# Effects of calcination upon properties of needle-cokes

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A green needle-coke was heated from 773 to 1323 K at 50 K intervals. The following properties were assessed: bulk dimensions, optical texture, fissure development, microstrength and elemental composition. It was observed that volumetric shrinkage of the green needle-coke commenced at about 900 K and appears to be largely complete at 1200 K. The shrinkage is 7%. The proportion of anisotropic components which make up the optical texture of needle-coke are unaffected by calcining. Contraction fissuring develops preferentially in domain optical texture, the shape of fissures being determined by lamellar orientation within the domain. Fissuring also appears to be complete at 1200 K. The microstrength of needle-coke increases continuously with calcining temperature.

## 1. Introduction

In a review of aspects of the science and technology of graphite manufacture, Ragan and Marsh [1] comment upon possible effects of oxidation of petroleum coke as it is being calcined in several types of calciner, e.g. rotary hearth furnace or a rotary kiln. The calcined coke, often needle-coke, is used as the grist or filler phase, together with pitch to make graphite of arc-electrode quality. During the calcination process several properties of the coke change irreversibly, e.g. resistivity, true density and strength [2, 3]. During the heat treatment the ingress of air into the calciner may cause oxidation of the coke with resulting deterioration in coke properties.

This paper assesses changes shown by a green needle-coke, upon heat treatment in an inert atmosphere to calcination temperatures. The properties assessed are bulk dimensions, optical texture, strength and elemental analysis. Subsequent studies examine effects of oxidation and fracture mechanics [4, 5]. The kinetics of coke shrinkage during calcination are reported by Wallouch and Fair [6].

## 2. Experimental
### 2.1. Materials used

The cokes used were green and calcined needle-coke (ex Shell). Analyses are given in Table I.

### 2.2. Changes in bulk dimensions of green needle-coke with heat treatment

For examination of changes in bulk dimensions of green needle-coke upon heat treatment a series of oblong blocks of green coke were prepared. The blocks were produced from coke lumps by rough grinding upon a corundum wheel and then squared and finished upon 600 grit corundum paper. The symbols of the block dimensions ($x$ width, $y$ length and $z$ height) and the positions for dimensional measurement were marked upon the block sides. Block dimensions were measured before and after heat treatment by means of a vernier caliper, accurate to $\pm 20\,\mu m$.

The finished green coke blocks were placed in a silica boat ($12\,cm \times 2\,cm$) which was placed in a horizontal tube furnace and continuously flushed with nitrogen. Temperature and rate of heating were controlled by a Stanton Redcroft Linear

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TABLE I Properties of green and calcined needle-cokes

|  | Green coke | Calcined coke |
|---|---|---|
| Sulphur (wt %) | < 0.4 | 0.26 |
| Hydrogen (wt %) | 3.5 | 0.04 |
| Ash (wt %) | – | < 0.1 |
| Vanadium (wt ppm) | – | 2.0 |
| Real density (kg m$^{-3}$) | – | 2.13 |
| Tap density (kg m$^{-3}$) | – | 0.77 |
| Cube coefficient of thermal expansion ($K^{-1}\alpha_{473}$) | $4.2 \times 10^{-5}$ | $4.0 \times 10^{-6}$ |

Variable Programmer. A heating rate of $4\,K\,min^{-1}$ was used. The green coke blocks were heated separately in the temperature range of 773 to 1323 K at 50 K intervals. Each block was allowed to soak at its respective heat treatment temperature for 1 h, cooled under nitrogen and then reweighed and remeasured.

## 2.3. Changes in optical texture and fissure development of green needle-coke with heat treatment

The optical texture of coke (see Table II) is a description of the sizes of isochromatic areas revealed by examination of a polished coke surface by polarized reflected light optical microscopy [7]. After heat treatment each of the coke blocks was examined by optical microscopy to assess any changes in optical texture and fissure development within the coke.

The heat treated coke blocks were each separately mounted in "Metset" fast setting polyester resin, the resin was allowed to cure overnight until set, and then sectioned to expose a coke surface.

The first stage of polishing the coke surface was carried out on a water-lubricated "Metserv" hand grinder using four grades, in turn, of corundum paper; 220, 320, 400 and 600 grit rotating the specimen to remove grinding marks. The coke surface was thoroughly washed to remove residual grit. The fine polish of the coke surface, necessary for good reflectivity, was produced on a "Metserv" Universal Polisher' using three rotating laps, covered with Selvyt cloth, and alumina polishing powders, of progressively smaller particle size, 5/20, 3/50 and gamma, lubricated with distilled water. The coke surface was cleaned by distilled water in an ultrasonic water bath between each lap to prevent carry over of alumina particles. The polish of the coke surface was checked using an optical microscope at the end of polishing on each lap.

