Studies on the Graphitization II. Sub-structure and Crystallite Growth of Carbon Black

By Haruo KURODA and Hideo AKAMATU

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The Graphitization is a process of crystallite growth and continuous improvement of the crystal structure of carbon to graphite with heat-treatment. The most powerful method of investigation is the X-ray diffraction by which not only the crystallite growth but also the ordering of crystal structure can be well defined[1].

In the previous paper[2], we have examined the graphitization of several kinds of carbon and found that petroleum-coke as well as coal-tar-coke are well graphitized, but carbon blacks are less graphitized with heat-treatment even in the same conditions. With heat-treatment up to 3000°C, the crystallites grow up to 444Å (L_a) for petroleum-coke and their lattice layers are stacked in graphitic orientation, while for Kosmos Carbon Black, for example, the crystallites grow to only

1) R. E. Franklin, *Acta Cryst.*, **3**, 107 (1950); **4**, 253 (1951); *Proc. Roy. Soc.*, **A209**, 196 (1951).
C. R. Houska and B. E. Warren, *J. Appl. Phys.*, **25**, 1503 (1954).
B. E. Warren, "Proceeding of lst. and 2nd. Conference on Carbon", University of Buffalo, p. 49 (1956).

2) H. Akamatu, H. Inokuchi, H. Takahashi and Y. Matsunaga, This Bulletin, **29**, 574 (1956).

129Å and about 89 per cent of their layers still remains in disordered stacking. The strongest characteristic for carbon blacks is the fact that the crystallite growth does stop. L_a as well as L_c attain to a limited size respectively at about 2500°C, and these values depend on the original particle size of raw carbon blacks. It is widely known that the maximum value of layer diameter, L_a, is about one-third of the original particle size.

The results with both these cases of soft-cokes and carbon blacks, with violanthrone-coke and polyvinyl chloride-coke, show that there is a wide variety in graphitizability, and this should be attributed to the difference in micro-structures or sub-structures of these original cokes or carbons. In this paper, the sub-structures of carbon blacks and their change with heat-treatment will be discussed, from the results of investigation by means of X-ray small-angle scattering and electron microscopy. The sub-structures of soft-cokes will be discussed in the following paper.

Materials and Heat-Treatment.—Three kinds of commercial carbon black were used in the present investigation; Kosmos-15A (LFT, United Carbon Co.), Tokyo Gas Carbon (Tokyo Gas Co.) and Thermax (MT. Thermatomic Co.). The average particle size of Kosmos-15A is 400Å, that of Tokyo Gas Carbon 350Å, and that of Thermax 3000Å. The heat-treatment has been made in vacuo at several temperatures from 1000 to 3000°C. The data for crystallite size, by X-ray diffraction method, are summerized in Table I.

TABLE I
GROWTH OF CRYSTALLITE DIMENSION WITH HEAT-TREATMENT

	Temperature of H.T. (°C)	L_a(Å)	L_c(Å)
Kosmos-15A	original	33.6	15.9
	1570	50.4	19.1
	1750	56.3	27.8
	1960	68.8	34.0
	2500	124	44.6
	3000	129	44.7
Tokyo Gas	original	30.6	13.3
	1350	38.0	15.9
	1750	51.3	24.0
	2040	77.5	32.3
	2500	113	36.6
	3000	118	39.4
Thermax	original	38.5	17.0
	1500	47.5	20.2
	1900	78	73
	2500	326	152
	3000	320	177

The crystallite sizes are similar to one another in these original carbon blacks. This is the case even after being heat-treated below 2000°C. However, after being heated over 2000°C, where generally crystallite growth proceeds rapidly, the crystallite size of Thermax becomes much greater than that of the other blacks. The diffractometer records show that, for Kosmos and Tokyo Gas Carbon, (10) and (11)-diffraction still maintain the wedge-like profiles characteristic of the random orientation of layers even after heated to 3000°C, while for Thermax a remarkable modulation of the diffraction profile can be observed after being heated to 3000°C, and the ordering parameter shows that 50 per cent of layers are in the graphitic orientation.

