ANISOTROPIC STRAIN-LIKE LINE BROADENING DUE TO COMPOSITION VARIATIONS

A. Leineweber and E. J. Mittemeijer

Max Planck Institute for Metals Research, Heisenbergstraße 3, 70569 Stuttgart, Germany

ABSTRACT

The line-broadening of a sample of a powder of non-stoichiometric hexagonal ε-iron nitride with the average composition FeN_{0.433} was analysed by X-ray diffraction. A nearly Gaussian purely strain-like broadening was observed. The broadening is strongly orientation dependent. For each direction of the diffraction vector relative to the crystallographic axes the width of the reflections varies proportional to tan θ, with 2θ as the diffraction angle. The shape of the observed anisotropy could be fitted by a model based on the assumption of small differences between the compositions of the different powder particles. The observed extent of the anisotropy was found to be compatible with the known composition dependence of the hexagonal cell parameters of ε-FeN_y. It was shown, that for all crystal systems strain-like line broadening caused by composition variations can be conceived as a special case of the phenomenological description of anisotropic strain broadening often used in Rietveld refinement programmes (P. W. Stephens, J. Appl. Cryst. 1999, 32, 281-289.).

INTRODUCTION

In the course of a Rietveld refinement procedure it is in principle possible to extract microstructural information from the broadening of the diffraction lines incorporated in the analysis [1]. To this end a suitable model for the description of the line-profile shape for all reflections is needed. This profile shape function should be able to express anisotropic structural line broadening, i.e. broadening dependent on the direction of the diffraction vector relative to the crystal axes. In several Rietveld programmes it is possible to extend the adopted pseudo-Voigt profile-shape function with parameters to account for isotropic size and strain broadening (the latter being dependent linearly on tan θ, with 2θ as the diffraction angle) [2]. Anisotropic size and strain broadening can be implemented as well. Especially popular for anisotropic strain broadening is a model proposed by Stephens [3] (see also preceding work [4, 5]), which allows static fluctuations of the components of the reciprocal metrical matrix (cf. Eq. (3) in section 2) according to a distribution density function varying between Gaussian and Lorentzian shape. Correlations between the fluctuations of the different components are restricted by the crystal symmetry. The Stephens model is a phenomenological one; it is not related to specific physical origins of the strain broadening, although possibilities have been suggested [3].

In the present paper the powder diffraction analysis of composition variations in a solid solution powder sample, without concentration gradients within the coherently scattering domains, is presented. The proposed approach was applied to the anisotropic strain-like broadening observed from hexagonal ε-iron nitride powder of the composition FeN_{0.433}. This nitride has a hexagonal crystal structure based on a hcp arrangement of Fe with N distributed over the octahedral sites. Superstructures due to nitrogen ordering (e.g. see [6]) are not considered here; all cell parameters and hkl values used here refer to the hcp unit cell of the Fe substructure.
THEORY OF LINE BROADENING DUE TO COMPOSITION VARIATIONS

For a review on diffraction-line broadening by composition variations, see Ref. [7]. In the present case a powder consisting of particles of variable composition is considered. Each powder particle may be constituted of a number of (coherently scattering) crystallites. An individual crystallite can have the composition indicated by \( y \) in the formula \( AX_y \) (binary case). The average composition of the powder sample is \( y_0 \). The overall probability density function of the composition, \( p_\xi(\xi) \), obeys

\[
\int p_\xi(\xi)\,d\xi = 1
\]

(1)

with \( \xi = y - y_0 \), where integration is performed over the physically relevant range of \( \xi \).

The composition \( \xi \) in each coherently diffracting crystallite is assumed to be constant, but is allowed to differ from crystallite to crystallite. If now only the structurally broadened profile is considered (which has to be convoluted with the instrumental profile in order to give the experimentally observed diffracted intensity profile), and if other sources of line broadening (e.g. crystallite size) are not present, the diffraction profile for each crystallite is a delta function occurring at \( 2\theta_{hkl}(\xi) = 2\theta_{0,hkl} + \Delta 2\theta_{hkl}(\xi) \), where \( 2\theta_{0,hkl} \) is the peak position for \( \xi = 0 \). To calculate \( 2\theta_{hkl}(\xi) \) the \( \xi \) dependence of the d-spacings has to be known. For a distribution density function \( p_\xi \) the structural line broadening due to the composition variations in the sample can then be calculated by the superposition of the different diffraction profiles of the individual crystallites according to their weight, leading to a probability density function for the intensity on the \( \Delta 2\theta_{hkl} \) scale, \( p_{\Delta 2\theta_{hkl}} \). If \( p_\xi \) is, furthermore, symmetric with respect to \( \xi = 0 \), the functional form of \( p_{\Delta 2\theta_{hkl}} \) is always equal to that of \( p_\xi \), only the widths \( \delta \Delta 2\theta_{hkl} \) of the peaks change as a function of \( hkl \). The width \( \delta \Delta 2\theta_{hkl} \) can, e.g., be taken as the integral breadth or the FWHM.

