EVALUATION OF SUBSTRUCTURE PARAMETERS BY PEAK PROFILE ANALYSIS OF HIGH-RESOLUTION NEUTRON DIFFRACTION SPECTRA

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ABSTRACT

The peak profile shape analysis has been preferentially used in evaluation of X-ray and synchrotron powder diffraction pattern. However, neutron diffraction facilities of new generation frequently offer the instrumental resolution high enough to study efficiently the effects of broadening of neutron diffraction profiles. The present paper describes the procedure for a detailed evaluation of Bragg peak shape based on the method of transformed model fitting (TMF) which has been recently developed particularly for treatment of neutron diffraction profiles. Microstructure modeling is performed in the reciprocal space and the convolution of the model with the instrumental resolution curve is fitted to the profiles recorded in the diffraction experiment.

INTRODUCTION

X-Ray and synchrotron peak profile analysis is well known and efficient tool for characterization of macro- and microstructural parameters in studies of polycrystalline materials. Use of these methods is however of great importance in the case of neutron diffraction. Neutron diffraction technique is preferentially used in the case when a deep penetration depth of the radiation probe is necessary. Beams of diffracted neutrons can bring structural information from bulk of the material. This feature is successfully used in many in situ methods employing various sophisticated sample environments of the neutron diffraction facilities such as deformation testing machines, furnaces, cryostats and high-pressure cells. Comparing neutrons with X-Ray and synchrotron radiation, as a limiting factor of neutron experiments seems to be usually a lower flux of neutron sources and lower resolution of neutron diffractometers which typically results in longer counting times of neutron diffraction spectra. Characterization of dynamic behavior of the studied system is then more difficult. However, the intensive neutron spallation sources of the new generation and modern efficient powder diffractometers help to overcome this basic problem. The instrumental resolution limit necessary for successful peak profile analysis lies roughly in the range $\Delta d/d < 2.5 \cdot 10^{-3}$.

CONVENTION EVALUATION METHODS

Large variety of profile analysis evaluation methods has been developed in last decades. Before referring some frequently used approaches, let us discuss the general scheme of the scattering experiment. Fig. 1. shows a generalized diagram relating the original examined material microstructure and their resulting image obtained by a scattering experiment.
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figure of the material microstructure in real space is projected by the Fourier transform into
the 3d scattering length density distribution (in the case of neutron diffraction) in reciprocal
space (see Fig. 2.). This figure is consequently observed by a scattering instrument, e. g.
by the cross-section with the Ewald sphere (Fig. 2.). After this step, resulting ideal signal from
specimen microstructure is modified by further effects connected with the nature of the
radiation probe and specimen size and shape (absorption, multiple scattering) and properties
of the scattering instrument (wavelength distribution, aberration, detector smearing, etc.).

After assuming the last transformations, background addition and statistical noise
smearing, we will receive the real measured signal. Although the schematic link “microstructure -
experimental data” shown in Fig. 1. seems to be rather simple, the
way how to reconstruct
microstructural information from
the real measured pattern is
particularly difficult. Most
frequent evaluation methods are
based on inverse transformations
directly applied to the measured
pattern. These direct procedures
are rarely usable in the case of
neutron diffraction, mainly due to
lower statistics and noise. Especially deconvolution is ill-
conditioned operation in this case.

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Fig. 1. Schematic diagram of the scattering experiment.

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Fig. 2. Scheme of powder diffraction in reciprocal space, horizontal cut, no texture.
An experimentally observed diffraction profile is actually a convolution of the instrumental profile and the specimen broadened profile

$$F_{\text{exp}}(2\theta) = [F_{\text{inst}} \otimes F_{\text{spec}}](2\theta).$$

(1)

The instrumental profile $F_{\text{inst}}$ includes all the instrumental corrections e.g. mentioned in Fig.1. whereas the specimen broadened profile $F_{\text{spec}}$ is connected with the specimen properties only. Various deconvolution methods are used to subtract the instrumental profile from experimental data [1]. The specimen broadened profile $F_{\text{spec}}$ is assumed to correspond to the “ideal signal” shown in Fig 1. and it is further used for evaluation of microstructural parameters. In general, the profile $F_{\text{spec}}$ is mainly affected by the size effect discovered by Scherrer (1918) and strain effect described by Stokes & Wilson (1944). For the purpose of profile analysis of X-Ray diffraction pattern, different methods of separation of size and strain effects from $F_{\text{spec}}$ has been developed, e.g. integral breadth technique [2,3], Warren & Averbach method [4,5] and Williamson-Hall plot [6].

