JOURNAL OF MATERIALS SCIENCE 15 (1980) 909–917

Characterization by electron microscopy of carbon phases (intermediate turbostratic phase and graphite) in hard carbons when heat-treated under pressure

S. DE FONTON, A. OBERLIN
Laboratoire Marcel Mathieu, ER 131 du C.N.R.S., UER Sciences, 45046 Orleans, France
M. INAGAKI
Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi 440, Japan

As hard carbons are heat-treated under pressure (1 h, 5 kbar) an intermediate thermally stable carbon phase ($d_{00.2}$ = 3.39 Å, turbostratic) appears above 1100° C. Its proportion increases up to 1600 or 1700° C depending in the initial sample (saccharose or glassy-carbon). The morphology of this new phase has been determined by HREM to be similar to crumpled sets of paper sheets, it is thus highly porous. When heat-treated under pressure above 1600 or 1700° C, this phase is suddenly transformed into graphite, i.e. the porous texture flattens into lamellae.

1. Introduction

Under a pressure of 5 kbar, non-graphitizing hard carbons are transformed into graphite above 1600° C [1, 2]. In a previous work [3] the results obtained in the case of glassy carbon spheres* have been reported. Heat-treatment under pressure has been carried out under the same conditions as before, i.e. at temperatures ranging from 1000 to 1800° C, for 1 h, in a piston-cylinder type apparatus [4]. As in the previous studies [4–6], the crystalline graphite structure was first detected by X-ray diffraction techniques. Two remarkable changes were found. The first, at 1300° C, corresponds to the development of a peak at a 3.39 Å interlayer spacing, and the structure is still turbostratic [3]. The second takes place at 1700° C and is due to the sudden occurrence of a crystalline phase with the same $d_{00.2}$ spacing as graphite, i.e. 3.36 Å. Between 1600 and 1700° C the 1 0 . and 1 1 . bands suddenly become three-dimensional sharp $hk.l$ lines. The samples were then studied by high-resolution transmission electron microscopy techniques such as selected-area diffraction (SAD), bright- and dark-field and lattice-fringes imaging [7].

The purpose of this paper is to present the results obtained in the case of a very pure carbon (sugar coke) and to compare them to that obtained in the case of commercial glassy carbon (Tokai glassy carbon spheres).

2. Experimental details

2.1. Electron microscopy

The main advantage of the electron microscope compared to X-rays is to produce directly the Fourier synthesis of the object through the image. The Abbe image, situated in the back focal plane of the objective lens, corresponds to the diffraction pattern, i.e. to the first Fourier transform of the object. The optical image corresponding to the diffraction pattern of the diffraction pattern, i.e. the second Fourier transform, is formed in the Gaussian plane. Because the objective lens introduces phase shifts (transfer function),

---

* Commercial Tokai Carbon Co sample, made from furfuryl alcohol condensate carbonized up to 1300° C.

0022–2461/80/040909–09$02.90/0

the final image is only a restricted Fourier synthesis of the object which, in carbon samples, is reduced to two terms. In this case, interference between the undeviated 0 0 0 electron beam and the 0 0.2 scattered beam produces lattice-imaging. If an aperture large enough to let through these two beams is used and if a suitable defocus of the objective lens is introduced, a set of dark and bright fringes will be obtained in the Gaussian plane. In first approximation they are an enlarged projection of the graphite layer planes onto the observation plane. Since with electrons the Bragg angles are very small, 0 0.2 fringes result from lattice planes nearly parallel to the incident beam, i.e. the carbon layers are seen edge-on. It has to be kept in mind that only a projection is obtained which precludes the three-dimensional shape of the graphitic layers to be known. Therefore, another technique has to be used for obtaining additional data. Phase contrast can be replaced by amplitude contrast, i.e. the image of the object can be obtained by using only one scattered beam. An aperture is chosen small enough to let through only one beam at once. The region which issues this scattered beam thus appears bright on a dark-field. The main advantage of such a dark-field technique is to image crystallites diversely oriented in the object. Consequently, the three-dimensional object texture can be determined.

In the present work, lattice imaging, dark-field imaging, selected-area electron diffraction and bright field as well were used to determine the mechanism of hard carbon graphitization when heat-treated under pressure.

2.2. Sample preparation

Sugar coke to be compared with the Tokai commercial sample was prepared from very high purity saccharose heat-treated under nitrogen up to 340° C and then in a vacuum. From room temperature to 1000° C the material was heat-treated at a rate of 4° C min^{-1} in a nitrogen gas flow. The residence time was 1 h.

Both sugar coke and glassy carbon spheres were subjected to high pressure in a piston-cylinder type apparatus described elsewhere [4]. Heat-treatment runs were carried out at a rate of 400° C min^{-1}, followed by a 1 h residence time. The samples were then quenched by a rapid cooling in the apparatus. The containers are made of polycrystalline pure graphite insulated from the pyrophyllite external shield by boron nitride walls.

