Anisotropy of Needle Cokes

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(Received July 30, 1975)

The anisotropic properties of several lump needle cokes were studied by means of a X-ray diffractometer, a dilatometer, and a reflected microscope in order to evaluate the anisotropic factors of the needle cokes and to discuss the relations among them. Among them several relations were found, which were well understood on the basis of the structure of the uniaxial arrangement of the crystallites. The change in these factors upon heat treatment was also investigated in order to find how these factors depended on the crystal-growth of the needle coke. Some anisotropic properties of the extruded sample were compared with those of the filler coke, which were observed in a lump shape. The results indicate that the extruded sample had its anisotropic properties considerably lowered. The structure and crystal-growth of the needle cokes are discussed based on these observations.

The carbons used for the ultra-high-power electrodes have been required to be so-called needle-like cokes, which should have not only a good crystallinity but also a highly oriented structure.[1] It is recognized that the needle cokes exhibit high anisotropy in various properties, such as thermal expansion, thermal and electric conductivity, and Hall current.[2]

Mrozowski[3] and other researchers[4] described the structure of the needle cokes. The anisotropic properties of needle cokes in extruded or molded samples have been extensively studied, and the relations among them have been discussed.[2,5] However, some problems regarding the nature and structure of the needle cokes seem to be still open. A study of lump cokes may help us to understand the needle cokes, because there is no disturbance brought about by binder cokes and different degree of preferred orientation at the shaping.

In the present study, the anisotropy of lump needle cokes has been observed by means of microscopic observation, CTE measurement, and X-ray diffraction,[6–8] and the relations among the anisotropy factors have been studied on cokes heat-treated at graphitizing temperatures. The methods of measuring the anisotropy of powdered cokes have also been surveyed because the small batch reactors often give powdered cokes, even though they are needle-like. We also intend to discuss the structure of needle cokes on the basis of these data.

Experimental

Sample Cokes. Five kinds of filler cokes (A, B, C, D, E) and three kinds of extruded samples (B, F, G) were used in the present study. They were all commercially available; some of their properties are summarized in Table 1.

Table 1. Description of cokes used in the present study

Sample	Source	Starting pitch	Structure	Shape
A	Petro Cokes Ltd.	petroleum	needle	lump
B	GLW	petroleum	mosaic	lump, extruded
C	Koa Petro Co.	petroleum	needle	lump
D	Nittetsu Chem Co.	coal tar	mosaic	lump
E	Nittetsu Chem Co.	coal tar	needle	lump
F	Petro Cokes Ltd.	petroleum	needle	extruded
G	Petro Cokes Ltd.	petroleum	needle	extruded

Experimental Procedure. *Calcination and Graphitization*: Cokes were calcined at 1300 °C under a nitrogen flow. The calcined cokes were further graphitized at 2000 °C or 2500 °C for 0.5 hr under an argon flow. The heating rates were 20 °C/min up to 2000 °C and 10 °C/min up to 2500 °C.

Microscopic Observation and Measurement of Thermal Expansion: The optical structure of cokes and the graphites were observed using a Leitz Ortholux microscope with reflected polarized light under crossed nicols. The cokes were cut both parallel and perpendicular to the direction of the needle. They were then mounted in a cylinder of epoxy resin in order for the desired plane to be fixed on the surface of the cylinder, and were ground with several grades of alumina. As for mosaic cokes, the direction of cutting made no difference in the value of CTE or the features of microscopic observation, so each specimen was cut arbitrarily.

Thermal expansion was measured between 350° and 450 °C with a specimen heated at the rate of 10 °C/min in a vacuum. A dilatometer of a comparative type referring to the standard sample of silica (Shinku-Riko DL-1500H) was used. A cylindrical specimen 8 mm in diameter and 20 mm long was cut both parallel and perpendicular to the direction of the needle-like texture in order to obtain values of CTE parallel and perpendicular to the texture.

X-Ray Diffraction Analysis. *Measurement of Crystallographic Parameters*:[9] The calcined cokes and graphitized carbons were analyzed by X-ray powder diffraction Cu$K\alpha$ produced at 30 KV and 15 mA being used. The lattice constant (C_0) and the average crystallite thickness (L_c) were determined from the (002) diffraction peak. Silicon was used as the internal standard.

