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GRAPHITIZATION PROCESSES IN COKE AND CARBON BLACKS

by

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ABSTRACT

The effects of heat treatments of 2000 to 4650 F on the structure of carbons from several sources have been investigated, using X-ray diffraction. Of particular interest was the effect of temperature on the degree of graphitization. The process of graphitization results in a larger graphite crystallite size in the a_0 direction, the plane of the layers, than in the c_0 direction. No correlation was found between the structure of the coke heated at 2000 F and the degree of graphitization attained at 4650 F. Materials coked in a closed retort yielded a more perfect graphite structure than the same material coked with access to air. Carbon blacks yield graphite with a greater c_0 lattice constant than cokes with comparable crystallite sizes.

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INTRODUCTION

The structure of carbons and artificial graphites depends upon the source material and its method of heat treatment. A study has been made of the degree of graphitization of carbons from several sources produced by heat treatments of from 2000 F to 4650 F. Source materials were coal-tar pitches, petroleum asphalts, phenolic resins, sugar, and liquid or gaseous fuels.

The structures of the carbons and graphites were determined from analyses of their X-ray diffraction patterns. The disordered cokes and carbon blacks have an X-ray diffraction pattern of diffuse bands appearing about at positions for the (00.2) and (10.0) reflections of graphite. Warren⁽¹⁾ has shown that carbon black has a two-dimensional layer structure and his theory⁽²⁾ of diffraction by random layer lattices accounts for the asymmetry of the two-dimensional (10) and (11) bands. The resolution of (hkl) graphite reflections from the diffuse (hk) carbon bands was taken as the criterion for the formation of graphite. The formation of graphite from coke is a process of crystal growth. This growth causes a decrease in diffraction-line breadth which was used as a measure of the crystal growth.

PREPARATION OF MATERIALS

The sources of the materials selected for study are shown in Table 1.

Cokes were prepared in the laboratory from the petroleum asphalts and coal-tar pitches by two different methods: (1) in a rotary drum with air flowing through the drum during coking, and (2) in a closed retort.

In the first method, a 6-gal-capacity metal drum was partly filled with the material to be coked and then heated while being rotated, in a horizontal position, about its central axis. The asphalt adhering to the inner walls of the drum provided a large surface area for removal of volatiles. The temperature of the drum was gradually increased to about 950 F while the drum was being revolved and flushed with air. The volume of air passed through the drum was about 0.7 cfm. The temperature was measured by means of a thermocouple inserted into the asphalt from one end of the drum. Heating was continued until all condensable volatiles were removed. This usually required about 16 hr when starting with an initial volume of about two gallons of the material to be coked.

In the second method, the materials were reduced to coke by heating to approximately 950 F in a covered cast iron retort having an exhaust

(1) References given at end of report.

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TABLE 1. SOURCE MATERIALS FOR COKES AND CARBON BLACKS

Material Designation	Source
Coke from soft pitch	Coal tar pitch
Coke from medium pitch	Ditto
Coke from hard pitch	"
"K" coke, commercial	"
"B" coke, commercial	Petroleum asphalt, low sulfur
"C" coke, commercial	Petroleum asphalt, high sulfur
Coke from air-blown asphalt	Petroleum asphalt, low sulfur
Coke from straight-run asphalt	Petroleum asphalt, low sulfur
Ditto	Petroleum asphalt, high sulfur
Coke from "O" Korite	Petroleum asphalt
Coke from No. 4 Korite	Ditto
Coke from Stanolite	"
Coke from 79 LHS resin	Phenol-formaldehyde
Coke from sugar	Sucrose
Thermax carbon black	Gas
Vulcan No. 3 carbon black	Liquid fuel (oil)
Spheron N carbon black	Gas
Philblack carbon black	Liquid fuel (oil)
Statex 93 carbon black	Gas

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vent. The escape of volatiles from the closed retort essentially prevented contact of the asphalt with air during coking.

As a further heat treatment, the cokes obtained by each of these methods were calcined by heating to 2000 F or higher in a closed refractory container.

The coke prepared from phenol-formaldehyde resin was the carbon residue obtained upon calcining the cured resin at 2000 F in the closed refractory container.

The coke derived from sugar was the residue obtained after carbonizing cane sugar with hydrofluoric acid and then calcining at 2000 F. The carbon yield by this process was about 20 per cent of the original sugar.

The carbon blacks studied were commercial products resulting from the thermal decomposition of liquid or gaseous fuels.

HEAT TREATMENT AND PREPARATION OF SPECIMENS

The samples prepared for X-ray studies consisted of (1) unbonded cokes and carbon blacks, and (2) specimens formed from these materials by compression molding.

In the fabrication of molded specimens, the calcined cokes were pulverized to a fine flour, and then mixed with a binder consisting, in most cases, of the pitch or asphalt from which the coke was made.

The amount of binder used was adjusted to provide a suitable mixture for compression molding. The molded specimens then were heated at 2500 F for 4 hr to set the binder carbon and were subsequently heated to a temperature of about 4650 F for 4 to 6 hr. In addition, some of the specimens were heated to a lower temperature of 3700 F for 4 hr.

