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Note

Crystallite Size and Lattice Distortion Determination of Graphite

S. Popović

Institute »Ruđer Bošković«, Zagreb, Croatia, Yugoslavia

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A graphite sample was prepared by heating chemically purified petroleum coke powder to 3000°C in an argon atmosphere and its structural characteristics were determined by various X-ray diffraction methods[1-5]. The validity of the values obtained for the crystallite size and the lattice distortion proportion is discussed.

EXPERIMENTAL

X-ray diffraction line profiles were recorded using a Philips diffractometer fitted with a scintillation counter and a single-channel pulse-height analyser. In order to eliminate the instrumental broadening, a method of mixing the sample under examination with a standard was used[1].

As standard germanium powder was selected for two reasons: 1) The germanium lines are located close to the graphite lines, and equality of the instrumental functions for two neighbouring lines of both samples can be assumed; 2) Germanium powder was prepared from a single crystal of high purity and very regular crystal lattice.

In addition to the fact that the electrical resistivity of the germanium single crystal used (40 Ω cm.) was almost equal to the intrinsic value (47 Ω cm.), the above conclusion was confirmed from our measurements of the unit cell dimension[6] and line breadths. The fraction of germanium powder from 300 to 325 mesh gave lines narrower than those of a series of other substances we intended to use as standards.

In order to avoid the additional background produced by germanium and gum tragacanth binder and to record low intensity lines, we attempted to find a standard whose absorption coefficient was equal to that of the sample examined; it would thus be possible to take the patterns of graphite and a standard separately under the same experimental conditions. Diffraction lines of our germanium powder were about 15% narrower than the lines of natural Ceylon graphite. We intended to use natural graphite as a standard because of the equal absorption coefficients of this and the examined sample. In order to increase the crystallinity and remove the impurities, Ceylon graphite was chemically treated (with hydrofluoric acid) and heated (to 3000°C) in an argon atmosphere. Such treatment produced a decrease in the interlayer spacing by 0.0015 Å and an increase in the angular separation of the (100) and (101) lines. The doublet resolution of the (004) and (006) lines was more pronounced for the treated sample. However, the lines of the treated Ceylon graphite were about 10% wider than those of germanium.

Figures 1, 2 and 3 show the graphite (002), (004) and (110) lines with closely located germanium lines. The profiles of the (002)K β, (002)K α and (004)K α lines were corrected for the instrumental broadening by Stokes' method[2], using the strips of Lipson and Beevers[7] and by dividing the angular range of the lines into 60 intervals. Pure diffraction profiles, obtained by Stokes' method, were almost symmetrical in relation to the maximum intensity.

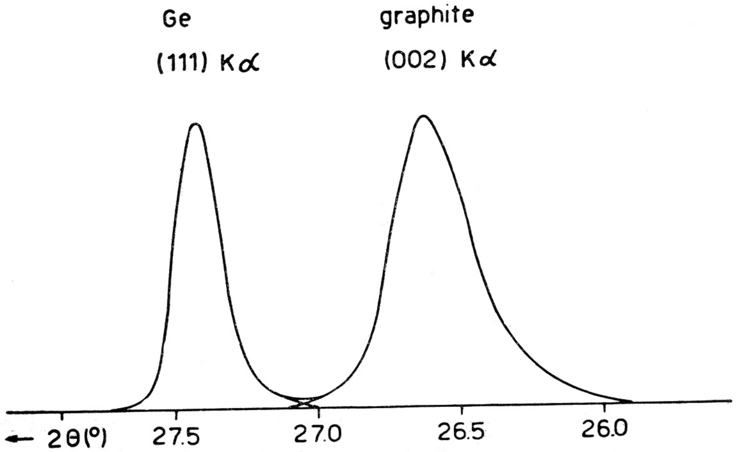

Fig. 1.

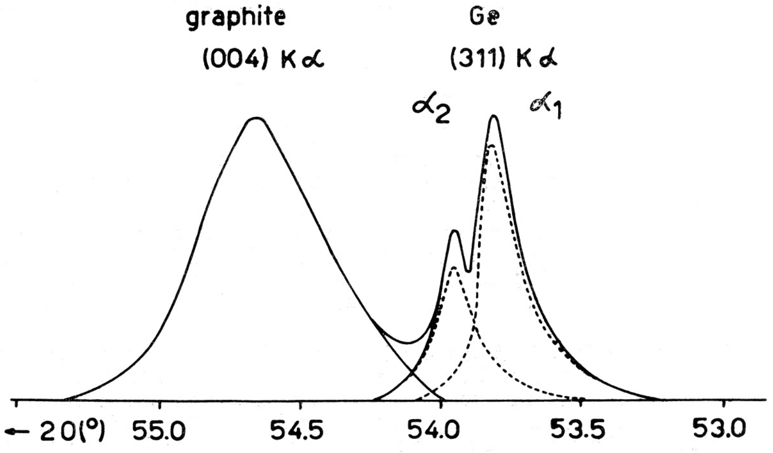

Fig. 2.

