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A MICROGRAPHIC STUDY OF CARBONIZATION AND GRAPHITIZATION OF AN EXTRACTED COAL-TAR PITCH

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J.L. WHITE, J. DUBOIS and C. SOUILLART

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Joint Nuclear Research Center
Petten Establishment - Netherlands

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KEYWORDS

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CARBONIZATION
GRAPHITIZATION
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COAL
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STACKING FAULTS
ANISOTROPY
HEAT TREATMENTS
HARDNESS
SHRINKAGE
CRACKS
LAYERS

ABSTRACT

Polarized-light micrography has been employed to investigate the microstructures formed in the carbonization and graphitization of a coal-tar pitch from which the insoluble particles have been removed by solvent extraction. Prominent features in the polarized-light extinction contours are the nodes and crosses, which are identified as four types of linear defects in the stacking of the aromatic layer planes. The coalescence process produces mostly cross-type stacking defects, but the deformation of the plastic mesophase caused by the percolation of gas bubbles results in an abrupt increase in the number of stacking defects and the formation of highly oriented regions with many folds in the layer planes. The principal effects of further heat-treatment may be summarized as hardening and formation of shrinkage cracks, fold sharpening, and finally the formation of mosaic blocks and kinks. By relieving boundary restraints and providing void space for small displacements of bulk material, the process of shrinkage cracking appears to be an essential precursor to fold-sharpening. In this latter process, the curved layer planes in the folds adjust to form sharp and approximately linear boundaries which may be twin boundaries in the ideal case. At temperatures near 3000°C, mosaic blocks and kinks are formed on a fine scale as the final step in graphitization.

INTRODUCTION

Recent studies by several groups (1 - 4) on the structural conditions for graphitization, and most notably the work by Brooks and Taylor (1), have demonstrated the significance of the mesophase transformation that takes place in graphitizable organic materials during pyrolysis to about 450°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 objectives in the micrographic studies reported here were to obtain further evidence of the structures formed during the relatively short lifetime of the plastic mesophase, and to relate these structures to those which are formed at various stages of the graphitizing heat treatment.

In the initial stages of nucleation and growth, the mesophase appears as spherules with the simple structure first demonstrated by Brooks and Taylor (1). As illustrated by Fig. 1, the polarized-light response of the mesophase may be employed (4) to show that the layer planes of the simple spherules are stacked perpendicular to a polar diameter and curve to meet the interface with the isotropic phase normally.

As carbonization progresses, the growing mesophase spherules, which are more dense than the isotropic parent phase (2), sink to the bottom of the container where coalescence takes place as illustrated by Fig. 2. When viewed microscopically with crossed polarizers, the bulk mesophase displays a complex ensemble of extinction contours. Two prominent features are the nodes and crosses, which are found to remain fixed in position on the specimen when the plane of polarization of the incident light is rotated.

In a previous paper (4) it was shown that the nodal regions correspond to two different types of linear defects in the stacking of the mesophase layer planes. The present paper extends this classification of defect structures to include the cross regions, and then undertakes a micrographic description of the effects of deformation, hardening, shrinkage, and graphitization when the mesophase is heat-treated to 3000°C. As in the previous work (4), this study is limited to a coal-tar pitch from which the insolubles have been removed by solvent extraction.

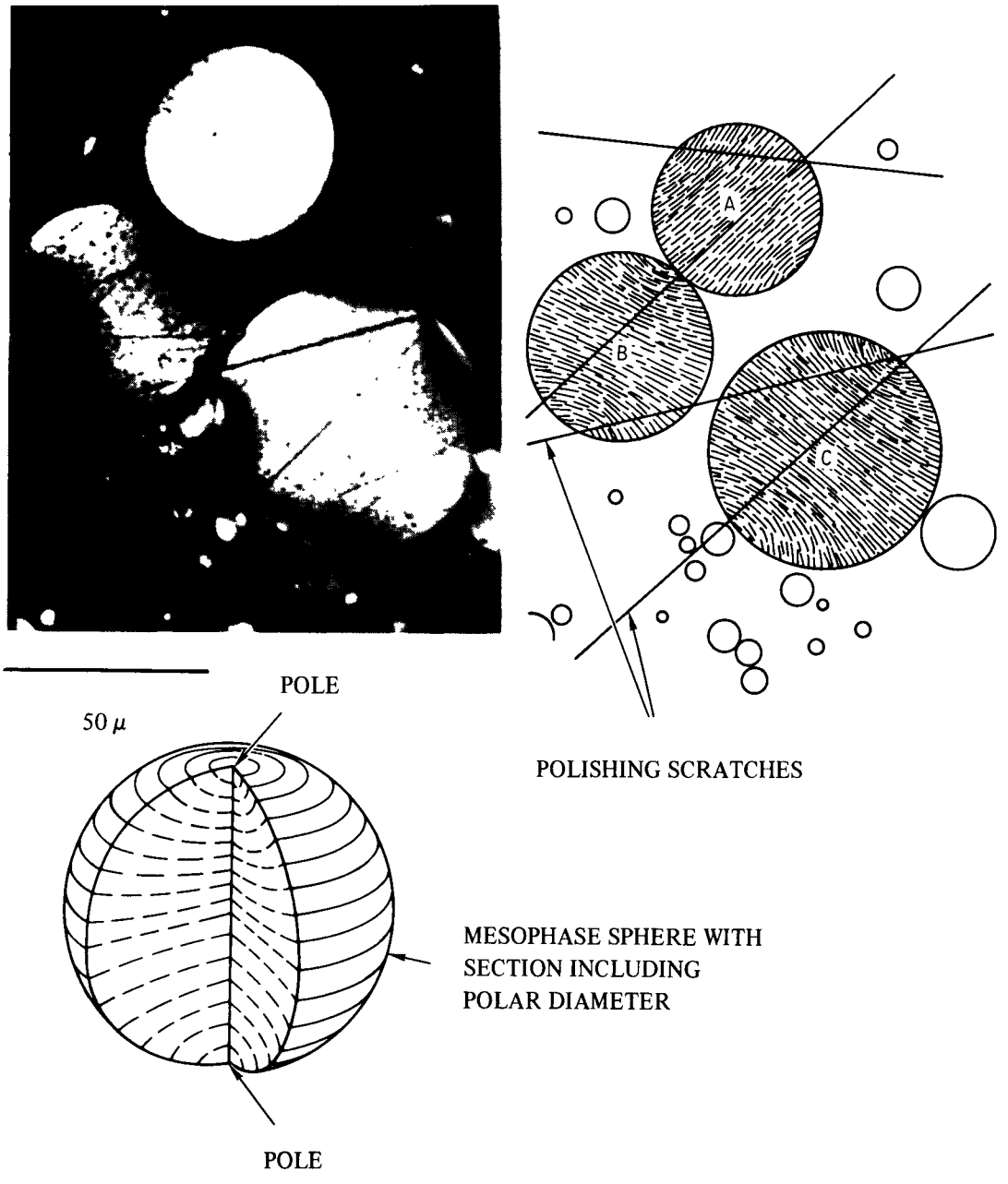

Fig. 1 – Structure of mesophase spherules nucleated and grown in an extracted coal-tar pitch. Spherule C has been sectioned fortuitously at the polar diameter.
Photomicrograph taken with crossed polarizers.

