

X-Ray Diffraction Studies on Carbon Gasification

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TO DATE there has been no attempt to correlate the important structural factors of the carbon crystallite with its gasification rate or to follow any possible change in these factors as gasification proceeds. Two of the most important structural factors of a carbon crystallite are its size and the spacing between the layer planes that make up the crystallite. In this work, these two factors have been followed during the gasification of an artificial graphite in an attempt to relate their importance to the gasification mechanism.

Their importance has been previously suggested by other authors. Long and Sykes (13) postulated that the top and bottom edge carbon atoms of a crystallite are more reactive than the others. It is then seen that the smaller crystallites, with their higher concentration of edge atoms per unit weight, should be more reactive than the larger crystallites. As it is known that carbons are composed of a range of crystallite sizes, which is determined by the nature of the carbon and its past thermal history, possible preferential reaction of the smaller crystallites during gasification could play an important part in its reactivity and produce a change in the average crystallite size of the carbon. In this investigation, therefore, the change in average crystallite size—as determined by x-ray diffraction line broadening—with degree of gasification has been explored in an attempt to get information on possible preferential reactivity of the small carbon crystallites.

In regard to interlayer spacing in carbons, both Bacon (5, 6) and Franklin (9) have shown that true graphite has a spacing of 3.354 Å. and that amorphous carbons which are graphitizable have a spacing of 3.44 Å. at 15° C. A carbon with an intermediate spacing is considered to be composed of certain fractions of graphitic and nongraphitic (or amorphous) carbon, which may be estimated from the interlayer spacing. Therefore, by following the progress of the average interlayer spacing (*c*-dimension) of carbon during gasification, it is possible to obtain information on the trend of the remaining carbon toward more or less graphitic material.

APPARATUS AND CARBONS USED

In the present investigation, a 164° (2θ) General Electric x-ray diffraction unit, XRD-3, with copper radiation was used. Throughout the work an x-ray slit width of 1° and a detector slit width of 0.1° were employed. The intensities at selected angles were determined by a Geiger counter connected to an electric timer which allowed counting a preselected number of counts and recording the time. The Geiger counter was mounted on a goniometer, so that patterns could also be plotted over a desired range of angles on a recording Leeds & Northrup potentiometer.

The carbon samples, rods 0.5 inch in diameter and 2 inches long, were gasified with carbon dioxide at 1100° C. in the apparatus described in connection with earlier studies of reaction rate (17).

For the majority of the gasification work, an artificial graphite produced at 2500° C. was used. Several samples of commercial "gas-baked" carbon, similar to that from which the graphite was made, were also investigated. This carbon was an admixture of approximately 87% gas-baked carbon formed at 1000° C. and 13% of the artificial graphite. Detailed descriptions of these carbons have been published (17).

In order to establish the quality of the artificial graphite both before and after gasification, No. 635 finely powdered natural Ceylon flake graphite (27.5 ± 7.5% on 200-mesh screen, U. S. sieve series, 25 ± 5% through 325-mesh screen) and No. 200-09

air-spun micronized Ceylon graphite (having an average particle size of 5 microns), both supplied by the Joseph Dixon Crucible Co., were used as standards representing pure graphitic carbon.

EXPERIMENTAL PROCEDURE

Both the reacted and unreacted carbon samples were prepared for x-ray diffraction measurements by first grinding them with an agate mortar and pestle to pass through a 200-mesh screen and thoroughly mixing them before sampling. A sample of the carbon was then intimately combined with high-purity grade (-200-mesh) sodium chloride, 18 ± 0.1% by weight. Then 30.5 ± 0.3 mg. of the mixture was weighed on each glass slide to give the desired number of samples. The mixture was dispersed in collodion and amyl acetate over an area of 3/8 sq. inch of the slide and allowed to dry. The sample thickness on the slide was measured by a micrometer as 0.006 to 0.010 inch, depending upon the density of the carbon.

DETERMINATION OF INTERLAYER SPACING. Figure 1 presents a typical x-ray diffraction pattern for a mixture of the artificial graphite and sodium chloride. The admixed sodium chloride was used as an internal standard to determine both crystallite size and interlayer spacing of the carbons—that is, for each sample, in addition to determining the graphite peaks, the sodium chloride angles and corresponding *d*-values were determined for the (200), (220), and (222) peaks. These experimental *d*-values were then compared with the absolute values calculated from the sodium chloride lattice constant of 2.8200 Å. at 25° ± 1° C. [This lattice constant was determined experimentally using a General Electric powder camera which has a diameter of 143.2 mm. The sodium chloride was smeared over a glass tube, less than 0.5 mm. in diameter, after being admixed with collodion. The film was mounted in the Straumanis position. The lines were read off to the nearest 0.1 mm. and the data were extrapolated to 180° (2θ) by the technique of Nelson and Riley (14). The value reported above was the average of two determinations and agrees well with the value of Straumanis (16).]

In order to determine the absolute spacing of sodium chloride at temperatures other than 25° ± 1° C., its coefficient of expansion was taken as 4.02×10^{-6} (10). The error in angle was plotted against angle over the range 31.7° to 56.5°, and the experimental *d*-spacings of the carbon, determined from the (004) diffraction peak (54.6°), were then corrected using this correlation to give an absolute *d*-spacing.

