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An extinction-free technique for pole density measurements of textures by XRD

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Pole density is a fundamental parameter of the diffraction pole figures used for calculation of orientation distribution functions that characterize the physical properties of textures. To gain accuracy and, hence, physical reality of the data, an approach is elaborated to derive experimental pole-density values, which are free of extinction effects. The approach is based on the intrinsic invariability of the empirical extinction coefficient *k* at a series of levels of interaction of the diffraction process. The invariability of *k* is a precondition for nullifying the extinction effects by equating couple of its expressions defined with the intensities measured at the same series of the levels of interaction. A nickel sample representing <100> texture component is investigated. The resultant derived series of data for the distribution of pole density *P* of the {200} diffraction pole figure is in exact accord with kinematic theory.

Key words: extinction, texture, diffraction pole figures, texture goniometer.

INTRODUCTION

Characterization of textural anisotropy is based on using pole density *P* that is defined by relative volume fraction of crystallites contributing with their <*hkl*> poles to the *hkl* reflection [1]. As diffraction and extinction are indissolubly linked [2], the pole density P_m determined by using the well-known definition $P_m = I_m/I_m^r$ suffers an extinction-induced systematic error caused by the measured intensities I_m and I_m^r of the same reflection of textured sample and powder standard, respectively. To overcome the inherent deficit of precision in the above definition, a pioneer technique is developed for *analytical* nullification of the extinction effects of diffraction pole-figures measured with texture goniometer. The technique is based on the invariability of the empirical extinction coefficient *k* with respect to the level of interaction of the diffraction process. Practically, the nullification of the extinction effects is attained by equating two expressions of *k* defined properly by measured intensities. To realize the purposes of this study, our concern here is essentially with exact relationship between diffraction and extinction at a series of levels of interaction attained by controlled variations of suitable physical parameters as in [3].

ANISOTROPY OF EXTINCTION COEFFICIENTS: NULLIFICATION OF THE EXTINCTION EFFECTS

Bragg *et al*. [4] and Darwin [5] have supposed that the empirical extinction coefficient *k* and the secondary extinction coefficient *g*, respectively, are constants for the crystal, i.e. they have considered *k* and *g* as parameters independent of crystallographic direction. Accounting for the crystal and textural anisotropy, the nature of *k* and *g* is reconsidered here. To this end, two definitions given by Darwin-Zachariasen [5, 6] and Bunge [1], respectively, are used:

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

$$I_{kin} = PI_0QS/2\mu\,. \quad (2)$$

Here ε is the secondary extinction (SE) correction, *g* is a dimensionless quantity, p_n (n=1,2,...,) is the polarization factor for incident X-ray beam [6, 7], I_0 is the intensity of the incident beam, *S* is the cross

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section of the beam, Q is the reflectivity per unit crystal volume, μ is the ordinary linear absorption coefficient. Combining (1) and (2) yields

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

where the expression

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

shows that k and g are mutually connected. Reforming (4) gives an expression for

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

illustrating that g depends on reciprocal way of the same parameters. Thus, the coefficients k and g should show different behaviour with respect to the diffraction process, whose level of interaction is controlled for any particular case by both P and I_0. First, at $PI_0 \rightarrow 0$, the lower limiting values of $I_{kin} \rightarrow 0$ (2) and $g \rightarrow 0$ (5) show, respectively, that in the only case of no diffraction, there is no extinction. Second, whereas g is proportional to the product PI_0, the coefficient k e is proportional to the ratio g/PI_0. Therefore, by virtue of the interdependence between g and PI_0, any change of P or I_0 or both does not cause change of the ratio g/PI_0 and, hence, k is constant for any measured point of a pole figure and, hence, independent of the level of interaction of the diffraction process. To prove this deduction suppose the pole density changes from P to P^r=1 under I_0=const. Following (4), k is transformed respectively into k^r, i.e.

$$k^r = 2\mu g^r / I_0S\,. \tag{6}$$

Here, it is accounted that g^r is proportional to P^r which corresponds to random distribution of crystalline orientations. Dividing (4) by (6) and taking into account that P=g/g^r yields

$$k = k^r\,, \tag{7}$$

irrespective k and k^r correspond to different crystalline orientation distributions. Whereas k corresponds to $\{hkl\}$ diffraction pole figure (intensity distribution function) of a texture, k^r corresponds to hkl reflection of a sample representing the same substance with random orientation distribution.

The invariability of k constitutes its capability to nullify the extinction effects by equating two its expressions that are defined by the intensities of a pole figure measured at a series of levels of interaction. By virtue of the mathematical logics, the condition (7) has to be in exact accord with the kinematical theory and the resultant derived data will be then extinction-free.

