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Structure and formation of shot coke – a microscopy study

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A series of shot cokes and sponge cokes from industrial delayed cokers was examined by scanning electron micrsocopy (SEM) and optical micrscopy (OM) of external, fractured internal and polished surfaces. Calcined cokes were etched with chromic acid solution and etching behaviour related to the optical texture of the cokes. The shot coke spheres have an inner structure of fine-grained mosaic and a smooth external skin, ~ 50 μm thick, of coarse-grained mosaic and small domains. Sponge cokes can be heterogeneous with inclusions of well-ordered carbon within the matrix mosaics. It is considered that the feedstock leading to shot coke in the delayed coker forms a high viscosity fused pitch/mesophase system which is subject to significant disturbance by volatile evolution. The "paste-like" system breaks up into fragments as a result of deep agitation by volatile release and movement through the system. The viscosity of the fragments is too high to permit their coalescence and reform a continuous system. Instead, they remain as fragments > 1.0 μm diameter. Structure of cokes from delayed cokers and the associated manipulation of the system by the volatile evolution within the coker. These two factors are inter-related. Differences between cokes arise from differences between viscosities of the mesophase from the feedstock and control the balance between fragmentation and re-coalescence of the charge, as a result of manipulation by volatile release, leading to the two extremes of shot and needle coke.

1. Introduction

Delayed coking is one of several types of commercial coking processes used to convert petroleum residues to a solid coke material [1]. Delayed coking is a semicontinuous process operating at about 480 to 500° C. It has a short contact-time preheater, the heated petroleum residues then "soaking" in a large drum and gradually forming coke until the drum is filled [2]. The operator of the delayed coker has limited control over the final properties of the coke, where the overall chemical composition of the feedstock is of paramount importance. Whereas initially delayed cokers were employed to maximize gasoline and distillate yields, today they can produce the high-value needle cokes, used in graphite production, as a major product. To this end, the petroleum or coal-tar pitch feedstock is not a residue material but is specially prepared for the process. Usually these feedstocks are of high aromaticity and are low in sulphur, mineral matter and quinoline-insoluble material. These needle cokes are characterized by their large sized optical texture as studied by optical microscopy, with anistropic isochromatic areas maximizing to ~ 500 μm diameter. Such needle cokes have low coefficients of thermal expansion (CTE).

As with all graphitizing anisotropic cokes, their

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structure results from the formation of planar (lamellar) aromatic nematic liquid crystals within the fluid phase of the carbonizing systems [3–7]. These liquid crystals originate usually as small spheres detected by optical microscopy at about 0.5 μm diameter. However, they originate as clusters of molecules with the dimensions of < 5 nm [8, 9]. The subsequent growth of these spheres of liquid crystals (also called mesophase [4]) and resultant coalescence into large spheres or of fusing on contact without loss of identity is a function of the viscosity of the mesophase. Ultimately in the delayed coking process, the fluid pitch phase is converted totally into the fluid (plastic) liquid crystal phase (mesophase) which solidifies to give the macrocrystallinity or optical texture of the resultant coke. Thus, this optical texture can be large in size (domains, $> 100\,\mu$m) or small in size (fine-grained mosaics, ~ 1 μm diameter). It is this wide variation in size of optical texture which accounts for the wide variation in properties and applications of cokes which are available commercially [1, 2].

Studies of the chemistry of formation of mesophase by Yokono and Marsh [10] and Marsh and Neavel [11] indicate that the viscosity of the mesophase controls its coalescence properties. The viscosity, in turn, is dependent upon the chemical composition of the pitch where the availability of transferable hydrogen to "cap" reactive radicals assists in maintaining the relatively low viscosities of mesophase which leads, for example, to needle cokes [10]. Reduced availability of transferable hydrogen leads to cokes of smaller sized optical texture. The pressure of inert solids, asphaltenes, etc., also leads to reduced size of optical texture [8, 12].

The processes which occur in the delayed coker leading to needle-coke, for example, are not clearly understood. Markovic and Marsh [12, 13] using microscopy of etched surfaces of needle cokes have made initial proposals to model the process.

Other forms of cokes which are made in the delayed coker have such names as amorphous coke, regular coke, sponge coke and shot coke. The former three names probably refer to the product which finds extensive application in the manufacture of carbon anodes for the electrolysis smelters of aluminium production cells. Here electrical conductivity is essential but mechanical stressing is less than with the arc-electrodes. The optical texture of sponge is smaller than that of the needle cokes. Shot coke is somewhat an undesirable product of the delayed coker. This type of coke has the appearance of lead shot, i.e. exists as spheres ~ 1 to 10 mm in diameter. It is undesirable because: (i) on opening the delayed coker, this shot coke can pour uncontrolled from the drum; (ii) it is of relatively low electrical conductivity; and (iii) it usually contains amounts of sulphur and metals in excess of industrially acceptable levels.

The objectives of this paper are (a) to examine, by microscopy methods, structure in shot cokes, and (b) to comment on how shot coke may be formed in the delayed coker.

2. Experimental details

2.1. Materials used

Four types of coke were separated from a single

TABLE I Analyses of cokes from Port Arthur Refinery

Property (wt%)	Sponge coke (I)	Shot coke		
		< 3 mm (II)	> 3 mm (III)	Cluster (IV)
Moisture	0.18	0.37	0.52	0.12
Volatile matter	12.32	13.14	8.49	13.01
Fixed carbon	87.21	86.48	90.79	86.82
Ash	0.29	0.01	0.20	0.05
Carbon	87.97	88.58	88.57	88.19
Hydrogen	3.85	3.60	3.72	3.54
Sulphur	3.85	3.98	3.85	3.94
Nitrogen	1.74	1.75	1.76	1.67
Oxygen	1.60	2.26	2.21	1.99
Nickel	0.045	0.045	0.047	0.049
Vanadium	0.118	0.112	0.124	0.115
Iron	< 0.010	< 0.010	0.010	0.014
Silicon	< 0.010	< 0.010	< 0.010	< 0.010
Density in mercury ($\mathrm{g\,cm^{-3}}$)	1.320	1.549	1.322	1.620

TABLE II Analyses of cokes from Lake Charles Calcining Plant

Property (wt %)	Sponge coke (V)	Shot coke (VI)
Moisture	0.50	0.21
Volatile matter	8.24	8.32
Fixed carbon	91.16	91.26
Ash	0.10	0.21
Carbon	88.53	88.27
Hydrogen	3.96	3.92
Sulphur	5.19	4.61
Nitrogen	1.07	1.25
Oxygen	1.93	2.33
Ash	0.10	0.21
Silicon	< 0.1	< 0.1
Vanadium	0.033	0.078
Nickel	0.013	0.023
Iron	0.024	0.044
Density in mercury (g cm^{-3})	1.292	1.302
Density in helium (g cm^{-3})	1.345	1.359
Total pore volume (cm^3)	0.031	0.032

lot of coke obtained from the Port Arthur Refinery, USA (PAR) of Gulf Oil Corporation. These are a sponge-coke (I), shot coke < 3 mm diameter (II), shot coke > 3 mm diameter (III), and cluster shot coke (IV).

