The Behavior of Heat-treated Graphitizing Carbons in Wet Oxidation[1]

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The chemical property of carbon may vary considerably according to the nature of the original carbonaceous material and the conditions under which it has been carbonized. Although the problem of the chemical reactivity of solid carbon is very complex, the reactivity of carbon which is free of ash and appreciable amounts of hydrogen and oxygen may be thought to depend mainly on such structural factors as the crystallinity and the state of the condensed system of aromatic carbon.

The wet oxidizability of carbon in a solution of potassium dichromate in phosphoric acid has been studied by Riley et al.[2-5], Akamatu et al.[6], Tamaru[7], and Honda and Hirose[8]. It has been reported by Riley et al.[2-5] that differences in the oxidation rate for various cokes are due largely to differences in graphite content and give a semiquantitative measure of the degree of graphitization. Akamatu et al.[6] have investigated the reactivity of various kinds of carbon in wet oxidation and have concluded that the rate of reaction depends on the type of carbon and on the modes of the aggregation of crystallites.

The relationship between the chemical reactivity of carbon and its structure has been studied only from the standpoint of carbon species of different degrees of graphitization. In order to obtain a general view of that relationship, the wet oxidation of three kinds of graphitizing carbon graphitized by heat treatment is here examined in the solution of potassium dichromate in phosphoric acid.

Experimental

Materials and Heat Treatments.—Petroleum coke (Union Oil Co., U. S. A.), coal coke used as the industrial raw material of calcium carbide (Kinki Cokes Co., Japan) and anthracite (Hongay, Viet-nam). The proximate analysis of these substances and the chemical analysis of ashes are listed in Tables I and II respectively. The specimens were prepared by preheating these substances for 2 hr. at 900°C in a laboratory electric furnace in a nitrogen atmosphere and by then heating them, in vacuo, to the higher temperatures of 1100, 1380, 1660, 1950 and 2250°C. The maximum temperature for each preparation was maintained for 2 hr. Heat treatments at 2600 and 2800°C were also made in the industrial graphitizing furnace for about 15 min. This latter procedure was undertaken in the Nagoya Factory of the Tokai Electrode Manufacturing Company to which our thanks are due. The heat-treated specimens were pulverized and graded for wet oxidation between a 180∼200 tyler mesh sieve. The ashes in the carbon decreased with the rise in temperature, showing 6.4 and 2.0% at 1660°C and 0.3 and 0.04% at 2250°C for coal coke and anthracite respectively.

TABLE I. PROXIMATE ANALYSIS OF CARBONS (%)

	Petroleum coke	Coal coke	Anthracite
Moisture	6.7	1.4	1.8
VM	11.5	2.3	6.6
Ash	0.7	7.9	6.9
Fixed carbon	81.7	88.4	84.7

TABLE II. CHEMICAL ANALYSIS OF ASHES (%)

	Petroleum coke	Coal coke	Anthracite
SiO_2	12.89	49.02	50.83
Fe_2O_3	45.84	13.90	5.43
Al_2O_3	9.63	27.27	37.51
CaO	14.67	5.93	4.37
MgO	2.87	2.65	1.28
P_2O_5	0.20	0.90	—
SO_3	4.86	0.69	0.74
MnO	0.51	—	—
Cr_2O_3	0.51	—	—
NiO	6.83	—	—
TiO_2	0.84	—	—

X-Ray Measurements.—Changes in the interlayer spacing and crystallite growth were observed as a function of the heat treatment temperature. The X-ray diffraction patterns were recorded by an automatic recording X-ray spectrometer (Rigaku Denki Co., Japan) and were calibrated by reference to a standard quartz specimen. As the diffraction

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[1] This investigation was already published partly in *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **63**, 1690 (1960); **65**, 1220 (1962).

[2] H. E. Blayden and H. L. Riley, *J. Soc. Chem. Ind. London*, **54**, 195T (1935).