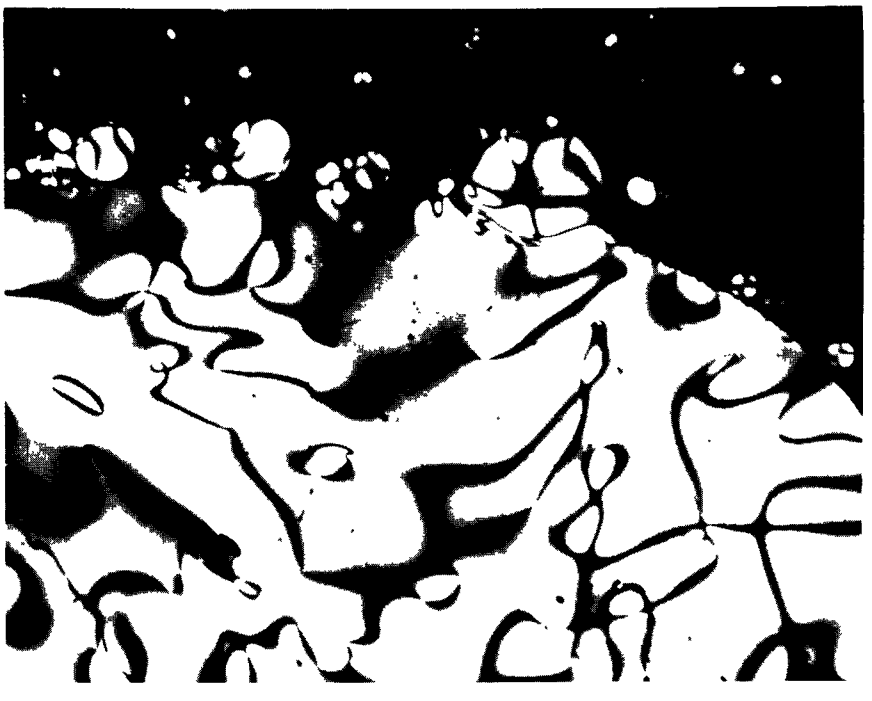

Fig. 2 Polarized-light extinction contours in coalesced mesophase.

EXPERIMENTAL

A commercial coal-tar pitch used for the impregnation of conventionally processed graphites was selected for these studies because of its relatively low content of insoluble particles. This starting material was Reilly Tar and Chemical Corporation Type I Impregnating Pitch, containing less than 3 wt. - % insoluble in quinoline. The insoluble particles were removed by extraction with tetrahydrofuran and filtration through a 2-micron sintered glass filter. The yield from this extraction process was 78%.

The extracted pitch was analyzed for carbon, hydrogen, oxygen, and sulfur, and the results are given in Table I. A spectrochemical analysis revealed the presence of no other elements in significant concentration.

Since the mesophase transformation and its hardening process are quite sensitive to time and temperature (1, 2), a temperature-gradient heat-treatment technique was used to obtain a series of specimens representative of slightly varying degrees of heat-treatment. The temperature gradient is maintained in a large steel bar in which a series of glass pyrolysis cells are inserted. The bar is heated slowly to avoid excessive bubbling in the pitch specimens. A gently moving argon atmosphere is used to carry away the gaseous pyrolysis products and to protect the specimens from oxidation.

A baking furnace with programmed temperature control was used to prepare coalesced mesophase in bulk form relatively free from deformation by percolating gas bubbles. A high thermal inertia was employed to damp out thermal fluctuations in the furnace before they reached the pyrolysis specimen. The heating schedules were determined from preliminary runs with the temperature-gradient heat-treatment facility. A typical heat-treatment involved 50 hours to traverse the temperature interval of 400 to 500°C.

The heat treatments to higher temperatures were made using a graphite resistance furnace capable of reaching 3000°C. Pieces of the hardened mesophase (baked to 600°C) were placed in graphite cups designed to be stacked vertically in the furnace. Successive heat-treatment runs were made at 100° intervals to 1000°C, 200° intervals to 1400°C, and 400° intervals to 3000°C. The temperature was measured by an optical pyrometer sighted on a black-body cavity in the graphite cup selected for removal after each heat-treatment. In each case, the maximum temperature was held steady for one hour.

Structural sketches of selected mesophase microstructures were prepared using an overlay technique applied to a series of polarized-light micrographs taken at various angles of the plane of polarization (4). The microstructure is thus defined in terms of the intersections of the mesophase layer planes with the micrographic plane of section.

TABLE 1

Analysis of Extracted Impregnating Pitch		
Element	**Content (wt. - %)**	**Analytical Method**
Carbon	91,3	Chemical Analysis
Hydrogen	5,1	Chemical Analysis
Oxygen	1,7	Activation Analysis (General Atomic)
Sulfur	0,4	Activation Analysis (General Atomic)