For examination by optical microscopy the polished coke surfaces were mounted onto glass slides by "blue tak" and levelled. The coke surfaces were examined using a Vickers M17 polarized reflected light microscope, in plane polarized light with a half-wave retarder plate in the column of the microscope so producing a coloured image. This image shows the presence of fissures developed in the coke and coloured photomicrographs of each coke were taken with exposure settings controlled by a Vickers J.S. 37 Auto Exposure controller.

## 2.4. Changes in microstrength of green needle-coke with heat treatment

The changes in strength of green needle-coke upon heat treatment were assessed using a microstrength testing apparatus [8]. Coke tested in the microstrength device was of particle size

TABLE II Nomenclature to describe optical texture in polished surfaces of cokes

| | |
|---|---|
| Isotropic (I) | No optical activity |
| Very fine-grained mosaics (VMf) | $< 0.5\,\mu m$ in diameter |
| Fine-grained mosaics (Mf) | 1.5 to 0.5 $\mu m$ in diameter |
| Medium-grained mosaics (Mm) | 5.0 to 1.5 $\mu m$ in diameter |
| Coarse-grained mosaics (Mc) | 10.0 to 5.0 $\mu m$ in diameter |
| Supra mosaics (SM) | Mosaics of anisotropic carbon orientated in the same direction to give a mosaic area of isochromatic colour |
| Medium-flow anisotropy elongated (MFA) | $< 30\,\mu m$ in length; $< 5\,\mu m$ in width |
| Coarse-flow anisotropy elongated (CFA) | 60 to 30 $\mu m$ in length; 10 to 5 $\mu m$ in width |
| Acicular flow domain anisotropy (AFD) | $> 60\,\mu m$ in length; $< 5\,\mu m$ in width |
| Flow domain anisotropy elongated (FD) | $> 60\,\mu m$ in length; $> 10\,\mu m$ in width |
| Small domains, isochromatic (SD) | 60 to 10 $\mu m$ in diameter |
| Domains, $\sim$ isometric (D) | $> 60\,\mu m$ in diameter |
| $D_b$ is from basic anisotropy of low-volatile coking vitrains and anthracite. | |
| $D_m$ is by growth of mesophase from fluid phase. | |
| Ribbons (R) Strands of mosaics inserted into an isotropic texture. | |

TABLE III Changes in block dimensions of green needle-coke with heat treatment to 1323 K

| Heat treatment temperature (K) | Block dimensions | | | | | |
| --- | --- | --- | --- | --- | --- | --- |
| | $x$ | | $y$ | | $z$ | |
| | $\Delta L$ | $\Sigma\%$ | $\Delta L$ | $\Sigma\%$ | $\Delta L$ | $\Sigma\%$ |
| 873 | − 0.019 | − 0.94 | − 0.023 | − 0.70 | − 0.003 | − 0.02 |
| 923 | − 0.044 | − 1.96 | − 0.028 | − 2.05 | − 0.014 | − 1.70 |
| 973 | − 0.306 | − 1.69 | − 0.053 | − 2.48 | − 0.006 | − 0.46 |
| 1023 | − 0.113 | − 5.14 | − 0.612 | − 9.5 | − 0.077 | − 3.86 |
| 1073 | − 0.112 | − 4.95 | − 0.122 | − 5.09 | − 0.061 | − 4.98 |
| 1123 | − 0.119 | − 6.69 | − 0.233 | − 8.57 | − 0.084 | − 5.78 |
| 1173 | − 0.126 | − 7.06 | − 0.164 | − 6.84 | − 0.089 | − 6.55 |
| 1223 | − 0.182 | − 7.30 | − 0.199 | − 7.71 | − 0.125 | − 6.91 |
| 1273 | − 0.125 | − 6.6 | − 0.132 | − 4.8 | − 0.076 | − 7.10 |
| 1323 | − 0.165 | − 7.3 | − 0.221 | − 5.7 | − 0.089 | − 7.20 |

14 to 25 BS mesh (1180 to 600 $\mu$m). To produce coke of this size range, lumps of green and calcined coke were ground by pestle and mortar and sieved for 3 min upon a mechanical sieve shaker. Grinding of the green coke was carried out in a fume cupboard, disposable gloves and dust masks being worn. Ten 10 g batches of the correctly sized green coke were prepared and heated as described previously in the range 773 to 1323 K at 50 K intervals. Green coke and the ground calcined coke were weighed into 2 g charges for use in the microstrength test.

