

# ANALYTICAL DETERMINATION OF CARBON VARIETIES AND GRAPHITIZABILITY OF BINDER PITCH IN GRAPHITIZED CARBON PRODUCTS

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Some of electrographitized carbon products, such as carbon brushes, are made from mixtures of different raw carbon materials; coke, carbon black and binder pitch. The (001) diffraction profiles of these products were found to be asymmetrical<sup>1)</sup>, as shown in Fig. 1. It is well known that the graphitizability of carbon black is distinctly different from that of coke. For example, the value of  $c_0$  of a pitch coke heat-treated at 3,400° C was 6.718 Å, while the value of  $c_0$  of carbon black, such as thermal black, channel black, etc. were 6.76~6.85 Å even when they were heat-treated up to 3,400° C<sup>2)</sup>. It was revealed under electron microscope that

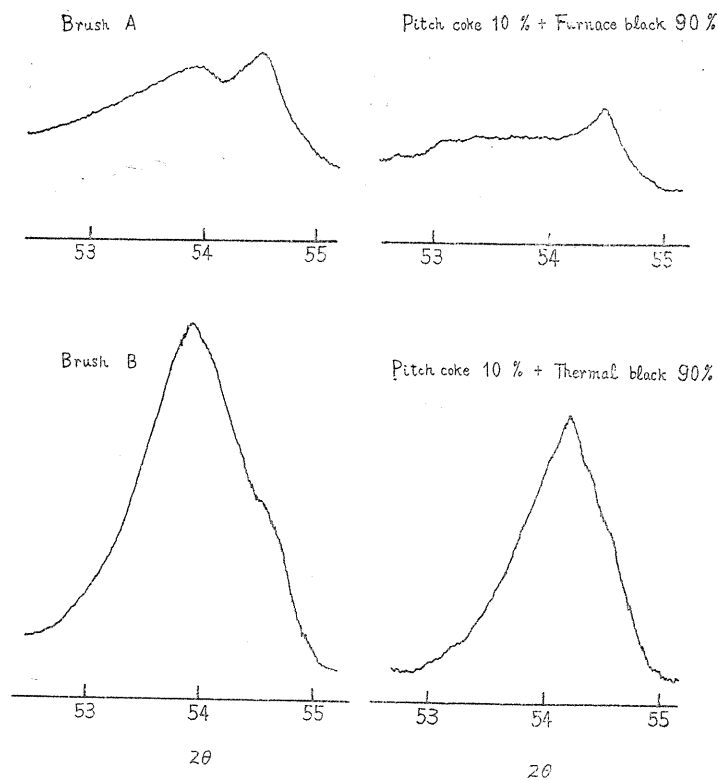


FIG. 1. Diffraction profiles of commercial brushes and of mixed powders of coke and carbon black.

carbon black particles preserved their original individuality and were sharply distinguishable from coke derived from binder pitch in the graphitized products which were made from carbon black and binder pitch<sup>3</sup>). As shown in Fig. 1, the diffraction profiles of mixtures of an electrographitized pitch coke powder and a furnace black or a thermal black were found to be considerably similar to those of commercial carbon brushes.

Therefore, the observed asymmetry of diffraction profiles of electrographitized carbon products is supposed to result from the overlapping of profiles of differently graphitized carbon materials. By separating these asymmetrical profiles into profiles of component carbons, such as coke, carbon black and coke derived from binder pitch (binder coke), it may be possible to determine the raw carbon materials analytically and to discuss the graphitizability of binder pitch in graphitized products.

### Corrections of diffraction profile

*Correction for crystallite orientation*—With the intensity of (001) diffraction, the effect of preferential orientation of graphite crystallites should be taken into consideration. An 'orientation function'  $I(\phi)$ , which was proposed by Bacon<sup>4</sup>, can be obtained from the measurement of the intensity of (002) diffraction by using a recording diffractometer<sup>5</sup>.

