The Wet Oxidation and the Structure of Carbon

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Introduction

In recent years, the view that the so-called amorphous carbon consists of minute crystallites of graphite has been modified(1) in the strict sense of the word. Most kinds of carbon give the characteristic X-ray powder photographs known as "carbon pattern." This shows that the molecular structure of carbon is made of a layer plane of condensed aromatic rings. However, it is thought that the plane molecules do not arrange themselves in a regular manner as in graphite, namely, it is thought that they are paralleled to each other in layers equally spaced along the *c* axis, but are otherwise disordered along the *a* and *b* axis. Thus, the true three-dimensional atomic lattice as in graphite is not built up in amorphous carbon. Such a structure is called by the term of "turbostratic."

Associating with physico-chemical properties of carbon, measurements of the sizes of their crystallites have been carried out by the X-ray examination. The dimension of the crystallite is the order of 10 ~ 60 Å. along the *a* axis, and 10 ~ 40 Å. along the *c* axis, for most industrial carbon. Now, there remains a problem which must be investigated hereafter;

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(1) U. Hofmann and D. Wilm, *Z. Elektrochem.*, **42**, 504 (1936); A.H. White and L. H. Germer, *J. Chem. Phys.*, **9**, 492 (1941); J. Biscoe and B. E. Warren, *J. Appl. Phys.*, **13**, 364 (1942); H. Akamatu, *J. Chem. Soc. Japan*, **64**, 1251 (1943); H. Akamatu and K. Nagamatsu, *J. Colloid Science*, **2**, 593 (1947).

that is, in what manner do these crystallite micelles aggregate themselves? For the larger part of the properties, by which types of carbon are characterised, is considered to be attributed to those inter-micellar aggregations.

H. L. Riley and his co-workers,⁽²⁾ for example, have carried out a series of experiments on the measurements of the change of dimensions of crystallites by heat treatment of carbon. Their results gave much informations about the inner structure of carbon which can not be expressed merely by the statements of the crystallite sizes. We have also carried out a series of experiments on the wet oxidation of carbon, that is, on the reactivity of carbon for the oxidizing solution, and also followed the changes in dimensions of crystallites under the oxidation process by the X-ray examination.

Reactivity to the Wet Oxidation and the Types of Carbon

Carbon is oxidized to carbon dioxide by the solution of potassium dichromate in phosphoric acid. The velocity of this reaction is very slow at the room temperature, but accelerated by moderate heating. It also varies widely depending upon the kind of carbon. This fact can be used to compare the features of carbon with each other.

The oxidizing solution was made by dissolving 20 g. of potassium dichromate into 100 cc. of phosphoric acidd of which density is 1.75. Each experiment was carried out with 0.03 ~ 0.05 g. of carbon, which had been powdered below 140 mesh, and 7 cc. of the oxidizing solution. A small glass vessel containing the reactants was dipped into a water bath at 100°, and then the volume of carbon dioxide produced was measured by a gas