EXPRESSING POLE DENSITY P BY NULLIFICATION OF EXTINCTION EFFECTS

To express P by nullifying extinction effects, a proper procedure is designed to data collection (Figure 1). In this respect, the $\{hkl\}$ diffraction pole figure of textured sample and hkl reflection of a powder standard with random crystalline distribu-

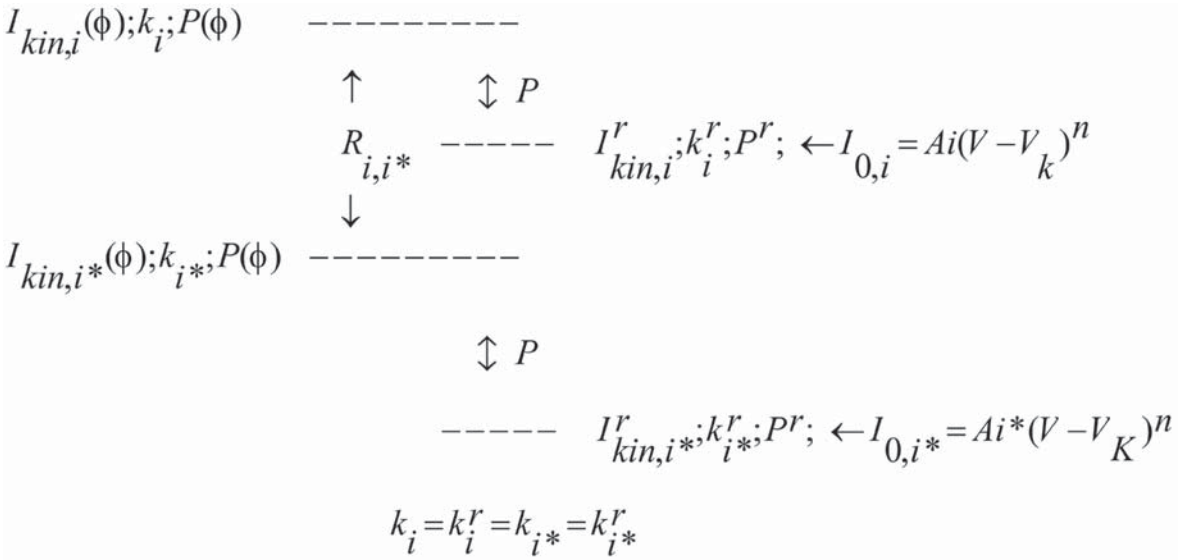

Fig. 1. Data collection procedure that is designed by the levels of interaction of the diffraction process. The $\{hkl\}$ pole figure of textured sample and hkl reflection of powder standard are measured at the incident beam intensities $I_{0,i}$ and $I_{0,i*}$ cased by the generator current i and i*. Here ϕ is the angle to the sample normal direction.

tion are measured at the incident beam intensities $I_{0,i}$, I_{0,i^*} caused by stepwise reduction of the generator current values i and i^* (i=2i^*).

In the equations listed in Figure 1, A is a constant, V_K is the critical excitation potential of the $K\alpha$ radiation, and n=1.5 [8]. As a whole, the measurement procedure is carried out at constant generator tension V. Any of the particular levels of interaction is characterized by kinematic intensities, $I_{kin}(\phi)$ and I^r_{kin}, of the texture and power standard, respectively, the pole densities, $P(\phi)$ and P^r, and the coefficient k. Let us focus our attention that k is the same for each of the levels of interaction, and P^r is equal to unit. Then, the pole density $P_i(\phi)$ is express by the kinematic intensities corresponding to the first couple of levels of interaction measured at the intensity $I_{0,i}$:

$$P_i(\phi) = I_{kin,i}(\phi) \big/ I^r_{kin,i} \tag{8}$$

The relation (8) is valid for the interval $0° < \phi < 70°$ of the pole figure measured at the intensity $I_{0,i}$. As shown in the paper [3], the kinematic intensities are defined by the respective measured intensities I_m:

$$I_{kin,i}(\phi) = \left\{\mu \Big/ \left[\mu - k_i I_{m,i}(\phi)\left(p_2 / p_1^2\right)\right]\right\} I_{m,i}(\phi), \tag{9}$$

$$I^r_{kin,i} = \left\{\mu \Big/ \left[\mu - k^r_i I^r_{m,i}\left(p_2 / p_1^2\right)\right]\right\} I^r_{m,i}. \tag{10}$$

Solving the system of equations (9) and (10) for $k_i = k^r_i$ (see (7)) yields the expression:

$$k_i = \frac{\mu\left[P_i(\phi) - \left(I_{m,i}(\phi)/I^r_{m,i}\right)\right]}{I_{m,i}(\phi)\left(p_2/p_1^2\right)\left[P_i(\phi) - 1\right]}. \tag{11}$$