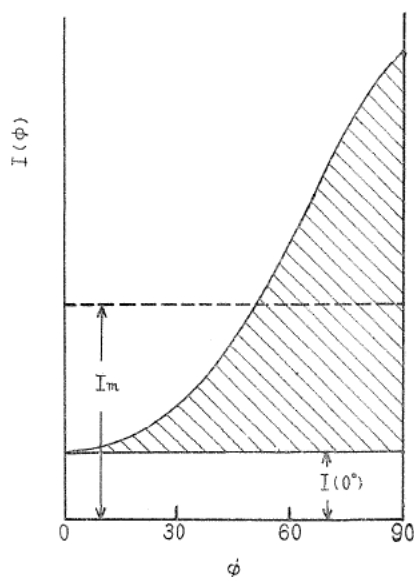


FIG. 2. Orientation function  $I(\phi)$  and average intensity  $I_m$ .

If the average intensity  $I_m$  is calculated from the area under the orientation function curve (refer to Fig. 2), it corresponds to the intensity which is to be obtained when graphite crystallites are randomly oriented. It must be noted that the diffraction intensity obtained by the usual reflection method is the intensity which is measured in the direction perpendicular to pressing, because a specimen with its plane parallel to the pressing direction is cut out from a sample. And so it corresponds to  $I(0^\circ)$  in the orientation function (refer to Fig. 2). When the reflected intensity is multiplied by a coefficient  $f$  which is calculated as

$$I_m/I(0^\circ) = f \quad (1)$$

the reflected intensity can be converted into the intensity which is to be obtained when the crystallites are randomly oriented. In this paper, the coefficient  $f$  is called the orientation coefficient.

*Relation between intensities of two specimens*—In addition to the correction for the crystallite orientation, diffraction profiles, particularly low-angle diffraction profiles as (002), should be corrected for various intensity factors, such as the

absorption factor, the Lorentz-polarization factor and the square of the atomic scattering factor<sup>6</sup>). In the present work, (004) diffraction profile was used, because it was hardly necessary to be corrected for the various intensity factors mentioned above, and because the higher order diffractions of (00*l*) were not always detectable in all electrographitized carbons.

The relation between the intensity of incident ray  $I_0$  and that of diffracted ray  $I$  is usually described as

$$I = I_0 \cdot V \cdot (1/2 \mu') \cdot \{1 - \exp(-2 \mu' t / \sin \theta)\} \quad (2)$$

where  $V$  is the irradiated volume,  $t$  is the thickness,  $\mu'$  is the linear absorption coefficient of a specimen, and  $\theta$  is the Bragg angle of (004) diffraction. The linear absorption coefficient  $\mu'$  can be calculated from

$$\mu' = (\mu/\rho) \cdot \rho' \quad (3)$$

where  $(\mu/\rho)$  is the mass absorption coefficient of carbon and  $\rho'$  is the bulk density of a specimen.

If two specimens  $A$  and  $B$  contain the same raw carbon material in different concentration, each diffraction intensity  $I_A$  or  $I_B$  for the same carbon material in the specimen  $A$  or  $B$  may be represented by Eq. 2. Therefore, assuming that the ratio of weight contents of the carbon material  $X_A/X_B$  can be used in place of the ratio of the volumes  $V_A/V_B$ , the ratio of  $I_A$  to  $I_B$  can be calculated from

$$f_A \cdot I_A / f_B \cdot I_B = (X_A/X_B) \cdot [\{1 - \exp(-2 \mu'_A t_A / \sin \theta)\} / \{1 - \exp(-2 \mu'_B t_B / \sin \theta)\}] \quad (4)$$

where  $f_A$  or  $f_B$  is the orientation coefficient,  $X_A$  or  $X_B$  is the weight content of the carbon material, and  $t_A$  or  $t_B$  is the thickness of each specimen. The second term of the right hand in Eq. 4 represents the ratio of the absorption factors of the two specimens.

