Influence of Bulk Graphite Thickness on the Accuracy of X-Ray Diffraction Measurement

Jane Y. Howe[1], Burl O. Cavin[1], Amy E. Drakeford[2], Roberta A. Peascoe[1], Tracy L. Zontek[2], and Douglas J. Miller[3]*
[1]Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[2]Health Sciences Department, Western Carolina University, Cullowhee, NC 28723, USA
[3]GratfTech International Ltd., 12900 Snow Road, Parma, Ohio 4413, USA

Abstract

X-ray diffraction (XRD) data were collected from a highly crystalline graphite material with increasing thickness (0.3, 0.4, and 0.5 mm) using a diffractometer in the Bragg-Brentano geometry. The diffraction peak widths are narrower for thinner samples. The peak widths that taken from a sample ground into powder form are slightly narrower than those from the bulk sample. The interplanar spacings from the 0.3 mm thick bulk samples are found to be reasonably close to the those of the powder data, which in most cases, are the average of the bulk data from the "with the grain" and "against the grain" directions. This sensible relationship between the bulk and powder data from the highly ordered graphite implies that this bulk measurement method is valid for materials with lesser degrees of order such as isotropic nuclear graphite. Therefore, it is recommended that the 0.3 mm thickness be used for bulk graphite XRD measurements. Additionally, the 002 and 004 peak widths from SP-1 graphite are comparable to the widths obtained with the NIST silicon standard. The NIST SRM640c silicon is a preferred standard because 1) it is a light element, like carbon; 2) its diffraction peaks are adjacent to those of carbon; 3) acceptance by the carbon community; and 4) high availability and relative low cost.

I. Introduction

In this letter, we report our research on the X-ray diffraction (XRD) of a highly crystalline commercial graphite material in bulk form. The purpose of the study is to understand the influence of sample thickness on the accuracy of XRD analysis, and to determine the optimum thickness for a future ASTM standard. The current ASTM stand only recommends carrying out XRD on a powder sample (ASTM 1997). It has been suggested that in the new ASTM standard, X-ray diffraction (XRD) be taken from a thin slice of bulk graphite material in addition to the powder diffraction method. The bulk method is advantageous as a bulk sample retains structural information such as texture in as-prepared state; no time required for grinding and sieving; and eliminates any artifacts created by the grinding process. Further, the porous, random nature of the bulk graphite greatly reduces the (00*l*) preferred orientation typically seen in powder samples. That is, non (00*l*) diffraction peaks, ie., (100), (101), and (110), are readily observed.

For certain applications, it is important to monitor the anisotropy of the bulk graphite materials introduced during the manufacturing process. In this context, anisotropy refers to texture, ie, a difference of structure in the direction of the extrusion axis (with grain) versus the direction normal to it (against grain). The structural anisotropy (texture) manifests itself in properties such as the coefficient of thermal expansion (CTE) as well as thermal and electrical conductivities. In the past, the CTE in "with grain" (WG) and "against grain" (AG) directions has been used to monitor the degree of anisotropy. The following table compares isotropic nuclear graphite grade PCEA with the highly anisotropic electrode pinstock grade measured and reported in this study. The isotropic nuclear graphite is less crystalline, and higher in CTE.

The properties required for electrode connecting pins are much different from those needed for nuclear graphite. Pinstock is used to make the threaded connection (pinstock is threaded male on both ends) of two graphite steel furnace electrodes with female sockets. It must be very low in CTE in order to keep the electrical joint between the two low CTE electrodes tight as the column heats to over 2000 °C. Raw materials and processing conditions for pinstock are selected to give the lowest possible CTE (see Table I).

When the graphite is to be used as a core block in a High Temperature Gas Cooled Reactor (HTGRs) it must be isotropic in order that irradiation induced changes in properties are the same in the transverse and longitudinal directions. CTE data directly correlates to the structural anisotropy that can be measured by XRD. Inevitably, there are trade-offs on XRD of a bulk low Z material such as carbon. X-ray diffractometers with a Bragg-Brentano

geometry are the most widely used type in industry and academia. This configuration renders a divergent incident X-ray beam and a convergent diffracted x-ray beam (Jenkins 1989). Since X-rays penetrate deeply into a low Z materials, XRD data taken in the Bragg-Brentano geometry usually display skewed peak shapes and asymmetrically expanded peak widths (viz. the "sample displacement and transparency" effect) (Bish and Reynolds 1989).