Measurement of Degree of Preferred Orientation: 1) Bacon Anisotropy Factor (BAF): The preferred orientation of both filler and extruded samples was measured by transmission X-ray diffraction according to the method proposed by Bacon.[6] A rectangular specimen 1 mm thick and 1 cm square was cut parallel to the direction of the needle-texture of the cokes. The intensity of the (002) reflection, $I(\phi)$, was observed at angles of every ten degrees from the normal direction of the texture. The area which was exposed to the X-ray was a circle 3 mm in diameter. BAF was calculated by the numerical integration of $I(\phi)$ based on the following equation:[6]

$$\mathrm{BAF} = \frac{1}{2}\,\frac{\int_0^{\pi/2} I(\phi)\sin^3\phi\,\mathrm{d}\phi}{\int_0^{\pi/2} I(\phi)\cos^2\phi\sin\phi\,\mathrm{d}\phi}$$

A random distribution of the crystallites will give equal intensities of (002) peaks against every ϕ, so that BAF is unity.

2) Method proposed by Noda and Inagaki[7] and Walker

et al.[8)]: The following equation of the anisotropy factor (γ_1) was used in the present study:

$$\gamma_1 = \frac{\dfrac{I(002)_{/\!/}}{I(002)_{/\!/}+K\{I(100)_{/\!/}+I(101)_{/\!/}\}}}{\dfrac{I(002)_{\perp}}{I(002)_{\perp}+K\{I(100)_{\perp}+I(101)_{\perp}\}}}$$

where $I_{/\!/}$, and $I_{\perp}$ represent the intensities from the (002), (100) and (101) diffraction peaks in the planes parallel and perpendicular to the direction of the needle texture respectively. The constant, K, was fixed at 5.56 so as to set the γ_1 of the completely non-oriented sample as unity. Because the intensities of the (004) and (110) peaks were as weak as for cokes calcined below 2000 °C, the (002), (101), and (100) peaks were used instead, modifying the equation proposed by Noda and Inagaki.[7)] The area exposed to X-ray in the reflection method was roughly 1 cm square.

Results

Comparison of Filler Cokes. The reflected micrographs and physical and structural properties of five cokes calcined at 1300 °C are shown in Photo 1 and Table 2 respectively. Cokes A, C, and E consisted of a flow-pattern structure, small values of CTE parallel to the direction of the texture, and large values of the anisotropic factors of both BAF and γ_1. In contrast, Cokes B and D, which showed a disordered mosaic unit-structure of several ten microns, have large CTE values and anisotropic factors near unity. The CTE values seem related to the anisotropy factors, although CTE should depend not solely on the anisotropy factor. The similar values of L_c and C_0, regardless of the kind of coke, might play some roles for such a relation, because Engle,[5a)] Matsumoto and Sasaki[10)] showed a slight dependence of CTE on Lc. Closed porosity should also be taken into account, as has been pointed by several researchers.[11)] Thus, the microscopic observations and the values of BAF, γ_1, and CTE may be considered to be indications of the needle-like structure of the cokes.

Dependence of Properties of the Needle Coke on the Calcination Temperatures. Because Table 2 indicates that A coke is the best needle coke in regard to CTE, BAF, and γ_1, the dependence of its properties on the calcination temperatures was investigated in order to clarify the relation among these properties. The reflected microscopic photographs of the plane parallel or perpendicular to the direction of the needle texture are shown in Photo 2. The preferred orientation of the crystallites is clearly observed on the parallel plane, whereas a disordered mosaic structure is shown on the perpendicular plane. No essential change in the visible structure was observed upon further heat treatment up to 2500 °C, except for the development of cracks along the needle texture on the parallel plane at higher calcination temperatures. The orientation of the cracks was not observed at all on the perpendicular plane, although they run along the anisotropic boundary.

