Changes of the Lattice Constants and Crystallite Sizes of Various Types of Carbons with Heat Treatment

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Measurements of the lattice constants and crystallite sizes of a number of raw carbon materials, heat-treated at various temperatures, have been carried out by many investigators. However, in most of the investigations, the heat treatments were made in a vacuum or in an inert atmosphere, such as of nitrogen or argon, using laboratory-type furnaces. On the other hand, the present authors thought it necessary to study the effect of the atmosphere of heat treatment on the graphitization of carbon, because it had previously been reported that carbon was only with difficulty graphitized in a vacuum[1,2]. For the present work, several kinds of raw carbon materials were heat-treated at temperatures between 1500 and 3400°C in a resistance furnace under atmospheric pressure. The lattice constants and crystallite sizes of these carbons were measured by means of the X-ray diffraction method in order to investigate their changes with heat treatment. The heterogeneity of the inter-layer spacing in a parallel layer group and the relation between the crystallite size and the particle size of carbon black will also be discussed.

Experimental

Heat Treatment of Raw Carbon Materials.—The raw carbon materials used in the present work are shown in Table I, together with technical analysis data of these materials. Each of the raw carbon materials was placed in a graphite crucible and heat-treated in a carbon granular-resistance furnace of a type similar to the industrial graphitizing furnace. The temperature of the crucible was measured with an optical pyrometer focusing through a graphite tube. Because it was difficult to keep the heating temperature constant during the heat treatment, the arithmetical mean of the temperature, t_{20}, at which the crucible was kept for 20 min. and the highest temperature, t_h, in the run was taken as the temperature of the heat treatment, t_m, as is illustrated in Fig. 1. The calibration of the scale of the optical pyrometer and the correction for the absorption by the window glass of the sighting pipe were made by using a standard lamp for the optical pyrometery.

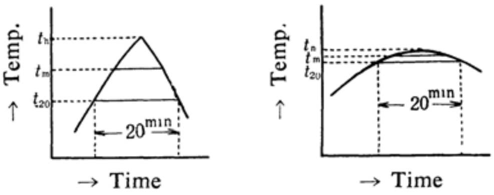

Fig. 1. Scheme of determination of heat treatment temperature.

X-Ray Diffraction Analysis.—Each sample was pulverized to pass through a 150-mesh sieve and mixed with an extra-pure silicon powder as an inner standard to the amount of 10%. The particle sizes of the standard silicon powder used were from about 20 to 40 μ, and its lattice constant, a_0, was measured as 5.4310 ± 0.0004 Å. For X-ray diffraction analysis, a recording diffractometer and CuK_α

TABLE I. TECHNICAL ANALYSIS DATA OF RAW CARBON MATERIALS

Sample	Moisture %	Volatile matter %	Vanadium p. p. m.	Free carbon %	Ash %	Sulfur %	Apparent density g./cm³	Powder resistance Ω·cm.
Petroleum coke	0.13	0.52	278	99.03	0.32	1.54	2.043	0.128
Pitch coke	0.13	0.19	20	99.43	0.25	0.45	2.009	0.218
Thermal black	0.15	1.72	12	97.26	0.87	0.186	1.895	0.911
Lamp black								
Furnace black A	0.87	1.88	13	97.07	0.18	0.686	1.822	0.452
Furnace black B	0.30	2.13	13	97.45	0.12	0.766	1.854	0.311
Channel black	2.38	4.65	11	97.96	0.14	0.339	1.790	0.325
Acetylene black	0.47	1.43	11	92.85	0.12	0.783	1.740	3.137
Charcoal	2.33	13.77	10	82.94	0.96	0.186	1.414	—

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radiation were used. All the profiles of the (422) and (331) diffractions, and some profiles of the (311) diffraction, of standard silicon, were graphically separated into the α_1 and α_2 profiles by means of the Rachinger method[3], the α_1 profiles were used for the present measurements. The lattice constant, c_o, and the thickness of the graphite crystallite along the c-axis, L_c, were obtained from the (002) and (004) diffractions of carbon, the lattice constant, a_o, and the width of the crystallite along the a-axis, L_a, from the (110) diffraction, and the spacing, d_{112}, and size of three-dimensional crystallite, L_{112}, from the (112) diffraction. The crystallite sizes were calculated from half-maximum breadths of the diffraction profiles[4]. The profile of the (002) diffraction was corrected for various intensity factors, such as the Lorentz-polarization factor, the absorption factor and the square of the atomic scattering factor, by using a method similar to Ruston's[5].