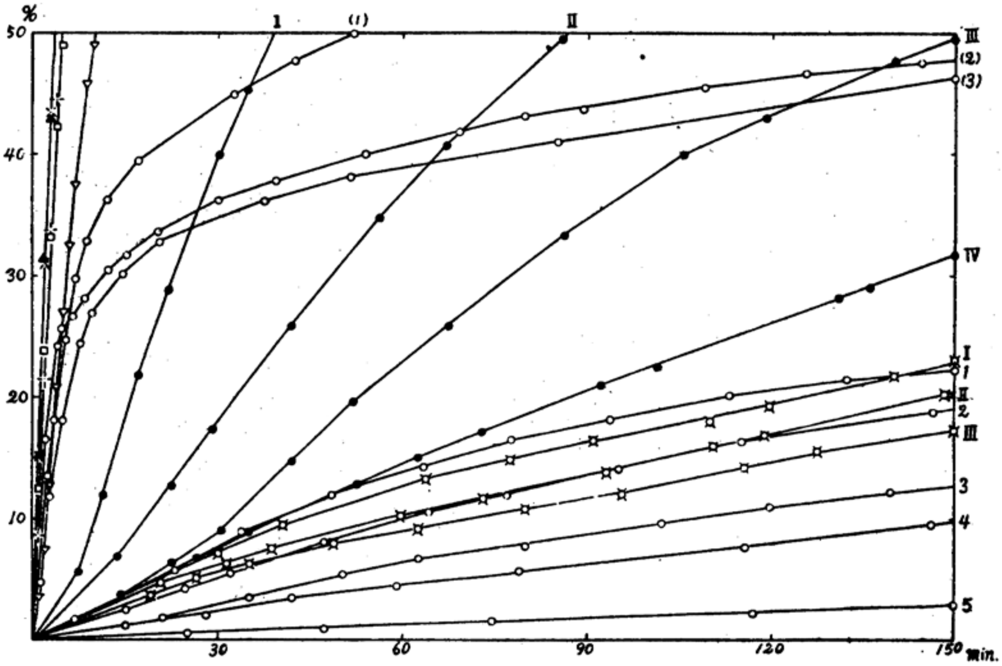

Fig. 1.—The rate of oxidation of various kinds of carbon by the solution of potassium dichromate in phosphoric acid. The fraction of carbon oxidized is shown in percentage against the reaction time in minutes.
Carbon Black: —×—×—, Micronex; —▲—▲—, Tokyo Gas Co.; —□—□—, Nippon Kasei Co.; —+—+—, Nippon Sekiyu Co.; —▽—▽—, acetylene black. Graphite: —●—●—, I, Acheson graphite; II, a natural graphite in Japan; III, flake graphite in Japan; IV, Ceylon graphite. Active carbon: —○—○—, (1), Norit; (2), Active carbon Takeda; (3), Supra-Norit. Pitch coke: —¤—¤—, I, an industrial product in Japan; II, Great Lake; III, an industrial product in Japan. Charcoal: —○—○—, 1, char prepared from filter paper at 390°C.; 2, char prepared from filter paper at 500°C.; 3, wood charcoal; 4, carbonaseous substance prepared from cane sugar and sulfuric acid; 5, carbosaccharose Kahlbaum.

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(2) J. Gibson, M. Holohan and H. L. Riley, *J. Chem. Soc.*, 1946, 456.

burette following the time.

The results are shown in Fig. 1, where the fraction of carbon oxidized are plotted against the time.

The types of carbon which were used in this experiment are as follows. (1) Carbon blacks, containing several kinds of commercial carbon black made in Japan and also "Micronex" made in U. S. A. (2) Active carbons, containing "active carbon Takeda," "Norit" and "Supra-Norit." (3) Charcoals, containing wood charcoal, chars prepared at 390° and 500° from filter paper, and "Carbosaccharose-Kahlbaum." It also contains carbonaseous matter prepared from cane sugar and concentrated sulfuric acid. (4) Pitch cokes, containing commercial products in Japan and U. S. A. (5) Graphites, containing Acheson graphite, Ceylon graphite and two kinds of natural graphite in Japan.

Of all these types of carbon, carbon blacks were oxidized with the highest rate of reaction. Most of them have the same order of the reactivity to the oxidizing solution. The samples of graphite were oxidized with moderate velocities. We can not estimate the crystallite sizes of these samples, because they are all infinitely large under the X-ray scale. However, the curves seem to be arranged in the opposite order of the apparent crystallisation, namely, the velocity of artificial Acheson graphite is the highest and that of Ceylon graphite is the lowest. Between them two kinds of natural graphite in Japan are situated.

The charcoal group has the lowest reactivity to the oxidizing solution, nevertheless the crystallites of these carbons are very small as it is well known. Hence, the fact that they have a large resistance to the wet oxidation, suggests that there must be some important difference in the inner structure between charcoals and carbon blacks. The reactivity of pitch cokes is in the same order as that of charcoals. This suggests that these two kinds of carbon have common characteristics in the inner strucuture.

The curves of active carbons are distinguishable from others by their shapes. At the first part of the reaction, active carbons were oxidized with the velocity as rapidly as carbon blacks were. After 20 ∼ 30 per cent of carbon was oxidized, however, the velocity dropped down to the value of charcoals. These activated carbons must not be different substantially from charcoals in their main structures, but it seems, from these results, that they have certain portions of which strucutre and that of carbon black are alike. This is supposed to be attributed to the process by which these carbons were activated.

H. L. Riley assumed,(3) in his paper, that the resistance of carbon to the oxidizing solution is attributed mainly to the presence of the bonding of hydrogen between the layer planes of crystallites, and that the rate of oxidation will be higher as the species is progressively graphitized. In the series of his experiments, however, data on carbon blacks have not been found.

