JOURNAL OF MATERIALS SCIENCE 19 (1984) 3287–3300

Structural components in needle-cokes as studied by etching with chromic acid

Part 1

V. MARKOVIC
Boris Kidric Institute, Vinca, Institute of Materials Science — 170, PO Box 522,
11001 Beograd, Yugoslavia

S. RAGAN, H. MARSH*
Northern Carbon Research Laboratories, School of Chemistry, Bedson Building,
University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, UK

Structures within commercial calcined needle-cokes are characterized by optical microscopy to reveal optical texture and by scanning electron microscopy before and after etching with chromic acid solution at 400 to 423 K. The needle-cokes exhibit an optical texture of medium and coarse-grained mosaics, acicular flow domains and flow domains. The etching studies indicate that the acicular flow domains are made up of rolled and convoluted lamellae which etch to form laths (needle-like) ~ 3 μm across. The mosaics appear when the rolled structures are viewed microscopically sectioned perpendicular to the lamellae. The acicular flow domains appear in longitudinal section. The etching of the flow domains shows that they have a sedimentary structure, 1 to 2 μm layer thickness, suggesting that mesophase coalesces within a layer but not between layers. A model is proposed to explain the origin and separation of structures in needle-cokes as created in the delayed coker.

1. Introduction

Needle-cokes are essential to the production of the graphite arc electrode as used in the steel industry. Needle-cokes are produced in delayed cokers as a premium grade coke. Their specification must include (a) a low coefficient of thermal expansion, (b) high strength after calcination, and (c) high electrical conductivity.

Recent research [1–16] into the formation of needle cokes has been devoted, in the main, to describing and characterising feedstocks. The actual processes leading to carbon formation, as needle-cokes, within a delayed coker are not clearly understood and discussions are speculative. The use of a highly aromatic feedstock seems to be essential.

The structure of a needle-coke can be controlled somewhat by operation conditions within the delayed coker. For example, Hackley [7] in 1960 emphasized this dependence upon coking conditions but suggests that a high temperature gradient within the coker creates excessive thermal circulation and turbulence which may prevent the formation of needle coke. This probably occurs in the upper regions of the delayed coker. It is now generally thought that some degree of turbulence is necessary in the delayed coker to create the characteristic structures found within needle-coke. The structures within needle-coke result directly from the physical and chemical properties of the nematic liquid crystal phase of carbonization and its mechanical manipulation.

Brooks and Taylor [14, 15] were the first to report the formation of liquid crystals during coking of coal and of pitch. This phase, which is termed mesophase, has been observed in the

---

*To whom correspondence should be addressed.

0022–2461/84 $03.00 + .12

coking of petroleum and coal-tar pitch by many workers [17, 18].

During coke formation complex chemical and physical changes occur in the pitch leading principally to dehydrogenative polymerisation reactions [19]. There is an increase in size and concentration of polynuclear aromatics, and with further condensation reactions mesophase is formed initially as spheres (usually). As these spheres of mesophase continue to grow they coalesce initially reforming a spherical shape. Later they fuse into each other and lose their individual identity as "bulk mesophase" is formed.

It must be stressed that the bulk mesophase is initially a fluid and hence can be caused to flow. This process of flow creates within the mesophase changing patterns of "macrocrystallinity" which are observed in optical microscopy as optical texture [20]. Within mesophase there appear to be optimum conditions of flow, dependent on viscosity, to create maximum sizes of macrocrystallinity. The chemical composition of the parent pitch (dominantly) and conditions of carbonization (secondarily) determine the viscosity of the resultant mesophase.

With increasing flow or movement of mesophase, associated with a decreasing viscosity caused perhaps by increasing temperature of the system, the size of the macrocrystallinity (optical texture) can increase. Coke with the largest size of optical texture has probably passed through a mesophase of relatively low observable viscosity.

However, as the flow or movement of mesophase is increased beyond that discussed above, e.g. by a more energetic mechanical manipulation, then the size of the optical texture is reduced [18] (but never to zero). Further, unique conditions of mesophase manipulation can cause unique structures to develop. It is probable that the delayed coker manipulates mesophase in a unique way. This paper speculates on aspects of this behaviour.

Discussions of structures in needle-coke were made first by White *et al.* [21] and Zimmer *et al.* [22]. The authors analysed the polished surfaces of cokes using polarized-light optical microscopy and hot-stage microscopic techniques to examine the formation of deformed microstructures during mesophase development. They described deformed microstructures such as the fibrous or acicular and lamellar structures of needle coke. White *et al.* [21] suggested that deformation of mesophase may result from internal stresses created by bubble percolation as well as by the flow of input parent pitch through mesophase within the drum of the delayed coker.

Buechler *et al.* [23, 24] showed that needle coke structures could be formed by mechanical deformation of mesophase. They produced an acicular flow type of anisotropy (optical texture) which quickly relaxed, returning to undeformed domain type optical texture. Obviously, in the delayed coker there is no mechanism for this relaxation and acicular structures persist.

Later Balduhn *et al.* [18] studied the influence of shear stress upon mesophase deformation in a viscometer and showed that needle-coke (acicular) structures were formed. These structures are very similar to those found by mechanical deformation of spherical mesophase [23].

Essential features of the microstructure of anisotropic carbon include disclinations [25] which are introduced during the formation and deformation of the carbonaceous mesophase. They are the result of realignment of structure (constituent lamellae) probably during coalescence processes. They are structural imperfections of low energy extending over distances of micrometers. Actual disclinations in bulk mesophase may vary in character from pure twist to pure wedge. White [26], for his carbonization systems, reports that pure wedge disclinations are characteristic of the acicular microconstituent while mixed disclinations with various levels of twist component are characteristic of the lamellar (domain) microconstituent. Disclination density may be increased by deformation as well as by spontaneous generation in tightly folded regions [26].

The acicular type of optical texture is an extensively deformed microconstituent of needle coke. This deformed microstructure must have developed before the transformation of fluid mesophase to semi-coke was complete. Once semicoke is formed then its structure is established and cannot be changed by subsequent heat treatment.

Disclinations play a very important role in properties such as fracture, graphitizability and thermal expansivity. The presence of recognisable disclinations in the bulk mesophase of needle coke feedstock was regarded as being responsible for micropore formation and for the low coefficient of thermal expansion (CTE) [26, 27].

Fitzer and Holley [28] studied the influence of different shear rates upon the thermal expansion behaviour of resultant coke. They found that lower shear rates do not influence or disturb the formation of disclinations. However, if higher shear rates were applied these brought about an increase in CTE.

Tamaka and Yamasaki [29] studied the contents of a pilot delayed coker and concluded that the behaviour of the liquid level could be correlated with the yield and properties of the coke produced, and that the application of kinetics to the change of the liquid level is feasible.