For microstrength testing one each of two, 2 g charges was placed into a stainless steel cylinder (305 mm long, 25 mm internal diameter) with twelve ball bearings (8 mm diameter). The ends of the steel tubes were sealed with stainless steel dust sealing caps. The cylinders were then placed onto an electrically driven holding frame which rotated the cylinders around their short axes. The speed of rotation was monitored to be constant at 25 ± 1 revolutions per minute, the speed necessary for the ball bearings and the coke to fall freely the full length of the cylinders. In testing of green and industrially calcined coke the duration of the test was varied from 200 to 800 revolutions. Test duration was standardized at 600 revolutions for laboratory heat treated cokes.

After completion of the rotations the broken coke was swept from each cylinder onto a sieve set, aperture sizes 600 $\mu$m (25 BS mesh), 212 $\mu$m (72 BS mesh) and a catch pan. The whole sieve set was then shaken for 3 min upon a mechanical sieve shaker. The broken coke retained on each of the sieves, and the catch pan was weighed. The procedure was repeated on 4 to 5 charges of each coke and an average weight of coke retained on the sieves and pan recorded.

## 2.5. Changes in elemental composition of green needle-coke with heat treatment

After microstrength testing, 2 g of 212 to 600 $\mu$m (25 to 72 BS mesh) sized needle-coke product, of each treatment temperature, was retained for assessment of changes in its carbon, hydrogen and nitrogen elemental analysis. The analyses were on a dry basis determined using a Perkin Elmer 240 B analyser.

## 3. Results
### 3.1. Changes in bulk dimensions of green needle-coke with heat treatment

The measurements of the change of the three principal block dimensions $x$, $y$, $z$ are given in Table III. The changes in block dimensions are expressed as percentages. Weight loss is similarly expressed as a percentage. Results are shown against heat treatment temperature in Figs. 1 to 4.
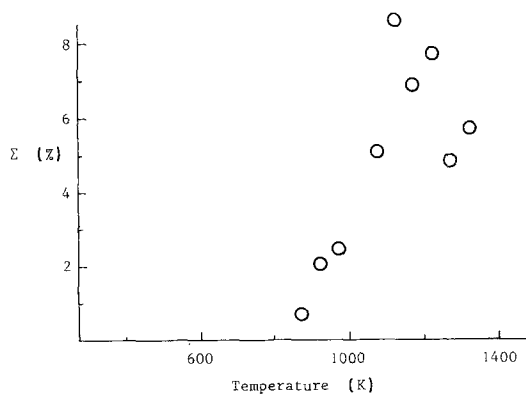


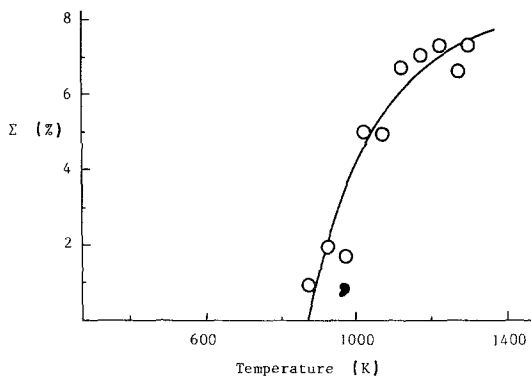Figure 1 Variation of shrinkage, $x$-dimension, with HTT for green needle-coke.

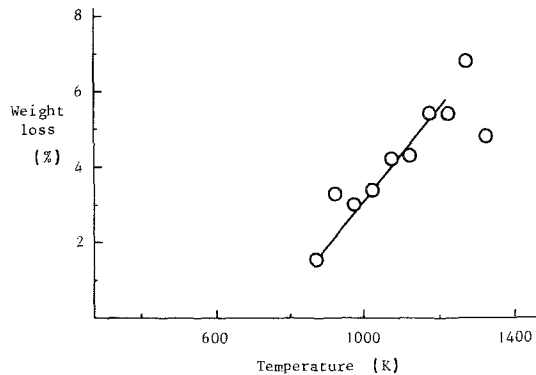*Figure 2* Variation of shrinkage, *y*-dimension, with HTT for green needle-coke.



*Figure 4* Variation of weight loss with HTT for green needle-coke.

## 3.2. Changes in optical texture and fissure development of green needle-coke with heat treatment

Figs. 5 and 6 are optical micrographs of green needle-coke. Fig. 5 shows a typical optical texture, Position A, of domains surrounded by areas of acicular flow domain, Position B, which, upon grinding, produces the acicular coke particles responsible for the term "Needle-Coke". Fig. 5, Position C, shows medium-grained mosaics associated with the transverse sectioning of the acicular flow domains of Position B. Fig. 6, Position D, shows detail of the interface between domain and acicular flow domain anisotropy. The optical texture of the green needle-coke possesses few cracks or fissures apart from small fissures in the domain optical texture.

