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

Part 2

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Structure within calcined and graphitized cokes from a delayed coker is investigated by optical microscopy, etching with chromic acid solution and scanning electron microscopy. The grains of mosaics of a coal extract delayed coke are clearly identifiable. Etching studies of needle-cokes are informative giving the detail of pore wall structure, of the sub-divisions of structure within the macro-needles (1 mm diameter) of needle-coke, i.e. the acicular flow domains, of disclinations within domains and of a layered "sedimentary" structure within domains. The etching characteristics of graphitized needle-cokes are quite distinct from those of calcined needle-cokes. In the former, basal planes of acicular flow domains etch into small bundles, 1 to 2 μm in length, with development of fissures every 1 μm apart and some 0.1 μm across. Features observed in the topography of etching may assist in the understanding of how needle-cokes accommodate thermal and mechanical stresses.

1. Introduction

Anisotropic graphitizable carbons (cokes) are usually formed from pitch-type precursors which are fluid during the carbonization process. They possess sufficient macrocrystallinity (i.e. the alignment of stacked lamellae of carbon atoms extends over distances 0.1 to 500 μm) such that they graphitize on heat treatment to ~ 3000 K [1]. Crystallographic order can be monitored by X-ray diffraction with macrocrystallinity being assessed as optical texture observed by optical microscopy [2].

The macrocrystallinity (optical texture) within a particular coke can vary in size from 0.1 to 500 μm. The boundaries between the macrocrystallinity are often not sharp and exhibit acute folding or distortion. The size and shape of the macrocrystallinity can be seen using reflected polarized light microscopy of polished surfaces [2]. This technique enables the macrocrystallinity to be seen as isochromatic areas with yellow and blue colours from prismatic edge presentation and with purple from the isotropic basal plane presentation at the polished surface. The colours can be used to assess the orientation of the constituent lamellae of carbon atoms.

The alignment of the lamellae in the coke can be further assessed by etching [3, 4]. Atomic oxygen or other etchants have been used to produce surface topography on coke surfaces so that the structural units can be viewed directly in the SEM [3, 5].

The technique of chromic acid oxidation was originally used in kinetic assessments of oxidation phenomena [6]. However, the technique has been re-assessed and applied to investigations of structure in anisotropic carbons [7, 8].

Constituent lamellae of macrocrystallinity which are folded and convoluted are preferentially oxidized and it would appear that fissures widen preferentially [9]. Disclinations within the coke structure show preferential etching [10]. As a consequence of selective oxidation within anisotropic carbon, the development of a surface topography shows the general orientations of constituent lamellae. Chromic acid has a low comparative reactivity towards optically isotropic carbons [3].

The preferential oxidation of anisotropic carbon with chromic acid may result from differences in structural perfection within and between layers. According to Balfour *et al.* [6] rates of oxidation increased as the degree of graphitization increased. Oberlin and Mering [11] using Simon's reagent (silver dichromate in sulphuric acid) concluded that four rate constants exist, attributable to four structural forms of carbon. Marsh *et al.* [3] verified that chromic acid etches preferentially the more graphitic material of metallurgical cokes and anisotropic carbons from pitches in the reactivity order: domains > mosaic > isotropic.

It is reported that reactivities of anisotropic carbon towards gasification by oxygen and carbon dioxide depend upon the degree of ordering, size and planarity of constituent lamellae, it being found that the smaller is the size of optical texture, the lower is the degree of ordering, size and planarity of lamellae and the greater is the number of defects and sites for gasification [12].

The objectives of this study are:

1. To develop an experimental method of etching which is meaningful and which can be carried out simply in the laboratory without recourse to vacuum technology, i.e. argon ion etching.
2. To promote an understanding of structures in several cokes.
3. To investigate structures associated with graphitized coke.

2. Experimental details

2.1. Materials used

The cokes used were:

Calcined coal-extract delayed coke (NCB No. 18) from extract of Annesley coal (NCB rank 702).

Ashland A240 petroleum coke, HTT 1123 K. (i.e. green coke heated to 1123 K in the laboratory)

Calcined petroleum needle-coke (NCB No. 1).

Calcined Conoco needle-coke.

Calcined petroleum needle-coke (NCB No. 23).

Shell graphitized needle-coke (HTT 3173 K).

2.2. Microscope analyses

Pieces of coke ~ 2 cm in size were mounted in cold-setting polyester resin. Polishing was carried out using a series of alumina powders (5/20, 3/50 and γ-grades). For examination by optical microscopy the polished coke surfaces were mounted on glass slides by "Bluetak" and levelled. The surfaces were examined by polarized reflected light microscopy with a half-wave retarder plate and parallel polars using an M41 Vickers optical microscope. Resultant coloured images show the optical texture of coke. Coloured photographs were taken from selected areas of the cokes prior to gold-coating (to reduce sample charging). The samples were then examined by scanning electron microscopy (JEOL T20 SEM). Care was taken so that the areas photographed by SEM were those photographed by optical microscopy.

After SEM examination of selected areas the gold-coating was carefully removed by light polishing with γ-alumina powder. The polished samples were etched with chromic acid (10 g potassium dichromate in 50 ml ortho-phosphoric acid) at 423 K for 1 h. The etched surfaces were recoated with gold and resultant structural features in the selected areas were examined by SEM.