Recently, needle cokes from coal-tar pitch can be produced by the delayed coking method from pitch feedstock having a low content of quinoline insoluble matter [30, 31]. The properties of coal-tar pitch needle-coke are similar or better (lower CTE) to those produced from petroleum pitch [30].

The literature does not contain authoritative descriptions of structures or components found within commercial needle-cokes, nor is there much speculation or knowledge as to how these structures may have been formed.

Etching with chromic acid is a very useful technique to study structures in cokes of diverse origins [32–34]. Originally, etching with chromic acid was used to obtain comparative kinetic data of oxidation rates of cokes with different contents of graphitic carbon [35, 36]. Oberlin and Mering [37] reported a relationship between rates of oxidation by Simon's reagent and the degree of graphitization of essentially graphitic materials.

The principal objective of this paper is to study structures within petroleum needle cokes as revealed by oxidation (etching) with chromic acid in conjunction with "same area" examination by OM and SEM techniques [38]. Also, it describes a possible model for the formation of needle-coke within the delayed coker using knowledge of mesophase formation and structural components within needle-coke.

2. Experimental procedure

2.1. Materials used

Calcined petroleum needle-coke, NCB2, Shell calcined needle-coke, Conoco calcined needle-coke.

2.2. Microscopic examinations

Piecies of needle-coke ~ 50 mm size were photographed to show bubble structures and the needle morphology characteristic of needle cokes.

Pieces of needle-coke (2 cm in size) were mounted in a thermosetting polyester resin and highly polished for good optical reflectivity. The optical textures of the cokes were examined using a Vickers M41 polarized light microscope with a half-wave retarder plate (550 nm) in order to produce coloured images [20]. The term "optical texture" is a description of the size, shape and position of adjacent isochromatic areas which are defined by the orientations of the constituent lamellae of hexagonally arranged carbon atoms (with various imperfections).

The polished surface of the coke was first examined by OM to characterize the optical texture. It was then oxidised in chromic acid at 423 K (150° C) for 1 h. The chromic acid was prepared using 10 g potassium dichromate in 50 ml orthophosphoric acid.

The same area of coke surface was re-examined before and after oxidation to correlate the surface topography seen by SEM with the optical texture of the cokes deduced from optical microscopy [33].

3. Results

Needle coke, on the macroscopic scale, is porous with heterogeneity of pore size and shape. Viewing of pieces of needle-coke shows that they possess the characteristic bundles of needles (~ 50 × ~ 1 mm diameter) as well as a porous type carbon. These needles contain smaller associations (~ 200 μm diameter) which constitute the acicular flow domain of optical texture. The porous type carbon corresponds to the domain anisotropy of optical texture. Boundaries between the two macro components are distinct.

3.1. Microscopic examinations

Table I lists the nomenclature used to describe the optical texture of the cokes.

TABLE I Nomenclature: optical texture in cokes

Isotropic	I	No optical activity
Very fine-grained mosaic	VMf	$< 0.5\,\mu$m diameter
Fine-grained mosaics	Mf	0.5 to 1.5 μm diameter
Medium-grained mosaic	Mm	1.5 to 5.0 μm diameter
Coarse-grained mosaic	Mc	5.0 to 10.0 μm diameter
Supra-mosaics	SM	Aligned mosaics
Medium flow anisotropy	MFA	$< 30\,\mu$m length; $< 5\,\mu$m width
Coarse flow anisotropy	CFA	30 to 60 μm length; 5 to 10 μm width
Acicular flow domain anisotropy	FD	$> 60\,\mu$m length; $< 5\,\mu$m width
Small domains	SD	10 to 60 μm diameter
Domains	D	$> 60\,\mu$m diameter

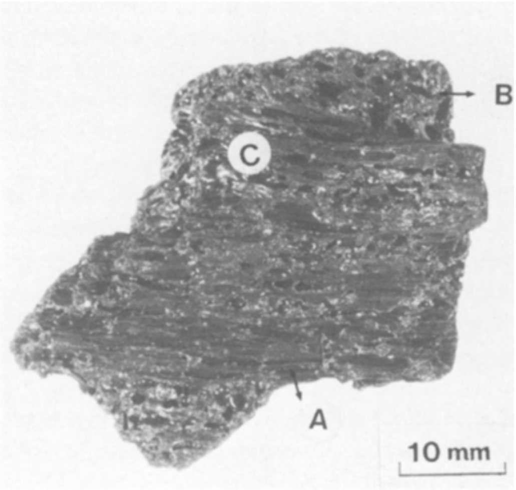


Figure 1 Petroleum needle-coke. (A) bundles of needles; (B) porous carbon; (C) bundles of needles containing elongated fissures.

Fig. 1 shows a photograph of the bulk appearance of petroleum needle-coke. Bundles of needles (A) correspond to acicular flow anisotropy. Porous structure (B) corresponds to the domain anisotropy and (C) to needles containing elongated fissures.

3.1.1. Petroleum coke NCB2

Figs. 2 and 3 are optical micrographs of the selected areas of calcined needle-coke (NCB2). Fig. 2 shows acicular flow domain (D), small domains (E), and medium-grained mosaic (F). Fig. 3 shows interfaces between the above components (G) and between domains (H).

Figs. 4–9 are SEM micrographs of the same selected areas of the needle-coke before and after etching with chromic acid. Fig. 4 shows the porosity of the coke and illustrates that with SEM it is difficult to distinguish structural orientations of the optical texture prior to etching. The interface (G) between acicular flow domain and small domains is shown in Fig. 3.

Fig. 5 shows acicular flow anisotropy with shrinkage fissures running parallel to prismatic edge presentation (from analysis of optical texture). Open porosity exists as fissures and pores which are thought to be locations of preferential oxidation. Fig. 6 is an SEM micrograph of the "same area" as Fig. 2, showing (G) features produced by oxidation with chromic acid for 1 h at 423 K. The detail of the parallel orientation of lamellae in acicular flow domain is shown (D), with (G) showing the interface to be preferentially etched (Fig. 7).

Fig. 8 shows the domain as folded lamellae running parallel to fissures (H). (I) shows basal planes (which are optically isotropic) of the domain to be unetched whereas optically anisotropic areas have been heavily etched. The lamellae within domains are exposed with prismatic edge presentation (J). (K) shows basal plane presentation (Fig. 9). Etching at (J) (Fig. 9) occurs preferentially within fissures extending their size.

3.1.2. Shell calcined coke

Figs. 10 and 11 are optical micrographs showing the major structural components of domain anisotropy (L), medium-grained mosaics (M) (Fig. 10) and acicular flow domain (N) (Fig. 11).