3. Results

3.1. Occurrence of a new phase and its importance

The sample heat-treated under pressure to 1600° C has the usual aspect of graphite. In bright-field the particles look like lamellae. In 1 0 . 0 dark-field they present very large Moiré patterns which may extend over 5000 Å. The SAD patterns prove that it is polycrystalline graphite since $h\,k\,.\,l$ reflections

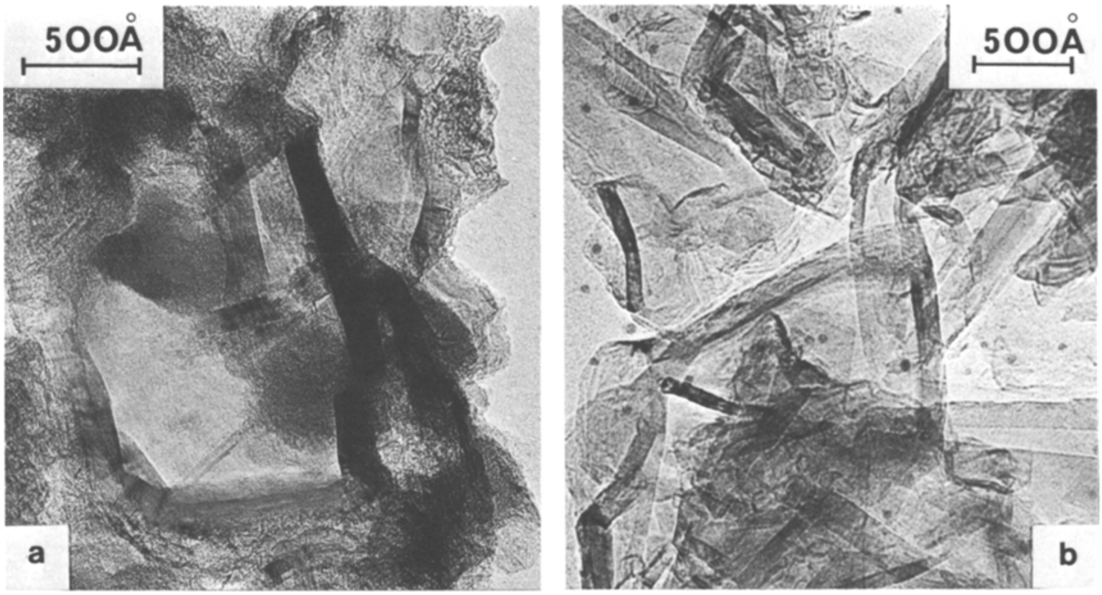

Figure 1 Intermediate carbon phase obtained under pressure (sample heat-treated to 1300° C under 5 kbar).

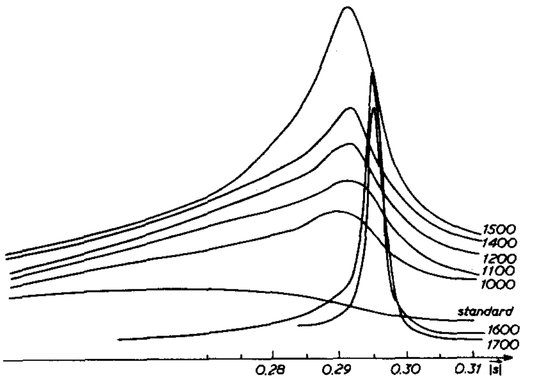

Figure 2 Variation of the X-ray profiles of the 0 0.2 reflection with the heat-treatment temperature ($P =$ 5 kbar).

appear. In the same sample, other types of particles can be noticed. Next to residues of hard carbon porous matrix, a new phase can be seen, which is illustrated in Fig. 1. The morphology of these particles will be described in detail below, but at this point it is possible to say that they are very different from both hard microporous carbon and graphite lamellae. They will be called "spherules". In addition, this new phase is turbostratic, as proved by the fact that no three-dimensional $hk.l$ reflections can be observed on the SAD patterns. It may thus be expected to be the intermediate phase between matrix and graphite.

Let us consider now the samples heat-treated at lower temperatures. Fig. 2 shows the evolution of the X-rays 0 0 . 2 reflection profile. Whereas the standard, which has just been heat-treated to 1000° C under normal pressure, produces a very broad line, a well-defined though broad line is superimposed from 1000 to 1500° C in the case of the samples heat-treated under 5 kbar. It corresponds to an interlayer spacing of 3.39 Å (at 1600° C a sharp peak, corresponding to an interlayer spacing of 3.36 Å appears, as also observed in the case of glassy carbon). At the same time, an increasing quantity of spherules, similar to that observed in the 1600° C sample can be seen under the electron microscope. At 1000° C they are very few, but their number grows as the temperature increases, and at 1500° C the transformation is almost complete and only a few are left at 1600° C. Comparing with X-ray data, we may conclude that the d_{002} of these spherules is 3.39 Å. X-rays and SAD agree to show that they are turbostratic. These spherules are a new carbon phase, characterized by a biperiodic structure and $d_{002} = 3.39$ Å.

