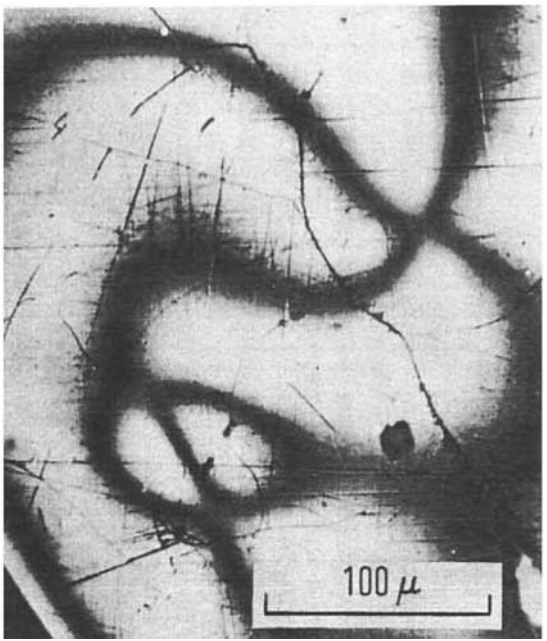


FIGURE 9 Coarse lamelliform morphology of freshly coalesced mesophase. Reproduced by permission from *J. Chim. Phys.*, special number, 33 (April 1969).



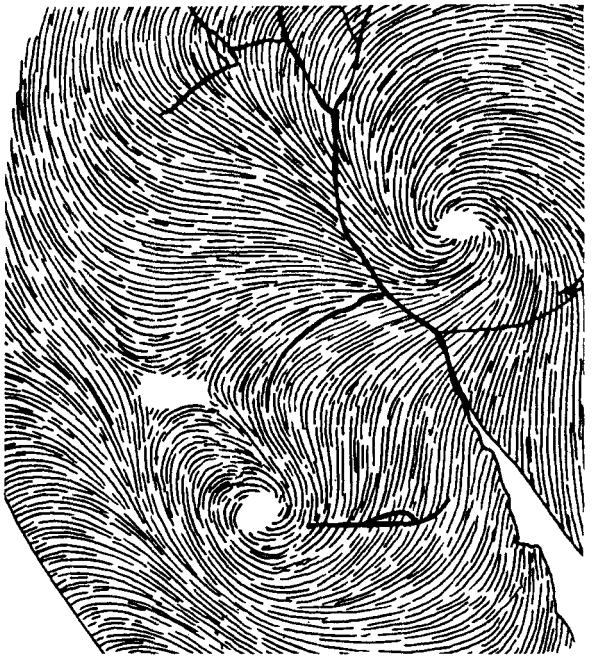


FIGURE 10 Disclination structures underlying extinction crosses of strength $S = \pm 1$ in freshly coalesced mesophase. Polarizers crossed at vertical and horizontal orientations. Reproduced by permission from *J. Chim. Phys.*, special number, 33 (April 1969).

extinction contours observed with crossed polarizers are the nodes of strength $S = \pm\frac{1}{2}$, where the extinction contours pinch down sharply, and the crosses of strength $S = \pm 1$ which appear as intersections of contours. When the plane of polarization of the incident light is rotated, the extinction contours sweep over the surface of the specimen, but the nodes as well as the centers of the nontransitory crosses remain fixed at particular points as the extinction contours rotate about these points either with or against the direction of rotation of the plane of polarization. Honda *et al.*[18] proposed the symbols U, Y, O, and X to suggest the layer configurations in the immediate neighborhood of the respective disclinations.

A structural map of a typical section of coarse undeformed mesophase[16] is given in Figure 9. In this region, the four types of node and cross appear in approximately equal number. A more detailed map of disclination structures underlying extinction crosses in freshly coalesced mesophase[16] is illustrated in Figure 10. Under crossed polarizers, core regions approaching 20 μm show extinction at all angles of the plane of polarization, indicating that the cores comprise either disordered regions or layers lying parallel to the plane of section. Note that the extinction contours of the O-type crosses of Figure 10 appear at angles relative to the directions of the crossed polarizers; the underlying helical nature of these disclination structures is commonly found in freshly coalesced mesophase.