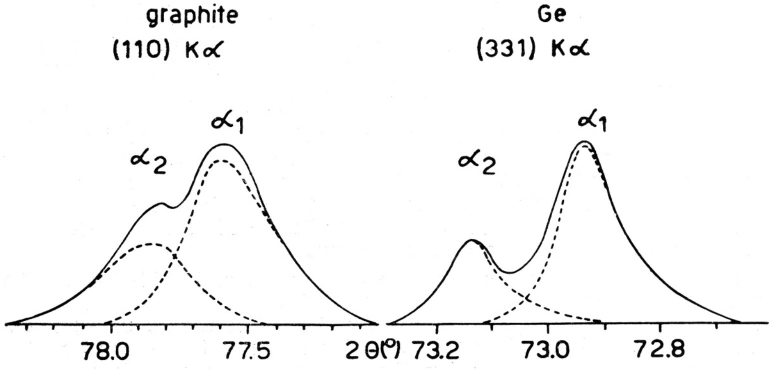

Fig. 3.

RESULTS AND DISCUSSION

a) Crystallite size and lattice distortion

Pure diffraction breadths (the angular width where the intensity is half its maximum value, $\beta_{1/2}$, or the integral breadth, β_i), determined both by Alexander's procedure[5] and by Stokes' method[2], are given in Table I.

The crystallite dimensions $L\,(L = D_{hko})$ and $H\,(H = D_{ool})$ were evaluated by means of Scherrer's equations[5], neglecting the broadening caused by the lattice distortion. Because of the presence of the lattice distortion, true crystallite dimensions are certainly greater than those given in Table I.

TABLE I

line	Alexander's method		Stokes' method	
	$\beta(^0)$	D_{hkl} (Å)	$\beta(^0)$	D_{hkl} (Å)
(002)Kβ	$\beta_{1/2} = 0.145$ $\beta_i = 0.166$	$H = 500$ $H = 490$	$\beta_{1/2} = 0.165$	$H = 440$
(002)Kα	$\beta_{1/2} = 0.163$ $\beta_i = 0.184$	$H = 497$ $H = 494$	$\beta_{1/2} = 0.180$	$H = 450$
(004)Kα	$\beta_{1/2} = 0.390$ $\beta_i = 0.422$	$H = 228$ $H = 235$	$\beta_{1/2} = 0.405$	$H = 218$
(110)Kα	$\beta_{1/2} = 0.167$ $\beta_i = 0.180$	$L = 605$ $L = 630$		

As seen from Table I, the value of *H*, derived from the (004) line, is about half those obtained from the (002)Kβ and (002)Kα lines. This can be explained only by the presence of the lattice distortion: the proportion of lattice distortion broadening increases with the reflection order *l*.

The values of the line breadths obtained by Alexander's procedure are smaller than those obtained by Stokes' method. One can conclude that pure diffraction profiles cannot be described by $(1 + k^2\,\varepsilon^2)^{-1}$, which is assumed in Alexander's procedure (ε is the angular deviation from the true Bragg angle Θ).

The pure diffraction profile is the convolution of the crystallite size profile, $p(\varepsilon)$, and the lattice distortion profile, $s(\varepsilon)$. If β_{ip} and β_{is} are the integral breadths of the profiles $p(\varepsilon)$ and $s(\varepsilon)$ respectively, the resultant integral breadth will be[1]

$$\beta_i = \frac{\beta_{ip}\;\beta_{is}}{\int p(\varepsilon)\,s(\varepsilon)d\varepsilon} \tag{1}$$

In order to determine the relationship between β_i, β_{ip} and β_{is} in explicit form, one must assume an analytical expression for the functions $p(\varepsilon)$ and $s(\varepsilon)$[8,9]. Such an assumption, however, affects the final result of the separation of line broadening effects.

In the case when the lattice distortion may be characterized by some proportion of disoriented layers[10], one can suppose that[11]

$$\beta_{is} = 2 \frac{\Delta c}{c} tg\, \Theta \tag{2}$$

where c is the lattice constant corresponding to the reflection *(00l)*. In order to find *H* and $\frac{\Delta c}{c}$, one must have at least two orders of reflection *(00l)*. For our sample we can use the (002) and (004) lines.

If we assume that the forms of the profiles $p(\varepsilon)$ and $s(\varepsilon)$ are[8]

$$p(\varepsilon) = (1 + k_1^2\, \varepsilon^2)^{-1} \qquad s(\varepsilon) = (1 + k_2^2\, \varepsilon^2)^{-1} \tag{3}$$

from equation (1) we obtain the following relationship between the integral breadths:

$$\beta_i = \beta_{ip} + \beta_{is} \tag{4}$$

Using two equations (4), for two reflections, we obtained the following values for *H* and $\frac{\Delta c}{c}$:

$$H = -5200\ \text{Å} \qquad \frac{\Delta c}{c} = 0{,}007$$

The negative value obtained for *H* indicates the non validity of assumption (3).

