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The primary factors which determine the microstructures of pyrolytic carbons deposited in a tumbling bed

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Microstructures of pyrolytic carbons deposited in a tumbling bed from propane gas have been examined by polarized light microscopy, scanning electron microscopy, and transmission electron microscopy. Isotropic, laminar, and columnar structures were obtained. These structural varieties, which could be produced by changes in the deposition conditions and the substrate geometry, were investigated to select more reasonable deposition mechanism. Two essential factors are found directly related to determine the microstructure of pyrolytic carbon. One is the degree of supersaturation of pyrolysis products in a gas phase. The other is the gas flow pattern of recirculation within a deposition zone. The overall deposition process of pyrolytic carbon can be explained by the factors independent of various coating systems. This paper gives the experimental evidences that the above two factors are inter-related and simultaneously contribute to form pyrolytic carbons, and the cracks formed in deposits are closely related to their fracture mechanism. Due to the cracks the fractured surfaces of isotropic deposits are round and those of columnar deposits are laminated. Laminar deposits have both round and laminated fracture surfaces.

1. Introduction

In earlier work [1] the changes in the optical microstructures deposited in a fluidized bed were thought to be due to the gradients in temperature and hydrocarbon concentration within a bed. When small gradients were present, the orderly growth of carbon rarely occurred so that the formation of isotropic deposit without appreciable preferred orientation was more favorable.

Lee *et al.* [2] obtained isotropic deposits using tumbling bed within large temperature and concentration gradients being present. By depositing pyrolytic carbon in a static cold-wall system Luleich *et al.* [3] postulated the cause of structural appearances in a fluidized bed; that the interaction of the plasma layers formed just adjacent to hot surfaces plays a main role in determining the microstructures of deposits. However, this gave no distinct explanation for the formation of pyrolytic carbon in a region where the interaction of Langmuir zones did not occur.

Kaae *et al.* [4] and Kaae [5, 6] suggested by using transmission electron microscopy (TEM) that the structural changes were due to the changes in the proportion of the solid particles formed in a gas phase and the directly deposited molecular carbons.

In a rotating tumbling bed developed by Je and Lee [7] the transitional structures deposited in a slowly rotating tumbling bed were observed. A deposition mechanism was suggested for the formation of pyrolytic carbons; that the recirculation of the pyrolyzing gas flowing within a bed is one of the important factors determining the microstructure of a deposit.

Besides these, there have been many suggestions on the mechanism of pyrolytic carbon formation. Some of them were briefly summarized by Je and Lee [7]. However, the essential factors directly related to the determination of the microstructural appearances are not yet evident.

This paper gives experimental evidence that deposition mechanisms of pyrolytic carbon are fundamentally explicable by the essential factors independent of various coating systems. Some experimental results contribute to find these factors. In addition, the cracks in deposits are investigated and compared with fractured surfaces to consider the fracture mechanism.

2. Experimental procedure

Fig. 1 is a schematic diagram of the tumbling bed apparatus used to deposit pyrolytic carbon on various substrates. The graphite reaction tube was rotated with a variable motor to over 120 rpm. In the central part of the reactor, four grooves parallel to the reaction tube axis were made to promote mixing and tumbling of substrates (Fig. 1b). The length of a groove was 5 cm.

Propane gas was used as a carbon source with argon as a carrier gas. The total pressure was ambient and the reaction temperature was between 980 and 1150° C. The concentration of propane gas was varied from 5 to 40% with constant total flow rate of 2.0 l min^{-1}.