3. Results

Fig. 1 shows the optical texture of delayed coke from a coal-extract to be dominantly medium-

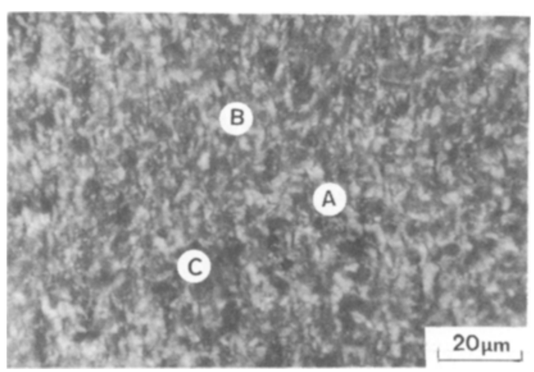

Figure 1 Optical micrograph of calcined delayed coke from extract of Annesley coal (NCB rank 702, No. 18). Position A: porosity, position B: prismatic edge presentation of mosaic, position C: basal plane presentation.

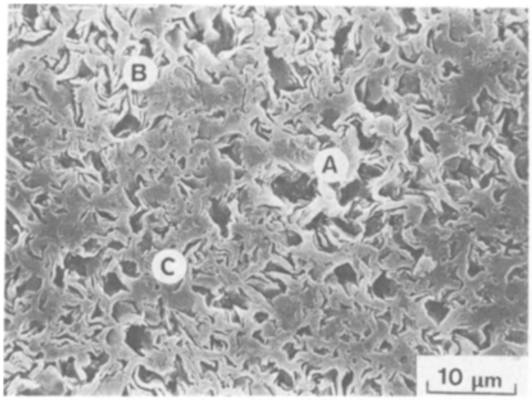

Figure 2 The surface of Fig. 1 after etching with chromic acid, 423 K, 1 h. The positions are as Fig. 1.

grained and coarse-grained mosaics. Porosity is seen at position A with position B showing the mosaics with prismatic edge presentation and position C showing basal plane orientation.

The SEM topography of the surface of coal-extract delayed coke after etching (Figs. 2 and 3) is determined by the mosaic size, i.e. ~ 5 to 10 μm. Fig. 2, position A shows etching within existing porosity or pits (< 7 μm). Position B shows etching of prismatic edges of mosaics. Position C shows the unreactive basal plane presentation of mosaics. On further etching with chromic acid (423 K, 2 h) the resultant SEM micrograph (Fig. 3) shows that the original features have been lost and the topography now consists largely of the more unreactive basal planes of the mosaics. Position D refers to a particular mosaic showing basal plane and prismatic edge presentation.

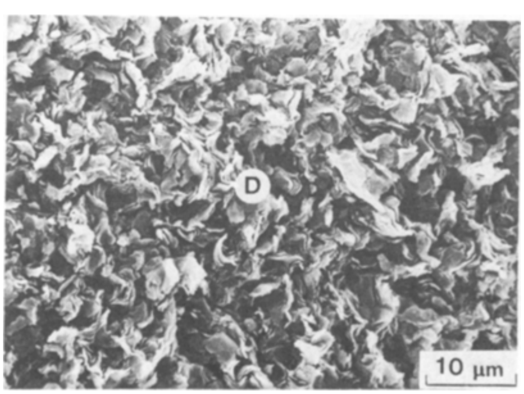

Figure 3 The surface of Fig. 1 after etching with chromic acid, 423 K, 2 h. Original features are lost. The mosaic presents mainly basal planes, position D.

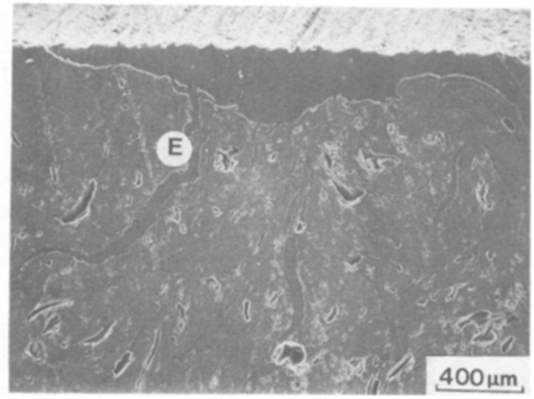

Figure 4 SEM micrograph of polished surface of Ashland coke (HTT 1123 K) prior to etching. Position E: porosity and fissures.

Fig. 4 is the SEM micrograph of a selected area of Ashland A240 coke (HTT 1123 K) before etching with chromic acid showing a smooth surface with open porosity pores and fissures, e.g. position E. Figs. 5, 6 and 7 are SEM micrographs of the "same" area of coke after etching. Fig. 5 shows that preferential oxidation occurs within existing porosity, position E. Fig. 6, position F shows basal plane presentation, position G shows the stacking of parallel lamellae with edge presentation and position H shows a convoluted structure with a sharp change in orientation of lamellae, i.e. acute folding.

Fig. 7, position H shows folding of lamellae with pitting at folds; position I shows basal plane surface of porosity with position J illustrating the layers of "sandwich-like" structures [9].