Figs. 7 and 8 are optical micrographs of green needle-coke heated to 1023 K with Fig. 7, Position E showing domain optical texture surrounded by acicular flow domain anisotropy, Position F. Com-

parison of Figs. 7 and 8 with Figs. 5 and 6 shows the development of small fissures within the domain optical texture of the heat treated coke. The shape of the fissures in Fig. 8 are thought to be directly related to the orientation of the lamellar stacking through which they have developed.

Figs. 9 and 10 are optical micrographs of green needle-coke, HTT 1123 K, with Fig. 9, Position G showing domain optical texture and Position H showing acicular flow domain anisotropy. Comparison of Fig. 9, Position G with Position H shows there to be markedly more fissuring within the domain optical texture than in the acicular flow domain anisotropy. Comparisons of Figs. 9 and 10 with Figs. 7 and 8 show that the optical texture of the heat treated coke differs only in the larger number and size of fissures developed in the domains of Figs. 9 and 10.

Figs. 11 and 12 are optical micrographs of green needle-coke, HTT 1323 K with Fig. 11,
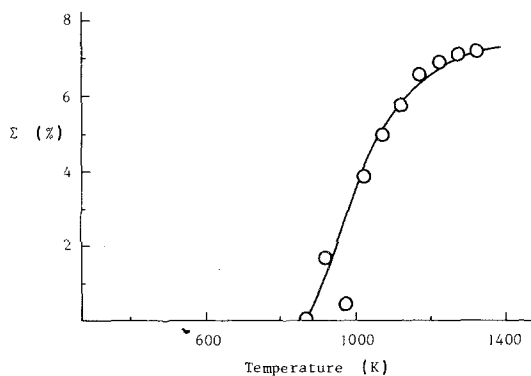


*Figure 3* Variation of shrinkage, *z*-dimension, with HTT for green needle-coke.
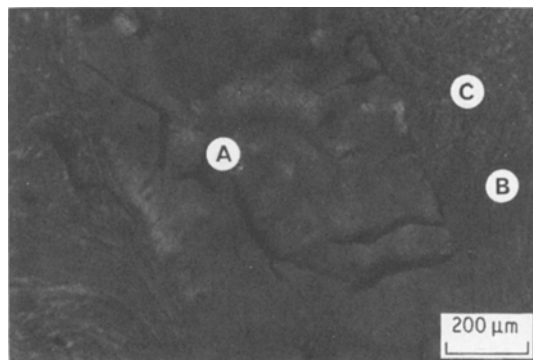


*Figure 5* Optical micrograph of green needle-coke. Position A is of domain optical texture. Position B is of acicular flow domain. Position C is of medium-grained mosaics.
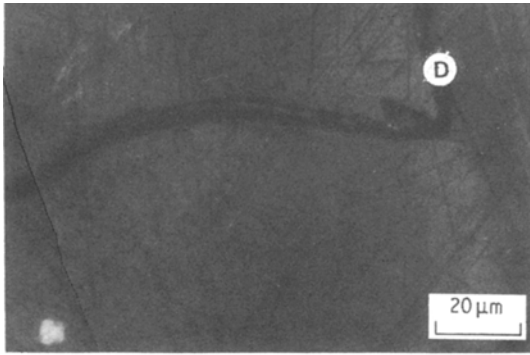
Figure 6 Optical micrograph of green needle-coke. Position D shows interface between domain and acicular flow domain anisotropy. Note the lack of fissuring in the domain.



Figure 8 Optical micrograph of needle-coke, HTT 1023 K. Note the fissure development in this domain.

Position I showing an area of domain optical texture and Position J showing acicular flow domain anisotropy. Comparison of Fig. 11, Position I, with Fig. 12, Position J, shows continued fissure development only in the domain optical texture. Comparison of Figs. 11 and 12 with Figs. 9 and 10 shows there to be no significant differences in optical textures or in fissure development between these cokes despite the different heat treatment temperatures (1323 K and 1123 K, respectively).

### 3.3. Changes in microstrength of green needle-coke with heat treatment temperature

The results of increasing duration of the micro-strength test, i.e. number of revolutions, upon the weights of the resultant sizes of green and calcined needle-coke are in Figs. 13 and 14, where:
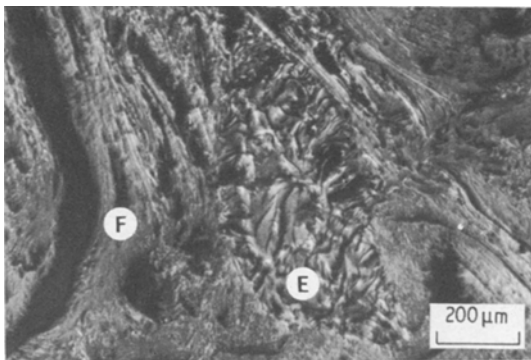
$$R = \frac{W_r}{W_0} \times 100, \qquad (1)$$



