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I. TOMOV*, S. VASSILEV**, P. TZVETKOV***

ACCOUNTING FOR SECONDARY EXTINCTION IN A NOVEL X-RAY ABSORPTION METHOD USED FOR THICKNESS MEASUREMENTS OF THIN FOILS

UWZGLĘDNIANIE EKSTYNKCJI WTÓRNEJ NOWĄ METODĄ ABSORPCJI PROMIENI X W POMIARZE GRUBOŚCI CIENKIEJ FOLII

A new approach accounting for secondary extinction (SE) is proposed for calculating the thickness of a foil mounted on textured substrate. To this end, the extinction-affected intensities of a strong substrate reflection are measured at different levels of interaction between X-radiation and crystal medium and, hence, these intensities suffer different extinction. Making use of such a series of measured intensities, the effect of extinction on the calculated foil thickness is eliminated by a proper definition of the zero-extinction condition. In this case, the definition is based on the incident-bean intensity independence of the empirical extinction coefficient k which is expressed by the measured intensities. The more precise interpretation of the experimental data leads to defining an extinction-free foil thickness, which results in improvement in the accuracy of the foil thickness determination.

Keywords: XRD, extinction, texture, foil, thickness

Zaproponowano nowe rozwiązanie dotyczące obliczeń grubości folii osadzonej na steksturyzowanym podłożu, uwzględniające ekstynkcję wtórną (SE). W tym celu, intensywności silnego odbicia dyfrakcyjnego od podłoża obarczone ekstynkcją mierzone są przy różnych poziomach oddziaływania pomiędzy promieniami X i materiałem krystalicznym folii. Wpływ ekstynkcji na mierzoną grubość folii można wyeliminować poprzez właściwą definicję warunku zero-ekstynkcji, stosując serię zmierzonych intensywności. W takim przypadku, definicja oparta jest na niezależności intensywności wiązki pierwotnej od współczynnika doświadczalnej ekstynkcji k wyrażanego przez mierzoną intensywność. Interpretacja danych doświadczalnych prowadzi do dokładnego wyznaczenia grubości folii pozbawionej wpływu ekstynkcji.

1. Introduction

Thickness measurement by X-rays is one of the fundamental techniques applied to thin films and foils [1–7]. From technical point of view, it is more convenient to use a foil as a model sample instead of a thin film. For example, powder diffraction techniques were applied for measuring the thickness of metal foils by mounting the foils on a polycrystalline substrate and decreasing the diffraction angle until the substrate reflection disappeared [2]. A relative error of 8-20% was obtained by employing a set of standards. Using standards with known thickness, the authors [2] illustrate implicitly the capabilities of the techniques used by them for characterizations of polycrystalline materials. However, the assumption that such substrates are effectively in accord with the classical definition for the case of powdered samples (as specified in *International Tables of X-Ray Crystallography* [8]), leads to a lack of precision in the interpretation of the experimental results. For this reason, the applicability of the powder diffraction techniques is restricted to the case of samples with *random orientation distribution* of crystallites [4]. However, such a distribution is not always the case. Actually, bulk and film materials used as substrates may represent texture whose reflection(s), corresponding to the main component direction, as a rule are strongly affected by secondary extinction (SE) [9, 10]. Therefore, analysing the observed intensities of strong reflections with methods ignoring SE of the measured intensities could completely compromise the foil-thickness determination by X-ray absorption. Thus, the aim of this paper is to develop and test a novel X-ray absorption method

* JORDAN MALINOWSKI CENTRAL LABORATORY FOR PHOTOGRAPHIC PROCESS, BULGARIAN ACADEMY OF SCIENCES, ACAD. G. BONCHEV ST., BLOCK 10, SOFIA 1113, BULGARIA
** INSTITUTE OF ELECTROCHEMISTRY AND ENERGY SYSTEMS, BULGARIAN ACADEMY OF SCIENCES, ACAD. G. BONCHEV ST., BLOCK 10, SOFIA 1113, BULGARIA
*** INSTITUTE OF GENERAL AND INORGANIC CHEMISTRY, BULGARIAN ACADEMY OF SCIENCES, ACAD. G. BONCHEV ST., BLOCK 11, SOFIA 1113, BULGARIA

based on the reduction of both the measured intensity and the SE correction whose changes depend on the path length of the X-ray beam inside the foil. In this connection, an extended version of the single reflection method (SRM) is applied to account for the SE [11]. Since the solution of the so-defined problem is connected with a basic term – 'freedom from extinction', below an operational definition of this term is briefly reminded.