Two types of coke were separated from another lot of coke obtained from the Lake Charles Calcining Plant, USA (LCCP) of Gulf Oil Corporation. These are a sponge coke (V) and a shot coke (VI).

These six types of coke are green, uncalcined. Available analyses of these six cokes are in Tables I and II. These analyses indicate that the cokes contain from 7.4 to 8.4 wt % of nitrogen, sulphur, oxygen and metals. The details of coke structure cannot be related directly to these anlyses which are indicative of the nature of the parent feedstock.

Three cokes, PAR (II) and LCCP (VI) shot cokes and LCCP sponge coke (V) were calcined to 1273 K in nitrogen and used in etching studies.

2.2 Scanning electron microscopy (SEM)

Both the external surfaces and internal fracture surfaces of the sponge cokes (I) (V) and shot cokes (II) (III) (IV) (VI) were examined by SEM using a JEOL SEM T20 instrument. Surfaces of cokes were gold-coated prior to examination.

2.3. Optical microscopy

All six cokes were mounted in a polyester resin which, after hardening, was polished with several grades of alumina finishing with γ-alumina and a Selvyt cloth. The optically polished coke surfaces were examined by plane polarized light optical microscopy using a Vickers M41 research microscope fitted with a half-wave retarder plate in the reflected light path in order to obtain interference colours to reveal optical texture [14, 15]. Anisotropic carbon, formed via mesophase, is seen as coloured areas of blue, yellow or purple, the colours being dependent upon the crystallographic projection of the carbon at the surface relative to the plane of the polarized light of the microscope. The isochromatic areas can vary in size, according to the coke being examined, from $< 0.5\,\mu$m to $\sim 500\,\mu$m, the combined effect being assessed by optical microscopy as the *microstructure, optical texture* or *macrocrystallinity* of the coke. The nomenclature used to describe the range of size optical texture is listed in Table III. Selected representative areas of surfaces were photographed.

TABLE III 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)	$< 1.5 > 0.5\,\mu$m in diameter
Medium-grained mosaics (Mm)	$< 5.0 > 1.5\,\mu$m in diameter
Coarse-grained mosaics (Mc)	$< 10.0 > 5.0\,\mu$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 (CF)	$< 60 > 30\,\mu$m in length; $< 10 > 5\,\mu$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)	$< 60 > 10\,\mu$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.

The optical textures of sponge cokes (I) and shot cokes (II) and (VI) were assessed by a point-counting technique. A Swift point-counter was attached to the stage of the optical microscope and 400 positions assessed for size of optical texture using the nomenclature of Table III. The optical texture of the coke is described in terms of percentage of components within the coke.

2.4. Surface etching

Polished surfaces of the cokes (calcined to 1273 K under nitrogen) were initially characterized and photographed by optical microscopy. The calcining to 1273 K was undertaken to enhance the etching behaviour. The same areas were then photographed by SEM, an approach necessary to be able to relocate areas of study after etching [12]. These surfaces were then etched in a solution of 10 g of potassium dichromate in 50 cm^3 of orthophosphoric acid at 393 K for 1 h. After washing and drying, the same area of surface was relocated and examined by SEM. This etching procedure allows preferential gasification of the more ordered parts of the anisotropic carbon and is extremely useful to demonstrate extent and direction of orientation of anisotropic carbon within a carbonaceous material [16, 17].

3. Results and discussion

3.1. Point-counting of optical texture

The point-counting analyses of shot cokes, PAR (II) and LCCP (VI) are given in Table IV. They indicate that mosaics constitute 91.3 and 95.7% of the optical texture of these shot cokes, the PAR (II) coke having a larger average size (more coarse-grained mosaics, 5 to 10 μm diameter). Overall the sponge coke PAR (I) has a larger-sized optical texture than the shot cokes.

3.2. Scanning electron microscopy

The three shot cokes, PAR (II), (III), LCCP (VI) all had the morphology of Fig. 1a, for PAR (II) shot coke, that is, they were almost spheroidal (2.5 mm diameter) with most of their surfaces being quite smooth, Position A. The surfaces of the spheres were pitted with pores (100 to 200 μm diameter) entering into the spheres, Position B. The fracture surface across an equatorial plane is seen in Fig. 1b. The pores originate about 0.5 mm from the surface. Position C shows an internal bubble forcing itself to the surface. An essential feature of that porosity is that, like the outside surface, it is quite smooth. This is seen more clearly in Fig. 2a, Position D, but also in an internal pore, Fig. 2b, Position E. The implications of these observations are that the spheres were plastic/fluid subsequent to their formation and that voltaile matter was being released in significant quantities to create the pipe-like macroporosity which did not collapse after the passage of the bubble. Fig. 2c shows the smooth wall of the pore, Position D, extending about 10 μm into the sphere of the shot coke. The roughness features of the surface of Fig. 2c are indicative of structural features within the coke, i.e. ~ 5 μm in size, equivalent to that of the mosaics of the optical texture.

Figs. 3a and b are of the PAR cluster shot coke (IV). The morphology is similar to shot cokes PAR (II), (III) and LCCP (VI), Fig. 1a, with individual spheroidal identities, but these having fused to form a cluster. The external surface skin is smooth, Fig. 3a Position F, and is continuous over the surface even where particles are fused, Fig. 3b, Position G.

Fig. 3b, Position H, H′ illustrate the internal (fracture) surface across the fusion bridge between two particles. The structural constituents of this bridge are similar in texture to the bulk particles i.e. mosaics [18]. Further particles were fused or adhered together at Positions H, H^1 before fracture. The evidence suggests that the individual particles were formed first, followed by a fusion or bridging

TABLE IV Point-counting analyses of optical texture

Coke	Optical texture component* (%)						
	Mf	Mm	Mc	SD	MFA	CFA	FD
Shot coke PAR (II)	0.4	55	36	5.3	0.9	1.4	1.0
Shot coke LCCP (VI)	2.5	69	24	1.4	2.7	0.2	0.2
Sponge coke PAR (I)	0	11	26	22	11	16	14

*See Table III for description of nomenclature.