[3] A. E. Balfour and H. L. Riley, *J. Chem. Soc.*, **1935**, 1723.

[4] A. E. Balfour, H. E. Blayden, A. H. Charter and H. L. Riley, *J. Soc. Chem. Ind. London*, **57**, 1 (1938).

[5] H. L. Riley, *Trans. Faraday Soc.*, **34**, 1011 (1938).

[6] H. Akamatu, R. Takahashi and K. Tamaru, This Bulletin, **24**, 27 (1951).

[7] K. Tamaru, *Kolloid-Z.*, **133**, 97 (1953).

[8] H. Honda and Y. Hirose, *Fuel*, **37**, 323 (1958).

maxima did not directly give the true interlayer spacing in the case of low graphitic carbon, the correction factors given by Ruston were used[9]. These factors were negligibly small for the specimens treated above 2250°C.

The crystallite size was obtained from the broadening of the X-ray diffraction lines according to the procedure described by Klug and Alexander[10]. The crystallite dimension was calculated according to the following equation;

$$L=K\lambda/\beta\cos\theta$$

where L is the average effective dimension of the crystallite in the direction perpendicular to the reflecting plane at the glancing angle θ, λ is the wavelength of the X-ray, K is a shape factor, and β is defined as the half-value breadth. The L_c-dimension, the thickness of the parallel packets of layers, was obtained from the (002) line using $K=0.9$, while the L_a-dimension, the width of the graphite-like layer, was obtained from the (10) band using $K=1.84$, as well as from the (110) lines using $K=0.9+(1.84-0.9)p$ for highly graphitizing specimens[11], where p as defined by Franklin[12] meant the fraction of the amorphous part in graphitic carbon and was given as the following equation; $d_{002}=3.44-0.086(1-p^2)$.

The diffration conditions employed were as follows: The target, copper, filtered by nickel; filament voltage and current, 40 kV. and 15 mamp. respectively; divergent slit 1°; receiving slit 1° and 0.1 mm.; time constant, 4 sec., and scanning speed, 1/4°/min.

Wet Oxidation Procedure. — Carbon is oxidized to carbon dioxide in the solution of potassium dichromate in phosphoric acid. The reactivity of carbon can be known from the quantity of carbon dioxide evolved per unit time or of the carbon decomposed, which is calculated from the quantity of carbon dioxide evolved. The author used the volumetric method, which gives reproducible results.

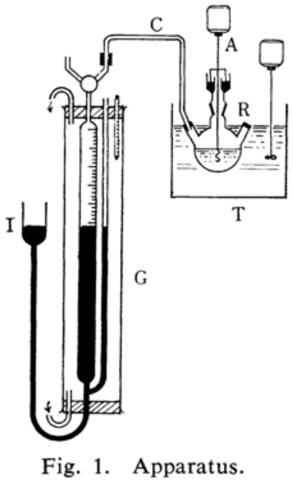

Fig. 1. Apparatus.

The apparatus used in these experiments is shown in Fig. 1. It consists of the temperature-controlled bath, T, a reaction vessel, R, and a gas burette, G. The reaction vessel was a 100 cc. three-necked flask with a mercury-sealed stirrer, S, of the constant speed. The gas burette, 80 cc. in volume, was kept at a constant temperature with flowing water in order to avoid the effect of any change in room temperature. The gas burette was connected to the levelling bulb I, filled with mercury, and to the reaction vessel with a glass capillary tube, C. The bath temperature was measured with a mercury thermometer and was maintained at a desired value within 0.1°C by the aid of an automatic temperature controller, although this is not shown in the figure.