By analogy of equations from (8) to (11), the coefficient $k_{i^*} = k^r_{i^*}$ corresponding to the second couple of levels of interaction is expressed by using the next three definitions:

$$P_{i^*}(\phi) = I_{kin,i^*}(\phi) \big/ I^r_{kin,i^*}. \tag{12}$$

$$I_{kin,i^*}(\phi) = \left\{\mu \Big/ \left[\mu - k_{i^*} I_{m,i}(\phi)\left(p_2 / p_1^2\right)\right]\right\} I_{m,i^*}(\phi), \tag{13}$$

$$I^r_{kin,i^*} = \left\{\mu \Big/ \left[\mu - k^r_{i^*} I^r_{m,i^*}\left(p_2 / p_1^2\right)\right]\right\} I^r_{m,i^*} \tag{14}$$

$$k_{i^*} = \frac{\mu\left[P_{i^*}(\phi) - \left(I_{m,i^*}(\phi)/I^r_{m,i^*}\right)\right]}{I_{m,i^*}(\phi)\left(p_2/p_1^2\right)\left[P_{i^*}(\phi) - 1\right]}. \tag{15}$$

Solving (11) and (15) for $P_{i,i^*}(\phi) = P_i(\phi) = P_{i^*}(\phi)$ under nullifying the extinction effect by equating the coefficients $k_i = k_{i^*}$ yields an extinction-free value for the pole density for the ϕ-angle of the diffraction pole figure:

$$P_{i,i^*}(\phi) = \frac{I_{m,i}(\phi) I_{m,i^*}(\phi)\left(I^r_{m,i} - I^r_{m,i^*}\right)}{I^r_{m,i} I^r_{m,i^*}\left(I_{m,i}(\phi) - I_{m,i^*}(\phi)\right)}. \tag{16}$$

Therefore, starting from kinematic definitions (8) and (12) for the pole density, an operative formula (16) that is in exact accord with the kinematic theory is derived using measured intensities. This procedure has to be repeated for any ϕ-angle of the measured interval $0° < \phi < 70°$.

EXPERIMENTAL, RESULTS AND DISCUSSION

As model samples, an electrodeposited nickel coating (Ni1) and a nickel powder standard with random crystalline distribution were used. The nickel coating represents fiber texture with a main <100> component. The {200} pole figure and 200 reflection corresponding to the respective samples were measured with texture goniometer using Ni filtered CuK_α radiation. The two-step measurement procedure, shown in Figure 1, was carried out in such

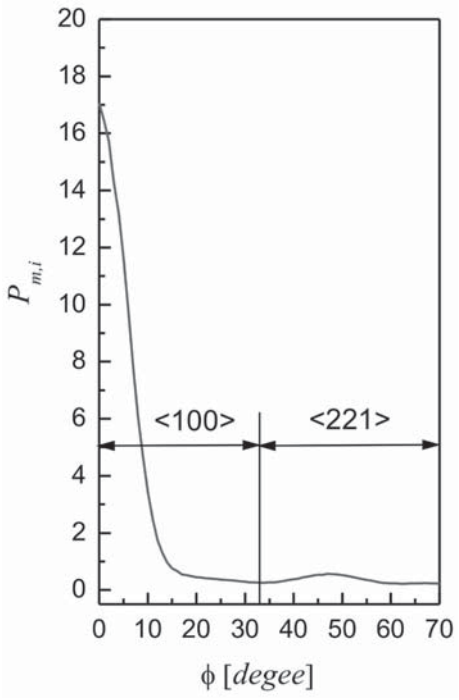

Fig. 2. {200} pole figure of an electrodeposited nickel (Ni1) measured at generator current i. It represents the distribution of strongly extinction-affected pole densities: $P_{m,i}(\phi) = I_{m,i}(\phi)/I^r_m$, ϕ is the angle to the sample normal direction.

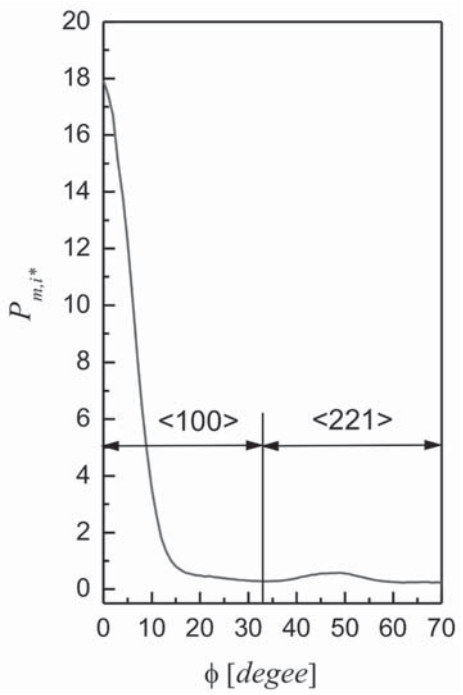

Fig. 3. {200} pole figure of an electrodeposited nickel coating (Ni1) measured at generator current i^*. It represents the distribution of less extinction-affected pole densities: $P_{m,i^*}(\phi) = I_{m,i^*}(\phi)/I^r_m$.

