A Correction for the Effect of a Low Absorption Coefficient on the X-ray Line Profiles

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Penetration of X-rays into the sample produces an asymmetric broadening and displacement of the measured diffraction line profile. Distortion of the line profile due to a low absorption was corrected by extrapolation to zero thickness of the sample (D equal to zero). The form of the extrapolation curves is discussed mathematically. Exactness of presented method for strong lines was verified by correcting for instrumental broadening by the Jones mixture procedure.

INTRODUCTION

In the X- ray diffractometer technique with the Bragg-Brentano[1] parafocusing arrangement the sample face is flat, the primary and diffracted beams make equal angles with the sample face, the distances from the source to the sample and from the sample to the receiving slit of the counter are equal (Fig. 1).
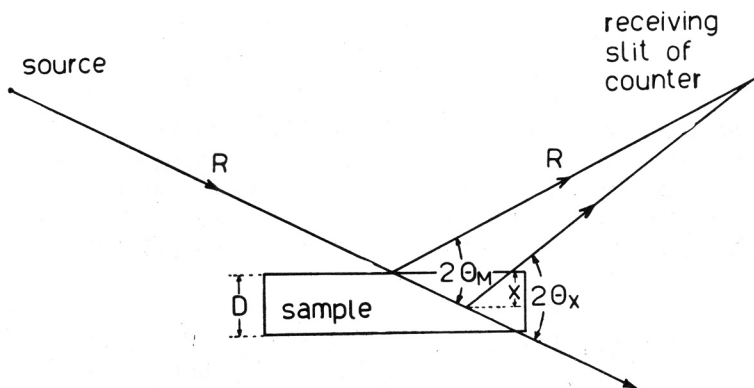

Fig. 1. Usual geometric arrangement in the X-ray diffractometer technique

When the sample absorption coefficient is small, diffraction also takes place in the interior of the specimen and there is both an asymmetric broadening and a displacement of the measured peak. Therefore, in addition to corrections of line profile for other instrumental functions, a correction for the penetration of X-rays into the specimen must be made. For strong peaks with sufficient intensity Jones'[2] mixture method for the examined sample and a suitably selected reference powder, with lines representing only instrumental broadening, can

be used. However, using this method the relative intensity of the reflections becomes too weak, and low intensity lines cannot be detected with sufficient accuracy. The profiles of such lines can be corrected by means of separately recorded lines of a standard if absorption coefficients of the examined sample and the standard are equal.

In the present paper a method for corrections of the graphite line profiles for the penetration of X-rays into the specimen is described. Corrections for other instrumental functions were made by separately recorded lines of a standard with large absorption.

<center>THEORETICAL PART</center>

If S is the cross-section area of the primary beam of X-rays, the effective irradiated volume between depth x and $x + dx$ is[3]

$$dV = \frac{S}{sin \; \Theta_o} \; dx \tag{1}$$

where Θ_o is the Bragg angle. Let $\Theta_M \; (\Theta_M = \Theta_o + \varepsilon_M)$ be the difraction angle of a ray diffracted at the surface of the specimen, i. e. Θ_M is the angle which is observed on the scale of a X-ray goniometer. A ray diffracted at a depht x from the specimen surface will come to the receiving slit of the counter at an angle $\Theta_x \; (\Theta_x = \Theta_o + \varepsilon_x)$. Since the distance R from the sample to the receiving slit of the counter is much greater than x, it follows

$$\Theta_x = \Theta_M + \frac{x \; cos \; \Theta_o}{R}$$

and

$$\varepsilon_x = \varepsilon_M + \frac{x \; cos \; \Theta_o}{R} \tag{2}$$

Let $h \, (\varepsilon)$ represent an experimentally observed line profile, and $h_o \, (\varepsilon)$ the intensity distribution which would be measured at the receiving slit if the absorption coefficient of the sample was very high, or, what is the same, the function which describes the line profile for the sample with thickness D equal to zero. Since the path through the specimen of a ray diffracted at a depth x equals $2 \, x/sin \, \Theta_o$, we have

$$h \, (\varepsilon_M) = \int_O^D exp \left(-\frac{2 \, \mu \, x}{sin \; \Theta_o} \right) h_o \, (\varepsilon_x) \; \frac{S}{sin \; \Theta_o} \; dx$$

where μ is the linear absorption coefficient. Using this equation and switching to the variable ε_x, according to (2) we got

$$h \, (\varepsilon_M) = \int_O^{\varepsilon_M + Dcos \, \Theta_o/R} C_1 \, exp \, (-C_2 \, \varepsilon_x) \, h_o \, (\varepsilon_x) \; d \, \varepsilon_x \tag{3}$$

where C_1 and C_2 are constant factors for a given angular position Θ_M:

$$C_1 = exp\left(\frac{4\,\mu\,R\,\varepsilon_M}{sin\,2\,\Theta_o}\right)\frac{2\,SR}{sin\,2\,\Theta_o} \qquad C_2 = \frac{4\,\mu\,R}{sin\,2\,\Theta_o}$$

