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A new evaluation method and its application are discussed in detail for the determination of some important statistical parameters of a dislocation assembly, namely the average dislocation density, the average fluctuation of the dislocation density and the average polarization, from the X-ray diffraction line profile. The method is based only on the analytical properties of the strain field of dislocations, regardless of the actual form of the dislocation distribution, so it can also be applied to inhomogeneous dislocation structures. The applicability of the evaluation procedure is demonstrated for broadened Bragg peaks of deformed Cu single crystals and of nanocrystalline Cu produced by inert-gas condensation.

1. Introduction

To characterize the microstructure of plastically deformed crystalline materials, it is important to describe quantitatively the dislocation structure evolving during the deformation process. X-ray line broadening analysis is frequently applied in the investigation of dislocation assemblies. It has been applied successfully to study the dislocation structures in plastically deformed materials (Ungár et al., 1984; Ungár, 1999; Hacker et al., 1997; Klimanek & Kuzel, 1988). Ungár, Révész et al. (1998) have even recently applied X-ray line broadening analysis in such studies of ball-milled nanocrystalline metals, while the misfit dislocation density in multilayers has been studied by Kaganer et al. (1997), opening new perspectives in this field.

The first method for interpreting strain-induced Bragg peak broadening was developed by Warren & Averbach (1950, 1952), who, from the Taylor expansion of the Fourier coefficients of the intensity distribution, concluded that the strain-induced broadening is proportional to the spatial average of the square of the strain. However, as pointed out first by Krivoglaz and coworkers (Krivoglaz & Ryboshapka, 1963; Krivoglaz, 1969; Krivoglaz et al., 1983), if the strain is caused by dislocations, the Warren–Averbach method cannot be applied, since in this case the space average of the square of the strain is infinite. For a completely random dislocation distribution, they derived an analytical expression, which, however, cannot be applied directly because the derived Fourier coefficients diverge logarithmically as the crystal size approaches infinity. This problem was first resolved by Wilkens (1962, 1969a,b, 1970, 1976, 1987) by introducing the concept of the restricted random dislocation distribution. For small Fourier coefficients, the expression derived by Wilkens has the same form as that obtained by Krivoglaz and coworkers, but the crystal size is replaced by a correlation length. A significant restriction of the applicability of Wilkens’ theory arises from the fact that it predicts symmetrical line profiles, while in many experiments asymmetric line profiles are observed (Ungár et al., 1984). Although asymmetric broadening can be understood within the framework of the theory of Wilkens in terms of the quasi-composite model (Ungár et al., 1984), its disadvantage is that it is based on several a priori assumptions. Furthermore, as was shown by Gaál (1984), a randomly distributed polarized dislocation dipole assembly also leads to an asymmetric profile, so asymmetric broadening can appear under more general conditions than those considered in the quasi-composite model.

The origin of the asymmetry was investigated by Groma et al. (1988) in terms of dislocation dipole polarization. In that work, an asymptotic expression was deduced for the Fourier coefficients and an evaluation method was developed for the determination of the parameters of the dislocation structure (see Ungár et al., 1989). Recently it has been shown (Groma, 1998) that from the analysis of the tail of the line profiles three important parameters of the dislocation distribution (average dislocation density, average dislocation fluctuation and formal dislocation polarization) can be evaluated without any a priori assumption with regard to the dislocation distribution. The mathematical foundation of the theory outlined by Groma (1998) is similar to the model described earlier by Groma et al. (1988). It is shown, however, that the result obtained earlier is valid only if the dislocation–dislocation correlation is weak enough. The theory of Groma (1998) is based only on the analytical properties of the displacement field of straight dislocations. As a result, it can be applied for the inhomogeneous dislocation distributions frequently observed in experimental investigations.

In the present paper, an evaluation method for the determination of three parameters characterizing the inhomogeneous dislocation distribution is proposed. The method is based on the analytical results outlined by Groma (1998). It
can be considered as a generalization of the variance method first proposed by Wilson (1955) for particle size broadening (see also Langford, 1968).