### Experimental and Discussion

*Profiles of mixtures of graphitized coke and carbon black*—Samples were prepared in the following way. A calcined pitch coke, a thermal black, a furnace black and a channel black were heat-treated independently at about 2,900°C in a carbon granular resistance furnace\* and pulverized to pass a 150 mesh sieve. The pitch coke was mixed at various ratios with the thermal black, the furnace black or the channel black. These mixtures were moulded by using polyester resin as binder. For X-ray analysis, flat specimens of  $0.750 \pm 0.005$  mm. thick with their planes parallel to the pressing direction were cut out from these moulded blocks. Mixing ratios, bulk densities and orientation coefficients of the specimens are shown in Table I.

The (004) diffraction profiles of all specimens were obtained by the usual reflection method using a recording diffractometer. The profiles of the mixtures of the pitch coke and the thermal black (CT-series) are shown in Fig. 3 with solid lines. In this paper, a profile of a mixture of different raw carbon materials is

\* The heat treatment of the carbons was described in detail elsewhere (Ref. 2)

TABLE I. Mixing ratio, bulk density, orientation coefficient and intensity ratio of mixtures of graphitized coke and carbon black

Specimen number	Raw carbon materials	Mixing ratio	Bulk density (g/cm <sup>3</sup> )	Orientation coefficient <i>f</i>	Intensity ratio
CT-1	Pitch coke : Thermal black	100 : 0	1.27	1.79	100 : 0
CT-2	Pitch coke : Thermal black	79 : 21	1.63	1.55	82 : 18
CT-3	Pitch coke : Thermal black	58 : 42	1.69	1.28	62 : 38
CT-4	Pitch coke : Thermal black	40 : 60	1.75	1.19	40 : 60
CT-5	Pitch coke : Thermal black	20 : 80	1.82	1.09	24 : 76
CT-6	Pitch coke : Thermal black	0 : 100	0.76	—	0 : 100
CF-1	Pitch coke : Furnace black	100 : 0	1.27	1.79	100 : 0
CF-2	Pitch coke : Furnace black	80 : 20	1.34	1.69	85 : 15
CF-3	Pitch coke : Furnace black	40 : 60	1.57	1.32	42 : 58
CF-4	Pitch coke : Furnace black	0 : 100	0.40	—	0 : 100
CC-1	Pitch coke : Channel black	100 : 0	1.29	1.58	100 : 0
CC-2	Pitch coke : Channel black	80 : 20	1.61	1.42	82 : 18
CC-3	Pitch coke : Channel black	40 : 60	1.63	1.27	43 : 57
CC-4	Pitch coke : Channel black	0 : 100	0.42	—	0 : 100

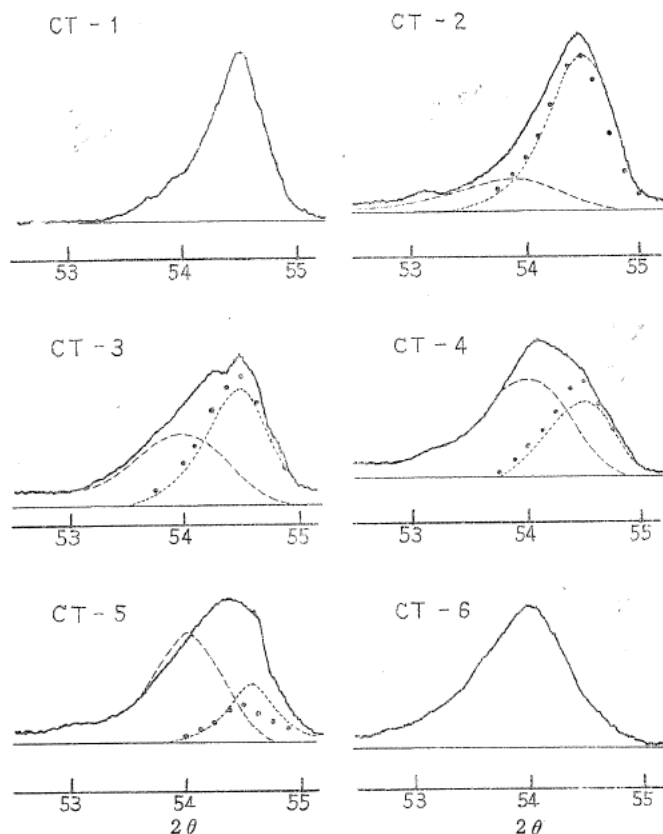


FIG. 3. Diffraction profiles of mixtures of graphitized coke and carbon black.