If we assume that[9]

$$p(\varepsilon) = (1 + k_1^2\, \varepsilon^2)^{-1} \qquad s(\varepsilon) = (1 + k_2^2\, \varepsilon^2)^{-2} \tag{5}$$

it follows from equation (1) that

$$\beta_i = \frac{(\beta_{ip} + 2\,\beta_{is})^2}{\beta_{ip} + 4\,\beta_{is}} \tag{6}$$

Solving two equations (6), for two reflections, we obtained:

$$H = 530\ \text{Å} \qquad \frac{\Delta c}{c} = 0.0012$$

The validity of the above values will be discussed together with the results obtained by the method of Warren and Averbach.

The Fourier coefficients of the (002)Kβ, (002)Kα and (004)Kα lines were determined by Stokes' method. By plotting the coefficients of these lines against the harmonics of the Fourier series[3] we obtained curves, the initial slopes of which gave the following values of *H* for our sample:

$$H_{(002)K\beta} = 574\ \text{Å} \qquad H_{(002)K\alpha} = 565\ \text{Å} \qquad H_{(004)K\alpha} = 560\ \text{Å}$$

Thus, using the method of Warren and Averbach, we obtained almost the same values for *H* from the (002) and (004) lines, differing from the results obtained by a simple application of Scherrer's equations[5]. We can conclude that one must take into account the distortion broadening, if the examined samples are less perfectly crystallized graphites.

Using the Fourier coefficients[3] for the (002) and (004) lines we obtained the value 0.003 for $\frac{\Delta c}{c}$.

The above results for H and $\frac{\Delta c}{c}$, obtained by the method of Warren and Averbach, are similiar to those obtained using assumption (5). It is noticable that the value $\frac{\Delta c}{c} = 0.0012$ is too small in relation to that obtained by the method of Warren and Averbach. The definition (2) for β_{is} is evidently not quite correct, and just that definition substantially affects the numerical values of $\frac{\Delta c}{c}$ which we get from (6).

We can conclude that the derivation of the pure diffraction profile by Stokes' method, and the interpretation of the Fourier coefficients according to Warren and Averbach, is undoubtedly the most adequate method for the determination of the structural characteristics of polycrystalline materials.

b) Proportion of disoriented layers

By an approximate treatment of the case of random errors in layer stacking, Wilson[12] deduced the following equation

$$\beta_1 = \frac{\lambda^2 l}{c^2 sin 2\Theta} p \tag{7}$$

which gives the integral line breadth of the (hkl) reflection in terms of p, the probability of an error of stacking between successive planes. If we intend to detect low intensity (110), (101), (112) and (114) lines with sufficient accuracy, we cannot use the mixture method. In order to avoid the additional background, we used graphite specimens without standard. The line profiles of these samples were corrected for absorption by extrapolation to zero thickness of the specimen[13]. The influences of other instrumental functions were eliminated by Stokes' method using separately recorded nearly located lines of germanium. As the linear absorption coefficient of germanium is about thirty times greater than that of graphite, one can suppose that the X-rays were diffracted only at the surface of the germanium powder.

We applied Wilson's formula (7) to the integral breadths of the (110), (112) and (114) lines (obtained by the above method) and obtained the value 0.23 for the proportion of disoriented layers. This result is in good agreement with the value 0.26 deduced from Bacon's equation[14] for the mean interlayer spacing.

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IZVOD

Određivanje veličine kristalita i distorzije kristalne rešetke grafita

S. Popović

Profili rendgenskih difrakcionih linija grafitiziranog petrolkoksa snimani su difraktometrom sa scintilacionim brojačem i jednokanalnim amplitudnim diskriminatorom. Korigiranje profila linija zbog instrumentalnog proširenja vršeno je Stokesovom metodom i Alexanderovim postupkom uz korištenje blizu položenih linija praška germaniuma (visoke čistoće i veoma pravilne kristalne rešetke). Veličina kristalita i distorzija rešetke određena je metodom Warrena i Averbacha. Potvrđeno je da je ta metoda adekvatnija od drugih postupaka, kod kojih se profili linija opisuju analitičkim funkcijama.

U cilju smanjenja šuma i registriranja slabo intenzivnih linija (101), (112) i (114), korišteni su uzorci grafita bez standardne tvari. Korigiranje profila zbog apsorpcije izvršeno je ekstrapolacijom na debljinu uzorka jednaku nuli. Čiste difrakcione širine tih linija služe za određivanje udjela neorijentiranih slojeva.

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