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ACCOUNTING FOR SECONDARY EXTINCTION IN XRD CHARACTERIZATIONS OF TEXTURE AND MICROSTRUCTURE WITH ANISOTROPY — RESPONSIVE METHODS

UWZGLĘDNIENIE EKSTYNKCJI WTÓRNEJ W TEKSTURZE WARSTW ORAZ MIKROSTRUKTURZE METODAMI ODPOWIEDZI ANOZOTROPOWEJ W TECHNICE DYFRAKCJI RENTGENOWSKIEJ

In studying textures of films extended knowledge is acquired about the anisotropy of the secondary extinction (SE) coefficient *g*. It is deduced that the anisotropy of g is quantified by texture factor. The texture factor accounts comprehensively for the crystallographic orientation and microstructural anisotropies of the sample. A dependence of coefficient g on the incident beam intensity is found too. Taking advantage of a reflection pair, the constituent reflections of which represent the same texture factors, anisotropy-responsive methods are developed. These methods are used for improved XRD measurements of both the SE coefficient and the texture factor of electrodeposited silver films.

Furthermore, the effect of SE on the reflection broadening is considered and a method is described for eliminating the extinction induced enlargement in the integral breadth of reflection. For the same films, a substantial increase of integral breadths is established for the strong 111 and 200 reflections, while the weak 222 and 400 reflections do not change their integral breadths under the same conditions..

Keywords: XRD, secondary extinction, texture factor, integral breadth, film, silver

Określenie współczynnika *g* ekstynkcji wtórnej (SE) ma istotne znaczenie w badaniach tekstur cienkich warstw. Stwierdzono, że anizotropia *g* jest określana ilościowo przez czynnik tekstury, który w pełni uwzględnia orientację krystalograficzną oraz anizotropię mikrostruktury próbki. W pracy określono również zależność współczynnika *g* od intensywności wiązki padającej. Opracowano metody odpowiedzi anizotropowej wykorzystując parę odbić, która reprezentuje taki sam czynnik tekstury. Metody te ulepszają pomiary tekstury techniką dyfrakcji rentgenowskiej uwzględniając zarówno współczynnik SE jak i czynnik tekstury dla warstw srebra wytworzonych metodą elektroosadzania.

Ponadto, rozważany jest wpływ SE na poszerzenie odbicia oraz opi8sano metodę eliminacji ekstynkcji, która powoduje zwiększanie szerokości profilu odbicia bragowskiego. Dla

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takich samych warstw ustalono zasadniczy wzrost szerokości odbicia dla silnych refleksów 111 i 200, podczs gdy słabe refleksy 222 i 400 nie zmieniają swojej szerokości w tych samych warunkach pomiarowych.

1. Introduction

Extinction-affected intensities cause substantial systematic errors in the measured quantities. Extinction was introduced to account for the reflecting power of a real crystal with respect to the power described by kinematic diffraction [1]. Extinction in a mosaic structure is power loss caused by the production of the diffracted beam. Depending on the block size, one has to distinguish between primary extinction, which is extinction within a single crystal block, and SE, which occurs when a ray reflected by one mosaic block is subsequently reflected by another block with the same orientation [2].

As inherent property of spherical crystals the isotropic extinction was considered to be only dependent on the Bragg angle [3]. It was found that the anisotropy of SE coefficient, handled for the purposes of x-ray crystallography, depends on both the anisotropy of domain orientation distribution and the anisotropy of domain shape [4, 5]. The influence of extinction and anisotropy of grain size on texture measurements of 3% Si-Fe sheet textures was analyzed by Birson & Szpunar [6].

Considering the anisotropic behaviour of textured materials, Bunge [7] showed that macroscopic anisotropies result from the microscopic crystal anisotropies which are averaged with the texture as weight function. Evidently, in the case of XRD measurements the microscopic crystal anisotropies are related to the volume fraction of identically oriented crystallites contributing to the probing direction of the sample, i.e. by means of the texture factor of the same direction.

