Studies on the Graphitization. I. Changes of Crystallinity, Diamagnetic Susceptibility and Electrical Conductivity in the Process of Graphitization[*]

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Introduction

Graphites are made by heat treatments of carbonaceous materials such as soots or cokes. It is widely known, however, that even under the similar conditions of heat treatment the degree of graphitization varies according to the sort of starting materials. In an extreme case, "non-graphitizable" carbons are known[1]. It is frequently said in the manufacturing process, that soots are less easy to be graphitized than pitch cokes, and among the cokes, petroleum-cokes are more facile than coal-tar-cokes. On the other hand, some questions arise when we intend to define the degree of graphitization. This is due to the fact that the graphitized materials are in multi-crystalline states and their physico-chemical properties can not be determined by their crystallinity alone, but depend upon functions of the system as a whole.

In this paper, the degree of graphitization has been studied from the viewpoints of crystallinity, magnetic susceptibility and

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[*] The principal part of this paper was presented at the 7th annual meeting of the Chemical Society of Japan on April 1954 at Tokyo, excepting the data by X-ray. The photographic measurements were revised by a Geiger counter X-ray spectrometer.

[1] R.E. Franklin, *Compt. rend.*, 232, 232 (1951).

electrical conductivity, and comparison will be made among various starting materials concerning their tendency to graphitization.

Materials and Heat Treatments

The following substances were selected as the starting materials of graphitization; they are classified into three groups.

I. Pitch cokes:
  - I–1. Petroleum-coke (Great Lake Co. U.S.A.)
  - I–2. Coal-tar-coke (Yahata Seitetsu Co. Japan)

II. Carbon blacks:
  - II–1. "Thermax" (Thermatomic Carbon Co. U.S.A.)
  - II–2. "Kosmos-15A" (United Carbon Co. U.S.A.)
  - II–3. "Tokyo Gas" (Tokyo Gas Co. Japan)

III. Simple organic compounds:
  - III–1. Violanthrone ($C_{34}H_{16}O_2$)
  - III–2. Polyvinyl chloride

All the commercial carbonaceous products (from I–1 to II–3) were heated in vacuum at several temperatures from 1000 to 2000°C in an electric furnace of Arsem type. The duration at a peak temperature was about ten minutes. Violanthrone and polyvinyl chloride were treated preliminarily at 600°C in the ordinary atmosphere and thereafter the carbonaeous substances obtained were heated in the same way as mentioned above. The heat treatments at 2500 and 3000°C were made in an electric furnace of which the principle nearly resembles that of the industrial graphitizing furnace excepting the fact that the dimension was a laboratory scale[2]. The duration at a peak temperature was about five minutes. This procedure was made in Ohmachi manufactory of Showadenko Co., to whom our thanks are due.

X-Ray Measurements

Changes in the inter-layer spacings, $d(002)$, as the function of the heat treatment, were carefully observed. A Geiger counter X-ray spectrometer (Norelco) with copper anticathode was used. The diffraction maxima were estimated by referring to that of lead nitrate. For this purpose, (220), (211), (210) and (200) spacings of lead nitrate were used, the corresponding values of 2θ were 32.211°, 27.849°, 25.390° and 22.670° for CuK$_\alpha$ radiation respectively. These values had been calibrated referring to a standard quartz specimen. It has been known that in the case of low graphitized carbons, the diffraction maxima do not give directly the true inter-layer spacings[3]. Further corrections are necessary for the transformation of recorded diffraction curve into $|F^2|$ curve. This procedure was made by using the correction factors given by Ruston[4]. In the present case, however, these correction factors did not become large even in the specimens treated at lower temperatures, and they were negligibly small for the specimens treated at higher temperatures.

Following Franklin[5], in the graphitic carbons the graphite-like layers are grouped in parallel packets within which there is a random distribution of orientated and disorientated layers. In the orientated layers the inter-layer spacing is constant and equal to that of graphite 3.354 Å; in the disorientated layers the inter-layer spacing is equal to that in the non-graphitic carbons 3.44 Å, and there is a spacing of intermediate value among the first disorientated layers on either side of each orientated group.