3.2. Description

As the correlation reported above proves that the spherules constitute the intermediate phase between matrix and graphite, it is necessary to know their true morphology. Fig. 3 shows pictures of the same particle in bright-field, 0 0.2 and 1 0 dark-field. In bright-field (Fig. 3a) the particle appears to be limited by dark bands, the central part showing only a weak contrast. In 0 0 . 2 dark-field (Fig. 3b), for position 1 of the aperture (Fig. 3 insert) some of these areas appear bright. If the aperture is moved about 60° around the 0 0.2 ring, for instance to position 2 (Fig. 3c), the bright areas direction also turns about 60°. It is possible by this method to light up the whole contour of the particle. This proves that it is limited by carbon layer stacks seen edge-on, and parallel to the contour. Finally, the existence in 1 0 dark-field of Moiré patterns extending over the whole area between the walls (Fig. 3d) shows that there are large carbon layers more or less parallel to the supporting film in all this area. The carbon layers are straight and parallel to each other, i.e. perfect, on a long range as seen in lattice plane imaging in Fig. 4. This equally implies a large diameter of the carbon layers. This assumption is verified by SAD patterns where 1 0 and 1 1 bands have a dotted appearance.

This set of results suggest for the particles the shape of a distorted and flattened balloon, i.e. a large distorted pore. However, since the images obtained, thanks to a microscope, are only a projection along the optical axis, it is necessary to obtain additional information on the third space dimension by using other techniques. Consequently, two other techniques were employed in order to point out the relief of the spherules: shadow casting and stereoscopy.

To evaluate the thickness of the particles themselves, a film of germanium was deposited by evaporation under a low incidence angle. The particles are very inhomogeneous in thickness: as particle size ranges from 4000 to 9000 Å, the total thickness is about 3000 Å with 500 to 1000 Å steps. Germanium is very easy to evaporate but the film obtained tends to coalesce. A good resolution being necessary for studying details, a film of carbon–platinum was deposited under a high-incidence angle. Fig. 5a shows that sometimes no shadow appears on the upper side of the particles. The walls of the pores appearing dark in bright-field are thus hidden by a continuous film of carbon layers. Fig. 5b shows that sometimes holes or folds