Due to high density of imperfections [8, 9], the textured materials exhibit pure SE [10-13]. In addition, for the same reason, reflection broadening caused by crystalline size and strains in textures is about two orders of magnitude larger than that in single crystals which amounts to a few ten of seconds of arc [8, 14]. Moreover, one has to point out that in the case of Gaussian distribution the standard deviation is employed for determination of SE coefficient of single crystals, the reflection broadening of which is however described by orientation distribution of crystalline blocks alone [15]. That is why, it is not justified to be expected that the structural model, used for determination of the SE coefficient of single crystals [15], would adequately account for the structural peculiarities of textures. So far, there has been no adequate method for determination of SE coefficient in textures. Thus, for the purpose of measurements of both the SE coefficient and the texture factor, anisotropy-responsive methods will be developed which account adequately for structural peculiarities of textures. Further, considerations will be made about the effect of SE leading to reflection broadening and, in this connection an appropriate method will be described for eliminating the extinction — induced enlargement in the integral breadth of reflection.

2. Method for measurements of SE coefficient g in texture

According to theory [1-3, 15, 16], the extinction decreases the measured intensity I_m of a reflection with a factor y, the extinction factor, defined by

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

The factor y is always less than unity. However, its upper limiting value of unity corresponds to extinction-free conditions, and the measured intensity is then equal to the kinematic one, i.e. $I_m = I_{kin}$. Hence, I_{kin} is the intensity that a Bragg reflection would have if kinematic theory would apply exactly to the system being examined. In the symmetrical Bragg geometry I_{kin} has to be 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 ordinary linear absorption coefficient, and P is the texture factor defined by the volume fraction dV/V of crystallites whose $< hkl >$-poles fall into a (infinitely small) space-angle element $d\Omega$ [17 - 20], i.e:

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

Equation (2) is analogous to the well-known one

$$I_r = I_0QS/2\mu, \tag{4}$$

which is derived under assumption of *random distribution*, i.e. P=1.

In the case of pure SE, Chandrasekhar [21] gave an expression for the extinction factor y:

$$y = \mu/\mu_\varepsilon, \tag{5}$$

where μ_ε is an effective absorption coefficient. In the symmetrical Bragg geometry with a plane parallel plate sample one should use the effective absorption coefficient as a first order approximation for the SE correction ε [16]:

$$\mu_\varepsilon = \mu + gQ\left(p_2/p_1^2\right) = \mu + \varepsilon. \tag{6}$$

Here g is the SE coefficient which depends on crystallographic orientation and microstructure in the probing direction of textured sample. The symbol p_n denotes the polarization factor for incident x-ray beam that is monochromatized [16]:

$$p_n = \left[1 + \cos^2(2\theta_0)\cos^{2n}(2\theta_B)\right]\Big/\left[1 + \cos^2(2\theta_0)\right], \tag{7}$$

where n =1,2,..., θ_B and θ_0 are the Bragg angles of both the sample reflection and the monochromator reflection, respectively. From (4) a formula follows for the SE correction ε which has been derived by Darwin [1] and later, the polarization p_2/p_1^2 of the incident x-ray beam has been incorporated in ε by Chandrasekhar [21] and Zachariasen [16]:

$$\varepsilon = gQ\left(p_2/p_1^2\right). \tag{8}$$

Since the SE correction has the dimension of absorption, it introduces an enhancement to the effective absorption in the range of reflection (see right-hand side of 4). The above equations will be used further for development of a new method for determination of the SE coefficient.

