Studies on the Graphitization. III. The Sub-Structure of Heat-Treated Coke*

By Haruo KURODA

(Received January 29, 1959)

Carbons made by carbonizing organic substances at a temperature lower than 1000°C are made up of minute crystallites of non-graphitic structure and disordered phase consisting of carbon, hydrogen and oxygen. The heat-treatment at a higher temperature causes in carbons the decrease of disordered phase and the crystallite growth as well as the improvement of the stacking order of the layer lattice in crystallites.

The progress of the structural change in the heat-treatment differs greatly depending on the characters of carbons even if they are heat-treated under the similar conditions. The crystal structure of carbons can be well defined by the analysis of their X-ray diffraction pattern¹⁾. Graphitization has been discussed hitherto mainly based on the knowledge concerning the crystal structure. The difference in graphitizability, however, can not be explained by comparing the crystal structure alone.

In the previous papers²⁾, we pointed out that the particular features in graphitization of carbon blacks are due to the substructure of carbon black particles. It might be natural that the graphitizability of carbon is strongly influenced by the character of crystallite boundaries, alignment of crystallites or other similar aspects of its structure which we shall call micro-structure distinguished from crystal structure. From such a point of view, we investigated the micro-structure and its change after heat-treatments in petroleum coke, which is known to be one of the well-graphitizable carbons.

Experimental and Results

Heat-Treatment and Crystal Structure.—Petroleum coke of Great Lake Co. was heat-treated in vacuo at several temperatures from 1000°C to 3000°C. X-ray diffraction was studied using a commercial X-ray diffractometer, with Cu K_α radiation. Diffractometer records of 10 diffraction are reproduced in Fig. 1. As seen in this figure, the raw coke has non-graphitic structure, and the improvement of the stacking order of layer lattice starts at a temperature around

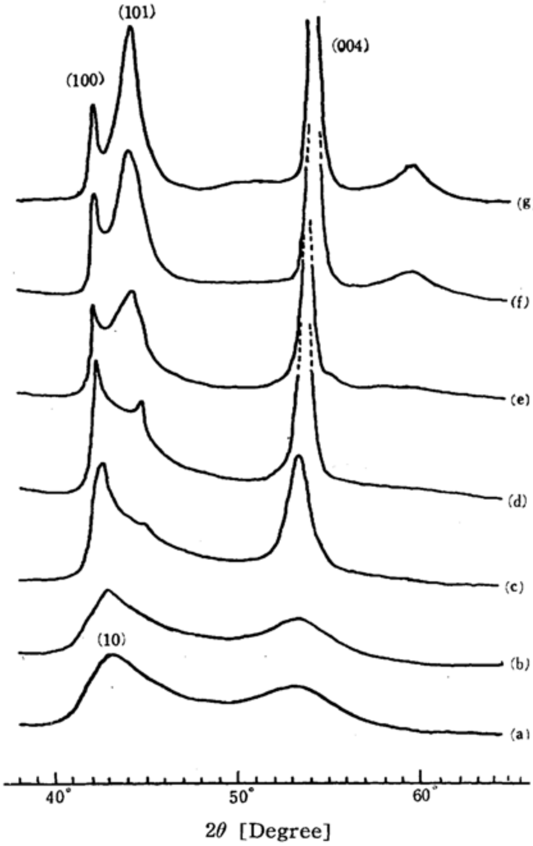

Fig. 1. X-ray diffraction pattern of petroleum coke. The effect of heat-treatment on the profile of (10) diffraction peak. (Cu K_α, Ni-filtered). (a) Raw state. (b) 1400°C. (c) 1850°C. (d) 1900°C. (e) 2040°C. (f) 2500°C. (g) 3000°C.

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* This work is a part of a research project on carbons, supported by the 117 Committee in Nippon Gakujutsu Shinkokai, directed by Prof. H. Akamatu. Part I, This Bulletin, **29**, 574 (1956); Part II, ibid., **32**, 142 (1959).