X-Ray Small-Angle Scattering.—*Experimental.*—A X-ray small-angle scattering camera is designed[3] which consists of collimation system, specimen holder and camera body. The collimation system is made of metal tube with two apertures separated by 500 mm.. Several sizes of aperture are prepared; the smallest one is 0.09 mm. in width and 0.1 mm. in length. Each aperture is fixed on a holder which can be fitted to the collimator tube and is easily exchangeable with others without a rearrangement of setting. Thus we can use a selected pair of apertures. The specimen is packed into a circular cavity of 10 mm. diameter in a flat metal plate of 0.5 mm. thickness, and placed immediately behind the second aperture. The camera body is made of a metal tube with a film cassette at one end. The distance from specimen to film is 549 mm.. A beam stopper is placed in front of the film, the thickness of which is controlled so that the image of the direct beam can be registered faintly on the film. The apparatus is evacuated except for the specimen. Cu-K_α radiation filtered with a nickel foil is used.

About twenty diagrams are usually registered for each specimen, with various exposure times from 5 minutes to 20 hours and with different aperture sizes. Of a microphotometer trace, only a restricted range of the photographic density is used for an intensity curve, so that a linear relation can be assumed between the incident energy of X-rays and the corresponding photographic density. A series of intensity curves for each specimen are combined by graphical matching to a complete scattering angle.

Results.—The results for the heat-treated samples of Kosmos and Tokyo Gas Carbon are shown in Fig. 1 and Fig. 2, where the scattering intensity in logarithmic scale is plotted against the scattering angle.

The geometrical condition of our camera, using filtered X-rays, is not applicable to the correct investigation of a very small angle part. We omitted Thermax, since its particle size is too large and the

3) H. Kuroda, *J. Chem. Soc. Japan Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 1298 (1956).

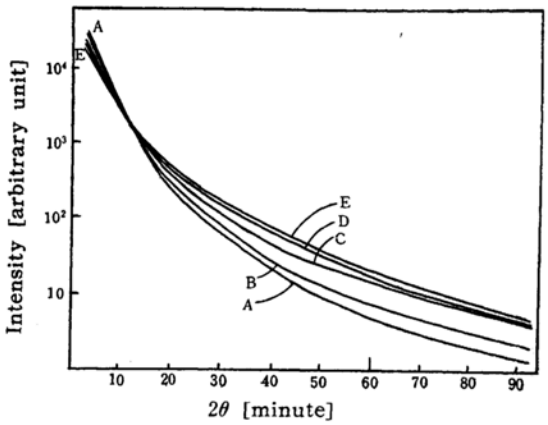


Fig. 1. Intensity curves of small-angle scattering by heat-treated Kosmos-15A Carbon Black.
(A) original, (B) 1325°C, (C) 1570°C, (D) 1950°C, (E) 2500°C.

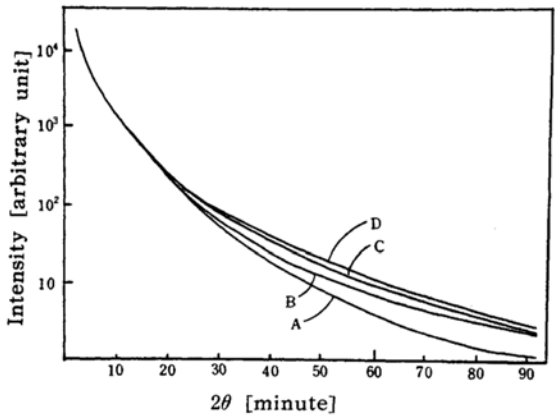


Fig. 2. Intensity curves of small-angle scattering by heat-treated Tokyo Gas Carbon Black.
(A) original, (B) 1350°C, (C) 2100°C, (D) 3000°C.

important part of scattering is presumed to be in such a very small angle part.

It can be seen in Fig. 1 and Fig. 2 that the intensity increases in higher angle part as the heat treatment temperature is higher, while in the lower angle part no remarkable change or slight decrease in intensity is observed. It can be assumed qualitatively that the scattering at a higher angle is due to smaller particles or heterogeneity of smaller dimension, and at lower angle due to larger particles or heterogeneity of larger dimension.