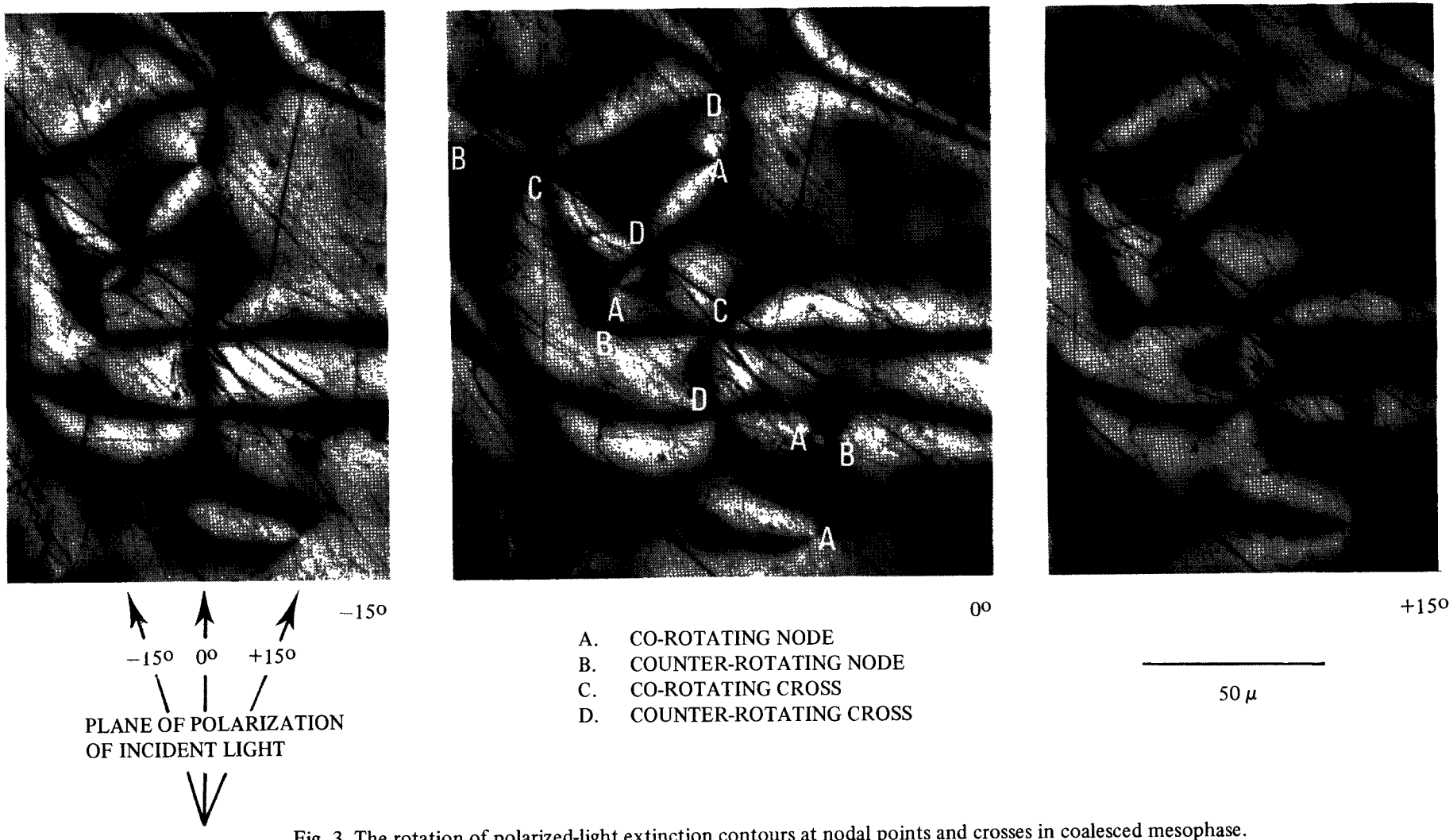

Fig. 3 The rotation of polarized-light extinction contours at nodal points and crosses in coalesced mesophase.

MESOPHASE DEFECT STRUCTURES

A region of bulk mesophase containing crosses as well as nodes when observed with crossed polarizers is shown in Fig. 3. When the plane of polarization of the incident light is rotated, the extinction contours move around the fixed centers of the crossed and nodes to define four types of behaviour:

A. co-rotating node
B. counter-rotating node
C. co-rotating cross
D. counter-rotating cross

It is noteworthy that the rate of rotation of the crosses half that of the nodes, i.e. for one complete revolution c the plane of polarization of the incident light, th extinction contours make two complete revolutions aroun either type of node but only one complete revolutio around either type of cross.

Fig. 4 is a structural sketch of the region shown by Fig. 3 The four types of nodes and crosses correspond to fou specific classes of linear defects in the stacking of th mesophase layer planes.

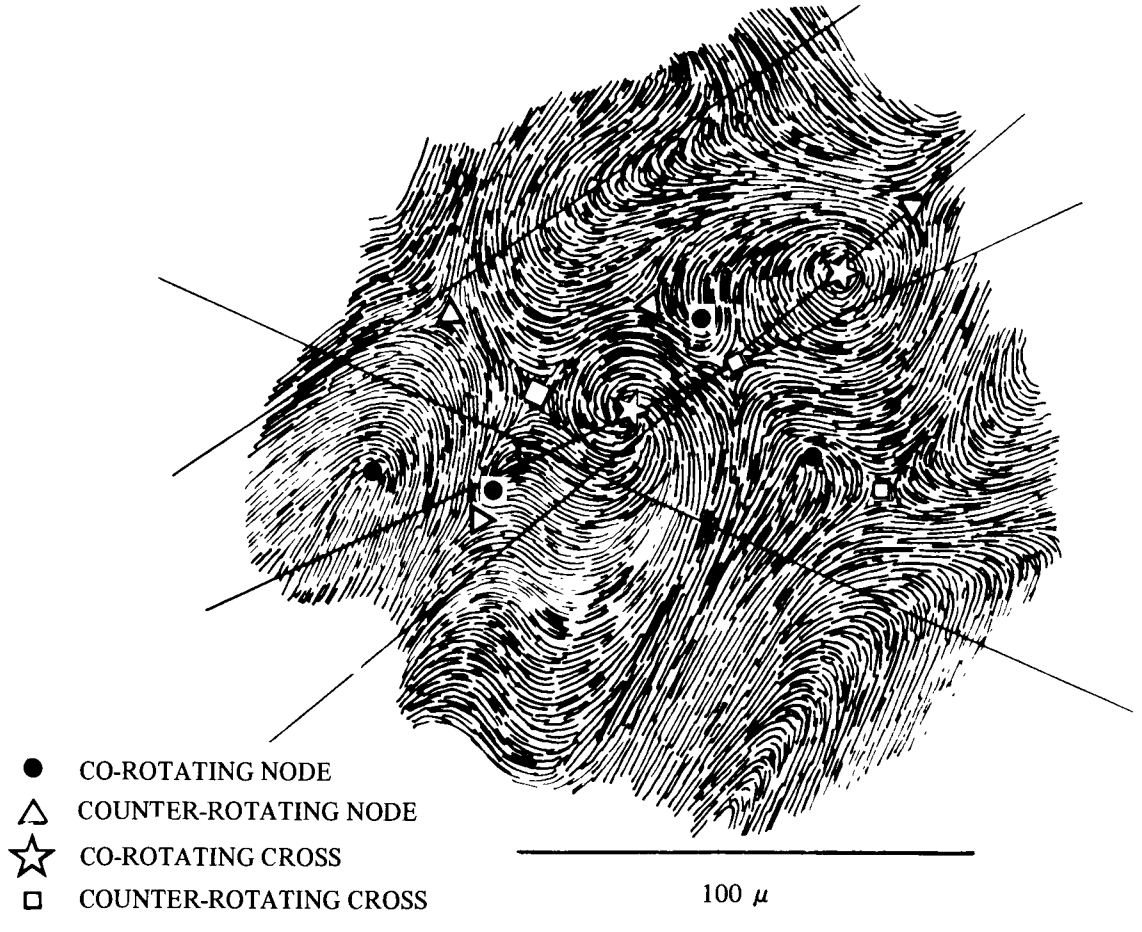

Fig. 4 Structural sketch of bulk mesophase; same area as shown in Fig. 3.

For clarity, these four classes of defects are diagrammed in Fig. 5, in which the directions of rotation of the polarized-light extinction contours are also indicated. Using the rule that extinction occurs with crossed polarizers when the layer-plane intersections lie either parallel or perpendicular to the plane of polarization of the incident light, the relative directions and rates of rotation of the extinction contours around each type of defect may be verified by consideration of Fig. 5. Thus the polarized-light behaviour offers a simple means of characterizing the four types of mesophase stacking defect.

As previously shown (4), both types of nodal structures involve the stacking of layer planes perpendicular to one another at the center of the nodes. The co-rotating node corresponds to a simple arch structure, with the layer planes lying concave or radial relative to the center of the node. The counter-rotating node possesses a delta structure with three-fold symmetry in the idealized case, and the curved layer planes lie convex relative to the center of the node.

