On the basis of known equations for calculating X-ray diffraction intensities from a given number of unit cells of a crystal phase in polycrystalline material, as due to: (i) Bragg reflections; (ii) average diffuse scattering caused by thermal plus first-kind disorder; and (iii) incoherent scattering, a relationship has been found that ties, in the Rietveld analysis, the Bragg scale factor to a scale factor for ‘disorder’ as well as incoherent scattering. Instead of fitting the background with a polynomial function, it becomes possible to describe the background by physically based equations. Air scattering is included in the background simulation. By this means, the refinement can be carried out with fewer parameters (six fewer than when a fifth-order polynomial is used). The DBWS-9006PC computer program written by Sakthivel & Young [(1990), Georgia Institute of Technology, Atlanta, GA, USA] has been modified to follow this approach and it has been used to refine the crystal structures of the cubic form of Y₂O₃ and of α-Al₂O₃. Peak asymmetry has been described by a function based on an exponential approximation. The results from refinements using polynomial physically based background function are, in terms of final structural parameters and reliability indices, very close to each other and in agreement with results reported in the literature. The reconstruction and optimization of the background scattering by means of physically based equations helps the implementation in the Rietveld code of other possible specific diffuse scattering contributions, such as that due to an amorphous phase.

Abstract

In the Rietveld structure refinement of polycrystalline materials from X-ray diffraction powder data, the background scattering is usually fitted with polynomials of a suitably high order (usually up to the fifth order). In this and the following paper (Riello, Fagherazzi, Canton, Clemente & Signoretto, 1995), in which we determine the degree of crystallinity of some semicrystalline materials, we have developed a Rietveld-analysis code for the calculation, on a physical basis, of the three most important background scattering components: air scattering, incoherent scattering and average diffuse scattering due to thermal disorder plus first-kind lattice disorder. The last contribution is expressed through a formula that takes the average isotropic atomic displacements into account (Warren, 1969; Sabine, 1980; Gehrke & Zachmann, 1981; Von Dreele, Jorgensen & Windsor, 1982; Schneider, 1988; Polizzi, Fagherazzi, Benedetti, Battaglieri & Asano, 1990; Suortti, 1993). Fluorescence effects can be generally neglected when a suitable X-ray tube target and a diffracted-beam monochromator are used. We have not included the contribution of the structured thermal diffuse scattering components that can be computed (Warren, 1969; Suortti, 1967, 1993) only for very simple structures for which Rietveld refinement may not be important. We preferred to test our approach on two fairly complex structures: an yttrium sesquioxide powder (cubic form), the crystal structure of which has been determined from single-crystal neutron diffraction data (O'Connor & Valentine, 1969), and an α-Al₂O₃ (corundum) powder, for which basic structural parameters can be found in the text of Hyde & Andersson (1989).

Introduction

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The Rietveld-refinement results obtained by our approach were compared with corresponding ones from a refinement in which the background was fitted by a fifth-order polynomial, all the remaining conditions being equal. The DBWS-9006PC computer program (Sakthivel & Young, 1990), which is an updated version of that of Wiles & Young (1981), was modified in such a way that the theoretically defined X-ray diffuse scattering components could be inserted and taken into account in the optimization routine, through a relationship that ties the Bragg scale factor to a scale factor for 'disorder' as well as incoherent scattering. In the following paper, the procedure is extended to semicrystalline materials by the inclusion of intensities from an amorphous phase, suitably scaled, based on experimental intensities from a pure amorphous specimen. For the moment, the modified program does not take account of the short-range-order scattering due to noncrystalline substances (see Richardson, 1993) or to nonstoichiometry [modulated diffuse scattering, as shown by Schneider (1988) in the case of NaTI]. As a matter of fact, our main purpose was to derive a general mathematical expression for the background scattering from a polycrystalline material, to which scattering due to an amorphous phase can be added in order to determine the degree of crystallinity in semicrystalline materials (see Riello et al., 1995). In principle, all specific types of diffuse scattering contributions caused by static disorder, as well as the structured thermal diffuse scattering peaks from acoustic phonons, could be included in the procedure proposed here by adding other specific terms to the background expression, suitably scaled to the total number of scatterers. Note that, although the equations and formulas reported here have been developed for X-ray powder diffraction, most of the general considerations, as well as many of the previously cited papers, relate also to neutron diffraction.