X-RAY DETERMINATIONS

The samples were examined on a Norelco X-ray spectrometer using filtered CuK α radiation. For the coke samples with a diffuse band pattern, the white radiation was eliminated by use of balanced filters of nickel and cobalt.⁽³⁾ The diffraction-line breadths at half-maximum height were measured and corrected for instrumental broadening by the method of

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Jones⁽⁴⁾. The instrumental corrections were obtained from measurement of diffraction lines of annealed tungsten powder which was mixed with the powdered sample in amounts up to fifteen weight per cent. From the breadths at half-intensity, the crystallite dimensions were calculated assuming only particle-size broadening and no effect of lattice distortion caused by micro strains. Only in well-developed graphites would the contribution of lattice distortion become appreciable.

The dimension in the direction of the c_0 axis is denoted "C" while that in the direction of the a_0 axis is "A". The "C" dimension was calculated from the (00.2) line. In general, the (00.4) line showed increased broadening, indicative of some distortion of the layer spacing. The "A" dimension was calculated for disordered carbons from the (10) and (11) diffuse bands using Warren's⁽²⁾ equation for two-dimensional lattices. For graphite samples the "A" dimension was calculated using the normal particle-size equation.

The graphitized cokes exhibit a varying amount of disorder in the stacking of the layers. This disorder may be in the form of random translation or rotation of the carbon layers or variation in interlayer spacing. Either type of disorder will cause increased broadening of general (hkl) reflections. As a measure of this stacking disorder, the average distance "t" between stacking mistakes in the direction of the c_0 axis was determined from the breadth of the (11.2) line using Wilson's equation⁽⁵⁾. This measure is an inverse function of the proportion of disoriented layers as determined by Franklin⁽⁶⁾.

RESULTS

The data on crystallite size and structure of the carbons examined are listed in Tables 2 and 3 under their corresponding temperatures of treatment. Figures 1 and 2 show a correlation of crystallite sizes "C" and "A" with the lattice constant, c_0 . Specimens with crystallite dimensions greater than 220 Å were not shown on the curves in order to have an expanded ordinate scale. There is a marked increase in crystallite size for specimens with a lattice constant, c_0 , of 6.75 Å or less. Using, as criterion for graphitization, the resolution of (hkl) graphite lines from (hk) carbon bands, it was found that specimens with c_0 greater than 6.75 Å were not graphitized. Considering the "t" as a measure of disorder, it is shown that c_0 decreases with increasing perfection of the layer stacking. The "t" dimension was derived from the (11.2) line; however, analysis of the breadth of the (10.1) line in patterns of the more-graphitized specimen gave comparable values of "t" dimension. This agreement of "t" values for different lines would indicate that the distribution of stacking disorders is random, as concluded by Franklin⁽⁶⁾.

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TABLE 2. CRYSTALLITE SIZES OF VARIOUS CARBONS AS A FUNCTION OF HEAT TREATMENT

No.	Material Type	Remarks	Crystallite Dimensions, Å											
			2000 F (a)			2500 F			4050 F					
			A	C	c_0	A	C	c_0	A	C	c_0	A	C	c_0
1	79L-115 Resin	Coked in refractory container	55	9	7.4	44	11	7.1	60	30	6.90			
2	Sugar carbon		46	11	7.6				60	39	6.30			
3	"B" coke	Bonded with "O" Korite	27	22	7.0	47	39	6.8	> 1000	425	6.75	24		
4	"B" coke	Bonded with "O" Korite				60	38	6.9	> 1000	650	6.73	27		
5	"B" coke	Bonded with No. 4 Korite							> 1000	450	6.71	29		
6	"C" coke	As received	16	24	7.0									
7	"K" coke		36	22	7.0	51	34	6.9	330	250	6.74	11		
8	Hard coal-tar pitch	Rotary drum coked with air accen	45	22	6.95	50	34	6.9	470	330	6.74	11		
9	Soft pitch	Ditto	41	18	7.0				165	115	6.75	11		
10	Medium pitch	-	37	12	7.3				195	130	6.82	11		
11	Air-blown asphalt	-	26	18	7.1	51	33	6.9	435	187	6.36	11		
12	Straight-run asphalt, low sulfur	-	35	18	7.05	49	26	6.9	475	156	6.77	10		
13	Straight-run asphalt, high sulfur	-	40	15	7.15				145	110	6.78	11		
14	"O" Korite	-	40	14	7.15				85	75	6.82			
15	4 Korite	-	42	16	7.05				40	36	6.82			
16	Stanolite	-	52	18	7.05				90	100	6.74			
17	Straight-run asphalt, low sulfur	Coked in a retort				47	31	6.90	240	244	6.74	11		
18	Straight-run asphalt, high sulfur	Ditto				76	38	6.88	190	213	6.75	11		
19	"O" Korite	-				44	33	6.90	250	220	6.76			
20	4 Korite	-				49	32	7.00	279	206	6.87	11		
21	Stanolite	-				49	33	6.90	130	220	6.71			

(a) The specimens heated at 2000 F were unbonded coke.