DETERMINATION OF CRYSTALLITE SIZE. For the determination of crystallite size of the carbon, the admixed sodium chloride was assumed to consist of infinitely large crystallites. The sodium chloride was not subjected to rigorous grinding procedures; and although no data on particle size distribution were obtained, it is thought to have an average particle size, on a weight basis, well above 1 micron. Since the crystallite size of sodium chloride essentially equals the particle size, this would suggest an average crystallite size also in excess of 1 micron, which is well above the size that causes detectable line broadening. The large size of the sodium chloride crystallite makes it possible to determine from its (200), (220), and (222) diffraction peaks the half-peak-intensity line broadening produced by the inherent x-ray machine factors [called *b₀* by Alexander and Klug (4)], exclusive of broadening from the crystallites, at angles of 31.5°, 45.6°, and 56.7°. By interpolation of these data, it is possible also to determine the line broadening, *b₀*, which the ma-

TABLE I. INTERLAYER SPACING OF ARTIFICIAL GRAPHITE RODS

Description of Graphite	Spacing 15° C., A.	Average Spacing, A.
Unreacted rod 1 1/16-inch outside scrapings - 1/16-inch scrapings	3.3601	3.3601
	3.3600	
	3.3602	
	3.3599	
Unreacted rod 2, whole rod used as sample	3.3603	3.3602
	3.3602	
Rod 3, 10% gasified Outside 1/16-inch scrapings Inside 1/4-inch plug	3.3576	3.3579
	3.3581	
	3.3599	
	3.3599	
Rod 4, 45% gasified, whole rod used as sample	3.3582	3.3581
	3.3579	
	3.3583	
	3.3583	
Rod 5, 85% gasified, whole rod used as sample	3.3577	3.3579
	3.3580	
	3.3580	
	3.3580	

chine factors give the carbon x-ray diffraction peaks at their particular angles. The half-peak widths of the carbon diffraction peaks [the (002), (100), and (004) peaks corresponding to angles of 26.6°, 42.5°, and 54.5° were used] can also be determined.

The broadening of the carbon peaks is caused by a combination of machine factors and the diffraction from the crystallites [called B_0 by Alexander and Klug (4)]. Because the diffraction peaks under study occur at relatively low Bragg angles, the correction for the $K\alpha$ doublet line broadening (11) can be neglected, thereby resulting in b_0 and B_0 equal to b and B , respectively. By then using the graph of Alexander and Klug (3) for the new spectrometer [similar to Figure 1 (4) for the older spectrometer], which plots β/B against b/B , one can determine β , the true half-peak width line broadening produced by the average crystallite size in the sample. The average crystallite size is then calcu-

lated from the line broadening by the von Laue equation (7), $\bar{L} = \frac{0.89 \lambda}{\beta \cos \theta}$, where λ is the wave length of the copper radiation and θ is the Bragg angle at which the peak occurs. Both \bar{L}_c and \bar{L}_a , the average height and diameter of the crystallites, can be calculated from the above equation.

Both the carbon and sodium chloride x-ray diffraction peaks were measured by using the Geiger counter and timer to evaluate x-ray intensities. Sufficient counts were taken to permit determination of intensities with a probable error from counting statistics of 2% or less. The superior reproducibility of this counting technique over the recorder has been demonstrated by Klug, Alexander, and Kummer (12) in studies on pure quartz and verified by the authors in studies on carbons.

The initial step was to determine the intensity readings in counts per second at angles of 20°, 30°, 35°, 40°, 50°, and 58° in order to locate the background profile where no peaks existed. The angle could accurately be set to the nearest 0.01° on the machine. The next step was to locate the angles and intensities of the diffraction maxima for the peaks in question. With this information, the intensity of the peaks could be calculated by subtracting the background found by interpolating between the values of the angles listed above from the count at maximum intensity. The intensity of half-peak height then was calculated by adding one half the peak intensity to the background. Then counts were made on both sides of each peak above and below the half-peak intensity values. These data were plotted to a large scale (the sides of the peak over the small-angle increment were assumed to be straight lines), and the widths at the half-peak intensity determined.

These data served two purposes. The angles used in the Bragg equation to determine the spacing of the carbon and sodium chloride were taken as the middle of the half-peak widths and the widths themselves used for determinations of crystallite size.

DETERMINATION OF PEAK INTENSITIES. Some samples were also prepared to determine the intensities of the (002) and (100) diffraction peaks of the carbons.

In order to decrease orientation of the carbon particles and to get stronger intensities, -200-mesh carbon was dropped into a hole 0.5 inch in diameter contained in a nickel slide 1/16 inch thick. After the slide had been filled with carbon, a 50-gram weight was placed on top of the carbon pile to pack it to a constant pressure, and the excess was scraped from the top with a spatula. A glass slide was then taped over the hole, the slide was inverted, and a similar glass plate on which the sample had been dropped was taken from the bottom. The slide was now ready for the x-ray machine.