Theory

Many excellent papers have described and discussed Rietveld analysis (Rietveld, 1969) as applied to X-ray powder diffraction patterns (see, for example, Hill & Madsen, 1987; Hill & Howard, 1987; Bish & Howard, 1988; Hill, 1991, 1992; Young, 1993). Therefore, the general theory underlying this methodology is well known and is reviewed here only as required to explain our specific approach. The X-ray intensities, \( Y_{ci} \), diffracted at the \( i \)-th step of the \( 2\Theta \) diffraction angle, have been calculated by means of the following equation, which can, in the present computer program, be extended up to a mixture of eight crystalline phases:

\[
Y_{ci} = K^{\text{Bragg}} \sum_{n} |F_n|^2 O_n A_n L_n \Phi(2\Theta_i - 2\Theta_n) + Y_{bk}^n,
\]

with:

- \( K^{\text{Bragg}} \): Bragg scale factor
- \( \sum_n \): sum taken over all \( n \) reflections that contribute at the same \( i \)-th step
- \( |F_n|^2 \): squared structure factor for the \( n \)-th reflection
- \( O_n \): correction factor for the preferred crystal orientation [we used the March-Dollase function (Dollase, 1986)]
- \( H_{ni} \): correction function for peak asymmetry.

Here we modified the Sakthivel & Young (1990) program by using the following semi-empirical approximation:

\[
H_{ni} = 1 + \left[ K^4(2\Theta_i - 2\Theta_n)/\tan (\Theta_n) \right] \frac{\text{FWHM}}{\Theta_i},
\]

where \( K^4 \) is a constant to be fitted, \( 2\Theta_n \) is the peak maximum and FWHM is the full width at half-maximum of the \( n \)-th reflection. This function is properly normalized and does not give misfits due to truncation effects. Like the classical Rietveld asymmetry function, this function depends on one fit parameter so the Sakthivel & Young (1990) program could be modified easily for absorption.

The Lorentz, polarization and multiplicity factors; the polarization factor also takes the reflection from the graphite monochromator into account. The normalized profile function (pseudo-Voigt) background function, fitted at the \( i \)-th step with a fifth-order polynomial in the standard code and calculated as follows in our modified Rietveld code (Riello, Clemente, Fagherazzi & Canton, 1993):

\[
Y_{bk}^i = K^{\text{inc}} I_{i}^{\text{inc}} + K^{\text{dis}} [1 - \exp (-k s_i^2)] I_{i}^{\text{coh}} + Y_{i}^{\text{air}},
\]

with:

- \( s_i = 2 \sin \Theta_i/\lambda \): variable in reciprocal space
- \( K^{\text{inc}} \): scale factor for the incoherent scattering
- \( K^{\text{dis}} \): scale factor for diffuse scattering due to thermal and first-kind lattice disorder
- \( I_{i}^{\text{inc}} \): independent incoherent scattering at the \( i \)-th step, corrected by the polarization factor, by the Breit–Dirac factor, by specific absorption effects and by the bandpass function of the monochromator used in the diffracted beam (Ruland, 1961, 1964), independent coherent scattering at the \( i \)-th step, corrected by the polarization factor; it is given by \( \sum_{\text{cell}} |f_j|^2 \).\]
global disorder parameter used in the description of the diffuse scattering due to both thermal vibration and first-kind lattice disorder (Ruland, 1961; Gehrke & Zachmann, 1981). This parameter, relating to uncorrelated and isotropic atomic displacements (Warren, 1969), is equal to \( B/2 \), where \( B \) is the overall average isotropic thermal factor. When the isotropic thermal factor \( B_j \) for each \( j \)th atomic species in the unit cell is taken into account, (3) has to be generalized accordingly.

The air scattering contribution to the background, based on a fitted scattering calibration curve, then corrected for the presence of the specimen as well as for the air trapped inside the specimen, according to Ottani, Riello & Polizzi (1993). Both \( I_i^{inc} \) and \( I_i^{coh} \) intensities concern all atoms of the unit cell. The \( I_i^{inc} \) were computed by using the analytical expressions and the relevant parameters published by Smith, Thakkar & Chapman (1975). \( I_i^{coh} \) were computed on the basis of analytical approximations to the atomic scattering factors of \( Y^{3+} \) and \( Al^{3+} \), published in International Tables for X-ray Crystallography (1974; Table 2.28, p. 100), and parameters for the atomic scattering factor of \( O^{2-} \) from a recent paper by Azavant & Lichanot (1993).