1) J. Biscoe and B. E. Warren, *J. Appl. Phys.*, **13**, 364 (1942); C. E. Houska and B. E. Warren, ibid., **25**, 1503 (1954); R. E. Franklin, *Acta Cryst.*, **3**, 107 (1950); *Proc. Roy. Soc.* (*London*), **A209**, 196 (1951); H. Akamatu, H. Inokuchi, H. Takahashi and Y. Matsunaga, This Bulletin, **29**, 574 (1956).

2) H. Kuroda and H. Akamatu, "Proceeding of the 3rd Conference on Carbon", Pergamon Press, New York (1958), p. 381; This Bulletin, **32**, 142 (1959).

1900°C. When H.T.** is 2500°C, the observed value of layer spacing is 3.365 Å. This indicates that nearly 65% of layers are in graphitic orientation. It becomes 3.351 Å after the heat-treatment at 3000°C.

The crystallite sizes determined from the breadth of diffraction peak are given in Table I. At lower temperatures crystallite size increases only a little. The rapid growth starts at a temperature around 1900°C.

TABLE I. GROWTH OF CRYSTALLITE DIMENSION IN PETROLEUM COKE WITH HEAT-TREATMENT

H.T. (°C)	L_a (Å)	L_c (Å)
Original	38	37
1400	40	38
1550	42	49
1720	87	71
1850	110	93
2040	276	180
2500	392	202
3000	444	213

Grains of Coke Powder.—After the heat-treatment, coke was milled into a fine powder and observed under the electron microscope***. Minute flaky grains can be observed with the raw coke as shown in Fig. 2. They have a jagged outline and the appearance of the granular structure. Most of them are of several microns in transverse direction and less than 1000 Å in thickness. The granular appearance is removed by the heat-treatment. When H.T. is higher than 2000°C, it entirely disappears. After the heat-treatment with high H.T., the stepwise variation of electron transmission is seen at edges of grains. It can be found also at the inner part of grains when its thickness is very small. These facts indicate that each grain is a bundle of many thin lamellae. The thickness of one lamella seems to be in the order of 200~300 Å.

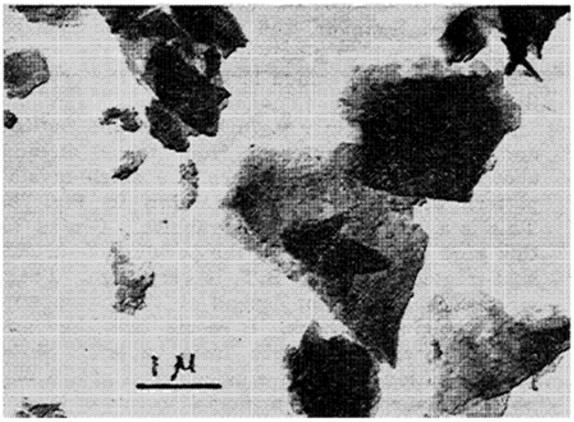


Fig. 2. Electron micrograph of coke grains, (raw state). (shadowed with Ge)