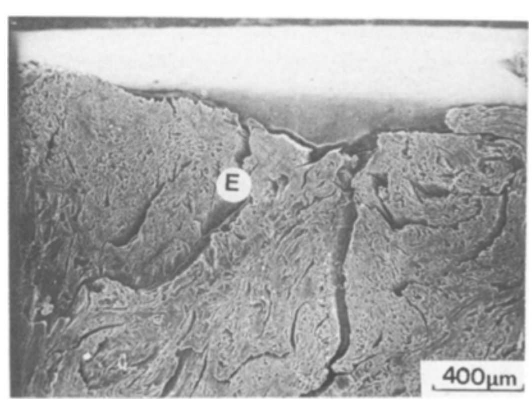

Figure 5 SEM micrographs of surface of Fig. 4 after etching with chromic acid, 423 K, 1 h. Position E: preferential etching of fissure, position F: basal plane presentation in fissure, position G: fissured domain anisotropy, position H: folding of lamellae within domain.

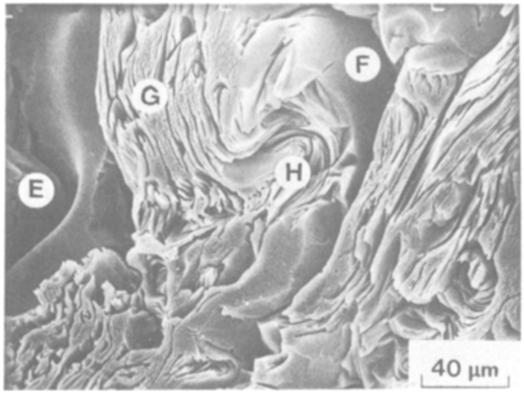

Figure 6 SEM micrographs of surface of Fig. 4 after etching with chromic acid, 423 K, 1 h. Position E: preferential etching of fissure, position F: basal plane presentation in fissure, position G: fissured domain anisotropy, position H: folding of lamellae within domain.

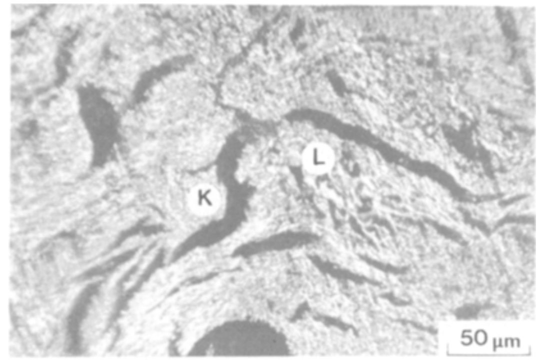

Figure 8 Optical micrograph of calcined petroleum needle-coke (NCB No. 1). Position K: medium-grained mosaics, position L: coarse-flow anisotropy.

The optical micrographs of calcined needle-coke (NCB No. 1) are Figs. 8 and 9. Fig. 8 shows optical texture of medium-grained mosaics (1.5 to 5.0 μm), position K, and coarse-flow anisotropy (30 to 60 μm length, 5 to 10 μm width), position L. Fig. 9 shows basal plane presentation, position M within coarse-flow anisotropy, as well as a $-\pi$ disclination, position N.

Figs. 10 to 13 are micrographs of the calcined needle-coke (NCB No. 1) examined by SEM after oxidation in chromic acid. Figs. 10 and 11 show medium-grained mosaic structure, position K, and coarse-flow anisotropy, position L. Figs. 12 and 13 show basal plane orientation, position M, as well as the $-\pi$ disclination, position N.

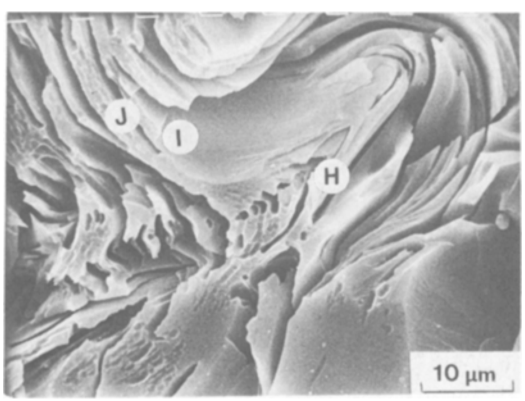

Figure 7 SEM micrograph of Ashland coke, (HTT 1123 K) as Fig. 6. Position H: folding of lamellae with pitting at folds, position I: basal presentation of wall of porosity, position J: "sandwich-like" structures.

Figs. 14 and 15 are micrographs of Conoco calcined needle-coke examined by SEM after oxidation in chromic acid. They show one of the two principal components of needle-cokes [11], i.e. the acicular flow domains to be convoluted structures, positions O, O′.

Fig. 14, in particular, shows clearly that the macro-needles visible to the eye (~ 1000 μm) within pieces of needle-coke are made up of lamellae in a convoluted basal plane presentation, positions O, O′. Fig. 15 shows the convoluted layers within the acicular structures, position O, and that etching occurs at sites of folding or distortion in these convoluted layers, e.g. position P, to create the so-called laths (not a constituent but created by the etching process).

Fig. 16 shows the optical texture of (NCB No. 23) needle-coke of domains (> 60 μm length, > 10 μm width). Position R shows pores and position S shows fissures in the domains.

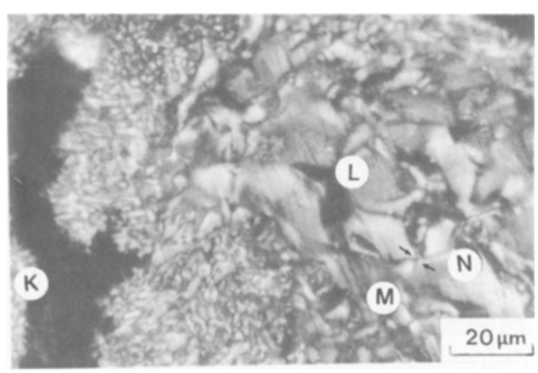

Figure 9 Optical micrograph of calcined petroleum needle-coke (NCB No. 1). Position K: medium-grained mosaics, position L: coarse-flow anisotropy, position M: basal plane presentation, position N, $-\pi$ disclination.