The CTE values of the cokes calcined at 600 °C were still very large on both the parallel and perpendicular planes, as is shown in Table 3, although the anisotropic nature ($\alpha_{\perp}/\alpha_{/\!/}>1$) had previously been observed. As the shrinkage of the needle texture and cracks parallel to the texture appeared at the calcination temperature of 1300 °C, the CTE value

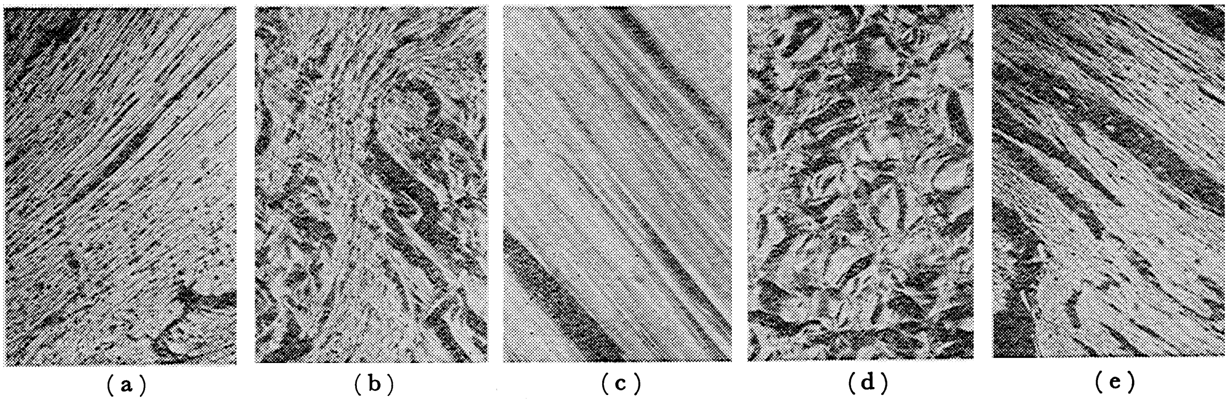
TABLE 2. PROPERTIES OF SOME COKES[a)]

	A coke	B coke	C coke	D coke	E coke
CTE[b)] ($\times 10^{-6}$/°C)	0.4	2.6	1.1	4.8	1.7
BAF	3.0	1.2	3.0	1.0	2.9
γ_1	4.8	1.2	6.0	1.0	7.1
C_0(002) (Å)	6.838	6.884	6.884	6.891	6.884
L_c(002) (Å)	21	28	47	27	41

a) Calcined at 1300 °C. b) Parallel to the axis of the needle if the samples are needle-like cokes.

TABLE 3. PROPERTIES OF A COKES CALCINED AT VARIOUS TEMPERATURES

HTT		600 °C	1300 °C	2000 °C	2500 °C
CTE ($\times 10^{-6}$/°C)	$\alpha_{/\!/}$	10.9	0.4	0.3	0.5
	$\alpha_{\perp}$	24.6	2.6	2.4	2.1
B. A. F.		2.7	3.0	5.6	5.1
γ_1		—	4.8	12.7	10.4
C_0(002) (Å)		6.885	6.835	6.842	6.732
L_c(002) (Å)		35	21	290	990



(a) (b) (c) (d) (e)

Photo. 1. Optical micrographs (crossed nicols, ×200) of various cokes calcined at 1300 °C. (a) A coke, (b) B coke, (c) C coke, (d) D coke, (e) E coke.
As for A, C and E cokes, photographs were taken parallel to the axis of the needle-texture.