Our results will be interpreted, at least qualitatively, by the following assumptions. The reaction to carbon dioxide proceeds through the formation of intermediate compounds as graphitic oxide, of which structure has been investigated by U. Hofmann.(4) Hence, the first step of the reaction is the entrance of oxygen atoms between the layer planes of crystallites. This is accompanied by the swelling of the crystallite micelles along *c* axis. An effect, caused by the formation of graphitic oxide and the swelling, can be presumed, by which the aggregations of micelles will be destroyed and crystallites will be dispersed into the solution. In reality, in the case of carbon black and graphite, it was found always that carbon was dispersed into the colloidal state in the process of the wet oxidation. In consequence of the dispersion, the surface area of carbon in contact with the oxidizing solution becomes larger, and it will progressively increase as the carbon is made of smaller crystallites. The order of the rate of oxidation from carbon black to Ceylon graphite will be interpreted by this assumption.

In the case of charcoals and pitch cokes, on the other hand, we could not find any dispersion of carbon into the colloidal solution. The small reactivity of these substances to the oxidizing solution will be attributed to the fact that their crystallite micelles seem to be prevented to dispersion. It is further assumed that this restriction is due to the binding of micelles with some cross-linkages between them. These cross-linkages are supposed to be caused by the residual carbon atoms, or some others, which are not completed to the aromatic condensation under the carbonisation process.

The assumption that carbon black is made of independently mobile micelles as in graphite and that charcoal is made of non-mobile micelles bridged to each other with cross-linkages, seems to be plausible when we

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(3) H. L. Riley, *Trans. Faraday Soc.*, **34**, 1011(1938); Blaydan and H. L. Riley, *J. Soc. Chem. Ind.*, **54**, 159 T (1935).

(4) U. Hofmann, A. Frenzel and E. Csalán, *Ann. Chem.*, **510**, 1(1934).

remember the origin of these kinds of carbon. Carbon black or soot is prepared from substances of low molecular weight through the gas phase, on the other hand, charcoal or pitch coke is prepared in liquid or solid phase, from materials or at least through certain intermediate substances of high molecular weight.

X-ray Examination of the Oxidizing Process

To get further informations, we carried out the X-ray examination of carbon following the process of the wet oxidation. The results support the assumption described in the preceding section. Experimental procedure was as follows.

By controlling the amount of potassium dichromate in the oxidizing solution, it is able to stop the reaction at any desired step of oxidation, before all the amount of carbon is consumed. Thus, after a part of carbon which is equivalent to the amount of potassium dichromate in the solution disappeared, a certain amount of carbon still remains in the solution. This residual part of carbon was used as the specimen of the X-ray examination, after being purified from salts by repeated decantation with water or by dialysis.

X-ray powder photograhps were made by using a cylindrical camera (radius is 50.4 mm.) and copper-K_α radiation filtered by nickel foil. Powder photographs of carbon consist of diffused bands. By measuring the half-peak widths of the diffraction bands, *i. e.* its width at half the peak intensity, it is possible to know the dimensions of the crystallites. The intensities of the patterns have been found for this purpose from the photographic film using a microphotometer. In this case, however, as the blackening on the photographic film is not simply proportional to the X-ray intensity curve. Several devices have been proposed for the means of this correction. The procedure which was devised by us was as follows. The cover of the photographic film was made of three parts side by side in the X-ray camera, the two parts were covered with aluminium foils differing in thickness to each other, in addition with a paper envelope which was commonly used in all three parts. In consequence, a photograph is divided into three parts such as shown in plate 1.

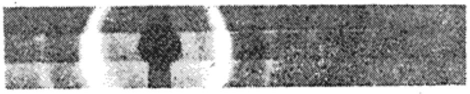

Plate 1.—Powder photograph of pitch coke "Great Lake," 60% oxidized. Photograph is divided into three parts, the intensities at the corresponding points in these parts are in ratio 1:0.625:0.344, theoretically.

From the value of the coefficient of absorption of aluminium, $\mu = 130.3$,(5) and the thickness of the foils used, 0.036 and 0.082 mm. respectively, the relative values of the intensities at the corresponding points in the three parts of a photograph can be known, as in ratio of 1:0.625:0.344. The further procedure is the same as that described by G. P. Thomson,(6) in its principle. The patterns were then microphotometered and groups of densities of the corresponding points on the three parts were tabulated. Each group of densities was plotted with density as ordinate and differences of abscissa equal to log 0.625 and log 0.344 respectively. Each group of points was then shifted parallel to the axis of abscissa until the whole lie on a smooth curve, which gives the relation between the blackening and the logarithm of the relative intensity of X-ray. From this a second curve was drawn giving density against the relative intensity itself. Basing on this curve, the corrected intensity distribution curve was obtained from a microphotometer curve.