Figure 7 Optical micrograph of needle-coke, 1023 K. Position E of domain optical texture. Position F is of acicular flow domain.
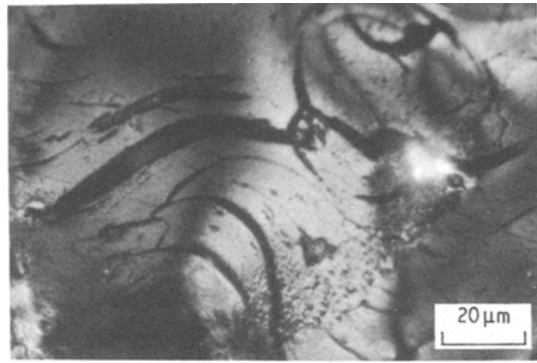
where $R$ is the reduction index, $W_r$ is the weight retained on sieve, and $W_0$ is the weight of original charge. The reduction indices are defined as $R_1$ for weight per cent of coke $> 600 \, \mu m$; $R_2$, for weight per cent of coke $< 600 \, \mu m$ and $> 212 \, \mu m$; $R_3$ for weight per cent of coke $< 212 \, \mu m$. Figs. 13 and 14 show the reduction indices plotted against increasing duration of test for green and calcined needle-coke. Figs. 15 to 17 show the reduction indices plotted against heat treatment temperature of green needle-coke, test duration 600 revolutions.

### 3.4. Changes in elemental composition of green needle-coke with heat treatment

The changes in elemental composition, in terms of the content of carbon, hydrogen and nitrogen of green needle-coke resulting from heat treatment are in Table IV. Changes in hydrogen/carbon (H/C) ratio for green needle-coke resulting from heat treatment are plotted against heat treatment temperature in Fig. 18.

TABLE IV Elemental analysis of green needle-coke with increasing heat treatment temperature

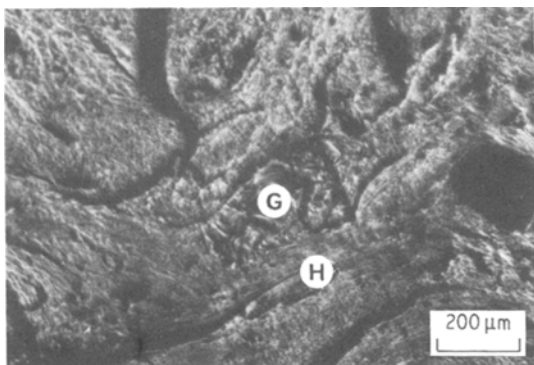| Heat treatment temperature (K) | Elemental analysis | | | |
|---|---|---|---|---|
| | %C | %H | %N | H/C |
| 773 | 94.29 | 3.52 | 0.11 | 0.37 |
| 923 | 97.29 | 2.54 | 0.13 | 0.26 |
| 973 | 97.54 | 2.03 | 0.17 | 0.21 |
| 1073 | 98.36 | 1.28 | 0.16 | 0.13 |
| 1123 | 98.86 | 1.15 | 0.15 | 0.12 |
| 1173 | 98.87 | 0.91 | 0.15 | 0.09 |
| 1223 | 98.89 | 0.77 | 0.12 | 0.08 |
| 1273 | 98.96 | 0.68 | 0.13 | 0.07 |
| 1673 | 99.02 | 0.35 | 0.10 | 0.04 |

*Figure 9* Optical micrograph of needle-coke, HTT 1123 K. Position G is of domain optical texture. Position H is of acicular flow domain.
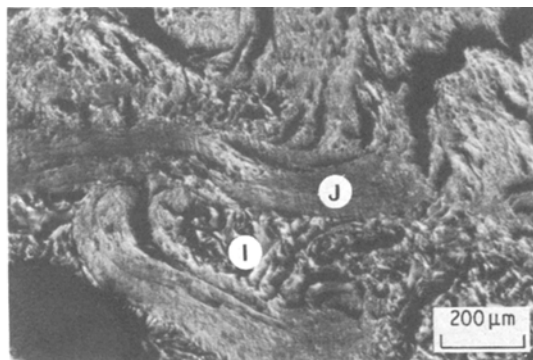


*Figure 11* Optical micrograph of needle-coke HTT 1323 K. Position I is of domain optical texture. Position J is of acicular flow domain.