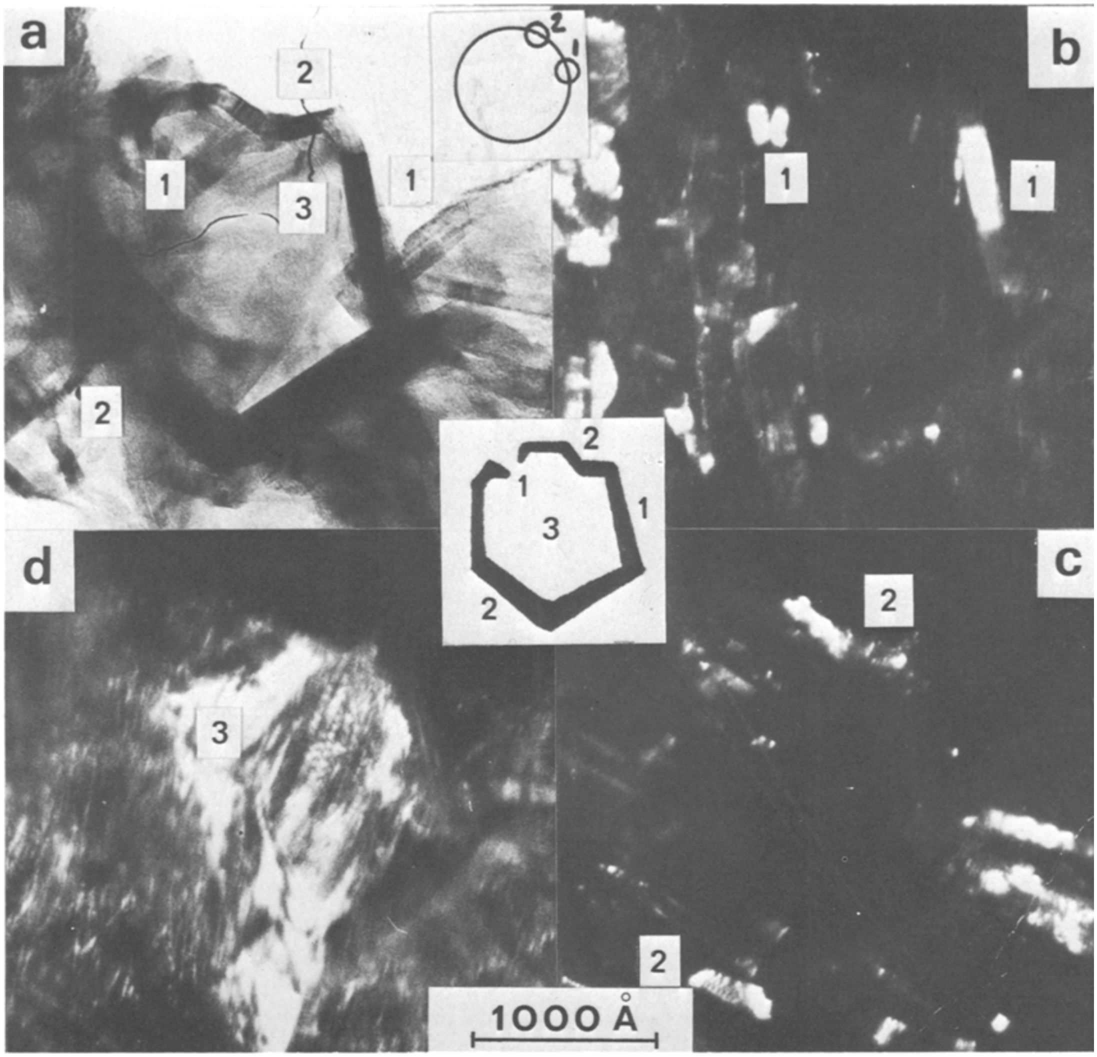

Figure 3 Analysis of the texture of a particle obtained under pressure: (a) bright-field, (b) and (c) 0 0.2 dark-field, (d) 1 0 dark-field. Inset, aperture position on the 0 0.2 ring.

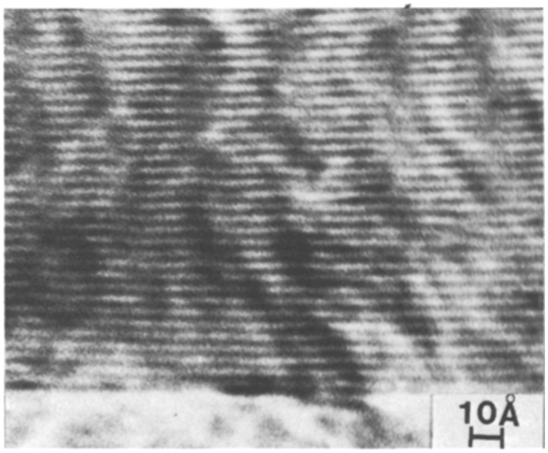

Figure 4 Lattice-plane imaging on a new particle wall.

in the particle produce visible shadows. Consequently, the shape of the particle is very complicated and distorted. Stereoscopy will reveal this in more detail.

In this technique, a goniometer stage is used for tilting the object with respect to the incident beam. Tilting was performed in 6° increments between + 60 and − 60°. Observing two consecutive pictures together with a stereoscope enables to restore the three-dimensional shape (Fig. 6). Observing the whole series proves that the walls of the spherules are continuous: in bright-field a part of a wall appears as a dark band when it is under the Bragg angle. Tilting the object brings under the Bragg angle a part next to the first one, and the dark band progressively moves along the wall.

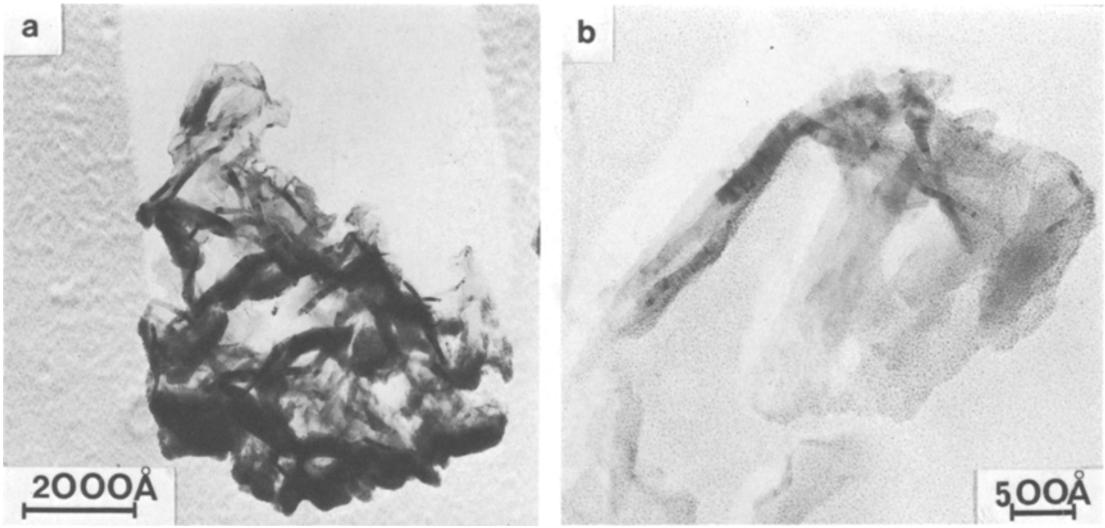

Figure 5 Shadow-casting. (a) Continuous carbon wall approximately parallel to the observation plane. (b) Folds of the carbon walls of spherules.

