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Secondary extinction correction used in a novel method for improved XRD characterizations of textured materials: The case of thin films

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Abstract. Synthesizing basic definitions of extinction theory and texture analysis, deeper knowledge is acquired about the anisotropic nature and behaviour of the empirical extinction coefficient k and the secondary extinction (SE) coefficient g. It is shown that the adequate accounting for the anisotropy of k and g requires XRD data acquired from reflection(s) corresponding to a crystallographic direction. Analyzing the relationship between these coefficients reveals that while g is *proportional* to the incident-beam intensity I_0, k is *independent* of this intensity. Based on the different behaviour of g and k with respect to I_0, a novel method using only one reflection, the single-reflection method, is developed for improved characterizations of textured materials. To verify the accuracy of the method, a new formula for thickness measurement of a thin foil is derived by means of an extended version of the same method.

Introduction

Methods accounting for SE correction in the measured intensities of single crystals are used for the purposes of X-ray crystallography [1−5]. Recent methods accounting for SE were developed for improved characterization of textured films [6,7]. To this end, a reflection pair corresponding to the main texture component has been used. However, if the particular preferred orientation of the texture predetermines only one strong reflection on the XRD pattern, the reflection-pair method employing first- and second-order reflections cannot be applied. Therefore, this method indicates a shortcoming due to discrepancy of both the necessity to use a reflection-pair and the possibility to observe only one reflection corresponding to the main texture component. To overcome this discrepancy, a novel method is developed which makes use of a single reflection. Hence, the applicability of the method to characterizing textures is independent of the particular preferred orientation. The development of the method is based on a SE-coefficient dependence on the incident-beam intensity.

Anisotropy and behaviour of the coefficients *k* and *g*

Bragg, James & Bozanque [1] deduced *a posteriori* that the SE correction ε is proportional to the kinematic intensity I_{kin} of reflection. To this end, they have supposed that the empirical extinction coefficient *k* is a constant for the crystal (see [4] as well). Accounting for the texture anisotropy, the nature of *k* is reconsidered here. In this connection two definitions given by Zachariasen [3] and Bunge [8], respectively, are used, i.e.

$$\varepsilon = gQ\left(p_2/p_1^2\right), \tag{1}$$

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

Here ε is the SE correction, *g* is the SE coefficient which is a dimensionless quantity, p_n (n=1,2,...,) is the polarization factor for incident X-ray beam [3], 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. Combining (1) and (2) yields

$$\varepsilon = kI_{kin}\left(p_2/p_1^2\right), \tag{3}$$

where the expression

$$k = 2g\mu/PI_0S \tag{4}$$

shows how the coefficient *k* depends on various parameters describing the measurement conditions: *k* has dimension of reciprocal volume. Reforming (4) gives the expression

$$g = kPI_0S/2\mu \tag{5}$$

which illustrates that *g* depends in different way on the same parameters. So defined the coefficients *k* and *g* throw additional light on the nature of SE. First, depending on the crystallographic anisotropy in terms of the texture factor *P*, *k* and *g* are anisotropic coefficients. The texture factor comprises the crystallographic and microstructure anisotropies of the crystallites contributing to reflection. Acting together, anisotropy parameters such as *size, shape, dislocation substructure, crystallographic orientation and crystallite arrangement* [9] synthesize the resulting anisotropy of *g* and *k*. Secondly, 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. Evidently, while the value of the SE coefficient *g* is related with the level of interaction between X-radiation and crystal medium defined by means of I_0, the value of *k* is independent of this type of interaction. Now let us analyze how the change of *g* on I_0 can be controlled.

Suppose a thin foil of thickness t^* and linear absorption coefficient μ^* crosses the path of the incident X-ray beam which results in reducing the intensity from I_0 to I_{0,t^*}. According to (5), this causes reduction of the SE coefficient from *g* to g_{t^*}, respectively. Then, by analogy with (5), we shall have

$$g_{t^*} = kPI_{0,t^*}S/2\mu , \tag{6}$$

where it is accounted that *k* does not change with I_0. Dividing (6) and (5) yields

$$g_{t^*}/g = I_{0,t^*}/I_0 . \tag{7}$$

Since $I_{0,t^*}/I_0$ is equal to the transmission factor $\exp(-\mu^* t^*)$ of the foil, we can rewrite (7) as

$$g_{t^*}/g = I_{0,t^*}/I_0 = exp\left(-\mu^* t^*\right), \tag{8}$$

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^*}, respectively.