4 ELECTRON MICROSCOPY

Although polarized-light micrography gives an indication of the disclination structures present in the carbonaceous mesophase, scanning electron microscopy can reveal directly the actual configuration of these disclinations to a finer level of resolution. The scanning electron micrograph is an exact representation of the surface features on a micrographic plane of section that has been properly etched. Such micrographs of oriented sections of needle coke[19] have been used to identify the geometry of the disclinations in the carbonaceous mesophase and graphite. In the ion-etching technique used to prepare the samples of needle coke, the carbonaceous mesophase is first graphitized. The graphitization introduces small intercrystallite cracks that identify the orientation of the adjacent layers, and the ion-etching with xenon of the polished surface enhances the details of the graphitic structure.

Scanning electron micrographs of the wedge disclinations in a graphitized specimen of needle coke are shown in Figures 11–13. In each figure, the intercrystallite cracks appear as dark lines separating the crystallites or packets of graphitic layers. The configurations of these disclinations correspond to those sketched in Figure 4 and those obtained from the analysis

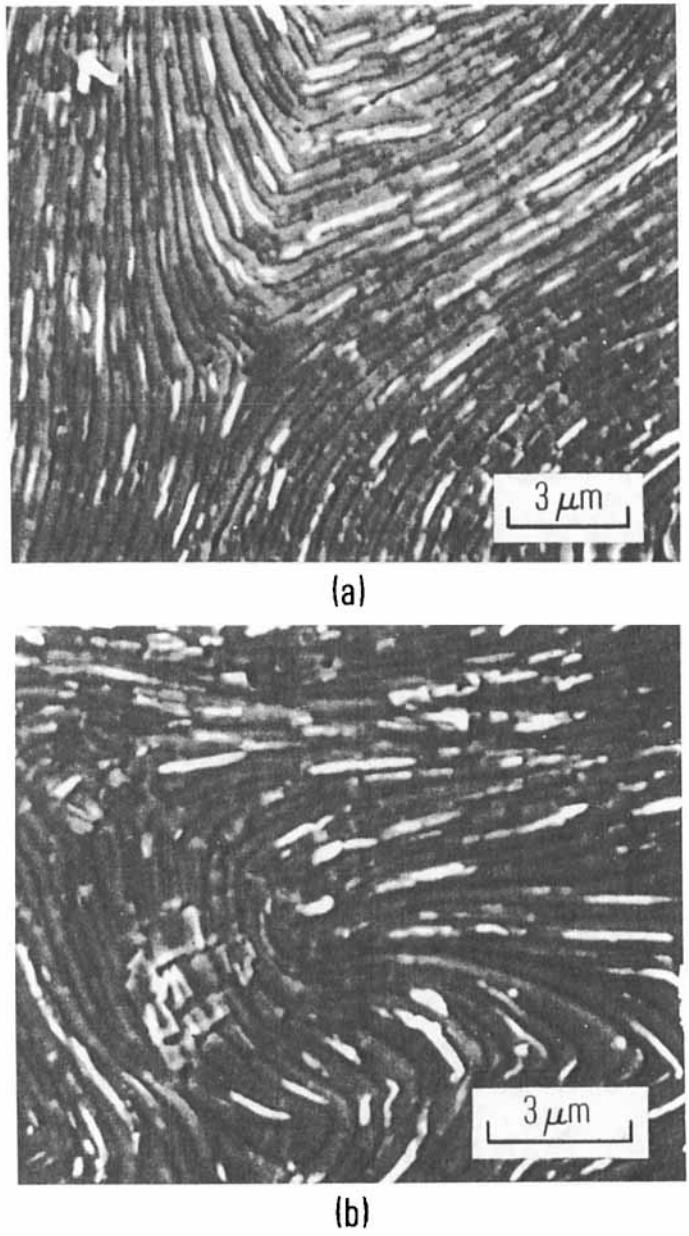


FIGURE 11 Scanning electron micrographs of wedge disclinations in graphite of strength (a) $S = -\frac{1}{2}$ and (b) $S = +\frac{1}{2}$.