By this formula, the apparent inter-layer spacing is in reality a mean value which depends upon the proportion of the number of disorientated layers to the total number of layers. Franklin has proposed an empirical equation which is expressed as

$$d=3.440-0.086(1-p^2),$$

where d is the mean inter-layer spacing observed and p is the fraction of the randomly disorientated layers. A similar formula has been concluded from a more theoretical point of view by Houska and Warren[6]. The value of p can be interpreted as a measure of the degree of non-graphitization, from the above point of view. The observed values of the inter-layer spacings and the p-values are shown in Table I.

TABLE I

INTER-LAYER SPACINGS AND CORRESPONDING P-VALUES OF GRAPHITIC CARBONS

Starting material	Heat-treatment temperature (°C)	Inter-layer spacing (Å)	p-value	$\frac{I(112)}{I(110)}$
Petroleum-coke	1550	3.413	0.828	0
	2040	3.385	0.600	0.40
	2500	3.365	0.358	0.62
	3000	3.351	0.000	0.73
Coal-tar-coke	1900	3.426	0.915	0.47
	2500	3.361	0.285	0.69
	3000	3.353	0.000	0.75
Thermax	1740	3.433	0.957	
	1960	3.423	0.896	
	2500	3.379	0.535	0.39
	3000	3.376	0.507	0.39
Kosmos	1960	3.428	0.900	0
	2500	3.422	0.890	0.12
	3000	3.422	0.890	0.18
		3.356	0.167	
Violanthrone	1520	3.436	0.976	
	1720	3.423	0.896	
	1960	3.420	0.876	
	2500	3.402	0.749	0.33
	3000	3.389	0.640	0.34
Polyvinyl chloride	1680	3.440	1.000	
	2020	3.428	0.925	0
	2500	3.384	0.586	0.40
	3000	3.371	0.441	0.45

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[2] S. Yamaguchi, T. Noguchi, S. Hatta and M. Hino, *Carbon*, **2**, 239 (1952).

[3] R.E. Franklin, *Acta Cryst.*, **3**, 107 (1950).

[4] W.R. Ruston, *Fuel*, **31**, 52 (1952).

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

[6] C.R. Houska and B.E. Warren, *J. Appl. Phys.*, **25**, 1503 (1954).

The crystallite size determination was made from the broadening of X-ray diffraction. The X-ray spectrometer profiles were used for this purpose. In order to get the broadening β of the line due to the finite size of the crystallites, the experimentally observed width B was corrected for the instrument width b. The instrument width was obtained from the lines of reference quartz powder (10–20 micron), and the correction curve of β/B against b/B for the X-ray spectrometer line breadths was used[7].

The crystallite dimensions were calculated by the formula,

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

where L is the mean dimension of the crystallite perpendicular to the set of planes giving rise to the line at the glancing angle θ, λ is the wave length of the X-ray and K is a shape factor. K is nearly 0.9 for ordinary three-dimensional lattice, provided β is defined as the half-maximum line breadth, while 1.84 for two-dimensional lattice[8].

The L_c-dimension, the thickness of the parallel packets of layers, was obtained from (002) line using $K=0.9$, while the L_a-dimension, the width of the graphite-like layers was obtained from (hk0) lines. Because the low graphitized carbons have the tarbostratic structure, they give nearly the two-dimensional reflections. In such a case, the L_a-dimension was obtained from (10) line using $K=1.84$. However, when the graphitization proceeded there appears the cross lattice (101) reflection, overlapping with the (100) line on the large angle side of the latter. This makes it difficult to estimate the half-width value of (100). Therefore, for highly graphitized specimens, (110) reflection was used for the determination of the L_a-dimension. Furthermore, there occurs some question concerning the value of the shape factor.