2. The evaluation method

The mathematical foundation of the proposed evaluation procedure is related to the fact that in the case of dislocations, regardless of the actual distribution of dislocations, for a small enough Fourier parameter \( n \) the Fourier transform of the measured intensity \( A(n) \) can be given with the following form up to the fourth order in \( n \) (see Groma et al., 1988; Groma, 1998):

\[
\ln A(n) = \Lambda \langle \rho \rangle n^2 \ln(n/R_1) + i\langle s^2 \rangle n^3 \ln(n/R_2) \\
+ (1/2)\Lambda^2 \langle \rho^2 \rangle - \langle \rho \rangle^2 n^4 \ln(n/R_3) \ln(n/R_4),
\]

(1)

where

\[
\langle \rho \rangle = (1/V) \int \rho(r) \, dr
\]

(2)

is the average dislocation density, \( \rho(r) \) is the local dislocation density at position \( r \), and \( V \) is the sample volume.

\[
\langle \rho^2 \rangle = (1/V) \int \rho(r)^2 \, dr
\]

(3)

is the average of the square of the dislocation density, and

\[
\langle s^2 \rangle = (2/V) \Lambda \pi (g_i g_j / |g|) \int \rho(r) \beta_{ij}^{\alpha\alpha} (r) \, dr,
\]

(4)

in which \( g \) is the diffraction vector and \( \beta_{ij}^{\alpha\alpha} (r) \) is the total distortion caused by the dislocation system. The \( \langle s^2 \rangle \) parameter measures the correlation between the internal strain and the dislocation density. It can be considered as a special measure of the dislocation polarization, since in the case of an unpolarized dislocation structure, the value of \( \langle s^2 \rangle \) would disappear. Therefore, the \( \langle s^2 \rangle \) parameter will be referred to in the following as the formal dislocation polarization. The influence of dislocation polarization in the general case will be discussed in a forthcoming paper. The parameter \( \Lambda \) describes the contrast effect of dislocations (Groma, 1998):

\[
\Lambda = (\pi/2) C |g| \sin^2 \Psi,
\]

(5)

in which for screw dislocations

\[
C = \cos^2 \Psi
\]

(6)

and for edge dislocations

\[
C = \sin^2 \Psi [1/8(1-\nu)^2][1-4\nu+8\nu^2+4(1-2\nu)\cos^2 \gamma],
\]

(7)

where \( \nu \) is the Poisson ratio, \( \Psi \) is the angle between \( g \) and the dislocation line vector \( \mathbf{l} \), and \( \gamma \) is the angle between the vectors \( \mathbf{b} - \mathbf{l} \cdot \mathbf{b} \) and \( \mathbf{g} - \mathbf{l} \cdot \mathbf{g} \). For the values of the contrast factors in the general case of anisotropic material see work by Ungár & Borbély (1996), Ungár, Révész et al. (1998) and Ungár, Ott et al. (1998). The quantities \( \langle \rho^2 \rangle = \Lambda \langle \rho \rangle \) and \( \langle s^2 \rho^2 \rangle = \Lambda \langle \rho^2 \rangle \) containing the contrast effect are usually referred to as the formal values of the dislocation density and the square of the dislocation density, respectively. The parameters \( R_1, R_2, R_3 \) and \( R_4 \) are characteristic length parameters of the dislocation assembly, but their actual values are difficult to determine.

The evaluation method applied earlier for the determination of the dislocation density and the other parameters mentioned above was based on fitting the form (1) to the Fourier transform of the measured intensity profile (Ungár et al., 1989). A major disadvantage of this procedure arises from the experimental finding that equation (1) describes with sufficient accuracy only about the first ten Fourier coefficients, resulting in a relatively large scatter of the obtained parameters. Furthermore, there is no well established criterion for the determination of the fitting interval.