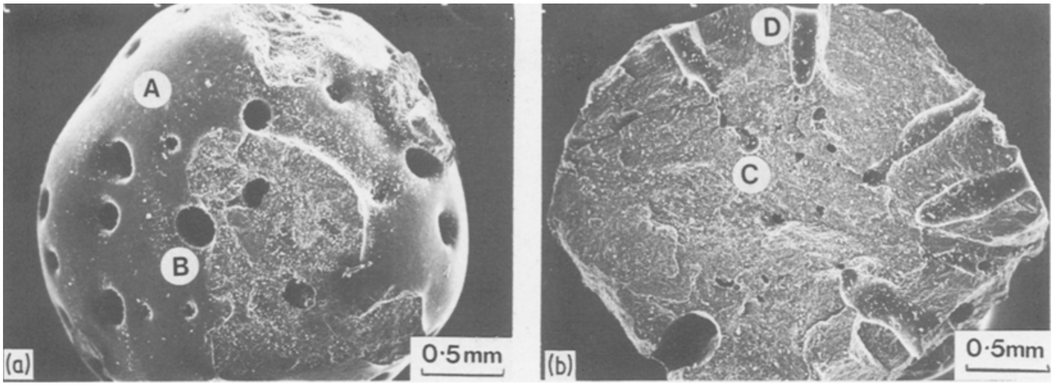


Figure 1 SEM micrographs of external and internal fracture surfaces of PAR shot coke (II). Position A, smooth external surface; Position B, entrance to internal porosity; Position C, porosity developing in interior of shot coke; Position D, internal appearance of porosity.

to 8 mm shot coke clusters towards the end of the coking process.

Figs. 4a and b illustrate the smooth surface, Position J and smooth walled porosity, Position L of LCCP shot coke (VI). With this variety of shot coke, the porosity is not as obvious as with PAR (II). Particles may have adhered together at Position K, Fig 4a, which has the characteristics of a fracture surface. The fracture surface of Fig. 4b, at the higher magnification of Fig. 4c, shows clearly the structural constituents of this shot coke, LCCP (VI). These features are characteristic of broken surfaces of mosaics [18]. In Fig. 4c, to the left of Position M, is a coarse grain, ~ 7 μm diameter and the left of Position N, is a smaller medium grain, ~ 4 to 5 μm diameter.

For the PAR sponge coke (I), Fig. 5a is quite informative. It represents, possibly, a half-way stage between the non-porous fluid phase and the individual spheres of Fig. 1a. Position P is about 1 mm in diameter. On either side, the significant porosity, caused by volatile release, has smooth surfaces seen at Positions Q. Fig. 5b looks at a bridge Position R between two developing spheres, Positions S. The bridge material is identical to the bulk material of the developing spheres and has the morphology of coarse-grained mosaics, ~ 10 μm diameter, Position T, Fig. 5c.

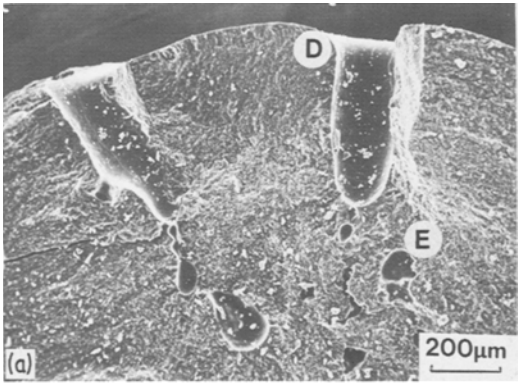
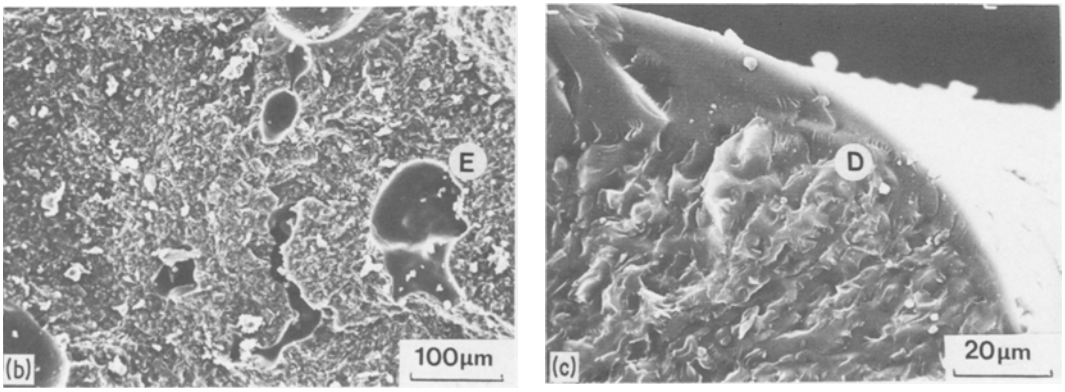


Figure 2 SEM micrographs of internal fracture surfaces of PAR shot coke (II). Position D, smooth skin of porosity; Position E, smooth skin of internal closed porosity.



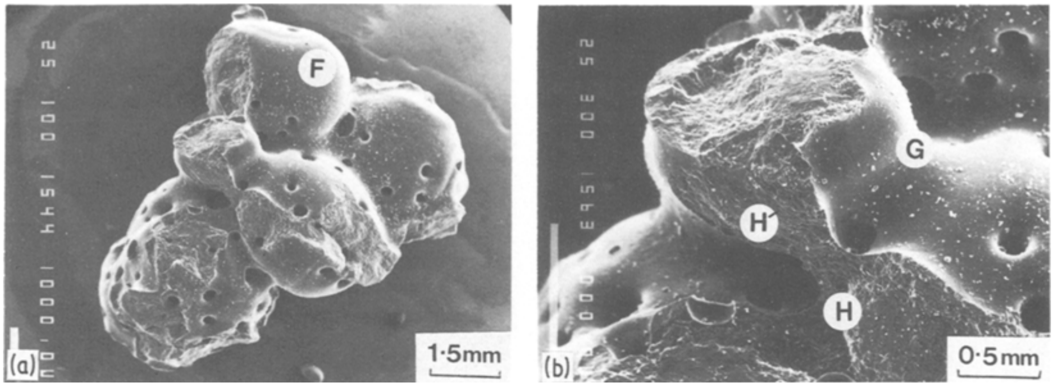


Figure 3 SEM micrographs of external and internal fracture surfaces of PAR clustered shot coke (IV). Position F, smooth external surface; Position G, smooth external surface continuous over bridging material between particles; Position H, H , internal fracture surface across fusion bridge between two particles.

It would appear that at a critical stage of the coking process within the delayed coker the fluid petroleum residue feedstock, because of the formation of relatively viscous growth of liquid crystals (mesophase), has assumed a "paste-like" quality. That is, it has little fluidity, has some *plasticity*, but with very restricted facility after deformation, to relax back into a continuous matrix. It would appear that these feedstocks, possibly because of a relatively high aliphatic composition, produce significant proportions of volatile matter. It is this volatile matter then, as it forces its way through this pastel-like plastic matrix, which breaks it up. The extent of this subdivision of material and the stability of the entities are a function of the feedstock and range from individual spheres, to the clusters, to sponge coke, PAR (I).