Replacing Q by its corresponding expression from (2) transforms (6) into

$$\varepsilon = kI_{kin}\left(p_2/p_1^2\right), \tag{9}$$

where

$$k = 2g\mu/PI_0S \tag{10}$$

is an *auxiliary extinction coefficient* having the dimension of reciprocal volume. As derived, (7) represents another form of SE correction which has been given *a posteriori* by Bragg et. al. [22]. From (7a) the expression

$$g = kPI_0S/2\mu, \tag{11}$$

follows which reveals explicitly the dependence of g on the texture factor P. The texture factor comprises implicitly the crystallographic and microstructural anisotropies of constituent crystallites contributing to reflection. Acting together, anisotropy parameters such as *size, shape, dislocation substructure, crystallographic orientation and arrangement of the crystallites* [7] synthesize the resulting anisotropy of g. Besides the texture factor, g depends on the measurement conditions in terms of both the energy I_0S of the incident beam and the wavelength which controls μ. The only way to unambiguously account for the anisotropic effect of the texture factor on the SE correction is to determine g using measured intensities corresponding to a single crystallographic direction. Thus, if k and I_{kin} are known, from (6) and (7) one obtains:

$$g = kI_{kin}/Q, \tag{12}$$

which defines an anisotropy-responsive method for determination of g. In contrast to Zachariasen's method [15] for determination of g, the new method is based on using the integral intensity and, hence, it accounts entirely for the structural peculiarities of the texture. Another anisotropy-responsive method for k, I_{kin}, and P determination will be described below.

3. Expressing the k, I_{kin} and P with measured intensities of a reflection pair

With (5), (6), and (7) introduced consecutively into (1), the measured intensity I_m is expressed by

$$I_m = \left\{\mu\Big/\left[\mu + kI_{kin}\left(p_2/p_1^2\right)\right]\right\} I_{kin}. \tag{13}$$

Equation (13) has two unknown quantities - the auxiliary extinction coefficient k and kinematic intensity I_{kin}. They will be expressed using a reflection pair. The reflection pair consists of two reflections corresponding to a single $< hkl >$ direction. Eq. (13) is then rewritten as:

$$I'_m = \left\{\mu\Big/\left[\mu + kI'_{kin}\left(p_2/p_1^2\right)'\right]\right\} I'_{kin}, \tag{14}$$

$$I''_m = \left\{\mu\Big/\left[\mu + kI''_{kin}\left(p_2/p_1^2\right)'\right]\right\} I''_{kin} \tag{15}$$

for the first and second order of reflections, respectively. These represent two independent equations. Since the crystallites contributing to a reflection pair are the same, the texture factors of the respective reflections are identical. Then the relation holds:

$$I'_{kin}\Big/I''_{kin} = I'_r\Big/I''_r \tag{16}$$

which connects the kinematic intensities I'_{kin} and I''_{kin} of a textured sample with those (I'_r and I''_r) corresponding to the same reflection pair of random distribution. For I'_{kin} and I''_{kin} we have:

$$I'_{kin} = \left\{\mu\Big/\left[\mu - kI'_m\left(p_2/p_1^2\right)'\right]\right\} I'_m, \tag{17}$$

$$I''_{kin} = \left\{\mu\Big/\left[\mu - kI''_m\left(p_2/p_1^2\right)''\right]\right\} I''_m. \tag{18}$$

Dividing the expressions for I'_{kin} and I''_{kin} from (12), respectively, and taking into account the connecting relation (16), yields

$$k = \mu\left[\left(I'_r\Big/I''_r\right) - \left(I'_m\Big/I''_m\right)\right]\Big/I'_m\left[\left(I'_r\Big/I''_r\right)\left(p_2\Big/p_1^2\right)' - \left(p_2\Big/p_1^2\right)''\right] \tag{19}$$

Once determined, the auxiliary extinction coefficient k can be employed for calculation of the kinematic intensities from (17) and (18), the SE coefficient from (12), the SE correction from (7), and texture factors defined below.

Using the ratio of only the kinematic intensities of textured sample (2) and random distribution (4), one defines extinction-unaffected texture factor P:

$$P = I_{kin}/I_r. \tag{20}$$

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

$$P_m = I_m / I_r. \tag{21}$$

Since P is the extinction-unaffected texture factor, the difference

$$P - P_m = \Delta P \tag{22}$$

is used as a measure of the extinction-induced systematic error in texture factor determination.