The X-ray small-angle scattering by raw carbon blacks has been discussed in a previous paper[4], where it has been reasonablly interpreted by Porod's theory[5]. According to this theory, a parameter called the distance of heterogeneity, l_c, can be known from the observed intensity curve by means of the following integration,

$$l_c = \pi \int_0^\infty h \cdot I(h) \cdot dh \Big/ \int_0^\infty h^2 \cdot I(h) \cdot dh$$

where $h = 4\pi \sin\theta/\lambda$ at scattering angle of 2θ, with X-ray wave length λ, and $I(h)$ is the intensity at h. There is the following relation between the distance of heterogeneity and the average diameter of particle,

$$D = \frac{4}{3} l_c$$

when the system consists of spherical particles and the inter-particle interference is absent.

It has been revealed that in the case of raw carbon blacks, the average diameter of particles estimated from the above relation is in good agreement with the particle size observed by electron microscope. This is the case also for untreated samples of Kosmos and Tokyo Gas Carbon. Therefore, in raw carbon blacks, the structural unit which is responsible for the greater part of the observed scattering is an individual carbon black particle which is observed directly by electron microscope. In consequence, one can assume that each particle is made of homogeneous material density. This is true, however, in the first approximation. According to the theory, the scattering intensity is expected to be proportional to h^{-4} in the higher angle region, when a system consists of particles of homogeneous density. In the case of raw carbon blacks, the region in which $h^4 I(h)$ is nearly constant is observed as seen on curve a in Fig. 3. However, this is realized only in a limited region below a certain scattering angle, and beyond this angle the intensity deviates from the prediction of the theory. This deviation in the higher angle region is presumablly due to the heterogeneity of electron density in a particle.

The change in the parameter l_c with heat-treated temperature is illustrated in Table II. The value of this parameter decreases as heat treated temperature increases. However, the geometrical significance of this parameter is not so simply

4) H. Kuroda, *J. Colloid Sci.*, **12**, 496 (1957).

5) G. Porod, *Kolloid-Z.*, **124**, 83 (1951); **125**, 51 (1952).

TABLE II
CHANGE IN DISTANCE OF HETEROGENEITY WITH HEAT-TREATMENT.

	Temperature of H.T. (°C)	l_c (Å)
Kosmos-15A	original	289
	1325	281
	1570	243
	1950	230
	2500	215
Tokyo Gas	original	261
	1350	232
	2100	216
	3000	208

interpreted as in the case of raw carbon blacks. The decrease in the size parameter can not be attributed to the shrinkage of carbon black particles, since their shape and size do not change appreciably, by electron microscope, below 2000°C, and so also the density even after being heated up to 3000°C.

In Fig. 3 the plot of $h^4I(h)$ versus h is shown. Although a horizontal part is realized for the untreated sample, the deviation from the constancy of $h^4I(h)$ becomes more and more serious as heat treated temperature is higher. This is presumablly due to the advancement of heterogeneity in a particle. Thus, after being heated, the structure unit responsible for the observed scattering is not the individual particle, but the sub-structures which developed in the particle; the sub-structure made of crystallites which grow in the particle.

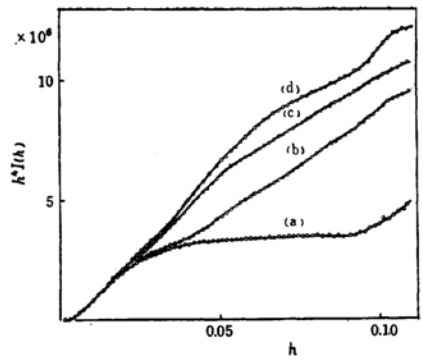


Fig. 3. Plot of $h^4I(h)$ versus h. Tokyo Gas Carbon Black.
(a) original, (b) 1325°C, (c) 2100°C, (d) 3000°C.

The distance of heterogeneity decreases as heat trated temperature is higher, while the crystallite size increases. Thus, at an extreme both these dimensions might approach each other. Neverthless, in reality they do not coincide with each other, since strong interference is likely to be present between crystallites.