However, the material described as LCCP sponge coke (V) is unlike sponge coke PAR (I). It lacks the apparent porosity of Fig. 5a and is a more continuous coke, but not necessarily homogeneous. It is in some ways a biphase coke. Within the general matrix material as reported in Fig. 5c for PAR (I) coke, there exist quite distinct structural units of much larger optical texture and structure. Fig. 6a

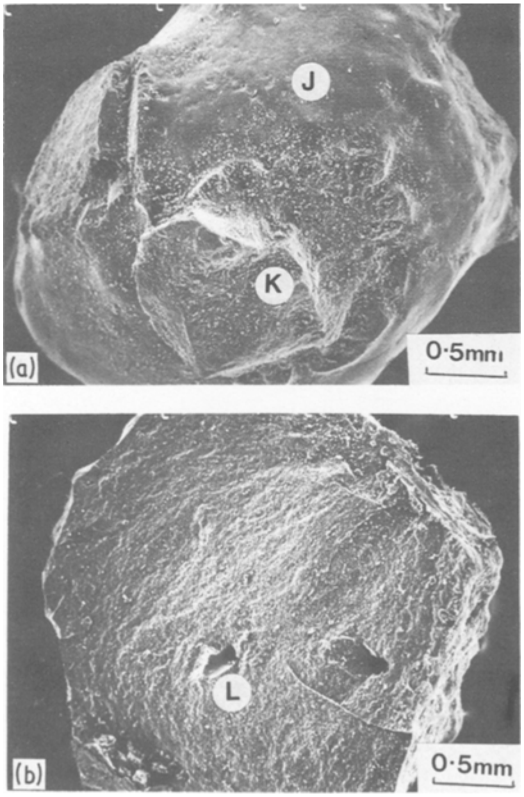
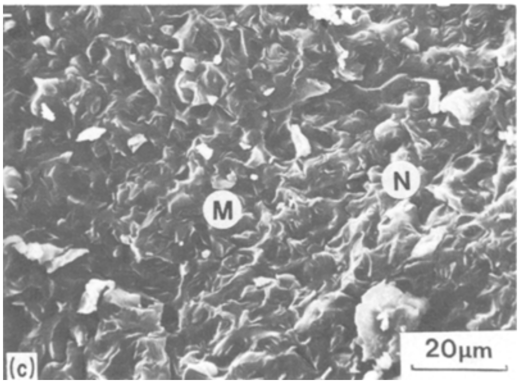
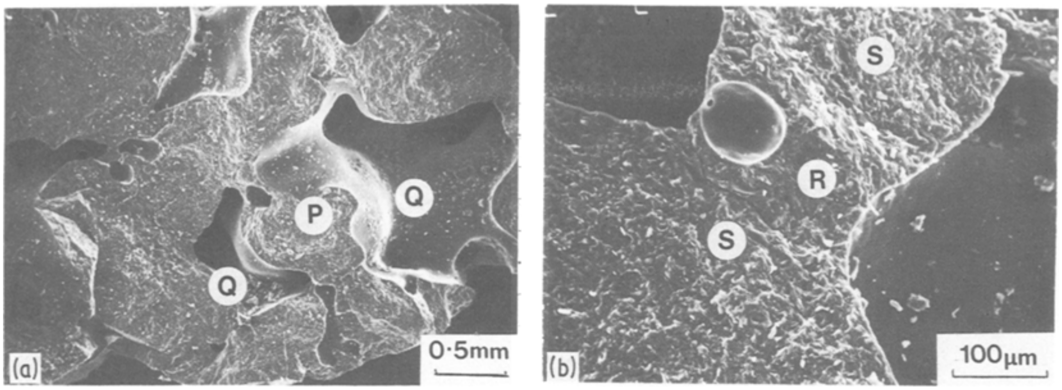


Figure 4 SEM micrographs of external and internal fracture surfaces of LCCP shot coke (VI). Position J, smooth external surface; Position K, fracture surface of particle; Position L, smooth skin of internal porosity; Position M, coarse grain of mosaic, ~ 7 μm; Position N, medium grain of mosaic, ~ 4 μm.





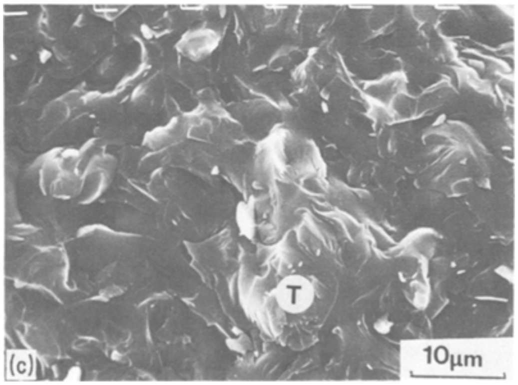


Figure 5 SEM micrographs of internal fracture surfaces of PAR sponge coke (I). Position P, partially separated fragment, ~ 1 mm; Position Q, smooth skin of internal porosity; Position R, bridging material; Position S, fracture surface of developing sphere; Position T, coarse grain of mosaic, ~ 10 µm.

shows such an inclusion, Position U, in the matrix, Position W, and Fig. 6b shows an elongated Position X, in the matrix material of Position W. A cone-shaped inclusion with smooth walls, presumably of basal planes, is seen as Position Y to Y′ in Fig. 6c, the matrix material being Position Z. The edge of the cone, Position A, Fig. 6d is of convoluted prismatic edges as reported for structures in needle cokes [12, 13].

Hence, the structure of this sponge coke, LCCP (V) shows features found in needle cokes, but not so well developed. The biphase structures of needle cokes could arise because of the influence of liquid flow behaviour and volatile evolution upon a mesophase of relatively low viscosity [12, 13]. The inclusions in this sponge coke may arise from a lack of total miscibility of components which make up the feedstock going to the delayed coker. The distinct components within fluid pitch apparently carbonize separately and their individual resultant cokes become incorporated into the sponge coke as distinct entities. Probably, the grade of this feedstock is superior to that used for the shot cokes.

3.3. Optical microscopy

This microscopy approach confirms and augments the findings based on SEM of the structures and origin of shot cokes. Fig. 7 shows two dominant features of the shot coke: Position B is of the fine-grained mosaics of PAR (II) (Table IV) 0.5 to 1.5 µm diameter. Position C is of the smooth skin of the shot coke particles (see Fig. 1a). This skin is about 50 µm thick and consists of coarse-grained mosaics (5 to 10 µm) and small domains (10 to 60 µm).