Thanks to these two techniques, it is possible to compare a particle formed by a complicated group of spherules to paper balls, obtained by crumpling a set of paper sheets. A very schematic model of such a texture is given in Fig. 7.

All the results obtained lead me to consider the material heat-treated to 1500° C under pressure as a new carbon phase structurally characterized by its d_{002} spacing (3.39 Å), its two-dimensional (turbostratic) structure and its large L_a value, joined to its very peculiar morphology (crumpled set of paper sheets). In order to define this new phase completely, it is necessary to know if it is stable under normal pressure, i.e. whether it is

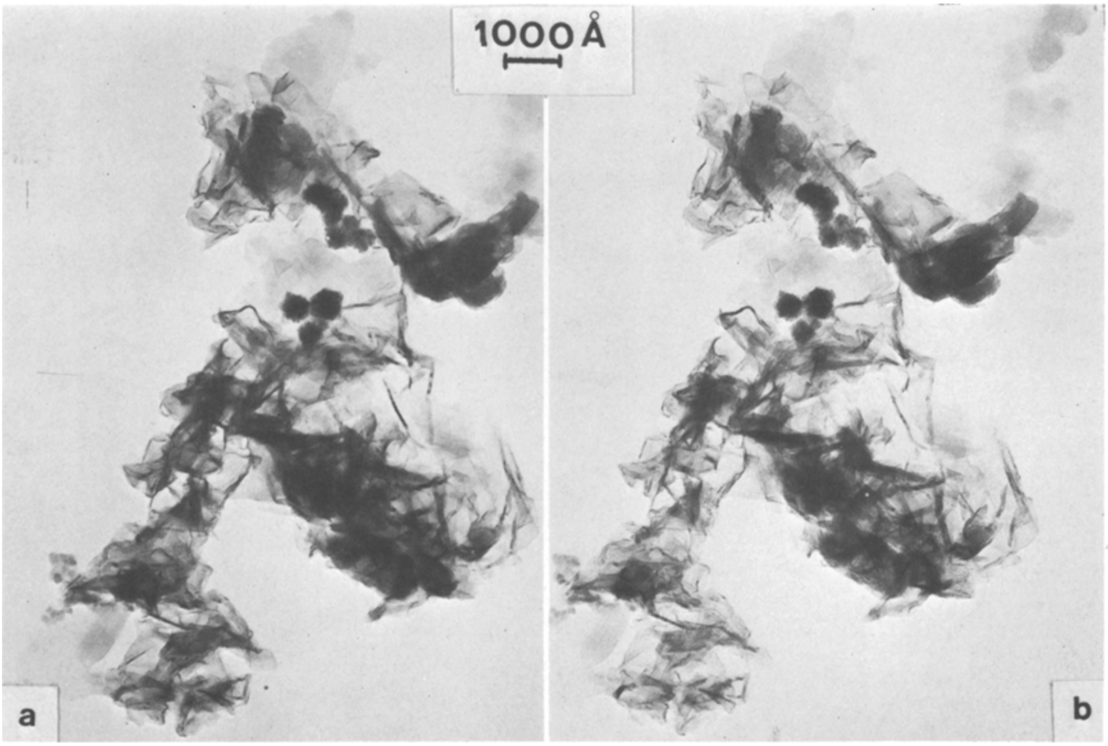

Figure 6 Stereoscopic pictures (to be observed with a stereoscope) tilting angle (a) 0 (b) 6°.