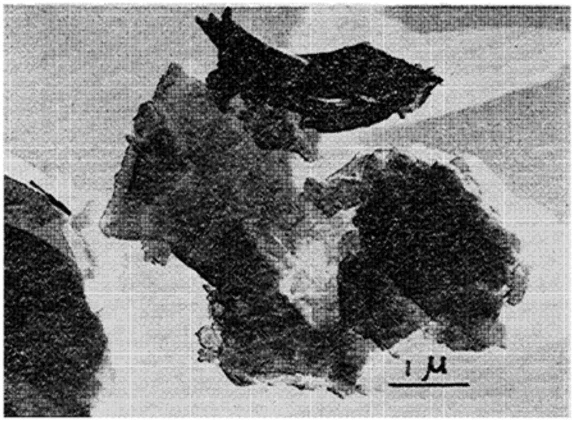
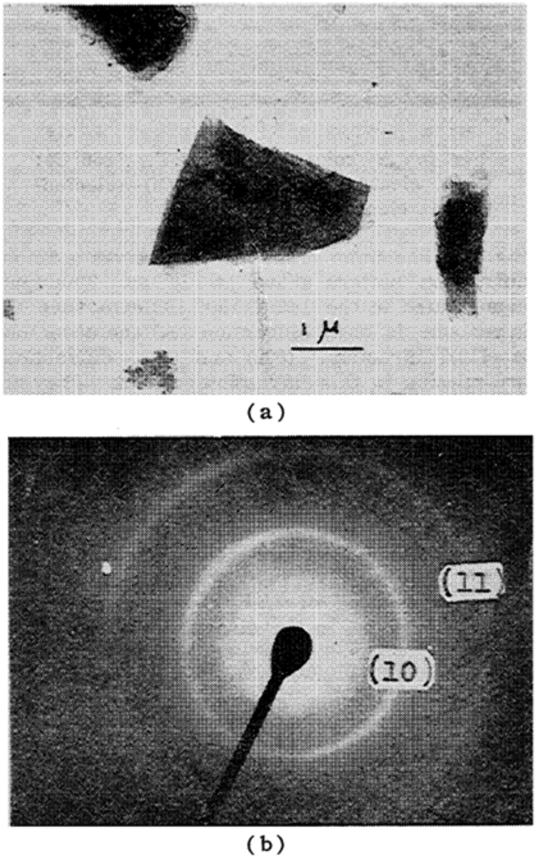


Fig. 3. Electron micrograph of coke grains, (H.T., 2500°C). (shadowed with Ge)

As can be seen in Figs. 3 and 6, in every coke grain are sub-boundaries, which are dividing it into smaller grains.

The electron diffraction pattern corresponding to each grain was studied by the method of selected-area electron diffraction. One of the typical results with the raw coke is given in



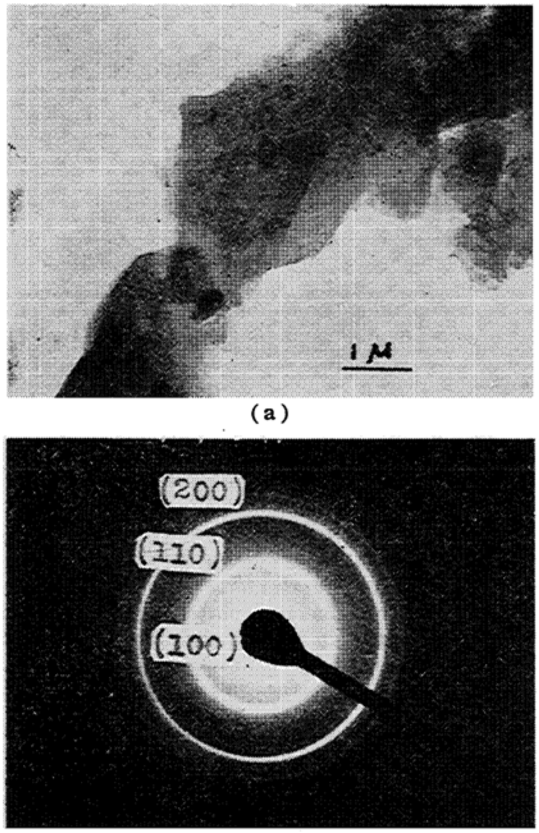
(a)

(b)

Fig. 4. A coke grain, (raw state): (a) electron micrograph, (b) selected-area electron diffraction.