4. Expressing the extinction-induced reflection broadening using the measured integral breadth

Here, considerations will be made about the effect of SE leading to reflection broadening and, in this connection an appropriate method will be described for eliminating the extinction-induced enlargement in the integral breadth of reflection. Taking into account (1), from (9) one obtains that

$$\varepsilon = k\,(I_m/y)\left(p_2\big/p_1^2\right) \tag{23}$$

depends explicitly on the measured intensity I_m. However, due to the variation of the measured intensity $I_{m,2\theta}$ along the reflection profile, the SE correction $\varepsilon_{2\theta}$ has to be presented as a quantity varying within the reflection range, i.e.

$$\varepsilon_{2\theta} = k_{2\theta}\,(I_{m,2\theta}/y_{2\theta})\left(p_2\big/p_1^2\right), \tag{24}$$

where 2θ is the diffraction angle and the particular values, $\varepsilon_{2\theta}$, fulfill the condition

$$\varepsilon = \int_0^{\Delta 2\theta} \varepsilon_{2\theta}\, d\,(2\theta). \tag{25}$$

The interval $[0, \Delta 2\theta]$ includes all $\varepsilon_{2\theta} > 0$. According to the right-hand side of (6), the effective absorption coefficient is thus also a quantity varying within the reflection range:

$$\mu_{\varepsilon,2\theta} = \mu + \varepsilon_{2\theta}. \tag{26}$$

Due to variation of the SE correction, the effective absorption coefficient $\mu_{\varepsilon,2\theta}$ attains highest value, $\mu_{\varepsilon,\max}$, at the maximum of reflection $2\theta_B$. This implies that the measured intensity $I_{m,max}$ at the reflection maximum suffers the highest reduction among all measured intensities.

Now, using the above knowledge we shall substantiate the extinction-induced broadening by means of the measured integral breadth of reflection. The integral breadth B_m is defined by the area ωI_m under reflection divided by the intensity $I_{m,max}$ at the maximum of reflection [23]:

$$B_m = \omega I_m / I_{m,\max}, \tag{27}$$

where ω is the scanning speed. Due to the extinction-affected intensities (I_m, $I_{m,max}$), B_m is also an *extinction-affected integral breadth.* Since the denominator, $I_{m,max}$, in the integral-breadth formula (27) suffers the highest reduction among all measured intensities, the integral breadth B_m has *a larger value* with respect to an integral breadth B, the correct one, corresponding to the extinction-free conditions.

The next considerations are intended to be derived a relationship between the reflection broadening affected by extinction and that one corresponding to extinction-free conditions. Introducing I_m from (1) transforms (27) into

$$B_m = y\omega I_{kin} / I_{m,\max}. \tag{28}$$

According to (1), one can write:

$$I_{m,\max} = y_{\max} I_{kin,\max}, \tag{29}$$

where $y_{\max}$ is the extinction factor corresponding to the reflection maximum, and $I_{kin,\max}$ is the kinematic intensity at the reflection maximum. Replacing $I_{m,\max}$ with its corresponding expression from (29) transforms (28) into

$$B_m = (y/y_{\max})\, B. \tag{30}$$

where the integral breadth

$$B = \omega I_{kin} / I_{kin,\max} \tag{31}$$

is defined by the *kinematic* intensities and, hence, it is not affected by SE. Thus, for the purpose of B determination one needs two extinction factors. While the y factor is an averaged over the range of the reflection, the factor $y_{\max}$ corresponds to the maximum of the reflection. The calculation of these factors can be done by using the reflection-pair method. The difference

$$\Delta B_\varepsilon = B_m - B \tag{32}$$

defines the *extinction-induced enlargement* $\Delta B\varepsilon$ which is actually an *extinction-induced systematic error* in the measured integral breadth of reflection.