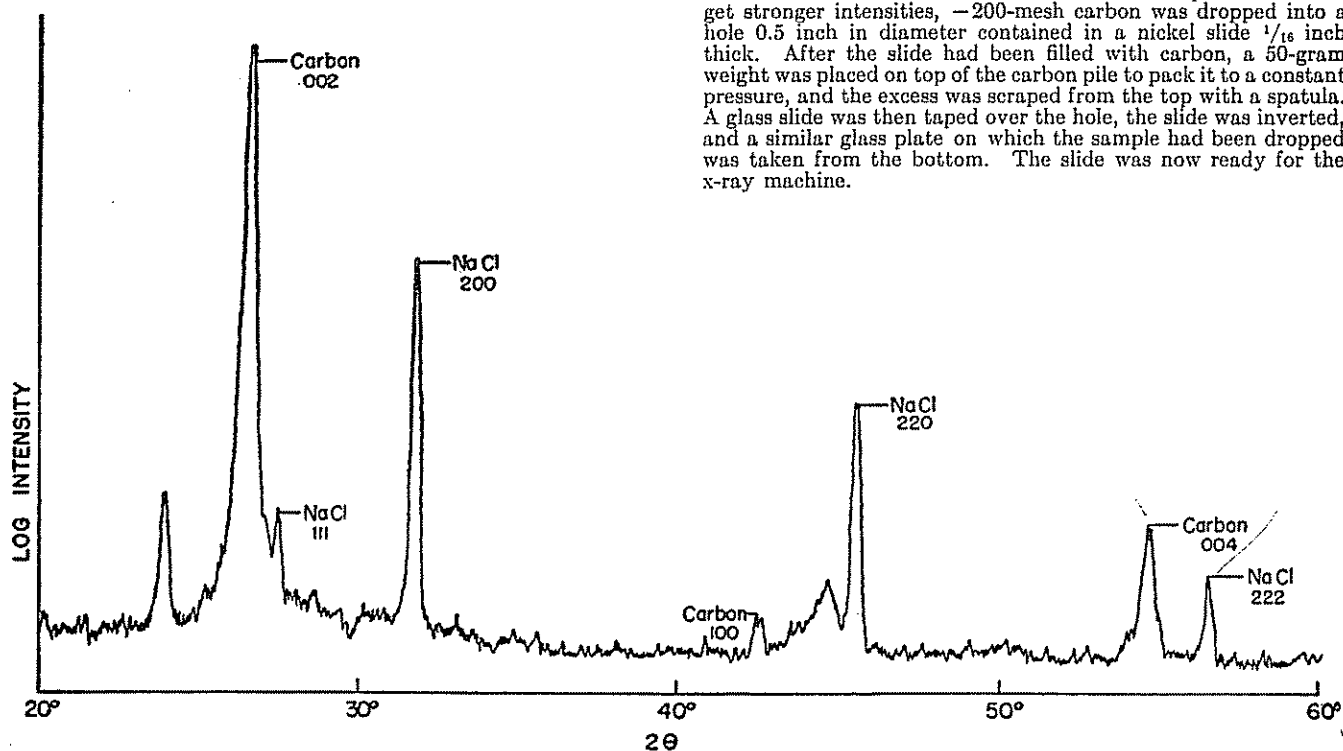


Figure 1. Typical X-Ray Diffraction Pattern of 18% Sodium Chloride-82% Graphite Mixture

Copper radiation

RESULTS

VARIATION OF INTERLAYER SPACING OF ARTIFICIAL GRAPHITE WITH GASIFICATION. Table I presents the data on the interlayer spacing at 15° C. of the artificial graphite before and after varying degrees of gasification. Initially it was necessary to determine how closely the *c*-spacing on the same material could be duplicated, in so far as it would be affected by x-ray diffraction technique and sampling procedure. With this information, possible true differences in interlayer spacing as caused by differences in the carbon could be ascertained.

To obtain an indication of how uniform the interlayer spacing was within a rod, $\frac{1}{16}$ inch was scraped from the exterior of a $\frac{1}{2}$ -inch rod, its interlayer spacing determined, and the interlayer spacing also determined on the remainder of the rod. This seemed to be the most logical way to test for homogeneity, since the interior of the rods are thought to be heated to a somewhat higher temperature during graphitization than the exterior. The results of duplicate determinations, however, indicate that a possible temperature gradient during graphitization had no significant effect on variations in interlayer spacing between the interior and exterior of the sample. The whole of a second un-

reacted rod was then ground up and two determinations of *c*-spacing were made. The *c*-spacings, as determined on the two rods, agree closely. The agreement between rods and within a rod is at least within ± 0.0004 A., which is in line with previous results of the authors (18) during studies on the thermal expansion of graphite.

The interlayer spacings of samples of graphite gasified to various weight losses were next investigated. It is seen for the samples gasified to either 45 or 85% weight loss that the average interlayer spacing has decreased. The decrease in neither case is marked but is considerably outside experimental error. There is only a slight decrease, probably of no significance, in interlayer spacing in going from 45 to 85% weight loss.

To test further this apparent decrease in *c*-dimension of the residual carbon upon gasification, a sample gasified to a weight loss of 10% was examined. Petersen (15) has shown that after 11.1% of the graphite rod has been gasified at 1100° C., an inside plug 0.222 inch in diameter has still not reacted. This is based on the fact that the apparent density of this carbon has not changed from that of the unreacted carbon. As this graphite becomes porous on gasification (17), this is felt to be direct evidence that no reaction occurs in this plug. On the other hand, the outer periphery of this sample is highly reacted, as indicated by a marked increase in the porosity of the carbon. This rod reacted to 10% weight loss was then separated into two parts. An outer sample $\frac{1}{32}$ inch thick was scraped off the rod and a $\frac{1}{8}$ -inch core was drilled from the center of the rod, presenting both a completely unreacted portion and a highly reacted portion. X-ray diffraction determinations made in duplicate on these samples again show a decrease in interlayer spacing of the carbon, on the same rod, upon gasification. It is seen that the interlayer spacing of the reacted annulus is comparable to that of the samples gasified to either 45 or 85% weight loss. This is to be expected, if it is realized that this sample is also very highly reacted, even though the entire sample has been gasified to only a 10% weight loss.

In an attempt to compare these artificial graphite spacings with those of pure graphitic carbon, *c*-dimensions were determined on several samples of Ceylon natural graphite. Table II shows the data for both the "200-mesh" natural flake graphite (similar in particle size to the samples of artificial carbon) and 5-micron natural graphite. The interlayer spacings of these two samples have been compared to obtain information on the possible effect of variation in particle size of the carbon on this spacing. This was thought desirable, because it was conceivable that the differences in *c*-dimensions found between the unreacted and reacted samples of artificial graphite might be due to some differences in particle size. Comparison of the interlayer spacing values for the two samples of natural

TABLE II. INTERLAYER SPACING OF NATURAL GRAPHITE

Graphite	Spacing, 15° C., A.	Average Spacing, A.
200-mesh	3.3545	3.3546
	3.3547	
	3.3545	
5-micron	3.3549	3.3541
	3.3550	
	3.3549	