An optical micrograph of the surface of Shell needle coke (Fig. 12) prior to etching with chromic acid shows the interface (O) between medium and coarse-grained mosaics (P) and domains (Q).

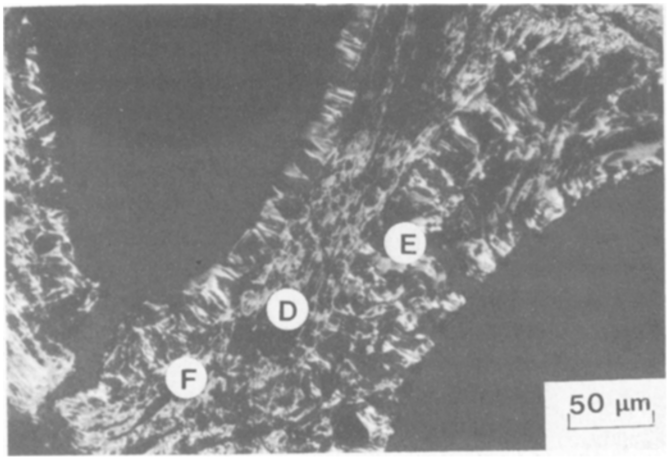


Figure 2 Optical micrograph of calcined needle-coke (NCB No. 2). (D) acicular flow domain; (E) domain anisotropy; (F) medium-grained mosaics.

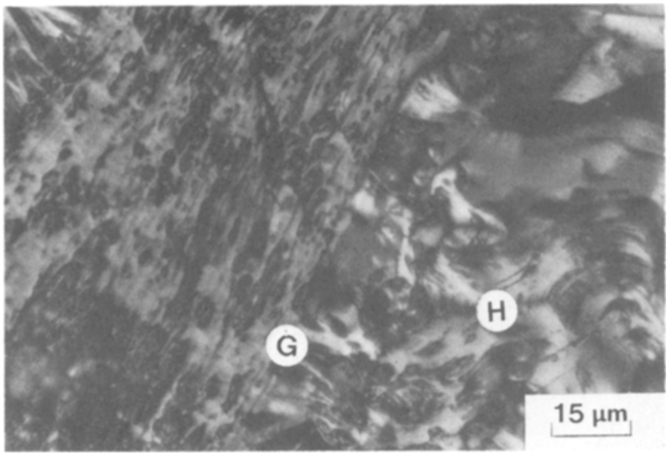


Figure 3 Optical micrograph of calcined needle-coke (NCB No. 2). (G) interface between acicular flow domain and domain; (H) interface between domains.

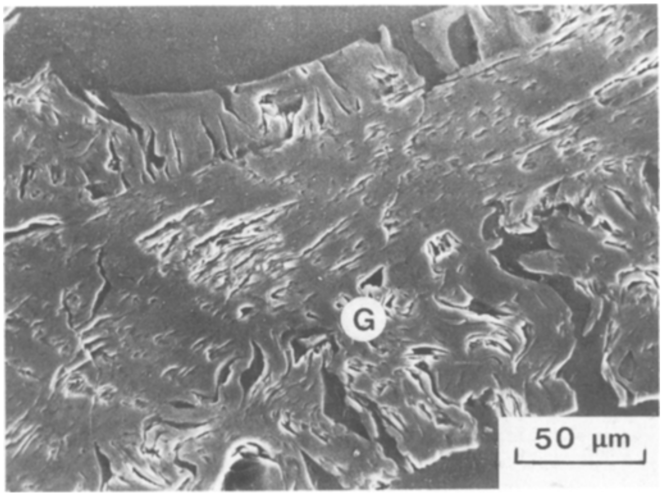


Figure 4 SEM micrograph of calcined needle-coke (NCB No. 2) prior to etching with chromic acid. (G) interface between acicular flow domain and domain anisotropy.

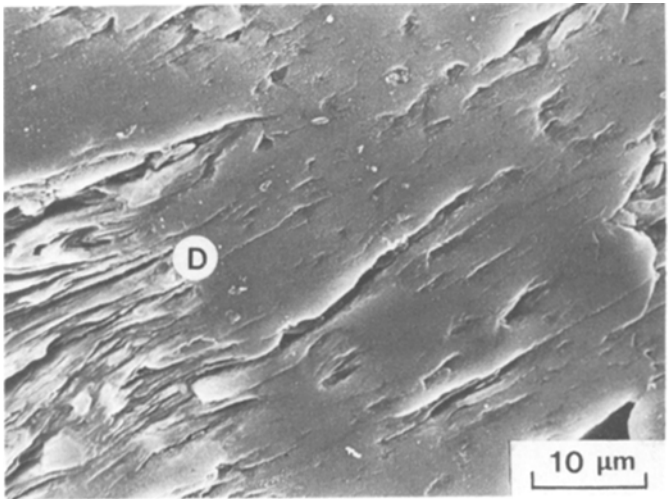


Figure 5 As Fig. 4. (D) contraction fissure in acicular flow domain.

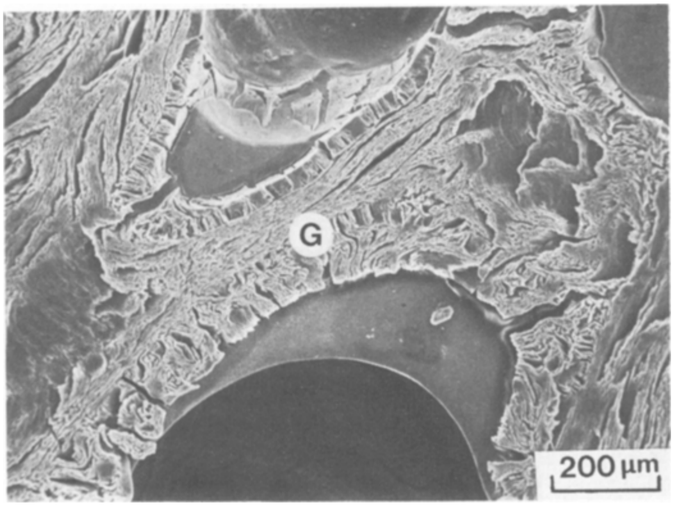


Figure 6 SEM micrograph of calcined needle-coke (NCB No. 2) after etching with chromic acid at 423 K for 1 h. (G) interface between acicular flow domain and domain anisotropy.