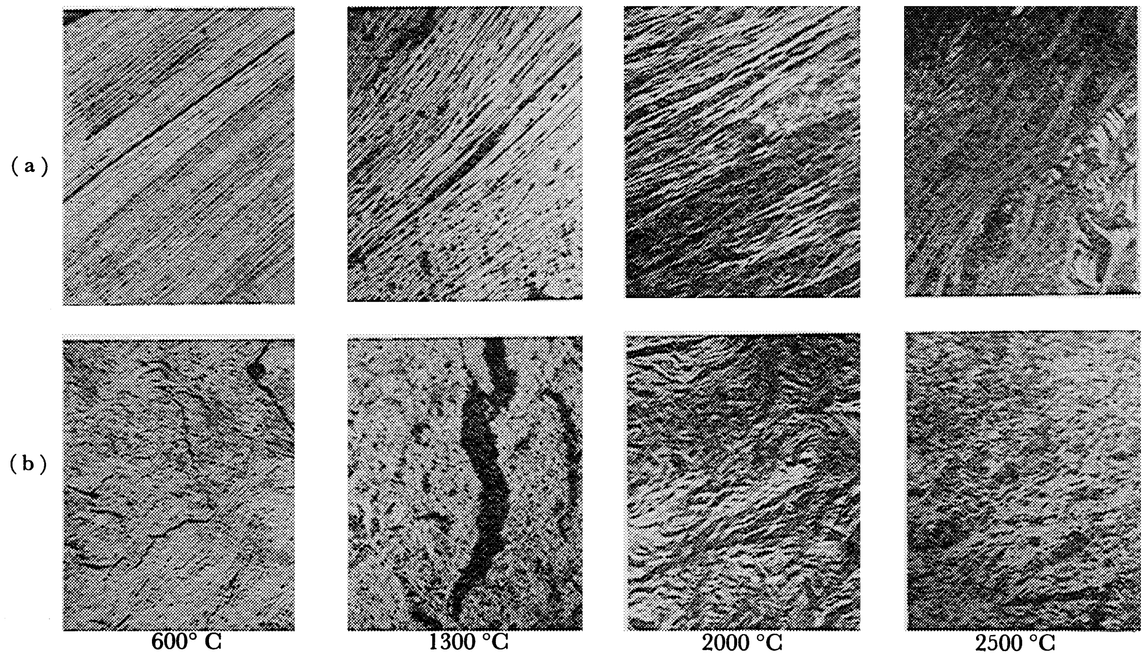


Photo. 2. Optical Micrographs (crossed nicols, ×200) of A cokes calcined at various temperatures. (a) Planes parallel to the axis of the needle texture. (b) Planes perpendicular to the axis of the needle-texture.

decreased. The value, however, did not decrease appreciably upon further heat treatment. Although the ratios of $\alpha_{\perp}/\alpha_{//}$ had a rather poor accuracy because of the difficulty of accurately measuring small $\alpha_{//}$ values of cokes calcined at higher temperatures, a significant increase in $\alpha_{\perp}/\alpha_{//}$ was observed at 1300 °C as the marked decreases of $\alpha_{\perp}$ and $\alpha_{//}$ occurred. In contrast, only slight changes were observable in the values of C_0, L_c, and BAF between 600 °C and 1300 °C, as is shown in Table 3. However, the background around 23°(2θ) in the X-ray diffraction pattern decreased for the sample calcined at 1300 °C, indicating that the amorphous part decreased upon heat treatment at this temperature. No more evolution of gas was observed above 1300 °C.

TABLE 4. DEGREE OF PREFERRED ORIENTATION AND GRAPHITIZATION OF WELL-ORIENTED COKES

HTT	C coke		E coke	
	1300 °C	2500 °C	1300 °C	2500 °C
BAF	3.0	4.9	2.9	3.5
γ_l	6.0	6.6	7.1	8.1
C_0 (Å)	6.884	6.739	6.884	6.743
L_c (Å)	47	750	41	570

TABLE 5. DEGREE OF PREFERRED ORIENTATION AND GRAPHITIZATION OF BADLY-ORIENTED COKES

HTT	B coke			D coke	
	1300 °C	2500 °C	3000 °C	1300 °C	2500 C
BAF	1.2	1.2	1.2	1.0	1.0
γ_l	1.2	1.2	1.1	1.0	1.2
C_0 (Å)	6.884	6.762	6.725	6.891	6.747
L_c (Å)	28	540	810	27	655

The two anisotropy factors obtained in turn by X-ray diffraction changed considerably between 1300 and 2000 °C, and both settled above 2000 °C. The crystal growth of the carbon continued up to 2500 °C, as is indicated by the increasing L_c(002) value and the decreasing C_0(002) value. The relation among these properties of cokes calcined at different temperatures will be discussed later.

The needle-like cokes, C and E, showed increases in the anisotropic factor and the crystal growth similar to those of the A coke (Table 4), although their starting pitches were different. In contrast, mosaic cokes showed no improvement in anisotropic factors at all up to 3000 °C, at which point a significant crystal growth was observed much as with needle-like cokes (Table 5).