For the case of crystals of cubic symmetry differential calculus via Bragg's equation shows that (cf. [8, 9])

\[
\delta \Delta 2\theta_{hkl} = 2 \left( \frac{180^\circ}{\pi} \right) \tan \theta_{0,hkl} \cdot \left| \frac{d \ln a(\xi)}{d\xi} \right|_{\xi=0} \cdot \delta \xi,
\]

(2)

with \( \Delta 2\theta_{hkl} \) in degrees, and with \( \delta \xi \) as the corresponding width of \( p_\xi \). For Eq. (2) it has been assumed that the structure factor and \( \left| \frac{d \ln a(\xi)}{d\xi} \right|_{\xi=0} \cdot \delta \xi \) with \( d_{hkl} \) as the lattice spacing of the reflection \( hkl \) is approximately constant over the range of \( \xi \) in which \( p_\xi \) is significantly larger than 0. The \( \tan \theta \) factor is the only \( \theta \)-dependent one in Eq. (2), indicating that composition broadening in this case of a one-to-one relation between \( \xi \) and \( \theta \) behaves like a typical case of strain broadening [10]. Since \( \left| \frac{d \ln a(\xi)}{d\xi} \right|_{\xi=0} \cdot \delta \xi \) is a constant for each reflection \( hkl \), line broadening due to the composition variations is strictly isotropic (i.e. not dependent on the direction of the diffraction vector relative to the crystal axes). In other words: the broadening depends on the length of the diffraction vector (\( \tan \theta \) factor; see above), but not on its orientation. For real cases an empirical function \( a(\xi) \) can be employed to determine \( \frac{d \ln a(\xi)}{d\xi} \) at \( \xi = 0 \). Then, using Eq. (2), an estimate for the composition variation \( \delta \xi \) can be calculated from the profile width \( \Delta 2\theta_{hkl} \). This procedure has been applied previously [9] to assess the inhomogeneity of nonstoichiometric defect-NaCl type transition metal carbides, like NbC_{0.83}.

For the general case (crystal systems down to triclinic), it is convenient not to use directly the lattice parameters \( a(\xi), b(\xi), c(\xi), a(\xi), b(\xi), c(\xi) \) in equations like Eq. (2), but, instead, to use them in the form as they are contained in the so-called reciprocal metrical matrix \( \mathbf{M} \).
\[
\begin{pmatrix}
\mathbf{a}^* \cdot \mathbf{a}^* & \mathbf{b}^* \cdot \mathbf{a}^* & \mathbf{c}^* \cdot \mathbf{a}^* \\
\mathbf{a}^* \cdot \mathbf{b}^* & \mathbf{b}^* \cdot \mathbf{b}^* & \mathbf{c}^* \cdot \mathbf{b}^* \\
\mathbf{a}^* \cdot \mathbf{c}^* & \mathbf{b}^* \cdot \mathbf{c}^* & \mathbf{c}^* \cdot \mathbf{c}^*
\end{pmatrix}
= 
\begin{pmatrix}
\alpha_1 & \alpha_6 & \alpha_5 \\
\alpha_{12} & \alpha_2 & \alpha_4 \\
\alpha_5 & \alpha_4 & \alpha_3
\end{pmatrix}
= \mathbf{M}(\bar{\xi}),
\]
(3)

from which \(1/d^2(\bar{\xi})\) can easily be calculated according to

\[
M_{hkl}(\bar{\xi}) = 1/d^2_{hkl}(\bar{\xi}) = \mathbf{h} \cdot \mathbf{M} \cdot \mathbf{h}
\]

\[
= \alpha_1(\bar{\xi}) \cdot h^2 + \alpha_2(\bar{\xi}) \cdot k^2 + \alpha_3(\bar{\xi}) \cdot l^2 + \alpha_4(\bar{\xi}) \cdot kl + \alpha_5(\bar{\xi}) \cdot hl + \alpha_6(\bar{\xi}) \cdot hk
\]
(4)

with \(\mathbf{h} = (h, k, l)^T\). The width, \(\Delta \theta_{hkl}\), may then be estimated as follows (cf. Eq. (2)):

\[
\delta \Delta \theta_{hkl} = \left( \frac{180^\circ}{\pi} \right) \tan \theta_{0,hkl} \left| \frac{d \ln M_{hkl}(\bar{\xi})}{d \bar{\xi}} \right|_{\bar{\xi}=0} \cdot \delta \bar{\xi}.
\]
(5)