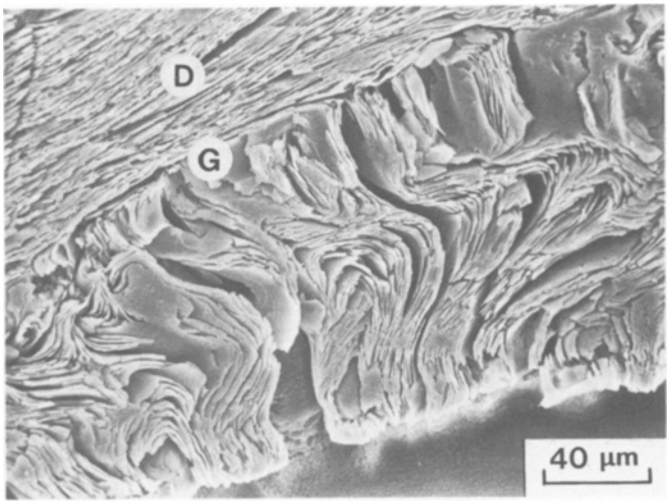


Figure 7 SEM micrograph of calcined needle-coke (NCB No. 2) after etching with chromic acid at 423 K for 1 h. (D) acicular flow domain; (G) interface with preferential etching.

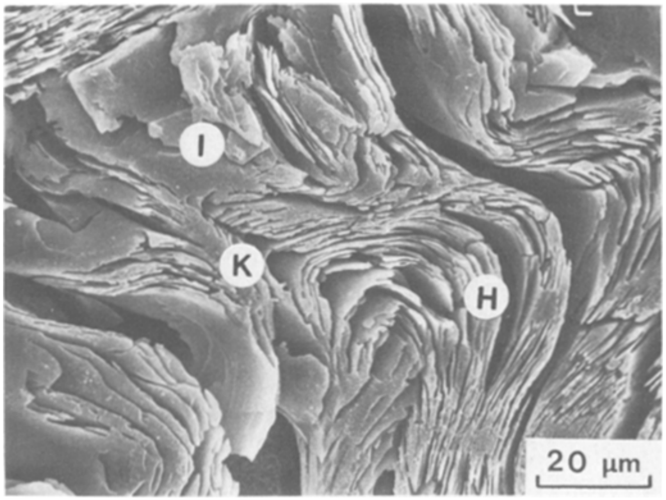


Figure 8 SEM micrograph of calcined needle-coke (NCB No. 2) after etching with chromic acid at 423 K for 1 h. (H) domain with fissures; (I) optically isotropic domain.

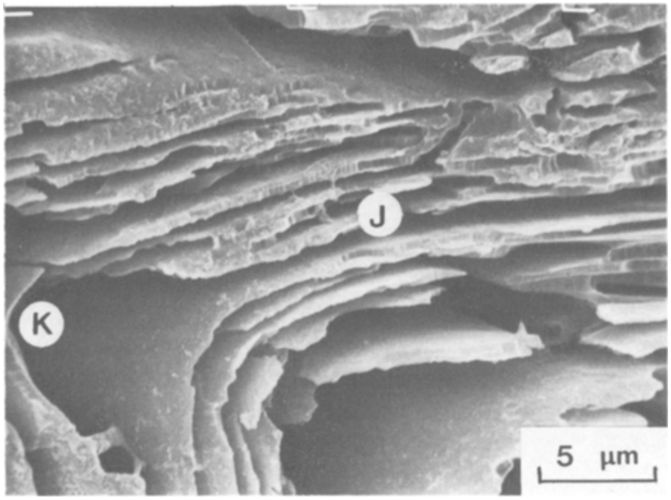


Figure 9 As Fig. 8. (J) prismatic edge presentation of domain; (K) basal plane orientation.

Figure 10 Optical micrograph of calcined Shell needle-coke. (L) domain anisotropy; (M) medium-grained mosaics.

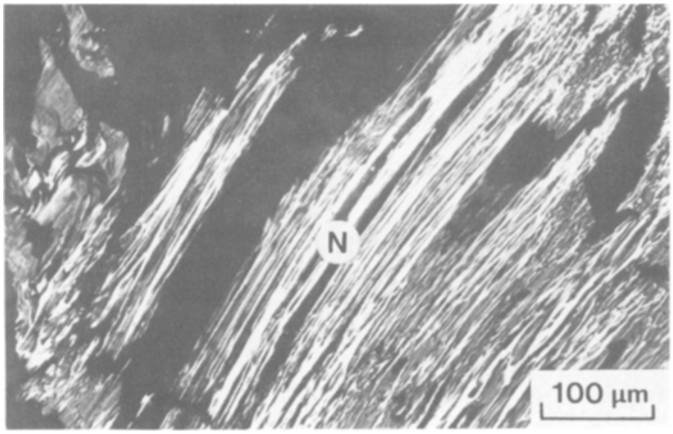


Figure 11 As Fig. 10. (N) acicular flow domain.

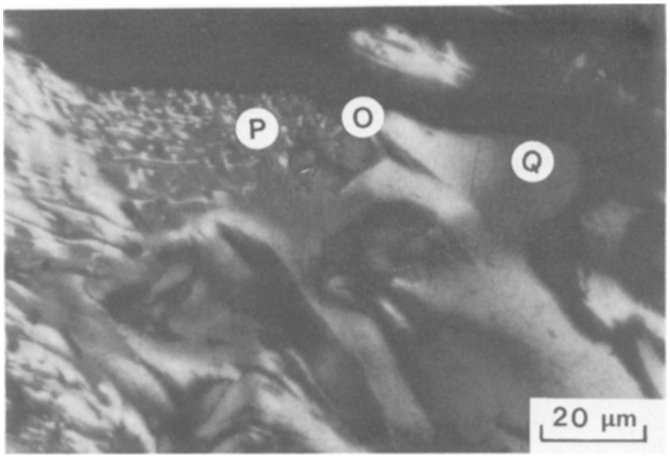


Figure 12 Optical micrograph of calcined Shell needle-coke. (O) interface between medium-grained mosaics at (P); (Q) domain anisotropy.

An SEM micrograph after etching (Fig. 13) shows that the interface (O) is preferentially etched. Coarse-grained mosaics (P) result from presentation at the surface of folded lamellae, i.e. acicular flow domains which have a near-vertical orientation to the polished surface. Hence these coarse-grained mosaics have considerable depth, and as such should not be confused with the medium-grained mosaics of e.g. metallurgical cokes [32] which are essentially isometric. Position Q shows domain structures which upon etching appear as arrays of folded and bent lamellae with edge presentation.

Figs. 14–16 are SEM micrographs of an etched domain, revealing preferential oxidation and fissuring of lamellae (R) as well as unchanged basal plane presentation (S) (Fig. 14). These domains after progressive etching show what is termed a "sandwich" structure (T) [31] as in Fig. 15.