Results and Discussion

Changes of Lattice Constants and Crystallite Sizes with Heat Treatment.—The lattice constant, c_o, and the crystallite sizes, L_c, L_a and L_{112}, of the samples are shown as a function of the temperature of heat treatment in Fig. 2. The c_o and L_c values of all raw carbon materials changed very slightly at temperatures above 2500°C, apparently approaching a finite value. The c_o values of a petroleum coke and a pitch coke, i. e., the so-called graphitizing carbons, were not less than 6.718 Å, even when they were heat-treated up to 3400°C. According to Walker and Imperial, the c_o values of four carbons heat-treated at about 3600°C under a pressure of 10 atm. of argon were not less than 6.714 Å[6]. The same c_o value as of natural graphite, 6.708 Å, was obtained only when carbon was melted[7]. From the results of our experiment and of the reported experiments, it can be concluded that the graphitizability of carbon is affected by the original texture of the carbon—crystallite arrangement, pore distribution, criss-cross linkage between crystallites, etc.—even at such a high temperature as 3600°C, in the same way as at 3000°C or below.

In carbon blacks heat-treated at 3400°C, i. e., a thermal black, a lamp black, two furnace blacks, a channel black and an acetylene black, the c_o values were 6.77, 6.76, 6.81, 6.83, 6.85 and 6.82 Å, and the L_c values obtained from the (002) diffractions, were 220, 190, 110, 89, 64 and 91 Å respectively. The particle sizes of these carbon blacks were about 3000, 5000, 500, 350, 300 and 300 Å respectively. These experimental results revealed that the c_0 value became smaller and the L_c value larger with the increase in the particle size of carbon black. Therefore, it can be said that the degree of graphitization of carbon black depends on its particle size. This is very interesting in regard to the mechanism of crystal growth in a particle of carbon black. This subject will be discussed below in more detail.

The a_o value increased with the increase in the temperature of heat treatment, approaching the a_o value of natural graphite, 2.461 Å. The a_o values of the cokes heat-treated at temperatures above 2400°C and the values of the thermal black and the lamp black heat-treated above 3000°C were 2.461 Å, but the values of other carbon blacks did not increase over 2.456 Å even when they were heat-treated up to 3400°C.

The value of spacing, d_{112}, was always 1.156 Å, independent of the temperature of heat treatment. The modulation of the (11) diffraction profile, which reveals the appearance of a three-dimensional (112) diffraction, was observed in the cokes heat-treated at temperatures above 1800°C, the L_a values of the cokes being larger than 100 Å. This experimental finding coincides with Warren's observation[8]. In the thermal black and the lamp black, the (112) diffraction was observed when the L_a value was more than 150~200 Å. In all the other carbon blacks, however, no (112) diffraction could be observed.

Heterogeneity of Interlayer Spacing in Crystallite.—Usually, the L_c value obtained from the (002) diffraction of a carbon, $L_{c(002)}$, is larger than that from the (004) diffraction of the same carbon, $L_{c(004)}$. The broadening of the (002) or (004) diffraction profile may be caused not only by the smallness of the crystallite but also by the heterogeneity of the interlayer spacing. The interlayer spacing of the turbostratic structure is said to be 3.44 Å and that of graphite structure, 3.354 Å, so the broadening for the (004) diffraction due to the heterogeneity of the spacing is twice as large as that for the (002) diffraction. The broadening due to the smallness of the crystallite should be the same for both the (002) and (004) diffractions, provided that the diffraction angle is taken into consideration. As the crystallite size is calculated from the observed broadening, the above discrepancy between $L_{c(002)}$ and $L_{c(004)}$ must be caused mainly by the heterogeneity of the spacing. If we put $\{L_{c(002)}-L_{c(004)}\}/L_{c(002)}$ as $\Delta L/L$, the

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[5] W. R. Ruston, *Fuel*, **32**, 53 (1953).