Table I. Coefficient of thermal expansion of PCEA and Pin Stock graphite materials

Grade	WG CTE ppm/^{o}C	AG CTE ppm/^{o}C	Isotropy Ratio (AG/WG) CTE
PCEA	3.5	3.7	1.06
Electrode Pinstock	0.05	1.8	36

CTE measured (30-100°C)

A previous XRD study on the thickness effect was carried out on the PCEA grade graphite from samples which were 0.3, 0.4, and 0.5 mm thick. It was found that thickness of 0.3 mm is appropriate. However, PCEA grade graphite does not have the highest degree of crystallinity among commercial bulk graphite materials. As the graphite becomes more crystalline, the peak width decreases, making the thickness effect more profound. The purpose of this study is to understand the influence of sample thickness on the accuracy of XRD analysis of graphitic materials, and to determine the optimum sample thickness for a future ASTM standard. XRD data from a bulk graphite material with highest degree of crystallinity will be gathered to determine what the thickness is appropriate. In order to evaluate the effect of sample displacement and transparency, the X-ray diffraction patterns were collected from ground graphite powder and SP-1 graphite, both mixed with NIST's SRM 640c silicon standard, using a zero-background holder. The comparison of peak width between SP-1 graphite and the silicon standard is also included in the study.

II. Experimental Procedures

A piece of highly crystalline graphite material (pinstock grade), approximately 3x10x10 cm^3 was supplied by GrafTech International, Ltd. (Parma, Ohio). A Buehler Isomet Low Speed Saw with a Buehler 5 LC blade was used to cut the graphite block into thin slices of 0.3, 0.4, and 0.5 mm thick along both the AG and WG directions. During the cutting process, Buehler Isocut Fluid was continuously dripped onto the blade for lubrication. After cutting, the slices were rinsed in acetone. The SP-1 graphite is a flaky material processed from purified natural graphite flakes (GrafTech International, Ltd. , Parma, Ohio formerly Union Carbide Corporation). As-received SP-1 has a mean diameter of 30 μm. The powder samples was prepared by gentle hand-grinding using an agate mortar and pestle, and sieved to remove particles larger than 45 μm. The SRM640c silicon was mixed with the powdered graphite as an internal standard to calibrate the peak width and position. The details of the sample preparation of SP-1 graphite specimen was reported elsewhere (Howe, Rawn et al. 2003). The XRD measure measurements were carried out on a Scintag PAD V powder diffractometer in the Bragg-Brentano geometry, using a Cu K$_\alpha$ radiation source at 45 kV and 40 mA, and an energy dispersive Si (Li) solid state detector. The data were collected in a continuous scan mode with a scan rate of 2°/ min with 0.02^o/step from 5 to 90° 2θ. The XRD data were analyzed using Jade software package (Materials Data, Inc., Livermore, California) . Profile fitting was applied to all the raw data by using the Peudo Voigt equation (ref). The diffraction peak width, measured as full width at half maximum (FWHM), are reported without corrections for absorption or instrument broadening. The reported peak positions have all been calibrated.

III. Results and Discussion

The 002 and 004 diffraction peaks reflect the degree of order normal to the graphene sheets. The 100 peak reveals the order within the graphene plane. The stacking order of graphene sheets in 3-dimension can be analyzed from the width of 101 and 110 peaks. The 100 peak is narrower because within a graphene sheet, the carbon atoms are connected by the strong covalent bonding. The 101 and 110 peaks are much wider due to the presence of stacking faults. These two peaks usually become wider even after gentle hand-grinding (Howe, Rawn et al. 2003).

The higher angle peaks are wider, mostly due to the divergent nature of the Bragg-Brentano geometry (Jenkins 1989).

Tables II and III present the peak widths as a function of sample thickness in AG and WG directions, respectively. In addition, the FWHM of the powder sample (ground from the bulk sample) are also listed for comparison. The standard error of the peak width is 8 to 10%. The FWHM decreases slightly with sample thickness. The powder diffraction peaks are narrower than those measured from bulk specimens. It is apparent that the thinnest sample, 0.3 mm, has peak widths closest to the powder sample.