The X-ray observations indicate that the anisotropy, one of important qualities of the needle-like cokes, is a property connected with the preferred orientation of the crystallites as well as with the crystallographic nature of the simple crystallite. Such a conclusion

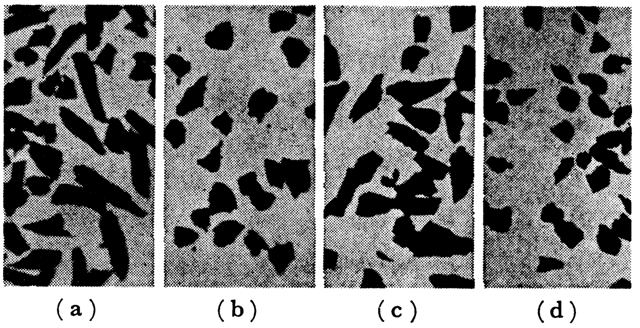


Photo. 3. Optical micrographs (×60) of the ground cokes calcined at 1300 °C. Particle size; 65—100 mesh. (a) A coke, (b) B coke, (c) C coke, (d) D coke.

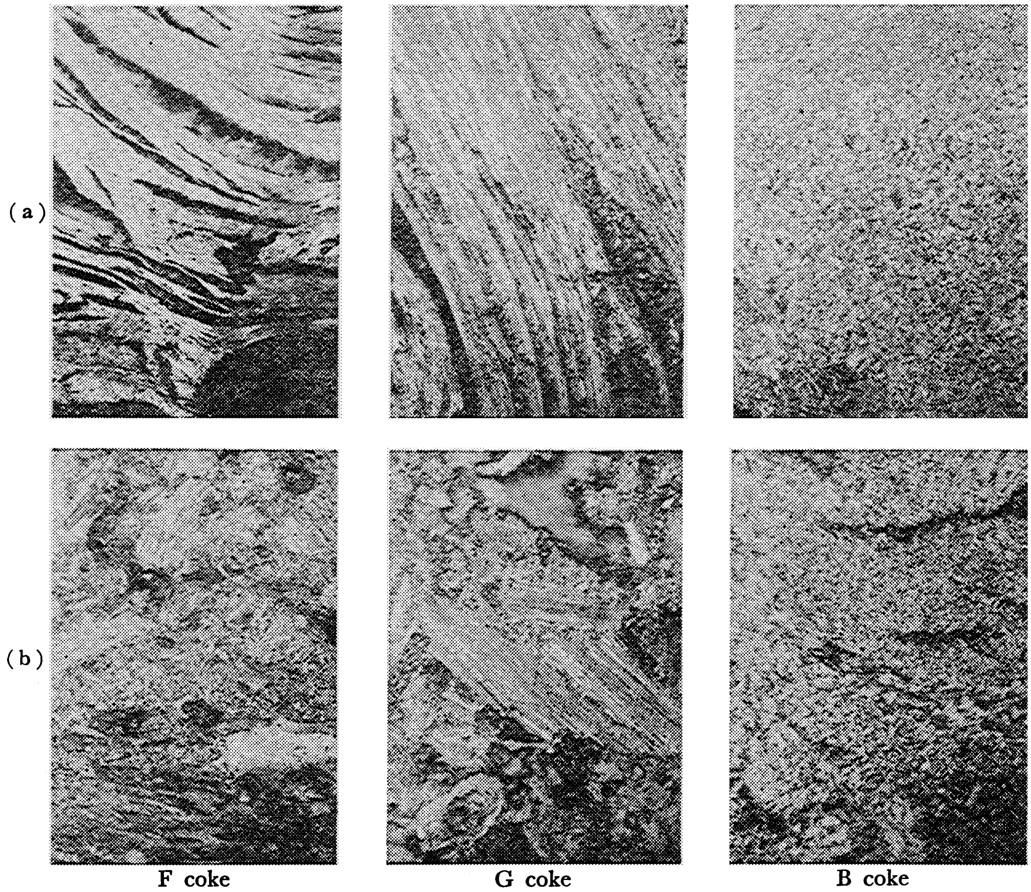


Photo. 4. Optical micrographs (crossed nicols, ×200) of F, G, B cokes, and their extruded samples. (a) Filler cokes, (b) Extruded samples.

has also been obtained in the discussion of the carbonized products from naphthalene and pyrene.[12)]