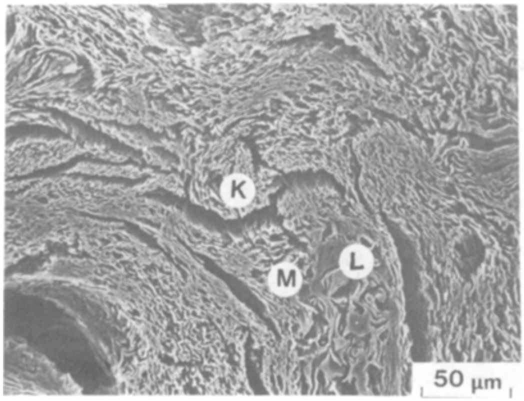

Figure 10 SEM micrograph of surface of Fig. 8 after etching with chromic acid, 423 K, 1 h. Position K: etching reveals acicular structures, positions L and M as Fig. 9.

SEM micrographs of the etched domains are Figs. 17 and 18 which show the other of the two principal structures in needle-coke, i.e. the so-called "sedimentary" or "sandwich-like structure" [11]. Position T shows the striations perpendicular to the basal planes with position T' showing residual etchings of the striations as serrations or "teeth-like" features. Fig. 18 illustrates how the sedimentary layers have grown. Position V shows (to the left) the growth of a new interposed layer as also to the left of position W. Position U shows the preferentially etched sedimentary structure.

Fig. 19 is an optical micrograph of Shell graphitized needle-coke (HTT 3173 K) showing medium-grained and coarse-grained mosaics (1.5 to 10 μm diameter), position X. SEM micrographs (Figs. 20 and 21) are of the "same area" after etching with

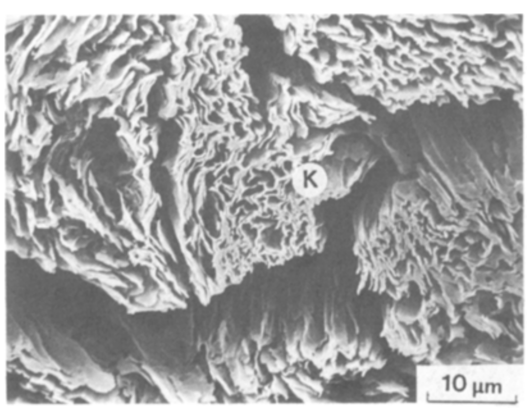

Figure 11 SEM micrograph of surface Fig. 9 after etching with chromic acid, 423 K, 1 h. Position K: etching reveals acicular structures.

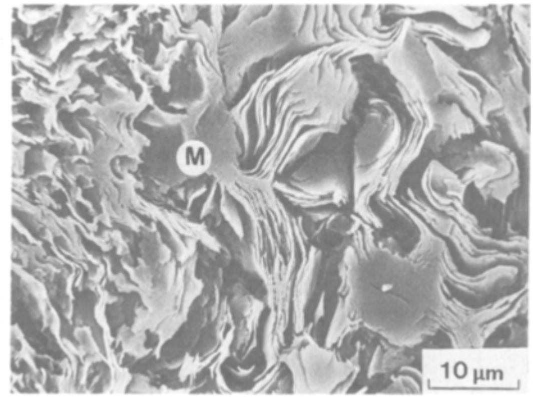

Figure 12 SEM micrograph of surface of Figs. 8 and 9 after etching with chromic acid, 423 K, 1 h.

chromic acid. They define the orientation of the graphitic layers, position X, as well as mosaics with their basal plane presentation, position Y (Fig. 20). Mosaics appear in optical micrographs of the graphitized needle-coke at positions which otherwise would be the isochromatic domains of the calcined needle-coke. Fig. 21, position Z shows the constituent units, mosaic size ($\sim 0.5\ \mu m$ length), and small graphitization cracks between mosaics, position A. Basal plane presentation is as seen at position Y.

Fig. 22 is a second area of optical texture of Shell graphitized needle-coke, showing flow domain anisotropy ($> 60\ \mu m$ length, $> 10\ \mu m$ width), positions B and C.

Figs. 23, 24 and 25 are SEM micrographs of Shell graphitized needle-coke after oxidation in chromic acid (723 K, 5 min). Fig. 23 shows

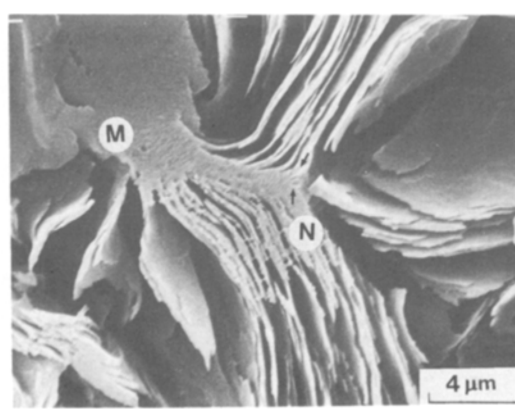

Figure 13 SEM micrograph of surface of Figs. 8 and 9 after etching with chromic acid, 423 K, 1 h. Position N: $-\pi$ disclination.