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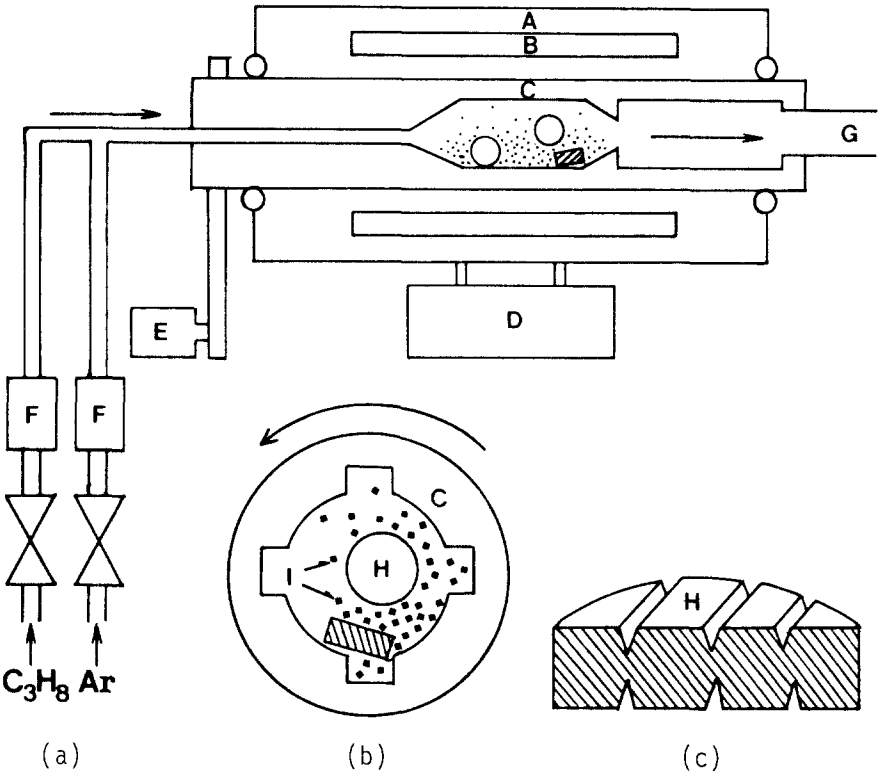


Figure 1 (a) A schematic diagram of tumbling bed deposition apparatus. (b) A cross-section of the centre of graphite reactor. (c) A half-section of a graphite disc on which parallel scratches are. A – resistance furnace, B – heating element, C – graphite reactor, D – temperature controller, E – motor, F – flow meter, G – gas trap, H – graphite disc, I – sea sand particles.

The total amount of bed particles in a charge was up to 10 g of 15 to 24 mesh sea sand, and the rotation speed of the reaction tube was ranged from 20 to 120 rpm. Deposits were obtained on 3 or 4 graphite disc substrates, 13 mm in diameter and 3 mm thickness, with the bed particles. Note that parallel scratches on the graphite discs, varying in size and shape, were made before deposition. (Fig. 1c).

The observation of the reactivity under polarized light reveals the types of optical microstructures and the degree of preferred orientation of bulk deposits. Specimens for SEM were fractured perpendicular to the deposition plane and then examined. Deposits were stripped from the graphite substrates, ground and polished until they were about 30 μm thick. They were then further thinned by argon ion sputtering. Examinations were carried out on the thin foils transparent to 160 KV electrons in a TEM. The local arrangement of crystallites was examined by selected area diffraction pattern technique.

3. Results

Figure 2 shows the transmission electron micrographs of a typical isotropic deposit in bright field (BF) and selected area diffraction pattern (SADP). In Fig. 2a the small spherical growth features exist about 0.5 to 1.0 μm in diameter. Microcracks are characterized by their transparency to the electron beam, arc-shape, and particular orientation parallel to the circumference of the growth features.

Fig. 2b shows close examination of the area A in Fig. 2a. This shows the presence of sub-growth features of globular shape in the central part of the growth feature. Fig. 2c is a SADP of A area in Fig. 2a and shows a ring-type (0 0 2) reflection. Similar SADPs were found in all central regions of another growth feature. Fig. 2d is a SADP of B area and shows an arc-shaped (0 0 2) reflection. This type of SADPs was always found on the edge regions and was the most common growth feature in the samples. Thus it arises that the crystallites are arranged with preferred orientation parallel to the circumference of the growth feature.

Shown in Fig. 3a–c are the TEM micrographs in BF and SADP of a laminar deposit. The viewing plane is parallel to the deposition plane and this shows somewhat different appearances from those perpendicular to the deposition plane [4, 5, 7, 8]. The growth features, unlike those which occur in the isotropic carbon, are not clearly distinguishable, but growth-feature-like regions including faint cracks are often observed. Sharp cracks are rarely observed anywhere.