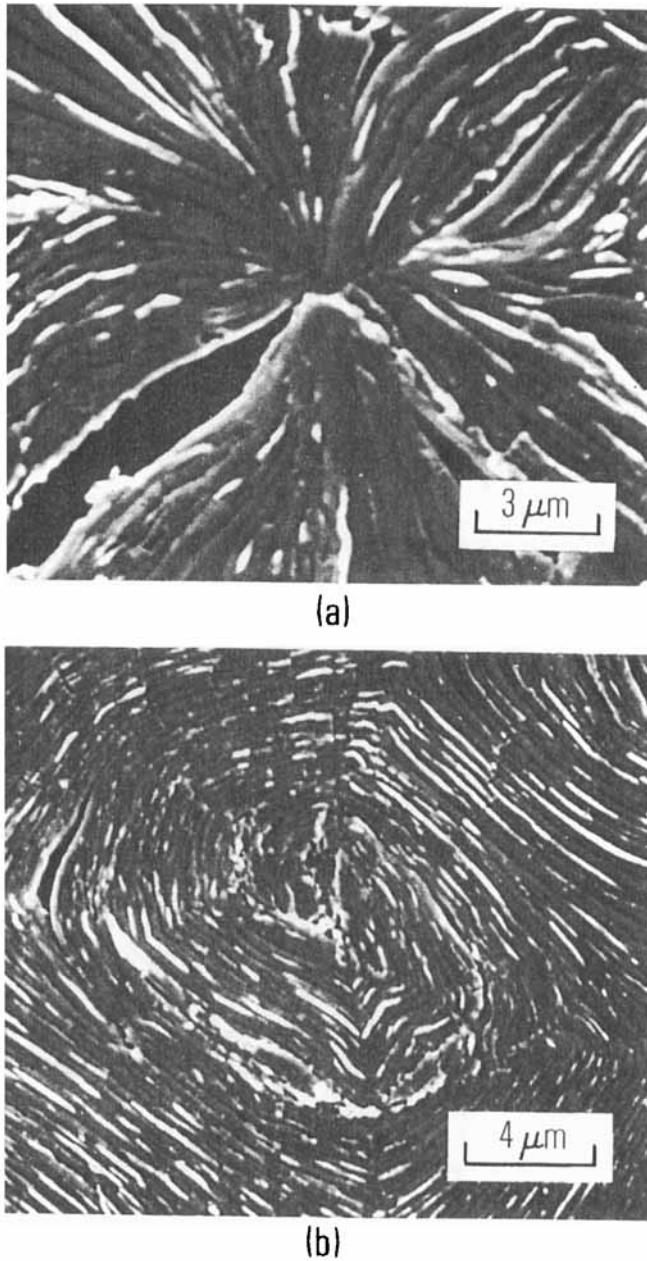


FIGURE 12 Scanning electron micrographs of wedge disclinations in graphite of strength $S = +1$. The sunburst configuration (a) involves mostly splay and (b) involves mostly bend.

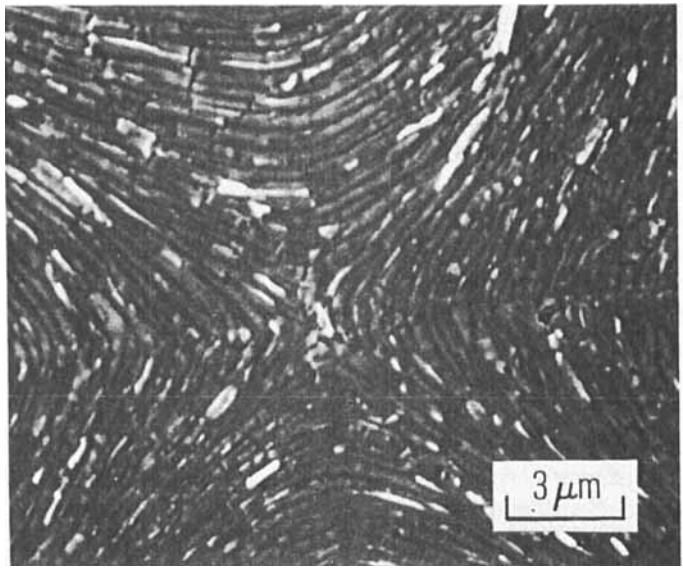


FIGURE 13 Scanning electron micrograph of wedge disclination in graphite of strength $S = -1$.

of the polarized-light response (Figure 9). The structures around the disclinations are little modified despite the extensive anisotropic shrinkage during graphitization.

