EXTRAPOLATION METHOD OF THE ELIMINATION OF INSTRUMENTAL BROADENING OF DIFFRACTION LINES

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1. Introduction

Kochanovská et. al. proposed a method for the determination of the intrinsic diffraction line width without a standard by means of extrapolation to zero diameter of the collimator [1]. They used the back-reflection arrangement with several collimators with suitably designed diameters. The film registration of diffraction patterns was used. The main advantage of this method is the absence of a standard sample. The standard sample of appropriate qualities may be sometimes a problem. The purpose of this contribution is therefore to propose an analogy of the mentioned film method for the conventional powder diffractometer with counter registration.

Keywords: XRD line broadening, instrumental broadening, powder diffraction

2. Instrumental factors affecting diffraction lines

Let us briefly summarize the instrumental factors which cause the broadening, the asymmetry and the shift of diffraction lines [2], [3].

(i) The source of radiation is not infinitely narrow, but its brightness can be approximated by

$$g_1(\varepsilon)=\exp(-k_1^2\varepsilon^2) \tag{1}$$

where ε is the angular deviation and k_1 is connected with the breadth of the source.

(ii) The flat specimen surface does not lie perfectly on the focal circle and the horizontal (equatorial) divergence causes the abberation described by

$$g_2(\varepsilon)=\sqrt{\frac{R^2}{2\sin 2\theta}}\frac{1}{\sqrt{\varepsilon}} \tag{2}$$

where R is the radius of the goniometer and θ is the Bragg angle.

(iii) The vertical (axial) divergence causes the abberation expressed by

$$g_3(\varepsilon)=\sqrt{\frac{2R^2}{\cot\theta}}\frac{1}{\sqrt{\varepsilon}} \tag{3}$$

(iv) Specimen transparency brings about the abberation with weight function

$$g_4(\varepsilon)=\exp(4\mu R\varepsilon/\sin 2\theta) \tag{4}$$

where μ is the linear absorption coefficient.

(v) Receiving slit with a width δ has the weight function

$$g_5(\varepsilon)=\begin{cases}1 & |\varepsilon|\le\delta/(4R)\\ 0 & |\varepsilon|>\delta/(4R)\end{cases} \tag{5}$$

(vi) The enumerated functions $g_1, \dots, g_5$ are not perfect descriptions of the individual instrumental factors. Further, no diffractometer is mechanically perfect and precisely adjusted. Therefore, the misalignment function g_6 was proposed in the form [2]

$$g_6(\varepsilon)=\frac{1}{1+k_6^2\varepsilon^2} \tag{6}$$

where k_6 is given by the degree of misalignment.

(vii) Besides these geometrical factors, also physical abberations should be considered such as refraction, response variation and dispersion [4, 5]. The spectral dispersion can be described by

$$g_7(\varepsilon)=\frac{1}{1+k_7^2\varepsilon^2} \tag{7}$$

in the first approximation for the separated $K_{\alpha1}$ or $K_{\alpha2}$ line or for the unresolved doublet at low Bragg angles. The parameter k_7 is connected with the angular width of the spectral profile [2].

The total instrumental function g is then the multiple convolution of these seven individual, specific instrumental functions $g_1, \dots, g_7$, i.e.

$$g(\varepsilon)=g_1*g_2*g_3*g_4*g_5*g_6*g_7 \tag{8}$$

Usually this instrumental function g enters into the convolution integral with an intrinsic (pure) diffraction profile f. The measured profile h is then

$$h(x)=\int_{-\infty}^{\infty}f(y)g(x-y)dy \tag{9}$$

It is clear, that the receiving slit (g_5) should be chosen as the factor the influence of which will be changed and extrapolated. More precisely, the width of the receiving slit (δ) will be stepwise changed analogically to the diameter of the collimator in [1]. Various values of δ can be adjusted easily and precisely with a high degree of reproducibility in a broad interval. The widths of the measured diffraction profiles (halfwidths or integral widths) will be then extrapolated to the value corresponding to the zero width of the receiving slit ($\delta = 0$).

3. Experiment

Two diffraction lines of the tungsten powder were measured on the conventional X-ray powder diffractometer with the Bragg-Brentano focusing geometry. The cobalt X-ray tube and the primary high-angle monochromator [6] were used. Only part of $K_{\alpha 1}$ spectral line fell on the sample. The Bragg angle was 23.52° and 43.78° for the measured diffraction lines (110) and (211) respectively. The width δ of the receiving slit had 8 and 5 different values, respectively for the lines (110) and (211) respectively. These values are indicated in Table 1 together with the corresponding values of halfwidths of the measured diffraction lines and they are also indicated in Fig. 1.

Table 1. Halfwidths $2w_h$ of the measured diffraction lines (110) and (211).

Width of receiving slit δ in mm	Halfwidths $2w_h$ in deg. (2θ)	
	line (110)	line (211)
0.1	0.2644	-
0.2	0.2636	0.3784
0.3	0.2768	-
0.4	0.2672	-
0.5	0.2780	0.3848
1.0	0.3388	0.4176
1.5	0.4248	0.5024
2.0	0.5240	0.5840

3. Results and discussion

The convolution in eq. (8) means that the individual factors are mutually independent. The elimination of one of these factors does not influence the others. However, it is evident, that the receiving slit is the dominant factor for high values of δ and the influence of the remaining factors is negligible. The extrapolation of widths of diffraction profiles measured with these higher values of δ leads obviously to the elimination of all instrumental factors. This means in principle that the extrapolation of the halfwidth beginning from high values of δ eliminates not only the influence of the receiving slit but all remaining instrumental factors. The obtained extrapolated values of diffraction line widths refer then to the intrinsic (pure) diffraction profile which has the direct physical interpretation. This situation is indicated in Fig. 1.