Besides Fourier analysis, a traditionally applied method to characterize a broadened Bragg peak is the determination of the different moments (Wilson, 1955) of the intensity distribution \( I(q) \):

\[
m_k = \int_{-\infty}^{\infty} q^k I(q) \, dq / \int_{-\infty}^{\infty} I(q) \, dq,
\]

(8)

where \( q = 4\pi \sin \Theta / \lambda_s \) (\( \lambda_s \) is the wavelength of the X-rays and \( \Theta \) is half the scattering angle). The relation between the different order moments and the Fourier transform of the intensity distribution is

\[
m_k = (i)^k [1/A(0)][d^k A(n)/dn^k] \big|_{n=0}.
\]

(9)

In the case of line broadening caused by dislocations, however, according to equation (1) the second- and higher-order moments are infinite, since the corresponding derivatives of \( A(n) \) are infinite. So they cannot be directly used to obtain the characteristic parameters of the dislocation structure. By analysing the dependence of the moments on the integration limit, i.e. the behaviour of the function

\[
v_k(q) = \int_{-q}^{q} q^k I(q') \, dq' / \int_{-\infty}^{\infty} I(q') \, dq',
\]

(10)

(referred to hereinafter as the \( k \)th-order restricted moment), at large enough \( q \) value the parameters \( \langle \rho \rangle \), \( \langle \rho^2 \rangle \) and \( \langle s^2 \rangle \) can be determined (Groma, 1998).

As explained in detail by Groma (1998), the asymptotic form of the second-order restricted moments and the intensity distribution can be obtained from equations (1) and (10) [similar asymptotic expressions for the intensity profile have been obtained by Wilson (1955) and Krivoglaz et al. (1983)],

\[
v_2(q) = 2\Lambda \langle \rho \rangle \ln(q/q_0)
\]

(11)

and

\[
I(q) = \Lambda \langle \rho \rangle 1/[q]^\frac{1}{2} \ldots
\]

(12)

allowing the average dislocation density to be determined by fitting a straight line to the asymptotic part of the measured \( v_2(q) \) versus \( \ln(q) \) relation. The method is illustrated on a measured 200 reflection profile of a Cu single crystal deformed by tension (Fig. 1b).

The line profiles are usually not symmetric, which results in a nonzero third-order restricted moment of the form

\[
v_3(q) = -6\langle s^2 \rangle \ln(q/q_1)
\]

(13)
with

\[ I(q) = \Lambda \langle \rho \rangle 1/|q|^3 - 3 \langle s^2 \rangle q/|q|^1 + \ldots \]  

allowing one to obtain \( s^2 \) from the slope of the \( v_3(q) \) versus \( \ln(q) \) relation in the large \( q \) regime (Fig. 1c). [The relatively large scatter of the data points in \( v_3(q) \) arises from the fact that it measures the asymmetry, so it is connected to the difference between the two branches of the measured profile.]

Both the fluctuation and the average dislocation density can be obtained from the fourth-order restricted moment (Groma, 1998):

\[ v_4(q) = \Lambda \langle \rho \rangle q^2 + 12 \Lambda^2 \langle \rho^2 \rangle \ln(q/q_3) \ln(q/q_3). \]  

[According to our experience, \( q_2 \) and \( q_3 \) are nearly equal, so they can be approximated by their harmonic average \( q_0 = (q_2 q_3)^{1/2} \). The parameters \( q_1, q_2, q_3 \) and \( q_4 \) are related to the \( R_1, R_2, R_3, R_4 \) characteristic length parameters of equation (1).]