Now, Rietveld refinement involves the calculation of the integrated intensities followed by the normalization to unit area of the profile functions. Starting from the power \( P \) per unit length of diffraction circle and taking into account the expression for the peak area above the background (Warren, 1969), which has to be properly compared with (1), it is possible to obtain for \( K_{Bragg} \), \( K_{inc} \) and \( K_{dis} \) the following expressions (Bragg–Brentano reflection geometry):

\[
K_{Bragg} = V(CI_0A_0/2\mu)r_0^2(180w/16\pi^2R^2)(\lambda^3/V)^2
\]

\[
K_{inc} = K_{dis} = VCI_0[A_0/(2\mu V_0)]r_0^2(w/R^2).
\]

with:

- \( C \): proportionality constant depending on counter efficiency
- \( I_0 \): primary-beam intensity
- \( A_0 \): primary-beam cross-sectional area
- \( \mu \): linear absorption coefficient of irradiated sample
- \( r_0^2 = (e^2/m_e c^2)^2 \): classical square radius of electron
- \( R \): receiving-surface-sample distance (goniometer radius)
- \( \lambda \): wavelength of the characteristic radiation used
- \( V \): unit-cell volume
- \( V_0 \): volume fraction of the crystalline phase under study
- \( w \): width of the receiving slit
- \( t \): length of the receiving slit.

Therefore, for each crystalline phase in the sample the following relationship holds:

\[
(K_{Bragg}/K_{inc}) = (K_{Bragg}/K_{dis}) = 180\lambda^3/(16\pi^2V). \tag{6}
\]

The same result can be obtained for neutron diffraction starting from the basic equations published by Sabine (1980). These constraints represent the basis of our modified version of the Sakthivel & Young (1990) program. Moreover, we have imposed another physical constraint by using the same \( B \) (or \( B_j \)) thermal factors to describe the decrease in crystalline peak intensities as well as the increase in diffuse scattering caused by ‘disorder’ (of which thermal diffuse scattering is usually the main component). This last constraint was also suggested by Suortti (1993), who, however, proposed to fit the diffuse scattering contribution by iterative procedures. \( K_{inc} \), \( K_{dis} \) and \( B \) (or \( B_j \)), and therefore \( Y_{ir} \), are automatically refined in our Rietveld code, together with all the structural parameters relevant to the crystalline phase under study. In this way, our optimization routine requires six fewer parameters than are needed in the procedure in which a fifth-order polynomial is used to fit the background. It is worth noticing that other authors have suggested using an average thermal-diffuse-scattering background in the Rietveld analysis (Von Dreele, Jorgensen & Windsor, 1982; Schneider, 1988), but as an analytical function, completely adjustable by the fit procedure, added to a suitably defined polynomial. The present procedure avoids the strong correlations that occur among the parameters when the background is described by a polynomial. When several phases are present, it becomes possible to attribute to every phase its own ‘disorder’ and incoherent background contribution. These results are particularly important for determining the degree of crystallinity of semicrystalline materials.

Experimental technique

Materials

The powder sample of \( Y_2O_3 \) examined, produced by Rhône-Poulenc (Courbevoie, France), was composed of the cubic (base-centred-cubic) form of yttrium sesquioxide and had a 99.99% purity. The \( \alpha \)-\( Al_2O_3 \) powder was produced by ALCOA (Pittsburgh, PA, USA) and had a 99.5% purity.

X-ray apparatus

For both polycrystalline materials, the same experimental conditions were employed. The patterns
Table 1. Unit-cell parameters, atomic coordinates, isotropic thermal factors and agreement indices (R_{wp} = weighted profile; R_{exp} = expected and R_b = Bragg) for the c form of Y_2O_3

The Rietveld e.s.d.'s are reported in parentheses. I: Rietveld refinement with the background calculated according to (3). II: Rietveld refinement with a fifth-order polynomial background. III: Neutron refinement on a single crystal by O'Connor & Valentine (1969).