Experimental values of the halfwidths $2w_{\mathrm{h}}$ of the measured diffraction lines were fitted by straight lines in the interval of the width δ of the receiving slit from $\delta = 2.0$ mm to $\delta = 1.0$ mm and extrapolated to $\delta = 0$. The extrapolated values 0.1514° and 0.2517° were obtained for the width of the diffraction lines (110) and (211), respectively. These extrapolated values can be considered as the halfwidths $2w_{\mathrm{f}}$ of the intrinsic diffraction profiles of the lines (110) and (211).

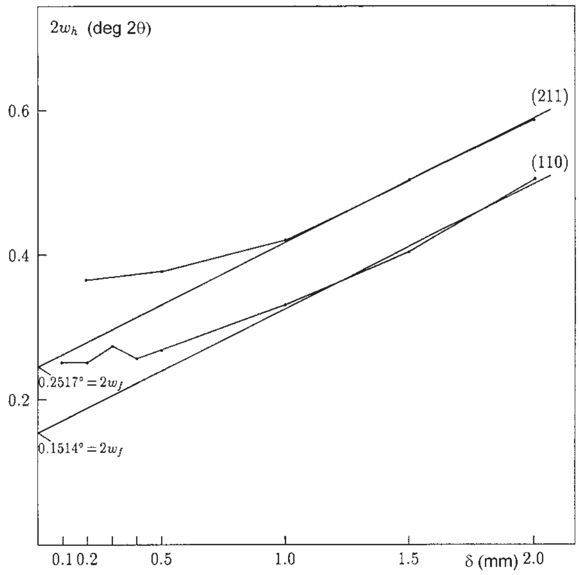

Figure 1. The extrapolation of the halfwidths $2w_{\mathrm{h}}$ of the measured diffraction lines to the zero width of the receiving slit.

The extrapolation method was tested by two ways. At first, the instrumental function was measured with the suitable standard sample that had very narrow diffraction lines. The width of the receiving slit had the value $\delta = 0.2$ mm during the measurements of the instrumental function for both diffraction lines, (110) and (211).

The halfwidths $2w_f$ of the intrinsic diffraction profiles were estimated by formulas which are based on assumption on the shapes of the intrinsic profile and instrumental profile. If these are assumed to be Cauchy-Cauchy (CC), Gaussian-Gaussian (GG) or Cauchy-Gaussian (CG), then [2, 7]

$$\text{(CC)} \quad 2w_h - 2w_g = 2w_f \tag{10}$$

$$\text{(GG)} \quad \sqrt{(2w_h)^2 - (2w_g)^2} = 2w_f \tag{11}$$

$$\text{(CG)} \quad 2w_h - \frac{(2w_g)^2}{2w_h} = 2w_f \tag{12}$$

respectively, where $2w_h$, $2w_g$ and $2w_f$ are the halfwidths (or the integral widths) of the measured profile, the instrumental profile and the intrinsic profile respectively. The numerical results of these computations are indicated in Table 2.

Our extrapolated values are in the best agreement with the results just of the equation (12) for both diffraction lines, (110) and (211). It is in a harmony with a general experience that eq. (12) - so-called parabolic correction - is very often the best formula for the widths of intrinsic profiles [8].

The second test of the extrapolation method was the physical interpretation of the halfwidths $2w_{\mathrm{f}}$ obtained by the extrapolation of the values $2w_h$. The Williamson-Hall plot [2]

$$\frac{2w_f \cos\theta}{K\lambda} = \frac{1}{D} + \frac{4e}{K\lambda}\sin\theta \qquad (13)$$

was used where $2w_f$ is in radians, K is the shape factor of the crystalline particles, λ is the wavelength (= 1.78892 Å), $e = (\Delta d/d)$ is the microstrain and D is the particle size. θ is the Bragg angle equal to 23.52 and 43.78 degrees in our case for the diffraction lines (110) and (211) respectively. The Willianson-Hall plot or the solution of the the system (13) for two values of θ gives for the unknown D and e the values $D = 1300$ Å and $e = 6.39 \times 10^{-4}$. The conventional powder diffractometry with the same measured and standard samples gives $D = 1500$ Å and $e = 5.55 \times 10^{-4}$ from six diffraction lines measured with CuKα radiation. The high resolution X-ray diffraction with triple axis diffractometer gives for the same measured sample the value $D = 1400$ Å [9]. It means that the results of all three methods are in the good agreement.

Both tests of the extrapolation method are positive, which is clear from:

(i) the comparisons of the halfwidths $2w_f$ obtained by extrapolation and by computation according to the formulas (10 - 12) and

(ii) the physical interpretation of these extrapolated values.

Table 2. Halfwidths $2w_f$ of the intrinsic diffraction profiles estimated according to formulas (10) - (12) and by the extrapolation.

Diffraction line	*Shape of profiles - formula*	*Halfwidth $2w_f$ in deg. (2θ)*	
		calculated	*extrapolated*
110	(CC) - (10)	0.1008	0.1514
	(GG) - (11)	0.2073	
	(CG) - (12)	0.1631	
211	(CC) - (10)	0.1784	0.2517
	(GG) - (11)	0.3212	
	(CG) - (12)	0.2727	

5. Conclusion

The extrapolation method for the elimination of the instrumental broadening of diffraction lines has been proposed. The absence of a standard sample is the main advantage of this method.

This method is based on the measurements of the widths of diffraction lines with several widths of the receiving slit. The influence of the remaining instrumental factors is reasonably suppressed.

The measurements with wide receiving slits should be made with a sufficient precision. Just results of such measurements are subjected to the linear or a convenient non-linear extrapolation.

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