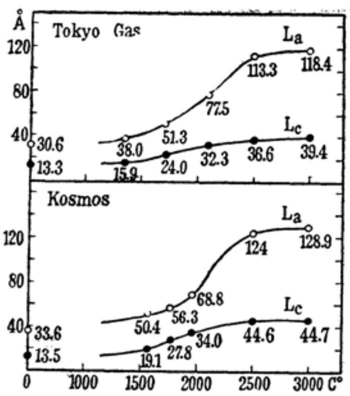

Fig. 1a. Growth of crystallites in graphitized carbon blacks.

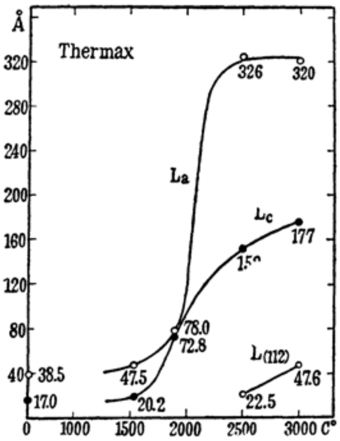

Fig. 1b. Growth of crystallites in graphitized carbon blacks.

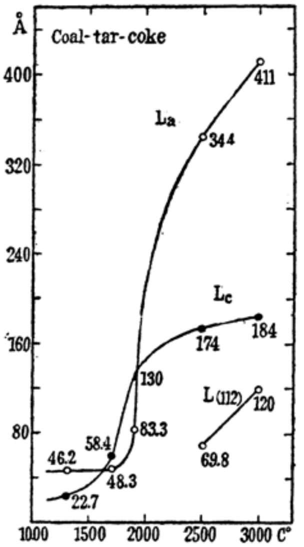

Fig. 2a. Growth of crystallites in graphitized pitch-cokes.

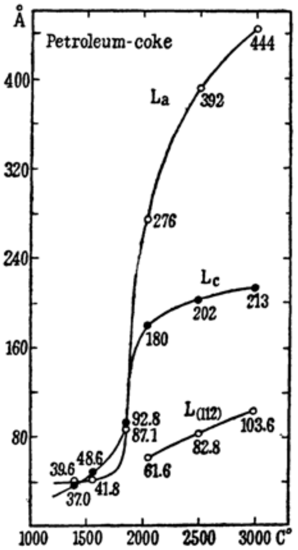

Fig. 2b. Growth of crystallites in graphitized pitch-cockes.

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[7] H.P. Klug and L.E. Alexander, "X-Ray Diffraction Procedures" (1954), p. 509.

[8] B.E. Warren, *Phys. Rev.*, 59, 693 (1941).

When the graphitization has proceeded, and the cross lattice reflection (101) and (112) has appeared, the structure of a crystallite consists of a stack of parallel planes composed of a random mixture of groups of perfectly orientated planes and groups of completely disorientated planes; the former gives the three-dimensional reflection while the latter gives the two-dimensional reflection. In such a case, K must be some average value between 0.9 and 1.84. Concerning the shape factor, we refer the p-value in the preceding section, and used $K=0.9+(1.84-0.9)p$. Another method is obtained by referring the intensity of (112) and (110) reflection. When the graphitization has been completed, the ratio of intensity of (112) to that of (110) is 1.61. Therefore in an intermediate state,

$$K=1.84-(1.84-0.9)\left(\frac{\mathrm{I}(112)/\mathrm{I}(110)}{1.61}\right),$$

can be used. The values of I(112)/I(110) are shown in Table I. The observed values of the crystallite dimensions are shown in Fig. 1, Fig. 2 and Fig. 3 as the function of the temperature of heat treatment.