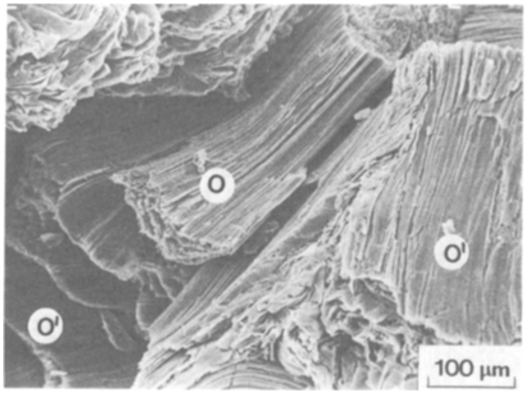

Figure 14 SEM micrograph of Conoco calcined needle-coke after etching with chromic acid, 403 K, 25 wt % loss. Positions O and O′: micro-needles, ~ 200 μm diameter.

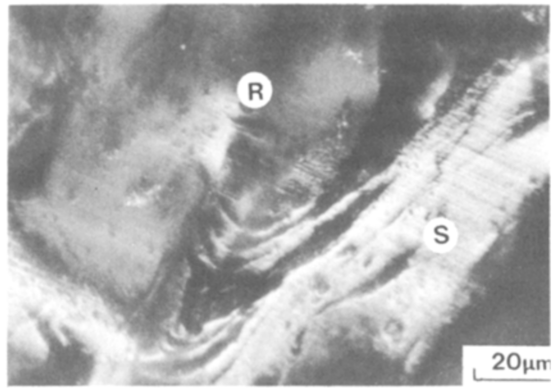

Figure 16 Optical micrograph of calcined petroleum needle-coke (NCB No. 23). Position R: porosity in domains, position S: fissures in domains.

that existing fissuring is enlarged (positions B, C and D). Fig. 24, positions D and E, shows lamellae (within domain anisotropy) which are presented as fine-grained mosaics (1 μm).

Fig. 25 shows the mosaic structure of graphitized layers present in domains. Basal plane orientation of mosaics is seen at position F. Porosity (space) between the graphitic layers or within the layers is seen at position G.

Fig. 26 is an optical micrograph of Shell graphitized needle-coke showing acicular flow domain anisotropy ($>60\,\mu$m length, $>10\,\mu$m width), position I.

Figs. 27 to 30 are SEM micrographs of etched Shell graphitized needle-coke. Fig. 27 shows clearly that the acicular flow domains appear with mosaic structures (seen in Figs. 21 and 24), position I. Fig. 28 shows the surface of heavily etched graphitized coke. There would appear to be large porosity (space) between the layers, seen at position J. Fig. 29 shows the stacking of graphitized lamellae (positions L and M) in the calcined coke shown as acicular flow anisotropy, position K, Fig. 11. Fig. 30, at higher magnification, shows that the graphitized basal plane etches into a "tortoise-shell" appearance, position L.

4. Discussion

4.1. Use of chromic acid

This study indicates that etching of cokes with chromic acid solution is a convenient and informative method to elucidate three-dimensional aspects of structure within a variety of cokes of different optical texture.

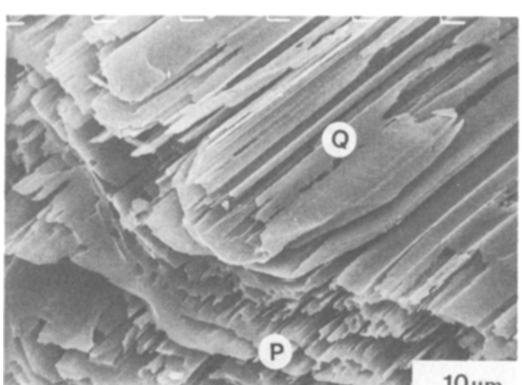

Figure 15 SEM micrograph of micro-needle of Fig. 14, position Q showing the distinct layering within the acicular structures. Position P shows etching into folds of basal planes of acicular structures to produce laths.

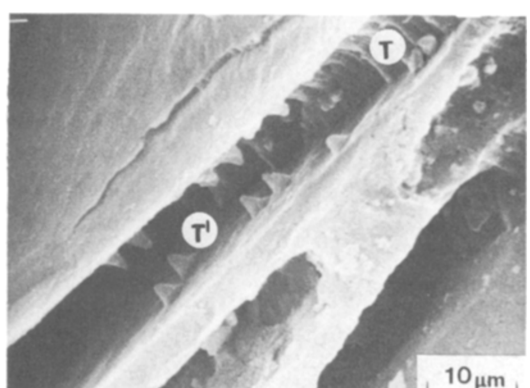

Figure 17 SEM micrograph of surface of Fig. 16 after etching with chromic acid, 423 K, 1 h. Position T: etching within "sandwich structure" to produce striations, position T′: residual teeth-like etching of sandwich striations.

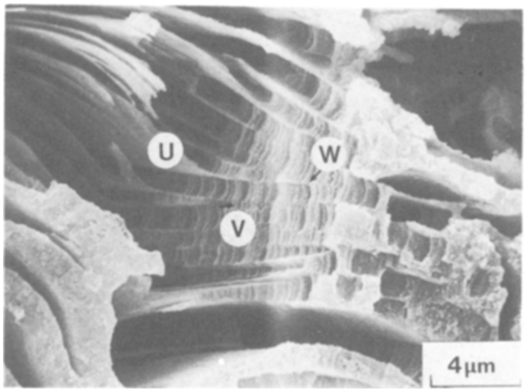

Figure 18 SEM micrograph of Fig. 16 after etching with chromic acid, 423 K, 1 h. Position U: basal plane presentation, positions V and W: development of layers (from right to left) within sandwich striations.