2. On freedom from extinction and the kinematical limit

Analyzing the process of X-ray scattering and the level of interaction between radiation and crystal medium, Mathieson [12] gives a general description of the relationship between diffraction and extinction in the limit of zero diffracted power, the kinematical limit. Since the process of diffraction removes energy of an X-ray beam, the author generalizes that "under diffraction conditions, just the *transmitted beam* is extinguished so also is the *diffracted beam.*" Such a relationship between the two beams results in weakening the level of interaction of the diffraction process so that the author states: "... *any measurement with finite diffracted intensity is affected by extinction*". Since diffraction and extinction are indissolubly linked and are simply two aspects of the process whereby X-radiation interacts with the crystal medium, the author concludes "... that *extinction is only identically zero when diffracted power is zero*".

3. Basic definitions of extinction theory and texture analysis

According to theory [13–17] and experiment associated with it [18], the extinction decreases the measured intensity I_m of a reflection with a factor y, the extinction factor, defined by

$$I_m = yI_{kin} \tag{1}$$

Here I_{kin} is the intensity that a Bragg reflection would have if kinematical theory would apply exactly to the system being examined. In the symmetrical Bragg geometry, I_{kin} is expressed as

$$I_{kin} = PI_0QS/2\mu, \tag{2}$$

where I_0 is the intensity of the incident beam, S is the cross section of the beam, Q is the reflectivity per unit crystal volume, μ is the linear absorption coefficient, and P is the texture factor defined by

$$(dV/V)/d\Omega = P, \tag{3}$$

where dV/V is the volume fraction of crystallites whose <*hkl*> poles fall into a (infinitely small) space-angle element $d\Omega$ [19, 20]. In the case of pure SE, Chandrasekhar [14] gave an expression for the factor y:

$$y = \mu/\mu_\varepsilon, \tag{4}$$

where μ_ε is an effective absorption coefficient. In the symmetrical Bragg geometry with a plane-parallel plate one should use the effective absorption coefficient as a first-order approximation for the SE correction ε [15], i.e.

$$\mu_\varepsilon = \mu + gQ\left(p_2/p_1^2\right) = \mu + \varepsilon. \tag{5}$$

Here g is the SE coefficient, which is a dimensionless quantity [13], and p_n denotes the polarization factor for incident X-ray beam [15]:

$$p_n = \left[1 + \cos^{2n}(2\theta_B)\right]/2, \tag{6}$$

where $n = 1, 2, ...$, and θ_B is the Bragg angle of reflection. From (5) formula follows for the SE correction ε, which has been derived by Darwin [13] and later the polarization p_2/p_1^2 of the incident beam has been incorporated in ε by Chandrasekhar [14] and Zachariasen [15], i.e.

$$\varepsilon = gQ\left(p_2/p_1^2\right). \tag{7}$$

4. Anisotropy and behaviour of the SE coefficients

Bragg, *et al.* [21] deduced *a posteriori* that the SE correction ε is proportional to the integrated intensity I_{kin} of reflection. To this end, they have supposed that the coefficient k is a constant for the crystal (see [16] as well). Accounting for the textural anisotropy, the nature of k is reconsidered here. Combining (2) and (7) yields

$$\varepsilon = kI_{kin}\left(p_2/p_1^2\right), \tag{8}$$

where the expression

$$k = 2g\mu/PI_0S \tag{9}$$

shows how the empirical extinction coefficient k depends on various parameters describing the texture, microstructure and measurement conditions: it has dimension of reciprocal volume [cm^{-3}]. As defined, k represents the volume in the scattering space that is scanned during measurement of reflection. Rearranging (9) gives the expression

$$g = kPI_0S/2\mu, \tag{10}$$

which illustrates that g depends in a reciprocal way on the same parameters. The so-defined coefficients k and g throw additional light on the nature of SE. First, depending on the texture factor P, k and g are anisotropic

coefficients. The anisotropy of the texture factor comprises the crystallographic, microstructural and textural anisotropies. Acting together for all crystallites contributing to reflection, anisotropy parameters such as *size, shape, dislocation substructure, crystallographic orientation and crystallite arrangement* [22] synthesize the resulting anisotropy of g and k. Second, whereas g is proportional to I_0, k is proportional to the ratio g/I_0. Therefore, by virtue of the proportionality between g and I_0, any change of I_0 does not cause a change of the ratio g/I_0 and, hence, k is independent of I_0. Moreover, in case of no interaction ($I_0 \rightarrow 0$), there is no diffraction and, hence, no extinction ($g \rightarrow 0$). By virtue of g and I_0 relation, the coefficient g quantifies the level of interaction for the whole range of the solid state (powders, textures, single crystals). In contrast to g, the coefficient k is independent of any change of the interaction controlled by I_0. In practical aspect, the k independence of I_0 implies that the reduction of the incident-beam intensity from I_0 to I_{0,t^*} by means of a thin foil crossed by the incident beam does not change k at each thickness $t* [= t_1, t_2, t_3, ...]$ of the foil.