The co-rotating cross is seen to correspond to a simple circular or, more generally, helical arrangement of layer planes. The counter-rotating cross is due to a more complicated structure, which possesses four-fold symmetry in the idealized case and in which the curvature of the layer planes is convex to the center of the cross. The counter-rotating cross is thus a four-fold version of the three-fold delta structure of the counter-rotating node.

This classification of the mesophase stacking defects into four basic types of linear defect structures appears to cover all such structures with an appreciable frequency of occurrence in pyrolyzed coal-tar pitch. Although a peculiar behaviour of the extinction contours is occasionally observed, it is believed that most if not all of these cases can be attributed to special angles of section, e.g. a co-rotating node sectioned nearly parallel to the nodal line.

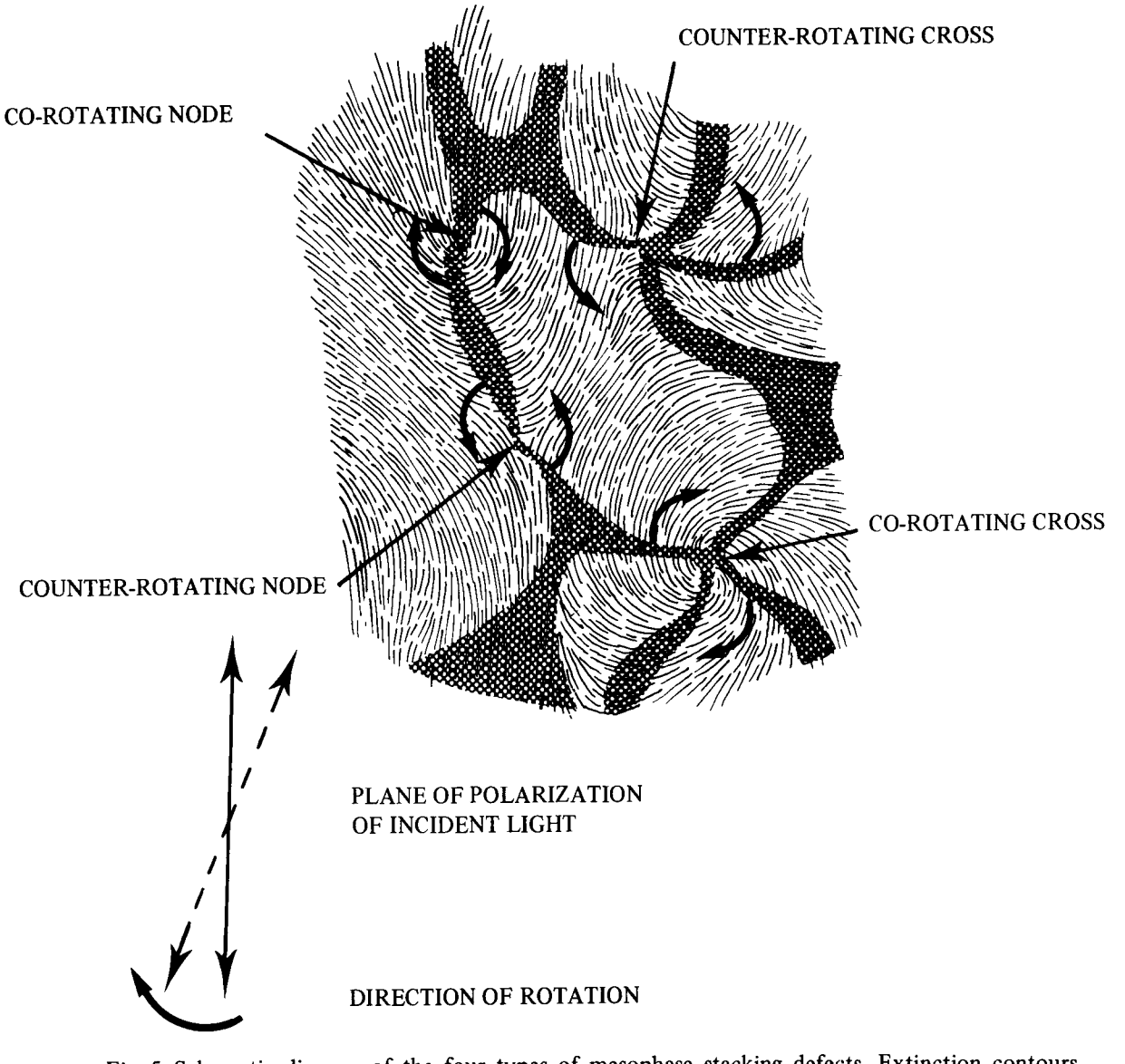

Fig. 5 Schematic diagram of the four types of mesophase stacking defects. Extinction contours are shown for the case of crossed polarizers.

COALESCENCE

Examinations of mesophase droplets at various stages in the process of coalescence were made to learn how the stacking defects originate. Fig. 6 illustrates several stages of coalescence observed in a specimen which was slowly pyrolyzed in the baking furnace and furnace cooled from the maximum pyrolysis temperature (465°C). The initiation of the coalescence process appears to depend on the mutual interleaving of layer planes of the contiguous bodies of mesophase.

The driving force for coalescence is the interfacial tension between the mesophase and the isotropic matrix (1). However the high viscosity of the mesophase severely retards the long-range structural rearrangements within the bulk mesophase which would be necessary to achieve a defect-free mesophase. Thus, even under conditions of very slow pyrolysis, freshly formed droplets arrive and begin to coalesce before the bulk mesophase can reach equilibrium. Accordingly a relatively complex mesophase microstructure is locked into the bulk mesophase by the continuing coalescence processes taking place at the interface with the matrix; this effect also leads to the occasional incorporation of small islands of untransformed pitch.

200 μ

Fig. 6 The coalescence of mesophase spherules to form bulk mesophase.