In Fig. 4, $\log I(h)$ is plotted against $\log h$. On this curve, the inclination of the curve is illustrated, the value of which is around 2 or 3. This value indicates that the intensity of scattering by heated sample to above 2500°C is nearly proportional to the inverse of the second power of the scattering angle. It can be expected, when a system consists of plate-like particles, that the intensity will be proportional to the inverse of the second power of the scattering angle in a wide

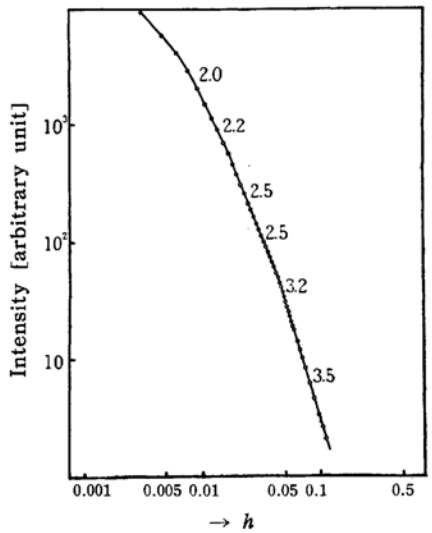


Fig. 4. Log $I(h)$ vs. Log h. Kosmos-15A heat-treated to 2500°C.

range[6]. One can conclude that the most part of the observed scattering for a heated sample above 2500°C is caused by crystallites which have a plate-like shape.

The results from X-ray small-angle scattering leads to the following conclusion. A particle of raw carbon black is made of nearly homogeneous density. With heat-treatment, sub-structures develop to plate-like crystallites; at an extreme, however, the carbon black particle does not grow to a large crystalline unit but splits into smaller crystalline units. These small crystallites are quite independent of each other, as each of them can be the center of scattering, but they are still in aggregation so tightly that interference between them is sure to be strong.

6) A. Guinier and G. Fournet, "Small-Angle Scattering of X-Rays" John Wiley, Chapt. 2, New York (1955).

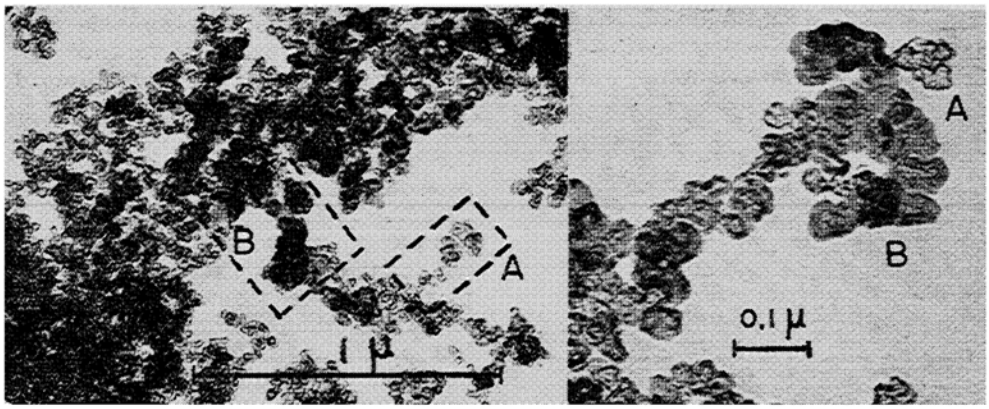


Fig. 5. Electron Micrograph of Tokyo Gas Carbon Black, heated to 3000°C. (Unshadowed).

Electron Microscopic Observation.— *Experimental.* — Electron micrographs were made with Hitachi Electron Microscope, Model-10-A. Special precautions are required to observe the details of structure, with high resolution as well as contrast, of such a minute particle as carbon black. Recently, Sakata[7] in our laboratory has developed a technique of making a collodion grid, whose pore size is one micron or less. This is called micro-grid. One can spread over a micro-grid a very thin collodion film, less than 50A in thickness. The specimen is mounted on this thin film. Thus, the undesirable effects from mounting the film is avoidable to a great extent. Experimental procedures were conducted so as to reduce the effects of contamination[8] to the minimum.