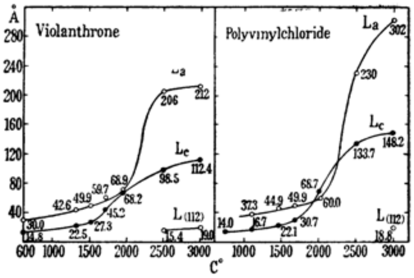

Fig. 3. Growth of crystallites in graphitized violanthrone- and polyvinyl chloride-base carbons.

Magnetic Measurements

The magnetic susceptibility at the room temperature has been measured by the Gouy method. The details of the method have been presented in a preceding paper from our laboratory[9].

To remove ash impurities which might have some effect on the magnetic susceptibility, each specimen was subjected to heating with hydrofluoric acid in a platinum crucible until the latter was evaporated up, then boiled with hydrochloric acid and finally washed with water throughly. Even after the purification, it was found in several specimens that a trace of ferromagnetic impurity still persisted, as a result the apparent susceptibility varied,depending on the magnetic field strength applied. In such a case, the ferromagnetic effect was calibrated by the formula,

$$\chi^{*}=\chi_{\infty}+2\sigma/H\,,$$

where χ^{*} is the apparent susceptibility observed, H is the field strength applied, σ is the saturation intensity of the ferromagnetic impurity, and χ_{∞} is the susceptibility proper to the sample itself.

When we plot the mass susceptibility against the temperature of heat treatment, we find that the features vary widely according to the sort of starting materials, especially of the groups. However, when we plot them as a function of the L_a-dimension, it is found that all points mount on nearly one curve, irrespectively of the sort of starting materials. This is shown in Fig. 4.

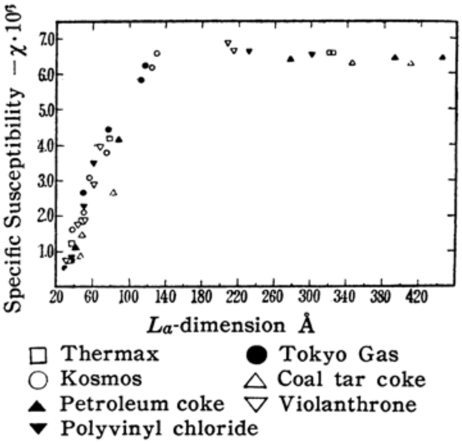

Fig. 4. Magnetic susceptibilites of graphitic carbons.

For comparison with the graphitized carbon, the magnetic susceptibility of natural graphite has been measured. Concerning the latter, there are many reports in the literature of the subject; however, they have given rather various values. The reason is presumably due to some contaminations in the graphite. In the present investigation, the purification procedure was made of two steps, e.g., in the first step specimens were subjected to alkali fusion with potassium hydroxide and carbonate at 300−400°C, and then accompanied by boiling with hydrochloric acid; in the second step the specimens which had been subjected to the above treatment were further treated with hydrofluoric acid and hydrochloric acid consecutively in the same manner as mentioned above.

The results are shown in the fourth column of Table II. The observed values are unexpectedly small; furthermore, the values for flake graphites are rather lower than those of amorphous graphites. This is due to the fact that when a graphite specimen is packed into the sample tube for magnetic measurement, the plate-like crystals take a preferred orientation with planes perpendicular to the axis of the sample tube; as a result, the measured value of susceptibility decreases, since in this direction the susceptibility has the least value. To avoid the orientation effect, the graphite powder diluted with γ-alumina was used. As an example, the mean gram susceptibility of the mixture of Korea flake graphite and alumina as a function of weight per-centage of graphite is shown in Fig. 5. A good linearity is found in the range of the lower concentration. This shows that the orientation effect of graphite crystals was almost cancelled.

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[9] H. Akamatu and Y. Matsunaga, This Bulletin, 26, 364 (1953).

The values in the last column in Table II are those which were obtained by using the mixture of graphite and alumina. Comparing those values to that in the preceding column, the difference, consequently the orientation effect, is large in the case of flake graphite, whilst in the case of amorphous graphite the effect is negligible.