It can be seen from equation (15) that it is useful to introduce the quantity \( f(q) = v_4(q)/q^2 \) since its asymptotic value is \( f_{\infty} = \Lambda \langle \rho \rangle \) and it has a maximum at \( q_m = eq_0 \) with a value of \( f_{\infty} = \Lambda \langle \rho \rangle + 12 \Lambda^2 \langle \rho^2 \rangle 1/q_m^2 \). So the difference between the maximum and the asymptotic value can be related to the relative fluctuation:

\[ f_{\infty} - f_{as}/f_{as}^2 = 12(\langle \rho^2 \rangle /\langle \rho \rangle^2)(1/q_m^2). \]  

In Fig. 1(d), the quantity \( f(q) = v_4(q)/q^2 \) is plotted as a function of \( q \) together with the fitted theoretical function obtained from equation (15). The fit of \( f(q) \), involving three free parameters, was performed between the limits indicated by the two arrows in Fig. 1(d). It is remarkable that the obtained curve follows the measured data points extremely well even for \( q \) values considerably larger than the upper fitting limit. It is important to note that the determination of the parameters requires a nonlinear fitting procedure, which demands an initial guess for the parameter values. For this the dislocation density and \( q_0 \) obtained from the second-order restricted moment can be applied. For the relative fluctuation, the condition \( \langle \rho^2 \rangle /\langle \rho \rangle^2 = 1 \) is usually a good initial guess.

In order to determine the regime where the asymptotic expression given above describes the tail of the profile, the measured profile and the calculated \( f(q) \) quantity are plotted.
in Fig. 2. It can be seen that at the maximum of \( f(q) \) the relative intensity is approximately \( 10^{-2} \) and the theoretical expression of equation (15) describes well the tail part of the intensity distribution from about \( 10^{-1} \) relative intensity.

Another important issue is the influence of the background of the intensity measurement. In Fig. 3, the effect of different artificially added constant backgrounds on the \( f(q) \) function is illustrated. It is clear that in order to obtain reliable results, the relative background should be less than \( 10^{-4} \). Considering Figs. 2 and 3, it can be stated that the new evaluation method can be applied if the profiles are measured up to \( 10^{-4} \) relative intensity, with backgrounds less than \( 10^{-4} \).

The advantages of the method can be summarized as follows. The regime from which the information is obtained consists of approximately 100 data points, so the results are more reliable than those of the earlier method using the Fourier coefficients directly. Furthermore, since \( \langle \rho \rangle \) can be determined from both the second- and the fourth-order restricted moments of the intensity distribution, the evaluation process offers the possibility to check the consistency of the results. Finally, it can be directly checked whether the profile is measured in a sufficiently wide range, because in order to obtain proper values of the fitted parameters, the downhill part of \( f(q) \) has to be reached.

3. Examples of experimental application

3.1. Plastically deformed Cu single crystal

In order to illustrate the application of the method described above, X-ray measurements were performed on Cu single crystals deformed by uniaxial compression in the [100] direction at \( 2 \times 10^{-4} \) s\(^{-1} \) constant strain rate up to resolved shear stresses of 40, 50, 60 and 65 MPa.

The X-ray line profiles of the 200 reflection were obtained by a double-crystal diffractometer using Cu Ka radiation. The three parameters \( (\rho^4), (\rho^2), (s^2) \) characterizing the dislocation arrangement are obtained by fitting the theoretical functions (11), (13) and (15) to the corresponding restricted moments calculated from the measured profiles.

Fig. 4 shows the \( v_4(q)/q^2 \) quantities for the different samples as a function of \( q \). In Fig. 5, the formal values of the dislocation densities are plotted versus the resolved shear stress. In Fig. 6, the measured \( \langle s^2 \rangle \) values (characterizing the dislocation polarization) are plotted versus the resolved shear stress, while in Fig. 7 the obtained relative fluctuations \( (\sigma^2 = \langle \rho^2 \rangle - (\rho^2)^2/(\rho^2)^2) \) are plotted versus the resolved shear stress.

Figure 2
The behaviour of the \( v_4(q)/q^2 \) function compared with the measured profile.

Figure 3
The effect of constant intensity background (bgr) on the \( v_4(q)/q^2 \) quantity of the profile of Fig. 1.