**TRANSFORMED MODEL FITTING PROCEDURE**

The TMF evaluation procedure [7] has been developed especially for treatment of single-line neutron diffraction profiles, exhibiting usually larger statistic errors with respect to X-ray diffraction profiles. Instead applying inverse transformations as indicated above, this evaluation method follows the scheme in Fig. 1. Block diagram of the TMF procedure is displayed in Fig. 3. The microstructure model created in the reciprocal-space is passing through a set of transformations resulting in the calculated profile corresponding to the experimentally observed diffraction profile. By conventional fitting procedure, the parameters of the microstructural models are refined to receive the best agreement between the calculated and experimental profile.

Until now, two models were developed for TMF procedure. The most simple model is based on modified integral breadth technique and enables to refine the root-mean-square strain (RMSS) $\sqrt{\varepsilon^2}$ [8] and the effective dimension of coherently diffracting domains $D_{\text{eff}}$ [8]. The specimen broadened profile $F_{\text{spec}}$ is modeled by the Voigt function, i.e. convolution of the Gaussian and the Lorentzian (or Cauchy) curves. The Gaussian function is used for characterization of microstrain in crystalline materials whereas the size contribution is related to the Lorentzian function [3,9]. This model was also used in modified version to describe strongly asymmetric peaks observed in strongly anisotropic shape memory CuAlZnMn alloy during stress induced martensitic transformation [10].

Although this simple models reproduces quite well real diffraction data in many cases [11,12], it has certain limits. For example, this procedure does not account for the anisotropy of diffraction line broadening which influences the correctness of the assessed microstructural parameters. Therefore, more sophisticated broadening models based on the Wilkens dislocation model [13] and a log-normal grain size distribution [14-16] was adopted for TMF procedure. This
new approach in modeling of the broadening effects in real space provides more realistic microstructure parameters. Using the Fourier transformation, this model is transformed to the reciprocal space, smeared by instrumental resolution, and compared with the measured data. Following the approach used by Warren & Averbach [4,5] for multiple reflections, the shape of each diffraction peak can be represented by a Fourier series. The Fourier coefficients of the peak profile, \( A(L) \), are the product of the distortion, \( A^D \), and size, \( A^S \), effects. If both types of broadening are present, the measured coefficient is the product of the coefficients for each effect

\[
A(L) = A^D(L)A^S(L),
\]

where \( L \) is the variable of the Fourier transform [5,14]. The distortion Fourier coefficients \( A^D \) can be expressed according to Warren & Averbach [5] as follows

\[
A^D(L) = \exp\left[-2\pi^2 g^2 L^2 \langle \epsilon_L^2 \rangle \right],
\]

where \( g \) is the absolute value of the diffraction vector, \( \langle \epsilon_L^2 \rangle \) is the mean square strain depending on the displacement of atoms relative to their ideal positions, and the angle brackets indicate spatial averaging. This relation corresponds to the Gaussian distribution of microstrain. Several authors worked on the determination of the mean square strain, assuming either random atomic displacement and/or stacking faults. Later, Krivoglaz [17] and Wilkens [13] assumed dislocations as the main source of peak broadening close to the fundamental Bragg positions. The model was improved afterwards by Wilkens by introducing the effective cut-off radius of dislocations \( R^*_e \), instead of the crystal diameter. The mean square strain has been derived in the following closed form [13], assuming infinitely long parallel screw dislocations with a restrictedly random distribution:

\[
\langle \epsilon_L^2 \rangle = \left( b / 2\pi \right)^2 \rho C f \left( L / R^*_e \right),
\]

where \( b \) is the Burgers vector, \( \rho \) is dislocation density, \( C \) is contrast factor, \( f \) is strain function (the Wilkens function), and \( R^*_e \) is the effective outer cut-off radius of dislocations as a second parameter characterizing the dislocation arrangement. The strain function \( f \) has an explicit form [13, in appendix A therein]. Strain anisotropy in that model is accounted for by the average contrast factors \( C \) of the dislocations, which depends on (i) the indices \( h, k, l \), (ii) on the relative orientations of the line and Burgers vectors of dislocations and the diffraction vector, (iii) on the elastic constants of the crystal [14,18].