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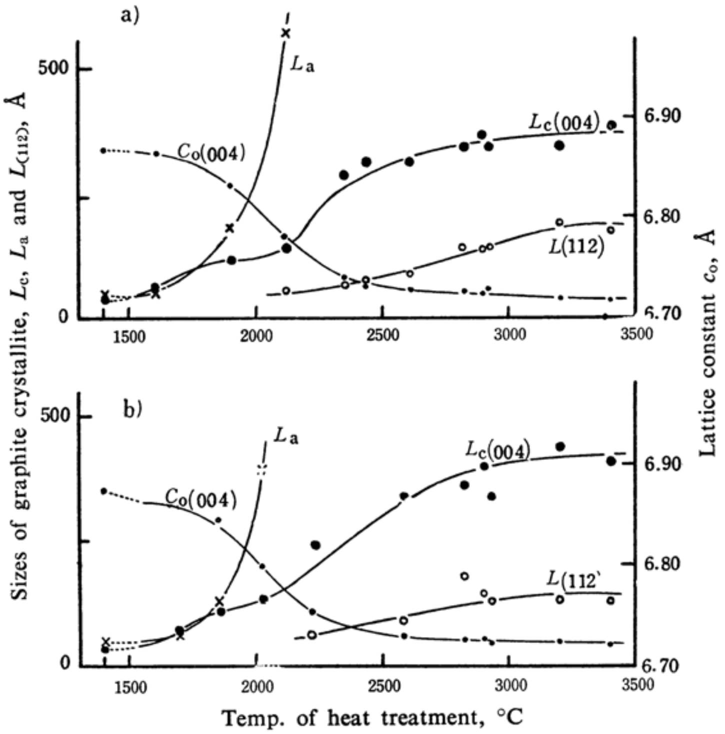
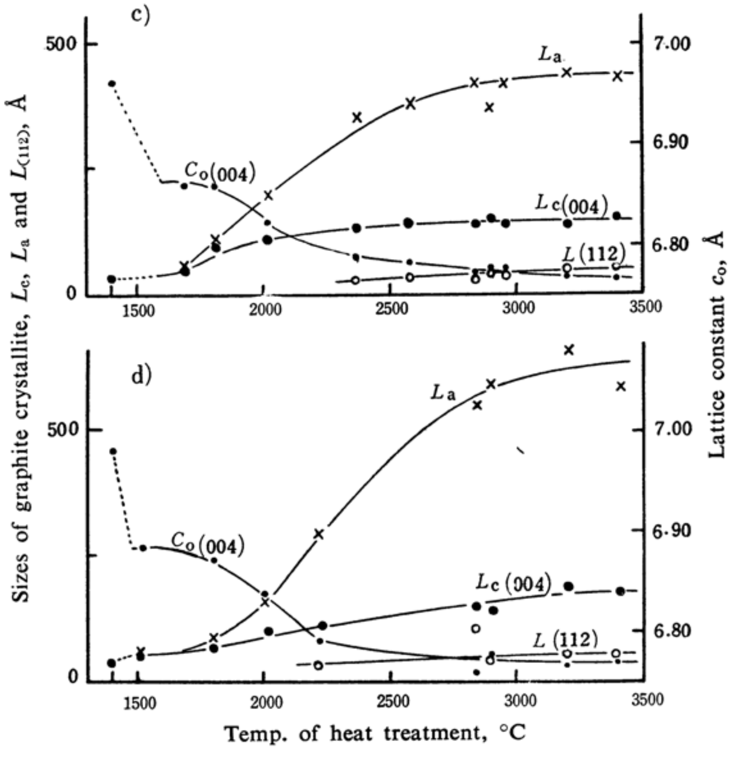

a)
L_a
$L_c(004)$
$C_o(004)$
$L(112)$
500
0
1500
2000
2500
3000
3500
6.90
6.80
6.70
b)
L_a
$L_c(004)$
$C_o(004)$
$L(112)$
500
0
1500
2000
2500
3000
3500
6.90
6.80
6.70
Sizes of graphite crystallite, L_c, L_a and $L_{(112)}$, Å
Lattice constant c_o, Å
Temp. of heat treatment, °C


c)
L_a
$C_o(004)$
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$L(112)$
500
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d)
L_a
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$L_c(004)$
$L(112)$
500
0
1500
2000
2500
3000
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Sizes of graphite crystallite, L_c, L_a and $L_{(112)}$, Å
Lattice constant c_o, Å
Temp. of heat treatment, °C