The SEM micrograph of acicular flow domains (Fig. 16) shows folded lamellae, i.e. bundles of rolled-up lamellar sheets. This type of structure is termed the "rolled newspaper" structure [31]. Comparison of the acicular flow domain (U) with the medium-grained mosaic ((L) in Figs. 10 and 11) shows that the medium-grained mosaics result from the "rolled newspaper" structure, ((U) in Fig. 16) inclined at a high angle to the polished surface. The longitudinal section (V) would give lamellae stacked almost parallel to a polished surface giving basal plane orientation with a striped appearance similar to that shown in Fig. 16 (W). Preferential oxidation in the folds of the lamellae then causes division into narrow laths ((W) in Fig. 16).

3.1.3. Conoco calcined coke

Optical micrographs of Conoco calcined coke are very similar to those of Shell coke.

Fig. 17 is an SEM micrograph of industrially

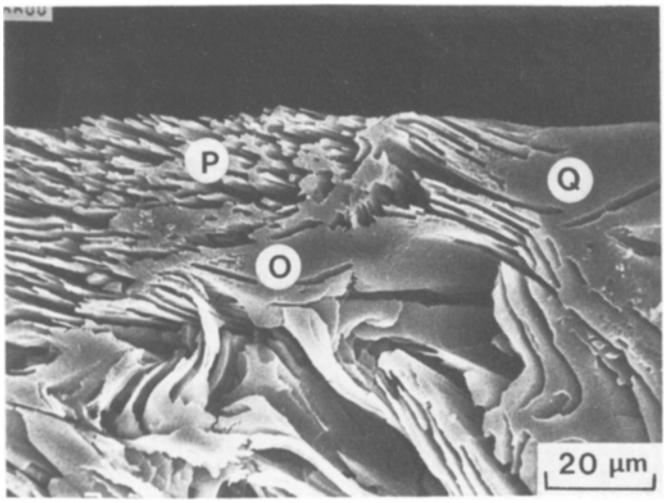


Figure 13 SEM micrograph of calcined Shell needle-coke after etching with chromic acid at 400 K for 5 h. (O) interface between medium-grained mosaics at (P); (Q) domain anisotropy.

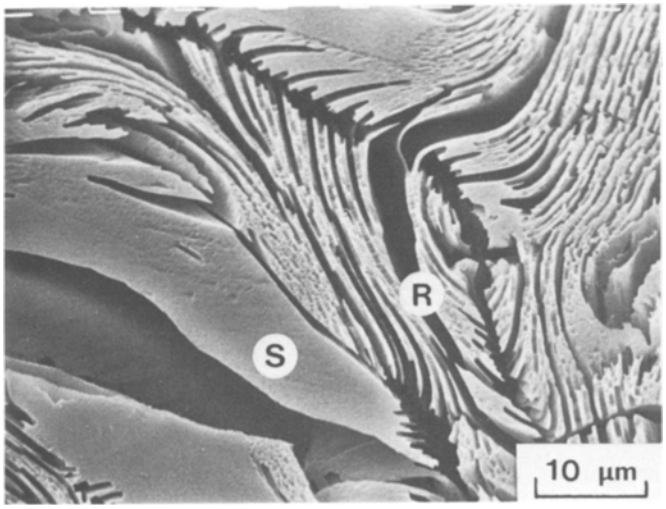


Figure 14 SEM micrograph of calcined Shell needle-coke after etching with chromic acid at 423 K for 1 h. (R) preferential oxidation of domain and fissuring; (S) basal plane presentation.

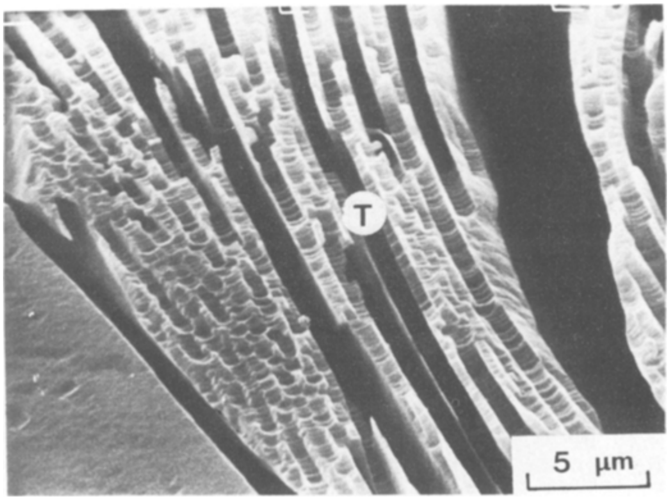


Figure 15 SEM micrograph of calcined Shell needle-coke after etching with chromic acid at 423 K for 1 h. (T) "sandwich" appearance of etched domain carbon.

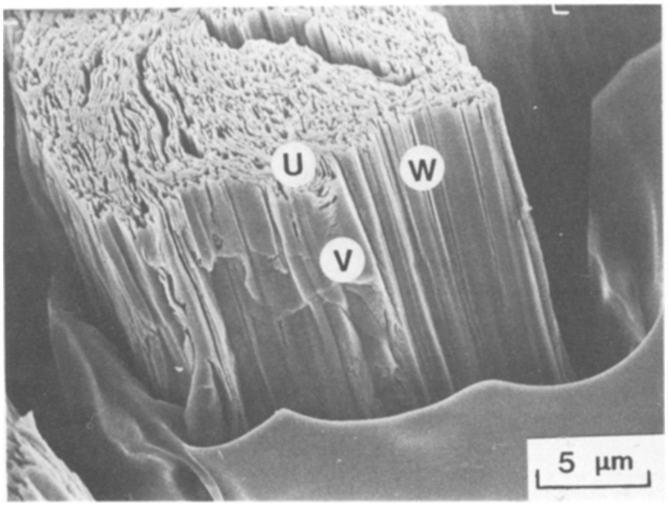


Figure 16 SEM micrograph of calcined Shell needle-coke after etching with chromic acid at 423 K for 1 h, showing rolled lamellae. (U) horizontal section through medium-grained mosaics; (V) longitudinal section of lamellae and external basal planes; (W) preferential etching in folds of basal planes.