5. Experimental

For the purpose of this study electrodeposited silver films were used as model samples. The films represent < 111 > (sample Ag2RE) and < 100 > (samples Ag2K and Ag3P) main texture components. To precisely indicate the extinction-induced broadening, the reflections are measured with a standard X-ray diffractometer using single-component CuK$_\beta$-radiation separated by graphite monochromator. The thickness of the films was about 40 μm.

The change in the effective absorption coefficient of a reflection will reflect in x-ray penetration depth [12]. Depending on the texture factor and energy I_0S of incident beam, the effective x-ray penetration depth of the samples under study vary between 6.7 μm and 8.7 μm for the low-angle Bragg reflections (111 and 200) and between 8 μm and 13.8 μm for the high-angle Bragg reflections (222 and 400).

6. Results and Discussion

In this section we shall accentuate successively on both the systematic error in texture — factor measurements and the anisotropic nature of the coefficient g. Figure 1 shows the 111↔222 reflection pair corresponding to the main <111> component of an electrodeposited Ag film (Ag2RE). With respect to the ordinary linear absorption coefficient, the SE correction amounts to about 16% for the 111 reflection and to about 2.4% for the 222 reflection. The texture factor P must be the same for a reflection

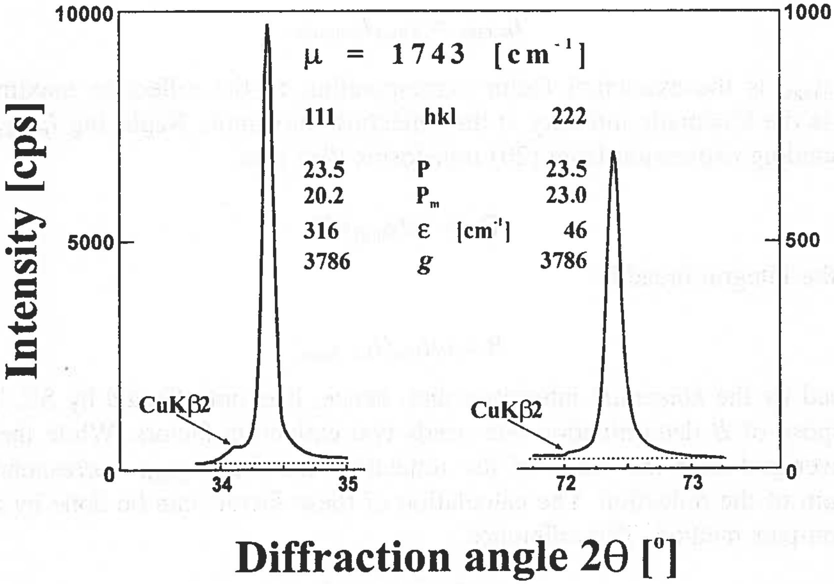

Fig. 1. 111↔222 reflection pair corresponding to the ideal direction of the main <111> texture component of an electrodeposited Ag film (Ag2RE): *hkl* are the Miller indices of reflection; *g* is the SE coefficient; ε[cm^{-1}] is the SE correction; P_m is the extinction-affected texture factor; P is the extinction-unaffected texture factor; μ[cm^{-1}] is the ordinary linear absorption coefficient of Ag. The measurements were performed with CuK$_\beta$-radiation separated by graphite focusing monochromator

pair since it is a sample property independent of the SE. In contrast to P, P_m is extinction-affected. Evidently, higher SE correction causes higher systematic error ΔP in the measurements of the texture factor P_m.

TABLE

Relative extinction-induced errors $(\Delta B_\varepsilon/B_m)$ % of 111 and 200 reflections measured under different x-ray tube ratings [W], B (minutes of arc) is the integral breadth unaffected by extinction and P_{hkl} is the texture factor of electrodeposited silver films representing respectively < 111 > and < 100 > main texture components

Sample	*hkl*	P_{hkl}	$(\Delta B_\varepsilon/B_m)$ %		
			240 W	400 W	560 W
Ag2RE	111	23.5	10	14	18
Ag3P	200	74.9	2	4	7

The value of the coefficient g is related to the texture factor P. Like P, g has the same values for the two reflections of the reflection pair corresponding to a crystallographic direction. This result confirms cogently the directional dependence of g and, hence, its anisotropic nature.