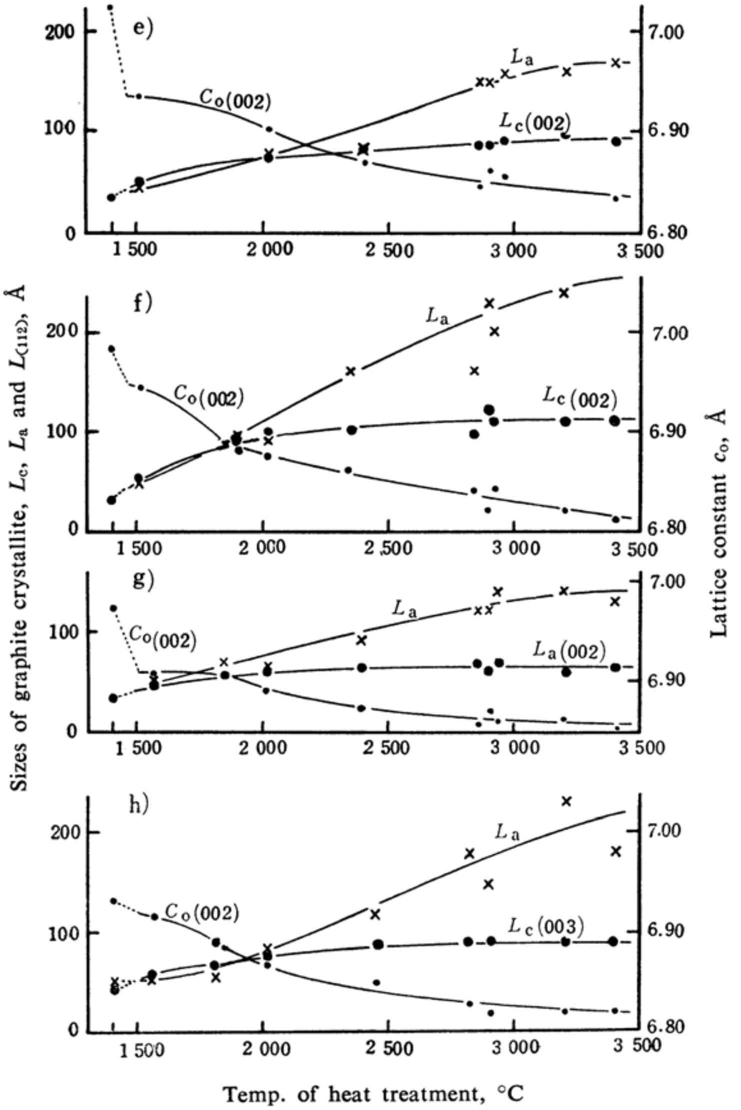

Fig. 2. Changes of lattice constant and crystallite sizes of carbon with heat treatment.
a) Petroleum coke, b) Pitch coke, c) Thermal black, d) Lamp black, e) Furnace black A, f) Furnace black B, g) Channel black, h) Acetylene black

value of $\Delta L/L$ may be taken as a measure of the heterogeneity of the spacing of the graphite-like layers in a parallel layer group.