Note that in Fig. 3c a certain crack, generated by handling, is propagated through a deposit. This crack goes through the interiors of growth features and many cracks in the interiors of growth features are related to its propagation. SADP reveals that most regions show no distinct arc-shaped (0 0 2) reflection in laminar deposit, except for the regions where some extent of cracks are present (see Fig. 3b).

A BF micrograph of columnar structure is shown in Fig. 3d. No spherical growth features are observable in sub-micron order, but the faint dividing regions are shown. Columnar structures are rarely composed of spherical growth features in TEM, and optical micrographs show the conical growth features which sizes range from a few micron to over several tens micron [7, 9]. No arc-shape SADPs of (0 0 2) reflection were found anywhere.

Fig. 4 shows the SEM of fractured surfaces of typical columnar, laminar, and isotropic structures. Columnar structures are characterized by layered appearances. Laminar structures are composed of round component and layered component over it. Isotropic structures are entirely composed of round component and rarely have layered component.

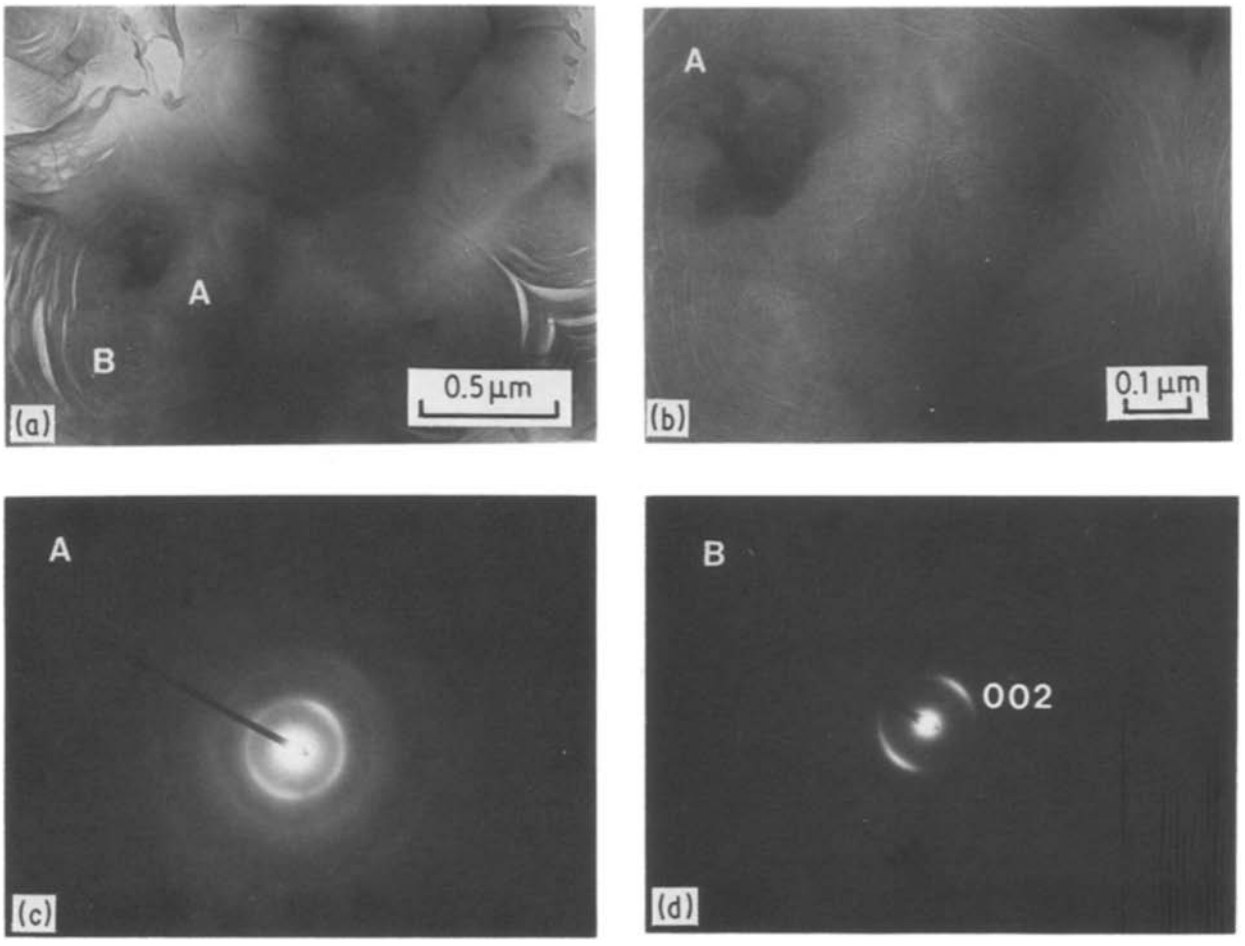


Figure 2 TEM of a typical isotropic deposit. Observation planes are parallel to the deposition planes.(a) and (b) are in bright field (BF). (c) and (d) are selected area diffraction patterns (SADP). Deposition conditions are a temperature of 1150° C, a propane concentration of 5%, a bed particle weight of 10 g, a rotation speed of reactor of 120 rpm, and a total gas flow rate of 2.0 l min^{-1}.

Fig. 5 shows the microstructural changes with deposition temperature and propane concentration under polarized light with other deposition conditions held constant; bed particle weight of 10 g and rotation speed of reaction tube of 120 rpm. A schematic diagram of a scratch and a bed particle sweeping over it is shown in Fig. 5f.

