Focusing x-ray optics and Rietveld refinement – a tool for local phase analysis?

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Abstract. Special x-ray optics is able to focus the X-ray beam. It is shown that such an unusual optic geometry can be handled by modern Rietveld programs using the “learnt profiles” approach. The results of local quantitative analysis are comparable with the results of a conventional device, and limitations like an even or large sample surface are cancelled.

Introduction

X-ray diffraction is the state of the art tool for the analysis of crystalline phases. Modern x-ray diffractometer for phase analysis are controlled by a computer, but the optical principles to focusing the x-ray beam are the same as described by Bragg-Brentano or Guinier. For that reason, a flat sample with an even area of some square centimetres is required. This well-known situation is easily handled by Rietveld [1] programs, especially by the “fundamental parameter” (FP) approach [2, 3] of modern software packages as BGMN®/AutoQuan® or Topas®. These programs calculate the peak shape and width for an ideal sample using the physical parameters of the diffractometer and store it in a device function. Therefore, the number of free parameters is lowered compared to conventional Rietveld programs and real structure parameters as crystal size or microstrain are determined with higher precision and safety. Together with the high numerical stability these programs are well suited for the quantitative phase analysis in routine applications [4, 5]. However, structured, coated or uneven compact samples require a local quantitative phase analysis. Devices with double point screens or x-ray capillaries are frequently used for the measurement of inherent stress or crystal texture. The present paper presents some experiences using such a texture stress diffractometer for the quantitative local phase analysis.

Main text

Two θ/θ-diffractometers 3003 TT by GE Insp. Techn. Ahrensburg GmbH & Co. KG (Ahrensburg, Germany) were used. Device A is equipped with a Cu long fine tube, an automatic divergence slit, a sample changer, a graphite secondary monochromator and a scintilla-
tion counter. It is only used here for comparison. Device B has a Cu fine focus tube working with point focus, a focusing x-ray capillary with a 1 mm focus, a x-y-stage on an Eulerian cradle and a position sensitive detector by Braun GmbH (Garching, Germany) with a registration range of 10 ° in 2θ. It was completed with a cross laser and a CCD camera to control the x-ray focus and to adjust the sample height. As mentioned above the Rietveld program AutoQuan®/BGMN® [4] uses a fixed device function which is generated for device A by the FP approach. The device function of device B was determined by measurements on line profile standard LaB₆ (SRM 660a) using the “learnt profiles” (LP) approach. The following examples illustrate the opportunities for local quantitative phase analysis.

Fig. 1 shows the diffraction patterns of an ATZ (alumina toughened zirconia) disk. Scan a) represents the measurement of the whole disk surface with device A, scan b) to d) the local measurements with device B. Fig. 1 shows a good agreement for the quantification of alumina, monoclinic YSZ and for the sum of t- and c-YSZ. The different ratio of the latter phases is caused by the bad angle resolution of device B and the insufficient separation of the reflexes of cubic and tetragonal YSZ. It should be noted that the standard deviations of a single measurement is comparable for both devices. The higher values listed in fig. 1 results from the coupling of the variances of single measurements. This example illustrates that both devices produce comparable results in spite of the different device function approach.

The second example depicted in Fig. 2 shows the diffraction patterns of a Ti sheet coated with an adhesive intermediate layer and with Hydroxylapatite by thermal spraying. The marked positions correspond to the diffraction patterns a) to c). The Hydroxylapatite coating at position a) is partially decomposed caused by the high process temperature. Similar results were obtained at further positions within the light grey areas. The BaAl₂O₄ at position b) is formed between the Ti sheet (Ti-Al alloy) and the glass layer (Ba glass). The reaction layer of BaAl₂O₄ is thinner than the penetration depth of the x-ray beam. For this reason the quantification is systematically distorted and gives only some hints on the thickness of the reaction layer. The Ti-Al alloy sheet on position c) shows a high deviation from a statistic orientation of the crystallites.

The presented examples demonstrate that the Rietveld refinement is also suitable for the
local quantitative phase analysis using diffractometers with an unusual optic geometry. However, the precision of a Rietveld quantification is strongly influenced by the counting statistic of the measured diffraction pattern. X-ray capillaries generate higher intensities than simple double point screens, but this is usually insufficient for a save Rietveld refinement. Much more intensity growth is obtained with a position sensitive detector because of the fact that it collects also reflex counts out of the Bragg condition. Moreover, this collection of reflections out of the Bragg condition also improves the orientation statistic of the crystals. Unfortunately, the combination of a capillary with a PSD is entailed with a bad angle resolution. Additionally, it has to take into consideration that an intensive Bragg reflex can overload the PSD. A following Rietveld refinement is than distorted by the lack of intensity. A true limitation for Rietveld refinement is the occurrence of large grains, large single crystals or strong preferred orientations. Corresponding to that it was frequently impossible to quantify salt crusts on building materials, not only because of the size of the salt crystals but also because of the grain size of the additives. Technical ceramics or metals are frequently much better suited, but some of these products as super conductors or rolled plates have a high crystal texture preventing a successful refinement.

Fig. 2  Local phase analysis on a Ti sheet with an intermediate layer and a bio-active Hydroxyapatite coating thermal sprayed

<table>
<thead>
<tr>
<th>Pos.</th>
<th>Formula</th>
<th>Content [w-%] ± threfold standard deviation</th>
</tr>
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<tbody>
<tr>
<td>a</td>
<td>Ti</td>
<td>35.13 ± 1.35</td>
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<tr>
<td>b</td>
<td>BaAl(_2)O(_4)</td>
<td>64.87 ± 1.35</td>
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<tr>
<td>b</td>
<td>Ca(_2)(PO(_4))OH</td>
<td>62.27 ± 1.53</td>
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<td>b</td>
<td>Ca(_3)(PO(_4))O</td>
<td>19.34 ± 1.05</td>
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<tr>
<td>b</td>
<td>Ca(_4)(PO(_4))O</td>
<td>18.39 ± 1.50</td>
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<tr>
<td>c</td>
<td>Ti</td>
<td>100.00</td>
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References