TABLE III. X-RAY DIFFRACTION DATA AND CALCULATED PARAMETERS FOR 45% GASIFIED GRAPHITE RODS

Back-ground	Counts per Second			Width, B	NaCl Width, b	b/B	β/B	β
	Peak	Peak above back- ground	Intensity at one- half peak					
SAMPLE 1								
15.8	64.5	48.7	40.1		0.249°			
15.6	107	91.4	61.3	Graphite 004 Peak 0.368°	0.246°	0.668	0.390	0.144
17.4	210	192.6	113.7	NaCl 220 Peak	0.233°			
18.2	31.7	13.5	25.0	Graphite 100 Peak 0.264°	0.225°	0.852	0.170	0.045
29.2	490	460.8	259.6	NaCl 200 Peak	0.198°			
34.0	2560	2526	1297	Graphite 002 Peak 0.260°	0.185°	0.713	0.335	0.087
SAMPLE 2								
15.7	61.8	46.1	38.8	NaCl 222 Peak	0.266°			
15.8	107	91.2	61.4	Graphite 004 Peak 0.358°	0.259°	0.725	0.325	0.116
17.2	218	200.8	117.6	NaCl 220 Peak	0.225°			
17.7	30.8	13.1	24.3	Graphite 100 Peak 0.259°	0.219°	0.848	0.175	0.045
29.6	460	430.4	244.8	NaCl 200 Peak	0.194°			
34.2	2420	2385.8	1226.6	Graphite 002 Peak 0.215°	0.183°	0.730	0.318	0.080
SAMPLE 3								
15.8	60.0	44.2	37.9	NaCl 222 Peak	0.289°			
16.2	120	103.8	68.1	Graphite 004 Peak 0.378°	0.277°	0.730	0.320	0.121
18.0	259	241	138.5	NaCl 220 Peak	0.222°			
18.8	34.3	15.5	26.5	Graphite 100 Peak 0.253°	0.217°	0.860	0.162	0.041
30.0	520	490	275	NaCl 200 Peak	0.198°			
35.0	2750	2715	1392.5	Graphite 002 Peak 0.259°	0.189°	0.730	0.318	0.082

graphite indicates that considerable variation in particle size below -200 mesh has an insignificant effect on layer spacing of the carbons. The interlayer spacing values checked exceedingly well within themselves. Furthermore, the slight increase in c -dimension concurrent with ultrafine sizing of the carbon is possible in line with some reduction in the crystallite size of the carbon. This possible decrease in crystallite size might be interpreted as characterizing a trend toward less graphitic material and increasing c -spacing.

VARIATION OF AVERAGE CRYSTALLITE SIZE OF ARTIFICIAL GRAPHITE WITH GASIFICATION. Next, the average crystallite size of the unreacted graphite rods was compared with rods gasified to 45 and 85% weight loss. The magnitude of the crystallite sizes reported is above 500 Å, which is stated as the limiting size for reasonable accuracy (4). According to Alexander and Klug, it is futile to attempt size measurements for crystallites larger than this, because the mandatory precision of the experimental measurements becomes too great for practical work. Despite these comments and because the experiments were carried out on a new and greatly improved spectrometer (not available for Alexander and Klug's earlier work), the possibilities of measuring crystallite sizes larger than 500 Å with some degree of consistency were investigated.

Table III presents the complete raw data for the three samples of artificial graphite gasified to a weight loss of 45%, in order to clarify the experimental procedure and to report the magnitudes of the line broadening at half-peak intensity which were measured. The intensity values in counts per second could be duplicated within 2%. For the broader peaks, particularly the (222) peak of sodium chloride and the (100) and (004) peaks of graphite, it was necessary to reproduce intensities with this accuracy in order to determine reasonably consistent values of crystallite size.

The intensities of the backgrounds for the three patterns are very consistent. There is some variation in maximum peak intensities and, consequently, like variations in the calculated intensities for the half peak. However, considering the possibilities of orientation of the graphite on the slides, slight variations in sample depth, and lack of complete mixing of the sodium chloride with the graphite, the intensity agreement is satisfactory. The sodium chloride widths, b , increase with increasing angle, necessitating an interpolation procedure to get b at the carbon angles, as discussed ear-

lier. The pronounced effect that a small error in line broadening angle can have on average crystallite size in this region is shown by the fact that changing the sodium chloride half-peak width value at the (002) diffraction peak of carbon sample 1 from 0.185° to 0.175° changes the calculated \bar{L}_c size from 930 to 820 Å.

Table IV presents data on crystallite size for the three samples of carbon. For each sample, diffraction peaks from three slides were counted in an effort to ascertain if there was any consistency in the results on the same carbon. The individual values vary from the average by as much as $\pm 15\%$ in some cases and as little as $\pm 5\%$ in others. In an effort to see if these variations were due to real differences in samples as well as in technique, samples 1 and 3 of the 85% gasified carbon were repeated; these duplicate runs failed to give results that were more consistent than results on different samples. The conclusion is that the deviation of the individual crystallite sizes from the mean for a