The relation between $\Delta L/L$ and the temperature of heat treatment is shown in Fig. 3. The curves of $\Delta L/L$ for the petroleum coke, the pitch coke, and the thermal black were similar. These curves might be interpreted as follows. Up to 2000°C treatment, the turbostratic structure of graphite-like layers predominates in the samples, but a part of the graphite-like layers begin to take on a three-dimensional ordering, i. e., the graphite orientation, from 1800°C treatment (this was proved by the modulation of the (11) diffraction as mentioned above). Therefore, the heterogeneity of the interlayer spacing in crystallite increases, and the value of $\Delta L/L$ increases rapidly from 1800°C upward. At temperatures above 2000°C, the graphite orientation predominates in the samples, while the turbostratic structure decreases; i. e., the heterogeneity in crystallite decreases with the increase in the temperature of heat treatment. Therefore, the value of $\Delta L/L$ becomes maximum at about 2000°C and then decreases as the temperature

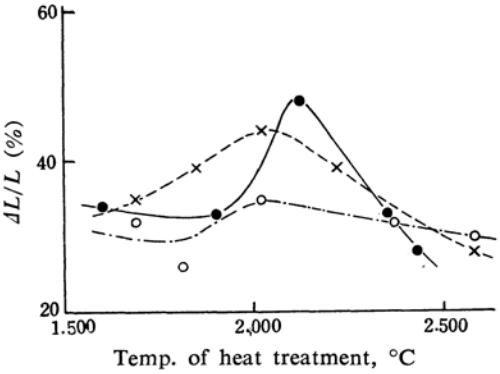

Fig. 3. Relations between $\Delta L/L$ and temperature of heat treatment of carbon.
—●— Petroleum coke
--×-- Pitch coke
-·○·- Thermal black

of the heat treatment increases. With samples heat-treated at temperatures above 2600°C and having crystallite sizes larger than 300Å, the error in $\Delta L/L$ was very large, so a discussion of the signification of $\Delta L/L$ may become meaningless. Tagawa and Nakashima⁹⁾ obtained a similar curve by investigating the relation between the temperature of heat treatment and the activation energy of the wet oxidation reaction of heat-treated petroleum coke.

Relation between the Particle Size and the Crystallite Size of Carbon Black.—It is said that particle size is the main limiting factor for the growth of graphite crystallite in carbon black¹⁰⁾. In Fig. 4, the crystallite size, L_c or L_a, of the thermal black, the two furnace blacks, and the channel black is represented as a function of the average particle size, $2R$. Because the lamp black had a peculiar distribution of particle size and because the acetylene black seemed to behave differently in its crystal growth from other carbon blacks, they were omitted from this discussion. From the two figures, it can be seen that the particle size has some effect on the crystal growth along the a-axis and also along the c-axis. This is consistent with the assumption that the minute crystallite whose layer plane is aligned parallel to the surface of the carbon black particle coalesces with its adjacencies into a larger crystallite¹¹⁾ and that, in consequence, the angle between the c-axes of adjacent parallel layer group is the main limiting factor for crystal growth in carbon black. If it is the only limiting factor, the value of $L_a/2R$, which corresponds to the average angle between the c-axes of adjacent parallel layer groups, should be the same in all carbon blacks. However, it can be seen in Fig. 5 that the value of $L_a/2R$ is larger as the particle size is smaller. Therefore, there must be another limiting factor besides the angle between the c-axes of adjacent crystallites. It might be the micropores between the crystallites.

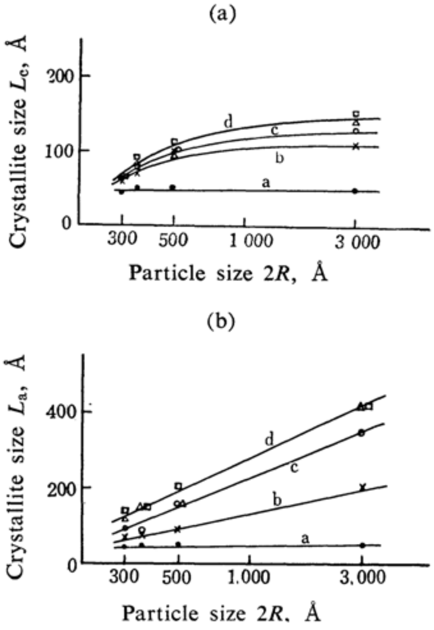

Fig. 4. Relations between particle size and crystallite sizes of carbon black.
a: 1550 b: 2020
c: 2400 d: 2800~3400°C