The experimental procedure was as follows: 1 g. of the sample was added to the reaction flask already containing 10 g. of potassium dichromate (G. R. Grade, Wako Chemicals Co.) and 50 cc. of concentrated phosphoric acid (d 1.70 g./cc.; E. P. Grade, Wako Chemicals Co.). While the water bath was being heated to the desired temperature, the three-way cock of the gas burette was opened to the air. When the vessel was dipped in the bath, the meniscus was adjusted to the zero mark of the burette and the stopcock was closed. The volume of gas evolved was measured with the burette as a function of time. It was found, by means of gas chromatography analysis, that all the gas evolved was carbon dioxide. The volume of gas was converted to the value in the standard state. Fifty cubic centimeters of carbon dioxide (N. T. P.) is equivalent to 2.68% of consumed carbon. The reaction temperatures were 62, 67, 73, 79, 85 and 89°C.

Results and Discussion

Graphitization.—The graphitization states of the specimens heated at several temperatures from 1100 to 2800°C were determined by means of the X-ray diffractometer.

The interlayer spacings obtained from the (002) line are plotted against the temperature of heat treatment in Fig. 2. The crystallite sizes determined from the breadth of the diffraction patterns of the (002) line and the (10) band or the (110) line are given against the heating temperature in Figs. 3 and 4. It has been found that the developement of crystallinity by heat treatment varies among different carbon species. The growth of crystallite proceeds with the most facility in petroleum coke. No remarkable difference, however, could be found between these three materials in the general features of graphitization.

Wet Oxidation. — The results for petroleum coke and anthracite at 85°C are shown in Figs. 5 and 6 respectively, where the gas evolved is plotted as a function of time. In Fig. 5, all the curves of the gas evolved vs. time are

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[9] W. R. Ruston, ibid., 31, 52 (1953).

[10] H. P. Klug and L. E. Alexander, "X-ray Diffraction Procedure", John Wiley, New York (1954), p. 491.

[11] H. Akamatu, H. Inokuchi, H. Takahashi and Y. Matsunaga, This Bulletin, 29, 574 (1956).

[12] R. E. Franklin, *Acta Cryst.*, 4, 253 (1951).

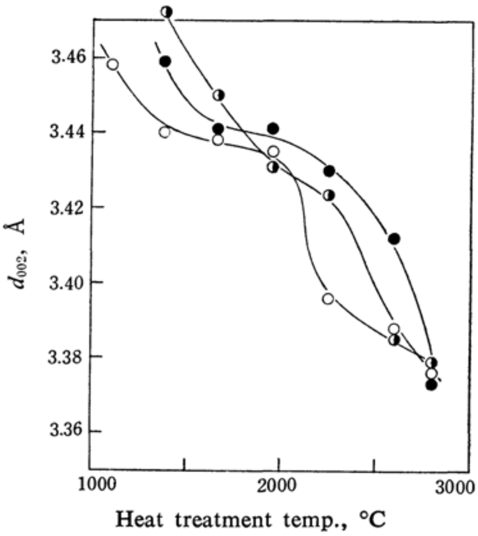

Fig. 2. Interlayer spacing of carbons as a function of the heat treatment temperature.

○ Petroleum coke ● Coal coke
◑ Anthracite

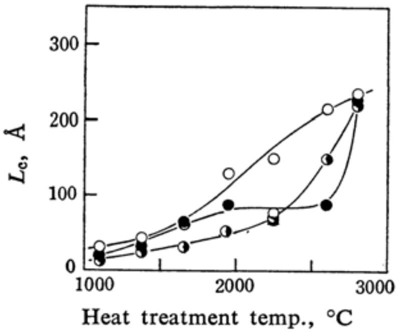

Fig. 3. L_c-Dimension vs. heat treatment temperature.

○ Petroleum coke ● Coal coke
◑ Anthracite

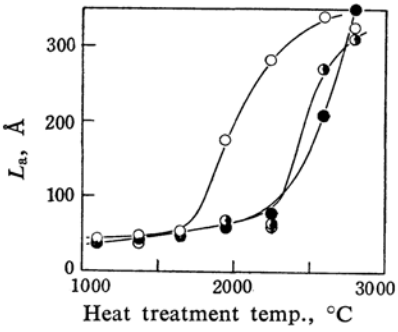

Fig. 4. L_a-Dimension vs. heat treatment temperature.