The solid lines show the composite profiles or single profiles, the dotted lines and circles the profiles of coke, and the broken lines the profiles of carbon black.

called a composite profile and a profile of only one raw carbon material is called a single profile.

A diffraction profile is modified by a degree of the preferential orientation of graphite crystallites in a sample, and the degree of the crystallite orientation may differ from sample to sample. But, in the case of carbon black, the crystallite orientation need not be taken into account and so the value of  $f$  in Eq. 4 may be taken to be 1. Therefore, the single profile of carbon black can be directly introduced to each composite profile by using Eq. 4. The result of introduction of the single profile of the thermal black into each composite profile is shown with broken line in Fig. 3. Each specimen was composed of the pitch coke and the thermal black, so the composite profile must also be composed of the single profiles of both carbons. Therefore, the balance should be the profile of the pitch coke when the profile of the thermal black was subtracted from each composite profile. The profile of the pitch coke thus obtained is shown with dotted line in Fig. 3.

The single profile of the coke can also be introduced quantitatively into the composite profiles by the use of the orientation coefficient and Eq. 4. The single profile of the coke thus obtained is shown with circles in Fig. 3. The coincidence of the results can be said to be satisfactorily well, taking account of errors in the measurement of the orientation coefficient and in the introduction of the single profile into the composite profile.

The integrated intensities of the separated profiles of coke and carbon black,  $I_{\text{coke}}$  and  $I_{\text{black}}$ , were obtained by measuring the areas under these profiles with a planimeter. Intensity ratios,  $f \cdot I_{\text{coke}} : I_{\text{black}}$ , are shown in Table I. It can be seen that the intensity ratio agrees closely with the mixing ratio of the component carbons.

From this experiment, the following conclusions can be drawn. First, the composite profile of electrographitized coke and carbon black can be separated into two profiles of the component carbons by the use of Eq. 4. Secondly, the ratio of the integrated intensities of these two component carbons is directly proportional to the mixing ratio of these carbons, when the effect of the orientation of graphite crystallites on the diffraction intensity is corrected for.

*Profiles of graphitized products*—So far, mixtures of graphitized coke and carbon black were used as samples. However, most of commercial products are made from coke, carbon black, or a mixture of these raw carbon materials bonded by binder pitch, and then baked and graphitized, that is to say, commercial products contain calcined or graphitized binder in addition to carbon fillers. Accordingly, (001) diffraction profiles of commercial products are composed of profiles of component carbons, such as coke, carbon black and coke derived from binder pitch (binder coke).

The following samples were prepared for the investigation. A calcined petroleum coke was mixed with a thermal black or a furnace black at various ratios. The mixtures were moulded by using the same proportion of binder pitch, baked at 850°C and graphitized in a carbon granular resistance furnace at 3,000°C. Mixing ratios of the component carbons and bulk densities of the graphitized products are shown in Table II. For X-ray analysis, flat specimens of  $0.750 \pm 0.005$  mm. thick with their planes parallel to the pressing direction were cut out