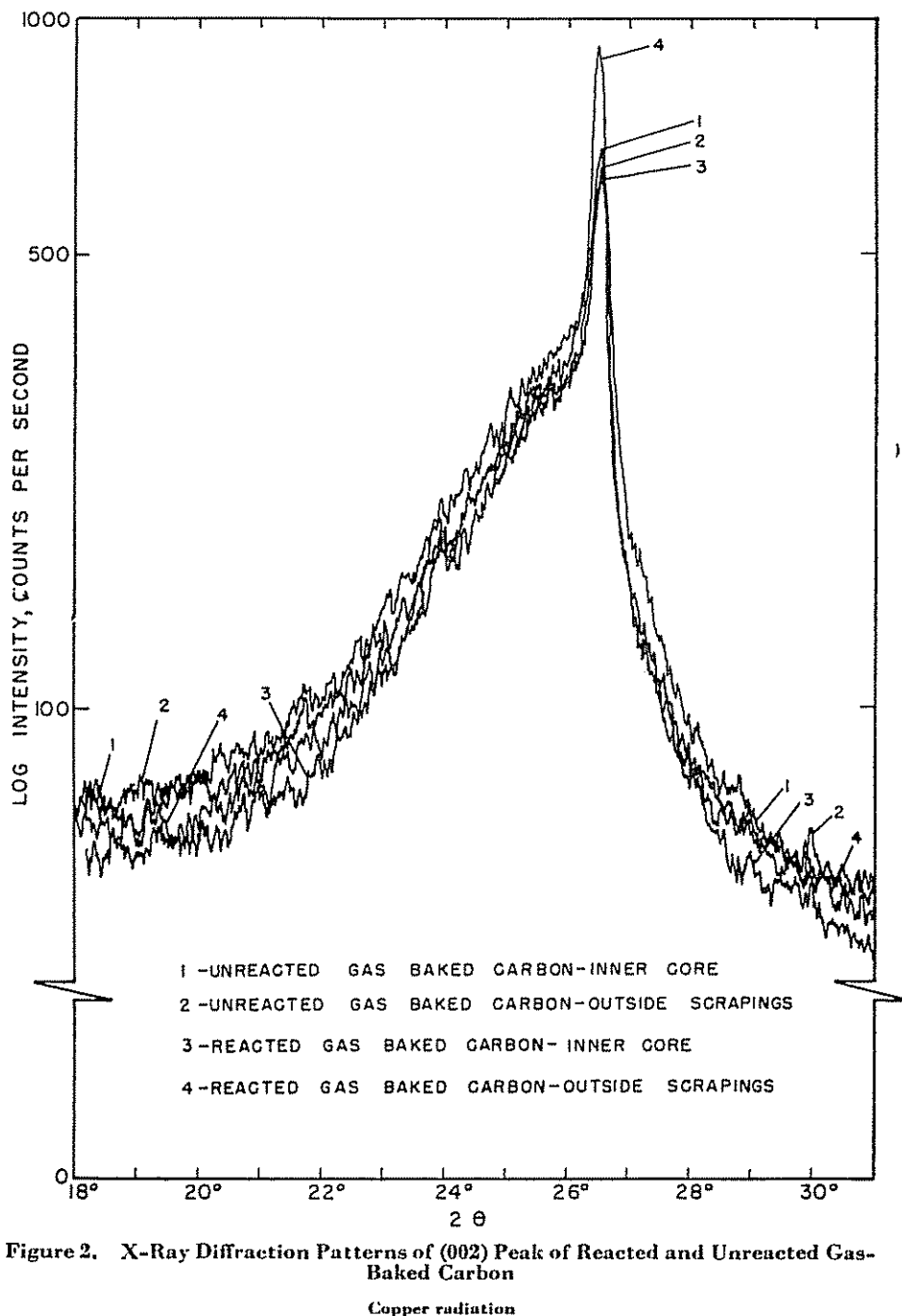


Figure 2. X-Ray Diffraction Patterns of (002) Peak of Reacted and Unreacted Gas-Baked Carbon

TABLE IV. CRYSTALLITE SIZE OF ARTIFICIAL GRAPHITE RODS

Graphite	Crystallite Size at Different X-Ray Diffraction Peaks, A.			Ratio of Crystallite Size of (100) to (004) Diffraction Peaks
	(002)	(004)	(100)	
Unreacted				
1	870	460	1000	2.17
2	830	610	1200	2.11
3	960	450	992	2.20
Av.	887	507	1094	2.16
45% gasified				
1	930	618	1890	3.07
2	1020	767	1860	2.42
3	980	734	2050	2.79
Av.	977	706	1933	2.74
85% gasified				
1	1120	825	1510	1.33
2	940	609	1190	1.96
3	1000	660	1700	2.57
Av.	1020	698	1466	2.12

TABLE V. CRYSTALLITE SIZE OF NATURAL GRAPHITES

Graphite	Crystallite Size at Different X-Ray Diffraction Peaks, A.	
	(002)	(004)
200-mesh		
1	1060	2460
2	1020	3240
3	1010	2740
Av.	1030	2813
5-micron		
1	1320	1270
2	1295	1370
3	1230	1320
Av.	1282	1320

given carbon is due to the lack of accuracy inherent in the technique and not to sampling errors.

Despite the spread of the data, general conclusions appear to be warranted. All the crystallite sizes except one for the graphite samples 45% gasified are larger than those for the unreacted carbon. All the crystallite sizes for the sample 85% gasified, with the exception of two, are larger than those for the unreacted carbon. There appears to be a definite increase in mean crystallite size, for both \bar{L}_c and \bar{L}_a , of the remaining carbon upon gasification. The average height of the crystallite, \bar{L}_c , appears to remain relatively constant between 45 and 85% of carbon gasified; but there appears to be a detectable drop in \bar{L}_a , the diameter of the average crystallite, upon more complete gasification. With the hope of getting some idea of a possible change in shape of the carbon crystallite upon gasification, the ratio of \bar{L}_a to \bar{L}_c has been calculated. The carbon rod 45% gasified appears definitely to have a higher ratio than the unreacted carbon; upon further gasification to 85% reacted there is a decrease in this ratio back to that approximating the unreacted carbon.

Again to compare the artificial carbon with a standard, the crystallite size of the natural graphites was determined and is presented in Table V. No \bar{L}_a size could be determined, as the (100) and (101) x-ray diffraction peaks, owing to sample orientation, were small. However, the crystallite sizes determined for \bar{L}_c are in all cases larger than those of the artificial graphite. Furthermore, the crystallite size determined from the (004) peak is larger than that determined from the (002) peak, which is the opposite to the finding for the artificial graphite. In investigating a series of carbons, Franklin (9) also found that the crystallite sizes determined from these two peaks differed widely. A possible clue to the reason for this difference in crystallite size, as determined from these two peaks, is given by data on the 5-micron graphite. Here there is a remarkable check between values, not only at the same angle ($\pm 4\%$ variation) but also between angles (2.9%). When this is compared with the considerable variation between the crystallite sizes determined for the 200-mesh natural graphite at the two different angles, the conclu-

sion would seem to be that reduction of the carbon to a fine size in some way removes the factors causing discrepancy between the crystallite size calculated from different diffraction peaks.

