Calculation of Diffraction Line Profiles in the Case of a Major Size Effect: Application to Boehmite AIOOH

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Abstract

A method allowing the calculation of the diffraction line profiles of a powder, whose crystallites are convex polyhedrons, is described. The decomposition of the crystallite volume into elementary prisms distinguishes three cases. The analytical expression of the results allows their derivation in the case of a linear size distribution. With instrumental broadening causes taken into account, an application of this method is given in restoring the whole X-ray diffraction pattern of samples of finely divided powders of boehmite, AIOOH.

1. Introduction

Very precise X-ray powder diffractometry has widely proved its interest in acquiring structural and textural information such as reticular distances, atomic coordinates or crystallite mean size (Langford, 1981). The aim of this paper is to present a method for calculating the profile of a whole powder diffraction pattern in the case of highly divided material. This method allows a preponderant size effect to be described and can be applied to general morphologies of crystallites.

The consequence of the size effect is a broadening of the lines approximately in inverse ratio to the thickness of crystallites, perpendicularly to the reflecting planes. It is usually estimated by measuring the width of the line, according to different definitions (Langford & Wilson, 1978; Langford & Louër, 1982). The relative ratios between the width of the line on the one hand, and the profile of each line, on the other, are a function of the morphology of the crystallites. This point has been thoroughly studied as far as rather simple crystalline shapes are concerned (rectangular parallelepiped, tetrahedron, octahedron, sphere, etc.) from the point of view of a variance analysis. Still, such a method is limited when experimental data are poor. That is, for example, the case of an important size effect, which involves an overlapping or an excessive weakening of the lines, and would make the measure of the above mentioned parameters quite impossible or very inaccurate.

The line-profile shape function has been directly analysed, either to answer specific needs, taking into account a determined morphology (for example, needle-like crystallites: Yucel, Rautureau, Tchoubar & Tchoubar, 1980; De Courville-Brenasin, Joyez & Tchoubar, 1981), or to study thoroughly the problem of a size distribution by the study of one diffraction line, and that only for an apparent crystallite size (Morawec, de Montgolfier & Renouprez, 1977; Le Bail & Louër, 1978).

In order to exploit the crystallographic data of series of boehmite powders (AIOOH) with a large range of sizes and morphologies, we have developed a method for calculation of the line-profile shape function from the classical theoretical approach of diffraction by small crystallites. This method is valid for any diffraction direction and any convex polyhedral morphology of crystallite, and consequently it can describe various samples.

2. Calculation method of the broadening of the diffraction line profile due to size effect

2.1. Theoretical principles

Calculation of the intensity diffracted by a small crystallite of a powder sample has already been developed (Guinier, 1964; Wilson, 1969). It leads to the general formula

\[ I(s) = U^{-1} \left| F \right| \int_{-T}^{T} V(t) \exp\{-2\pi ist\} \, dt, \]  

where \( U \) is the volume of the unit cell, \( F \) is the structure factor for the Bragg reflection considered, \( V(t) \) is the measure of the intersection of the crystallite volume with its ghost translated by \( t \) perpendicular to the reflecting planes, \( s \) is the deviation \( \theta(2 \sin \theta/\lambda) \) from the Bragg position. It is useful to formulate some remarks about this equation, which is the starting point of our calculation:

The function \( V(t) \) obviously presents the following...
properties: \( V(t) = V(-t), V(0) \) is the maximum value of \( V(t) \) and equals the real volume \( V_0 \) of the crystallite; there is a limiting value of \( t, T \) for and beyond which \( V(t) \) vanishes.

This equation results from an integration in the neighbourhood of the reciprocal-lattice point \( hkl \) using the following assumptions: the structure factor is quite constant on the integration field defined by the Fourier transform of the shape; the Ewald sphere can be confused with its tangent plane.

Equation (1) implies, on the one hand, the knowledge of the function \( V(t) \), which requires the choice of an adequate crystallite shape, and, on the other hand, the possibility to perform the integration for the crystallite shape considered. We have chosen such a shape so that it can easily be decomposed into several elementary crystalline volumes over which analytical integration of (1) is possible: it can be any convex polyhedral shape, which — according to the diffraction direction and on the basis of a triangulation of its ‘reflecting’ section — allows elementary truncated prisms to be considered.

On such a volume, we try to integrate the profile shape function:

\[
Z(s) = \int_{-T}^{+T} V(t) \exp\{-2\pi ist\} dt. \tag{2}
\]

2.2. Triangulation method and integration field

Let us consider the case of a convex polyhedral crystallite whose boundaries are defined by a set of reticular planes \((h, k, l)\). The position of each plane is fixed by its orthogonal distance from a point \(O\), chosen inside the crystal volume. In order to split the volume, we have to create fictive edges orthogonal to the reflecting plane \((H, K, L)\) above or below each summit (Fig. 1).