Two regions of depositions are apparent; one is a region where laminar or isotropic carbon is formed and the other only columnar carbon is formed. On the flat surfaces of graphite discs the changes proceeded gradually from fine bright laminar, A, to isotropic, H, as increasing the deposition temperature and propane concentration. A smooth transition is apparent between laminar and isotropic regions. In scratches only columnar structures are deposited independent of the deposition conditions. The deposition rate (deposition thickness per h) was lower for columnar structure than isotropic and laminar, and this resulted in enclosing the mouths of the scratches (see Fig. 5a and d). Deposition times are not same for all deposit layers.

Fig. 6 shows a porous deposit with rough deposit surface. In Fig. 6a under polarized light there are some bright regions extended to the growth direction. Most of them have pores at the end. Fig. 6b is a SEM fractograph of a pore. In this region the growth features are larger than in other regions.

4. Discussion

The various microstructures depicted in the previous section have implications pertaining to the discussion of the deposition mechanism and the fracture mechanism.

In isotropic structure the presence of the sub-growth features and their boundaries with nearer ones indicate that deposition might not occur in the liquid state but occur in the solid state. The crack formation was investigated to stem from the nature of anisotropic thermal contraction and curved arrangements of carbon layer planes [9]. Both the waviness of cracks in some growth features and the deviation from their sphericity arise from the random incorporation of sub-growth features during growth in a gas phase. The cracks in the interior of the growth features are related to their propagations. Round appearance of fractured surface of isotropic deposit must be due to the arc-shaped cracks within the globular growth features.

In previous studies [4–6, 8], observations perpendicular to deposition planes were carried out and it was seen that laminar structures consisted of small conical growth features with small solid particles at the apex of a cone. The fractured appearance of laminar deposits somewhat differ from that of isotropic deposit, it consists of not only round component but also additional layered component over it.