Procedure | I | II | III
--- | --- | --- | ---
a_0 (Å) | 10.60394 (2) | 10.60342 (5) | 10.604
u | 0.03244 (3) | 0.03247 (3) | 0.0327 (3)
x | 0.3907 (2) | 0.3911 (2) | 0.3907 (3)
y | 0.1526 (2) | 0.1526 (2) | 0.1520 (3)
z | 0.3807 (2) | 0.3809 (2) | 0.3804 (3)
B_{11} (Å^2) | 0.589 (15) | 0.513 (17) | 0.24 (4)*
B_{22} (Å^2) | 0.524 (8) | 0.487 (12) | 0.35 (6)*
B_{33} (Å^2) | 0.5078 (48) | 0.923 (49) | 9.3 (5)*
R_{wp} (%) | 7.63 | 7.59 |
R_{exp} (%) | 3.14 | 3.14 |
R_b (%) | 1.72 | 2.10 | 11.5

* Equivalent isotropic displacement factors calculated from the published anisotropic flit factors by B_i = [(4ag)/3](f_{ll} + f_{l2} + f_{l3}).

were recorded at 295 K for 2θ from 13 to 140° with step size 0.02°. The X-ray sample holders had the following dimensions: 25 × 15 × 2 mm. In order to minimize preferred orientation, the powders were gently pressed into the holder. The X-ray powder diffraction data were collected (10 s step⁻¹) with a Philips vertical goniometer PW1050/70 (Bragg–Brentano parafocusing geometry) and a Philips PW1394 and PW1390 diffractometer-controlled system and electronics, using nickel-filtered Cu Kα radiation (30 mA, 40 kV), a focusing graphite monochromator on the diffracted beam and a proportional counter with electronic pulse-height discrimination. A divergence slit of 0.5° and a receiving slit of 0.2 mm were used. The correction factor for asymmetry was applied up to 39° in 2θ. No correction was necessary for preferred orientation. The weights in the minimization formula were set as w_i = 1/Y_{oi}.

Methodology test cases: the structure refinement of Y_2O_3 and α-Al_2O_3

(1) Y_2O_3

The crystal structure of the C form of Y_2O_3 was determined by O'Connor & Valentine (1969) by neutron diffraction from a single crystal. Y_2O_3 crystallizes in the cubic system, centrosymmetric space group Ia3. Eight Y^3+ ions occupy the special Wyckoff positions 8(b) (1/4, 1/4, 1/4) (Y1), while the remaining 24 occupy the sites 24(d) (u, 0, 1/4) (Y2); the 48 O ions occupy the general Wyckoff positions 48(e) (x, y, z).

Table 1 shows a comparison between the parameters we obtained from the Rietveld refinement.

Procedure I refers to the background calculated on a physical basis; procedure II to that calculated by a conventional fifth-order polynomial. The results by O'Connor & Valentine (1969) are also recorded (procedure III).

Convergence was assumed to have been reached when the last-cycle shifts relative to the e.s.d. were below 5%. No large correlation involving the structural parameters was found.

Fig. 1 shows the output from the Rietveld analysis using our modified version of the Sakthivel & Young (1990) program (procedure I).*

For a visual comparison between the results of the two procedures employed, suitable magnifications of the best-fitted diffraction patterns are shown in Figs. 2 and 3.

While Figs. 2(a) and 3(a) show the result of the refinement procedure in which the polynomial is used, Figs. 2(b) and 3(b) illustrate the outcome of the refinement procedure when the background scattering is calculated according to (3). Note that the extremely weak reflection at 26.5°, not explained by the Rietveld refinement, is the Kβ1 residual peak of the very strong 222 yttria reflection.

The atomic parameters (positional and thermal) obtained by Rietveld refinement with procedures I and II are very similar. They agree also with those obtained from neutron diffraction on a single crystal (procedure III), while the thermal parameters calculated by Rietveld analysis are systematically slightly higher than the corresponding ones calculated by procedure

* The numbered intensity of each measured point on the profile has been deposited with the IUCr (Reference: HW0038). Copies may be obtained from The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester, England,
III. The agreement indices $R_{wp}$ and $R_B$ are very similar for the two Rietveld procedures. It is worth mentioning that, with the classical asymmetry function of Rietveld (1969) instead of (2), $R_{wp}$ and $R_B$ increase by some percentage points and become significantly worse for procedure I than for procedure II. It would seem that procedure I (physical background) is more sensitive than procedure II (analytical background) to possible deficiencies in the definitions of some terms or correction factors appearing in (1) and (3).