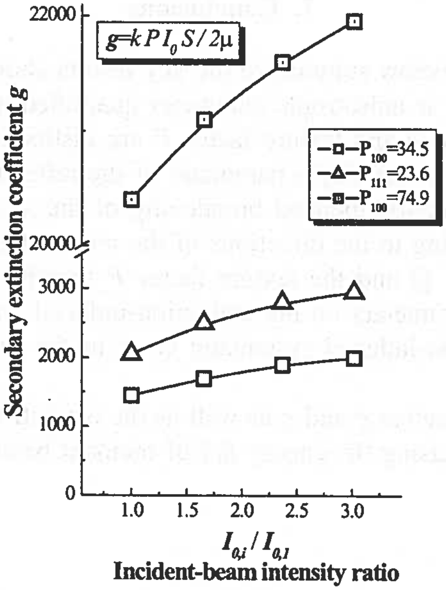

Fig. 2. Secondary extinction coefficient g *vs*. the ratio $I_{0,i}/I_{0,1}$, where $I_{0,1}$ is the incident-beam intensity corresponding to the lowest x-ray rating (=240 W) used by the first experiment, and $I_{0,i}$ is the incident-beam intensity of experiment i = 1,2,3,4. Three sets of experiments are performed under different values of the texture faxctor P. The measurements were perfomed with CuK$_\beta$-radiation separated by graphite focusing monochromator

Now let us point out that while the values of SE coefficient, observed in various single crystals, are in the range 200-1000 ([8] and references therein), the values of g, observed here, are in the range 1000 – 22000 as evident from Figure 2. Figure 2 presents a plot of g *vs.* the ratio $I_{0,i}/I_{0,1}$, where $I_{0,1}$ is the incident-beam intensity corresponding to the lowest x-ray tube rating (=240 W) used by this first experiment, and $I_{0,i}$ is the incident-beam intensity of experiment $i = 1,2,3,4$. The curves illustrate the dependence of g on both the texture factor and the incident-beam energy (see (11)). Evidently, the texture factor P is the parameter that contributes dominantly to the value of g.

Table 1 shows the texture factors and the relative extinction-induced reflection broadening $(\Delta B_\varepsilon/B_m)\%$ measured under different x-ray tube ratings W. For the 200 reflection of Ag3P film representing rather high texture factor P_{100}, the relative extinction-induced broadening $(\Delta B_\varepsilon/B_m)\%$ is less pronounced than that one measured at 111 reflection of another silver film (Ag2RE) representing more than three times lower texture factor P_{111} with respect to the former case. These results reveal that the reflectivity Q and texture factor P together contribute to the extinction-induced broadening of the strongest low-angle Bragg reflections. However, the reflectivity Q is the parameter that dominantly contributes to this effect.

7. Conclusions

The findings given below summarize the key results about the nature of SE:

- The SE coefficient g is anisotropic parameter quantified by the texture factor P.
- Since the reflectivity Q and texture factor P are distinctive features of reflection, the SE correction ε is formally a parameter of the reflection.
- There exists an extinction-induced broadening of the strong low-angle Bragg reflections corresponding to the directions of the main texture components.
- Both the reflectivity Q and the texture factor P together act respectively as first and second rank parameters on the extinction-induced enlargement ΔB_ε which is actually an extinction-induced systematic error in the integral breadth of reflection.
- The extinction parameters g and ε as well as the extinction-induced errors ΔP and ΔB_ε increase with raising the energy I_0S of incident beam.

OUTLOOKS

- The SE correction offers a possibility either existing methods to be reconsidered or new ideas to be developed.
- Future application of the SE correction in the diffraction pole figures would provide for their refinement and, hence, for improved quantification of the texture.
- No problem related to using the integral intensity can be solved correctly in textures if the SE is not taken into account.

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