TABLE II

GRAM SUSCEPTIBILITY OF NATURAL GRAPHITE

Sample	State of purification*	Ash content (%)	Gram-susceptibility in $-\chi\cdot10^6$.	
			From graphite alone	From mixture with alumina
Korea (flake)	Raw material	1.72		
	I-Step	0.02	5.07	6.22
	II-Step	0.07	5.38	
Korea (amorph.)	Raw material	5.47		
	I-Step	0.30	5.90	
	II-Step	0.28	5.95	6.12
	Without alkali fusion	0.36	5.77	
Ceylon (flake)	Raw material	0.74		
	I-Step	0.05	5.14	6.10
	II-Step	0.01	5.51	6.34
	Heated up to 3000°C			6.08
Madagascar (flake)	Raw material	19.85		
	I-Step	0.18	4.97	6.54
	II-Step	0.08		6.69
Mexico (amorph.)	Raw material	5.85		
	I-Step	0.14	5.57	
	II-Step	0.14	5.64	5.65

* Raw materials are commercial products which have been purified in the commercial sense.

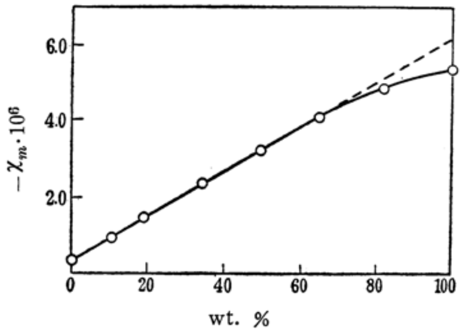

Fig. 5. The gram susceptibility of the mixture of graphite (Korea, flake) and alumina, against weight percentage of graphite.

It is seen in Table II that further purification makes increase of the diamagnetic susceptibility in every case; however, the difference is rather small. From this and the smallness of ash content, the observed value is presumably near the limiting value of the susceptibility of each specimen. In conclusion, the susceptibility of natural graphite can be assumed -6.4×10^{-6} in its good crystal form, and this agrees with the limiting values of the graphitized carbons.

Electrical Resistivity Measurements

The electrical resistivity at the room temperature has been measured by the usual potential drop method. Since the specimens are in powder form, the measurements were made under compressed states up to 200 kg/cm^2 in a bakelite cylinder. A nearly linear relationship was obtained between the resistivity and the reciprocal of the pressure, from which, by extrapolation, the value at the infinite compression was read as the resistivity of each specimen. The observed values are shown in Fig. 6 as the function of the L_a-dimension.

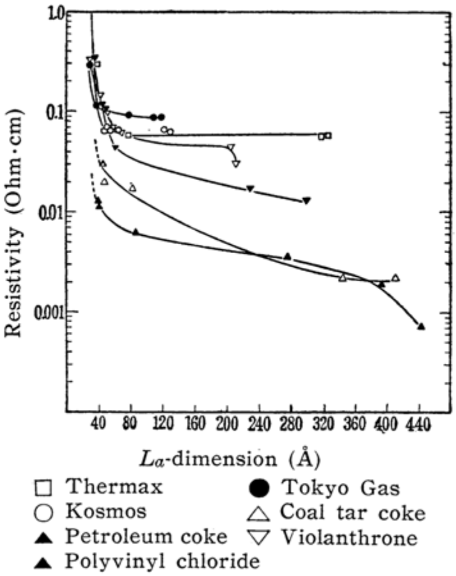

Fig. 6. Electrical resistivities of graphitic carbons.

Discussion

From the results of X-ray measurements, it has been found that the development of crystallinity by heat-treatment varies remarkably among the groups of the starting materials. This is seen from the growth of crystallites as well as the change of the inter-layer spacing or p-value.