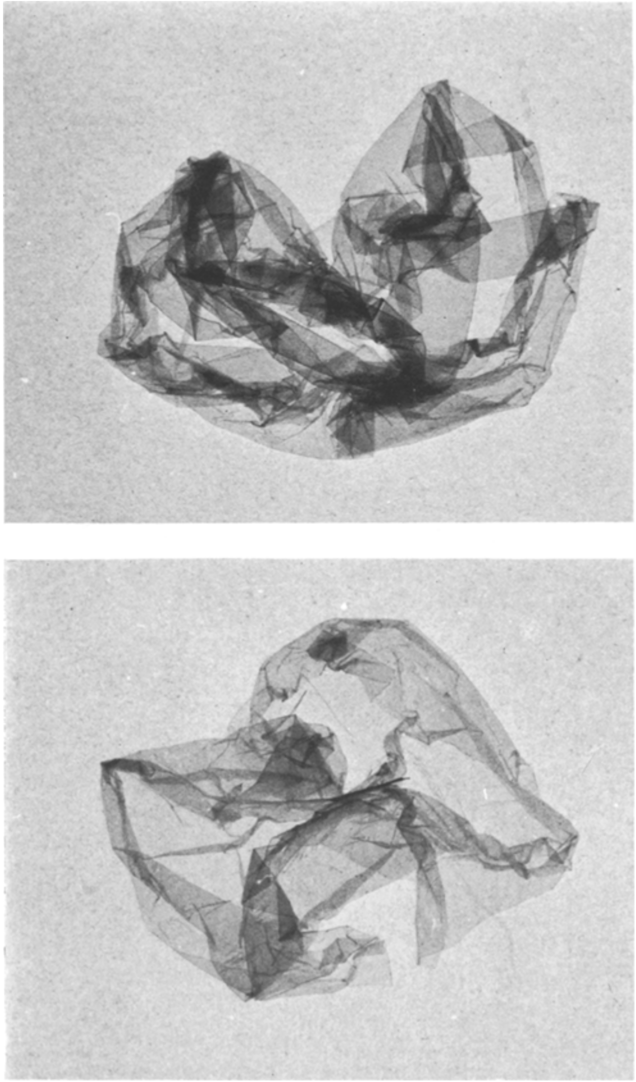

Figure 7 (a) and (b) Models of the morphology of "spherules" (crumpled set of cellophane sheets illuminated from behind).

progressively graphitizable or not. Samples almost completely transformed by heat-treatment under pressure were thus heat-treated to 2800° C under normal pressure. No change was observed either in structure or in texture and no graphite appeared. Hence this phase is thermally stable.

3.3. Comparison between two possible percursors: sugar coke and glassy carbon

Whereas the transformation into graphite under high pressure happened between 1600 and 1700° C in the case of glassy carbon it happens between 1500 and 1600° C in that of sugar coke. Thus sugar coke seems to be easier to transform. This can be seen also in observing the porous non-transformed matrix. There is almost no change in glassy carbon matrix heat-treated under pressure, but sugar coke matrix is transformed. Three SAD patterns are given in Fig. 8: Fig. 8a and c correspond to standard cokes heat-treated respectively to 1300 and 2000° C under normal pressure, and Fig. 8b corresponds to a sample heat-treated to 1300° C under 5 kbar. The latter is very similar to the second one, so far as 00.2 ring width is concerned: matrix heat-treated to 1300° C under 5 kbar is in advance with respect to that heat-treated under normal pressure, and this concerns the size of the diffracting elements as well as the spread of the d_{002} spacing [7].

4. Discussion and conclusions

In order to understand the results obtained by heat-treatment under pressure, we have to think

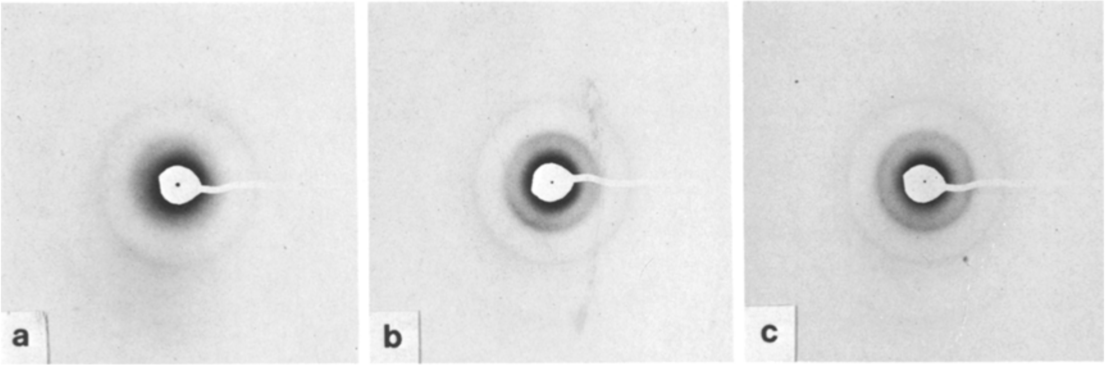

Figure 8 SAD patterns. (a) Standard coke heat-treated to 1300° C. (b) Sample heat-treated to 1300° C under 5 kbar. (c) Standard coke heat-treated to 2000° C.

again in detail about the behaviour of carbon when heat-treated under atmospheric pressure as it has already been described elsewhere [7–11].