## 4. Discussion
### 4.1. Changes in bulk dimensions of green needle-coke with heat treatment

Figs. 1 to 3 show the percentage strain term for the principal dimensions $x$, $y$, $z$ plotted against heat treatment temperature. Although Fig. 1 has scatter, the figures show that negative strain, i.e. shrinkage, of the coke commences at $\simeq 800$ K and rises rapidly to a maximum value of 7% at $\simeq 1200$ K. Where commercial calcination is carried out in the temperature range 1600 to 1700 K so as to pre-shrink the petroleum coke, the economic advantages of reducing calcining temperatures are considerable [9]. Figs. 3 and 4 would suggest, for the subject needle-coke, that shrinkage is largely complete at 1323 K and a reduction of calcining temperature is possible. However, calcination at $\sim 1700$ K may be necessary if thermal desulphurization of the coke is also required [3, 10].

Fig. 4 shows that the per cent weight loss has a linear variation with heat treatment temperature to about 1200 K. This weight loss may be associated with micro-fissure formation [4] or from heteroatom removal.

### 4.2. Changes in optical texture and fissure development of green needle-coke with heat treatment

Comparison of Fig. 5 with Figs. 7, 9 and 11 shows that over the temperature range 600 to 1300 K there is no change in the optical texture of the coke. There is, however, a marked development of fissuring, particularly in the domain optical texture, e.g. Fig. 7, Position E.

The fissuring within the optical texture results from the contraction stresses created by coke shrinkage. This development of the fissures via contraction stresses is supported by evidence of fissure morphology shown in Fig. 8. The fissures are "crescent-shaped" and follow the crystallographic orientation of the lamellae as deduced from changes in colour of the optical image.



*Figure 10* Optical micrograph of needle-coke HTT 1123 K. Note the fissure development in this domain.
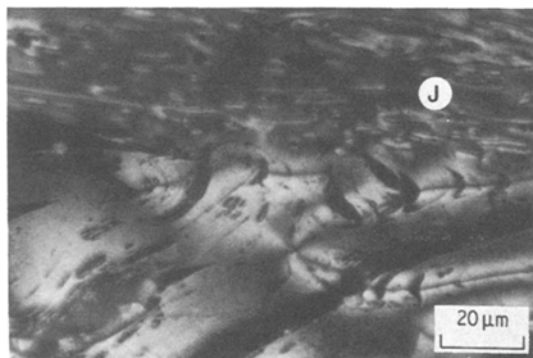


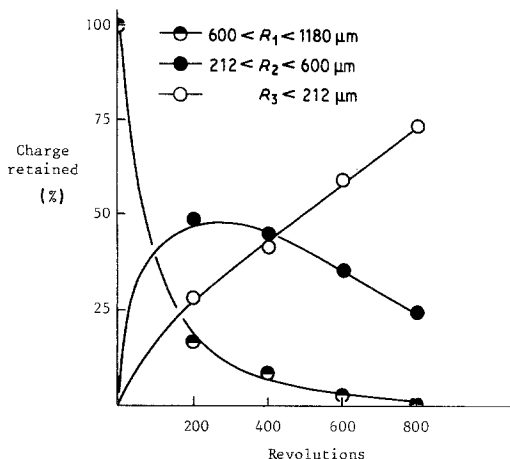*Figure 12* Optical micrograph of needle-coke HTT 1323 K. Position J is of acicular flow domain.

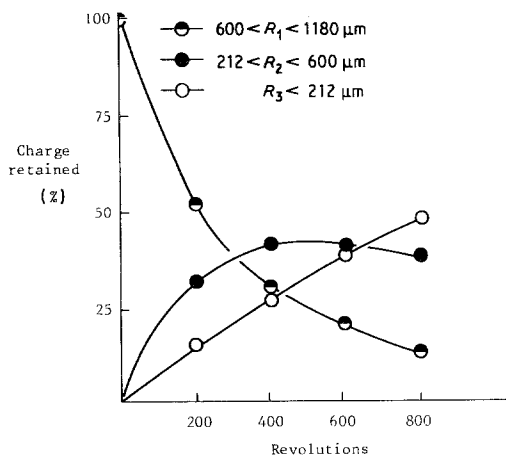*Figure 13* Variation of microstrength indices with test duration for green needle-coke.



*Figure 14* Variation of microstrength indices with test duration for calcined needle-coke.

Hence, the fissure morphology results from separation of lamellae under tensional stresses induced by shrinkage.

Comparison of Figs. 7 and 9 shows that at temperatures below 1123 K the fissure network increases in size and extent, reflecting the increasing shrinkage and contraction stresses acting within the coke. Above 1123 K, however, there is no observable increase in fissure development within the coke (cf. Figs. 9, 10, 11 and 12). Preferential development of fissuring within domains probably results from the long range of crystallographic orientation, deduced from the optical image, of lamellae within them. Under the contraction stresses induced by shrinkage the common orientation of the lamellae allow for the development of several fissures of identical morphology resulting from multiple lamellar splitting. In acicular flow domain anisotropy lamellar orientation is short range and exhibits rapid re-orient-ations; hence the "rod-like" extinction contours in the optical image. Fissure formation in such structures would be energetically less favourable and hence such acicular anisotropy remains relatively fissure free.