The growth of crystallites proceeds with the most facility in pitch-cokes, and so far as this point is concerned, a large difference can not be found between petroleum-coke and coal-tar-coke. In both specimens, p-values tend to zero when they have been treated at 3000°C. This means that in this state disorientated layers have been almost entirely transformed to orientated layers. However, the intensity ratio I(112)/I(110) was yet 0.75; therefore, the perfect graphite lattice has not been completed.

In the case of carbon blacks, the growth of crystallites is slow and limited. This is due to the fact that carbon black is made of individual particles and in each particle the growth of crystallites is limited by its particle size. The final diameters of crystallites are 118 Å, 129 Å and 320 Å in "Tokyo Gas", "Kosmos" and "Thermax" respectively, while their particle sizes estimated by electron microscopy are 400 Å, 400–500 Å and 2000-4000 Å respectively. Furthermore, the crystallinity is low; hence, the p-values were still large even in the state which was subjected to the heat-treatment at 3000°C. This might be partly due to the fact that for promoting the transformation of disorientated layers to orientated layers, the growth of crystallites in advance to a certain large size is needed. But even in the case of "Thermax" which has a pretty large dimension, the p-value is still large compared with pitch-cokes.

In the case of "Kosmos" treated at 3000°C, it was found that the (002) diffraction maximum was divided into two peaks. This is shown in Table I. It might be assumed that this carbon is made of two parts in itself in a heterogeneous manner; one is completely graphitizable and the other is less graphitizable and the graphitization proceeded suddenly in the former at this temperature.

Violanthrone is a typical polycyclic aromatic compound and polyvinyl chloride is made of linear chain molecules. No remarkable difference could be found between those materials in the general feature of graphitization. However, in the violanthrone-base carbon the growth of crystallites seems to have been attained to a saturation value already at 2500°C, while in the polyvinyl chloride-base carbon the growth is proceeding even after the heat-treatment at 3000°C. So far as this point is concerned, the former is rather like carbon black and the latter is like pitch-coke. In the case of violanthrone, all molecules themselves are stable and might become as nuclei for the aromatic condensation, and so many graphite-like layers would arise from the outset, but the development of them by the expense of nonorganized carbons, which are less in number in this case, would be rather obstructed. In order to develop each crystallite to a large one, it is desirable that there occur a small number of nuclei and a large number of nonorganized carbon atoms. This is presumably the case of polyvinyl chloride and pitch-cokes.

Since graphite is a substance having a large value of diamagnetic susceptibility, it is of interest to see how it changes the magnetic property during the process of the graphitization. The diamagnetic susceptibility increases with the size of crystallites, and this is most impressive when we plot the gram susceptibilities against the L_a-dimensions as shown in Fig. 4.

It is a noteworthy fact that all the values obtained lie on a curve irrespective of the sort of starting materials. This result agrees with the conclusion of Pinnick[10) who studied two types of carbons, while it disagrees with the result of Wynne-Jones, Blayden and Iley[11), whose curves for three types of carbons do not overlap but are shifted somewhat relative to one another along the horizontal axis. On the other hand, when we plot the gram susceptibilities against the L_c-dimensions we obtain the various curves, which do not overlap with each other, according to the sort of materials. Consequently, the present result shows that the gram susceptibility is principally determined by the value of L_a alone, and does not depend upon any other second-ordered structures in polycrystalline states. This is rather a natural conclusion when we remember the origin of the magnetism.

This result is useful to understand that the crystallite sizes obtained by the X-ray method are self-consistent with each other. The crystallite sizes estimated by the X-ray method are not necessarily in agreement with each other among the investigators. This is perhaps due to the difference in the method of calibration, apparatus and other factors. The characteristic feature of the curve of the magnetic susceptibility will be useful to make the adjustment for the differences in crystallite sizes among the investigators. Thus, in our result the rapid increment of the susceptibility begins at 30 Å and attains to the saturation value at about 130 Å, whilst in the work of Pinnick the corresponding range is 50−150 Å. Therefore, our crystallite sizes are shifted to somewhat lower values than that of Pinnick.