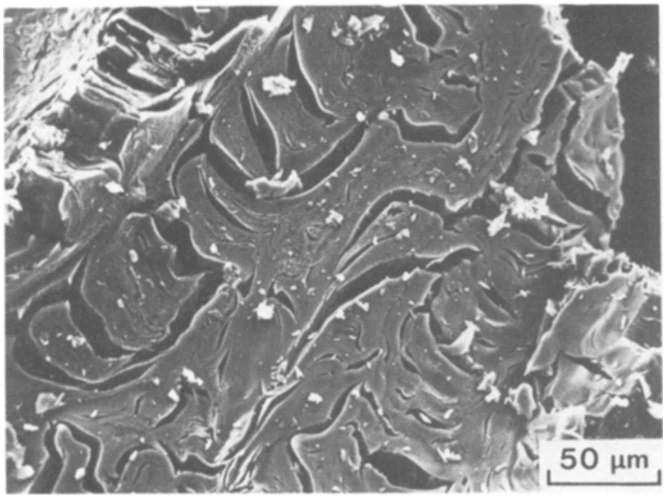


Figure 17 SEM micrograph of calcined Conoco needle-coke prior to etching with chromic acid, showing contraction fissures.

supplied Conoco needle-coke showing that needle-coke particles possess many contraction fissures probably introduced during the calcination stage. There exists a smaller series of fissures, ~ 3 μm in diameter, as well as larger fissures of ~ 12 μm diameter.

SEM micrographs taken after etching with chromic acid (Figs. 18–20) show acicular flow domains preferentially etched along the folds of basal planes to produce laths (needle-like) of material (~ 3 μm across), Fig. 18, (X), and Fig. 19, (Z).

Interfaces between folded lamellae and basal plane presentation of domain anisotropy (Fig. 19, (Y)) are also preferentially etched. Domains with edge presentation are shown in Fig. 20, (A). Between the lamellae there is a finer structure, termed 'sandwich' structure, which is preferentially etched (B).

3.1.4. Coal-tar pitch coke

Optical and SEM micrographs of some industrially supplied pitch coke have similar major structural features to petroleum needle-coke. A more detailed study will be published later.

4. Discussion

4.1. Etching with chromic acid

Chromic acid oxidation is a very useful technique in the study of macrocrystallinity of anisotropic carbon. It provides structural information on cokes mainly because it is a selective etchant in terms of different sizes of optical texture of anisotropic carbon and of differences in reactivity of prismatic edge and basal plane orientations.

4.2. Structure of needle cokes

Examination of the structure of needle-cokes by

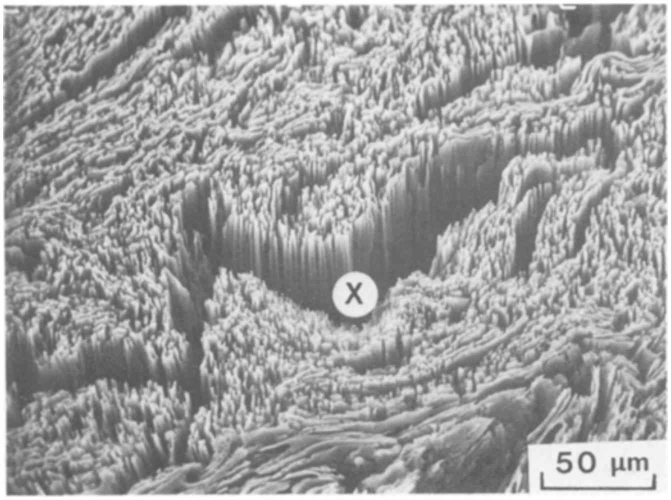


Figure 18 SEM micrograph of calcined Conoco needle-coke after etching with chromic acid at 423 K for 0.5 h. (X) acicular flow domain preferentially etched along the folds of the basal planes to produce laths of materials (~ 3 μm).

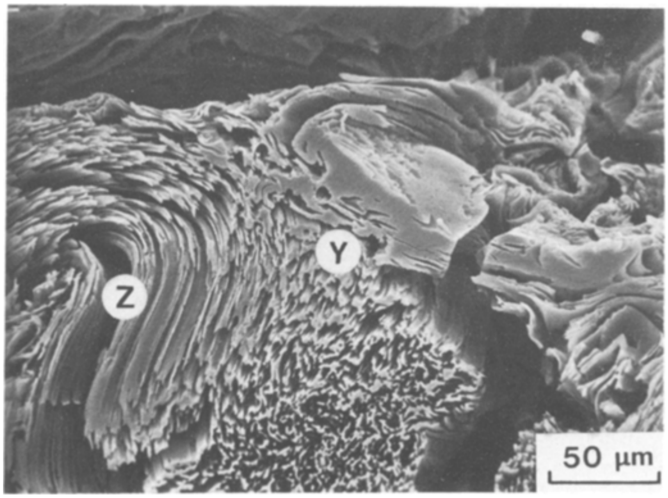


Figure 19 SEM micrograph of calcined Conoco needle-coke after etching with chromic acid at 423 K for 0.5 h. (Y) interface between domain and acicular flow domain; (Z) preferentially etched acicular flow domain.

optical microscopy shows a range of size and shape of optical texture. Etching with chromic acid shows that these optical textures result from complex associations of only two basic structures, acicular flow domains and domains.

4.2.1. Acicular flow domains

Etching of the acicular flow domains of needle coke (i.e. $> 60\,\mu$m long and $< 5\,\mu$m wide) shows that they consist of a series of folded lamellae which in longitudinal section present a basal plane orientation to the polished surface. This results in a striped or banded appearance in the optical microscope. However, when the lamellae are observed in transverse section or at a high angle to the polished surface then they appear as medium or coarse-grained mosaic (Fig. 2, (F)).

4.2.2. Domains

Comparison of Figs. 3 and 7 shows that the optically isotropic domains have lamellae with basal plane presentation to the polished surface; optically anisotropic domains have lamellae with a prismatic edge presentation, e.g. Fig. 14, (R). Prismatic edge carbon is more reactive to oxidation with chromic acid than basal plane carbon.

Domains, i.e. isochromatic areas $> 60\,\mu$m, tend to be associated with the porosity of needle-coke (Figs. 1, 3, 6 and 7), often in the form of a thin "skin" around the pore separated from more highly deformed mesophase by a distinct interface. Domains on etching show the "sandwich" structure [32] thought to result from a quiescent growth of mesophase, e.g. via settling of mesophase in the delayed coker.