Results.—The electron micrographs show that the appearance of particles does not change appreciably when the heat treated temperature is lower than 2000°C; particles keep their spherical shape, the average size being similar to those of untreated carbon black. Only a slight change of contrast is seen in the inner part of images of particles. However, after being heated up to 2500°C, the particles suddenly show a completely different appearance. This will be seen in Fig. 5. In these figures, one can see two modes of particle shape. Some particles have very irregular contours and are transparent to an electron beam. These are shown in the region lettered A. Other particles have rather round outlines and are less transparent to an electron beam. These can be seen in the region lettered B. The particles of mode-A have plate-like shape with sharp edges. The particle size is nearly 100 A, which is comparable to the crystallite size determined from X-ray diffraction pattern. Each of these minute particles might be a crystallite. The particles of mode-B show a heterogeneity of density; the inner part is more transparent than the peripheral part, which suggests a hollow structure of particle. They consist of minute grains whose size is also comparable to the crystallite size. These facts indicate that a particle of mode-B is a shell-like cluster of crystallites, with a loose packing in the inner part. Such a structure is presumably not different from the structure of heat-treated Thermax. It can be easily presumed that particles of mode-A are produced by disintegration from particles of mode-B.

Thermax is most advantageous for electron microscopic observation, for the particle size is very large. The electron micrographs of heat-treated Thermax have been presented by Ragoss, Hoffman and Holst[9], and by Kmetko[10]. Kmetko has given a polyhedron model of graphitized carbon black particles, based on electron microscopic observation by replica technique. In the present investigation, we used a high accelerating potential, 10 kV, in operating the electron microscope. This gives a clear internal structure of particles. Some typical micrographs are illustrated in Fig. 6, 7 and 8.

Below 1500°C of heat treated temperature, no appreciable change can be seen. However, at this temperature, fine contrast is seen in the images. This fine contrast develops to dark radiated strips along the periphery of particle as heat treated temperature is higher. Finally, above 2500°C, the dark strips grow up to trigonal or trapezoidal dark patterns. The

7) S. Sakata, *J. Electronmicroscopy*, **6**, 75 (1958).
8) J. H. L. Watson, *J. Appl. Phys.*, **18**, 153 (1947).
9) A. Ragoss, U. Hoffman and R. Holst, *Kollod-Z.*, **105**, 118 (1943).
10) E. A. Kmetko, "Proceeding of 1st. and 2nd. Conference on Carbon," University of Buffalo, 21 (1956).

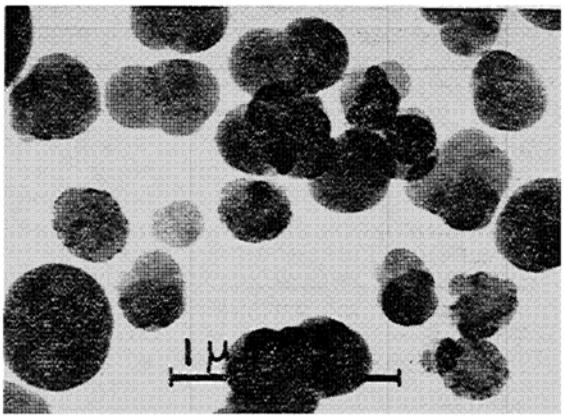


Fig. 6. Thermax heated at 1540°C.

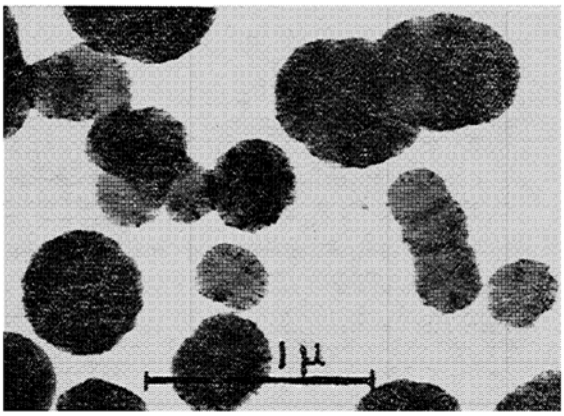
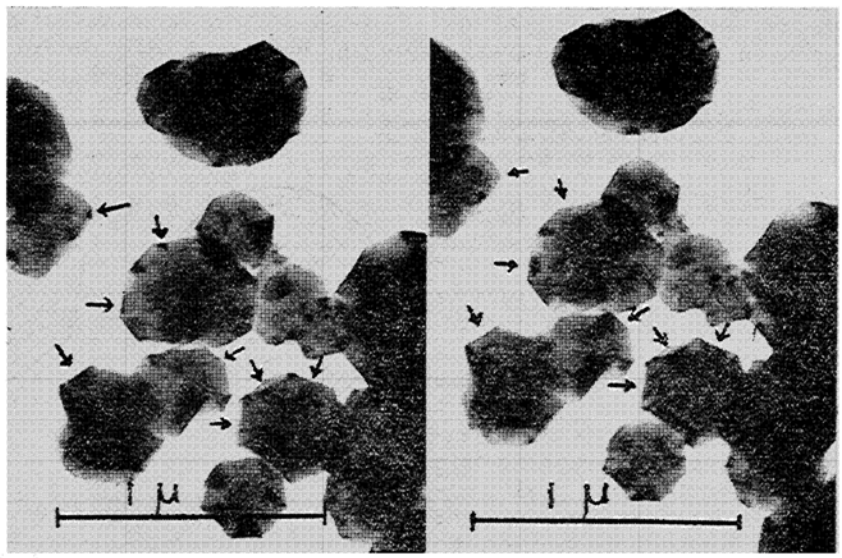