Single-reflection method

The knowledge acquired so far makes it possible to develop a new method for characterizations of textured materials using a single reflection. Suppose the reflection is measured two times by incident-beam intensities I_0 and $I_{0,t*}$ under otherwise equal conditions. As shown earlier [7], the intensity I_m of the first measurement has to be expressed by

$$I_m = \{\mu/[\mu + kI_{kin}(p_2/p_1^2)]\}I_{kin} \, . \tag{9}$$

To distinguish between the parameters of the first and second measurements, the parameters of the second one are designated with subscript $t*$. Equation (9) is then rewritten as:

$$I_{m,t*} = \{\mu/[\mu + kI_{kin,t*}(p_2/p_1^2)]\}I_{kin,t*} \, . \tag{10}$$

Since the two measurements are carried out in a probing direction, the texture factor is the same and, hence, the following relation holds

$$I_0/I_{0,t*} = I_{kin}/I_{kin,t*} = \exp(\mu * t*) \, . \tag{11}$$

For I_{kin} and $I_{kin,t*}$, we have from (9) and (10) following expressions:

$$I_{kin} = \{\mu/[\mu + kI_m(p_2/p_1^2)]\}I_m \, , \tag{12a}$$

$$I_{kin,t*} = \{\mu/[\mu + kI_{m,t*}(p_2/p_1^2)]\}I_{m,t*} \, . \tag{12b}$$

Dividing these expressions and taking into account (11) defines the empirical extinction coefficient k by means of measurement data corresponding to a single reflection i.e.

$$k = \mu[\exp(\mu * t*) - (I_m/I_{m,t*})]/I_m[(p_2/p_1^2)\exp(\mu * t*) - 1] \, . \tag{13}$$

Once determined, the coefficient k is employed for calculation of the kinematic intensities from (12), the SE correction from (3), and the SE coefficient

$$g = kI_{kin}/Q \, , \tag{14}$$

which was defined recently [7]. Using only the kinematic intensities I_{kin} of textured sample and I_r of sample with random orientation distribution of crystallites, one defines texture factor P that does not suffer extinction-induced error:

$$P = I_{kin}/I_r \, . \tag{15}$$

The texture factor P_m is defined by using the extinction-affected intensity I_m:

$$P_m = I_m/I_r \, . \tag{16}$$

Finally, a criterion is substantiated for verification of the accuracy of the method described above. To this end, an extended version of the single reflection method is used for thickness determination of the foil crossing the path of the incident X-ray beam. Suppose integrated intensities I_m, $I_{m,t*}$ and $I_{m,2t*}$ of a reflection are measured by using incident-beam intensities I_0, $I_{0,t*}$ and $I_{0,2t*}$, respectively, under otherwise equal conditions. While the measurement of I_m is performed without absorbing foil, the second and third measurements are carried out by means of absorbing foils of thicknesses $t*$ and $2t*$, respectively. The coefficient k is expressed by either of the couples, I_m, $I_{m,t*}$, and $I_{m,t*}$, $I_{m,2t*}$, of measured intensities. For the second couples of intensities, a relation, similar to that one given in (11), holds

$$I_{0,t*}/I_{0,2t*} = I_{kin,t*}/I_{kin,2t*} = \exp(\mu * t*) \, , \tag{17}$$

Hence, analogously to (13), k can be represented as

$$k = \mu[\exp(\mu * t*) - (I_{m,t*}/I_{m,2t*})]/I_{m,t*}[(p_2/p_1^2)\exp(\mu * t*) - 1] \, . \tag{18}$$

Solving (13) and (18) for $t*$ yields

$$t^* = (1/\mu^*)\ln\left[I_m\left(I_{m,t^*} - I_{m,2t^*}\right)/I_{m,2t^*}\left(I_m - I_{m,t^*}\right)\right]. \quad (19)$$

Since equation (19) is derived under condition for *zero* extinction (i.e. I_0 –independent k), the thickness t^* is an extinction-unaffected quantity. The effect of SE manifests itself through the foil thickness t^*_i (i =0, 1, 2) which, according to the kinematic theory, is given by

$$t_0^* = \left(1/\mu^*\right)\ln\left(I_m/I_{m,t^*}\right), \quad (20a)$$

$$t_1^* = \left(1/\mu^*\right)\ln\left(I_{m,t^*}/I_{m,2t^*}\right), \quad (20b)$$

$$t_2^* = \left(1/2\mu^*\right)\ln\left(I_m/I_{m,2t^*}\right). \quad (20c)$$

As the intensities I_m, I_{m,t^*} and $I_{m,2t^*}$ suffer different extinction, contrary to t^* each of the so-defined thicknesses t^*_i is affected by extinction-induced error of different value.

Experimental, results and discussion

As model samples vacuum-deposited silver films (Ag21, Ag22, Ag23) were used. They represent fibre textures with a main <111> component, twin-related <511> component, and a satellite <100> component [10]. Pole figures were measured in step scanning mode with texture goniometer using CuK_α radiation separated by nickel filter. Figure 1 represents the 111 pole entity which is typical of all the samples. Integrals of the 111 reflections were measured in continuous scanning mode with conventional X-ray diffractometer using CoK_β-radiation separated by focusing graphite monochromator. To reduce the intensity from I_0 to I_{0,t^*} or $I_{0,2t^*}$, the path of the incident beam was crossed by two Al foils of different thickness t^*=100 μm and $2t^*$=200 μm, respectively. The foils were mounted behind the divergence slit.