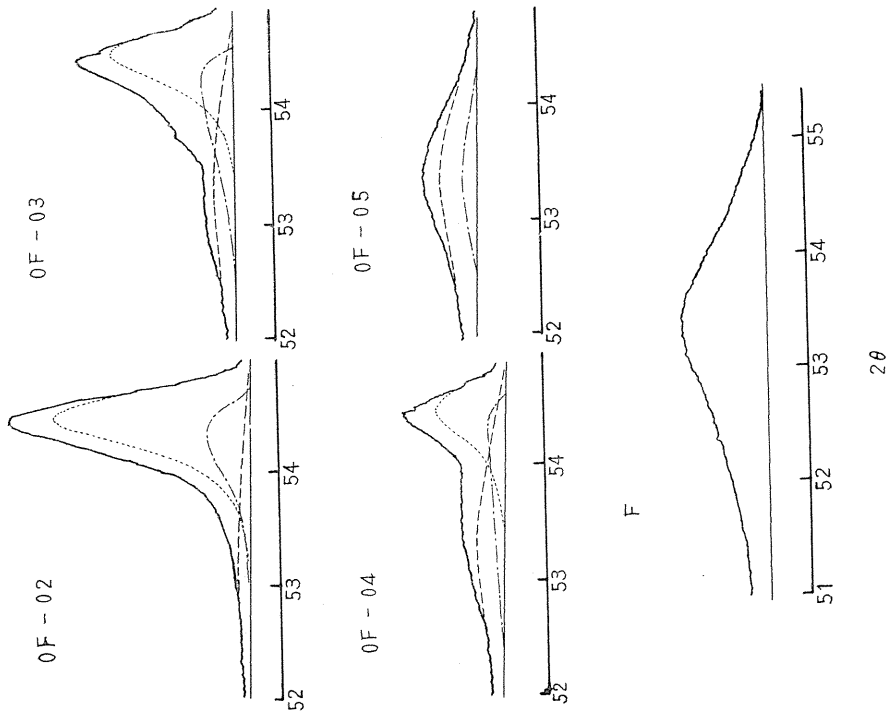


FIG. 4. Diffraction profiles of graphitized products. The solid lines show the composite profiles or the single profiles, the dotted lines the profiles of coke, the broken lines the profiles of carbon black and the chain lines the profiles of binder coke.

from the products. Using the same procedure as mentioned in the previous section, the (004) diffraction profiles and the orientation functions  $I(\phi)$  of graphite crystallites were obtained for all specimens. The composite profiles and the single profiles are shown with solid lines in Fig. 4, and the orientation coefficients which were calculated from the orientation functions of the products are shown in Table II.

TABLE II. Mixing ratio, bulk density, orientation coefficient and intensity ratio of graphitized products

a. bonded by polyester resin.

b. pulverized to pass a 150 mesh sieve.

c. T stands for thermal black and F for furnace black.

Specimen number	Mixing ratio			Bulk density (g/cm <sup>3</sup> )	Orientation coefficient	Intensity ratio		
	Coke	Carbon black <sup>c</sup>	Binder pitch			Coke	Carbon black	Binder coke
O <sup>a</sup>	100			1.60	1.37			
T <sup>b</sup>		F 100		1.00	1.00			
F <sup>b</sup>		F 100		0.42	1.00			
OT-01	100	T 0	40	1.56	1.21	100	0	18
OT-02	80	T 20	40	1.38	1.43	80	19	20
OT-03	60	T 40	40	1.57	1.38	60	39	18
OT-04	40	T 60	40	1.61	1.18	40	57	17
OT-05	0	T 100	40	1.66	1.00	0	95	25
OT-11	100	T 0	55	1.31	1.08	100	0	24
OT-12	80	T 20	55	1.49	1.08	80	19	26
OT-13	60	T 40	55	1.74	1.14	60	38	27
OT-14	40	T 60	55	1.43	1.10	40	58	28
OT-15	0	T 100	55	1.82	1.00	0	95	34
OF-01	100	F 0	40	1.56	1.21	100	0	18
OF-02	80	F 20	40	1.51	1.20	80	18	22
OF-03	60	F 40	40	1.43	1.21	60	35	26
OF-04	40	F 60	40	1.35	1.06	40	55	19
OF-05	0	F 100	40	1.25	1.00	0	90	18

Using Eq. 4, the single profiles of coke and carbon black were subtracted graphically from each composite profile. The balance should be profile of the binder coke. In Fig. 4, the profile of coke is shown with dotted line, the profile of carbon black with broken line and the profile of binder coke with chain line.

In introducing the profiles of the coke and the carbon black, the weight contents of the component carbons in the products were calculated on the assumption that the coking yield of binder pitch was 50%.