The orientation dependence of the line broadening is contained in the factor \(|d \ln M_{hkl}/d \bar{\xi}|_{\bar{\xi}=0}\). For a fixed direction in reciprocal space, the width is proportional to \(\tan \theta_{0,hkl}\) (see above discussion). Expressing \(|d \ln M_{hkl}/d \bar{\xi}|_{\bar{\xi}=0}\) in terms of the derivatives of \(\alpha_i\) with respect to \(\bar{\xi}\) gives

\[
\delta \Delta \theta_{hkl} = \frac{180^\circ}{\pi} \tan \theta_{0,hkl} \left| \frac{d \alpha_1}{d \bar{\xi}} \cdot h^2 + \frac{d \alpha_2}{d \bar{\xi}} \cdot k^2 + \frac{d \alpha_3}{d \bar{\xi}} \cdot l^2 + \frac{d \alpha_4}{d \bar{\xi}} \cdot kl + \frac{d \alpha_5}{d \bar{\xi}} \cdot hl + \frac{d \alpha_6}{d \bar{\xi}} \cdot hk}{\alpha_1 h^2 + \alpha_2 k^2 + \alpha_3 l^2 + \alpha_4 kl + \alpha_5 hl + \alpha_6 hk} \right|_{\bar{\xi}=0} \cdot \delta \bar{\xi}.
\]
(6)

Table 1 Symmetry restrictions of the components \(\alpha_i\) \((i=1..6)\) of the reciprocal metrical matrix according to Eqs. (3-4). Analogous restrictions hold for \(d \alpha_i/d \bar{\xi}\) in Eq. (6).

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Restrictions on metric parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>(\alpha_1=\alpha_5=\alpha_6=0)</td>
</tr>
<tr>
<td></td>
<td>(\alpha_2=\alpha_3=\alpha_4=0)</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>(\alpha_1=\alpha_2)</td>
</tr>
<tr>
<td></td>
<td>(\alpha_3=\alpha_4=\alpha_5=0)</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>(\alpha_1=\alpha_5=\alpha_6=0)</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>(\alpha_2=\alpha_3=\alpha_4=0)</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>(\alpha_1=\alpha_2=\alpha_3)</td>
</tr>
<tr>
<td></td>
<td>(\alpha_4=\alpha_5=\alpha_6=0)</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>(\alpha_1=\alpha_4=\alpha_5)</td>
</tr>
<tr>
<td></td>
<td>(\alpha_2=\alpha_3=\alpha_6=0)</td>
</tr>
<tr>
<td>Triclinic</td>
<td>no restrictions</td>
</tr>
</tbody>
</table>

For \(d \alpha_i/d \bar{\xi}\) the same symmetry restrictions are valid as for \(\alpha_i\); see results for each crystal system in Table 1. For the isotropic, cubic case Eq. (2) follows directly from Eq. (6) and then only one parameter is needed to describe the isotropic line broadening. For the most general triclinic case a maximum of six parameters are required to describe the anisotropic strain-like broadening according to Eq. (6). Note, that from a diffraction experiment alone, only the products \(d \alpha_i/d \bar{\xi} \cdot \delta \bar{\xi}\) can be determined. As for the cubic case (see above), the values of \(d \alpha_i/d \bar{\xi}\) have to be known in order to obtain \(\delta \bar{\xi}\).

**EXPERIMENTAL PROCEDURE**

10 mg \(\varepsilon\)-FeN0.433 powder (powder particles size 1-5 \(\mu\)m; for preparation see Ref. [6]) were suspended in iso-propanol and sedimented on a Si monocrystal slice cut with (510) parallel to the surface using a supporting brass ring. By this procedure a nitride powder layer of a thickness of roughly 10 \(\mu\)m was achieved. An analogous layer was prepared from NBS660a
LaB$_6$ standard powder. Both samples were investigated on a powder diffractometer Philips X'Pert MPD operating with Bragg-Brentano focussing geometry and using CoK$_\alpha$ radiation and a graphite secondary monochromator. In the range $40^\circ < 2\theta < 160^\circ$ all fundamental reflections of $\varepsilon$-FeN$_{0.433}$ and selected reflections of LaB$_6$ were recorded by measuring in $2\theta$ sub-ranges sufficiently large that at both sides of the reflections the background could be well determined. Step-widths and measuring times in these ranges were chosen with a view to the reflection intensities and to the peak widths.