Shape Factors of Ground Cokes. Microscopic photographs of ground samples from A, B, C, and D cokes are shown in Photo 3. Obviously, the needle cokes A and C were broken into elongated pieces in which the needle-textures ran lengthwise, as Mrozowski[3)] and Walker *et al.*[8)] recongnized. In contrast, the B and D cokes with the mosaic structure, gave rather spherical pieces. Walker *et al.*[8)] proposed to define the shape factor, k, by the following equation;

$$k = S_{\mathrm{v}}\mu$$

where S_{v} is the geometric surface area per unit of value and where μ is the arithmetic-average sieve-size diameter of the sample; they reported the relation between the shape factor and the anisotropic factors. Because their factors seem to have some ambiguity concerning the pore surface area, the ratios of the shortest and longest lengths of the particles were averaged for one hundred particles in the present study. We could not find any clear difference in the averaged ratios of ground cokes of A, B, C, and D, although distinct difference in shapes could be recognized at a glance.

Comparison of Anisotropic Factors between Filler Cokes and Their Extruded Products. The anisotropy factors of filler cokes and their extruded products were compared in an attempt to discuss how well the extrusion aligned the particles of needle cokes parallel to the axis of extrusion, and whether or not the anisotropy factor of the extruded products could represent that of filler cokes, because the elongated pieces of the needle cokes were expected to be arranged parallel to the direction of extrusion. The anisotropy factors measured by two ways of X-ray diffraction are summarized in Table 6. As for the needle cokes (F and G), a decreased anisotropy upon the extrusion was shown by both methods, although the extent of decrease was a little smaller by the reflected method (γ_1) than in the Bacon method(BAF). The arrangement of the needle coke particles in the extrusion products is shown by the micrograph[Photo 4]. When compared with the photographs of the fillers themselves, they could be easily distinguished from the binder cokes in the extrusion products, however, this arrangement was far from an uniaxial one along the extrusion axis. The disordered arrangement probably brings about the decrease in the anisotropic facors. Thus,

Table 6. Comparison of anisotropic factors between filler and extruded cokes

	B coke[a)]		F coke[b)]		G coke[c)]	
	Filler	Ext.	Filler	Ext.	Filler	Ext.
BAF	1.2	1.1	2.5	1.4	2.2	1.4
γ_1	1.1	1.2	3.4	2.0	2.6	2.3

a) Calcined at 3000 °C. b) Calcined at 1300 °C.
c) Calcined at 3000 °C.

the usual extrusion could not be expected to be sufficient to reproduce the anisotropic factors of filler cokes. The extrusion which forces the uniaxial arrangement of filler cokes more strictly is required for this purpose. In the case of cokes of the mosaic structure, the filler cokes were difficult to distinguish by the microscopic observation, and the X-ray data shown in Table 6[B Coke] indicate the unchanged isotropic natures of both filler and extruded cokes.

The different degree of decrease in the anisotropic factors observed by the two ways of X-ray diffraction measurement may be explained as follows. The values of BAF fluctuated with the exposed location, and sometimes the plots of $I(\phi)$ *vs.* ϕ gave a quite unsymmetrical curve. These facts may be the result of the small area exposed to X-rays, and may mean that the Bacon method is not suitable for the measurement of the extruded sample the fillers of which are not uniformally arranged. In contrast, the reflection method gave constant and reproducible values, perhaps because of the larger exposed area, as has been pointed out by Noda and Inagaki.[6] This method may give the averaged anisotropic factor against the filler cokes distributed in the area exposed to the X-rays.

Discussion

There have been several proposals with regard to the structures of the needle cokes. Franklin[13] considered the needle coke to be a platelet-like arrangement of crystallites with the crystallites parallel on a large plate. Mrozowski[3] defined the needle-coke in which the crystallites of carbon were well aligned with normals to the planes distributed in all directions, but approximately parallel to the axis of the needle, so that the crystallites were not at all parallel to each other. Photo 2 clearly supports such a structure. This structure can be compared to a paper-roll.[4b] On the basis of this structure, the fact that the profiles of Bacon plots are equal in two planes perpendicular to each other, but parallel to the axis of the needle, is understandable.

The data shown in Table 3 are of value in a discussion because they seem to indicate interesting relations among crystal growth, the orientation of the crystallites, and the physical properties of the needle coke. The significant decrease of CTE value between the calcination temperatures of 600 °C and 1300 °C is considered to be the result of the crystal growth of the incorporation of the disorganized phase,[3] as is indicated by the marked decrease in the amorphous part in the X-ray diffraction, although no real crystal growth such as is shown by L_c or C_0 was observed. The disappearance of amorphous carbon may improve the CTE of the carbon.