○ Petroleum coke ● Coal coke
◑ Anthracite

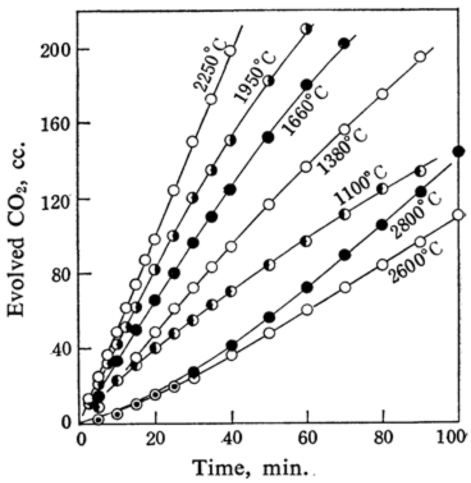

Fig. 5. Oxidation curve of petroleum coke at 85°C.

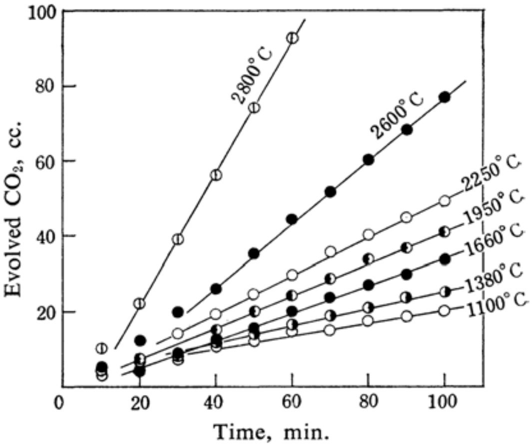

Fig. 6. Oxidation curve of anthracite at 85°C.

seemingly linear; however, the oxidation velocity for the petroleum cokes heat-treated below 1950°C decreased as the oxidation proceeded, while that for the specimens heat-treated above 2600°C increased with time.

These curves may be roughly classified into the following three types according to the heat treatment temperature:

(1) The oxidation rate decreases as the reaction proceeds for the specimens heat-treated below 1950°C.

(2) The rate is almost constant during the whole course of the reaction for the specimens heat-treated near 2250°C.

(3) The rate increases as the oxidation proceeds for the specimens heat-treated above 2600°C.

To examine whether these phenomena are expressed by a quantitative measure, all the curves in Fig. 5 are replotted in the logarithm

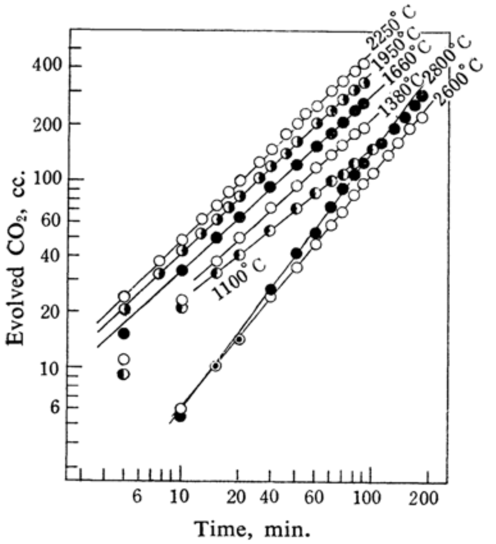

Fig. 7. Evolved carbon dioxide vs. reaction time.

scale in Fig. 7. The logarithm of the quantity of carbon dioxide evolved, *V*, becomes linear with that of time, *t*, and is expressed as the following equation at any reaction temperature:

$$V=at^b$$

where *a* and *b* are constant. The *b*-value depends on only the heat treatment temperature. Moreover, that value does not depend on the oxidation temperature; e. g., the values for petroleum coke treated at 2600°C were 1.49, 1.39, 1.43, 1.44 and 1.44 at the oxidation temperatures of 62, 67, 73, 79 and 85°C respectively.