The crystallite is then defined by a set of points \(A_i^0\) and thickness \(r_i\): \(A_i^0\) is the projection of the summit \(A_i\) on a cross section parallel to the reflecting planes \((H, K, L)\); \(r_i\) is the length of the fictive edges relative to the summit \(A_i^0\); it is defined and limited by the associated boundary planes \((hkl)\) and \((h', k', l')\). This is the thickness of the crystallite above or below \(A_i\), along the normal to the reflecting planes \(t\). The cross section itself is then divided by means of an algorithm into elementary triangles (Fig. 2). Consequently the whole crystalline volume is divided into triangular truncated prisms along the direction \(t\), over which the integration (2) can easily be performed. An example of this method is given in Fig. 3, which shows this
triangulation in the case of a boehmite crystallite for various diffracting directions.

2.3. Basic formulae of the profile function

On an elementary volume, (2) becomes

$$dZ(s) = \int_{-r}^{r} (r - |t|) \exp\{-2\pi i s t\} dt \, dA,$$

(3)

where \( r \) is the height of the prism and \( dA \) is the elementary reflecting area. Consequently, if \( s \) is non-zero:

$$dZ(s) = 2(2\pi s)^{-2} (1 - \cos 2\pi rs) \, dA.$$

(4)

On the volume defined in Fig. 4:

$$Z(s) = \int_{A} dZ(s),$$

(5)

where \( A \) is the projected area of crystalline volume on the reflecting plane. The calculation of this integral leads us to distinguish three cases according to the possible equality of the limiting thicknesses of the prisms \( r_1 = M_1 M_1, \quad r_2 = M_2 M_2, \quad r_3 = M_3 M_3. \) These mathematical cases can be rather frequent in practice, because the crystal faces are often lattice planes, and consequently they can often be in a particular position of parallelism or orthogonality in relation to the diffraction direction or with other boundary planes.

We may also find the directly calculated values for the case \( s = 0 \), (4) being undefined for this value.

The three cases are as follows:

(i) \( r_1 \neq r_2 \neq r_3 \neq r_4 \)

$$Z(s) = \frac{2A}{(2\pi s)^2} \left[ \frac{1}{2} + \frac{1}{2\pi s} \sum \frac{\cos(2\pi sr_i)}{(r_i \cdot r_j)(r_i \cdot r_k)} \right]$$

(6)

$$Z(0) = \frac{A}{12} \left[ \sum \frac{r_i^4}{(r_i \cdot r_j)(r_i \cdot r_k)} \right],$$

(7)

where \( \sigma \) represents the group of cyclic permutations of the set \( \{1, 2, 3\} \).

(ii) \( r_1 = r_2 = r_3 = r_0 \) and \( r_4 \neq r_0 \)

$$Z(s) = \frac{2A}{(2\pi s)^2} \left[ \frac{1}{2} + \frac{1}{2\pi s} \left\{ \frac{\sin(2\pi sr_0)}{2\pi (r_0 \cdot r_0)} \right\} \right]$$

$$+ \frac{\cos(2\pi sr_0) - \cos(2\pi sr_4)}{2\pi (r_0 \cdot r_0)} \right\} \right]$$

(8)

$$Z(0) = \frac{A}{12} \left[ 3r_0^2 + 2r_4r_0 + r_0^2 \right].$$

(9)

(iii) \( r_1 = r_2 = r_3 = r_4 \)

$$Z(s) = A(2\pi s)^{-2} [1 - \cos(2\pi sr_4)]$$

(10)

$$Z(0) = \frac{A}{2} r_4^2.$$

(11)

We can remark here that the three cases mentioned correspond, for example, to the cases where the first contact of a plane parallel to the reflecting planes will be made with a corner, an edge or a face. Then the profile shape function has different asymptotical behaviour; this has already been mentioned (Wilson, 1969) in the particular case of a function \( V(t) \) with constant coefficients and continuous derivatives; we can observe differences in the profile shape that essentially affect the line tails (Fig. 5). We can also verify that we are in agreement with the previous profile-shape functions already mentioned (Langford & Wilson, 1978) for simple morphologies. The cases of a tetrahedron (all \( hkl \)), of a cube (111 reflexion) and of an octahedron (100 reflexion) correspond to the juxtaposition of elementary triangular prisms of type (ii), with \( r_4 = 0 \) and \( r_0 \neq 0 \), and to a profile function

$$Z(s) = \frac{A}{(2\pi s)^2} \frac{2A}{(2\pi s)^4(r_0)^2} [1 - \cos(2\pi sr_0)].$$