** The temperature of heat-treatment is abbreviated to H. T.

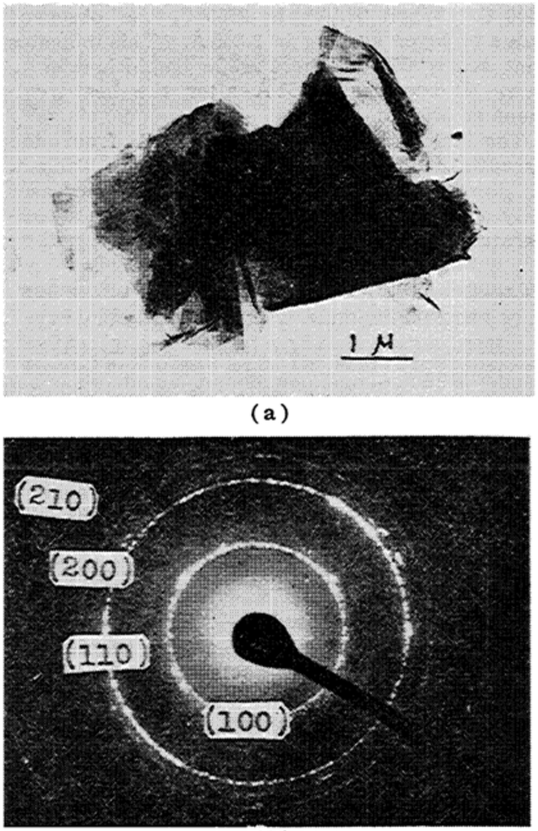
*** Electron microscopic studies were made using Hitachi Electron Microscope, Model 10-A.



(a)

(b)

Fig. 5. A coke grain, (H.T., 1850°C): (a) electron micrograph, (b) selected-area electron diffraction.



(a)

(b)

Fig. 6. A coke grain, (H.T., 3000°C): (a) electron micrograph, (b) selected-area electron diffraction.

Fig. 4. The flaky grain in Fig. 4a gives a diffuse diffraction pattern shown in Fig. 4b. The spacings related to the two halos indicate that the inner one is (100) diffraction and the outer one is (110) diffraction. (002) and (004) diffractions are missing in this diffraction pattern. They are always either missing or very weak in every selected-area electron diffraction pattern of the grain of the raw coke. After heat-treatment, diffraction rings become clear and sharp as seen in Figs. 5 and 6. In both of them, diffraction rings correspond to (100), (110), (200), (210) and (300) diffractions, respectively. Most of the grains give such a polycrystalline diffraction pattern consisting of $(h\,k\,0)$ diffractions alone. c-axis should be in the direction parallel to the incident electron beam, hence parallel to the direction that is normal to the surface of the grains, in order to give such diffraction patterns. Thus each coke grain is a group of many crystallites with a preferential orientation of c-axis. In Fig. 5a diffraction rings have homogeneous intensity distribution in all directions, hence a-axis direction is quite random in the plane of the grain. In Fig. 6b however, diffraction rings split into many spots. Many grains give such a pattern if H.T. is 2500~3000°C. There are some grains which give a diffraction pattern like that of a single crystal. They seem to be a quasi-single crystal. As shown in Table I, the crystallite size along a-axis determined from X-ray diffraction is only 400~500Å, even if H. T. is around 3000°C. From the selected-area diffraction, however, the average dimension of the area, in which a-axis direction is the same, seems to be very much larger than the crystallite size.

A grain shown in Fig. 7a has a round outline and looks quite different from those already shown. Its diffraction pattern is a single-crystal pattern with Kikuchi-lines as shown in Fig. 7b. This is a single crystal of graphite. Grains of this kind can be found in the powders of various heat-treated carbons if H.T. is very high. Their size and shape do not depend on the characters of the original carbons. It seems that they are due to the crystal growth from vapor[3]. Since the formation of such single-crystal grains has no essential role in the principal process of graphtiization, we shall not further discuss it in this paper.