VARIATION IN INTENSITY OF X-RAY PEAKS OF ARTIFICIAL GRAPHITE UPON GASIFICATION. In an attempt to reduce the part which orientation of the carbon plays in affecting peak intensity, hollow slides were used for this work and the carbon was dropped into the slides as previously described. The slides used all had the same sample volume, which meant that the weight of carbon packed varied with its density. It is understood that the simplified treatment of placing the intensities on the basis of a count per second per gram of carbon cannot completely remove the effect of density of packing. However, the nonlinear effects of variation in density on intensity values, as it affects absorptivity, for example, are thought to be minor in comparison to the intensity changes noted.

For the artificial graphites the same sample was used for both determinations—i.e., the slide was packed, read, removed, repacked, and read. For these duplicate determinations of the (002) and (100) diffraction intensities the maximum variation between readings was $\pm 1\%$. For the natural graphite samples two slides of each were used, and variations between the weights of carbon packed in the two slides were deliberately employed. When the intensities were placed on a unit weight basis, duplicate readings agreed within at least $\pm 2\%$.

Table VI presents the data for the duplicated x-ray peak intensities (the duplicate readings having been averaged). There is a 100% increase in intensity of the (002) peak of the 45% gasified carbon over the unreacted sample and a minor decrease in the (100) peak intensity. Gasification to a weight loss of 85% shows some decrease in the (002) intensity from that of the 45% gasified sample and no change in the (100) intensity. The ratios of intensities for the samples show a onefold increase for 45% weight loss and then a significant decrease for 85% weight loss.

The intensities of the natural graphite have also been determined. The 200-mesh graphite shows the maximum (002) intensity of all the samples and by far the weakest (100) intensity. The ratio of these two intensities is an order of magnitude higher than that for the artificial graphites. Drastic size reduction of this natural graphite to 5-micron material, however, produces marked changes in the intensities, with the sample returning close to that of the unreacted artificial graphite.

TABLE VI. VARIATION OF X-RAY PEAK INTENSITIES OF GRAPHITE WITH REACTION

Graphite	Intensity at Different X-Ray Diffraction Peaks, Counts/Sec./G.		Ratio of Intensities
	(002)	(100)	
Unreacted	9,150	259	35
45% gasified	18,400	241	77
85% gasified	15,200	245	62
Natural graphite, 200-mesh	22,300	50	446
Natural graphite, 5-micron	10,600	280	38

GASIFICATION OF GAS-BAKED CARBON-GRAPHITE SAMPLE. In order to substantiate further the preferential reaction of non-graphitic or graphitic carbon during gasification, a commercial sample of gas-baked carbon containing 13% artificial graphite was investigated. The difference between the gas-baked carbon-graphite sample and the artificial graphite sample previously discussed should be appreciated. For the former, the two types of carbon had been thermally treated at different temperatures, the nongraphitic carbon at 1000° C. and the graphitic carbon at 2500° C. These carbons had been mechanically mixed and gas-baked at 1000° C. For the artificial graphite, all of the original carbon had been graphitized at 2500° C. The nongraphitic carbon should be in more intimate contact with the graphitic carbon in the artificial graphite than in the gas-baked carbon-

graphite sample, where the nongraphitic and graphitic portions are essentially located in different particles and, hence, different crystallites.

The gas-baked carbon-graphite sample was gasified to a weight loss of 40% at 1100° C. Figure 2 shows four x-ray patterns of the (002) peak of the carbons. Patterns 1 and 2 represent the unreacted carbon, samples being taken from the outside and interior of the sample to test for homogeneity. The two peak intensities, as taken from the chart, agree within 10%. The superposition of the broader and weaker gas-baked carbon peak onto the sharp graphite peak is clearly seen. Patterns 3 and 4 represent the reacted sample. Because of the high reaction rate of the gas-baked carbon, reaction occurs almost entirely close to the surface (17) and, hence, it was easy to scrape a highly reacted outer layer from the sample, leaving the dense unreacted interior. Curve 3 gives the x-ray pattern for the inner core, and comparison with peaks 1 and 2 indicates its close duplication of maximum peak intensity (within 17% for the two unreacted samples). On the other hand, the highly reacted outer layer shows an increase of maximum intensity over the other samples from an average of 630 counts per second to 920 counts per second, or 46%. This would seem to be a clear indication that the percentage of graphitic carbon in the sample has been substantially increased upon gasification, owing to the preferential reaction of the nongraphitic carbon.

DISCUSSION

Prior to interpretation of the experimental results in an effort to explain the gasification mechanism, the character of the artificial graphite used should be clarified. The original raw materials used for the production of these graphite rods were 25% coal tar pitch and 75% calcined petroleum coke flour. According to Abbott (1), baking of these rods is a destructive distillation process whereby the pitch binder is gradually heated until it softens and melts, the lighter fractions are volatilized, and the residue is formed into a coke. The particles of calcined petroleum coke are coated with a layer of this pitch coke, which gives strength to the carbon rod. The rods are then graphitized and because the pitch coke is difficult to graphitize (2), each particle of the artificial graphite can be visualized as consisting of a highly graphitized inner core surrounded by a slightly graphitized outer shell. Furthermore, the distribution of the crystallite sizes should be bimodal (3), with the graphitized crystallites from the pitch coke having their maximum concentration of sizes at a significantly smaller size than the graphitized crystallites from the petroleum coke.