(8')

In the same way an octahedron in 110 reflexion is a juxtaposition of elementary triangular prisms of type
with $r_c \neq 0$ and $r_0 = 0$, and the profile function is
\[ Z(s) = \frac{A}{(2\pi s)^2} - \frac{2A}{(2\pi s)^4} r_c \sin(2\pi sr_c) \]
\[ + \frac{2A}{(2\pi s)^4} r_c^2 \left[ 1 - \cos(2\pi sr_c) \right]. \]

Expressions (8') and (8'') are equivalent to those reported in the literature.

2.4. The problem of size distribution

The calculated profile shape function is still an approximate one as far as it represents, for an idealistic diffraction experiment, the intensity diffracted by a powder, which should be a population of small identical crystallites perfectly homogeneous in their morphologies and sizes.

While keeping the previous formalism and the geometrical description of the crystallite volume, we introduce a statistical distribution of the crystallite size, and we calculate its effect on the previous equations, in the case of a very simple distribution law: a set of linear functions.

A more classical Gaussian distribution would have been more satisfactory to get a general analytical formulation of our new profile function. Nevertheless, 'negative thicknesses' would have had no physical significance and we would have had to introduce a truncation of our Gaussian distribution, which leads to insolvable integrals. On the other hand, a set of linear easily computed functions is a good approximation to various size distributions and allows us various settings of sizes.

For this calculation, we have supposed that each crystallite has the same general shape, its boundaries being made of the same reticular planes $(hkl)$; their respective distances from a point $O$, $D_{hkl}$ (Fig. 1), remain in the same relative ratios in such a way that we can write, for all $(hkl)$ planes, $D_{hkl} = xD_{0hkl}$, where $x$ is a common scale factor and $D_{0hkl}$ a standard distance from the plane $(hkl)$ to the point $O$. Then it is possible to keep exactly the same network in elementary volumes and the same triangulation, with a simple proportionality coefficient $x$.

Let us consider a statistical distribution of the form
\[ g(x) = ax + b \quad \text{for} \quad x \in [x_1, x_2], \]
where $x$ represents the common scale factor, and $x_1$ and $x_2$ are the extreme values of $x$. The calculation of the integral $Z_m(s)$, mean value of $Z(s)$,
\[ Z_m(s) = \int_{x_1}^{x_2} (ax + b)Z(x, s) \, dx \]
give the following results, for three distinct values of $r_1, r_2, r_3$. (The other cases are mentioned in the Appendix.)*

\[(i) s \neq 0 \]
\[ Z_m(s) = \frac{2A}{(\pi s)^2} \left[ 1 - \frac{1}{2} \left( x_1^4 - x_2^4 \right) \right] + \frac{2A}{(\pi s)^4} r_c^2 \left[ 1 - \cos(2\pi sr_c) \right]. \]

\[(ii) s = 0 \]
\[ Z_m(0) = Z(0) \left[ a \left( \frac{x_2^6 - x_1^6}{6} \right) + b \left( \frac{x_2^5 - x_1^5}{5} \right) \right]. \]

For a size distribution defined by a set of such functions,† we must calculate the weighted mean of the different linear contributions. It is also possible to take into account Dirac distributions with a weight that would correspond to their proportion of the total number of crystallites. So, numerous statistical distribution types can be approximated.

For example, Figs. 6 and 7 show some different size distributions and their calculated effect on the first line (020) of a boehmite (AlOOH) pattern. A general consequence of this statistical mean is to minimize the secondary fluctuations of the profile shape on the sides of the central peak. We also remark that the resulting profile is conditioned to a large extent by the most developed crystallites: as a matter of fact, their contribution is proportional to the diffracting volume and soon becomes preponderant.

3. Applications

In order to compare the calculated profile with the observed pattern, we have taken into account other

*The Appendix has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42167 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

†These functions are defined with the boundary scale factors $x_i$ and their respective values $g(x_i)$. 
broadening factors. Thus, the profile function has been
convoluted numerically, first by a spectral function
and then by instrumental representative functions.
The spectral distribution was assumed to be the sum
of purely Lorentzian lines \( K_{\alpha_1} \) and \( K_{\alpha_2} \). The instru-
mental and geometrical factors have been represented
according to the analytical formulations of Klug &
Alexander (1973) by five folding functions (X-ray
source width, axial divergence of the beam, flat speci-
men surface, specimen transparency and receiving-slit
width). If the different actual parameters of the diffra-
tion experiment are taken into account, as far as they
are checked and measured, gives an analytical form
valid for the whole extent of the diffraction pattern,
which would not be the case for an experimental
function measured with a reference sample for
example.