Above 1300 °C no amorphous part was present any more, but real crystal growth may occur, as is indicated by the significantly increased L_c and C_0. The small gas evolution or the small decrease in the H/C ratio may also indicate the crystal growth in this region at the expense of other crystallites, as was mentioned by Mrozowski.[3]

Microcrystallites of carbon calcined at 1300 °C (their average L_c was as small as 21 Å) may have a CTE value similar to that of complete graphite (L_c is several hundred Å) if the chemical bonds are the most important factor in the thermal expansion, because microcrystallines already consist exclusively of carbon–carbon bonds, as does complete graphite. This might indeed be the case, although many other factors should be considered to play some role in the thermal expansion. Several researchers have studied the relation of CTE or other anisotropic properties to the crystal size, as in shaped cokes. Engle[5a] claimed the dependence of CTE and its anisotropic ratio on the mean apparent crystallite size L_c. Matsumoto and Sasaki[10] investigated similar relations. The latter authors claimed a slight dependence of CTE on the crystal size (the size has no effect on the CTE value over 700 Å) and a linear relation between the CTE anisotropic ratio and the crystal size. According to the opinion of the present authors, however, there are some problems in the study of extruded or molded samples because shaped cokes may not always represent the filler cokes and because the factor brought about at the shaping probably often has significant effects. Furthermore, the mechanism how the crystal size influences the CTE is worth further study.

Although the CTE values did not change at the calcination of 2000 °C, where essential crystal growth was also noticed, a significant increase in anisotropic factors as measured by X-ray diffraction was observed. The anisotropic factor showed no increase at 2500 °C in spite of the marked crystal growth. These facts may mean that a critical value of the crystal size may be necessary to give the leveled anisotropy factor observed for the cokes calcined at 2000 or 2500 °C, because the intensity of the (002) diffraction is influenced very much by the crystal size. It is evident from Photo 2 that the alignment of the crystallites is already formed at the temperature of the solidification of the cokes and that is persists essentially unchanged up to the highest-temperature. In this sense, the anisotropy factor may be constant regardless of the later heat treatment; however, other anisotropy factors based on the other physical properties of cokes seem to change because of the dependence of the property on characteristics of the cokes other than alignment of crystallites.

The needle cokes produced by the reactor of an experimental size are often pulverized so that their anisotropic properties are difficult to measure, although the measurement is important in evaluating the quality of the needle cokes. There are two possible ways of measurement. First, an attempt is made to measure the anisotropic properties of a particle itself. Second, powdered cokes are molded or extruded into a lump of a suitable size with binders, and the properties of the filler cokes are estimated from those of the shaped sample. The first approach is possible by the use of a strong X-ray source and an automatic full-circle goniometer; however, it is still difficult to set the sample in the right direction, parallel to the needle-axis. The reflective index, as measured by a polarized light microscope, may also give the anisotropic factor of powdered cokes.[14]

In the second method, filler cokes should be arranged in the shaped sample, with the same symmetry as the filler cokes themselves have. The needle cokes are in an uniaxial arrangement in which the axis of the powdered needle is within a plate; however, this symmetry is completely different from the uniaxial one. Although the extrusion is considered a possible way to achieve this arrangement, the results shown in Table 6 and Photo 4 indicate that the present extrusion is not sufficient to arrange the powdered needle cokes in an uniaxial direction to the same extent as was observed in an original lump coke. Ubbelohde[15] succeeded in obtaining a highly anisotropic arrangement of cokes by applying compression and sherring forces to the cokes in a shaped binder-polymer at the same time. An extrusion with a large compression ratio seems to be an expedient way to obtain a lump composed of uniaxially arranged cokes which can represent the individual coke-particle; furthermore, it is interesting because anisotropic properties superior to those of original cokes can be realized in such a way.

Our thanks are due to Professor Ryohei Takahashi of our University and Mr. Juji Furumi, The Nittetsu Chemical Industrial Co., for providing the experimental facilities. The authors are also grateful to the Japan Securities Scholarship Foundation for its financial support.

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