Letters

Routine Method of Crystallite Size (L_a) Determination of Pyrolytic Graphite

For most graphite materials, the powder method is generally adopted for X-ray diffraction study of their crystal structures. However, powdered samples of pyrolytic graphite show a considerable degree of preferred crystallite orientation when mounted in a sample holder, making it impossible to obtain a complete powder diffraction pattern. The use of the transmission method is necessary to obtain the (11.0) line of pyrolytic graphite in bulk form, because a specimen sufficiently thick for the reflection method cannot always be easily prepared in an experimental apparatus. In the transmission method, since the measured width of the (11.0) line is considerably affected by the specimen thickness, it is very important to compare the line-width obtained by the transmission method with that obtained by the reflection method.

Guentert [1] examined the crystallite size (L_a) in the a-direction of pyrolytic graphite by means of a Fourier analysis of the profile of the (10) and (11) bands which were obtained by the transmission method from a 1 mm thick specimen. He pointed out that the determination of L_a was not complicated by strain in the pyrolytic graphite, and that the correction for instrumental broadening was important. Guentert's method is accurate but the performance of such analysis is rather tedious and time-consuming when applied to a large quantity of samples.

The purpose of the present experiment is simply to replace Guentert's method with a quick routine method suitable for quality control.

The pyrolytic graphites used in the present work (supplied by the Nippon Carbon Co) had been prepared by an indirect heating method at deposition temperatures of 1700, 1900, 2100 and 2300° C. Another sample was annealed at 3050°

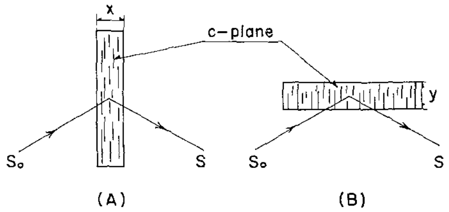

Figure 1 Transmitting (A) and reflecting (B) positions for solid samples. S_0 incident beam; S transmitted beam (A), reflected beam (B); x, y specimen thickness.

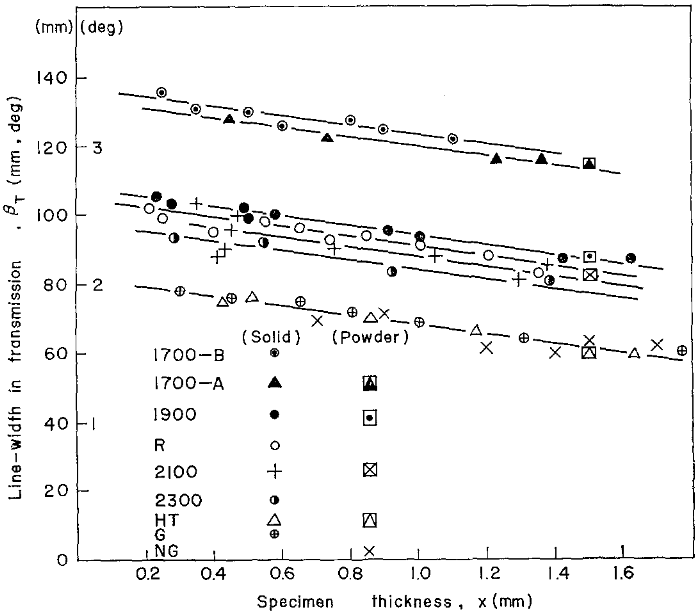

Figure 2 Effect of the specimen thickness x on the observed line-width in transmission β_{T_0}.1700, 1900, 2100 and 2300 deposition temperature (° C); R prepared by Raytheon Co; HT annealed at 3050° C after deposition at 2000° C; G reactor grade solid graphite; NG natural graphite powder.

C after deposition at 2000° C (indicated by the abbreviation HT). A pyrolytic graphite sample was also made available by the Raytheon Co (R). Reactor-grade solid graphite (G), natural graphite powder (NG) and high purity silicon powder were employed as standard samples.

X-ray measurements were carried out using Ni-filtered CuKα radiation. The (11.0) line was obtained by both the transmission and reflection methods, under the diffraction conditions specified in table I. The arrangements of the specimens in the transmitting and reflecting positions are shown in fig. 1.

TABLE I X-ray diffraction conditions

Reflection lines	(11.0)	(00.4)
Divergence slit (deg)	1	1
Receiving slit (mm)	0.15	0.15
Scatter slit (deg)	1	1
Time constant	1-2	1-2
Full scale (c/s)	200	400
Tube voltage (kV)	30	30
Tube current (mA)	10	10
Scanning speed (deg/min)	1/4	1/4
Chart speed (cm/min)	1	1

Fig. 2 shows the effect of the specimen thickness x on the observed line-width in transmission β_T, which was obtained by the position shown in fig. 1A. The x/β_T relation was found to be linear in all the cases. With increasing thickness, β_T decreases in accordance with the following experimental equation:

$$\beta_T = -0.35x\,(\text{mm}) + a \qquad (1)$$

expressed in degrees, where a is a constant for each sample. This relationship shows that the gradient is independent of the variation in structure. The line-width in transmission of powdered samples (200 to 325 mesh) of each type of graphite, mounted in the sample holder of 1.5 mm thickness, is indicated by the symbols ◮ ◙ ⊠ and ◬ which also lie on the same straight lines as the corresponding points for solid samples.