As well as the size distribution, they essentially
contribute to a smoothing of the profile. Nevertheless
we must notice here that in the case of highly divided
powders these instrumental broadening factors
become rapidly negligible in comparison with that of
size effect.

This method of diffraction line profile analysis has
been used for studying boehmitic samples (AlOOH)
whose structure is now well known, but whose mor-
phology and size can be very different. We shall give
two examples here:

(i) a well-crystallized boehmite prepared from
aluminium trihydroxide in hydrothermal conditions.
The crystallites are hexagonal platelets, which can be
up to 1000 Å thick and 1 µm long (sample 1);
(ii) a more divided product prepared by neutraliz-
ation of a solution of aluminium oxychloride
\( A_2(OH)_3Cl_3 \) and followed by an evolution in hydro-
thermal conditions (Grebille, 1982). The crystallites
are platelets (diameter = 600 Å, thickness = 100 Å)
(sample 2).

In the last case, size effect is preponderant, whereas,
in the first case, morphological and instrumental
factors are comparable.

The X-ray diffracted patterns have been recorded
on a prototype goniometer (Bérar, Calvarin & Weigel,
1980) with the doublet \( K_{\alpha_1}-K_{\alpha_2} \) of a copper rotating
anode. Owing to well defined characteristics of the
apparatus, we could take into account instrumental
factors, which described the real experimental con-
ditions (X-ray source width: 0.05 mm, goniometer
radius: 500 mm, radial divergence: 0.7°, axial diver-
gence: 1.0°). The receiving slit has been chosen at
1.0 mm for the first powder sample and at 1.5 mm for
the second.

The angular analysed field begins at 6.0°θ and ends
at about 33°θ. According to extinction rules, 21 lines
should exist in this interval. But only 12 of them are
actually observed or have non-negligible intensity.
The intensity values of these lines have been measured
with steps varying from 0.01 to 0.05°θ chosen to get an
at least 20 points on each line. Thereafter the back-
ground has been deduced from these values.

An estimation of the morphology and the size of the
products was first made by transmission electron
micrography. As a significant difference in the inten-
sity ratios of the lines between various samples has
been noticed, an important effect of orientation char-
acteristic of such platelet-like products must be taken
into account. The values of a preferred orientation
function* were first refined with the integrated inten-

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* A quadratic function has been chosen to describe this preferred
orientation effect.
CALCULATION OF DIFFRACTION LINE PROFILES

sity of the lines. Then, we compared the calculated and observed profiles, and we have looked for the best agreement by adjusting the size and the morphology, then refining the preferred orientation function and finally the size distribution.

The agreement between experimental and calculated profiles was measured by quadratic residual factor $R^2_P$, which is to be compared with the value of $R^2_B$ defined from the integrated intensity. Similarly, non-quadratic residual factors $R^1_P$ and $R^1_B$ have also been calculated.

$$R_{np} = \left( \frac{\sum_p \omega (I_o - I_c)^2}{\sum_p \omega I_o^2} \right)^{1/n}$$

$$R_{nP} = \left( \left\{ \sum \left( \sum_p \omega (I_o - I_c)^2 \right) \right\} / \left\{ \sum \left( \sum_p \omega I_o^2 \right) \right\} \right)^{1/n}$$

where $I_o$ and $I_c$ are respectively the observed and the calculated intensities at each point, and $\omega$ is a weight factor.

The diffractometric data and results are given in Table 1. The morphological results are in very good agreement with the micrography ones. The latter, coupled with electron diffraction experiments, helped us to define the orientation of our crystallites and, as a consequence, the indexing of the boundary planes. From the profile calculation we could conclude that these crystallites are coherent domains for X-ray diffraction. Enlarged line tails pointed to a statistical size distribution, which has been chosen a simple linear one. We have to conclude a broader one for sample 1 and this conclusion is also in good agreement with the general aspect of the two powders in micrography observations.

Some examples of observed and calculated profiles are given in Figs. 8 and 9 for lines 020, 150°002 and 132-200. Two remarks can be made:

(i) the integrated intensity ratios between the lines are quite different in our two samples, for the same structure. This difference has been explained by different preferred orientation coefficients in the powder;

(ii) the size-effect broadening is far more important in the most divided sample (2) and is mainly in this case from instrumental factors. This is not the case in sample (1), for which the two broadening causes have a non-negligible influence. Other refinements have been carried out successfully on still more divided materials (Grebille, Dupin, Berar & Gregoire, 1983). Refinements on such a scale of sizes (50-10 000 Å) have shown the efficiency of the method.