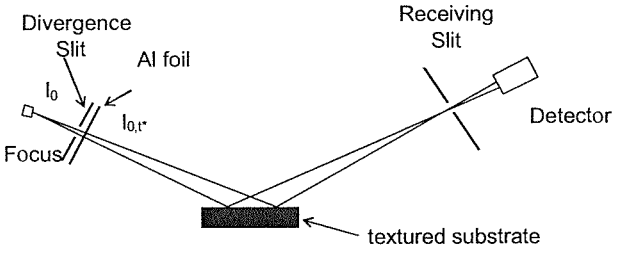

Fig. 1. Simplified sketch of a Bragg-Brentano diffractometer adapted for controlled reduction of the incident-beam intensity from I_0 to I_{0,t^*} by means of a thin foil of known thickness t^*

Now let us analyze how the change of g with I_0 can be controlled. Suppose a thin foil of thickness t^* and linear absorption coefficient μ^* is crossed by incident X-ray beam, which results in reducing the beam intensity from I_0 to I_{0,t^*} (Fig. 1). According to (10), this causes reduction of the SE coefficient from g to g_{t^*}, respectively. Then, by analogy with (10), we shall have

$$g_{t^*} = kPI_{0,t^*}S/2\mu, \tag{11}$$

where it is accounted that k does not change with I_0. Dividing (11) and (10) yields

$$g_{t^*}/g = I_{0,t^*}/I_0. \tag{12}$$

Since $I_{0,t^*}/I_0$ is equal to the transmission factor $\exp(-\mu^* t^*)$ of the foil, we can rewrite (12) as

$$g_{t^*}/g = I_{0,t^*}/I_0 = \exp(-\mu^* t^*), \tag{13}$$

which reveals that the reduction of the SE coefficient from g to g_{t^*} is controlled by the transmission factor which reduces the intensity from I_0 to I_{0,t^*}. The knowledge acquired in this section makes it possible to define the kinematical limit (extinction-free condition) by equalizing a couple of k values defined by intensities measured at different levels of interaction between X-radiation and crystal medium controlled by the incident-beam intensity.

5. Thickness measurement of a foil mounted on textured substrate

Knowing the thickness t^* of the foil crossed by the incident X-ray beam, we want to extend the applicability of the SRM [11] for the case of measurement of a foil mounted upon textured substrate. Suppose the foil and the substrate represent different phases. To determine the foil thickness, the integrated intensities I_m, I_{m,t^*} and $I_{m,t}$ are measured by a substrate reflection that is not overlapped by any reflection from the foil. Let the intensities I_m and I_{m,t^*} correspond to a clean substrate whose reflection is measured by using incident-beam intensities I_0 and I_{0,t^*}, respectively, i.e. without absorbing foil and with absorbing foil of thickness t^*. The measurement of $I_{m,t}$ is carried out by using incident-beam intensity I_0 and diffraction from the substrate underlaying the foil of thickness t (Fig. 2). To yield valid intensities, the substrate has to be a specimen appearing infinitely thick to the X-rays. With (4), (5) and (8) introduced in succession into (1), the intensity I_m of the first measurement is expressed by

$$I_m = \left\{\mu/\left[\mu + kI_{kin}\left(p_2/p_1^2\right)\right]\right\} I_{kin}. \tag{14}$$

To distinguish between the parameters of the first, second and third measurements, the parameters of the second and third ones are designated with subscripts t^* and t, respectively. Equation (14) is then rewritten as:

$$I_{m,t^*} = \left\{\mu/\left[\mu + kI_{kin,t^*}\left(p_2/p_1^2\right)\right]\right\} I_{kin,t^*}, \tag{15}$$