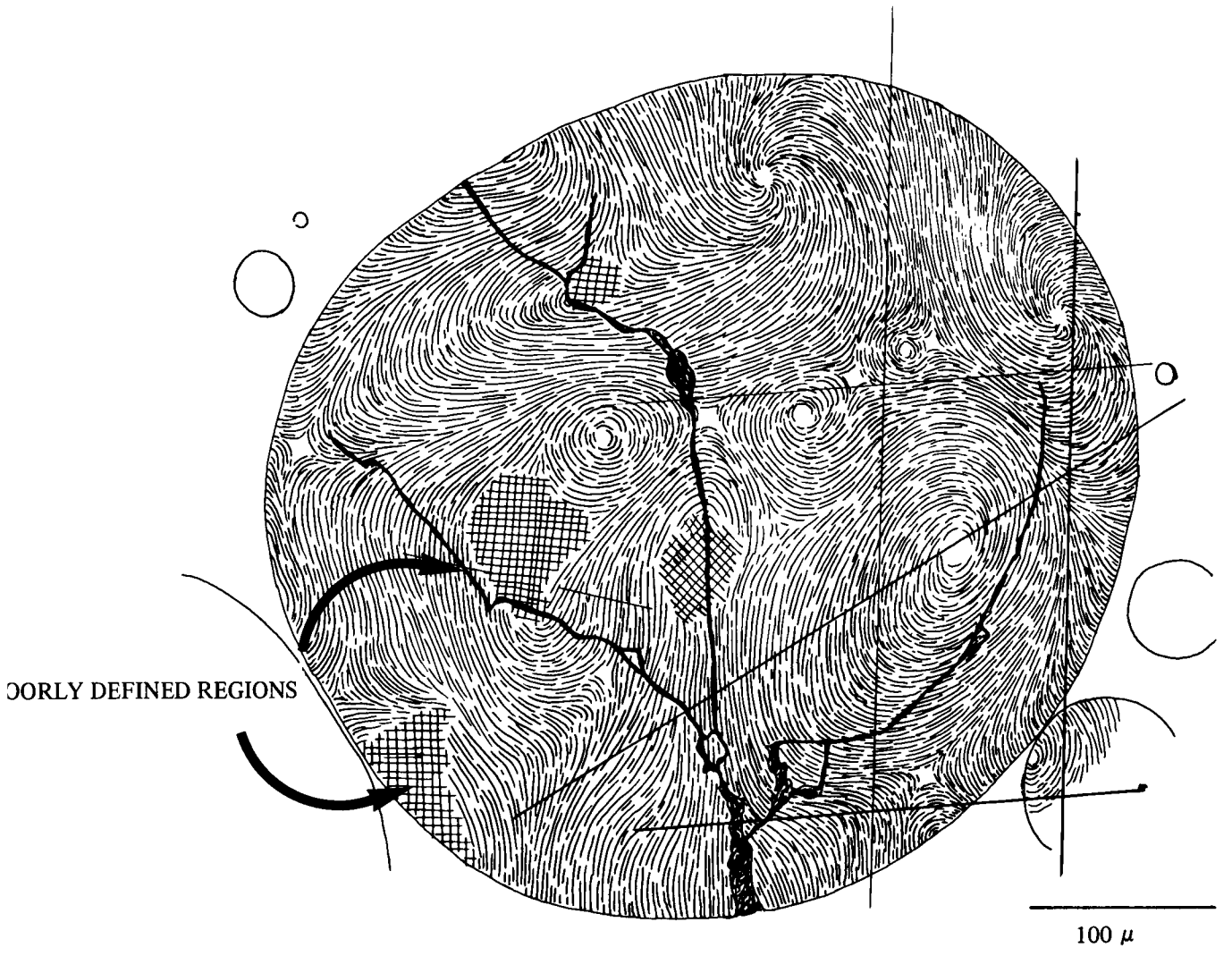

Fig. 7 The structure of a drop of coalesced mesophase.

Fig. 7 illustrates a freshly formed mesophase drop of a size large enough to display a complex ensemble of extinction contours but apparently not yet appreciably deformed by stirring or bubble formation. The structural sketch was made to identify the various defect structures and to see their relations to one another. These examinations indicate that the coalescence process by itself tends to produce cross structures preferentially and with spacings on the plane of section of 15 to 150 microns.

As may be noted from Fig. 3, the nodal structures contrast with the cross structures in the way in which the extinction contours pinch down sharply at the nodes. Fig. 8 represent an attempt to define three cross structures in a freshly coalesced droplet as carefully as the polarized-light sketch ing technique will permit. The defect structures are seen to consist of two co-rotating helical crosses and one somewha elongated counter-rotating cross. There is a region of the order of 20 microns in diameter at the center of each cross for which extinction is nearly complete at all angles of the plane of polarization. This evidence suggests the existence of an appreciable disordered region at the core of each cross structure.

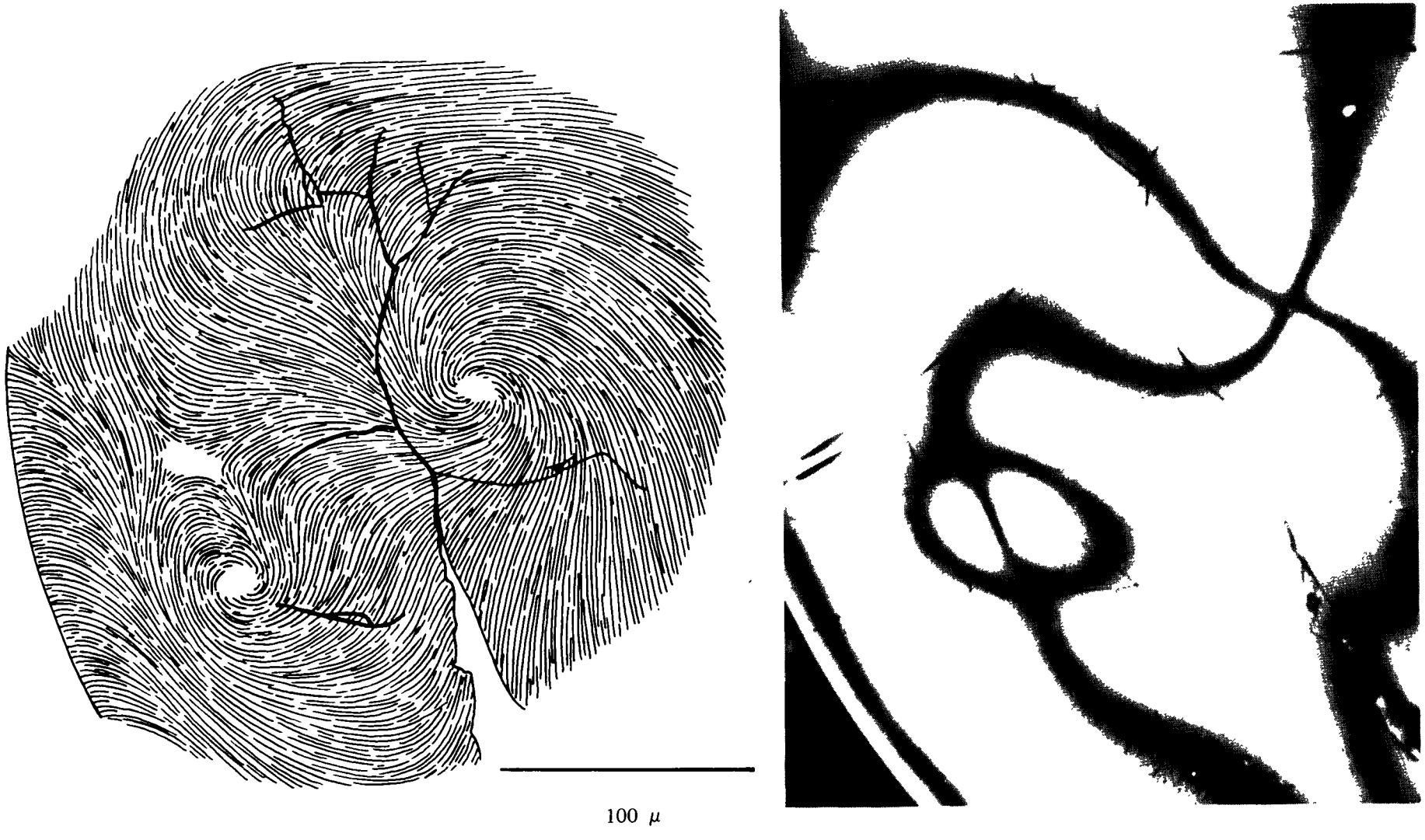

Fig. 8. Detailed microstructure of extinction crosses.