It is an established characteristic of liquid crystals and mesophase [4] that they will orientate parallel to and flow over available surfaces. Thus, it would appear that after the "paste-like" charge to the drum of the delayed coker has broken into the small particles (1 to 10 mm), the mesophase at the surface is still able to flow and hence establish the larger-sized optical texture as well as the smooth exterior surface of the particle. The porosity described in Fig. 2 also has the same smooth "skin" of larger-sized optical texture. This confirms the postulate that the porosity was formed by volatile evolution from within the still plastic particle after its formation from the overall paste-like charge to the drum.

Fig. 8 is of the PAR clustered shot coke (IV). It would appear from this typical micrograph that two particles of shot coke, Position D, D′, have become fused after their initial separation into two identities. Each of the particles has the skin of larger-sized optical texture, Position E, E′ and this continues around the particle even where the particles are fused, Position F. This suggests that

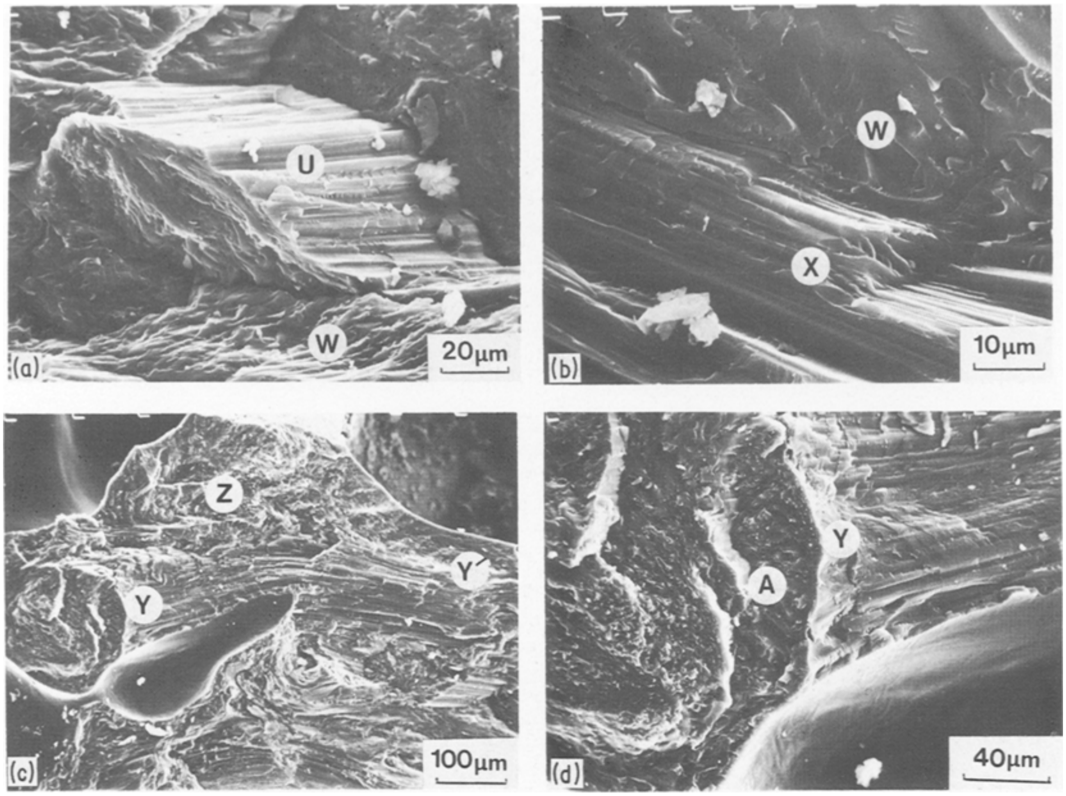


Figure 6 SEM micrographs of internal fracture surfaces of LCCP sponge coke (V). Position U, folded inclusion; Position W, matrix material; Position X, elongated folded inclusion; Position Y, Y′, cone-shaped inclusion; Position A, prismatic edge of cone-shaped inclusion.

during the formation of this particular coke there occurred the fragmentation of the paste-like charge. These fragments became the shot coke particles except that in the specific conditions of this charge there appear to have been formed smaller fragments, perhaps by breakage of larger fragments and these smaller fragments were able to fuse the particles together. Note that the bridging material, at Position F, itself has no skin of larger-sized optical texture. If the bridging took place to form the shot coke clusters towards the end of the coking process, then residual plasticity and flow properties would be too low for the bridging material to form the skin and so would project the fine-grained mosaics at the surface, as seen in Fig. 1b.

Figs. 9a and b are illustrative optical micro-

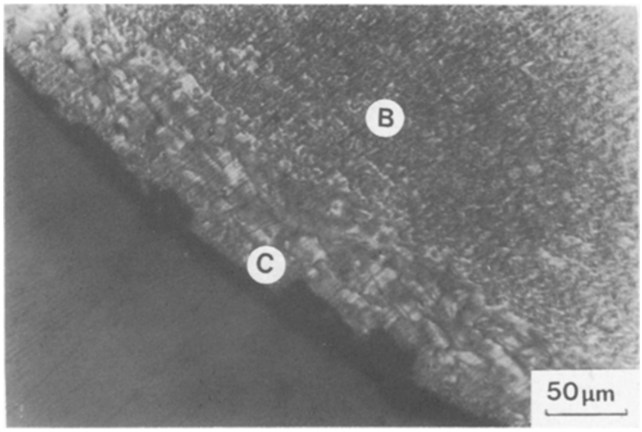


Figure 7 Optical micrograph of surface of PAR shot coke (II). Position B, fine-grained mosaic of centre; Position C, coarse-grained mosaic of skin of particle.

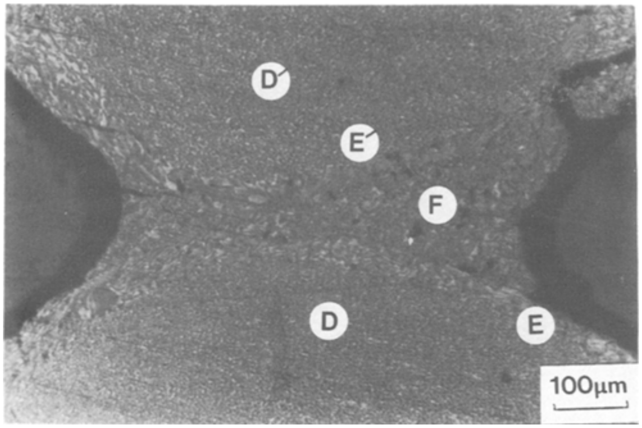


Figure 8 Optical micrograph of surface of PAR clustered shot coke (IV). Position D, D′, fine-grained mosaics of centre; Positions E, E′, coarse-grained mosaics of skin; Position F, bridging material between shot coke particles.

graphs of the type of heterogeneity seen in the structure of PAR sponge coke (I). [See also Figs. 6a to d of sponge coke LCCP (V).] In Fig. 9a, Positions J, J′ represent the more general matrix carbon of optical texture coarse grained mosaics and small domains. Within this matrix carbon exist bands, etc. of quite distinct material, Position G, H. These, in this particular cross-section, have the appearance of fine-grained mosaics (0.5 to 1.5 μm), but in reality, as observed with needle cokes [12, 13], are probably cross-sections of lamellar-flow material as indicated in Figs. 6c and d. The flow features of these inclusions into the coke are illustrated in Fig. 9b, Position K, between the matrix carbon, Positions L, L′.