Fig. 7. Thermax heated at 1900°C.

bases of trigons or trapezoids coincide with the edges of the polygonal outlines of the particles. These dark patterns are not due to the difference in thickness of material, but are produced by the diffraction effect. This is illustrated in two micrographs (a) and (b) of Fig. 8. Both the micrographs were made from the same field, but made with different inclination to incident beam by 12°. The dark patterns in each particle change the shape, or disappear, depending sensitively on the direction of incident beam. This is indicated by arrows. It can be easily presumed that these dark patterns are due to (002)-diffractions by the graphite-like crystals. This leads to the conclusion that crystallites are orientated with their c-axes being in the direction normal to the particle surface. The length of edges of the polygonal outlines is in the order of 1000Å, which is only a few times that of L_a-dimension determined by X-ray diffraction. Therefore, the area corresponding to each dark pattern might be a single crystal or a cluster made of a few crystallites with a common direction of their c-axes.

Discussion

Carbon black is deposited from a gas phase in the process of incomplete combustion or thermal decomposition of hydrocarbon gas or vapor. The resulting solid



(a) (b)

Fig. 8. Thermax heated at 3000°C.
(a) and (b) were made from the same field with different directon to incident beam by 12°. The dark patterns in each images are slightly different in (a) and (b).

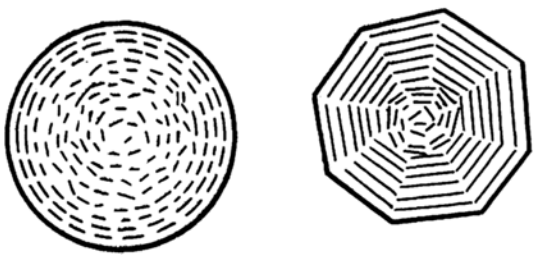
particles consist mainly of turbostratic carbon crystallites. However, the spheroidal shape suggests that the particles are in a fluid-state when they are produced at a higher temperature. The X-ray small-angle scattering by raw carbon black indicates that the material density is nearly homogeneous in the particle. The minute turbostratic crystallites may be imbedded among heavy hydrocarbon molecules or cross-linkages of disorganized carbon atoms. However, alignment of minute crystallites would not be at random, but may be in a preferential orientation. As this is due to the effective action of surface tension, which is responsible for the spheroidal shape, the preferential orientation should be most effectively conducted along the surface of the particle, with the basal planes of crystallites being tangent to the surface. Hall[11] found indications of such a preferential orientation at the surface of a raw carbon black. The schematic diagram of such a model is illustrated in Fig. 9, A.

In the process of heat-treatment, minute crystallites grow by the condensation process at the expense of the disorganized carbon atoms with liberating hydrogen. Meanwhile, the alignment of crystallites will be further improved. The crystallite growth proceeds mainly in such a way in an early stage of heat-treatment, presumablly below 1500°C. The rate of growth is not different between smaller particles and larger ones. No appreciable change can be seen in the particle shape nor size in electron micrographs, excepting a fine structure which can be seen in images of large particles of Thermax, which indicate rather clearly the preferential orientation of crystallites. The X-ray small-angle scattering can reveal the continuous development of heterogeneity which results from the crystallite growth.

When the heat treated temperature is over 2000°C, suddenly the rate of crystallite growth is greatly advanced. This is so, when the particle size is greater, while in small particles the growth attains very rapidly to a limited size. It is widely experienced that the degree of graphitization is primarily dependent on the peak temperature, but less dependent on the time of soaking. The remarkably accelerated rate of crystallite growth at the higher temperature demands an explanation other than the mechangism mentioned above.