The formation of fissures within the coke, as a result of heat treatment or calcination, although detrimental to its strength properties, e.g. crushing strength, may result in the improvement in coefficient of thermal expansion (CTE) seen in Table I. Closure of the fissure at elevated temperatures would absorb expansion, hence reducing CTE.

The continuing weight loss of the coke with increasing temperature which occurs with reduced shrinkage (cf. Figs. 3 and 4) cannot be accounted for by the formation of fissures within the optical texture. It is possible that continued heteroatom removal associated with heat treatment accounts for the continued weight loss. However, transmission electron microscopy of similar heat-
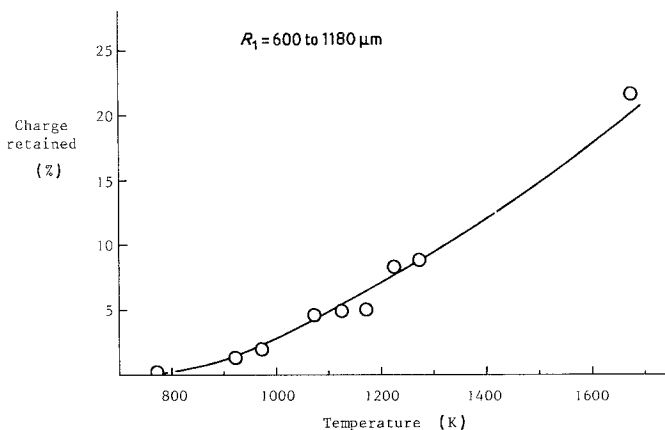


*Figure 15* Variation of $R_1$ microstrength index with HTT for needle-coke using 600 revolutions.
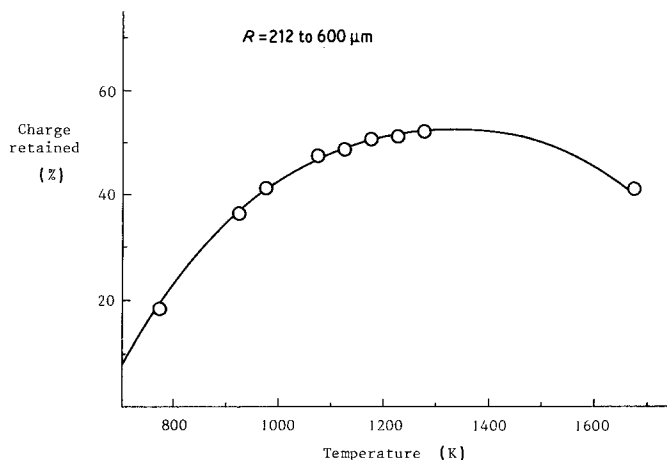
*Figure 16* Variation of $R_2$ microstrength index with HTT for needle-coke using 600 revolutions.

treated carbons [11] has shown re-orientation of lamellae and that this results in the formation of microfissures of only a few nanometres in size and not resolvable in optical microscopy. It is the formation of these micro-fissures which may account for continued weight loss without bulk shrinkage.

## 4.3. Changes in microstrength of green needle-coke with heat treatment

Figs. 13 and 14 show that the green needle-coke is weaker than the calcined coke. Over any duration of test the $R_1$ index, i.e. coke $> 600 \mu m$, for the green coke is smaller than that for the calcined coke. Also the $R_2$ index, i.e. coke $< 600 \mu m$ and $> 212 \mu m$, which shows a maximum at approximately 200 revolutions for green coke, shows a similar maximum at 400 revolutions for calcined coke.

The relationship of $R_1$ with test duration shows that for the green coke, Fig. 13, values of the $R_1$ index decrease exponentially with increasing duration. This type of curve results from the interaction of breakage of the $R_1$ size coke fragments early in the test with the "cushioning" effects of the small size coke ($R_2$ and $R_3$ size), produced by extended breakage at later stages of the test. During the first 200 revolutions breakage of the $R_1$ size coke is rapid (Figs. 13 and 14). However, with test duration in excess of 200 revolutions, the $R_1$ size coke becomes dispersed within coke of $R_2$, $R_3$ sizes.

The higher microstrength of the calcined coke modifies the shape of the curve in Fig. 14 but breakage of the $R_1$ size coke is identical for both green and calcined cokes.