For the calculation of the crystallite size from the value of half-peak width (B), the Laue-Brill-Pelzer's formula was used,

$$\eta = 0.0884\left\{B\cos\theta - \frac{1}{B}\left(\frac{\pi r}{R}\right)^2\cos^3\theta\right\}$$

where r and R is the radius of the cylindrical specimen and camera respectively, and θ is half the diffraction angle as defined in the Bragg law. η is a pure number related to the crystallite size by the expression $\eta = \lambda/4\pi ma_t$, where λ is the wave length and ma_t represents the extension of crystallite along the a or c axis in our case. From the (002) diffraction band we can estimate the c-dimension, *i. e.* the average height of layer lattices or of piles of plane molecules, and from the (100) diffraction band, the a-dimension(7) *i. e.* the average diameter of the plane molecules.

In Figs. 2 and 3 the c and a dimensions are shown respectively, plotted against the degree of oxidation which is shown as the fraction of carbon disappeared by the wet oxidation. Each figure shows a process which has been

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(5) E. W. Pike, *J. Appl. Phys.*, **12**, 206 (1941).

(6) G. P. Thomson, *Proc. Roy. Soc.*, **A125**, 352 (1929).

(7) If Warren's formula (*Phys, Rev.*, **49**, 693 (1942), $B = 1.84\lambda/L\cos\theta$ where L is the dimension of crystallite, is used for the calculation of the a-dimension, the value becomes larger than that calculated by L. B. P.'s formula in the amount of about 70~90 percent.

followed by crystallite micelles, when a solid disappeared by a chemical reaction.

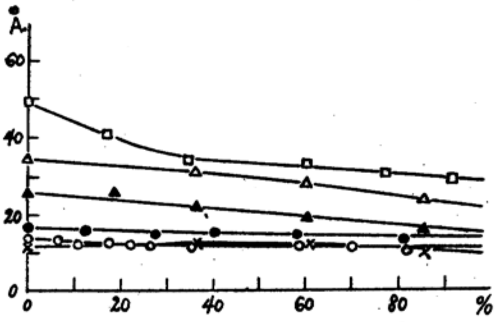

Fig. 2.—The crystallite dimension in Å. along the c-axis is plotted against the fraction of carbon oxidized in percentage.
□, acetylene black; △, pitch coke "Great Lake"; ▲, pitch coke, an industrial product in Japan; ●, carbon black "Miike"; ○, carbon black "Nippon Kasei"; ×, Supra-Norit.

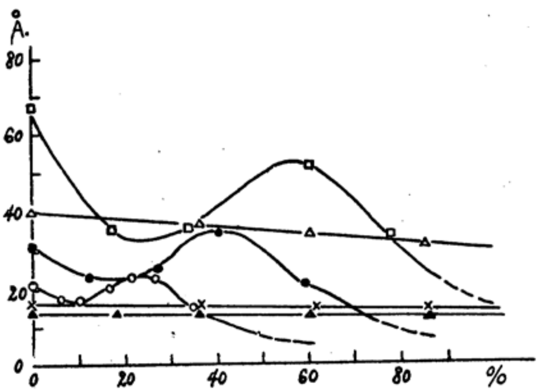

Fig. 3.—The crystallite dimension in Å. along the a-axis is plotted against the fraction of carbon oxidized in percentage. The same symbols as in Fig. 2.

In these figures, changes in the c-dimensions are small all over the degree of oxidation and for all the species of carbon, on the other hand, changes in the a-dimensions are remarkable. Namely, the a-dimension curve of carbon black has a minimum and a maximum. It seems to be a common character of carbon black.