The results may now be interpreted in the light of this simplified picture of the particles composing the artificial graphite rods.

INTERPRETATION OF INTERLAYER SPACING DATA. The interlayer spacing data show (1) that the spacing of the carbon decreases a measurable amount, from 3.3601 to 3.3581 Å., in going from the unreacted to the 45% reacted sample, whereas further gasification to 85% weight loss finds the spacing decreasing an insignificant amount to 3.3579 Å.; (2) that the spacing of the carbon after both 45 and 85% gasification indicates that there is a significant portion of nongraphitic carbon (15%) still present (9) which does not measurably decrease over this range of gasification. These results can be explained as follows:

Upon gasification to a certain weight loss, the less graphitic crystallites around the periphery of the particles (probably constituting about 10% of the original sample weight), are completely removed. As this less graphitic carbon, according to Bacon and Franklin, will have a larger *c*-spacing than the more graphitic carbon, its removal from the sample will lower the average *c*-spacing of the residual carbon. After essentially complete removal of this material at some percentage of gasification, the *c*-spacing of the residual carbon will be expected to remain constant with further gasification, under the conditions that the crystallites produced from the petroleum coke all contain the

same percentages of graphitic carbon and that subsequent reaction is not able to remove preferentially the nongraphitic material from these crystallites.

These conditions appear to be best satisfied if the picture of the residual carbon adopted is that postulated by Franklin (9). The nongraphitic carbon having the 3.44 Å. interlayer spacing is intimately mixed, in the same crystallite, with the carbon having the graphitic spacing of 3.354 Å.—the experimentally determined spacing giving the percentage of nongraphitic carbon in each crystallite. If the nongraphitic carbon is randomly dispersed in the crystallites, as Franklin believes (as opposed to being locally concentrated), it is extremely unlikely that the nongraphitic carbon will be preferentially removed from the whole crystallite. If the reaction removed entire nongraphitic planes from crystallites, the crystallites would be split apart into ones having a smaller \bar{L}_c dimension, which does not occur. Therefore, the following is suggested.

The initial lowering of the *c*-spacing upon gasification is due to the complete removal of the less graphitic carbon; the constancy of the *c*-spacing for high degrees of gasification is due to the presence of crystallites of uniform composition of graphitic and nongraphitic carbon and the fact that the nongraphitic carbon is not preferentially removed from these crystallites, because of its intimate mixture with the graphitic carbon.

INTERPRETATION OF CRYSTALLITE SIZE DATA. The data on crystallite size of the graphite samples show the following well-substantiated results. Gasification to either 45 or 85% weight loss produces an increase in both the \bar{L}_a and \bar{L}_c dimensions of the residual carbon over the unreacted sample; and gasification from 45 to 85% weight loss produces an insignificant change in \bar{L}_c but a measurable decrease in \bar{L}_a . The increase in average crystallite size of the residual carbon upon gasification can be accounted for by either crystal growth during reaction or the elimination of the small crystallites by reaction. Carbon graphitized to 2500° C. would hardly be expected to undergo further crystal growth during gasification at 1100° C. Therefore, the latter explanation would seem to be the more logical. It is clear that, if gasification has achieved only the reduction of crystallite sizes and has not completely eliminated the smaller crystallites, the average crystallite size of the carbon would have to decrease. Therefore, the major hypothesis here must be that increase in average crystallite size necessitates sufficient duration of gasification to eliminate at least some of the smaller crystallites. The extent of gasification required for the effective removal of the small crystallite sizes will depend in large measure upon two factors—the crystallite size distribution in the carbon and the presence of preferential reactivity of the smaller crystallites.

It is informative to explore the implications of preferential reaction by first considering the simpler cases of nonpreferential reaction.

Nonpreferential reaction means that the reaction rate of all crystallite sizes is directly proportional to their external surface area, or

$$R = KA \quad (1)$$

where *K* is a constant independent of crystallite size. Considering a crystallite shaped in the form of a disk (as can be roughly imagined when expressing \bar{L}_a and \bar{L}_c), its surface area can be given as $\pi L_a(L_c + L_a/2)$. If it is further assumed that $L_c = L_a/2$ over the range of crystallite sizes (this is not strictly true, but a sufficiently close approximation in this case), then the external area of a crystallite is given as πL_a^2 . Therefore, for nonpreferential reaction of crystallites, their rate of reaction is directly proportional to L_a^2 over the entire range of crystallite sizes or

$$R = K_1 L_a^2 \quad (2)$$

Furthermore, the weight of a carbon crystallite can be expressed as $1/4(\rho L_c)(\pi L_a^2)$ or $\rho L_a^3/8$, or the differential change in weight of a crystallite is given by Equation 3 as

$$dW = \frac{3\rho L_a^2(dL_a)}{8} \quad (3)$$

The rate of weight loss of a crystallite then can be expressed by Equation 4 as

$$dW/dt = (K_2 L_a^2) dL_a/dt \quad (4)$$

assuming ρ essentially independent of crystallite size. Equating the reaction rate Equations 2 and 4 and simplifying give

$$dL_a = K_3 dt \quad (5)$$

where K_3 is essentially independent of crystallite size. This indicates that for nonpreferential reaction the numerical change of L_a and/or L_c would be independent of crystallite size and solely a function of time.

Consideration must now be given to the nature of crystallite size distribution in the sample in view of the fact that the average crystallite size of the residual carbon increases with 45% gasification. If the distribution of crystallite sizes were of the normal Gaussian form, nonpreferential reaction would always cause a decrease in average crystallite size, despite the continuous disappearance of completely reacted crystallites during gasification. On the other hand, preferential reaction of the small crystallites would mean that they would begin to disappear at a time when the upper crystallite size value was greater than in the nonpreferential case. If the preferential reactivity was high enough, the average crystallite size of the residual carbon could increase after a certain fraction of the small crystallites had completely reacted. Earlier it was strongly suggested that the distribution of crystallite sizes in the carbon was bimodal. If there is sufficient difference between the sizes represented by the two modes, either preferential or nonpreferential reaction of the carbon to complete elimination of the mode representing the distribution of the smaller crystallite sizes could cause an increase in average crystallite size.