When heat-treated below or at 1000° C, both graphitizing and non-graphitizing carbons are made of the same elements, i.e. perfect mosaic domains formed by stacks of parallel layers. Their structure is turbostratic: within a domain, each layer is oriented at random relative to its neighbours. The diameter L_1 of a stack (Fig. 9) is less than 10 Å (4 to 10 aromatic rings) and the number N of layers is about 2 to 3. These mosaic domains gather into clusters, the local preferred orientation of which is roughly parallel to a plane (Fig. 9). Inside such a zone, L_2 in diameter, the domains are inter-connected by tilt and twist boundaries, thus forming larger wrinkled layers. From one cluster to its neighbours, the direction of the preferred orientation plane changes at random. It results in a porous texture where each cluster forms the wall of irregularly shaped pores. It is remarkable to notice that such a microtexture can also be represented by a model similar to that shown in Fig. 7. However, pore scale differs greatly, first when soft or hard carbon are considered and then if the carbon phase has been formed by heat-treatment under pressure. In soft carbons, the preferred parallel orientation occurs on a very long range and each cluster of parallel mosaic domains is larger than a few micrometers. In the "spherules" described here, the walls are about 1000 Å in size. In hard carbons, pores walls are less than 100 Å. In low temperature soft and hard carbons, pores walls have a striking zig-zag structure, while carbon layers are in "spherules", and are straight and perfect over a large extent.

As heat-treatment temperature increases, both soft and hard carbons behave in the same way. During the first step (pregraphitization stage), N

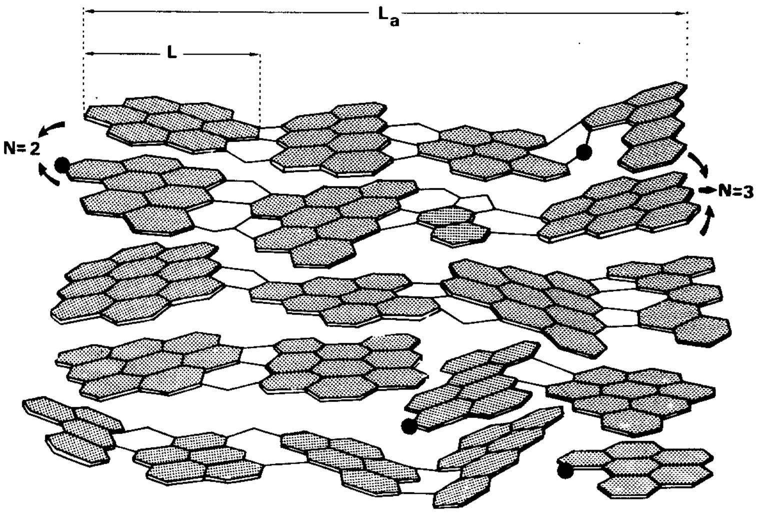

Figure 9 Model of low-temperature carbon: HTT ≃ 1000° C (from Villey [14]).

increases very quickly, L_2 does not increase much and the layers remain wrinkled. Above 2000° C, the layers suddenly dewrinkle and become straight. From this point (graphitization stage) in soft carbons, more and more pairs of layers reach the graphite order, and the crystallite size as well as the three-periodic order increase very fast. The sudden dewrinkling of the layers has been attributed to a sudden wiping out of the defects trapped at the tilt and twist boundaries between two perfect mosaic domains. This phenomenon is related to the mobility of carbon atoms which occurs at about 2000° C, inducing the mobility of the defects.

These data show that the final size of the carbon layers is limited by the extent of the clusters of parallel mosaic domains formed below 1000° C: a few micrometers in soft carbons, less than 100 Å in hard carbons. As a result, the graphitization process can only be achieved in soft carbons where crystal growth is practically unlimited. On the contrary, in hard carbons where L_2 is less than 100 Å, geometrical stresses preclude any rearrangement between two adjacent walls and graphitization does not occur. The carbon ability to graphitize is limited by the L_2 dimension in a manner similar to that of carbon blacks. The smallest ones are non-graphitizing carbons while the largest ones are graphitizing carbons.

The graphitization process has to be reconsidered if heat-treatment is conducted under pressure. Microporous hard carbons are thus suddenly transformed into a macroporous material below 2000° C. At the same time, even at such a low temperature, pore walls are made of straight and perfect layers. In such a transformation process, the leading force is probably the shear stresses which develop in pore walls as pressure is applied. This causes the boundaries between neighbouring stacks to break down. Free edges are thus created which are highly reactive. They necessarily recombine to lower the free energy of the system. This results in large straight layers which form the walls of larger pores. The crumpled sets of paper sheets described above can thus be considered as made of large distorted pores, a consequence of the coalescence of hard carbon small pores. The extent of the preferred orientation is thus considerably increased and this intermediate stage prepares for a new step which, by the same mechanism, suddenly leads to flat lamellar graphite.

This intermediate phase leads to graphite only when high pressure is maintained during the following heat-treatment. When heat-treatment continues in normal atmospheric pressure conditions, this phase remains stable and turbostratic. Its stability is due to the occurrence of perfect carbon layers of large diameter. Hence they cannot rearrange when carbon atoms become mobile.