(2) $\alpha$-Al$_2$O$_3$

The crystal structure of $\alpha$-Al$_2$O$_3$ (corundum) is hexagonal, space group $R3c$. Twelve Al$^{3+}$ ions occupy the site 12(c) (0, 0, $z$) and eighteen O$^{2-}$ ions occupy the site 18(e) ($x$, 0, $\frac{1}{4}$). The structural parameters and their associated e.s.d.'s determined here with procedures I and II are compared in Table 2 with the Rietveld analysis performed by Hill & Madsen (1986) (5 s step$^{-1}$ and 0.02° step size).

The parameters obtained with polynomial background and physically based background are, as in the case of Y$_2$O$_3$, very close to each other and also close to the corresponding ones obtained by Hill & Madsen (1986). Fig. 4 shows the output from the Rietveld analysis using our modified code. A suitable magnification of the best-fitted diffraction pattern is reported in Fig. 5 in order to compare the various diffuse scattering contributions calculated in our procedure (Fig. 5b) with the trend given by the polynomial background (Fig. 5a).

Table 2. Unit-cell parameters, atomic coordinates, isotropic thermal factors and agreement indices for $\alpha$-Al$_2$O$_3$

<table>
<thead>
<tr>
<th>Procedure</th>
<th>I</th>
<th>II</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$ (Å)</td>
<td>4.75939(5)</td>
<td>4.75950(5)</td>
<td>4.75980(3)</td>
</tr>
<tr>
<td>$c_0$ (Å)</td>
<td>12.9909(1)</td>
<td>12.9909(1)</td>
<td>12.9936(1)</td>
</tr>
<tr>
<td>$z_{Al}$</td>
<td>0.35210(3)</td>
<td>0.35210(3)</td>
<td>0.35211(5)</td>
</tr>
<tr>
<td>$x_O$</td>
<td>0.3065(1)</td>
<td>0.3074(1)</td>
<td>0.30644(18)</td>
</tr>
<tr>
<td>$B_{Al}$ (Å$^2$)</td>
<td>0.473(7)</td>
<td>0.491(8)</td>
<td>0.381(8)</td>
</tr>
<tr>
<td>$B_O$ (Å$^2$)</td>
<td>0.370(12)</td>
<td>0.489(15)</td>
<td>0.517(22)</td>
</tr>
<tr>
<td>$R_{wp}$ (%)</td>
<td>7.76</td>
<td>7.37</td>
<td>8.69</td>
</tr>
<tr>
<td>$R_{wp}$ (%)</td>
<td>3.18</td>
<td>3.22</td>
<td>4.03</td>
</tr>
</tbody>
</table>

Fig. 2. Magnified Rietveld refinement plot of Y$_2$O$_3$, in the range 13–80°, that illustrates (a) the background as fitted with a fifth-order polynomial and (b) the physically calculated global background (continuous line) with the contributions due to air scattering (dashed line) and to incoherent plus air scattering (intermediate line). Weighted residuals ($\times$ 3), calculated according to Young (1993), are shown.

Fig. 3. Magnified Rietveld refinement plot of Y$_2$O$_3$ for the angular range 80–140°. (a) and (b) as in Fig. 2.

Fig. 4. Rietveld refinement plot (Cu K$\alpha$ radiation) of $\alpha$-Al$_2$O$_3$ using the background modelled with (3). The residuals $Y_{\alpha}-Y_{\alpha}$ are shown.
Concluding remarks

The modified Rietveld procedure based on a physically defined background scattering gives results practically equivalent to (or slightly better than, for the \( R_B \) index) those from the conventional procedure for both the C form of yttria and corundum; therefore, our methodology can be considered as successfully tested. On the basis of these results, we can conclude that, if structured thermal diffuse scattering peaks could be appropriately modelled and incorporated in the framework of an absolute calculation of all scattering contributions, a further improvement in the precision in some parameters (especially the thermal parameters) might be reached in comparison with the classical Rietveld analysis with a polynomial background. The term describing the X-ray experimental structured scattering of the amorphous fraction of a semicrystalline material can be easily added to a physically defined background, provided the scattering pattern of the completely amorphous substance is available. Therefore, the present modified Rietveld code opens up a new approach for the determination of the degree of crystallinity in semicrystalline materials, as is shown in the next paper (Riello et al., 1995).

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