The observed line-widths of solid samples in reflection (β_R) are shown in fig. 3, which was obtained by the geometry shown in fig. 1B. The values of β_R were independent of the specimen thickness (y) and depend on the variation in structure. The difference $\beta_c = \beta_{T(x=0)} - \beta_{R(y=0)}$ between the line-widths measured in the two positions was, within experimental error, about 59 mm; except for the samples HT, G and NG, for which β_c was about 65 mm. It seems that the variance in β_c between as-deposited and samples HT, G and NG depends on the degree of graphitisation, which increases with heat-treatment [2].

In the case of an as-deposited sample of different thickness (x'), L_a is now determined as follows. The line-width in transmission (β'_T) is measured from the (11.0) transmitted line, and a is calculated from equation (1) using x' and β'_T. Then the line-width in reflection (β'_R) is decided from the following relationship:

$$\beta'_R = a - 1.47_5 \qquad (2)$$

expressed in degrees. The true line-width β is obtained after various corrections to β'_R (such as separation of α_1 and α_2, and the instrumental broadening, except for broadening due to specimen thickness). L_a is then calculated from the following equations:

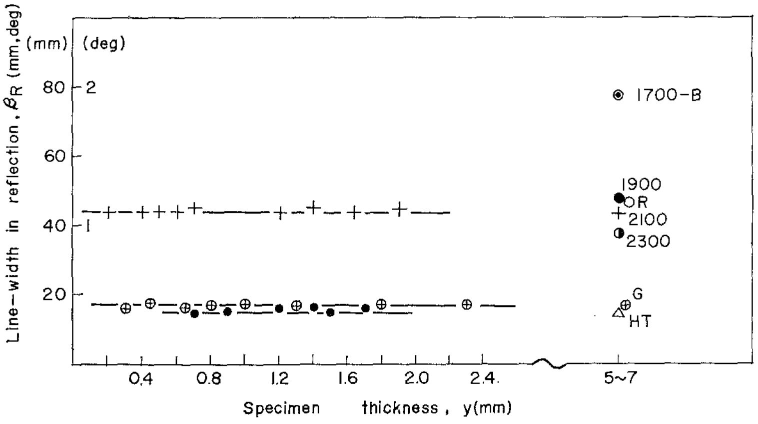

Figure 3 Effect of specimen thickness *y* on the observed line-width in reflection β_R.

$$L_a = K\lambda/\beta\cos\theta \tag{3}$$

$$K = 0.9 - (1.84 - 0.9)p \; [3] \tag{4}$$

$$1 - p^2 = (3.440 - c_0/2)/0.086 \; [4] \tag{5}$$

where K is the Scherrer constant, λ is the wavelength of the X-radiation, θ is the Bragg angle, p is Franklin's parameter [4], and $c_0/2$ is the inter-layer spacing. The values of $c_0/2$ for various samples were measured from the (00.4) reflection.

The values of L_a of various samples employed in the present experiment are shown in fig. 4 and listed in table II. Fig. 4 also includes values obtained by means of a Fourier analysis by Guentert [1], and from the measurement of diamagnetic susceptibility by Fischbach [2]. The difference between the results of the present experiment and the earlier values may be due to variation in structural features which depend on the conditions of preparation.

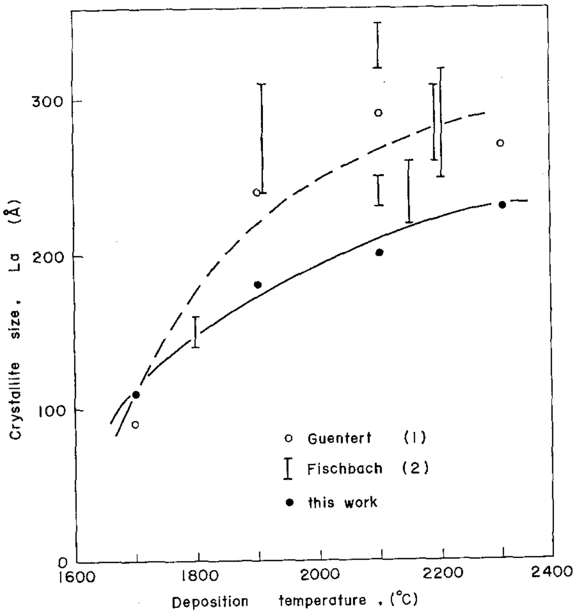

Figure 4 Crystallite size L_a of various samples.

TABLE II Crystallite size L_a of various graphites

Sample	L_a (Å)
R	190
HT	> 1000
G	750
NG	> 1000

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Twinning in Lead

Deformation-twinning does not ordinarily occur in fcc metals. In the case of pure fcc metals tested at normal rates of strain, deformation-twinning has been observed only at very low temperatures. However, very high strain rates, such as those associated with explosive loading or high velocity impact, may lead to the production of twins at room temperature [1]. Early attempts [2-5] to detect twinning in aluminium and lead were unsuccessful, even at temperatures as low as 4.2° K. Bolling *et al* [6] report the production of mechanical twins by the high compression of zone-refined lead single crystals at 77° K.

We were able to produce large numbers of twins in high purity lead single crystals by spark-machining and annealing. Lead of 99.999% purity, obtained from ASARCO, was melted and cast into square bars which were about 15 cm long and 1.3 cm on a side. Each bar was pointed