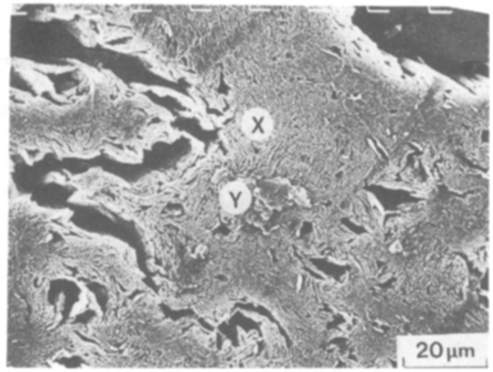

Figure 20 SEM micrograph of Shell graphitized needle-coke after etching with chromic acid, 423 K, 5 min. As Fig. 19, position X: direction of lamellae, position Y: basal plane presentation.

4.2. Etching of mosaics

Chromic acid solution selectively oxidizes mosaics which have prismatic edge presentation to the polished surface so creating pitting between the grains of the mosaic. This elucidates the size and shape of mosaics. Optical microscopy indicates that the mosaics are a continuum of anisotropic material with random relative orientation of the grains within the mosaics. In terms of macro-properties such as structure, this will promote strength and restrict crack propagation, following stress, through this type of material.

4.3. Etching of calcined needle-cokes

The information available from the etching studies of the Ashland, NCB and Conoco calcined cokes may be summarized as follows.

Figs. 4 and 5 indicate that etching extends the dimensions of existing porosity and fissures.

The basal plane presentation as walls of porosity/fissures is clearly established, as Fig. 6, position F. Such a basal plane is also seen in Fig. 7, position I. To the left of the pore (position I) can be seen the etched material which extends the dimensions of the pore. The etching reveals, very frequently, the layered or sedimentary type structure of coke recognizable as domains by optical microscopy. The preferential etching into layers, Fig. 7, position J, could indicate weak bonding between layers. If this is the case then during thermal and mechanical stressing slip movement may be possible between the layers to accommodate these stresses. Volume expansion can be accommodated within the range of porosity exhibited by the etching.

Within the cokes are volume elements of extremely convoluted material, i.e. extreme bend-

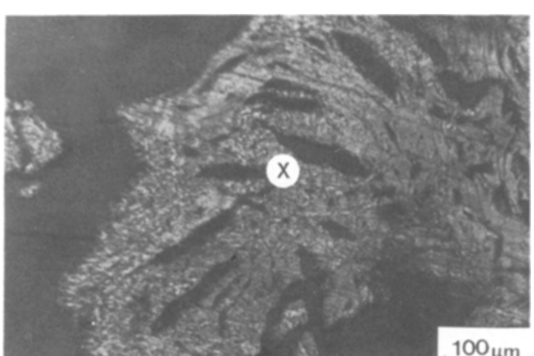

Figure 19 Optical micrograph of Shell graphitized needle-coke. Position X: medium-grained and coarse-grained mosaics.

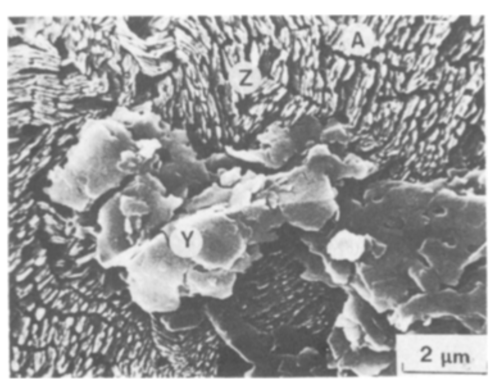

Figure 21 SEM micrograph of Shell graphitized needle-coke after etching with chromic acid, 423 K, 5 min. Position Y: basal plane presentation, position Z: etched units, 1 μm length, position A: graphitization cracks between mosaics.

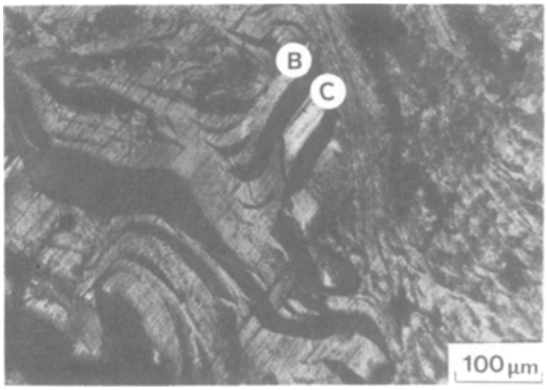

Figure 22 Optical micrograph of Shell graphitized needle-coke. Positions B and C: flow domain anisotropy.