According to the reactivity of columnar deposit

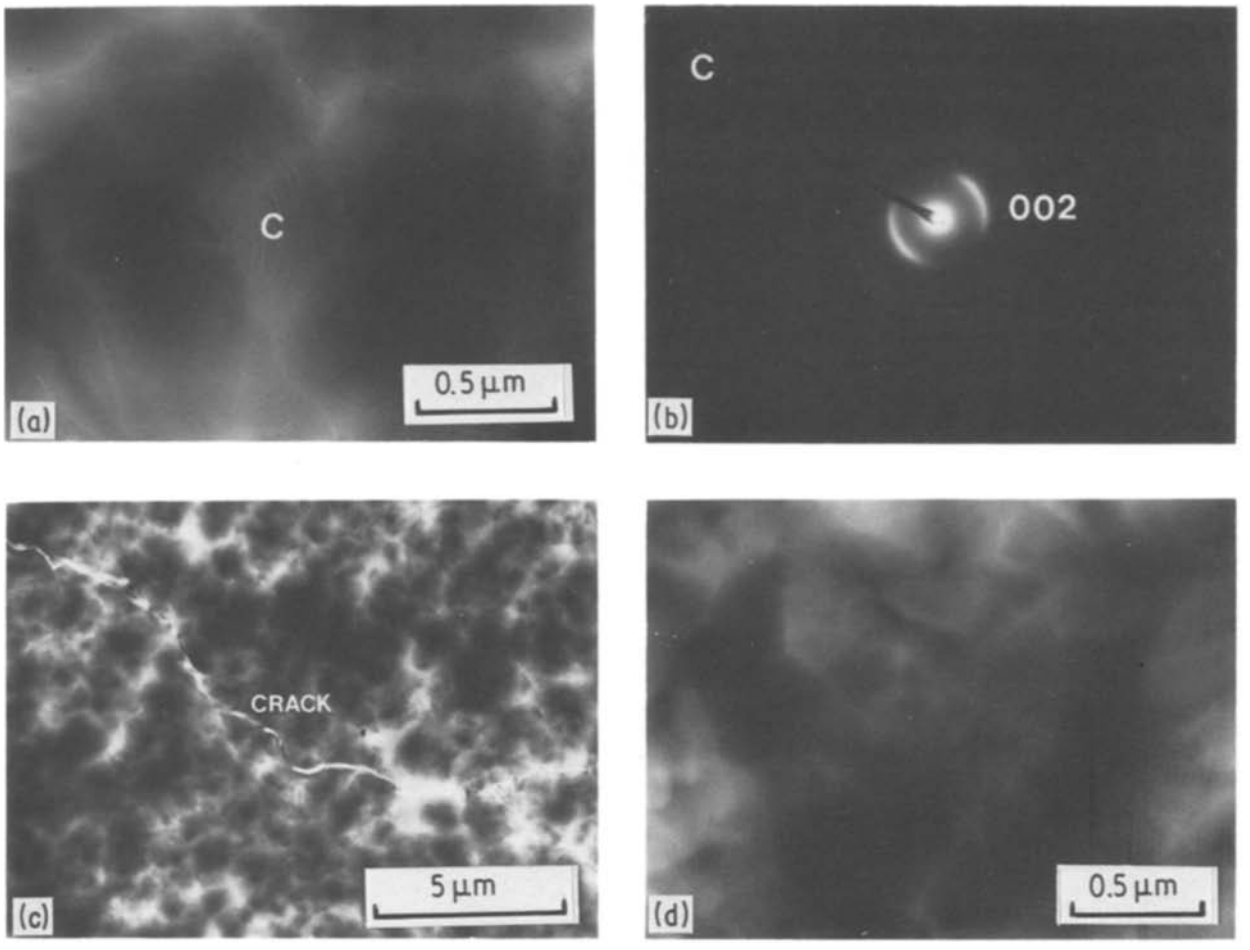
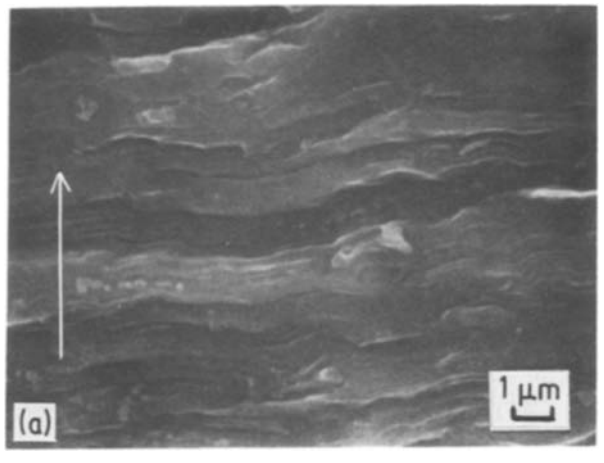