In a previous work[9), we have studied the diamagnetic susceptibility of polycyclic aromatic hydrocarbons. The large values of the diamagnetism of those compounds are due to the anisotropic components which are due to the closed-shell diamagnetism of the London type. This diamagnetic anisotropy increases with increasing the number of benzene rings. However, their magnetic properties are rather structure-sensitive, and even the paramagnetic contributions are found[12). In such a case, the diamagnetic susceptibility becomes smaller than the ex-

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10) H. T. Pinnick, *Phys. Rev.*, **94**, 319 (1954).

11) W. F. K. Wynne-Jones, H. E. Blayden and R. Iley. *Brennstoff-Chem.*, **33**, 268 (1952).

12) Y. Yokozawa and I. Tatsuzaki, *J. Chem. Phys.*, **22**, 2087 (1954).

pected value. Thus, $n\Delta K_b$ gives the upper limit of the molar anisotropy, where n is the number of aromatic rings and ΔK_b is the diamagnetic anisotropy of benzene (-54×10^{-6}). However, as pointed out by Mrozowski[13], the large values of graphitized carbons can not be explained by this London-type diamagnetism alone, because the susceptibility converges to -1.0×10^{-6}, when the molecule becomes a large one, and when it is expressed in the mass susceptibility per gram*.

Marchand[14] has observed the temperature dependence of the magnetism of graphitized carbons in the range of −200−1000°C. He found that the gram susceptibility χ, is nearly constant when the L_a-dimension is small such as 36 Å, but it becomes dependent upon the temperature when L_a becomes larger than 45 Å and when χ at the room temperature becomes above -2×10^{-6}. The susceptibility increases with decreasing the temperature and tends asymptotically to a limiting value, which is characteristic for each carbon and becomes larger with the increment in L_a. The whole behaviour is similar to that of graphite which was found by Ganguli and Krishnan[15] and interpreted as Landau diamagnetism due to the two-dimensional free electron gas having a low degeneracy temperature. The result of Marchand may be understood when we suppose the degeneracy temperatures of carbons are higher than that of graphite.

Our result, Fig. 4, corresponds to the points on Marchand's curves at the room temperature. They are in good agreement with each other. In conclusion, the large values of diamagnetic susceptibility of graphitized carbons are due to the anisotropic components, which are partly contributed from the closed-shell diamagnetism of London-type and mainly from the free electron gas diamagnetism of Landau-type. The former is related to the ground states and the latter is due to the exited states of electrons. However, a question is left how in the relatively small range of 30−130 Å of L_a the Landau diamagnetism rapidly takes place. It is of interest, at least, to see the rapid change in electronic states of graphitized carbons in this range of L_a.

However, the values of the gram susceptibility itself can not be used for the reference of the graphitization degree, as they converge so rapidly to a saturation value of graphite.

Whilst the magnetic property is determined solely by the size of the molecular plane regardless of the sort of carbon, the apparent electrical resistivity remarkably depends on the starting materials. This can be see in Fig. 6.

The general feature of the electrical resistivity of carbon at room temperature as a function of the heat-treatment has been well illustrated and discussed by Mrozowski[13]. The resistivity decreases very rapidly with increasing the temperature of heat-treatment up to about 1000°C, but above this temperature the decreasing stops and a flat plateau is generally observed. So in the present investigation, the resistivity decreases rapidly with increasing L_a in the region where L_a is small, but it comes to have a nearly constant value when L_a becomes above 40 Å. It is noteworthy that the plateau is formed at the L_a-demension where the Landau diamagnetism begins to take place. The values of resistivity at the plateau vary among the sorts of carbons. The graphitized pitch-cokes have less resistivity than the graphitized carbon blacks, and violanthrone- and polyvinyl chloride-base carbons have intermediate values. In the case of carbon blacks, each plateau is a completely flat one, while in the case of pitch cokes the resistivity gradually decreases as increase in L_a even in the range of the plateau formation. Concerning this behaviour, the polyvinyl chloride-base carbon is like pitch coke, and the violanthrone-base carbon is rather like carbon black again, as mentioned in the above discussion on the X-ray analysis. So far as the crystallite dimension is concerned, the graphitized "Thermax" at 3000°C is not different from the graphitized pitch-coke "Yahata" at 2500°C concerning both L_a and L_c, and the resitivity of the former is still twenty-five times as high as the latter.