**ANALYSIS OF LINE BROADENING AND QUANTIFICATION OF THE COMPOSITION VARIATIONS**

Each peak was fitted by a split pseudo-Voigt function with a full width at half maximum (FWHM) $B_{\Delta 2\theta,hkl}^h$, a mixing parameter $\eta_h^{lkl}$, and an asymmetry parameter $a_s^h$ (identical parameters for the $\alpha_1$- and $\alpha_2$-components; the superscript $h$ indicates uncorrected profile parameters including structural and instrumental broadening). The instrumental broadening (superscript $g$) parameters $B_{\Delta 2\theta}^g(2\theta)$, $\eta_g(2\theta)$ and $a_s^g(2\theta)$, were determined from the parameters of the LaB$_6$ reflections, which were described as function of the diffraction angle by polynomials of $\theta$ ($\eta_g$ and $a_s^g$) or of $\tan\theta$ ($B_{\Delta 2\theta}^g$). The $B_{\Delta 2\theta,hkl}^g$ values of the $\varepsilon$-FeN$_{0.433}$ reflections, and the fitted ones of the LaB$_6$ reflections are shown in Fig. 1, indicating the strong structural line broadening of the iron nitride. The reflections of $\varepsilon$-FeN$_{0.433}$ were corrected for the instrumental broadening via Voigt functions and their convolution rules as follows [11, 12]: The measured ($h$) and instrumental ($g$) pseudo-Voigt profile parameters were transformed to give the parameters of a "corresponding" (i.e. of "closest shape") Voigt function; the straight-forward deconvolution procedures of the Voigt function were then applied; thereafter, the Voigt parameters were again transformed into pseudo-Voigt parameters, now representing only the structural broadening: $B_{\Delta 2\theta,hkl}^f$, $\eta_{hkl}^f$ and $a_{s,hkl}^f$ for each $\varepsilon$-FeN$_{0.433}$ reflection $hkl$. Asymmetry was accounted for by treating the low- and high-angle sides of the reflections in the correction separately. A final $\eta_{hkl}^f$ was then determined by averaging. It was found that mostly symmetrical and slightly "super-Gaussian" ($\eta_{hkl}^f < 0$) parameters occurred for the only structurally broadened profiles of the different reflections.

Williamson-Hall plots made for different directions in reciprocal space indicate considerable strain-like broadening and negligible size broadening. Therefore, in the following, the structural line broadening is considered to be completely strain-like. The anisotropy of the structural line broadening is exhibited by plotting $B_{\Delta 2\theta,hkl}^f\tan\theta_{0,hkl}$ as a function of the angle between the diffraction vector and the [001] direction (Fig. 2). The largest broadening occurs in the [hk0] directions. All data apparently fall on a single curve. Identifying $\delta\Delta 2\theta_{hkl}$ and $\delta\xi_{hkl}$ in Eq. (6) with $B_{\Delta 2\theta,hkl}^f$ and $B_\xi$ (the FWHM of the probability density function of the composition, $p_\xi$), respectively, and using the symmetry restrictions of the hexagonal crystal system, gives for $B_{\Delta 2\theta,hkl}^f$

$$B_{\Delta 2\theta,hkl}^f = \left(\frac{180^\circ}{\pi}\right)\tan\theta_{0,hkl} \left[ \frac{B_\xi \cdot \frac{d\alpha_1}{d\xi} \cdot \left(h^2 + k^2 + hk\right) + \left[B_\xi \cdot \frac{d\alpha_3}{d\xi} \cdot l^2\right]}{\alpha_1 \cdot \left(h^2 + k^2 + hk\right) + \alpha_3 \cdot l^2} \right], \quad (7)$$