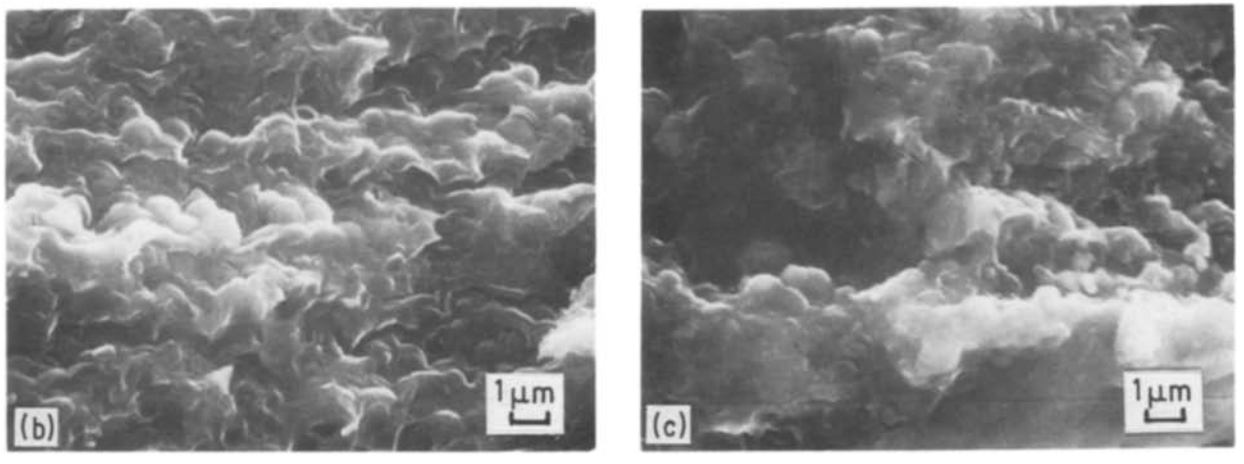
Figure 3 TEM micrographs of a laminar structure (a)–(c) and a columnar (d). Observation planes are parallel to the deposition planes. Deposition conditions of laminar are 1050° C, 5% propane, 10 g, 120 rpm and 2.0 l min^{-1}, and those of columnar are 980° C, 10% propane, no bed particles, 120 rpm and 2.0 l min^{-1}.



under polarized light, the layer planes are known to be oriented parallel to the cone axis and thus the cracks propagate in the direction parallel to the layer planes. As a result, the fractured surface of columnar shows a laminated appearance (see Fig. 4a).

From the above discussion the structural variations can be analysed by the combination of gas-born solid particles and directly deposited molecular carbons

Figure 4 SEM of the fractured surfaces perpendicular to the deposition planes of (a) columnar, (b) laminar and (c) isotropic deposits, at a constant total gas flow rate of 2.0 l min^{-1}. Deposition directions of all the deposits are denoted by an arrow in (a). Deposition conditions are (a) 1000° C, 5%, 0 g, 120 rpm, (b) 1050° C, 5%, 10 g, 20 rpm, (c) 1150° C, 5%, 10 g, 120 rpm.