DEFORMATION

When the coalesced mesophase is further pyrolyzed, gas bubbles nucleate and grow in the viscous mesophase and various regions are subjected to large plastic strains. As indicated by Fig. 9, this plastic deformation produces an increasingly fine texture of extinction contours. Two types of fine texture may be distinguished, fibrous and mosaic, but these may simply correspond to two ways of sectioning the same three-dimensional fibrous structure. The density of defect structures in the deformed mesophase is several orders of magnitude higher than in the freshly coalesced mesophase, and the nodal structures occur with higher frequency than the cross structures. However the appearance and behaviour of the nodal and cross structures in the deformed mesophase is essentially the same as observed at lower magnification for the same structures in the freshly coalesced mesophase.

100 μ

Fig. 9 Mesophase deformed by percolation of gas bubbles.

20 μ

A structural sketch was made of a fibrous region in a mesophase specimen in which bubble percolation had only just begun to deform the mesophase so that the fibrous regions were present at a sufficiently large scale to permit application of the sketching technique. The result given in Fig. 10 shows that the elongated extinction contours which produce the fibrous appearance of the deformed mesophase correspond to rather tight folds in the strongly oriented mesophase layers.

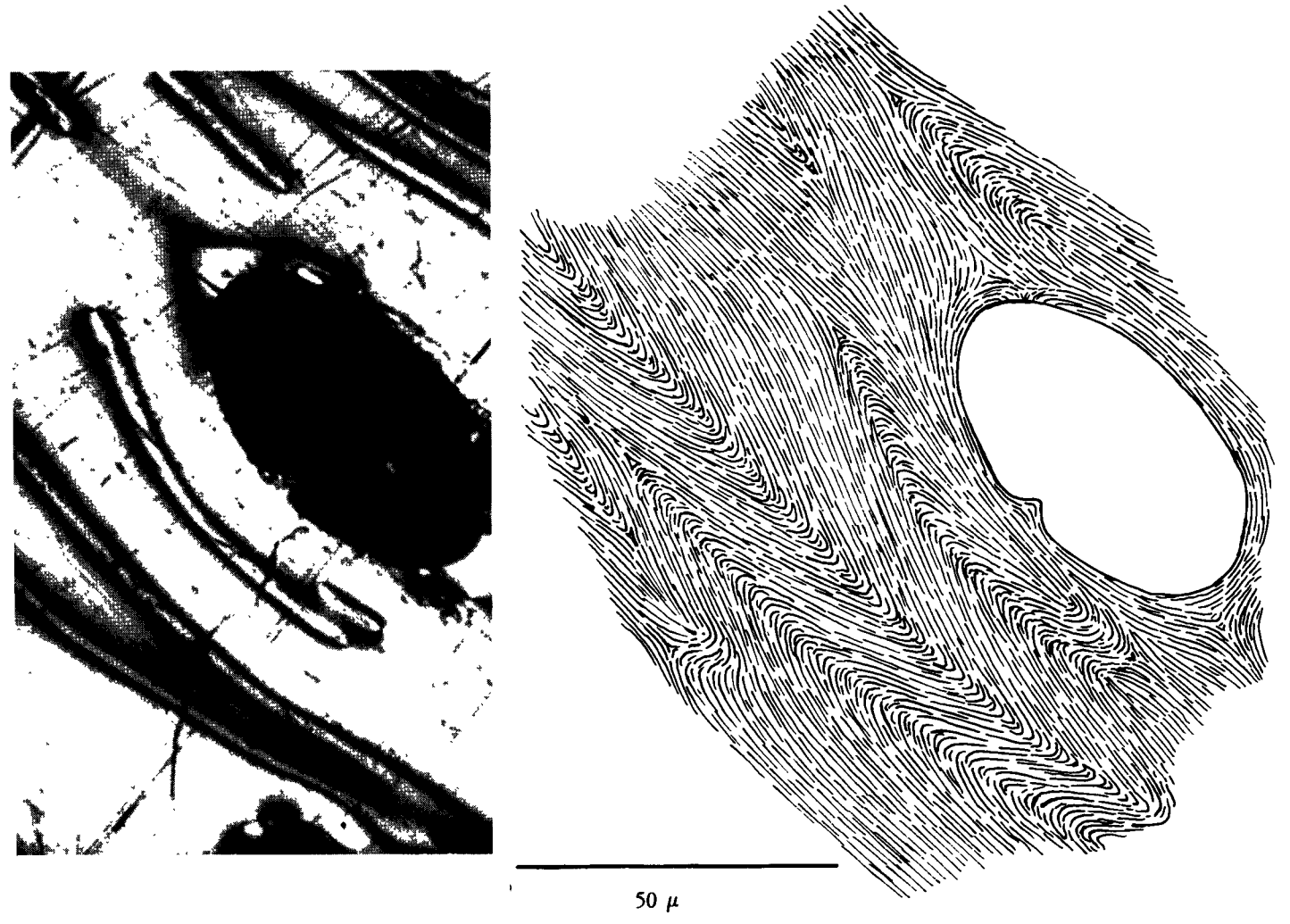

Fig. 10 The structure of mesophase after light deformation by bubble percolation.

HEAT TREATMENT

The foregoing work has demonstrated that the processes of coalescence and deformation of the mesophase produce two types of microstructural components, namely: structures resulting from defects in the stacking of layer planes, and highly oriented regions containing folds. It now remains to see how these characteristic structures are affected by heat-treatments up to and including graphitization at 3000° C. The phenomena observed may be summarized, in order of their occurrence as the temperature of heat-treatment is increased, as (1) the formation of shrinkage cracks, (2) the sharpening of curved and folded layers to form approximately linear boundaries, and (3) the formation of mosaic blocks.

The immediate effect of continued pyrolysis on the properties of the liquid mesophase is to increase the viscosity, resulting ultimately in the formation of a solid coke. This hardening process, which is the subject of a current study, prevents the bulk flow of material in response to the anisotropic shrinkage of the mesophase. The result is shrinkage cracking due to greater shrinkage in the direction perpendicular to the layer planes than in the direction parallel to the layer planes. This shrinkage cracking is illustrated at low magnification by the micrographs of Fig. 11. The first shrinkage cracks appear shortly after the mesophase has hardened, e.g. as early as 525°C, although dependent on time as well as temperature conditions. The cracks are relatively short until a temperature of about 700°C is exceeded. However by 800°C, the fibrous regions show extensive long-range cracking, frequently exceeding one millimeter in length. Further heat-treatments leads to some increases in number and size of cracks, but no important changes in the general crack texture as observed at low magnification.