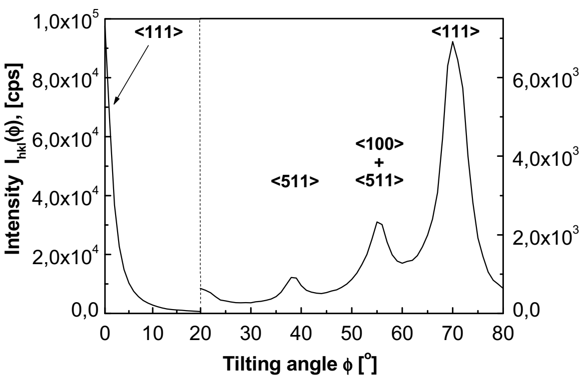

Figure 1. 111 pole figure of a silver film representing fibre texture with a main <111> component, twin-related <511> component, and a satellite <100> component.

In Table 1 values of both the texture factor and the SE correction ε of <111> reflection of Ag films are listed. By definition, the texture factor P is an extinction-free quantity. In contrast to P, P_m is extinction-affected. Evidently, a higher SE correction is related to a higher systematic error in the measurements of the texture factor P_m.

Table 1. Quantities corresponding to the main <111> texture component of vacuum deposited Ag films.

Sample	Quantity		
	P	P_m	ε $[cm^{-1}]$
Ag21	182.6	172.2	158.3
Ag22	96.6	94.9	43.9
Ag23	135.2	130.0	87.2

For an Al foil, thickness data analyzed by both the extinction and the kinematic theory are given in Table 2. The calculations show that t^* is very close to the *a priori* known thickness of the aluminium foil amounting to 100 µm. Contrary to the extinction-free thickness t^*, the data series t^*_0, t^*_1, and t^*_2 illustrates that each of the thickness values, defined by means of the kinematic theory (see (20)), has an extinction-induced error of different magnitude.

Table 2. For an aluminium foil, thickness data t^* and t^*_i (i =0, 1, 2) are analyzed by both the extinction and the kinemathic theory, respectively.

Sample	Thickness [μm]			
	t^*	t^*_0	t^*_1	t^*_2
Ag21	100.13	96.97	99.42	98.23
Ag22	99.90	97.92	99.81	99.11
Ag23	100.17	97.15	99.54	98.61

Evidently, the stronger the effect of the extinction on the intensities incorporated in each of the definitions, the greater the magnitude of the extinction-induced systematic error. Therefore, it can be considered that the proposed criterion for verification of the accuracy of the single-reflection method is sufficiently reliable.

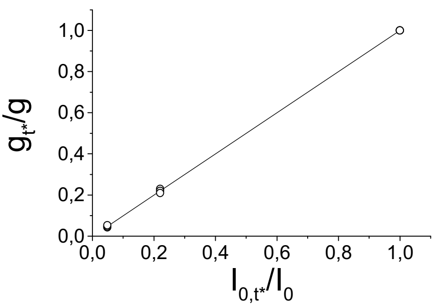

Figure 2. The relationship between the ratio g_{t*}/g and the incident-beam intensity ratio $I_{0,t*}/I_0$ whose reduction is controlled by the transmission factor $exp(-\mu^*t^*)$ which is defined at thickness t = 0, t^*, 2 t^* µm: t^*=100 µm is the thickness of an Al foil, and μ^* = 151.18 cm^{-1} is its linear absorption coefficient.

Figure 2 shows that the degree of the extinction effect is related to the level of interaction between X-radiation and crystal medium defined by means of the incident-beam intensity. The relationship, however, is illustrated by normalized quantities g_{t*}/g and $I_{0,t*}/I_0$ whose values are controlled by the transmission factor (see (8)). The SE-coefficient ratio g_{t*}/g assumes its lower limiting value of zero when the incident-beam intensity ratio $I_{0,t*}/I_0$ is zero. This is in accordance with Mathieson's statement that "*…extinction is only identically zero when diffracted power is zero*." [11]. However, the condition for zero extinction is also definable by *k*, which is the same at different levels of interaction (see (13) and (18)), due to its independence of the incident-beam intensity. Under condition of zero extinction, the kinematic approximation is exact so that experiment and theory become strictly compatible.

Concluding remarks

The secondary extinction is described by the anisotropic coefficients *g* and *k* whose definitions considered here extend the knowledge about the SE phenomenon. The SE coefficient *g* is quantified by the texture factor *P* and incident-beam intensity I_0. The empirical extinction coefficient *k* is quantified by the texture factor *P*, and is independent of the incident-beam intensity I_0.

A reliable criterion is proposed for verification of the accuracy of the single reflection method. Actually, it represents a method based on zero extinction for foil thickness measurement by X-ray absorption.

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