A choice between these two distributions of crystallite sizes in the unreacted artificial graphite can be made in the light of the trend of the crystallite size data from 45 to 85% gasification. If the increase in crystallite size from 0 to 45% gasification were due to preferential reaction of a sample having the normal Gaussian distribution, then further gasification to 85% weight loss would also be expected to produce an increase in \bar{L}_c and \bar{L}_a for the same reason. However, such is not the case, with \bar{L}_a decreasing significantly between 45 and 85% burnoff. This decrease in the \bar{L}_a dimension, while \bar{L}_c remains constant between 45 and 85% burnoff, suggests that the reaction is occurring almost entirely along the edges of the crystallite as opposed to across the basal planes. Such a mode of reaction would also be expected during the first 45% of gasification, but the increase in \bar{L}_c during this time can be attributed to the removal of the smaller crystallite material, with its effect on increasing \bar{L}_c considerably outweighing the reduction in \bar{L}_a due to reaction along the crystallite edges.

INTERPRETATION OF X-RAY PEAK INTENSITY DATA. Before the data on the variation of the x-ray peak intensities of graphite with reaction are discussed, the requirements for the production of x-ray diffraction peaks in the present experimental setup should be understood. The fundamental requirement for the appearance of a peak at a given Bragg angle is, of course, that there is a spacing of planes in the solid such that the Bragg equation, $n\lambda = 2d\sin\theta$, is satisfied. However, even though the solid in question does have a spacing of planes, d , such that a peak should occur at an angle, θ , this will not occur unless the reflecting planes in the solid are oriented parallel to the glass slide holding the sample. For example, for the (002) reflection, the atoms contained in the parallel layer planes of graphite are so spaced that a peak should occur at a Bragg angle of roughly 13.3°. The intensity of this peak is determined, among other things, by the number of these parallel planes which are "reflecting" the x-ray beam. Only those layer planes which are parallel to the glass mounting slide will produce an x-ray intensity at this angle. On the other hand, the (100) peak is produced by the reflection of x-rays by parallel planes of scattering centers which cut perpendicularly across the former planes. Again for these reflections

to be realized, the (100) planes must be parallel to the glass mounting slide.

Variations in intensities of x-ray diffraction peaks and, consequently, variations in ratios of peak intensities can be produced by preferential orientation of the sample on the mounting slide. Such orientation occurs with unsymmetrical particles where crystallite orientation within the particles is present. This phenomenon is clearly brought out by the intensity data on the 200-mesh natural graphite, where the ratio of intensities for the (002) to the (100) peak is an order of magnitude higher than for the other graphite samples. The long, flat flakes of this graphite tend to orient with their flat side parallel to the mounting slide. The apparent existence of crystallite orientation within the particle, such that the (002) planes are preferentially lined up parallel to the long, flat side of the particle, then produces a (002) peak of considerable intensity and a (100) peak of low intensity.

The data on the 5-micron natural graphite substantiate the view that particle size and shape affect the intensity ratio—that is, the severe reduction in particle size from 200-mesh to 5-micron would be expected to produce more symmetrical particles which would decrease their tendency for orientation. Furthermore, this reduction in size would, from the statistical sense, decrease the number of particles that would orient in a given direction. These factors would then produce a decrease in the ratio of the (002) to the (100) peak intensities, as is observed.

The trend of the intensity ratios for the artificial graphite samples can be explained in the light of the intensity results on natural graphite plus the crystallite size data. The data on crystallite size indicate that removal of the less graphitic carbon during the early stages of gasification leaves a residual carbon of a higher \bar{L}_c/\bar{L}_a ratio. The higher this ratio the more unsymmetrical the crystallites and the greater their tendency to orient parallel to the long side of the particle during graphitization. This increase in crystallite orientation will increase the number of (002) planes parallel to the mounting slide and, hence, increase the (002) intensity of the 45% gasified sample, as is found. Decrease in the (100) intensity would likewise be expected and is also recorded experimentally. Another point to consider, however, is the possible change in particle shape during reaction and its effect on intensities. If the major point of reaction of a crystallite is at the edges, as previously suggested, and if the long, flat sides of the crystallites are lined up parallel to the long, flat sides of the particles, reaction is going to produce not only more symmetrical crystallites but also more symmetrical particles. The production of more symmetrical particles will decrease their orientation on the mounting slide and, hence, decrease the (002) intensity and raise the (100) intensity, as is found in going from 45 to 85% gasification. During the early stages of gasification, the two above phenomena will be in competition, with the removal of the less graphitic carbon from the particles enhancing the average crystallite orientation and (002) intensity more than the trend toward symmetrical particle shape decreases (002) intensity. However, with the complete removal of this less graphitic carbon, the former phenomenon no longer exists and decrease in orientation is observed.

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This work was undertaken to investigate possible changes in interlayer spacing, average crystallite size, and intensity of x-ray diffraction peaks of an artificial graphite before and after various stages of gasification with carbon dioxide.

Upon gasification the interlayer spacing of the residual carbon decreases, the average crystallite size increases, and the ratio of intensities of the (002) to the (100) x-ray diffraction peak increases. These results all suggest that upon gasification the less graphitic carbon is, at least in part, preferentially reacted.

These results explain why the strength of graphite electrodes sometimes rapidly decreases with use. The almost complete reacting away of the binder material, even at low weight losses of carbon, substantially weakens the cohesion between particles and, hence, the strength of the solid structure.