Table II: Peak width at FWHM as a function of sample thickness in against grain (AG) direction (Unit of FWHM: degrees of 2θ)

Reflection Peak	0.31mm	0.43mm	0.55mm	Powder
002	0.20	0.22	0.23	0.16
100	0.11	0.16	0.13	0.12
101	0.62	0.62	0.64	0.43
004	0.26	0.31	0.33	0.20
110	0.18	0.21	0.23	0.22

Table III: Peak width at FWHM as a function of sample thickness in with grain (WG) direction (Unit of FWHM: degrees of 2θ)

Peak	0.35mm	0.43mm	0.55mm	Powder
002	0.19	0.23	0.22	0.16
100	0.13	0.11	0.14	0.12
101	0.55	0.60	0.62	0.43
004	0.28	0.27	0.33	0.20
110	0.17	0.21	0.24	0.22

Table IV tabulates the interplanar spacing data measured from the 0.3 mm bulk as well as the powder sample. The interplanar spacings from the powder sample are very close to that of the bulk data. In most cases, the powder data is the average of the AG and WG values. The powder data of 101 and 110 are not the average of the bulk data, likely due to the fact that more stacking faults were introduced during the hand grinding. The bulk data were taken from the pinstock graphite with a very high degree of crystallinity. Highly accurate bulk data achieved on highly ordered graphite, implies that this bulk measurement method is valid for materials with a lesser degree of order.

Table IV. d-spacings (Angstrom) of the pinstock graphite measured from bulk and powder

Peak	AG-0.31mm	WG-0.35 mm	powder
002	3.3617	3.3627	3.3625
100	2.1340	2.1302	2.1320
101	2.0315	2.0319	2.0284
004	1.6797	1.6801	1.6799
110	1.2311	1.2307	1.2316

The data in Table V contain the FWHM of the silicon standard and the ground pinstock graphite. The silicon peaks are adjacent to many graphite peaks, giving a well-spaced calibration curve for graphite (Cline, Deslattes et al. 2000). The FWHM of the powder are wider than that of the silicon standard. In Table VI, the peak width of SP-1, the graphite flakes with highest degree of order, is compared to that of the silicon standard. The SP-1 graphite has the same peak width as the silicon standard. This confirms that SP-1 graphite is indeed highly crystalline, validating the carbon community's choice of SP-1 graphite as the reference material for graphite (Howe, Rawn et al. 2003).

There are three NIST XRD line position standards, among them, silicon has the lowest atomic number. The other two line position standards are lanthanum hexaboride (LaB_6) and mica. Crystals with heavier elements tend to

have narrower peaks such as the LaB_6 standard (Cline, Deslattes et al. 2000). Silicon has wider peaks, comparable to those of pure graphite. This makes the peak width calibration a much easier task. The mica standard is mainly for large d-spacing (low angle) calibration, and more undesirably, its main peak almost directly overlays on the graphite 002. As of October 2006, the mica standard sells for $237 for 7.5 g as compared to $459 for silicon and LaB_6. However, for day-to-day use, it is an acceptable practice to use a high-quality pure silicon powder, after properly calibrated by the NIST standard, as the "daily in-house standard". The price of high quality silicon powder is very low because it is widely supplied to the semiconductor industry as a raw material. Without much compromise, this practice significantly reduces operating cost for laboratories that make numerous XRD measurements.

Table V. FWHM (in $^o2\theta$) of NIST SRM640c Silicon Standard and pinstock graphite Powder

Si Peak Position	Si FWHM
28.491	0.10
47.374	0.10
56.322	0.11
69.195	0.11
76.434	0.12

graphite Peak Position	Pinstock powder FWHM	SP-1 graphite
002	0.16	0.10
100	0.12	
101	0.43	
004	0.20	0.11
110	0.22	

Table VI. FWHM of SP-1 Graphite and NIST SRM640b silicon standard

Peak Position	FWHM
SP-1 Graphite 002	0.10
Silicon 111 (28.44^o)	0.10
Silicon 220 (47.30^o)	0.11
SP-1 Graphite 004	0.11

IV. Summary

In summary, X-ray diffraction data were collected from a highly crystalline graphite material 0.3, 0.4, and 0.5 mm thick using a diffractometer with a Bragg-Brentano geometry. The diffraction peak width decreases with the decrease of sample thickness. Comparing XRD data taken from ground samples, the bulk samples have slightly wider peaks. The d-spacings from bulk samples of 0.3 mm thick are reasonably close to the powder data and , in most cases, are the average of the bulk data from WG and AG directions. High accuracy of bulk data is achieved on a highly ordered graphite, which implies that the bulk measurement method is appropriate for materials with less degree of order. Therefore, it is recommended that the 0.3mm thickness be used for bulk XRD measurement. The silicon powder is a preferred standard because 1) it is a light element; 2) the diffraction peaks are close to those of carbon; 3) acceptance by the carbon community; and 4) high availability and relative low price. It is found that the SP-1 graphite has same peak width as the NIST silicon standard, which validates the wide practice in the carbon community of using SP-1 as a standard for pure graphite.

Acknowledgements

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