To find the equation relating $h\,(\varepsilon_M)$ with the thickness D of the specimen let us derive expression (3) by D, according to the rule for derivation of the integral by the upper limit:

$$\frac{dh\,(\varepsilon_M)}{dD} = C_3\,exp\,(-\,C_4\,D)\,h_o\,(\varepsilon_M + C_5\,D) \qquad (4)$$

where C_3, C_4 and C_5 are the constants:

$$C_3 = C_1\,exp\,(-\,C_2\,\varepsilon_M)\,\frac{cos\,\Theta_o}{R} \qquad C_4 = \frac{C_2\,cos\,\Theta_o}{R} \qquad C_5 = \frac{cos\,\Theta_o}{R}$$

For the function $h_o\,(\varepsilon)$ one can assume the following bell- shape angular intensity distributions:

$$sin^2\,(k\,\varepsilon)\,(k\,\varepsilon)^{-2} \qquad exp\,(-\,k^2\,\varepsilon^2) \qquad (1 + k^2\,\varepsilon^2)^{-1} \qquad (1 + k^2\,\varepsilon^2)^{-2}$$

Let us take, for example:

$$h_o\,(\varepsilon) = exp\,(-\,k^2\,\varepsilon^2)$$

Writing simply ε instead of ε_M we get

$$\frac{dh\,(\varepsilon)}{dD} = C_3\,exp\,(-\,C_4\,D)\,exp\,[-\,k^2\,(\varepsilon + C_5\,D)^2] \qquad (5)$$

EXPERIMENTAL

A series of specimens of thicknesses 1.95 mm., 1.45 mm., 1.00 mm., 0.50 mm., 0.34 mm., 0.25 mm. and 0.14 mm. were made by cutting from the graphite block and
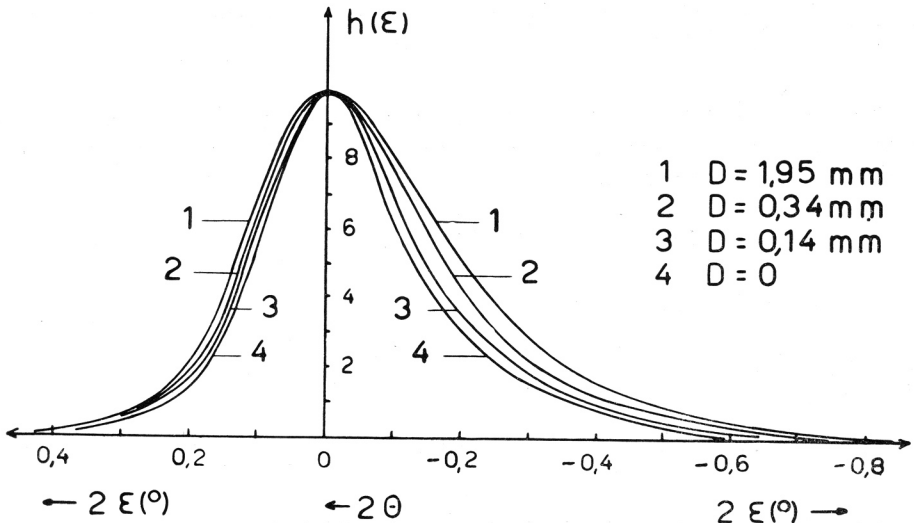

Fig. 2. Changes of (002) line profile $h\,(\varepsilon)$ with the thickness D of the specimen (ε is an angular deviation from true Bragg's position)