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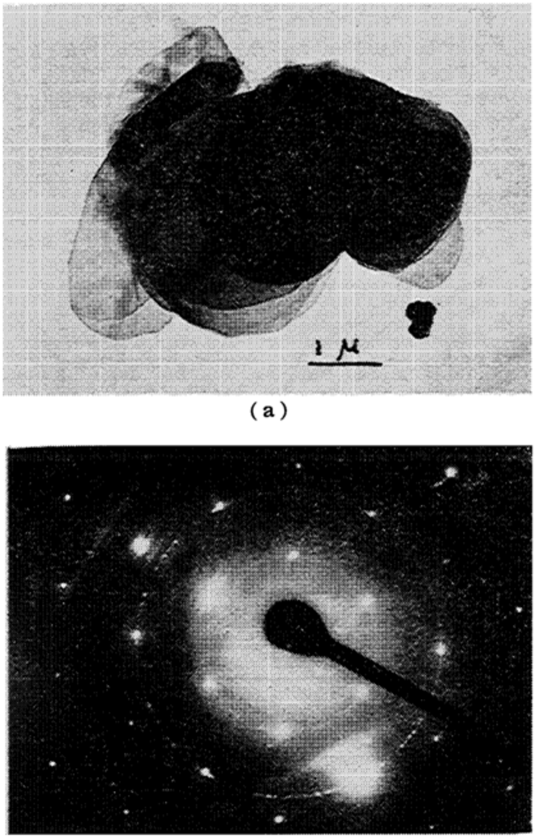
[3] The growth of graphite crystals by the dislocation mechanism was observed and discussed by T. Tsuzuku, *Tanso* (*Carbons*), **5**, 2 (1955); T. Tsuzuku and T. Komoda, *Acta Cryst.*, **9**, 90 (1956).



(a)

(b)

Fig. 7. A single-crystal grain: (a) electron micrograph, (b) selected-area electron diffraction.

Structure of Coke Grains.—If the direction of the incident electron beam is parallel to the texture axis, we can not find any difference between $(h\,k)$ two-dimensional diffraction and $(h\,k\,0)$ diffraction. This is the case in the diffraction patterns shown above. We studied the oblique diffraction pattern of coke grains in order to know their structure.

If coke grains have the textured polycrystalline structure, they should give oblique texture patterns[4]. The reciprocal lattice of non-graphitic structure consists of a series of $(0\,0\,l)$ points along c-axis and $(h\,k)$ lines parallel to it. Hence a grain should give an oblique pattern consisting of continuous ellipses if crystallites in it have non-graphitic structure. As the stacking order of layer lattice is improved, the structure factor has a periodic variation on each $(h\,k)$ line in the reciprocal lattice. Thus the stacking order in the crysallites can be known from the intensity variation on the elliptical pattern in the oblique texture pattern.

Fig. 8 is one of the diffraction patterns obtained with the raw coke. The long arc-patterns are (10) and (11) diffractions and the short ones are (002) and (004) diffractions. It can be seen from this diffraction pattern that the direction of the texture axis, c-axis, has fluctuation around that which is normal to the surface of the grain. Most of the grains in the raw coke give such diffraction patterns. This is the case also in the heat-treated coke if H.T. is low. The fluctuation of c-axis direction decreases as H.T. is raised, and it almost disappears when H.T. is higher than 1850°C. The indication of the improvement of the stacking order, however, is not observed with the grains which have appreciable fluctuation of c-axis direction. The improvement of the crystallite alignment seems to proceed in advance of the change in the stacking order.

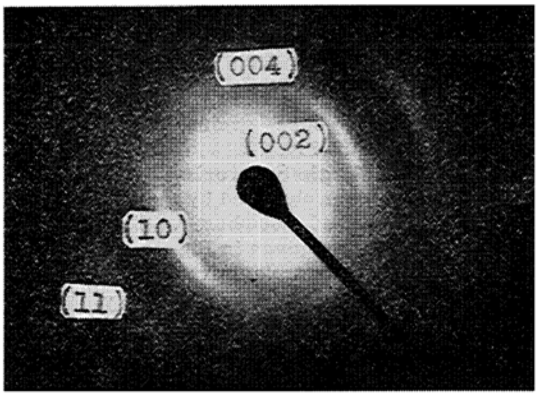


Fig. 8. An oblique pattern of a coke grain, (raw state). The oblique angle is larger than 80°.