The evident success of fitting Eq. (7) to the experimental data (continuous line in Fig. 2) indicates that the observed structural line broadening is compatible with the presence of composition variations as considered in section 2. The fit gives $B_\xi d\alpha_1/d\xi = 0.000966(5) \text{ Å}^{-2}$ and $B_\xi d\alpha_3/d\xi = 0.000173(2) \text{ Å}^{-2}$ (or the negative values of these). The extent of the
anisotropy in the line-broadening can be calculated from the known composition dependence of the cell parameters of ε-FeNₙ: a(y)/Å = 2.5828 + 0.3843·y and c(y)/Å = 4.2470 + 0.3834·y (fitted for data obtained from slowly cooled powders with 0.33 < y < 0.44 [13]), which gives dα₁/dξ = −0.0493 Å⁻² and dα₃/dξ = −0.0089 Å⁻² for y₀ = 0.433. The thus obtained ratio (dα₃/dξ)/(dα₁/dξ) = 0.181 agrees very well to the value obtained from the fitting parameters (0.180). Using the above given values for dα₁/dξ and dα₃/dξ as obtained from cell-parameter data, a value for Bξ can be obtained from the fitted values of Bξ·dα₁/dξ and Bξ·dα₃/dξ. It follows Bξ = 0.020 for the FWHM of the composition density function. Recognising the nearly Gaussian character of the line broadening, this gives 0.008 as the standard deviation of the composition distribution. Hence, the composition of the powder can be expressed as ε-FeN₀.₄₃₃±₀.₀₀₈.

Fig. 1  Full width at half maximum (FWHM) of the measured reflections of ε-FeN₀.₄₃₃ and LaB₆, with a fitted curve for the latter.

Fig. 2 The anisotropy of strain-like broadening of ε-FeN₀.₄₃₃: direction dependence of the corrected FWHM, Bf·Δ²θ₀, hkl⊥[001].

THE RELATION OF STRAIN BROADENING DUE TO COMPOSITION VARIATIONS AND THE STEPHENS ANISOTROPIC STRAIN BROADENING MODEL [3]

The model of strain-like line broadening due to composition variations presented here is related to the phenomenological anisotropic strain broadening model as given by Stephens [3]. Both models describe line broadening on the basis of equations like Eq. (2) and (5), i.e. assuming that the lattices distortions (cf. the αᵢ values in Eq. (4)) are constant within each coherently diffracting domain, but can vary from crystallite to crystallite. Thus, also in the description due to Stephens, for all reflections the structural broadening has the same shape and for a particular direction of the diffraction vector the line width varies proportional to tanθ. However, the factor describing the dependence of the line-broadening on the direction of the diffraction vector, i.e. |d ln M_hkl/dξ|·δξ in the model proposed here, is different in the description by Stephens. This difference is caused by the symmetry restrictions for αᵢ listed in Table 1 which for the case of composition variations have to be obeyed in each individual crystallite. For the Stephens description, however, only the ensemble of all diffracting crystallites, as an entity, has to obey the crystal symmetry conditions, and thus (i) the average values of αᵢ must directly reflect the crystal symmetry and (ii) certain correlations exist between the distribution functions for αᵢ. This leads finally to a description of the direction dependence of the strain broadening in terms of "SHKL parameters" with certain symmetry restrictions [3]. It can be shown [14], that for each crystal system Eq. (6) presents a special, physically founded case of the phenomenological line broadening description according to
Ref. [3]. In the case that Eq. (6) is valid, certain values $S_{HKL}$ of the Stephens description become redundant by additional equations between the $S_{HKL}$ values.

Therefore, in the course of a Rietveld refinement, structural line broadening due to composition variations can be evaluated using the Stephens' description as implemented in several Rietveld programmes. Thereby, the predicted redundancy of the $S_{HKL}$ parameters can be used to test whether the simpler model of composition variations is really applicable. Indeed, performing such a Rietveld refinement [15], incorporating the Stephens' description for strain broadening, to the current $\varepsilon$-FeN$_{0.433}$ diffraction data (using the LaB$_6$ data for describing the instrumental broadening), it could be shown that the refined values for the $S_{HKL}$ parameters gave the same amount of composition variation as obtained in section 4 and show the predicted redundancies. More details will be presented elsewhere [14].

CONCLUSION

- The anisotropic strain-like structural line-broadening observed in X-ray diffraction patterns of a powder sample of the hexagonal iron nitride, $\varepsilon$-FeN$_{0.433}$ can be fully ascribed to composition differences between the crystallites constituting the powder, taking the composition in each crystallite as constant.
- The extent of anisotropy as predicted by the composition dependencies of the cell parameters agreed very well with the experimental data. The composition variation of the powder was found to be near to Gaussian having a standard deviation of 0.008 so that the composition can be given as FeN$_{0.433 \pm 0.008}$.
- The structural line broadening caused by the composition variations can be regarded as a special, physically founded case of the phenomenological description of anisotropic strain-broadening due to Stephens [3].

ACKNOWLEDGEMENTS

The authors thank V. Petřiček, Prague, CZ, for valuable discussions.

REFERENCES