The broadening effect due to the crystallite size can be described in the real space as well. The Fourier transform of the intensity profile of the \( hkl \) diffraction peak equals to the common volume of the crystal and its ‘ghost’ obtained by a translation \( L \) in the direction normal to the reflecting lattice planes [14]. For the calculation of the Fourier transform of the peak profile originating from a crystallite, according to Guinier [19] the crystal is considered as divided into cylindrical columns normal to the lattice planes \( hkl \). Supposing \( d\sigma_\mu \) as the cross section of the columns, then the heights of these columns in the crystal lie in the interval between \( \mu \) and \( \mu + d\mu \). The common volume of the irradiated crystallites and their ‘ghosts’ shifted by \( L \) can be obtained by summing up of all the columns existing in the crystallites. Assuming
spherical crystallites and a log-normal crystallite size distribution, the common volume is defined as

\[
A^*(L) = \int \left[ \mu^2 - L |\mu| \text{erfc} \left( \frac{\log(\mu/m)}{2^{1/2}\sigma} \right) \right] d\mu, \quad (5)
\]

where \( \text{erfc} \) is the complementary error function [14], \( \sigma \) is the variance and \( m \) is the median of the distribution.

**COMPARISON OF X-RAY AND NEUTRON RESULTS**

To verify the dislocation model for TMF procedure, we performed comparative neutron and X-Ray diffraction experiments on the identical set of plain ferritic steel specimens prestrained up to 16% elongation. The chemical composition of the steel is given in Table 1. The microstructure of this steel consists of relatively large grains with the grain size of about 30 \( \mu \text{m} \) and the size effect on the profile broadening can be thus neglected.

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.100</td>
<td>0.400</td>
<td>0.400</td>
<td>0.035</td>
<td>0.035</td>
</tr>
</tbody>
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Neutron diffraction profiles were measured at the dedicated stress/strain diffractometer TKSN-400 in NPI Řež. Two reflections 110 and 211 were measured with a relatively high instrumental resolution of \( \Delta d/d \sim (2–2.5) \times 10^{-3} \). High instrumental resolution is achieved due to the curved Si-monochromator. The elastically bent perfect crystal monochromators work as a focussing element and enables to optimize the resolution of the selected reflections [20]. The example of the measured and treated neutron profile is given in Fig. 4.

Fig. 4. Example of measured and treated neutron diffraction profile, reflection 110, macroscopic deformation 16%.
X-Ray diffraction experiment was performed on the diffractometer Seifert FPM - XRD 7 in conventional powder diffraction Bragg-Brentano geometry with the secondary monochromator and also on the Panalytical X’Pert Pro with automatic divergence slit keeping the irradiated specimen area fixed and the secondary monochromator, both with Cu Kα radiation. In this case, the reflections 110, 200, 211, 220, 310, 222 were measured and analyzed. The Williamson-Hall plot (see Fig 5.) was used for the evaluation of corresponding dislocation densities [see also 21] in dependence on prestrain degree. The dislocation densities evaluated from individual neutron peaks by the TMF procedure are plotted together with X-ray data in Fig. 6. As it can be seen, a very good agreement was achieved.

**DISCUSSION**

The described TMF procedure for analysis of diffraction profiles exhibits a few very beneficial features. First of all, it enables us to avoid any deconvolution operation which is particularly very critical in the case of the neutron diffraction profiles which are characteristic by higher statistic errors with respect to the X-Ray and synchrotron profiles. However, this approach is nowadays used also in for total pattern modelling and fitting [22, 23].

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**Fig. 5.** X-Ray results - Williamson Hall plot of line broadening $\beta$ vs. $\sin \theta$, full symbols experimental data, open symbols calculated points.

**Fig. 6.** Dislocation densities as a function of macroscopic strain. Comparison of neutron results (TMF procedure) and X-Ray results (Williamson Hall plot).

**Fig. 7.** Measured and fitted diffraction edges in prestrained plain ferritic steel samples.
The TMF procedure also enables to analyze broadened profiles with arbitrary shape of the instrumental resolution function. This property is documented on the extreme case of the analysis of the shape of the neutron diffraction edges measured in energy dispersive transmission arrangement ($2\theta = 180^\circ$) [24]. Fig. 7 shows examples of the measured and fitted diffraction edges for deformation degree. Fig. 8 displays the resulting RMSS refined from both energy dispersive transmission experiment and Bragg diffraction peaks [24]. Also in this case, the results are in very good agreement.

Fig. 8. The root-mean-square strain in plain ferritic steel as a function of macroscopic strain. RMSS evaluated from the Bragg diffraction profile and from the transmission diffraction edge is compared.

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