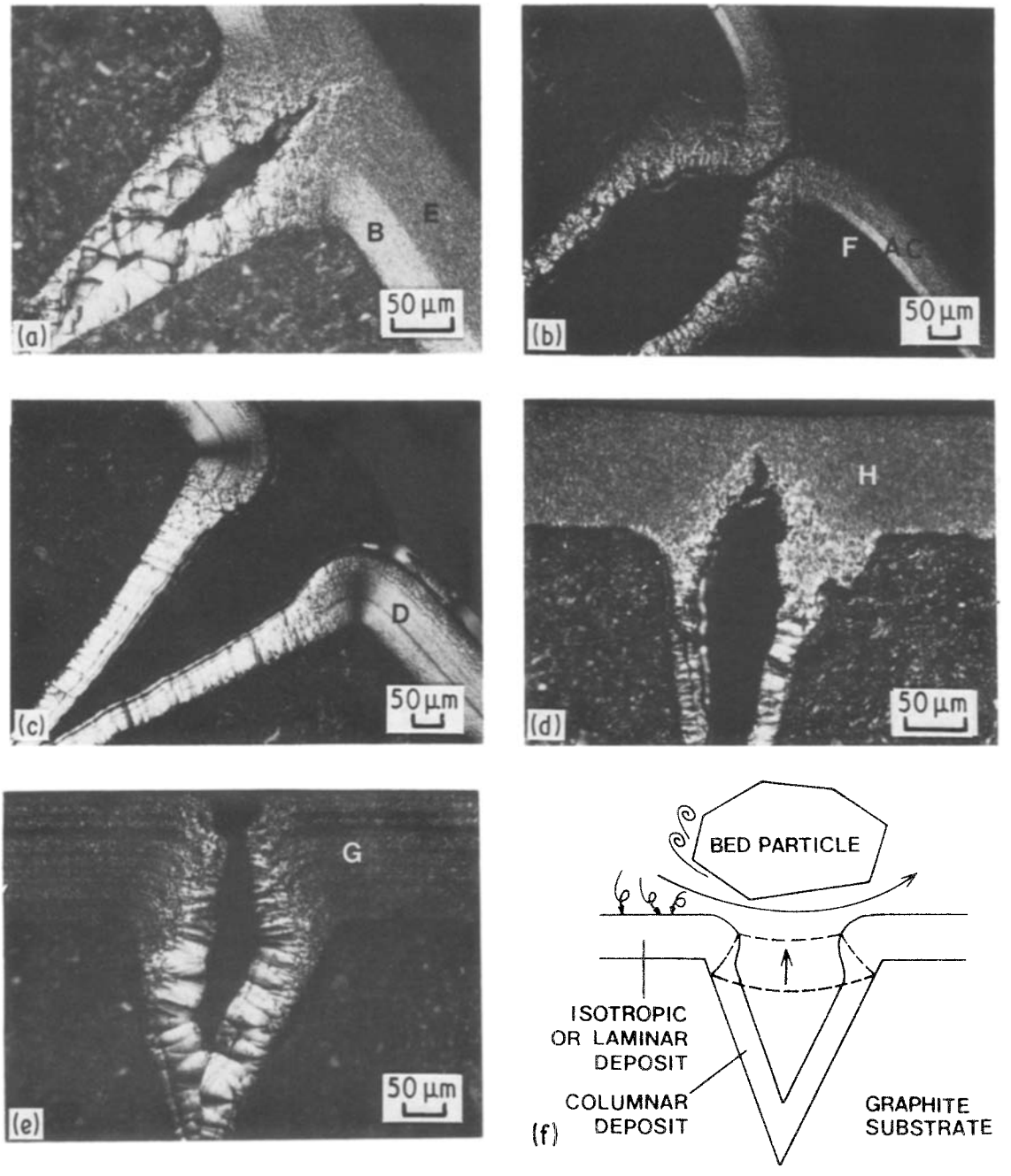


Figure 5 (a)–(e) Polarized light (PL) micrographs of pyrolytic carbons deposited at various temperature and concentration, other conditions kept constant; a bed particle weight 10 g, a rotation speed of reactor 120 rpm, and a total gas flow rate 2.0 l min^{-1}. (f) A schematic diagram of a scratch and a bed particle sweeping over it.

in them. The transition from laminar to isotropic depicted in Fig. 5 reflects that the relative amount of the gas-born solid particles in a deposit is increased with increasing temperature and propane concentration.

Under a constant tumbling situation more gas-born solid particles can be incorporated in a deposit at higher temperature and hydrocarbon concentration, this results in the formation of more isotropic deposit. Here we can choose one of the factors; it is chemical factor, the degree of supersaturation of pyrolysis products.

As pointed out from Fig. 5 the comparison of structures between deposits on the flat disc surfaces and deposits in the scratches suggests that the deposition variables, although important, are no longer the primary factors directly related to the changes in microstructures of pyrolytic carbon. The other factor is related to such differences.