The interpretation of the scanning electron micrographs is simplified by the use of specimens with a morphology that has a specific geometry including a strong preferred orientation. Disclination structures characteristic of the fine fibrous morphology[19] that results from uniaxial extension of the carbonaceous mesophase[20] are illustrated by Figures 11–13. The layers lie parallel to the fiber axis, and, in the plane perpendicular to this axis, the layers are tightly folded and bent. The normals to all the layers lie in this transverse plane, which is the plane of section in the electron micrographs. The wedge disclinations in needle coke have fibrous symmetry along their core, which is normal to the plane of the micrographs, and thus their geometry is uniquely defined.

5 PRACTICAL ASPECTS

The lamelliform morphology, with the attendant disclination structures, forms the basic structural framework of cokes and graphitic materials, and an understanding of the various types of morphologies formed when the carbonaceous mesophase transforms and hardens appears to be fundamental

to such practical characteristics as graphitizability, fracture behavior, and structure-sensitive properties such as thermal expansivity and dimensional stability under reactor irradiation.

Thermal graphitization, the conversion by heat treatment of a carbon to the equilibrium crystal structure of graphite with parallel planar layers spaced at 3.354 Å, must depend sensitively on the detailed structure at the starting point, i.e., the lamelliform structure frozen in place as the mesophase hardens to coke. Studies of x-ray scattering from carbonized coals[21] suggest that the molecular layers may be imperfect or wrongfully connected both in respect to the internal arrays of fused hexagons and in respect to their aromatic polymerization with neighboring molecules in the same or nearly the same layer. The layers may be buckled either because of layer wedge disclinations (Figure 8) or because, owing to cross-linking to other layers, two layers that join to form a larger one may not be able to come into perfect parallel alignment with the adjacent layers. The graphitization of such large, imperfect, buckled, and cross-linked layers is by no means a simple process of obtaining registry between the layers by small displacements or rotations.

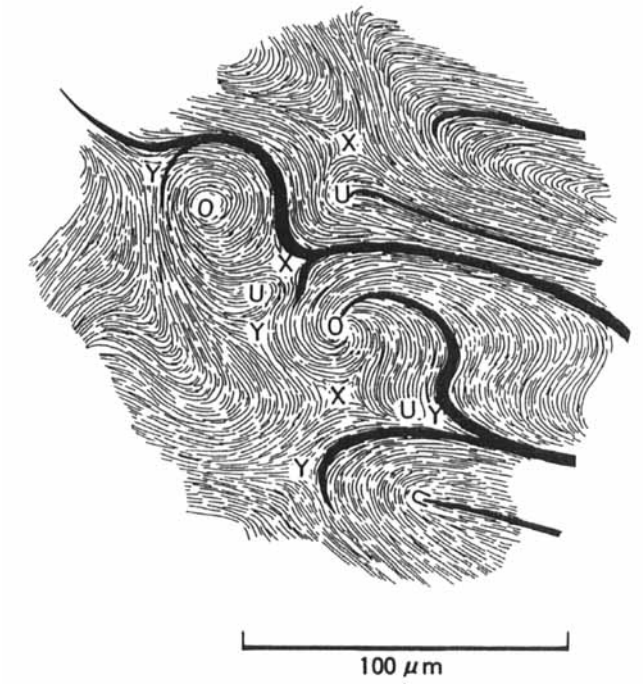


FIGURE 14 Fracture by cleavage through disclinated lamelliform morphology. Fractures produced by tensile stress are assumed to be propagating from right to left.

The dewrinkling of these curved layers during graphitization must necessarily involve mass transfer by diffusion within the layers.

The fracture of polycrystalline synthetic graphite is dependent upon the morphology of its microconstituents. When a cleavage crack attempts to follow a basal layer, it can become diverted into a nonpropagating direction[22] by the bends, folds, and discontinuities present in an array of disclinations. Multiple fracturing occurs often and frequently appears as splintered regions of needle coke grains. Graphite thus has a high work of fracture compared to most ceramic materials.[23]

Some mechanisms of energy absorption during the progression of a cleavage crack through a disclinated layer structure (the structure illustrated in Figure 9) are shown in Figure 14 by considering various possible cleavage paths. Disclinations offer means of stopping cracks or switching them to alternative directions. Curvature and folds can deflect cleavage to nonpropagating directions. Accordingly, only a few paths can be traversed successfully, and these may involve energy-absorbing diversions and false starts.

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