For the $R_2$ indices, Figs. 13 and 14 show that they rise quickly to maxima then slowly decay, the position of the maxima varying in the two cokes. The behaviour of the curve of $R_2$ against test duration results from a change in size distribution of the coke in the cylinders during the test.
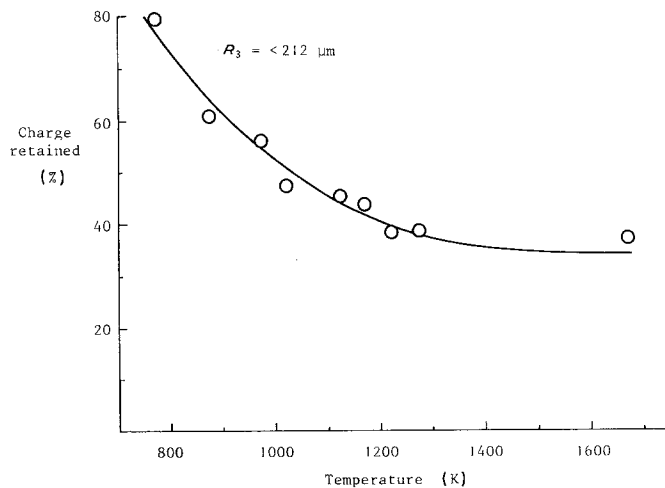


*Figure 17* Variation of $R_3$ microstrength index with HTT for needle-coke using 600 revolutions.
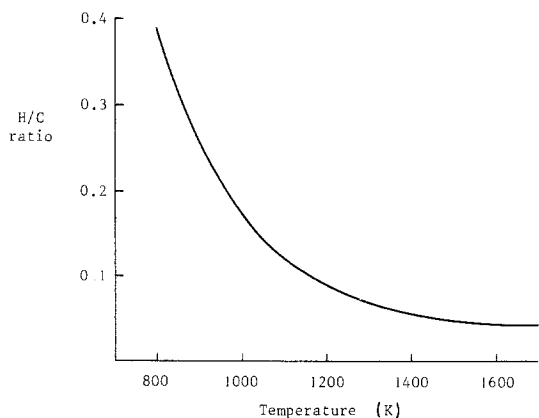
*Figure 18* Variation of H/C ratio with HTT for needle-coke.

Initially, coke breakage influences only the $R_1$ size coke which shatters to produce $R_2$ and $R_3$ size coke. The rate of formation of $R_2$ coke increases while there is a significant proportion of $R_1$ coke in the cylinders, i.e. $> 30\%$ $R_1$ for both green and calcined coke. However, the rate of production of the $R_2$ size coke decreases as breakage of $R_1$ size coke declines and the $R_2$ size coke becomes itself increasingly broken to $R_3$ size coke. The maximum seen in the $R_2$ curve is the point of transition where breakage of $R_1$ size coke is no longer dominant and breakage of $R_2$ size coke becomes prevalent.

For the $R_3$ curve in Figs. 13 and 14 the relationships are approximately linear. The gradient of the $R_3$ curve in Fig. 13 is greater than that of Fig. 14 as a result of the weakness of the green coke. The linearity of the $R_3$ curve results from the continuous production of this "fines" coke by the breakage of both the $R_1$ and $R_2$ coke size fractions. Figs. 13 and 14 indicate that the standard microstrength test duration for testing petroleum coke should be 600 revolutions. This value was chosen to avoid the maxima in the curve of the $R_2$ index.

Fig. 15 shows that the relationship between $R_1$ and heat treatment temperature is a continuous increase in the value of the $R_1$ index, i.e. microstrength of the coke. The increase in the $R_1$ index is about 8% in the temperature range 800 to 1200 K, but above 1200 K the $R_1$ index increases rapidly, i.e. some 15%, from 1300 to 1600 K.

The apparently more rapid increase of $R_1$ index, at temperatures above 1200 K, may result from a combined effect of the changes shown by the needle-coke upon heat treatment. Firstly, the coke shows an increase in microstrength resulting from the change toward a more crystalline ordering of lamellae as seen in transmission electron microscopy [11]. Secondly, increases in coke microstrength are counteracted by the formation of shrinkage fissures these acting as crack sources within the microstrength test so weakening the coke. In the temperature region 800 to 1200 K any possible increase in microstrength, due to increased crystalline ordering of lamellae, is reduced because of the formation of the weakening contraction fissures. However, at temperatures above 1200 K the development of crystallinity continues but fissure formation has largely stopped so causing a more rapid increase in microstrength. The rapid increase in the $R_2$ index in the temperature range 800 to 1200 K reflects the increase in microstrength of the coke seen for the $R_1$ index in Fig. 15.

## 4.4. Changes in elemental composition of green needle-coke with heat treatment

Analyses in Table IV show that increasing heat treatment temperature results in an increased content of carbon, a decreased content of hydrogen and H/C ratio, in the resultant needle-coke. This reflects the amounts of hydrogen in the volatile matter released in the early stages of calcining, Fig. 18.

## Acknowledgements

## References
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