Examinations at magnifications near the upper limit of optical methods were necessary to observe the other microstructural effects of heat-treatment. Fig. 12 illustrates the initiation of shrinkage cracks in the hardened mesophase. The structural sketch shows that the mesophase defect structure is similar to that of Fig. 4. The shrinkage cracks appear to form preferentially in the curved or folded regions and tend to run parallel to the layer planes. The mesophase stacking defects appear to play no important role in respect to the formation of the shrinkage cracks.

On heat-treating above 600°C, the shrinkage cracks multiply rapidly and appear in a wide range of sizes. The overwhelming majority of these cracks run parallel to the layer planes. The phenomenon of fold-sharpening has been observed at heat-treatment temperatures as low as 1200°C, and is illustrated in Fig. 13 by specimen heat-treatment to 1400°C. Each fold in the hardened mesophase is broken into segments by a series of shrinkage cracks at fairly regular intervals, and various segments of the original fold have sharpened up to form well-defined, approximately linear boundaries. The radius of curvature at these boundaries becomes too small to be resolved optically, thus introducing the possibility that the original fold has become a twin boundary.

As the heat-treatment temperature is increased, the amount of fold-sharpening increases. However, as shown by Fig. 14 the process is by no means complete at 3000°C, many curved regions still being observed in the original fold structures.

At 3000°C, a further step of structural refinement becomes apparent in several ways. The extinction contours develop a block structure indicating low-angle boundaries of the type associated with polygonization in metals. The crack surfaces, which generally appear as smooth curves in the mesophase heat-treated at 2600°C or below, show a tendency to develop straight segments. Finally thin structures, generally emanating from former folds, appear in a form suggesting the kink structures found in natural crystals (5) or in hot-worked graphite (6). These effects generally appear at a scale of a few microns or less, and thus appear to be the mosaic blocks and kinks observed by Woodruff (6) using electron-microscopy.

CONCLUSIONS

The pioneering work by Brooks and Taylor (1), Ihnatowicz et al (2) and Kipling and Shooter (3) indicates that the mesophase transformation is a general characteristic of graphitizable organic materials and thus appears to be an essential precursor to graphitization. Thus, although the present micrographic work has been limited to a single coal-tar pitch in the extracted condition, the results may be expected to be more broadly applicable to other graphitizable materials. Therefore we summarize below the results which are believed to be significant in furthering our understanding of the processes of carbonization and graphitization.

The processes of the formation, coalescence, and deformation of the plastic mesophase establish the basic elements of the graphite microstructure, namely, the parallel alignment of the aromatic layer planes and the arrangement of the complex folds in the fibrous regions. The nodal and cross structures, as linear stacking discontinuities analogous to dislocations in solid crystals, are essential features of the coalesced mesophase, and the nodal structures, at least, have been found to persist in their basic form to graphitization temperatures; cf. Fig. 15. However they do not appear to play a significant role in the more important processes occurring during heat-treatment: namely shrinkage cracking, fold sharpening, and the formation of mosaic blocks and kinks. In these respects, the formation of the highly oriented and folded fibrous regions is believed to be more important.

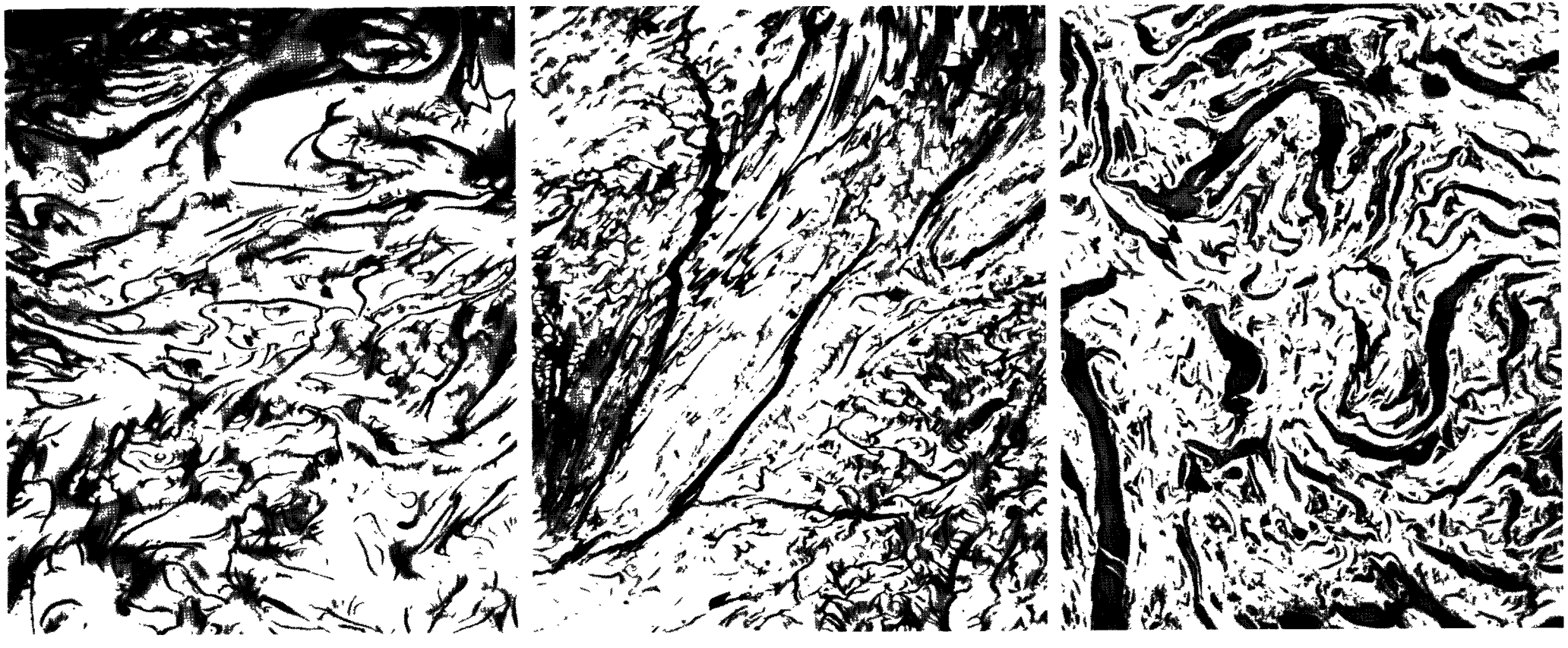

Fig. 11 The development of shrinkage cracks in hardened mesophase after heat treatment. Parallel polarizers.