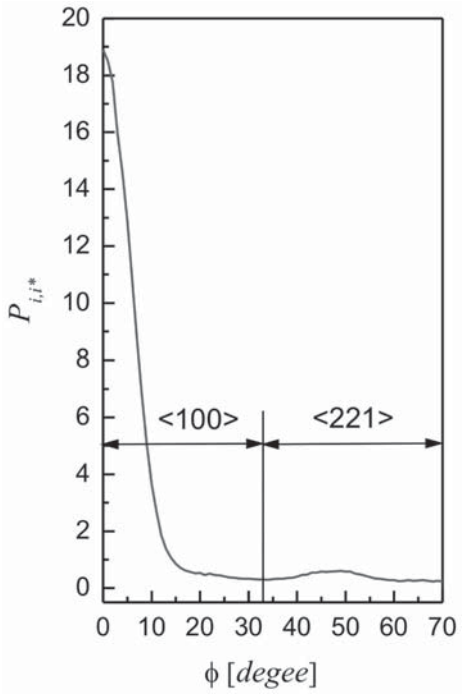

Fig. 4. {200} pole figure of an electrodeposited nickel coating (Ni1) representing extinction-free data calculated by (16).

a way to compensate the stepwise decrease of the generator current from i to i^* ($i = 2i^*$) by respective increase of the data collection time per scanned step from τ to τ^*, i.e. ($i\tau = i^*\tau^*$). The compensative condition ensures the same statistical errors in the respective ϕ-angles of the measured entity.

The pole density $P_m(\phi)$ distributions determined for the first and second measurements are shown in Figure 2 and Figure 3, respectively. Due to lower extinction effects, the $P_{m,i^*}(\phi)$ values (Figure 3) are higher than those of the $P_{m,i}$ (ϕ) distribution (Figure 2) that are strongly affected by extinction. The systematic error is higher at the higher level of interaction and lowest at the lowest level of interaction. This error depends on the absolute value P_m of the pole density as well. Figure 4 shows extinction-free data determined by (16). The percentage errors between the respective data listed in Figure 4 and that ones listed in Figure 2 and Figure 3 vary from about 5% to less than 1% for the whole measured interval $0° < \phi < 70°$.

CONCLUDING REMARKS

The main advantage of this approach is to gain accuracy and, hence, physical reality of the data. Accuracy can only be gained by care in the design and implementation of an experiment. Actually, this approach offers a possibility for existing methods both to be re-considered and improved for texture characterizations and to develop new ideas. In general, one can state that no problem related to using the integral intensities can be correctly solved in textures if secondary extinction effects are not nullified.

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REFERENCES

1. H. J. Bunge, *Textures and Microstructures*., **29**, 1, (1997).
2. A. McL. Mathieson, *Acta Cryst*. *A*, **35**, 50 (1979).
3. I. Tomov, in the same issue, submitted.
4. W. L. Bragg, R. W. James, C. H. Bosanque, *Phyl. Mag*., **42**, 1 (1921).
5. C. G. Darwin, *Phil. Mag*., **43**, 800 (1922).
6. W. H. Zachariasen, *Acta Cryst*. **16**, 1139 (1963).
7. S. Chandrasekhar, *Advances in Physics*, **9**, 363 (1960).
8. A. Guinier, Theorie et Techn. de la Radiocryst, 2nd Edition, Paris, Dunod, 1956.

ЕДНА ТЕХНИКА ЗА ИЗМЕРВАНЕ НА СВОБОДНИ ОТ ЕКСТИНКЦИЯ ПОЛЮСНИ ПЛЪТНОСТИ ЧРЕЗ РЕНТГЕНОВА ДИФРАКЦИЯ

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(Резюме)

Полюсната плътност е фундаментален параметър на дифракционните полюсни фигури, които се използват за изчисляване на ориентационните разпределителни функции, характеризиращи физичните и механични свойства на текстурите. За да се спечели точност, а оттук следва и физична реалност на данните, е разработен един подход за извличане стойностите на експерименталните полюсни плътности, които са свободни от екстинкционни ефекти.