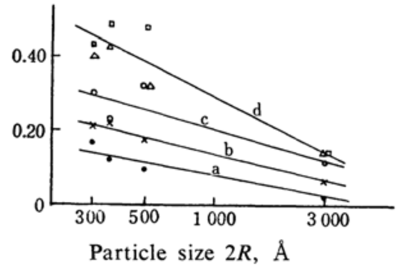

Fig. 5. Relation between particle size and $L_a/2R$ of carbon black.
a: 1550 b: 2020
b: 2400 d: 2800~3400°C

Graphitization of Charcoal.—All diffraction profiles of charcoals heat-treated at various temperatures are asymmetrical and seem to be composite profiles¹²⁾, as is shown in Fig. 6. The profiles can be separated into three different ones by appearance, i. e., two peaks at about 3.43 and 3.36Å and a broad band.

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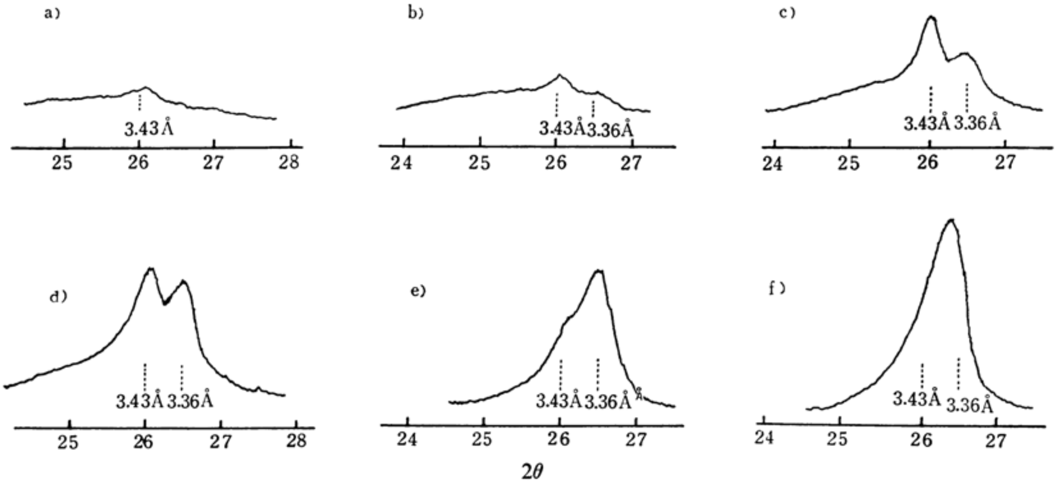

Fig. 6. Profiles of heat-treated charcoals.
a) 1820 b) 2120 c) 2370 d) 2450 e) 2820 f) 3200°C

The peak at 3.43Å increases its intensity up to 2500°C. The peak at 3.36Å, which is feeble as a temperature lower than 2000°C, increases its intensity with the increase in temperature of heat treatment and surpasses the peak of 3.43Å above 2500°C. Franklin[13] first noticed this phenomenon, calling it three-phase graphitization.

Summary

Two kinds of cokes, six kinds of carbon black and a charcoal were heat-treated at temperatures between 1500 and 3400°C in a resistance furnace under atmospheric pressure. The lattice constants and crystallite sizes of these carbons were measured by means of the X-ray diffraction method, using extra-pure silicon as an inner standard.

The c_0 values of the graphitizing carbons, such as the petroleum coke and the pitch coke, were not less than 6.718Å, even when these carbons were heat-treated at 3400°C. It was concluded that the graphitizability of carbon was affected by its original texture even at such a high temperature as 3400°C.

The c_0 value of carbon black became smaller and the value of L_c, larger with the increase in the particle size of carbon black. It has been said that the particle size is the main limiting factor for the growth of graphite crystallite in carbon black, but the experimental results suggest that such other properties as micropores may also be limiting factors.

The discrepancy between the L_c values calculated from the (002) and (004) diffractions was accounted for by the heterogeneity of the interlayer spacing in crystallite.

With the charcoal, so-called three-phase graphitization was observed.

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