For example, while the first twenty per cent of carbon was lost, the a-dimension of acetylene black decreased from 68 Å. to 35 Å. Such rapid decreasing in the a-dimension will not be expected when we conceive crystallites as small discs and the consumption takes place uniformly along the circumference inward. It is rather logical to assume, from this result, that a disc was split into smaller discs through cracking. Crystallite micelles may contain in their net planes unstable bonds as well as stable bonds. Consequently it is plausible to consider that the reaction proceeds preferentially along weak bonds, and micelles will be split into smaller ones. To interpret the next step, from the minimum to the maximum, it must be remembered that the reaction is an irreversible one, and the growth of crystallite consequently can not be conceived. It must be further remembered that the dimensions measured by the X-ray diffraction method are not other than the average values of the sizes of crystallites, which are even limited to the ordered parts of the micelles, overlooking the disordered parts. The apparent increasing of the a-dimension curve can be attributed to the fact that minute crystallites will be consumed preferentially leaving stable larger micelles behind, in consequence the average values of the dimensions increase. At the maximum point, there remain crystallites with relatively uniform dimensions, and thereafter they are consumed uniformly following the progressive reaction. The results of chemical analysis are shown in Fig. 4. Corresponding to the minimum and the maximum point of the a-dimension curve, there appeared also the minimum and maximum in the oxygen content curve. This supports the above interpretation of the a-dimension curve, because the oxygen content observed can be assumed to be proportional to the total surface of crystallites which can be combined with oxygen.

The behaviors of carbon black can be understood from the assumption that their micelles

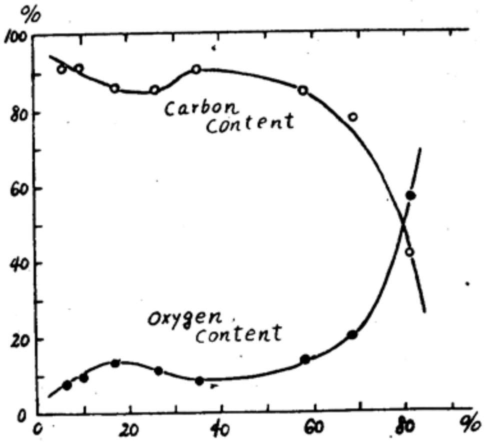

Fig. 4.—Carbon and oxygen content in percentage is plotted against the fraction of carbon oxidized. The sample is carbon black "Nippon Kasei."

are mobile and can be dispersed into the oxidizing solution. Furthermore each micelle can be attacked simultaneously by the oxidizing agent. On the other hand, the a-dimension of pitch-coke and Supra-Norit almostly did not change, even when about eighty percent of carbon had been lost by the reaction. This fact suggests that some micelles at the preferable positions of the total numbers of micelles are consumed preferentially leaving others unchanged, rather than that the total micelles are attacked simultaneously as in the case of carbon black. If the micelles are rigidly bridged with each other to a conglomeration, in which micelles can not move for dispersion and into which the oxidizing solution hardly penetrate, then the micelles being consumed by the reaction are limited to the outer ones of this conglomeration and inner micelles remain unchanged until the outer micelles are completely lost. In consequence, the constancy of the dimensions will be held all over the degree of oxidation.

In Table 1, the observed values of the half-peak widths of (002) and (100) band of Acheson graphite under the process of the wet oxidation are shown. The half-peak widths of the c-dimension increased rapidly rather than that of the a-dimension. This suggests that the crystallites of graphite split along the layer planes into thinner crystallites in the process of the reaction. The values of the spacings did not change through the reaction, until about 80 per cent of carbon was lost, when a new additional band at about 3 Å. appeared. The sample which remained after 99 per cent of carbon had been lost showed a pattern consisting of only two highly diffused halos at the position of 4.1 and 3.5 Å. respectively. This is a kind of amorphous carbon.

Table 1

The Half-peak Widths of (002) and (100) Band of Acheson Graphite, in the Process of the Wet Oxidation

Fraction of oxidized carbon	0%	25%	50%	80%	98%
	mm.	mm.	mm.	mm.	mm.
(002)	1.25	2.55	2.95	3.15	3.6
(100)	1.35	1.55	1.70	1.85	3.1

(Copper K_α-radiation, the radius of the cylindrical sample is 0.6 mm., the radius of the camera is 50.4 mm.)

Summary

The reactivity of various kinds of carbon to the solution of potassium dichromate in phosphoric acid was examined. The samples investigated contained carbon blacks, graphite, pitch cokes, and charcoals. The rate of the reaction varied depending on the types of carbon, and the order of the reactivity was found to be in the order shown above. This is attributed to the modes of aggregation of crystallites. It was assumed that, in carbon blacks the crystallites are mobile individually for dispersing or swelling, on the other hand, in pitch cokes as well as charcoals there are some linkages to bridge the micelles with each other. This is supported by the results of the X-ray examination which was carried out following the steps of the wet oxidation.

In conclusion, the authors wish to express their sincere thanks to Prof. J. Sameshima for his encouragement through the experiment. A part of the cost of this study was defrayed from the grant of the Ministry of Education, to which the authers' thanks are due.

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