As is shown in Fig. 6, the curves of carbon dioxide evolved vs. the time for anthracite were more linear than those for petroleum coke. The quantity of the gas evolved per unit time for anthracite and coal coke was much less than that for petroleum coke; therefore, the curve of three types. i. e., $b<1$, $b=1$ and $b>1$ in $V=at^b$, is not explicitly shown in Fig. 6 as in the case of petroleum coke in Fig. 5. Anthracite and coal coke heat-treated at 2250°C and below were oxidized at 100°C in order to obtain the *b*-value. The *b*-values for anthracite and coal coke heat-treated at 2600 and 2800°C were the average values at the reaction temperatures from 65 to 89°C.

The *b*-values for three kinds of carbon are plotted as a function of the interlayer spacing in Fig. 8. It is interesting that these *b*-values of all specimens compose one curve which increases monotonically as graphitization proceeds.

The oxidation velocity was obtained as follows: the reaction velocity for petroleum coke was measured from the time which it took for initial 50 cc. of carbon dioxide to evolve; for anthracite and coal coke, this was decided from the slope of each straight line which related the carbon dioxide evolved and the reaction time. The curve of the gas evolved vs. the time was apparently linear when the less reactive carbons such as anthracite and coal coke were oxidized.

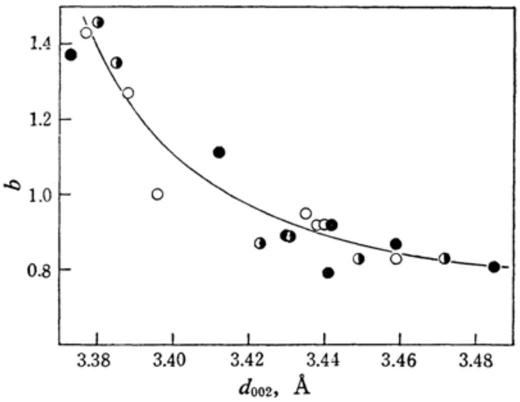

Fig. 8. *b*-Value vs. interlayer spacing.
○ Petroleum coke ● Coal coke
◑ Anthracite

The reaction velocities at 85°C of three heat-treated carbon are plotted against the interlayer spacing in Fig. 9. Of the three, petroleum coke was oxidized with the highest rate; the reactivity of coal coke was of the same order as that of anthracite. The velocity for petroleum coke heat-treated at 2600 and 2800°C was smaller than that heat-treated below 2250°C, but the reason can not be

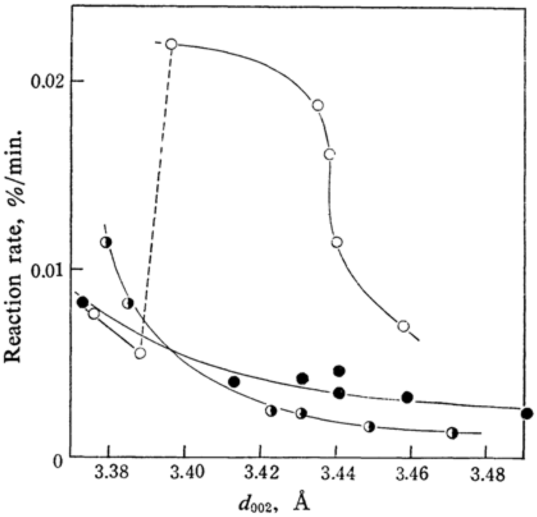

Fig. 9. Reaction velocity at 85°C vs. interlayer spacing.
○ Petroleum coke ● Coal coke
◑ Anthracite