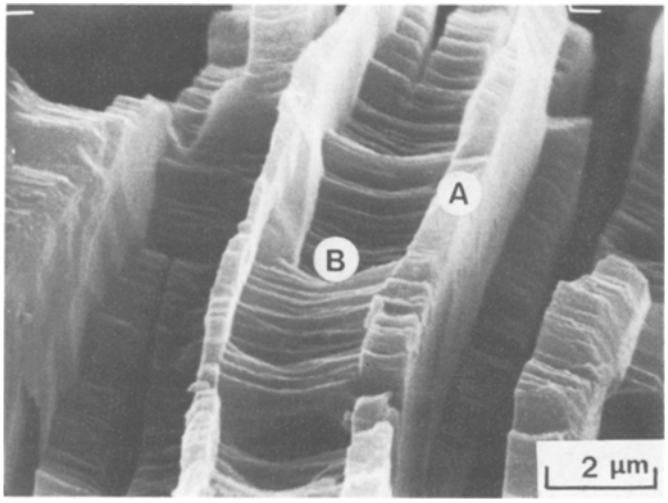
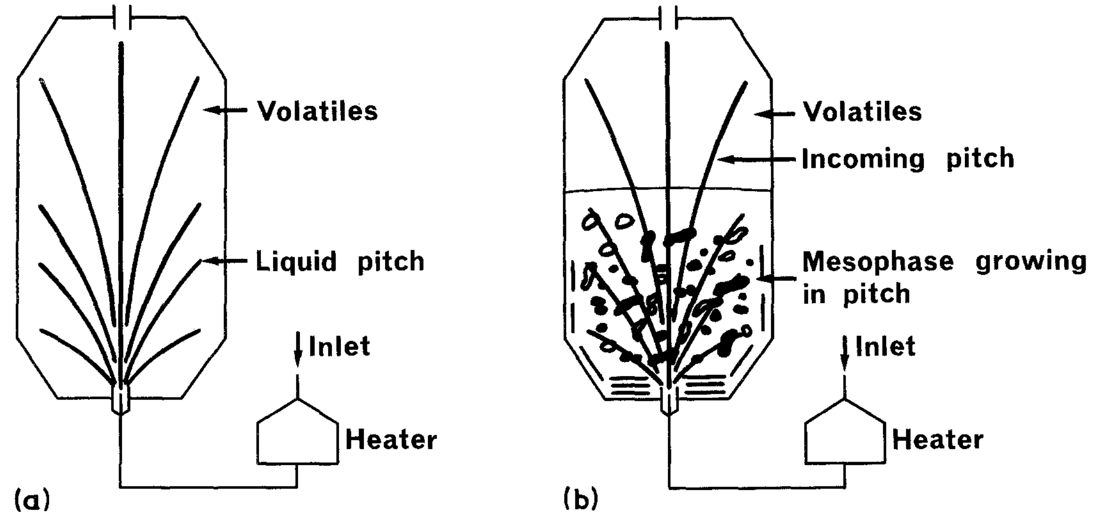


Figure 20 SEM micrograph of calcined Conoco needle-coke after etching with chromic acid at 423 K for 1 h, showing the "sandwich" structures. (A) edge presentation of lamellae; (B) preferential etching between the "sandwich" layers.



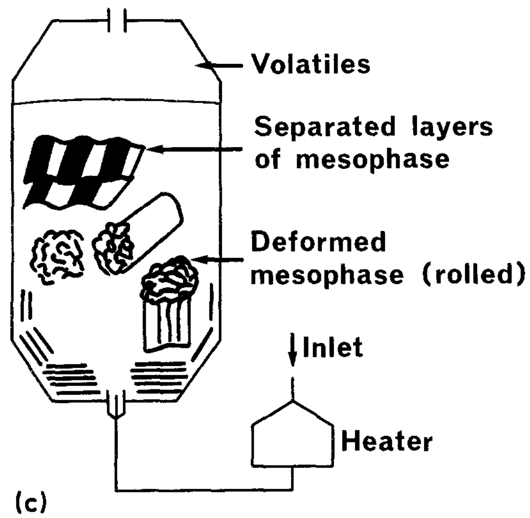


Figure 21 A model of the formation of needle-coke in a delayed coker.

In the early stages of bulk mesophase the resultant viscosity is low enough to enable spheres of mesophase to coalesce, to settle and to flow, so creating the sandwich structure. Mesophase formed later appears not to coalesce between the layers, which remain distinct.

The acicular structure may form later in mesophase development when deformation of mesophase, by upward percolating bubbles and incoming fresh feed, occurs in more "mature" mesophase which is plastic and hence retains the deformation. This deformation must occur just before solidification so that the deformation structures become frozen and incorporated into the needle-coke.

4.2.3. The interface

The interface between the two microstructural components, domain and acicular flow domain, is structurally very important as it separates apparently undeformed (domain) and severely deformed (acicular flow domain) components (Fig. 13, (O) and Fig. 19, (Y)). The interface appears discontinuous and fissured and is hence etched preferentially by chromic acid.

4.3. Model for formation of needle coke in the delayed coker

The various optical textures in needle-coke result from deformation of mesophase, formed from the feedstock pitch in the delayed coker.

The requirement that the mesophase in the coker has to be of relatively high viscosity so as to retain deformation would suggest that the microstructure of needle-cokes is fixed during the later stages of the operation, i.e. when the coke drum is almost full and a large proportion of the feed pitch has transformed to bulk mesophase. The complex folding of the lamellae seen in needle-cokes must result from significant deformation during the coking cycle within delayed cokers.

The results reported in this paper may help illustrate this aspect of formation of needle coke in the delayed coker. A simple scheme of the delayed coking process is shown in Figs. 21a to c.

The delayed coker feed is fed hot and over the period of time, typically 16 to 24 h [12] (Fig. 21a) growth units of mesophase form in the bulk pitch and enlarge at the expense of the surrounding pitch by coalescence. Any deformation of this mesophase by incoming feed or bubble percolation rapidly relaxes away, leaving an undeformed mesophase possessing "sandwich" structure, i.e. domain. However, as filling continues, a more continuous or bulk mesophase forms, of increasing viscosity. Turbulent flow of bubbles and incoming feed through this mesophase results in a more permanent deformation which does not relax away. The upward movement of bubbles or rapid movement of liquid through mesophase appears to be responsible for this deformation. Mesophase is deformed due to displacement around the bubble and often pairs of bubbles act to squeeze the mesophase resulting in the folded lamellae characteristic of acicular flow domain (Figs. 4 and 6).

The upward moving bubbles appear to draw along with them a skin or bubble wall of fresh feed or undeformed mesophase, resulting in the association of domains and porosity in the final needle-coke. The skin or bubble wall material is separated from the surrounding deformed mesophase by a shear zone, which also allows the bubble to move upward through the surrounding mesophase. This shear zone is typically the distinct interface between domains and acicular flow domains, preferentially etched by chromic acid. Rotation of lamellae associated with this shear zone may result in rolling of the lamellae as seen in the "rolled newspaper" structure (Fig. 16, (U)). Other more central parts of Fig. 16 show severe buckling of lamellae as a result of the shearing forces.

5. Conclusions

1. Chromic acid is a selective oxidation etchant preferentially reacting with anisotropic carbon. Basal plane oriented carbon is less reactive than prismatic edge oriented carbon toward oxidation. SEM observations of needle-coke after oxidation in chromic acid, show the structure of macro-constituents.

2. Needle-cokes after etching with chromic acid and examination by SEM are found to contain only two basic microstructures, i.e. the acicular flow domain (rolled) structure and domains ("sandwich") structure.