Figure 4
The \( v_4(q)/q^2 \) quantities of 200 reflections measured on single-crystal Cu samples deformed by compression up to the following resolved shear stresses: 40 MPa (stars), 50 MPa (empty squares), 60 MPa (filled squares), 65 MPa (circles).

Figure 5
The measured dislocation densities versus the resolved shear stress.
apparent from Fig. 4 that with increasing deformation, the asymptotic value of \( v_4(q)/q^2 \), i.e. the dislocation density, increases (Fig. 5), while the relative fluctuation [connected to the maximum of the \( v_4(q)/q^2 \) curves according to equation (16)] decreases (Fig. 7). The fact that the fluctuation decreases with deformation indicates that the dislocation network tends toward homogeneity.

### 3.2. Determination of grain size in nanocrystalline materials

Recent methods of grain size determination using X-ray line broadening analysis (Ungár, 2000; Ungár, Révész et al., 1998) are based on the fact that strain broadening and grain size broadening depend differently on the order of the reflection. The broadening induced by the strain fields of dislocations is different for the various type of reflections (contrast effect for dislocations), while size broadening is independent of the order of the reflection. The current method of grain size and dislocation density determination is based on a modification of the classical Warren–Averbach method by taking into account the reflection-order-dependent contrast factors of dislocations. According to this, the Fourier transform of the profile is (Ungár, 2000)

\[
\ln A(n) = \ln A^S(n) + \left(\pi b^2 \langle \rho \rangle n^2 / 2\right) \ln(n/R_1)(K^2 C),
\]

where \( A^S(n) \) is the term corresponding to size broadening, \( K = 2 \sin \Theta / \lambda \) and \( C \) is the average contrast factor of dislocations. Measuring the profile at different reflections and then plotting the Fourier coefficients against \( K^2 C \), the values of \( A(n) \) extrapolated to \( K^2 C = 0 \) give \( A^S(n) \), the part of the Fourier coefficients related to particle size. From the \( A^S(n) \) values, the particle size can be obtained as (Ungár, 2000)

\[
1/D = -(dA^S(n)/dn)_{n=0}.
\]

The variance method can be applied to determine the grain size in polycrystalline materials, using the fact that the effect of the finite grain size on the intensity of the X-ray reflection can be described as (Wilson, 1955)

\[
I(q) \propto (A/V)(1/q^2),
\]

where \( A \) is the surface and \( V \) is the volume of the grains. This grain size effect becomes significant below approximately 100 nm grain size. From this and equation (11), if the sample also contains dislocations, the second-order restricted moment of the intensity distribution is

\[
v_2(q) = (A/V)q + 2A \langle \rho \rangle \ln(q/q_0).
\]

Fig. 8 shows the line profile of the 311 reflection measured on nanocrystalline Cu produced by inert-gas condensation [this sample has been investigated in detail by Ungár, Ott et al. (1998)], while in Fig. 9, the second-order restricted moment of the profile and the fitted curve corresponding to equation (20) are drawn. The grain size was obtained as 15 nm, the dislocation density as \( 5 \times 10^{15} \text{ m}^{-2} \).

The advantage of this method is that it can provide the grain size and the dislocation density from one single reflection profile, in contrast to the modified Warren–Averbach method, but of course for checking the consistence of the results, measurement of several reflections is preferable.
4. Conclusions

A new evaluation method for the determination of parameters characterizing the statistical properties of dislocation arrangements from X-ray line profile analysis is proposed. The method is based only on the analytical properties of the strain fields of dislocations, without any further assumption on the distribution of dislocations, so it can also be applied directly to inhomogeneous dislocation networks.

The three parameters characterizing the dislocation arrangement (dislocation density, dislocation density fluctuation and polarization) are derived from the asymptotic behaviour of the restricted moments of different orders. The dislocation density can be obtained both from the second- and the fourth-order restricted moments, allowing one to check the consistency of the method. The method can be applied to determine the grain size and the dislocation density in nanocrystalline materials, by taking into account the effect of the finite size on the intensity distribution.

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