At this stage, the condensation process has been completed, leaving slight defects or distortions between neighboring crystallites. As the crystallites are in such an alignment in that their c-axes are in nearly the same direction among neighbors, they can easily be further rearranged with their c-axes in completely the same direction. This leads to the growth of crystallites, not accompanied by mass transfer nor the work of breaking bonds. The intermediate state is a cluster. The rearrangement would be forced thermally to relax the stresses caused from the distortions.

At a temperature higher than 2000°C, a plastic deformation or creep is known for carbons, therefore, the thermal relaxation would be advanced only at a higher temperature. Mrozowski[12] proposed a driving force of the crystallite growth, which is the anisotropic expansion of crystallites along c-axes. This leads to the creation of local stresses which lead to and become relieved by the growth and rearrangement of crystallites. This process, however, would be practically effective if the crystallites are in alignment in such a manner as mentioned above. The crystallite growth would be accelerated along the surface of the particle in preference to the inner part, as the alignment would be found primarily along the surface. This is what we observed. Thus, the polyhedral particle will result from the preferential orientation of crystallites, which developed with their c-axes being in the direction of normal to the surface. The schematic diagram is given in Fig. 9, B.



A B

Fig. 9. Schematic diagram of alignment of crystallites in a carbon black particle. (A) before heat-treatment, (B) after heat-treatment.

11) C. E. Hall, *J. Appl. Phys.*, **19**, 271 (1948).

12) S. Mrozowski, "Proceeding of lst. and 2nd. Conferences on Carbon", University of Buffalo, 31 (1956).

As the crystallite growth proceeds in this way, however, the mutual relation between the neighbors becomes different from the alignment mentioned above. This is easily seen when one compares the diagram (A) with (B). Moreover, great stresses would be stored up between crystallites, especially when the anisotropic expansion of crystallites are made at a higher temperature. We observed, for Tokyo Gas Carbon heated to 3000°C, a remarkably asymmetrical profile of (002)-diffraction, which suggests the presence of a large distorsion in lattice.

In this stage, the scheme proposed by Mrozowski must be modified, but becomes rather more important. When the stresses become too great, they are not likely to be relieved practically and the rearrangements of crystallites are not likely to be realized. There is no place for the energy dissipation within the particle, and this is the characteristic for carbon blacks which differ from soft-cokes. This would be so, as the size or the mass of a particle is smaller. Thus, the limited size of crystallite growth would be proportional to the original particle size. The result which would be expected from the further heattreatment is disintegration or rather bursting into individual crystallites, as this is the only way to relieve the stored stresses. This is the case we observed in the case of the small particles of Kosmos-15A and Tokyo Gas Carbon Black.

As the crystallites grow by the mechanism discussed, the turbostratic structures still remain unimproved. It is believed that the crystallite growth proceeds in advance of ordering of crystal structure. The crystal structure will be improved by the rearrangement of layers as pairs of the nearest neighboring layers take on graphitic orientation. The mechanism would not be far from that discussed above. However, this process begins when the layer diameter, L_a reaches a value of about 150Å. For small particies, the growth of crystallites stops for the reason discussed above, even when less than 150Å. In consequence, the crystal structure can not be improved. This is the reason why one can not make graphitization of carbon blacks with small particle size. A similar argument can be extended to hard carbons. The graphitization is primarily dependent on the sub-structures of raw materials.

Summary

The sub-structures of carbon black and its change with heat-treatment have been investigated by means of X-ray small-angle scattering and electron microscopy.

With heat-treatment, the X-ray small-angle scattering intensity increases in the higher angle region, indicating the development of heterogeneous sub-structures to minute crystallites. Above 2000°C, the crystallite growth is rapidly accelerated, and at an extreme, a carbon black particle disintegrated to smaller crystalline units. Electron microscopic observations, especially for Thermax which has a large particle size, revealed that the crystallites are in alignment with their c-axes being in the direction of normal to the particle surface. This alignment leads to the polyhedral shape of the heat-treated particles. From these observations, the sub-structures and the mechanism of crystallite growth in carbon black particles have been discussed.

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