The feedstock, for these sponge cokes, is such that the overall viscosity is relatively lower than that for the shot cokes. Consequently, the volatile

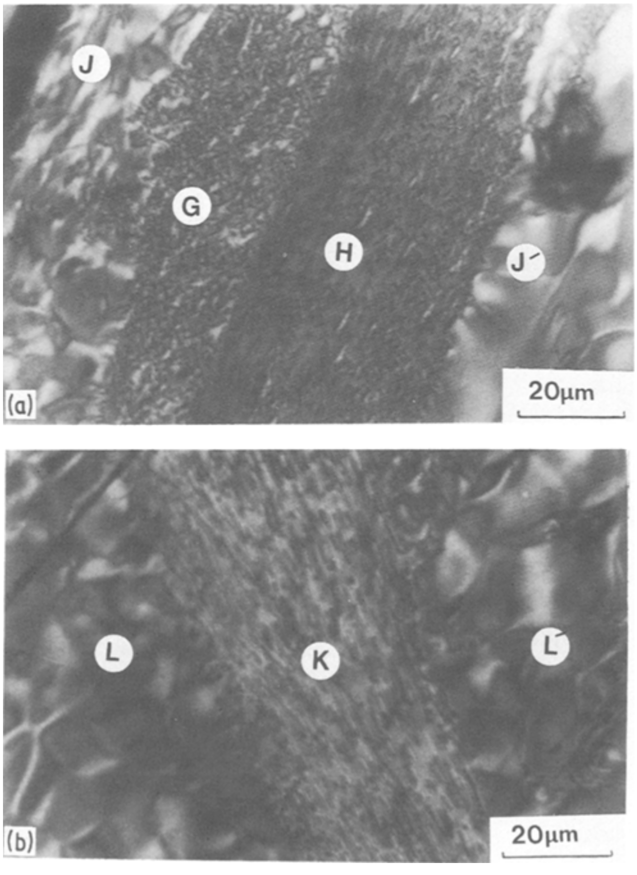


Figure 9 Optical micrograph of surface of PAR sponge coke (I). Positions G, H, transverse cross-sections of lamellar flow; Positions J, J′, matrix carbon of coarse-grained mosaic; Position K, longitudinal cross-section of lamellar flow.

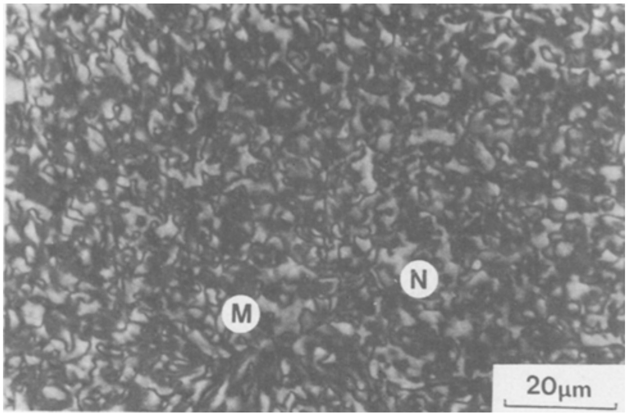


Figure 10 Optical micrograph of surface of *calcined* PAR shot coke (II). Position M, medium grain of mosaic with basal plane presentation; Position N, prismatic edge presentation of medium grain of mosaic.

evolution, or some equivalent force, is not able to fragment the charge into particles. Any fragmentation caused by volatile passage would be lost by coalescence of the fragments. However, two streams of liquid phase may exist together and carbonize independently to produce the illustrated inclusions. These streams of liquids (possibly multiphase) may result from blending of various residue petroleum feedstocks. That is, the blending may not result in complete mixing (solubilization) of the fluid phases. It is an aspect of blending which requires further research and may possibly be beneficial to coke production.

3.4. Etching of calcined cokes

This series of four studies provides further detail of the structure and origins of these shot cokes. Etching of calcined cokes is more informative than etching of green cokes.

Fig. 10 is an optical micrograph of the fine and medium grains of the mosaics of the optical texture of PAR shot coke (II). Above Position M is a grain with basal plane projection to the surface (purple in colour in optical microscopy). Above Position N is prismatic edge presentation over distances of ~ 5 μm. After etching of this surface by chromic acid [16, 17] the basal planes of Position M remain unaffected, Fig. 11, Position P. However, the anisotropic grains with prismatic edge presentation have etched, Position Q, but only over the dimensions of the isochromatic areas. Thus, this etching study confirms the mosaic structure of the shot coke, formed by the fusing (adhering) of growth units of mesophase of relatively high viscosity. If they had been of lower viscosity, then coalescence of the growth units would have occurred to cause loss of identity of these growth units and the production of a larger sized optical texture.

Figs. 12 and 13 examine more closely the skin structure of the surface of PAR shot coke (II). Fig. 12, before etching, is an optical micrograph of the internal structure of fine-grained mosaic, Position R, and the coarse-grained mosaic and small domains of the surface, Position S. After etching with chromic acid, the differences in size of etching patterns are seen in Fig. 13, Position R′, S′. However, the boundary between the skin and bulk of the particle has etched preferentially, Position T. This is indicative of movement, or shear, at this position to create a form of interface, which has etched preferentially, a phenomenon reported earlier [17]. Thus, this etching study confirms that the particles may have been formed by fragmentation of the paste-like charge to the drum and that surface movement of mesophase (and possibly rubbing together of particles) has created the smooth skin of larger-sized optical texture.

Figs. 14a and b illustrate another feature found

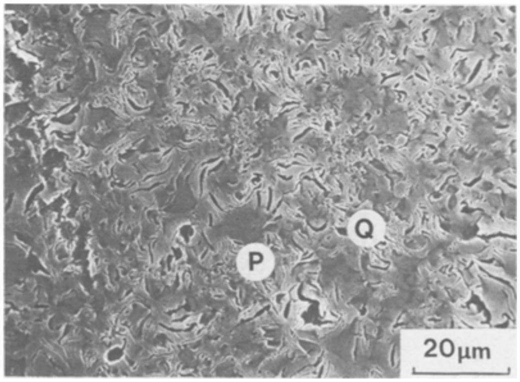


Figure 11 SEM micrograph of surface of *calcined* PAR shot coke (II) after etching with chromic acid. Position P, non-etched surface of basal plane of Position M, Fig. 10; Position Q, etched surface of Position N, Fig. 10.