4. Conclusion

A good agreement between experimental and theoretical diffraction line profiles has been reached, for two different samples of boehmitic products (AlOOH).

Table 1. Diffractometric data and results

<table>
<thead>
<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angular range (°θ)</td>
<td>7θ0-32θ2</td>
<td>6θ7-33θ5</td>
</tr>
<tr>
<td>Number of points in the calculated profile*</td>
<td>355</td>
<td>280</td>
</tr>
<tr>
<td>Angular step in the diffraction lines (°θ)</td>
<td>0.01 or 0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>Number of calculated diffraction lines</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Boundary planes and corresponding thickness</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(001) 1000 Å</td>
<td>(010) 160 Å</td>
<td></td>
</tr>
<tr>
<td>(010) 820 Å</td>
<td>(101) 600 Å</td>
<td></td>
</tr>
<tr>
<td>(101) 6400 Å (101) 600 Å</td>
<td>(101) 6400 Å</td>
<td></td>
</tr>
<tr>
<td>Size distribution at point i</td>
<td>(a) (b) (a) (b)</td>
<td></td>
</tr>
<tr>
<td>(a) scale factor $x_i$</td>
<td>0.7 1.5 0.7 1</td>
<td></td>
</tr>
<tr>
<td>(b) distribution function $g(x_i)$</td>
<td>0.3 0.3 1.1 1.5</td>
<td></td>
</tr>
<tr>
<td>Residual factors</td>
<td>$R^1_P$ $R^1_B$</td>
<td>9.90 4.72 12.29 3.97</td>
</tr>
<tr>
<td>$R^2_P$ $R^2_B$</td>
<td>7.65 5.18 8.82 4.17</td>
<td></td>
</tr>
</tbody>
</table>

*Most of these points contribute to profiles of observed lines; Larger angular steps have been chosen in the parts of the diagram where no significant diffraction line can be observed.
The theoretical profiles have been directly provided from the calculation of the diffracted intensity for a large angular range according to the structural, morphological and instrumental data, on the basis of a small restriction by a modelization of the morphology of the diffracting domains and of their statistical size distribution.

We have taken into account the usual different line-broadening causes and we could measure their specific influence on the line profiles on the entire range of a diffraction diagram. Consequently, it was not necessary to find any physical interpretation of a mathematical function, arbitrarily chosen to fit the experimental data. The first broadening cause to be studied is the size effect, which affects each direction of diffraction differently, according to the geometrical description of the coherent domains of diffraction. We have chosen to associate this calculation with the different experimental broadening causes rather than describe them by a Rietveld-type method. Refinements with two Lorentzian functions (with half width as a function of $\theta$) have given not such good accuracy ($R_{2p} = 11.7$, $R_{2B} = 4.4$) as with the five instrumental broadening convolutions, in the actual conditions of the diffraction experiments.

On the basis of the results of the refinement of the whole diagram, we isolated some lines (020, 021) to measure the accuracy on only one line profile. Before specific refinement of these profiles, we already had a good agreement [$R_{2p} (020) = 4.46$, $R_{2B} (021) = 7.40$], which was improved after refinement [$R_{2p} (020) = 4.10$, $R_{2p} (021) = 5.93$].

Another possible use of the method is the study of doublet lines. The restitution and refinement of such a complex profile can be an easy method of deconvolution.

We have noticed a residual and systematic discrepancy between observed and calculated profiles for the 020 line. This can be related to the analysis and characterization of more divided materials (Grebille et al., 1983), which showed an important broadening and shift of the 020 line. This effect has been explained on the basis of structural defects and stacking faults of the layered structure of a not perfectly stoichiometric boehmite and a model of such a stacking fault has been described and developed in this particular case (Grebille, 1982). This application is being prepared for publication. This type of defect has even been observed on well crystallized samples and has been related to a dilatometric anomaly (Bézar, Grebille, Gregoire & Weigel, 1984). Such structural defects, which are quite frequent in divided materials, can also be taken into account in our method of calculation by the introduction of new factors in the calculation of our profile function on the basis of an average value of the structure factor (Wilson, 1969) or by a convolution of the profile with already known distortion functions (Guinier, 1964). Here the problem lies in the fact that there is no general case and each particular case should be treated specifically. A convolution function or a general broadening factor can help to approach the observed pattern, but neither is obvious enough to be given a physical and realistic interpretation. Our method is a good basis for the development of such extensions and has proved its efficiency in the case of divided boehmite.

References