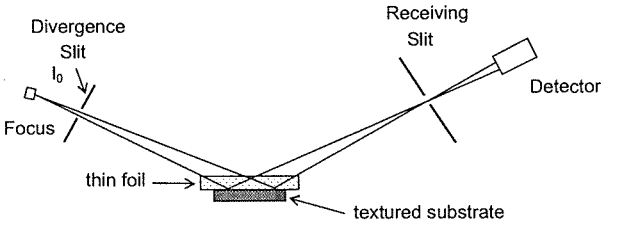

Fig. 2. Simplified sketch of a diffractometer used for thickness determination of a thin foil. It schematizes both transmission of the incident beam through the foil under study and the diffraction of X-rays from the substrate

$$I_{m,t} = \left\{\mu/\left[\mu + kI_{kin,t}\left(p_2/p_1^2\right)\right]\right\} I_{kin,t}. \qquad (16)$$

Since these measurements are carried out in a probing direction, the texture factor is the same and, hence, the following relations hold

$$I_0/I_{0,t^*} = I_{kin}/I_{kin,t^*} = \exp(\mu^* t^*), \qquad (17)$$

$$I_0/I_{0,t} = I_{kin}/I_{kin,t} = \exp\left(2\mu_f t/\sin\theta_B\right), \qquad (18)$$

where μ_f is the linear absorption coefficient of the foil mounted on the substrate. Due to its independence of incident-beam intensity (*cf.* § 4), the coefficient k is expressed by either of the couples, I_m, I_{m,t^*}, and I_m, $I_{m,t}$, of the measured intensities. Dividing (14) and (15) and taking into account (17) defines the coefficient k by means of the measurement data corresponding to the first couple of intensities:

$$k = \mu[\exp(\mu^* t^*) - (I_m/I_{m,t^*})]/I_m\left[\left(p_2/p_1^2\right)\exp(\mu^* t^*) - 1\right]. \qquad (19)$$

Analogously to (19), k can be expressed by (14), (16) and (18), i.e.

$$k = \mu\left[\exp\left(2\mu_f t/\sin\theta_B\right) - (I_m/I_{m,t})\right]/ I_m\left[\left(p_2/p_1^2\right)\exp\left(2\mu_f t/\sin\theta_B\right) - 1\right]. \qquad (20)$$

Solving (19) and (20) for t yields

$$t = \frac{\sin\theta_B}{2\mu_f}\ln \frac{\exp(\mu^* t^*)\left[\left(p_2/p_1^2\right)(I_m/I_{m,t}) - 1\right] + (I_m/I_{m,t^*}) - (I_m/I_{m,t})}{\left(p_2/p_1^2\right)(I_m/I_{m,t^*}) - 1}. \qquad (21)$$

This expression corresponds to the kinematical limit and, hence, t is an extinction-free quantity. The effect of SE manifests itself through the foil thickness t_0 which, according to the kinematical theory, is defined by

$$t_0 = \left(\sin\theta_B/2\mu_f\right)\ln\left(I_m/I_{m,t}\right). \qquad (22)$$

6. Experimental

A polycrystalline thin foil of nickel was used to test the method. The foil represents a sharp <100> texture obtained by electrodeposition on a copper substrate using conditions described elsewhere [23]. It is detached from the substrate by chemically dissolving the substrate in NH_4OH solution. Electrodeposited silver coatings (AgK1, AgK2 and AgK3) with a thickness of about 40 μm were used as substrates of the nickel foil under study. The coatings represent moderate <111> textures whose pole densities in the ideal <111> direction have values 31, 23 and 18, respectively. The XRD

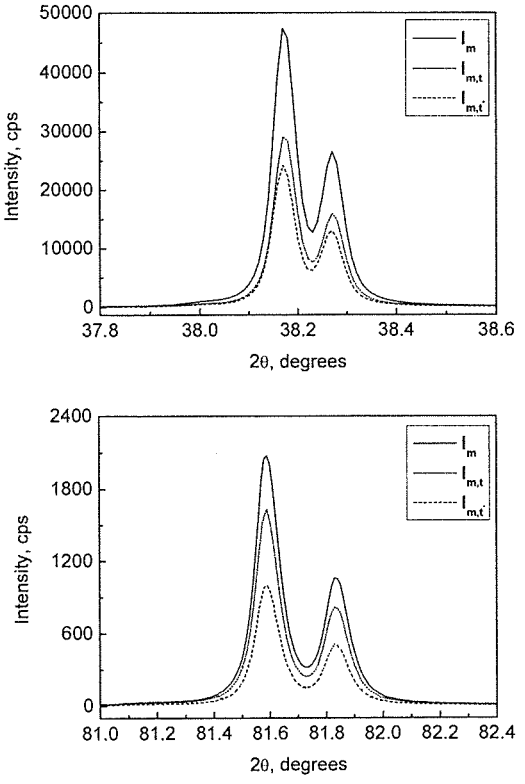

Fig. 3. Measured intensities of (a) the 111- and (b) the 222- reflections used for calculation of the foil thickness