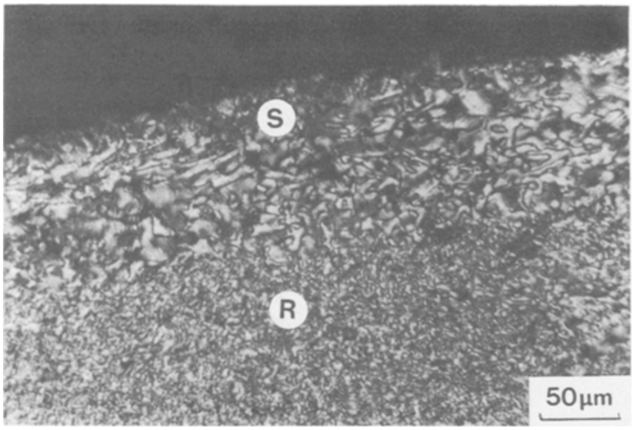


Figure 12 Optical micrograph of surface of *calcined* PAR shot coke (II). Position R, fine-grained mosaics of centre; Position S, coarse-grained mosaic of skin of particle.

in the LCCP shot coke (VI). The optical micrograph of Fig. 14a shows an open pore (not an enclosed bubble) within the shot coke particle, Position U. The wall of this pore has a composite structure. First the wall is composed of carbon of fine-grained mosaics, Position V; second, the wall now has a layer of carbon, Position W, arranged with the basal planes of the structure at right angles to the surface of the wall, i.e., prismatic edge bonding to fine-grained mosaic. The pore, with its two layers of carbon, is enclosed within the medium-grained mosaic matrix of the shot coke, Position Y. These structural features become obvious in the SEM micrograph of the etched surface. Fig. 14c, with the corresponding Positions U′, V′, W′, Y′.

The orientation of carbon, Positions W, W′, is such that it is probably not formed by growth of mesophase on the wall of a pre-existing wider pore. Deposition on the pore wall of mesophase would give material orientated parallel, that is, concentric, with the pore wall. The temperature of the drum is only 500° C, that is, too low for vapour cracking to give a pyrolytic graphitic carbon. A more plausible explanation is that a bubble of volatile matter uses the less viscous inclusion (as seen in Figs. 9a and b) as an easier escape route to the surface. These less viscous inclusions have significant orientation. A combination of the movement of the bubble and of the fluid inclusion in the dynamic system of the drum could lead to the radial spoke-wheel structure of Fig. 14a.

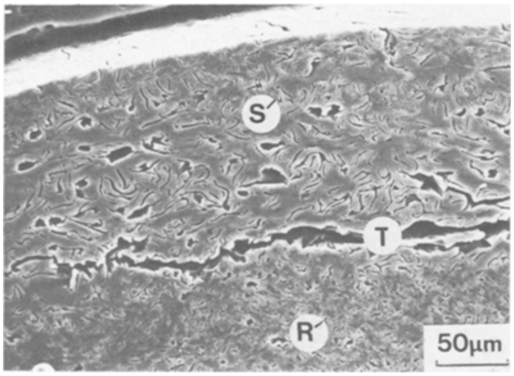


Figure 13 SEM micrograph of surface of *calcined* PAR shot coke (II) after etching with chromic acid. Positions R′, S′ correspond to Position R, S of Fig. 12. Position T etched boundary between the central mosaic and skin of particle.

However, at the interface between the vapour and wall, the turbulence appears able to break down the structure of the inclusion into the fine-grained mosaic, Position V, which is smaller than the medium-grained mosaic of Position Y. The interface between the fine-grained mosaic and the small domains appears to be continuous after etching. It does not have the appearance of two phases being superimposed upon each other.

Thus, Figs. 14a and c illustrate the extremely dynamic activity within the delayed coker caused by rapid and extensive volatile evolution in a pitch/mesophase system possessing considerable turbulence.

Figs. 15a to c illustrate the detail of structure found in the calcined sponge LCCP (V). In Fig. 15a, Position A, of this optical micrograph is a coarse grain of the mosaic, ~ 10 μm, and Position B is a thermal fissure possibly induced by calcining. After etching, the SEM micrographs, Figs. 15b and c, show the porosity at Position D with the coarse grain at Position E. This coarse grain etches through prismatic edges, Position F to reveal the same type of behaviour as reported earlier for needle cokes and cokes from a coal-extract [13].