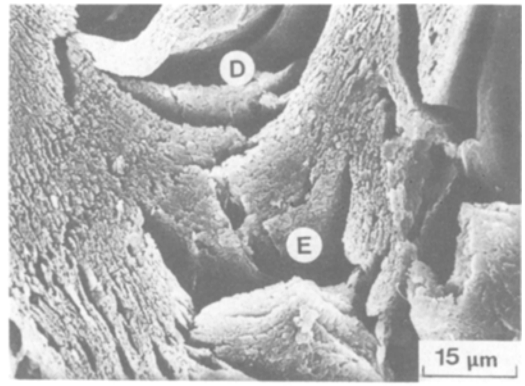

Figure 24 SEM micrograph of Shell graphitized needle-coke after etching with chromic acid, 423 K, 5 min. As Fig. 22, positions D and E: etched units ~ 1 μm in length which may appear as mosaics.

ing of lamellar stacking. Such volume elements, e.g. Fig. 7, position H, exhibit significant preferential etching by chromic acid. Presumably, other etchants or gasifying gases may show similar preferential etching.

Disclinations (i.e. structural defects) [13] are revealed by etching. Fig. 9, position N, an optical micrograph, clearly shows a $-\pi$ disclination. The lamellae arrangements which constitute this disclination are as in Fig. 13, position N. Position M, Fig. 9 (showing purple in colour micrography) is seen as basal plane presentation by SEM. The etching technique confirms interpretations of structure based on colour analysis of optical texture.

Further detail is made available of acicular structures. A previous study [9] illustrates the macro-needles (~ 1 mm diameter) of bulk pieces of needle-coke. Within these macro-needles are substructures as illustrated in Fig. 14, positions O and O′. Position O is a micro-needle, ~ 200 μm diameter, and extending into the coke piece. Position O′ illustrates further larger micro-needles. It would appear that the macro-needle observable to the naked eye [9] is fabricated of bundles of this type of micro-needle.

These acicular structures are composed of enclosed volumes, exhibiting longitudinal basal planes of highly convoluted lamellae, Fig. 11, position K. Again, porosity between these lamellae can accommodate thermal stresses (expansions) as well as slip between the layers. The convolutions result from acute bending of lamellae and preferential etching at folds in the convolutions

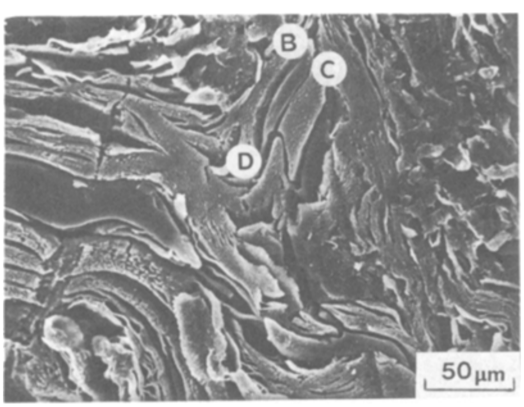

Figure 23 SEM micrograph of Shell graphitized needle-coke after etching with chromic acid, 423 K, 5 min. As Fig. 22, positions B and C: development of porosity, position D: etched units ~ 1 μm in length which may appear as mosaics.

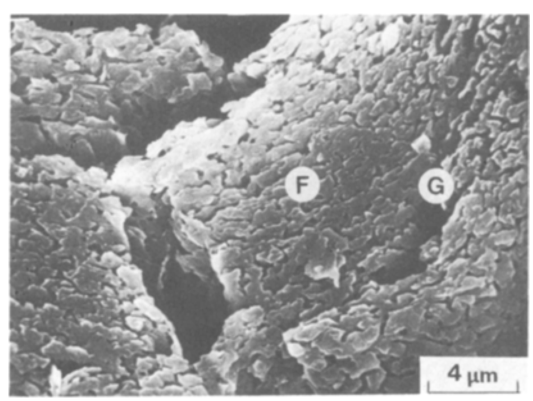

Figure 25 SEM micrograph of etched domain surface of Fig. 22. Position F: etched units ~ 1 μm in length. Position G: porosity between graphitic layers.

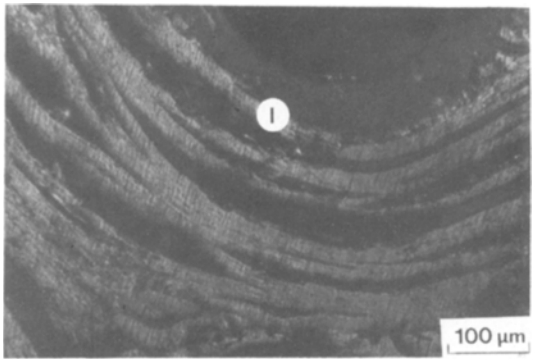

Figure 26 Optical micrograph of Shell graphitized needle-coke. Position I: shrinkage fissures within flow domain anisotropy.

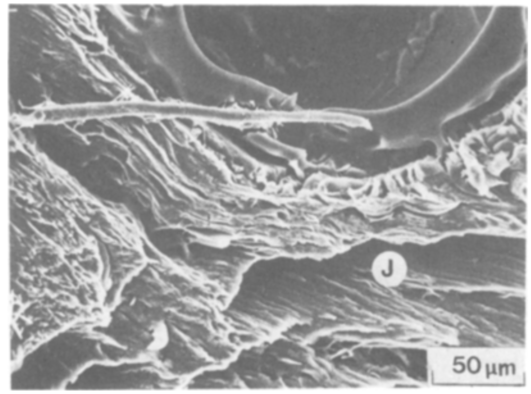

Figure 28 SEM micrograph of Shell graphitized needle-coke after etching with chromic acid, 423 K, 15 min. Position J: fissures between layers in acicular flow anisotropy.

results in laths (~ 1 μm) in width, Fig. 15, positions P and Q.

