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Modified Statistical Regularization in X-Ray Line Profile Analysis

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In X-ray diffraction experiments smearing effects due to instrumental resolution are appearing. Correction of these effects is not simple because of the statistical disturbances and limited a-priori informations. A recursive algorithm is produced from the Bayes estimation theory. The regularization process is interpreted as a certain a-priori information on the degree of smoothness of the real diffraction pattern.

Bei Röntgenbeugungsexperimenten treten Verschmierungseffekte aufgrund der instrumentellen Auflösung auf. Die Korrektur dieser Effekte ist nicht einfach wegen der statistischen Störungen und begrenzten a-priori-Informationen. Es wird ein rekursiver Algorithmus aus der Bayes-Theorie abgeleitet. Der Regularisierungsprozeß wird als eine gewisse a-priori-Information über den Grad der Glattheit des realen Beugungsbildes interpretiert.

1. Introduction

The mechanical properties (strength, plasticity, etc.) depends on the grain structure of polycrystalline metals. The polycrystalline structure is characterized by its dispersiveness and microdistortions.

The line-profile investigations of the diffraction patterns are one of the powerful tools for the determination of the polycrystalline structure. To obtain the original diffraction line, the experimental errors have to be eliminated. Unfortunately the widely applied "reciprocal" method [1 to 3] is mathematically incorrect [4].

Our aim in the present paper is to modify the method of statistical regularization to facilitate the analysis of X-ray data without losing pertinent information. The results so obtained are compared for W and Mo powders with those obtained by the direct deconvolution method.

2. The Methods of Evaluation

A line-broadening analysis generally consists of three stages:

1. Measurement of X-ray line profiles and application of a special correction (regularized Kalman filter [5]).

2. Separation of the structural broadening. This consists of the elimination of the instrumental and spectral imperfections. This elimination can be done by using a breadth measurement (Voigt deconvolution [6]) or – more exactly – using discrete Fourier transformation (DFT) (Stokes deconvolution) [7, 8].

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3. Evaluation of the structural broadening. The structural broadening is usually subdivided into broadening due to size effects and to the lattice distortions (microstrains) [9].

The structural broadening can be approximated with the single-line Voigt method [7, 8], representing the shape of the structurally broadened profile by its integral breadth and half-width. To separate size and strain broadening by this method assumptions have to be made: the broadening caused by the crystallite size is described by a Lorentz function and the microstrain broadening by a Gauss function [7].

Assuming only a size (or strain) effect in the sample we can determine the structural broadening by the Warren-Averbach method, [6] based on the description of the structurally broadened profile by its set of DFT values. To separate size and strain broadening by this method we use a physical condition [7, 10] requiring at least two orders of reflections from the same lattice plane for crystal-size broadening.

The analyses based on line breadths and DFT values yield different results: the single-line Voigt method yields the volume average of the crystal size, while the Warren-Averbach analysis yields an area (surface) average. The results so obtained should be considered complementary, not contradictory.

Our modified method of statistical regularization gives a high accuracy and the possibility of smoothing the anomalous overshoots as well. This method gives the highest accuracy in the determination of mosaic sizes (D_{eff}) [11, 12] by the determination of true X-ray diffraction spectrum.

3. The Modification Suggested

We consider now the linear system of equations for X-ray diffraction as follows:

$$I_0 = Kp + \xi\,, \tag{1}$$

where K is the matrix of the X-ray diffraction pattern, $\boldsymbol{I}_0$ the total X-ray diffraction measurement vector, $\boldsymbol{p}$ the estimated vector of the unknown real diffraction, ξ the vector of statistical (white) fluctuations and errors with a zero mean value in time average.

Moreover, let ξ and $\boldsymbol{p}$ have an a-priori Gaussian distribution. In this case, the minimum variance estimator and the maximum a-posteriori estimator are identical.

In order to obtain the maximum a-posteriori estimator p_{map}, $E[\boldsymbol{I}_0/\boldsymbol{p}]$ (the mean value) has to be calculated first. From (1) we have [10 to 12]

$$\begin{aligned} E[\boldsymbol{I}_0/\boldsymbol{p}] &= E\{\xi = \boldsymbol{I}_0 - K\boldsymbol{p}\} \\ &= (2\pi)^{-n/2}\,[\det(\xi)]^{-1/2}\exp\{-0.5\,\|\boldsymbol{I}_0 - K\boldsymbol{p}\|^2\,\xi^{-1}\}\,. \end{aligned} \tag{2}$$

After some simple manipulation the Gaussian density $N\{M[p],\,p\}$ results for $E[p/I_0]$ with

$$\boldsymbol{p}_{\text{map}} = \boldsymbol{M}[\boldsymbol{p}] = \boldsymbol{M}\{K^{\mathrm{T}}\xi^{-1}\boldsymbol{I}_0 + \boldsymbol{M}^{-1}(0)\,\boldsymbol{M}[\boldsymbol{p}(0)]\}\,, \tag{3}$$

$$\boldsymbol{M} = [\boldsymbol{M}^{-1}(0) + K^{\mathrm{T}}\xi^{-1}K]^{-1}\,. \tag{4}$$

In this case where no a-priori information is known about $\boldsymbol{p}$, $\boldsymbol{M}(0) \to \infty$ (3) yields

$$\boldsymbol{p}_{\text{p}} = \boldsymbol{M}K^{\mathrm{T}}\xi^{-1}\boldsymbol{I}_0\,, \tag{5}$$

$$\boldsymbol{M} = [K^{\mathrm{T}}\xi^{-1}K]^{-1}\,. \tag{6}$$

Equation (1) may be solved with respect to vector p using the statistical regularization method [3, 11, 12],

$$p_\alpha = [K^T \xi^{-1} K + \alpha \Omega]^{-1} K^T \xi^{-1} I_0 , \tag{7}$$

where Ω is a matrix stabilizer [1], introduced to take into account the a-priori information on the degree of smoothness of the solution sought for p_α, α is a regularization parameter, $0 < \alpha < 1$.

The Fourier coefficients can be written as [4, 8, 9]

$$\mathrm{Re}\,[F(k)] = \frac{2H_p}{L_p} \sum_{i=1}^{N} p_\alpha(S_i) \cos(2\pi k/L_p)\, S_i , \tag{8}$$

$$\mathrm{Im}\,[F(k)] = \frac{2H_p}{L_p} \sum_{i=1}^{N} p_\alpha(S_i) \sin(2\pi k/L_p)\, S_i , \tag{9}$$

where L_p is the value of the experimental interval of expansion (for the pattern), and $S_i = 2\theta$, where the θ is the Bragg angle.

The argument is $S_i = S_i + (i - 1) H_p$, where H_p is the step of discretization. Distance $L(k)$ in the crystal lattice has been connected with the number of Fourier coefficients as [7 to 9]

$$L(k) = \frac{\lambda}{L_p \cos\theta} K , \tag{10}$$

where λ is the wavelength of the radiation, θ the Bragg angle of the reflection (centre of gravity of the pattern), the Fourier coefficients being normalized to $F(0) = 1$. The normalized Fourier coefficient is given by

$$A^D(k) = \frac{F(k)}{F(0)} . \tag{11}$$

In order to correct the value of D_{eff} and considering the error arising from the inaccurate determination of the background level, a linear regression of $\ln A^D(L)$ versus L is plotted,

$$\ln A^A(L) = \langle \ln A^D(L) \rangle + \mu(L - \langle L \rangle) , \tag{12}$$

where $A^D(L)$ are the normalized Fourier coefficients of the function of real physical spreading from fine particle dispersity $p_\alpha(s)$ [1 to 3],

$$L = \sum_{i=1}^{M} L_i/M , \tag{13}$$

$$\langle \ln A^D(L) \rangle = \left(\sum_{i=1}^{M} \ln A^D(L_i) \right) \Big/ M , \tag{14}$$

M is the number of significant Fourier coefficients of the function $p_\alpha(s)$.

Using the method of least squares the well-known Gaussian strategy minimizes the differences between the experimental values (intensities, absorption values, etc.) and the model function see (12). We obtain for the linear regression coefficient the following

expression [13]:

$$\mu = \frac{\sum_{i=1}^{M} [\ln A^{\mathrm{D}}(L_i) - \langle \ln A^{\mathrm{D}}(L) \rangle] (L_i - \langle L \rangle)}{\sum_{i=1}^{M} (L_i - \langle L \rangle)^2}. \tag{15}$$

To clarify the degree of linear relation we shall calculate a correlation coefficient for the values $\ln A^{\mathrm{D}}(L)$ and L [9],

$$\varrho = \frac{\sum_{i=1}^{M} [\ln A^{\mathrm{D}}(L_i) - \langle \ln A^{\mathrm{D}}(L) \rangle] (L_i - \langle L \rangle)}{\sqrt{\sum_{i=1}^{M} [\ln A^{\mathrm{D}}(L_i) - \langle \ln A^{\mathrm{D}}(L) \rangle]^2} \sqrt{\sum_{i=1}^{M} (L_i - \langle L \rangle)^2}} \tag{16}$$

and residual dispersion [13]

$$E_{\min} = (1 - \varrho^2) \sum_{i=1}^{M} [\ln A^{\mathrm{D}}(L_i) - \langle \ln A^{\mathrm{D}}(L) \rangle] \tag{17}$$

as criterion of the correctness of the hypothesis concerning the presence of a linear relation [13] was used. The standard deviation of the linear regression is

$$T = \varrho \sqrt{(M - 2)/(1 - \varrho^2)}\,. \tag{18}$$

Further, according to [13], for the critical points t_c [13] the distributions were determined for the criterion of the so-called significance level (18) which is equal to 0.001 and degree of freedom is $K = M - 2$.

If the condition

$$|T| > t_c \tag{19}$$

is not fulfilled, then for all $i = 1, 2, \ldots M$ the following condition should be checked [13]:

$$|\ln A^{\mathrm{D}}(L_i) - \langle \ln A^{\mathrm{D}}(L) \rangle - \mu(L_i - \langle L \rangle)| \leqq \sqrt{E_{\min}/M}\,. \tag{20}$$

Those $\ln A^{\mathrm{D}}(L_i)$ values for which the condition (20) is not fulfilled are excluded and all calculations (13) to (20) are repeated until (19) is satisfied.

The value D_{eff} is calculated by $D_{\mathrm{eff}} = -1/\mu$. The number of significant Fourier coefficients of the function $p_\alpha(S)$ which provide a linear relation between $\ln A^{\mathrm{D}}(L)$ and L are generally between 8 and 10 when the spectral method is used.

In calculations applying the developed modified regularization method the number of necessary Fourier coefficients was 25 to 30 at a discretization step depending upon the lattice parameter in an interval which is equal to $L = 1.5$ to 2.5 nm.

4. The Model

For a "pure" spectral line such as $K_{\alpha 1}$ or $K_{\alpha 2}$ of the unresolved K_α doublet at low Bragg angles, the real diffraction function may be represented by the Cauchy form [9 to 11],

$$p_\alpha(S) = \frac{A}{1 + 1/c^2(S - W)^2}, \tag{21}$$

where A is the amplitude of the function of the true physical broadening, C the half-width of the true physical broadening, W the position of the maximum.

To separate size and strain broadening, we modify our statistical regularization method with the following physical assumption: broadening due to the mosaic size is independent, while microstrain broadening depends on the order of reflection.

This method is used on the following basic equation involving the Stokes-corrected Fourier coefficients, $A(k)$, of a harmonic number (number of the term in the Fourier expansion) k [7, 9],

$$A(k) = A^{\mathrm{D}}(k)\, A^{\mathrm{s}}(k)\,, \tag{22}$$

where $A^{\mathrm{s}}(k)$ is the microdistortion coefficient, $A^{\mathrm{D}}(k)$ the mosaic size coefficient.

The first-order reflection can be written by (22) as

$$A^{\mathrm{I}}(k) = A^{\mathrm{DI}}(k)\, A^{\mathrm{SI}}(k)\,. \tag{23}$$

The second-order of reflection can be written as

$$A^{\mathrm{II}}(k) = A^{\mathrm{DII}}(k)\, A^{\mathrm{SII}}(k)\,. \tag{24}$$

5. Conclusion

Our results lead to the conclusion that the modified method of statistical regularization developed by us can be successfully applied for the determination of microstrains and mosaic sizes by X-ray line profile analysis in deformed polycrystals. The instrumental broadening of the measured X-ray signals leads to the solution of Fredholm's integral equations of the first kind.

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