Among previous deposition mechanisms, the recirculation of gas flow within a bed, proposed by Je and Lee [8], is the most appropriate model to explain the above results. When bed particles sweep the surface of graphite disc, (see Fig. 5f) carbon particles formed in the flowing gas can collide with the graphite disc surface by the action of gas recirculation.

On the other hand, in the scratches there is no action of gas recirculation and this region is a 'stagnant point'. As pointed out previously [10] there is a denuded zone immediately adjacent to a hot surface to prevent homogeneous nucleation of carbon particles. The independence of columnar structure on deposition conditions is a consequence of the lack of gas recirculation breaking the denuded zone. Deposition occurs by the direct attachment of molecular carbons. Therefore we can choose the other factor; it is mechanical factor, the gas flow pattern of recirculation.

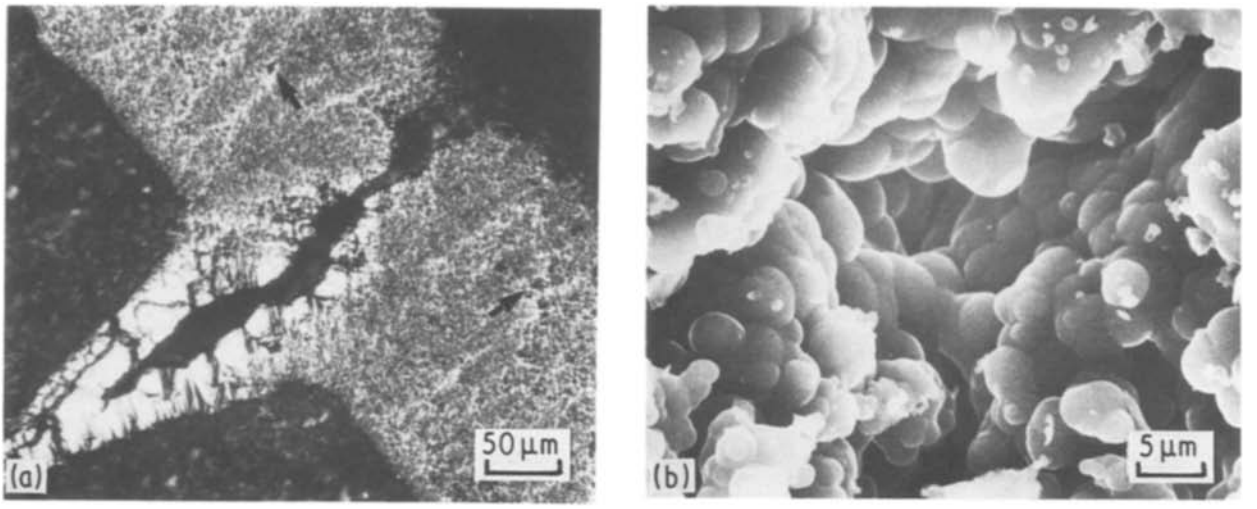


Figure 6 A porous deposit obtained at 980° C, 10% propane, no bed particles, and 120 rpm. (a) under polarized light and (b) SEM micrograph of a pore region.

In Fig. 6 it is considered that as deposition occurs the initial surface is further roughened to develop a hill and valley structure. Continual attachment of gas-born particles only occurs at hills and this preferential growth finally covers the retarding valley regions to form pores. In valley regions only mass transfer of pyrolysis products promotes the orderly growth which results in the extended bright region under polarized light.

5. Summary

The critical phenomena of depositions are observed in experiments to distinguish two essential factors which are directly related in determining the microstructures of pyrolytic carbons. One is the degree of supersaturation of pyrolysis products in a gas phase and the other is the gas flow pattern of recirculation within a deposition zone. Two factors simultaneously contribute to form pyrolytic carbons. Therefore the structural variations are not interpreted solely by one of two factors and both are inter-related.

Many cracks in the deposits are closely related to the fracture mechanism. Cracks in isotropic structures are mostly arc-shaped so that the fractured surfaces are mostly round. Fractography of columnar structures have a laminated appearance due to the lack of globular growth features. Fractography of laminar deposits show both round component and laminated component.

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