All of those facts suggest that not only the crystallites dimension but also the higher-ordered structures of multi-crystalline states are reflected on the resistivity. Carbon black is made of particles, furthermore, in each particle the crystallite micelles aggregate in such a manner that they are independent of each other. On the other hand, pitch cokes are made of a continuous massive material in which the crystallite micelles are bridged with cross-linkages, such as C-C valence bonds, to neighbors. The difference in the mode of the aggregation between those two

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13) S. Mrozowski, *Phys. Rev.*, 85, 609 (1952).

* When a molecule becomes large, the increment in number of carbon atoms is two per ring, and the limiting value of gram susceptibility is

$$-\chi\cdot10^6=n(2\times3.36+\Delta K_b/3)\div n(2\times12)=1.0 \text{ (cf. (9))}.$$

14) M.A. Marchand, *Compt. rend.*, 238, 1645; 239, 1609 (1954).

15) N. Ganguli and K.S. Krishnan, *Proc. Roy. Soc.*, **A** 177, 168 (1941).

groups has been well illustrated in the rate of wet oxidation of them[16]. This difference will persist or even be exaggerated in the graphitized state. In consequence, conserning the resistivity, the contact resistance or boundary scattering will be high in the case of carbon black, but it will be less in the case of pitch coke because of the transparent linkages between crystallites.

To explain the formation of the plateau, Mrozowski has assumed that the expected decrease of the resistivity due to growth of crystallites is compensated by a decrease in concentration of excess electrons or holes, which are responsible for the rapid decrease in the resistivity before the formation of a plateau, and the presence of which is due to the peripheral atoms which happen not to be bonded to neighbouring crystallites. This explanation may be applicable to the case of pitch cokes, in which the recombination among atoms at the peripheries of plane molecules will continue as long as the linkages remain, and the chance of occurrence of excess electrons or holes will persist. The decrease in the resistivity in a gradual manner in the region of a plateau may be understandable. But, such a flat plateau as observed in the graphitized carbon black is rather incomprehensible.

It has been found from the small angle scattering of X-ray that the fine structures are different between the graphitized carbon blacks and pitch cokes. In the graphitized carbon blacks, microporous parts arose and developed following graphitization. We are inclined to suppose that the expected decrease of the resistivity due to growth of crystallites is compensated by decrease in the number of contact points between crystallites due to the development of microporous parts. Further studies on the fine structures will be presented in the second part of this work.

Summary

Three sorts of carbon black, two sorts of pitch coke, violanthrone, and polyvinyl chloride have been subjected to heat treatment up to 3000°C. Changes in crystallinity during the graphitization have been studied by X-ray referring to inter-layer spacings and growth of crystallites. It was found that pitch cokes are graphitized with more facility than carbon blacks, and the other two substances are intermediate.

The magnetic susceptibility is determined solely by the size of plane molecules (L_a) irrespective of the sort of carbons, and tends to a limiting value -6.5×10^{-6} per gram which is coincident with the value of natural graphite, when L_a grows above 130 Å.

The electrical resistivity decreases as growth of crystallites, but there is a region when L_a becomes above 40 Å, where it tends to a nearly constant value for each carbon. Those values are different among the groups of carbons, and graphitized pitch cokes have less resistivity than graphitized carbon blacks. It was discussed that fine structures of multi-crystalline states are reflected on the resistivity.

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[16] H. Akamatu, H. Takahashi and K. Tamaru, This Bulletin, 21, 27 (1951).