In the X-ray diffraction pattern, the modulation of two-dimensional diffraction peak appears when H.T. is around 2000°C. The indication of the change in the stacking order can be observed also in electron microdiffraction from H.T. around 1900°C. One of the typical diffraction patterns corresponding to the earlier stage of graphitization is shown in Fig. 9. As H.T. is raised, the diffraction pattern becomes that of the textured polycrystalline structure of graphite. Some grains

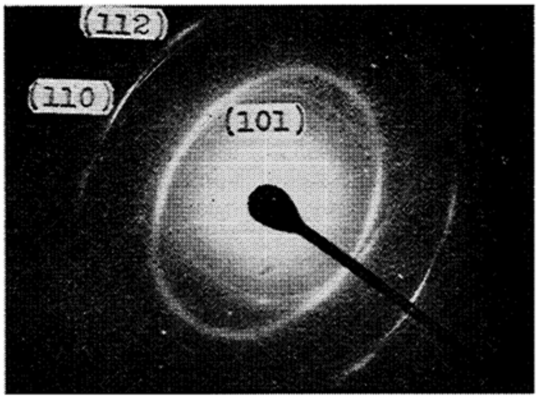


Fig. 9. An oblique pattern of a coke grain, (H.T., 1850°C). The oblique angle is 43°.

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[4] Z. G. Pinsker, "Electron Diffraction", Butterworths Scientific Publications, London (1953), p. 93.

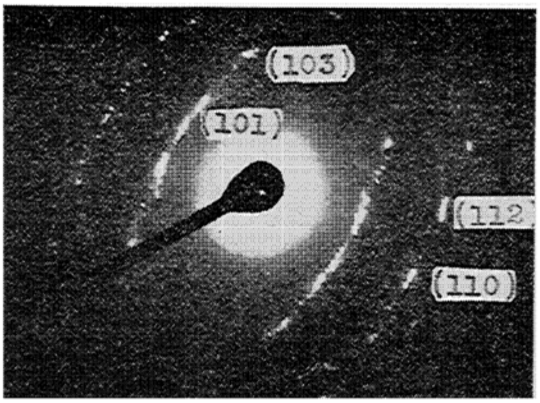

Fig. 10. An oblique pattern of a coke grain, (H.T., 2500°C). The oblique angle is 62°.

give a single crystal pattern. A typical diffraction pattern for coke grains heat-treated at 3000°C is shown in Fig. 10.

X-ray Small-Angle Scattering.—X-ray small-angle scattering was observed by the experimental procedures described elsewhere⁵⁾. The observed intensity curves are given in Fig. 11. The small-angle scattering of petroleum coke is very weak, and, as H.T. is raised, the gradient of the intensity curve becomes very steep. It is difficult to make an accurate measurement when H.T. is high. As can be seen from Fig. 12, the intensity is nearly proportional to $h^{-2.3} \sim h^{-2.5}$ throughout the observed range of scattering angle. Such a relation can not be expected if the system is made up of spherical particles. The result seems to suggest that the structural units responsible for the observed scattering are thin plates.

Kratky and Porod⁶⁾ have derived an approximate formula for the scattering function of a thin disk of thickness $2H$ and diameter $2R$****.

$$\overline{F^2(h)} = (2n^2/h^2R^2)\exp(-h^2H^2/3)$$

This can be used in the range of angle, $1/R < h < 1/H$. When the system consists of thin plates of different sizes and random orientation, the small-angle scattering intensity might be roughly expressed by the following formula at the angle where h is large with respect to $1/\overline{R}$ but small with respect to $1/\overline{H}$.