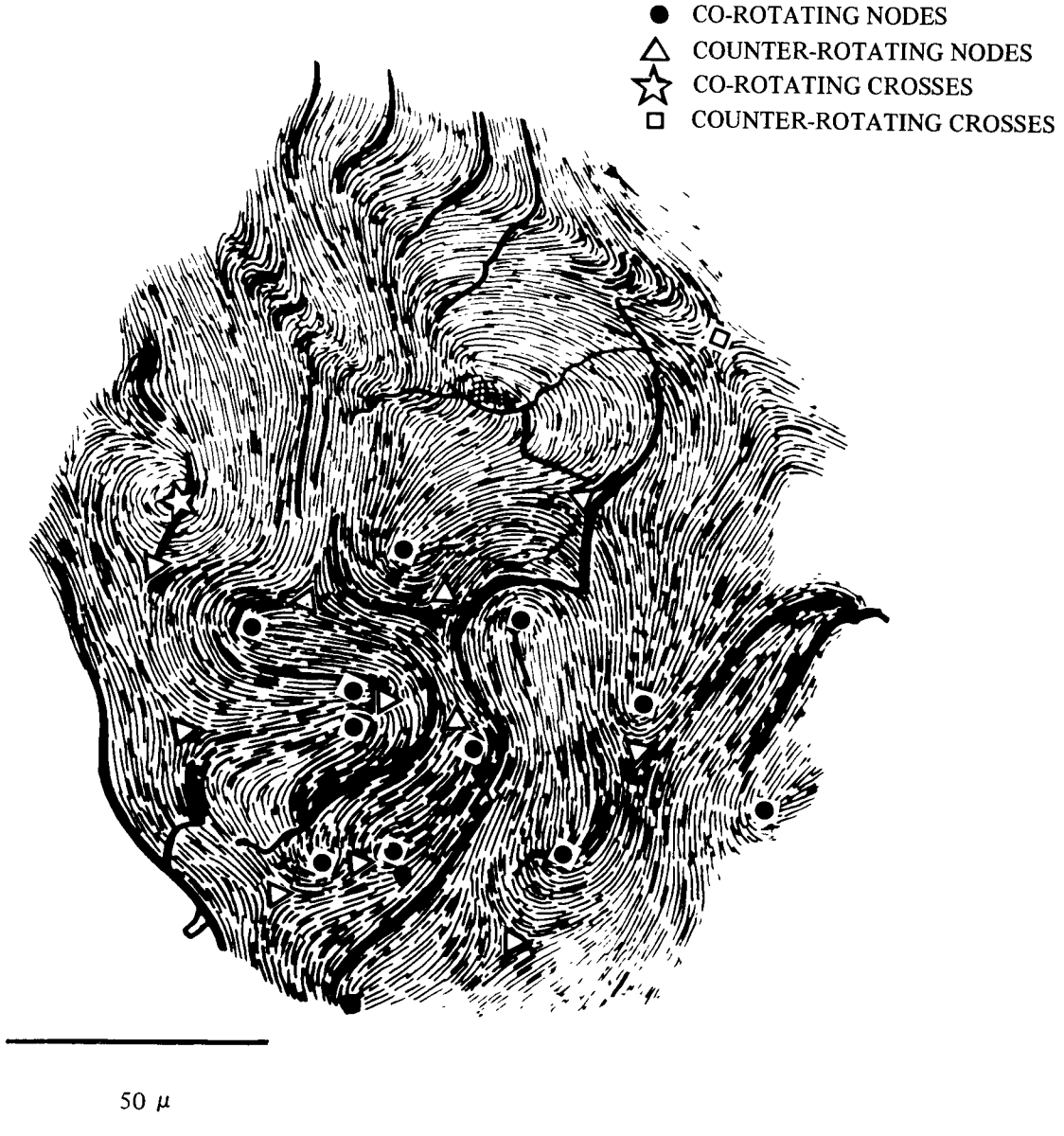

Fig. 12. The structure of mesophase heat-treated to 620°C

50 μ

Fig. 13 Fold-sharpening in mesophase heat-treated to 1400°C. Crossed polarizers.

20 μ

50 μ

Fig. 14 Sharpening of folds and formation of mosaic blocks in mesophase heat-treated to 3000°C. Crossed polarizers.

20 μ

.50 μ

Fig. 15 – Electron micropgraph of a nuclear graphite (graphitized at 3.000° C.), illustrating folds and nodal structures; from E.M. Woodruff of the Battelle Memorial Institute.

The differential shrinkage between the directions parallel and perpendicular to the layer planes, combined with the ease of delamination cracking, leads to a large porosity consisting almost entirely of exposed layer planes rather than planar edges. However, in respect to subsequent processes of graphitization, the significant result of the extensive shrinkage cracking is the removal of restraints around the folds and the formation of an appreciable voidage which allows the small bulk displacements which take place during fold-sharpening.

The phenomenon of fold-sharpening appears to be the first step in final graphitization wherein proper atomic registry is achieved from plane-to-plane. The existence of curved arrays of layer planes precludes the graphitic registry except for local arrangements, but, as the boundary restraints are reduced by shrinkage cracking, it is possible to see that small lamellar displacements will permit folds to form sharp boundaries, which in the ideal case may be twin boundaries with the appropriate graphitic registry existing in the layer planes on either side of the twin boundary. The fact that fold-sharpening is observed to take place over a wide range of temperature, beginning as low as 1200°C and still far from complete at 3000°C, is believed to be due to the wide range of curvatures and residual restraints existing at various points in the microstructures.

The formation of mosaic blocks and kinks at temperatur above 2600°C occurs on such a fine scale as to requi electron microscopy for effective study. However the processes appear to represent the final stages of graphi zation wherein even slight curvatures in the layer planes a replaced by polygonized blocks and local compressi stresses are relieved by the formation of kinks.

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

1. Structure of mesophase spherules nucleated and grown in an extracted coal-tar pitch. Spherule C has been sectioned fortuitously at the polar diameter.
   Photomicrograph taken with crossed polarizers.

2. Polarized-light extinction contours in coalesced mesophase.

3. The rotation of polarized-light extinction contours at nodal points and crosses in coalesced mesophase.

4. Structural sketch of bulk mesophase; same area as shown in Fig. 3.

5. Schematic diagram of the four types of mesophase stacking defects. Extinction contours are shown for the case of crossed polarizers.

6. The coalescence of mesophase spherules to form bulk mesophase.

7. The structure of a drop of coalesced mesophase.

8. Detailed microstructure of extinction crosses.

9. Mesophase deformed by percolation of gas bubbles.

10. The structure of mesophase after light deformation by bubble percolation.

11. The development of shrinkage cracks in hardened mesophase after heat-treatment. Parallel polarizers.

12. The structure of mesophase heat-treated to 620°C.

13. Fold-sharpening in mesophase heat-treated to 1400°C.
    Crossed polarizers.

14. Sharpening of folds and deformation of mosaic blocks in mesophase heat-treated to 3000°C.
    Crossed polarizers.

15. Electron micrograph of a nuclear graphite (graphitized at 3000°C) illustrating folds and nodal structures; from E. M. Woodruff of the Battelle Memorial Institute.

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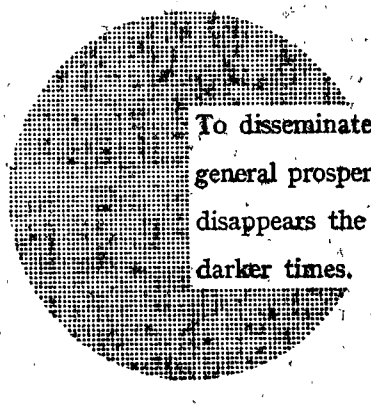

To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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