Thus, these micrographs suggest that the mech-

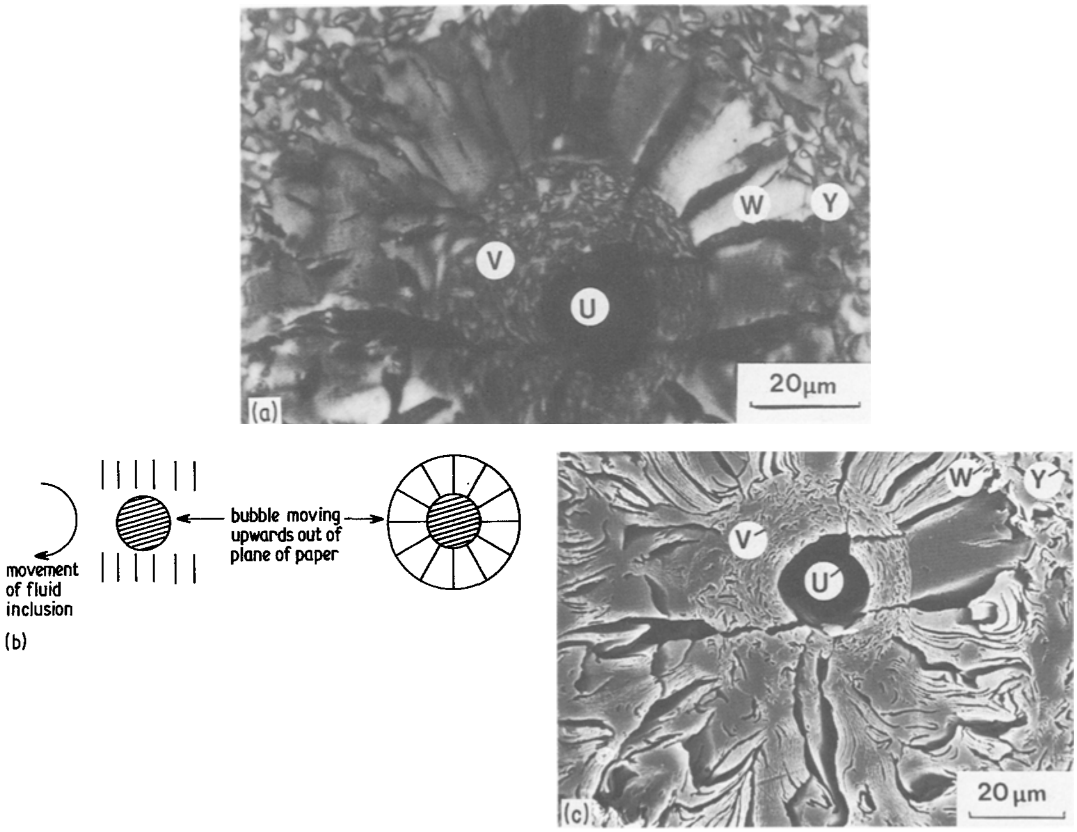


Figure 14 Optical and SEM micrographs of *calcined* LCCP shot coke (VI) showing effects of etching on a pore structure. Position U, U′, cross-section of pore; Position V, V′, fine-grained mosaic of pore wall; Position W, W′, carbon orientated with prismatic edges bonding to fine-grain mosaic; Position Y, Y′, medium-grained mosaic matrix of the shot coke. (b) shows the orientation in (a).

anism of formation of the sponge coke is via the creation of mesophase within the feedstock of the delayed coker.

4. Conclusions

The shot coke spheres have an inner structure of fine-grained mosaic and a smooth external skin, 50 μm thick, of coarse-grained mosaic and small domains.

The sponge cokes vary in appearance from a continuous coke to an intermediate between this and shot coke. The optical textures of the sponge cokes are coarse-grained mosaics or less. However, more ordered inclusions of carbon exist within the sponge cokes, possibly arising from incomplete mixing (lack of homogeneity) of the blend which constitutes the feedstock.

It is considered that the shot coke is formed from feedstocks which have high levels of heteroatoms, i.e. nitrogen, sulphur and oxygen, and high asphaltene levels with associated metals as indicated by the analyses of Tables I and II. Presumably there exists a sufficiently high content of aliphatic carbon and hydrogen and this could lead to significant volatile evolution within the coking drum.

The petroleum feedstock carbonizes to coke via the formation of liquid crystals and mesophase. High heteroatom content, high reactivity and presumably low facility for hydrogen transfer reactions all promote the formation of high viscosity growth units of mesophase which do not grow beyond $\sim 1\,\mu$m diameter and fuse on contact to form mosaics.

The high viscosity fused pitch/mesophase system is subject to significant disturbance by volatile evolution or some equivalent force. The "paste-like" system breaks up into fragments as a result of the deep agitation and movement through the system. Bubble size and content is related to shot coke size. The viscosity of the fragments will be too high to permit their coalescence to reform a continuous system. Instead, they remain as fragments $> 10\,\mu$m

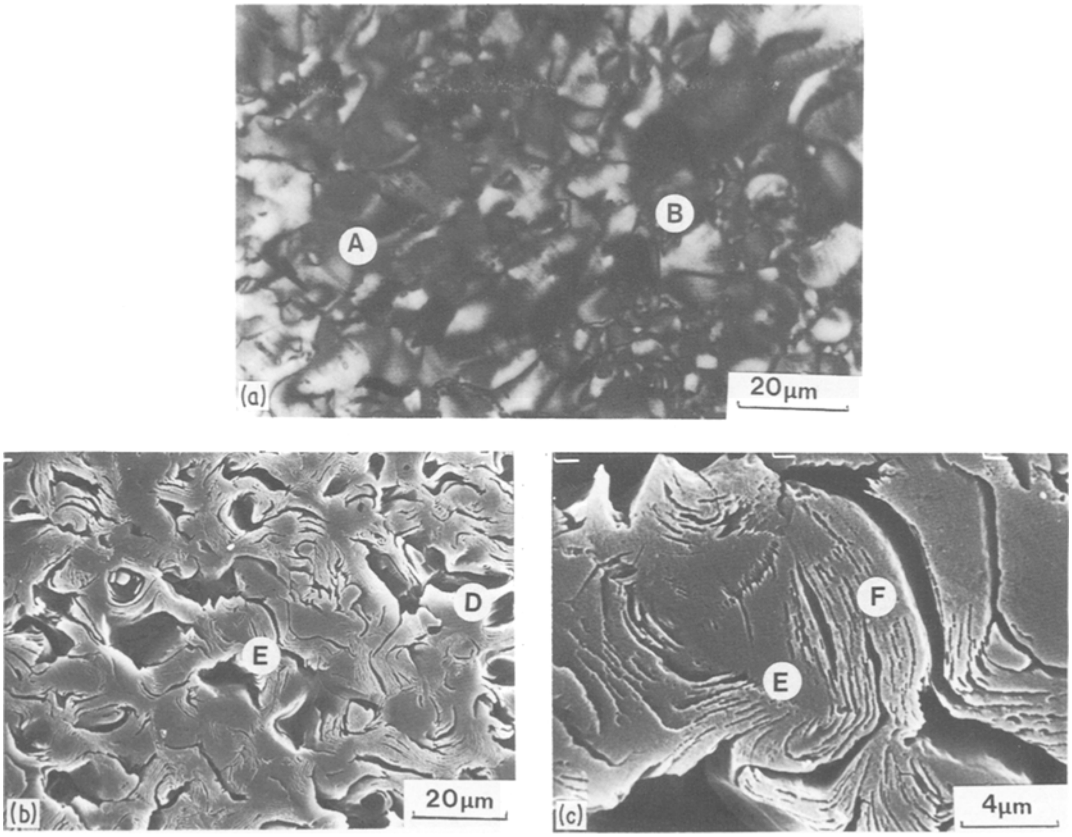


Figure 15 Optical and SEM micrographs of surface of *calcined* LCCP sponge coke (V) showing effects of etching on mosaic structure. Position A, coarse grain of the mosaic; Position B, thermal fissure; Position D, thermal fissure (SEM); Position E, F, etched coarse grain showing elongated etch fissures characteristic of prismatic edge presentation of carbon [13].

diameter. The residual viscosity/plasticity within the fragments permits a rounding of the shape of the particles and the establishment of a smooth skin by surface flow of mesophase. Volatile evolution continues within the particle to create a porosity ~ 200 μm diameter.

The chemical composition of the feedstock is the controlling factor with regard to coke structure. The "worst" feedstocks as described above lead to shot cokes. As the feedstock changes to lower levels of nitrogen, sulphur, oxygen, asphaltenes and to high levels of aromaticity, so the coke type changes from shot coke, to clustered shot coke, to the porous sponge coke and continuous sponge coke with inclusions of high relative structural order, and ultimately to the needle cokes. Structure is thus dependent upon the composition of the feedstocks as well as the associated manipulation of the system by the volatile evolution within the coker. These two factors are inter-related.

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