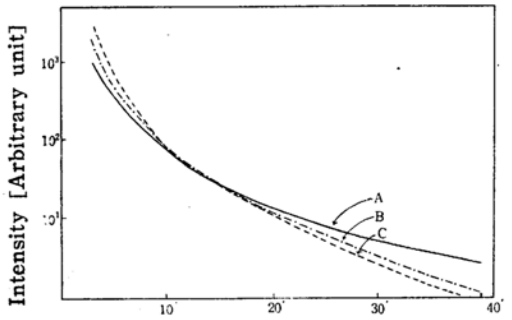

Fig. 11. Intensity curves of X-ray small-angle scattering: (A) raw state, (B) H.T., 1725°C, (C) H.T., 1850°C.

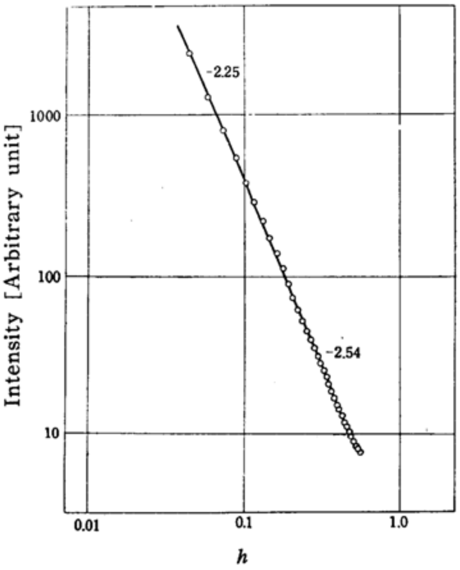

Fig. 12. Plot of $\log I(h)$ versus $\log h$, (raw state). The numbers on the curve indicate the inclination.

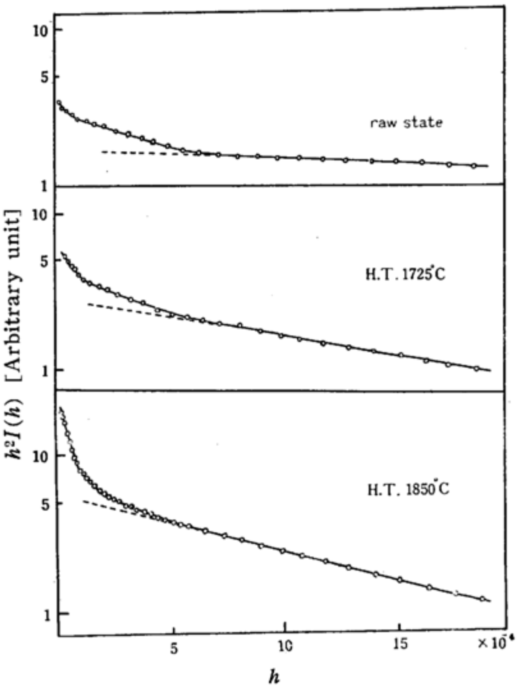

Fig. 13. Plot of $\log h^2I(h)$ versus h^2.

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5) H. Kuroda, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 1298 (1956); *J. Colloid Sci.*, **12**, 496 (1957).

6) O. Kratky and G. Porod, ibid., **4**, 35 (1949).

**** $h=4\pi\sin\theta/\lambda$ and n is the number of electrons in the particle.

$$h^2I(h)=\text{const}\sum M(H_i)H_i\exp(-h^2H_i^2/3)$$

where $M(H_i)$ is the mass-fraction of plates with thickness of $2H$, and $\bar{R}$, $\bar{H}$ are the average value of R and H, respectively.

The curves of $\log h^2I(h)$ versus h^2 are shown in Fig. 13. There is a wide linear part in each curve. The value of $2H$ corresponding to the inclination of this part is given in Table II. They are of the same magnitude with crystallite size.