3. Acicular flow domains exhibit extremely folded lamellae with external basal plane presentation. When lamellae are folded vertically to the polished surface then the optical texture appears as mosaics. When the folded lamellae are parallel to the polished surface of the coke they appear, microscopically, as the acicular flow anisotropy. The complex folding and tilting of lamellae in these structures indicate that the parent mesophase has been subject to significant deformation during coking.

4. After etching with chromic acid, domains show parallel stacking of lamellae as their general orientation. Layered sedimentary structures indicate that deformation processes are less severe than for the acicular structures, although some bending occurs.

5. Aspects of needle coke formation can be modelled as follows. Movement of incoming fluid feed and bubbles creates turbulence within the coker. Mesophase forms and its growth units coalesce into a bulk mesophase. This bulk mesophase is deformed by the turbulent movement of feed and bubbles through it. Mature mesophase is plastic and retains the deformation. The bubbles draw with them a thin skin of mesophase isolated from the deformed mesophase by the shear zone around the bubble, which allows bubble movement through the bulk mesophase. The mesophase in the bubble wall solidifies with little deformation developing a domain-type microstructure with a "sandwich" type lamellae structure. The strongly deformed mesophase develops the acicular flow domain-type microstructure with a folded basal-plane type lamellae structure. This two-phase structure of needle-coke becomes frozen into the semi-coke and recently formed mesophase.

Acknowledgements

VM is grateful for financial support from the Serbian Scientific Council and The ALCOA Foundation of the USA, and for leave of absence from the Boris Kidric Research Institute, Vinca, Yugoslavia, enabling her to study in the Northern Carbon Research Laboratories. The assistance of Miss Bridget A. Clow is acknowledged.

References

1. D. H. STORMONT, *Oil Gas J.* 67 (1969) 75.
2. C. B. SCOTT, *Chem. Ind.* (1967) 1124.
3. H. W. NELSON, *Ind. Eng. Chem. Prod. Res. Dev.* 9 (1970) 176.
4. R. R. JAKOB, *Hydrocarbon Process.* (1971) 132.
5. V. HEKLER and H. E. BROOKS, *Pet. Refiner* 38

(1959) 169.
6. F. L. SHEA, US Patent 2,775,549 (1956).
7. R. C. HACKLEY, US Patent 2,922,755 (1960).
8. GREAT LAKES CORPORATION, US Patent 1,194,985 (1970).
9. M. JANIK and M. KALOC, *Hutn. Listy* (1980) 378.
10. E. KURAMI, *Sekiyu Gakkai Shi* **16** (1973) 366.
11. W. L. NELSON, *Oil Gas J.* **76** (1978) 68.
12. K. E. ROSE, *Hydrocarbon Process.* (1971) 85.
13. N. P. LIEBERMAN, *Oil Gas J.* **78** (1980) 15, 71.
14. J. D. BROOKS and G. H. TAYLOR, *Carbon* **3** (1965) 185.
15. *Idem*, in "Chemistry and Physics of Carbon" Vol. 4 edited by P. L. Walker Jr (Marcel Dekker, New York, 1968) p. 243.
16. H. HONDA, H. KIMURA, Y. SANADA, S. SUGAWARA and T. FURUTA, *Carbon* **8** (1970) 181.
17. H. MARSH and P. L. WALKER JR, in "Chemistry and Physics of Carbon" Vol. 15 edited by P. L. Walker Jr and P. A. Thrower (Marcel Dekker, New York, 1979), p. 299.
18. R. BALDUHN and E. FITZER, *Carbon* **18** (1980) 155.
19. I. C. LEWIS and L. S. SINGER in "Chemistry and Physics of Carbon" Vol. 17 edited by P. L. Walker Jr and P. A. Thrower (Marcel Dekker, New York, 1981) p. 1.
20. H. MARSH and J. SMITH in "Analytical Methods for Coal and Coal Products" Vol. 2 edited by Clarence Karr Jr (Academic Press, New York, 1978) p. 371.
21. J. L. WHITE, G. JOHNSON and J. E. ZIMMER, Extended Abstracts of 12th Biennial Conference on Carbon, Pittsburgh, 1975 (American Carbon Society, 1975) p. 492.
22. J. E. ZIMMER and J. L. WHITE, *Mol. Cryst. Liq. Cryst.* **38** (1977) 177.
23. M. BUECHLER, C. B. NG and J. L. WHITE, Extended Abstracts of the 15th Biennial Conference on Carbon, Pennsylvania State University, 1979 (American Carbon Society, 1979) p. 433.
24. *Idem*, Extended Abstracts of 15th Biennial Conference on Carbon, Philadelphia, 1981 (American Carbon Society, 1981) p. 182.
25. J. E. ZIMMER and J. L. WHITE, *Advan. Liq. Cryst.* **5** (1982) 157.
26. J. L. WHITE, Proceedings of International Symposium on Carbon, New Processing and New Applications, Toyohashi, 1982 (Kagaku Gijutsu-sha, 1982) p. 149.
27. J. E. ZIMMER, *ibid.* p. 131.
28. E. FITZER and C. HOLLEY, Extended Abstracts of 16th Biennial Conference on Carbon, San Diego, 1983 (American Carbon Society, 1983) p. 104.
29. H. TANAKA and Y. YAMASAKI, Reprints, Carbon '80, Baden-Baden, 1980 Deutsche Keramischen Gesellschaft, p. 397.
30. H. MURATA. T. MIYAZAKI, H. HIRAOKA, I. KOIDE and S. HIRAGA Proceedings of International Symposium on Carbon, New Processing and New Applications, Toyohashi, 1982 (Kagaku Gijutshusha, 1982) p. 543.
31. W. MIGITAKA, Y. TASHIRO and M. IWASA, *ibid.* p. 553.
32. V. MARKOVICH, H. MARSH and S. RAGAN, Extended Abstracts of the 15th Biennial Conference on Carbon, Philadelphia, 1981 (American Carbon Society, 1981) p. 492.
33. H. MARSH, M. FORREST and L. A. PACHECO, *Fuel* **60** (1981) 423.
34. V. MARKOVIC and H. MARSH, *J. Microsc.* **132** (1983) 345.
35. A. F. BALFOUR, H. E. BLAYDEN, A. H. CARTER and H. L. RILEY, *J. Soc. Chem. Ind.* 57 (1938) 1.
36. H. MARSH, *Fuel* **50** (1971) 280.
37. M. OBERLIN and J. MERING, *Carbon* **1** (1964) 471.
38. V. MARKOVIC and H. MARSH, *J. Mater. Sci.* **19** (1984) 3301.

Received 1 December
and accepted 21 December 1983