by grinding carefully. Lines of all samples were recorded, using the scintillation counter, under the same experimental conditions and they were corrected for absorption by extrapolation to zero thickness of the specimen. Fig. 2 represents changes of (002) line profile $h(\varepsilon)$ with the thickness D of the specimen (ε is an angular deviation from true Bragg's position Θ_o). Extrapolation procedure of
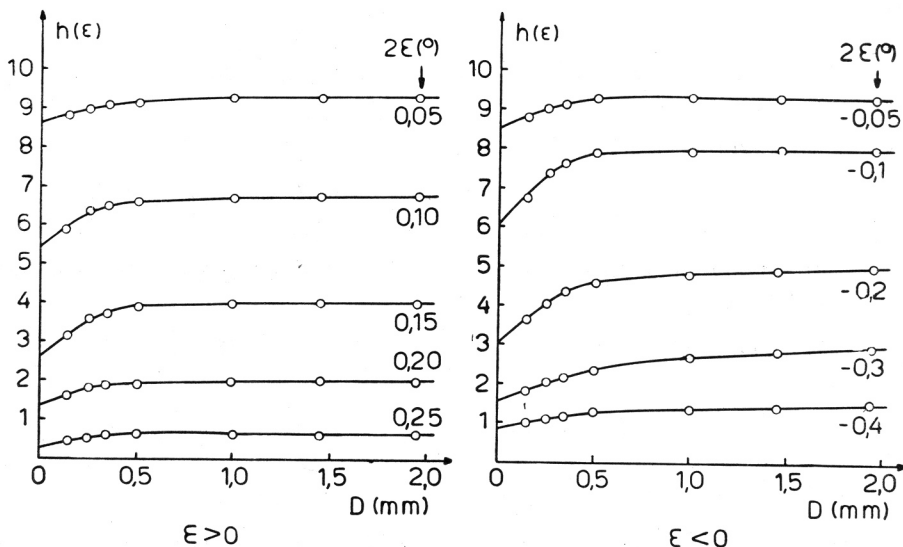

Fig. 3. Extrapolation procedure of derivation of the »zero« profile, i. e. the relation between h (ε), for a series values of ε, and the thickness D of the specimen

derivation of »zero« profile (for $D = 0$), i. e., the relation between $h(\varepsilon)$, for a series values of ε, and D is illustrated in Fig. 3. It can be seen that line profile begins to change substantially when sample thickness becomes less than 0.5 mm.

By graphical integration of the expression (5) one gets curves analogous to the extrapolation curves in Fig. 3.

RESULTS

Keating and Warren[3] have shown that profile $h_o(\varepsilon)$ could be deduced using experimentally recorded peak shape $h(\varepsilon)$ and its derivative by means of the following expression:

$$h_o(\varepsilon) = U_1 \left(h - \frac{h'}{U_1} \right)_\varepsilon + U_1 \left(h - \frac{h'}{U_1} \right)_{\varepsilon + U_2} \, exp\,(-\,U_1\,U_2) +$$

$$+ U_1 \left(h - \frac{h'}{U_1} \right)_{\varepsilon + 2\,U_2} exp\,(-\,2\,U_1\,U_2) + \ldots$$

where

$$h' = \frac{dh(\varepsilon)}{d\varepsilon} \qquad U_1 = \frac{4\,\mu\,R}{sin\,2\,\Theta_o} \qquad U_2 = \frac{D\,cos\,\Theta_o}{R}$$

We applied this formulae to the high intensity (002) line of the specimen with thickness 1.95 mm.; the result was in good agreement with the profile h_o

deduced by means of our extrapolation method. For other lines with low intensity the method of Keating and Warren cannot be used because of uncertainity in the graphical determination of derivative h'. Correction of the profile for the absorption by extrapolation to zero thickness of the specimen was applied for graphite lines (002), (004), (110), (112) and (114). The influences of other instrumental functions were eliminated both by Stokes'[4] method and by Alexander's[5] procedure using separately recorded nearly located lines of a germanium powder of high purity and a very regular crystal lattice[6]. Diffraction lines of our germanium powder were about ten per cent narrower than the lines of the chemically treated (with hydrofluoric acid) and heated (to 3000° C) natural Ceylon graphite which we had intended to use as a standard because of the equality of its absorption coefficient with the absorption coefficient of the examined graphite. As the linear absorption coefficient of germanium is about thirty times greater than the one of graphite, one could suppose that X-rays were diffracted only at the surface of the germanium powder. Validity of the described method of correcting line profile for absorption was also confirmed by the fact that the pure diffraction profile of the high intensity (002) line deduced using our procedure was in very good agreement with the profile (of the same line) obtained by Jones' method of mixture of graphite and germanium, using Stokes' evaluation for elimination of the instrumental broadening.

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IZVOD

Korigiranje efekta malog koeficijenta apsorpcije na profil rendgenskih linija

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Prodiranje rendgenskih zraka u uzorak uzrokuje asimetrično proširenje i pomak mjerenog profila difrakcione linije. Distorzija profila linije uslijed male apsorpcije korigirana je ekstrapolacijom na debljinu uzorka jednaku nuli. Dan je matematički izraz za oblik ekstrapolacionih krivulja. Ispravnost metode provjerena je za linije velikog intenziteta korigiranjem instrumentalnog proširenja Jonesovim postupkom smjese.

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