Aspects of growth of the sedimentary structures are revealed by etching. Fig. 18 shows significant layering of structures within domains. To the left of positions V and W are seen the development of new layers of structures. This must reflect in some way carbon formation in the delayed coker.

The etching process to reveal the layered arrangements of structures appears also to produce structures which are perpendicular to the planes of the lamellae, Fig. 17, position T. Progressive etching at the interface results in "teeth-like" remnants of stacked lamellae, Fig. 17, position T′.

4.4. Etching of graphitized needle-cokes

It is established that heat treatment of needle-cokes to 3173 K produces a graphitized material. However, changes in optical texture become apparent. The large isochromatic areas of calcined needle-cokes, e.g. Fig. 16, exhibit mosaics on graphitization.

The etching of these graphitized cokes exhibits features which are significantly different from the calcined cokes. The most pronounced differences are seen in Figs. 21 and 25. The lamellae now etch into small bundles, 1 to 2 μm, as around position Z, Fig. 21. There are also cracks or fissures, 0.1 μm across, as seen at position A, Fig. 21. It would appear that Fig. 21 is the etched cross-section of a graphitized acicular structure, compared with Fig. 11. Position Y, Fig. 21 is residual graphite of basal plane presentation. In large structures subject to thermal stress, e.g. the arc-electrode, which contain graphitized needle-cokes, accommodation of stress may be related to the structures of Figs. 21 and 25, thermal

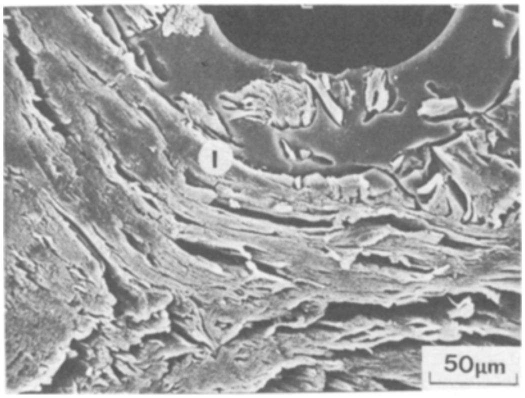

Figure 27 SEM micrograph of Shell graphitized needle-coke after etching with chromic acid, 423 K, 15 min. As Fig. 26, position I: etched flow domain anisotropy.

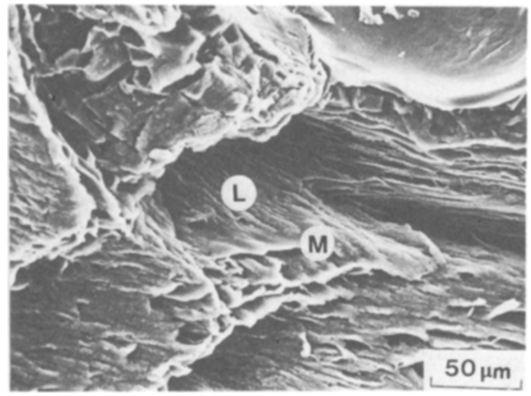

Figure 29 SEM micrograph of etched Fig. 26. Positions L and M: graphitized lamellae of flow domain anisotropy.

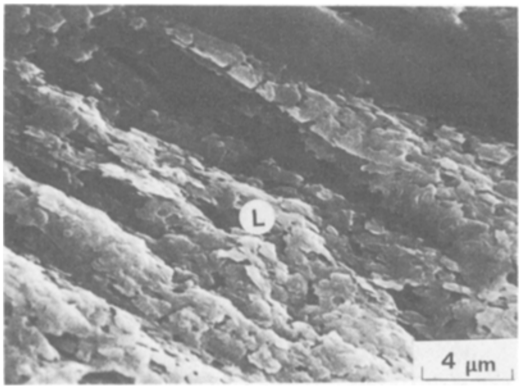

Figure 30 SEM micrograph of etched Fig. 26. Position L: tortoise-shell appearance, 1 μm within basal planes.

expansion being absorbed by closure of such cracks.

Figs. 26 to 30 examine the surfaces (longitudinal) of the graphitized structures (seen as in Fig. 14 for calcined material). The basal planes, as seen at positions L, Figs. 29 and 30, exhibit a "tortoise-shell" appearance. The planes have also etched into areas ~ 1 to 2 μm^2 separated by micro-cracks. Hence the lamellae in the flow domain also develop graphitization cracks similar to those seen in domains. Fig. 30 shows that these lamellae retain their convoluted form. Chromic acid etching therefore reveals aspects of structure in graphitized basal planes not otherwise apparent.

5. Conclusions

Chromic acid solution is a convenient etchant with which to examine structure in cokes, calcined and graphitized. Cokes with optical textures of coarse-grained mosaics and acicular anisotropy have been examined, the detail of structure of mosaics being clearly revealed. Etching of needle-cokes reveals many relevant features including structure of porosity, the sedimentary nature of the structure within domains, the preferential etching revealing extreme bending of lamellae and the presence of disclinations. Acicular structures, from 1 mm to < 0.1 μm are discussed in detail. The growth process of sedimentary coke (domains) can be assessed. It is suggested that slip between layers of the sedimentary structures may assist in the accommodation of thermal stresses. Etching of graphitized needle-coke, in particular the acicular structures, reveals features quite different from calcined needle-coke, the basal planes etching into isolated areas, ~ 1 to 2 μm^2 area.

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