The integrated intensity ratio was obtained by measuring the areas under the separated profiles and correcting for the crystallite orientation. The results are shown in Table II. It can be seen in the table that the intensity value for carbon black is somewhat smaller than the mixing value. This may be explained by the assumption that the weight loss of carbon black in the course of baking and graphitization is larger than that of coke.

The expected intensity value of binder coke is 20 or 27.5 parts for the samples listed in Table II, because the coking yield of the binder pitch was assumed to be 50%. The intensity values of binder coke of all samples except two are ap-



proximately equal to the expected values. Accordingly, it can be concluded that the integrated intensity ratio is directly proportional to the mixing ratio of component carbons if the crystallite orientation and the weight loss in the course of heat treatment are taken into consideration. For samples OT-05 and OT-15, the intensity values of binder coke are higher than the expected values. This can be inferred, however, from the presumption that the coking yield of pitch is greater than 50% in the sample which contains carbon black only.

*Graphitizability of binder pitch in graphitized product*—It has been surmised from many investigations that pitch is difficult to be graphitized when it is used as binder of carbon fillers. In applying a similar procedure to graphitized products, which were made from mixtures of coke, carbon black and binder pitch, the values of  $c_0$  of binder coke in the products were found to be 6.80~6.76 Å<sup>7)</sup>. In the present work, the profiles of binder coke were accurately separated and the lattice constant  $c_0$  and the size of graphite crystallite  $L_c$  of the coke were measured. The results are shown in Table III. The value of  $c_0$  of the binder

TABLE III. Lattice constant  $c_0$  and crystallite size  $L_c$  of binder coke in graphitized products

Specimen number	Lattice constant $c_0$ (Å)	Crystallite size $L_c$ (Å)
OT-01	6.76	260
OT-02	6.76	190
OT-03	6.75	220
OT-04	6.79	170
OT-05	6.80	170
OT-11	6.74	280
OT-12	6.77	130
OT-13	6.77	200
OT-14	6.77	190
OT-15	6.82	140
OF-01	6.76	260
OF-02	6.74	240
OF-03	6.76	170
OF-04	6.76	140
OF-05	6.83	150
Binder coke without the admixture of carbon fillers	6.71	340

coke in the graphitized products was from 6.74 Å to 6.83 Å, while the value of  $c_0$  of the coke derived from the same pitch without the admixture of carbon fillers was 6.71 Å. From this result, it can be seen that pitch is less graphitizable when it is heat-treated with the admixture of carbon fillers than without it. This fact may be explained by the following reasoning. When pitch softens in the process of coking, large molecules having graphite-like layer structure may move and orient themselves along the flowing line. When binder pitch is mixed with carbon fillers, it may form thin films around carbon particles and consequently its flow may be so restricted that the degree of preferential orientation of the layer molecules is largely decreased. It was already shown that, in the grains of

graphitizing carbons, the graphite-like layers roughly aligned with their c-axes approximately normal to the layer axis of the grain, but this structure was not observed in the non-graphitizing carbons<sup>8)</sup>. So this preferential orientation of the graphite-like layers is one of the most important factors in the graphitization of carbon. Furthermore, pitch may be more oxidized in a filmy state than in a bulky state<sup>9)</sup>. Therefore, a less graphitizable coke results from both the poor orientation of graphite-like layers and the oxidation of pitch.

When pitch is used as binder of coke filler, the lattice constant  $c_0$  of binder coke turns out to be a little smaller than when pitch is used as binder of a carbon black filler. Moreover, the size of crystallite  $L_c$  is larger in the former case.

### Conclusion

The profile of the (004) diffraction of graphitized carbon products can be separated graphically into the profiles of component carbons, such as coke, carbon black and binder coke. The intensity ratio is directly proportional to the mixing ratio of the component carbons, if the intensity is corrected for the effect of the preferential orientation of graphite crystallites and for the weight loss in the course of heat treatment. It is also found that pitch is less graphitizable when it is heat-treated with the admixture of carbon fillers than without it.

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