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TABLE 3. CRYSTALLITE SIZES OF CARBON BLACKS AS
A FUNCTION OF HEAT TREATMENT

No.	Material Type	Crystallite Dimensions, A											
		As Received			2500 F			3700 F			4650 F		
		A	C	c ₀	A	C	c ₀	A	C	c ₀	A	C	c ₀
22	Thermax	39	16	7.12	47	30	7.04	79	80	6.90	150	160	6.85
23	Spheron N	29	12	7.42	39	17	7.50	54	35	6.94	54	22	7.13
24	Philblack	29	13	7.32									
25	Statex 93	27	16	7.13									
26	Vulcan 3	25	15	7.36	33	26	7.04	58	18	7.13	52	47	7.0
27	Thermax ^(a)				50	32	7.00	109	124	6.86	100	138	6.86
28	Spheron N ^(a)				48	18	7.13	58	30	7.03	62	34	6.94

(a) Specimen bonded with hard coal-tar pitch.

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FIGURE 1. PLOT OF CRYSTALLITE SIZE C VERSUS LATTICE CONSTANT C_0 FOR COKES

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FIGURE 2. PLOT OF CRYSTALLITE SIZE A VERSUS LATTICE CONSTANT C_0 FOR COKES

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Figures 3 and 4 show the variation of crystallite size with lattice constant, c_0 , for the carbon black specimens. Only the Thermax developed a graphite structure. In the case of the carbon blacks, there was a sharp increase in crystallite size in specimens with c_0 values of 6.85 to 6.90 Å. The curves of Figures 3 and 4 are shifted toward higher values of c_0 as compared with those of Figures 1 and 2, representing values for the coke specimens. Thus, a carbon black has a greater interlayer spacing than a coke with comparable crystallite size. This would indicate greater stacking disorder in carbon blacks, perhaps with interstitial carbon atoms lying between carbon layers, hindering alignment of the layers into the graphite structure.

The relation of crystallite size "A" to "C" has been plotted in Figures 5 and 6. These show a greater increase in the layer dimension "A" than in the stacking dimension "C", with increased crystallite size. Figure 5 shows the data for specimens heated at low temperatures and for those which were not graphitized at higher temperatures.

CONCLUSIONS

A comparison of the Figures 1, 2, 3, and 4 reveals that both the cokes and carbon blacks have a crystallite dimension, A, in the a_0 direction about twice that of dimension C, in the c_0 direction. With graphitization, this proportion is maintained, and even increased, in the case of the cokes prepared with access to air. However, the same asphalts, when coked in a retort without access to air, gave graphites with crystallite dimensions "A" and "C" approximately equal. The cokes thus prepared also had less stacking disorder when graphitized. This variation in graphitization between samples coked in air and in a closed retort may be caused by the relative effect of oxidation versus dehydrogenation. Oxidation of the asphalts coked in the presence of air may have caused a disruption of incipient graphite layers, with an increase of oxygen bound to the carbon, and an increase in porosity. The retort coking is essentially dehydrogenation under partial reducing conditions and would result in less breaking of carbon-carbon bonds, lower oxygen content, and less porosity.

The high oxygen content of the sugar carbon and resin carbon may produce porosity and disrupted carbon-carbon bonds, and thus prevent the development of graphite from these materials. These conclusions are, in general, similar to those of Franklin⁽⁷⁾. However, her classification of carbons into two classes, (1) graphitizing and (2) nongraphitizing, is not borne out for our materials. The curves of Franklin for the two classes of carbons are drawn in Figures 5 and 6. It is evident that very few of our specimens lie on the lower curve for graphitizable carbons. There was no

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FIGURE 3. PLOT OF CRYSTALLITE SIZE C VERSUS LATTICE CONSTANT C_0 FOR CARBON BLACKS

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FIGURE 4. PLOT OF CRYSTALLITE SIZE A VERSUS LATTICE CONSTANT C FOR CARBON BLACKS

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FIGURE 5. PLOT OF CRYSTALLITE SIZES A VERSUS C FOR COKES AND CARBON BLACKS
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FIGURE 6. PLOT OF CRYSTALLITE SIZES A VERSUS C FOR
COKE AND CARBON BLACKS

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difference in crystallite sizes of the low-temperature specimens of cokes which graphitized well, as compared with cokes which did not graphitize at 4650 F. It should be noted that the curve shown by Franklin for graphitizable carbon would indicate a greater increase of the "C" dimension than of the "A" dimension. This, however, has not been observed with either the cokes or the carbon blacks used in these studies. Franklin advances the concept of graphitization by movement of whole layers of carbon atoms, with a higher probability of their being oriented parallel to the basal plane, rather than becoming attached to the edge-atoms of a layer. However, the greater growth of the layer dimension would indicate that in graphitization the layers join edgewise more frequently than by alignment of layers in stacking.

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