TABLE II. VALUES OF $2H$

H.T. (°C)	Range of the linear part (h)	Inclination of the linear part	$2H$ (Å)	L_c (Å)
Original	$>7.3\times10^{-4}$	3.48×10^2	49	37
1720	$>5.8\times10^{-4}$	10.72×10^2	86	71
1850	$>5.1\times10^{-4}$	14.51×10^2	100	93

$2H$ was calculated assuming that the inclination is equal to $-0.434H^2/3$.

Although we are not sure whether the structural units responsible for the observed small-angle scattering are the groups of crystallites or the voids between them, the results seem to suggest that petroleum coke has some kind of lamellar units in its structure even in the raw state and after heat-treatment at low temperatures.

Discussion

It has been found that petroleum coke can be disintegrated into minute flaky grains. When H.T. is high, it has been observed that each coke grain is made up of smaller grains or lamellae in which carbon crystallites are aligned so as to make their c-axes normal to the plane of the lamella. When H.T. is low, the lamellar structure can not be seen, but the alignment of crystallites is already not at random, c-axis direction being nearly perpendicular to the surface of grain. X-ray small-angle scattering suggests also the presence of lamellar units in the structure of petroleum coke.

It has been frequently presumed hitherto as the structural model for cokes that carbon crystallites are randomly linked to one another with chain-like molecules in disordered phase. Such a model, however, is not satisfactory for petroleum coke, since it is disintegrated into grains as mentioned above, and it must be made up of lamellar groups of crystallites with the preferential orientation concerning c-axis.

As mentioned already, the textured structure can be found even in the raw coke. It seems to have been formed during the carbonization process. If each crystallite is separated from the neighboring ones by a large amount of disordered phase, it might be difficult to form a large group of crystallites in which c-axis direction is nearly the same. The textured structure will be explained if we presume that there is a comparatively small amount of disordered phase between neighboring crystallites.

It has been known that the disordered phase is made up of mainly aliphatic C–C bonds, C–H bonds, C–O, bonds etc. Since these chemical bonds are thermally unstable compared with aromatic C–C bond, they can be broken at a lower temperature which can not provide a sufficient energy to break up residual bonds of aromatic character. Thus, when H.T. is low, the crystallite growth will proceed solely at the expense of disordered phase. This will cause only a slight increase of crystallite size. This is actually the case as seen in Table I. The crystallite alignment, however, is to be improved well in this stage. At the extreme of the crystallite growth of this mechanism, there should be only a very narrow disordered region or slight structural defects between the neighboring crystallites. The remaining residual bonds might be of aromatic character at this stage. If H.T. is high enough to provide sufficient energy to break them up, the rapid growth will proceed by the condensation of the neighboring crystallites. Actually it starts at a temperature around 2000°C which is known to be a temperature at which the plastic deformation can occur in various carbons. If we presume such a mechanism of crystal growth, the structural change in petroleum coke will be explained well.

In a carbon black particle, c-axis direction of crystallites is considered to be nearly normal to the surface of the particle. When crystallite grows well, a carbon black particle becomes polyhedrone. If the crystallite size increases too much, a stress will be created in the particle. As has been shown in the previous papers, this situation sometimes causes the disintegration of carbon black particle into smaller units. There is no situation like this in the crystallite growth in petroleum coke if it proceeds within each textured polycrystalline group.

The micro-structure pictured in this paper is not to be considered as the special one that can be found only in petroleum coke. The similar structure can be found widely in soft cokes. In hard cokes, the textured polycrystalline group does not exist, or, if it exists, the crystals are of small dimension. The large difference in graphitizability seems to be due to such a situation.

The author wishes to express his thanks to Professor H. Akamatu for his kind direction, and to Dr. H. Takahashi for his valuable advice. He is also indebted to Mr. S. Sakata for his kind help in the experiment.

Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo