phys. stat. sol. (a) **125**, 459 (1991)

Subject classification: 61.10; S1

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Analysis of the Broadening of X-Ray Diffraction Line Profiles of Polycrystalline Tungsten

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A statistical regularization approach is applied to calculate the real X-ray diffraction line profile from the measured convolution. Results are applied for tungsten powder.

Es wird ein statistisches Regulierungsverfahren benutzt, um das reale Röntgenbeugungslinienprofil aus der gemessenen Faltung zu berechnen. Die Ergebnisse werden auf Wolframpulver angewendet.

1. Introduction

The mechanical properties are connected with the polycrystalline structure, with internal stresses and strengths, as well as with dispersiveness and microdistortions. The information about the polycrystalline parameters can be obtained from the X-ray diffraction line profile. The task is experimentally complicated, which is connected with the noises and errors included in the measurements. To get the original form of the profile (to deconvolute the overlapping and mixed functions) there exist numerous approaches, requiring to solve certain integral equations of the first kind.

To determine the polycrystalline fine structure, a so-called "reciprocal" method is often encountered in X-ray investigations, but this is mathematically incorrect [10]. To solve such a problem some additional information is required about the functions being convoluted.

In our present paper a statistical regularization method is used and applied for the X-ray diffraction fine structure of polycrystalline tungsten powders.

In the analysis of the measured X-ray diffraction spectra, smearing effects due to the instrumental resolution are generally present. This situation can be represented by the following mathematical model:

$$I_0(s) = \int_{-\infty}^{\infty} I(s - s')\, P(s')\, ds' + \xi(s) \tag{1}$$

or

$$\boldsymbol{I}_0 = K\boldsymbol{P} + \xi\,,$$

where K is an $(n \times m)$ matrix, $\boldsymbol{I}_0(s)$ the measured value of the X-ray spectrum at point s, $I(s)$ the resolution function of the instrument, $P(s)$ the true, unknown, spectrum, and $\xi(s)$ the statistical noise of the X-ray diffraction measurement.

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From a set of measurements on $I_0(s)$ we calculate the true function of $P(s)$. This is complicated because

1. non-negligible statistical noise $\xi(s)$ is always present;
2. often the specification of a physically reasonable model for the function $\xi(s)$ is not possible;
3. the resolution function $I_0(s)$ is not exactly known, but usually obtained from measurements only with statistical disturbance.

As the first approach a least-squares approximation is possible, with the advantage that it requires practically no knowledge of the statistical properties of the disturbances. For the more accurate treatment some general assumptions about the true X-ray spectrum have to be made, for instance, using expansions by orthogonal functions. This method has been widely used in control theory [1] and applied in the treatment of smearing problems [4]. These solutions can have severe oscillations with no physical significance, because of the few X-ray diffraction measurements and the errors involved.

Several authors have suggested different solutions. Weise [8] added terms to the standard deviation function of the least squares in order to damp these oscillations, Green [2] used Fourier transformations and excluded the higher frequencies, Grosswendt [3] smoothed the data using a simple averaging technique.

In terms of statistical estimation theory, these methods have no meaning, so a distortion of the signal may result. Wiener [9] has given forms of optimal filters for smoothing data, which have been applied [6, 7] for deconvolution. Unlike to least-squares techniques, the a-priori information about the X-ray diffraction spectrum has to be introduced in a statistical way.

This seems to be the avoiding oscillations for a small number of X-ray diffraction measurements. Nevertheless, the classical treatment with Fourier transformation, used by these authors, is very cumbersome and a solution for the general case (1) is not easily obtained. Kalman and Busy [5] have developed a Wiener filter for the sequential treatment. These equations have a special application in Bayes estimation methods.

The application of the method of regularization [10 to 12] can considerably facilitate the analysis of X-ray data without losing pertinent information. We have applied our method to samples of tungsten and compared with those obtained by the direct deconvolution method.

2. Experimental Procedure

Tungsten was selected as a sample material, since it has b.c.c. lattice, the diffraction maxima from this crystal lattice being spaced quite far from each other, that practically rules out the possibility of their not overlapping even under strong expansion, which results from high plastic deformation. The sample material was prepared by the refinement of the tungsten powder by a laboratory vibrating mill during 10, 20, 30, 50, 100. To prevent powder oxidation the milling was carried at in ethyl alcohol. Diffraction data were obtained with an X-ray diffractometer DRON-3, using filtered CuK_α radiation, the reflections selected for the analysis were (110) and (220) (Fig. 1, 2). The scanning step for discrete modes was selected such as to provide not less than 200 to 250 points for each diffraction line. The exposure in each point on the first-order reflection was 10 s, on the second-order reflection was 20 s. As a standard there was used an original tungsten powder, for which the size of the coherent scattering area (CSA) was obviously larger than 200 nm and the value of the relative root-mean-square microdeformation (RRMS) was equal to zero.

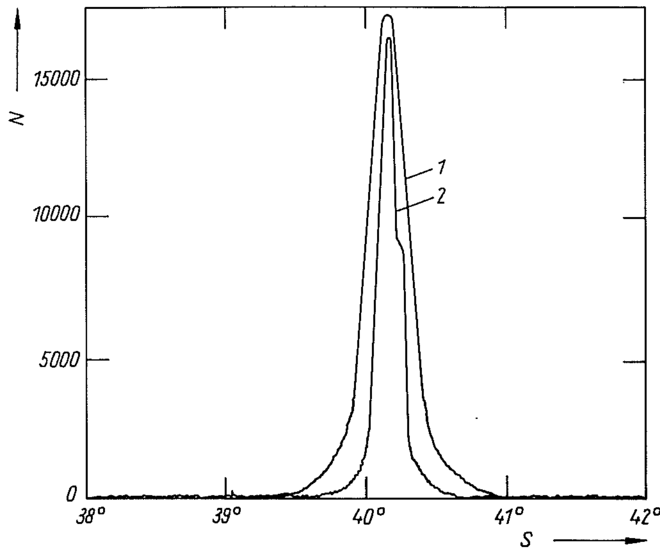


Fig. 1. Real X-ray diffraction profile of (1) pattern and (2) standard for first-order reflection (110). For pattern and standard $S_1 = 38.36°$, $S_n = 42.46°$

Equations (1) may be solved with respect to the vector $\boldsymbol{P}$ using the statistical regularization method [10 to 14],

$$P_\alpha = [\boldsymbol{K}^T \xi^{-1} \boldsymbol{K} + \alpha \Omega]^{-1} \boldsymbol{K}^T \xi^{-1} \boldsymbol{I}_0 , \tag{2}$$

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

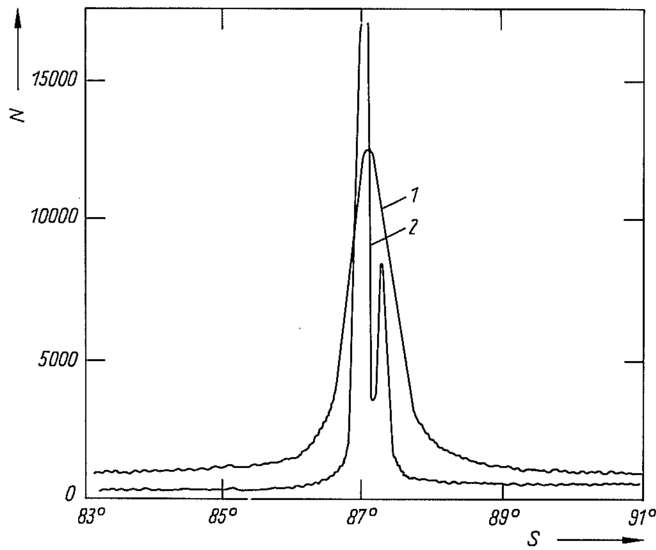


Fig. 2. Real X-ray diffraction profile of (1) pattern and (2) standard for second-order reflection (220); $\tau = 20$ s. For pattern and standard $S_1 = 86.31°$, $S_n = 90.31°$

3. Determination of the CSA

To correct the error, resulting from an inaccurate determination of the background level a linear regression of $\ln A^D(L)$ versus L is used,

$$\ln A^D(L) = \langle \ln A^D(L) \rangle + r(L - \langle L \rangle)\,, \tag{3}$$

where L is the distance in crystal lattice, $A^D(L)$ the normalized Fourier coefficients of the function of smearing caused by the fine particle dispersity $P_\alpha(s)$,

$$L = \left(\sum_{i=1}^{M} L_i \right) / M\,, \tag{4}$$

$$\langle \ln A^D(L) \rangle = \left(\sum_{i=1}^{M} \ln A^D(L_i) \right) / M\,, \tag{5}$$

M is the number of significant Fourier coefficients of the function $\boldsymbol{P}_\alpha(s)$.

Using a regression analysis, the well-known Gaussian strategy minimizes the differences between the experimental values (intensities, absorption values, etc.) and the model function from (12). We receive for the linear regression coefficient the following expression;

$$r = \left(\sum_{i=1}^{M} [\ln A^D(L_i) - \langle \ln A^D(L) \rangle]\,(L_i - \langle L \rangle) \right) \Bigg/ \left(\sum_{i=1}^{M} (L_i - \langle L \rangle) \right)^2 . \tag{6}$$

To clarify the degree of linear relation we shall calculate a correlation coefficient for the values in $A^D(L)$ and L,

$$\varrho = \frac{\sum_{i=1}^{M} [\ln A^D(L_i) - \langle \ln A^D(L) \rangle]\,(L_i - \langle L \rangle)}{\sqrt{\sum_{i=1}^{M} [\ln A^D(L_i) - \langle \ln A^D(L) \rangle]^2} \cdot \sqrt{\sum_{i=1}^{M} (L_1 - \langle L \rangle)^2}}\,, \tag{7}$$

and residual dispersion,

$$E_{\min} = (1 - \varrho^2) \sum_{i=1}^{M} [\ln A^D(L_i) - \langle \ln A^D(L) \rangle]\,. \tag{8}$$

As a criterion of the correctness of the hypothesis, i.e. the existence of a linear relationship, serves the characteristic quantity T [2],

$$T = \varrho \sqrt{(M - 2)/(1 - \varrho^2)}\,. \tag{9}$$

Further we determined the distributions for the criterion of the significance level of (9) which is equal to 0.001 and the degree of freedom number, $K = M - 2$.

If the condition

$$|T| > t_c \tag{10}$$

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

$$[\ln A^D(L_i) - \langle \ln A^D(L) \rangle - r(L_i - \langle L \rangle)] \leqq \sqrt{E_{\min}/M}\,. \tag{11}$$

Table 1
The mosaic block sizes and concentration of crystal lattice defects in six tungsten powders

N	milling time (h)	D_{100} (nm)	D_{200} (nm)	D_{100}/D_{200}	$1.5\alpha + \beta$	D_{1st} (nm)
1	10	57	30	1.90	0.0058	112
2	20	45	25	1.80	0.0066	81
3	30	41	24	1.71	0.0064	68
4	50	34	24	1.42	0.0046	45
5	100	30	23	1.30	0.0038	36
6	fillings	17	12	1.42	0.0091	21

Those values $\ln A^D(L_i)$ for which the condition is not fulfilled (20) are excluded and all calculations (4) to (11) are repeated until the condition (10) is fulfilled.

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

In calculations applying the developed modified regularization method the number of necessary Fourier coefficients was 25 to 30 at $L = 1.5$ to 2.5 nm.

The effective block sizes determined for two crystallographic directions ⟨110⟩ and ⟨100⟩ are shown in Table 1. The anisotropy of CSA sizes found during the powder investigation apparently is connected with the density of packing defects resulting from mechanical treatment.

In metals with b.c.c. lattice the possibility of crystal defect formation is very small, as they have high values of crystal defect energy. In this paper the isotropy of CSA sizes for tungsten refinement powder was estimated for all crystallographic directions.

4. Determination of the Relative Root-Mean-Square (RRMS) Microdeformation Value $\langle \varepsilon^2 \rangle$ (L)

Until now the question of RRMS distribution type along the length of a deformed column in the crystal lattice is still open. As a rule it is considered that RRMS distributions are inhomogeneous, the value of root-mean-square microdeformation $\langle \varepsilon^2 \rangle^{1/2}$ (L) increases quickly for $L \to 0$ [15]. In [17], e.g. it is assumed that $\langle \varepsilon^2 \rangle^{1/2}$ (L). Such a RRMS distribution corresponds to the presence of single dislocations in the material or their flat pile-ups. Some authors [16, 18] however, claim that the RRMS distribution is homogeneous, i.e.

$$\langle \varepsilon^2 \rangle^{1/2} (L) = \text{const.} \tag{12}$$

The deviations from (12) are caused by errors of background level determination of the first-order reflections, that lead to a sudden increase of $\langle \varepsilon^2 \rangle^{1/2}$ (L) at small L, the second-order reflections of background level lead to the condition

$$\langle \varepsilon^2 \rangle^{1/2} (L) \to 0 \quad \text{at} \quad L \to 0 \,.$$

In this paper for the purpose of framing a hypothesis concerning the dstribution type of RRMS in metals the background was artificially set too high and too low in the first- and second-order reflections. Setting too high the background level on the first-order reflection (110) and setting too low on the second-order reflection (220) by 1% from the maximum

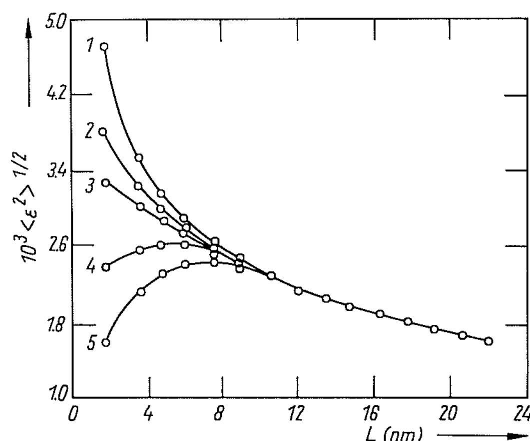


Fig. 3. The dependence of RRMS value in direction ⟨110⟩ on distance in the crystal lattice (for tungsten powder after 100 h milling)

peak value caused a sudden increase of $\langle \varepsilon^2 \rangle^{1/2}$ (L) at $L \approx 1.5$ to 6 nm (curves 1, 2 in Fig. 3). Setting too high the background level on the second-order reflections (220) by 0.5 and 1% from the maximum peak value caused a decrease of $\langle \varepsilon^2 \rangle^{1/2}$ (L) at $L \approx 1.5$ to 6 nm (curves 4, 5 in Fig. 3). Curve 3 gives an undeformed RRMS distribution, the averaged value of background level on both reflections (110) and (220). As one can see on the figures, all five curves coincide in the interval $L \approx 6$ to 23 nm, and the RRMS value decreases with increasing distance in the crystal lattice.

So, we can conclude that the errors in the background level determination distort only a primary area of the distribution $\langle \varepsilon^2 \rangle^{1/2}$ (L), and the distribution $\langle \varepsilon^2 \rangle^{1/2}$ (L) is not homogeneous. From a correlation coefficient calculation according to (7) for ln $\langle \varepsilon^2 \rangle^{1/2}$ (L) a value 0.998 was received, that at the significance level (9) equaled to 0.001 and at the degree of freedom number equal to 6 to 8 permitted to make the conclusion that the linear relation

$$\ln \langle \varepsilon^2 \rangle^{1/2} (L) = \langle \ln (\varepsilon^2)^{1/2} (L) \rangle + r(L - \langle L \rangle) \tag{13}$$

is valid, from (13) we get

$$\langle \varepsilon^2 \rangle^{1/2} (L) = \varepsilon_{hkl} \exp(-\alpha_{hkl} L)\,, \tag{14}$$

where the atomic plane defect presence is characterized by

$$\varepsilon_{hkl} = \exp(\ln \langle \varepsilon^2 \rangle^{1/2} (L) \rangle - r(L))\,. \tag{15}$$

Here α_{hkl} is a parameter depending upon the material nature and the direction in the crystal lattice ($\alpha_{hkl} = -r$).

Using the offered approximate relation (14) we determinated RRMS and ε_{110}, ε_{100}, α_{110}, α_{100} for the tungsten powders after different times of milling and filing (Table 2). As one can see from the obtained results, the value α_{hkl} in all cases for a certain direction in the crystal lattice is constant, therefore α_{hkl} is a physical constant of this material, which depends upon the direction in the crystal lattice. The value ε_{hkl} changes depending upon the material conditions, it becomes higher with increasing defect presence. Therefore, ε_{hkl} characterizes the condition of a material substructure which is present in this particular case. The determination of the RRMS distribution type makes it possible to find $\langle \varepsilon^2 \rangle^{1/2}$ (L) only

Table 2
The coefficients ε_{hkl} and α_{hkl} in (14) and RRMS size for tungsten powder of different milling times and fillings

milling time (h)	⟨110⟩ ε_{110}	α_{110} (nm^{-1})	$\Delta d/d$	$\langle \varepsilon^2_{5\,nm} \rangle^{1/2}$	$\langle \varepsilon^2_{D_{eff}} \rangle^{1/2}$	⟨100⟩ ε_{100}	α_{100} (nm^{-1})	$\Delta d/d$	$\langle \varepsilon^2_{5\,nm} \rangle^{1/2}$	$\langle \varepsilon^2_{D_{eff}} \rangle^{1/2}$	$\frac{\varepsilon_{110}}{\varepsilon_{100}}$
10	0.00197	0.033	0.00196	0.00167	0.0003	0.00182	0.0425	0.00181	0.00147	0.0005	1.08
20	0.00245	0.033	0.00243	0.00208	0.0006	0.00213	0.0425	0.00212	0.00172	0.0007	1.15
30	0.00279	0.033	0.00277	0.00237	0.0007	0.00253	0.0425	0.00251	0.00205	0.0009	1.10
50	0.00303	0.033	0.00301	0.00257	0.0010	0.00265	0.0425	0.00263	0.00214	0.0010	1.14
100	0.00318	0.033	0.00316	0.00268	0.0012	0.00277	0.0425	0.00275	0.00224	0.0010	1.15
fillings	0.00362	0.033	0.00359	0.00307	0.0021	0.00315	0.0425	0.00313	0.00265	0.0019	1.16

based on one interplanar distance,

$$\langle \varepsilon^2 \rangle^{1/2} (d) = \frac{\Delta d}{d}, \tag{16}$$

where d is the interplanar distance.

The value $\Delta d/d$ for all investigated powders, calculated on the basis of (16) is given in Table 2. As one can see from the obtained results, the value $\Delta d/d$ in each particular case practically does not differ from the value ε_{hkl}.

On this basis one can speak about the parameter ε_{hkl} as the degree of atomic plane defect presence. In Table 2 RRMS values, are given measured on the basis of 5 nm and D_{eff}. RRMS on the basis of 5 nm ($\langle \varepsilon^2_{5\,\text{nm}} \rangle^{1/2}$ (L)) is most frequently given in literature [19], and the values RRMS measured on the basis of D_{eff} may be used in the determination of the average inner energy in the material at plastic deformation. As well we found a small anistropy of microplastic deformation for the tungsten powders ($e_{110}/e_{100} = 1.08$ to 1.16) though the ratio of Young's moduli for these crystallographic directions equals unity [19].

5. Conclusion

Thus, here a method for CSA determination was offered according to which the determined CSA value does not depend upon the selection of the X-ray diffraction line background level.

The increase of profile measuring accuracy of X-ray diffraction lines by application of the modified statistical regularization method leads to the increase of number of Fourier coefficiens of the real physical expansion function used for the determination CSA and RRMS up to 20 to 30. For the investigated metals an analytical relation was found from various mechanical treatments (rolling, milling, filling) providing the same RRMS relation.

Fourier coefficient values of the real physical spreading function for the coherent scattering area (CSA) and microdistortions during tungsten powder milling for 100 h for the spectral

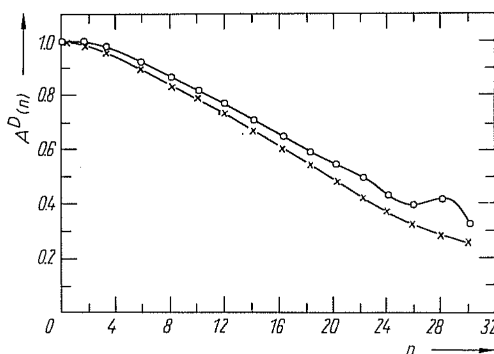


Fig. 4.

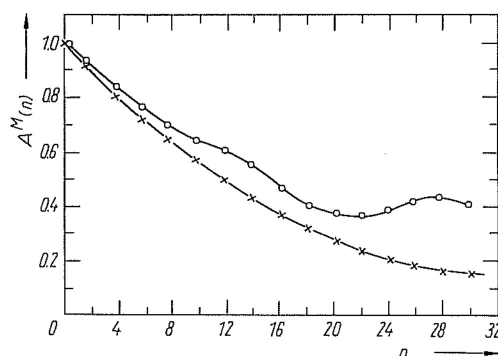
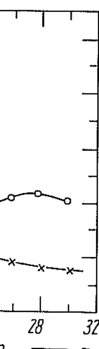


Fig. 5.

Fig. 4. Fourier coefficient values as a function of true physical broadening (due to lattice distortions) for ○ spectral method and × modified method of statistical regularization (tungsten pattern, 100 h milling)

Fig. 5. Fourier coefficient values as a function of true physical broadening (due to size effects of the crystallites) for ○ spectral method and × modified method of statistical regularization (tungsten pattern, 100 h milling)

method and the modified statistical regularization method are given on Fig. 4 and Fig. 5, respectively. From these figures one can see that for the spectral method 6 to 8 Fourier coefficients are stable and then the series is divergent, using the modified statistical regularization method we receive 25 stable Fourier coefficients.



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(Received December 7, 1990)