It is very interesting to now consider a different type of carbon: catalytic carbons. If hard carbons are heat-treated with catalytic agents such as Fe, Si, V,... , new phases appear, which are either turbostratic, graphite, or crystalline with a $d_{00.2}$ spacing larger than that of graphite. They are always obtained at temperatures much lower than 2000° C. When heat-treated at high temperature, these new phases are stable, i.e. they are not transformed into graphite [12]. We observed, under the electron microscope, a sugar coke heat-treated to 2800° C with silicon, and found particles exactly similar in morphology to those obtained under high pressure. The morphology is not only the same, but also the SAD patterns show no $h\,k\,.\,l$ reflections and the carbon layers are straight and perfect. The mechanism of pore-coalescence, leading to that shape, is probably the same, but in this case stack boundaries are broken by a chemical effect and not by a mechanical one. The absence of progressive graphitization is, in any case, explained in the same way.

A comparison can be drawn between the behaviour of anthracites and of hard carbons heat-treated under pressure. Anthracites are a microporous material similar in texture to hard carbons [13]. As in hard carbons, the clusters of parallel mosaic domains which form the pore walls are very small (less than 100 Å), but a large statistical preferred orientation is superimposed which is induced by tectonic stresses*. This parallel orientation of carbon layers stacks widely developed is due to pore flattening along the bed plane which brings more carbon layers parallel to that direction. During heat-treatment, this peculiar texture favours pore coalescence; flat regions thus suddenly appear at the expend of the porous ones. From 2000 to 2500° C their number increases and over this temperature transformation

---

* So they could be expected to be graphitizable. In fact, they are graphitizable only above 2500° C, and moreover they have a porous texture below 2000° C.

into graphite is complete. In anthracite as well, the shear stresses which develop at the mosaic domain boundaries are responsible for wall breakage and coalescence of neighbouring pores.

The effect of that very peculiar preferred orientation is destroyed if anthracites are heat-treated under pressure, because pressure is applied in any direction with respect to the bedding plane. Anthracites in that case behave like hard carbons: the intermediate phase occurs at 1600° C, followed then by a sudden change into graphite.

All these examples lead to a few general conclusions. The evolution of carbons with heat-treatment depends on their microtexture at a temperature lower than 2000° C, i.e. on the mutual position of neighbouring carbon layer stacks (mosaic domains less than 10 Å). In soft carbons, two characteristics co-exist: a large preferred orientation produced at low temperature and the possibility for defect at the frontiers between stacks to be swept off at higher temperature ($> 2000°$ C). In hard carbons, defects are swept off above 2000° C, but this happens only inside a cluster of homogeneously oriented stacks, i.e. over a short range since there is no largely extended parallel orientation. In the case of high pressure or catalytic agents, there is a rather large preferred orientation occurring at a low temperature, as carbon layers are straight over a long range in the "spherule" walls, but because of this very property they cannot be rearranged above 2000° C. In this latter case though, it is possible to obtain graphite by increasing the heat-treatment temperature under high pressure or the catalyst concentration, which leads to a phase transition, but there is no progressive and homogeneous graphitization: more and more spherules are suddenly transformed into graphite.

References

1. K. KAMIYA, M. INAGAKI, M. MIZUTANI and T. NODA, *Bull Chem. Soc. Japan* **41** (1968) 2169.
2. M. INAGAKI and S. NAKA, *J. Mater. Sci.* **10** (1975) 814.
3. M. INAGAKI, A. OBERLIN and S. DE FONTON, *High temp. High press.* **9** (1977) 453.
4. M. INAGAKI, S. HAYASHI, K. KAMIYA and S. NAKA, *ibid* **3** (1971) 355.
5. M. INAGAKI, Y. TAMAI, S. NAKA and K. KAMIYA, *Amer. Ceram. Soc. Bull.* **52** (1973) 856.
6. M. INAGAKI, K. HORII and S. NAKA, *Carbon* **13** (1975) 97.
7. A. OBERLIN, G. TERRIERE and J. L. BOULMIER, *Tanso* **80** (1975) 29; **83** (1975) 153.
8. M. INAGAKI, A. OBERLIN and T. NODA, *ibid* **81** (1975) 68.
9. M. VILLEY and A. OBERLIN, *Carbon* **17** (1979) 77.
10. G. TERRIERE and A. OBERLIN, in preparation.
11. J. GOMA and M. OBERLIN, *Thin solid films* (1979).
12. A. OBERLIN, M. OBERLIN and J. R. COMTE-TROTET, *J. Microsc. Spectrosc. Electron* **1** (1976) 391.
13. A. OBERLIN and G. TERRIERE, *Carbon* **13** (1975) 367.
14. M. VILLEY, Thesis, Orleans (1979).

Received 28 February and accepted 13 June 1979.