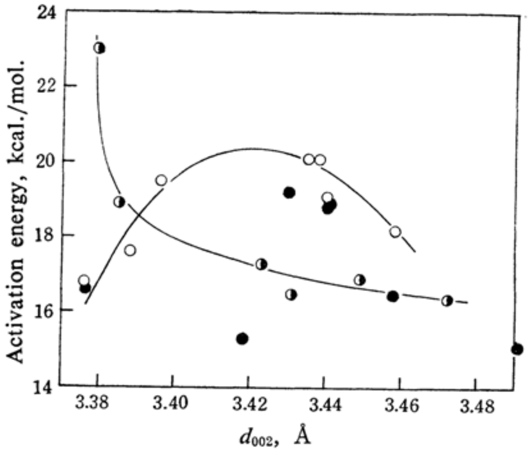

Fig. 10. Activation energy in wet oxidation vs. interlayer spacing.
○ Petroleum coke ● Coal coke
◑ Anthracite

understood from only the standpoint of the graphitization.

The activation energy obtained from the Arrhenius plot is shown as a function of the interlayer distance in Fig. 10. The standard deviation of activation energy for the three carbons obtained from the method of least squares was 0.7 kcal./mol. at most, although this is not shown in the figure. The activation energy for anthracite increased monotonically with the decrease of d_{002}, but for petroleum coke and coal coke there was a maximum at about 3.42 Å of the interlayer spacing. The different behavior of the activation energy mentioned above seems to come from the nature of the original carbonaceous materials.

It has been reported that petroleum coke, anthracite and coal coke are non-graphitic graphitizing carbons. These carbons graphitize easily upon heat treatment. The difference of the graphitization between petroleum coke and anthracite and coal coke seems to be attributable to the original carbonaceous materials. As is shown in Fig. 2, of the three specimens, the graphitization of these carbons proceeds with the most facility in petroleum coke. The structure of anthracite is seemingly similar to that of coal coke, although anthracite has been carbonized naturally.

The difference in structure between petroleum coke and anthracite and coal coke appears in the wet oxidation, as is shown in Fig. 9. As far as our experiments show, the oxidation velocity of the carbon graphitized increases toward graphite. Of the three kinds of carbon, the dioxidation velocity of petroleum coke is five times as large as that of the other, and coal coke is of the same order as anthracite in oxidation velocity.

As has been mentioned above, the behavior of the oxidation velocity of three different types of carbon in accordance with the reaction time has been classified. For non-graphitizing carbon of d_{002} 3.44 Å, the oxidation velocity decreases as the reaction proceeds.

As for the graphitic carbon of d_{002} 3.44 Å, the oxidation velocity, which increases with the degree of graphitization, has a tendency to increase as the reaction proceeds. The reason for the increase in the reaction velocity may be thought to be that the carbon heat-treated disperses into the colloidal state in the process of the wet oxidation and that its surface area in contact with the oxidizing solution increases progressively. It seems that the increase in the surface area is closely connected with the rigidity of the cross-linkage bridged between crystallites. Moreover, the linkage between them weakens as the graphitization proceeds.

It is considered that the b-value, which is a unique function of the degree of graphitization, as is shown in Fig. 8, becomes one measure of the rigidity of the crystallite linkage. Akamatu et al.6) have found that such carbons as carbon black and graphitic carbon disperse into the colloidal state during the wet oxidation, whereas no colloidal dispersion occurs in the case of charcoal and pitch coke. It is shown that their conclusion is in good agreement with our experimental results given in Fig. 8.

Summary

The wet oxidation of three kinds of heat-treated graphitizing carbons, petroleum coke, anthracite and coal coke, in a solution of potassium dichromate in phosphoric acid has been studied in order to clarify the relationship between the chemical reactivity and the carbon structure.

Changes in the interlayer spacing and crystallite size, which are used as a measure of graphitization, have been examined by X-ray diffraction method for each specimen over the range of heat treatment temperatures from 1100 to 2800°C.

The oxidation velocity increases with the degree of graphitization. The quantity of carbon dioxide evolved, V, is generally expressed by the following equation, $V=at^b$. The b-value depends on only the degree of graphitization and varies from 0.8 to 1.5 according to the increase of graphitization, but it does not depend on the oxidation temperatures.

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