measurements of the 111 and 222 substrate reflections were carried out in step-scanning mode with a Bruker θ-θ diffractometer using CuK_α radiation detected by solid-state detector (SOLX D8 Advance). Due to the particular preferred orientations of the substrate, its 111 and 222 reflections are not overlapped with neighbouring reflections of the foil so that the measured interval of each of the reflections was not restricted for crystallographic reasons. However, to measure the same interval in the scattering space corresponding to each of the reflections of a reflection pair, the scanned area was defined in $\sin\theta$ scale, i.e.

$$\sin\theta_2' - \sin\theta_1' = \sin\theta_2'' - \sin\theta_1''. \qquad (23)$$

Here the magnitude of the angle interval (θ_1 to θ_2) is selected in such a way that in the limits the intensity reaches the background level. The superscripts "prime" and "double prime" denote the first- and second-order reflections, respectively. Further, to reduce the intensity

from I_0 to I_{0,t^*}, the Al foil of thickness t^* = 54.5 μm was used. This foil was mounted behind the Soller slit assembly. The well-known ordinary absorption equation based on using incident-beam intensities I_0 to $I_{0,t}$

$$t = \left(1/2\mu_f\right) \ln \left(I_0/I_{0,t}\right) \tag{24}$$

was used as reference to verify the thickness t of the Ni foil under study. An average foil thickness of t = 4.19 ± 0.05 μm was found.

7. Results and discussion

Table 1 compares the results obtained for thickness determination of the Ni foil by X-ray diffraction from 111 and 222 reflections of silver substrates. The measurement data are analyzed by both extinction theory (Eq. (21)) and kinematical theory (Eq. (22)). Since equation (21) is derived by using first-order approximation for the SE correction, its applicability is restricted to the case of weak extinction effects [15]. Although the extinction of the 111 reflection is expected to be strong, the average thickness, t = 3.97 ± 0.07 μm, is in reasonable agreement with the thickness value, t = 4.19 ± 0.05 μm, obtained by the reference Eq. (24). Due to weak extinction effect in the measured intensities of the 222 reflection, the thickness of the Ni foil amounting to t = 4.23 ± 0.07 μm is in fairly good agreement with the average thickness value obtained with the reference (Eq. (24)). Therefore, it can be considered that the proposed formula for foil-thickness determination is capable to give sufficiently reliable results in the case of both weak and relatively strong extinction effects. The advantages of this technique can be gained by greater attention to data collection.

TABLE 1
Thickness determination of a nickel foil by X-ray diffraction from silver substrates (AgK1, AgK2, AgK3). The data for t and t_0 are analyzed by both extinction theory (Eq. (21)) and kinematical theory (Eq. (22)), respectively

hkl		Thicknesses t & t_0 [μm]				Systematic error, %
		AgK1	AgK2	AgK3	Average	
111	t	3.89	3.94	4.08	3.97 ± 0.07	5.3
	t_0	1.62	1.80	2.17	1.86 ± 0.18	56
222	t	4.17	4.22	4.32	4.23 ± 0.07	1.3
	t_0	2.63	2.74	2.98	2.82 ± 0.13	20

As the intensities I_m, I_{m,t^*} and $I_{m,t}$ of the 111 and 222 reflections of the substrates suffer different extinction, each of the thicknesses t_0 defined by the kinematical theory (Eq. (22)) is affected by extinction-induced error of different value. With respect to the thickness t obtained by the reference (Eq. (24)), the thickness t_0 (Table 1) suffers a systematic error of 56% for the data obtained by the 111 reflection and of about 20% for the data obtained by the 222 reflection.

8. Conclusions

A novel X-ray absorption method is proposed for foil-thickness measurement. Its development is based on a new criterion for zero extinction. It is shown that the kinematical limit is also attainable on the basis of the independence of the coefficient k of the incident-beam intensity. To effecting this approach, the coefficient k is expressed with intensities acquired at different levels of interaction. Actually, the method accounts for the SE in the intensities of reflections corresponding to the main component of textured substrate appearing infinitely thick to the X-rays. Accounting for the first-order approximation for the SE correction, the operative formula (21) is suitable for elimination of weak extinction effects. Particularly, it gives reliable results for the foil thickness determined from intensities of the weak 222 reflection and even for the strong 111 reflection.

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