EXPANDING FOX FOR MICROSTRUCTURE ANALYSIS

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Abstract

Program FOX for structure solution from powder diffraction was extended by routines for X-ray microstructure analysis of small-grain or defected materials, thin films or strained and textured samples in different diffraction geometries. General interface for convolution of various profile broadening models was created. It is possible to handle both physically relevant and phenomenological broadening models. The second part of extensions involves intensity corrections for texture and absorption in the layered samples. General texture calculator can be used for other purposes such as pole figure simulation. Program was applied to strongly deformed metal (Cu) samples and to nanocrystalline TiO_2 powders and thin films.

Introduction

Program FOX [1] is originally devoted for structure solution from powder diffraction. It is based on the object-oriented crystallographic library ObjectCryst++ [2]. The FOX program itself is not the tool for microstructure analysis, but in principle it contains all the necessary functions for powder pattern computation and refinement. Objects describing profiles shapes can easily be substituted by extended structures representing arbitrary shapes of the diffraction peaks. In this way, the idea of the whole powder pattern modelling proposed by Scardi & Leoni [3] or the anisotropic dislocation line broadening developed by Kuzel & Klimanek [4] and Ungar *et al*. [5, 6] can be introduced in the FOX pattern calculation. Arbitrary modifications can be applied also to intensities and positions of the diffraction peaks. By using the build-in LSQ algorithm the extended FOX can be used as a Rietveld-like program for microstructure analysis.

At present time, materials with nano-size grains are interesting. For instance, the catalytic properties of TiO_2 powders are connected not only to its crystal form (lattice symmetry) but also with the grain size (surface fraction). A strong peak overlap is the main complication in the analysis of nanocrystalline powders. Simultaneous fitting of the whole powder pattern, with crystallographic restrictions applied on peaks positions and intensities, is usually a very good solution how to overcome this problem. The same is true for extremely deformed metals (Cu). The type and the amount of present defects determine mechanical properties of such materials. Physically relevant models can be used for description of the defects induced broadening in these materials.

Nanocrystalline thin films represent the second class of interesting materials here. Presence of texture or stress is rather typical than exceptional for these materials. Therefore, the choice of correct texture or stress model makes another problem for Rietveld type analysis. Furthermore, application of such models to data from various experimental geometries could be non-trivial. It is surprising that with the exception of Maud [7], none of the several existing Rietveld programs, which are widely used for diffraction data refinement, is adapted for microstructure analysis of layered samples nor non-conventional scans (2).

Implemented extensions

For the purpose of the profile analysis an object encapsulating the general interface for convolution of various broadening effects described in real or reciprocal space was created. In particular, phenomenological asymmetrical pseudo-Voigt function, size-broadening model of spherical crystallites with lognormaly distributed diameter [3] and dislocation broadening effect [3] were implemented into the library.

Absorption in the layered structures was introduced by using simple absorption model accounting for absorption in the layer of finite thickness and absorption in the upper-laying part of the sample. Sample layers are characterised by their absorption coefficient, thickness and position in the sample.

In order to handle texture, an object for the numerical calculation of the projection of an arbitrary orientation distribution function (ODF) in any direction was created [8]. Unfortunately, the ODF function is only an internally build-in function now but there are no restrictions on this function and almost any particular model can be implemented and its parameters can be refined.

Program is using the LSQ algorithm from the original FOX and it can be used for analysis of powder diffraction data measured in both the Bragg-Brentano and the parallel beam geometry.

Experiment

Performance of developed FOX extensions is demonstrated on three types of samples. TiO_2 anatase nanopowders and strongly deformed Cu samples were measured in the focusing symmetrical Bragg-Brentano geometry. For TiO_2 thin films samples the parallel beam geometry with a mirror in the primary beam was used. Resolution in this geometry is about three times worse than in the Bragg-Brentano arrangement but the intensity enhancement and better signal to background ratio is the great advantage. Polycapillary optics was used for pole figure measurements of TiO_2 films. Analysed TiO_2 films prepared by magnetron sputtering reveal texture, which can not be

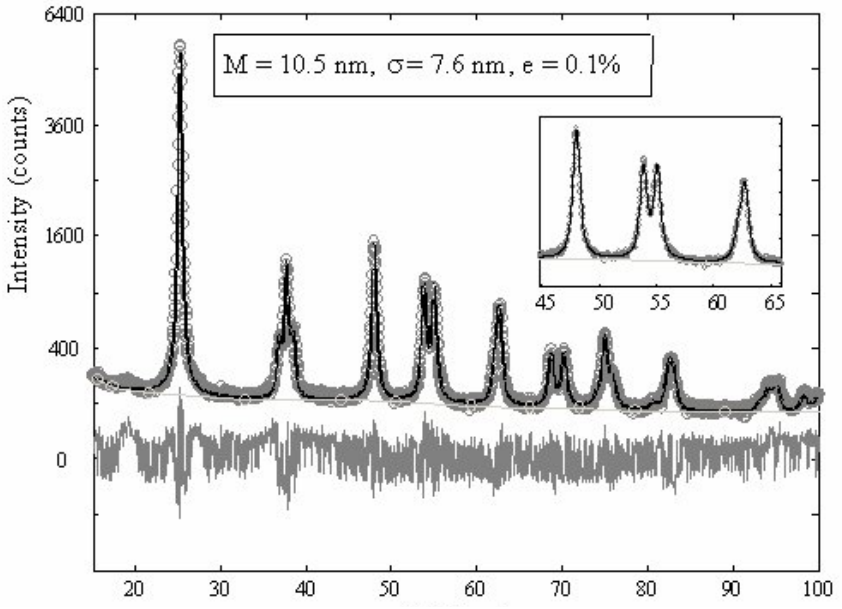

Figure 1. Result of the FOX LSQ-refinement of the small-crystalline powder sample of TiO_2 prepared by the sol-gel technique – BB geometry, WPPFitting approach, diffraction intensities constrained by the crystal structure, the crystal structure model not refined. *M* is the medain of grain size distribution, is the mean-square deviation, *e* is microstrain.

generally simply interpreted. Due to the strong overlap of very broad anatase peaks, only two reflections can be measured independently. Laboratory Cu-K radiation was used in all cases.

Application of the program on several problems

TiO_2 anatase powder sample (Fig.1) measured in the Brag-Brentano geometry is the simplest example of the program application for microstructure analysis. It was possible to refine all relevant parameters including isotropic temperature factors and both parameters of the log-normal distribution of crystallites (the median of the crystallites diameter distribution *M* and the square root of the distribution variance). There is no physically relevant model for microstrain broadening in the anatase structure. Hence the pseudo-Voigt function was used to describe defect induced part of the broadening effect. Only one of the Caglioti coefficients was set non-zero (U), so FWHM (in the reciprocal space units) was linearly proportional to the length of the diffraction vector. It was also possible to refine the shape parameter of the pseudo-Voigt function to find out if the deformation broadening has more Gaussian or Lorentzian character, respectively. However, the deformation broadening had minor effect in this case. Size and microstrain effects were convoluted with another pseudo-Voigt function describing instrumental resolution determined from the measurement of LaB_6 standard with the same experimental arrangement. In this point, the method is similar to the whole powder modelling approach [3] with one exception that the diffracted intensities are

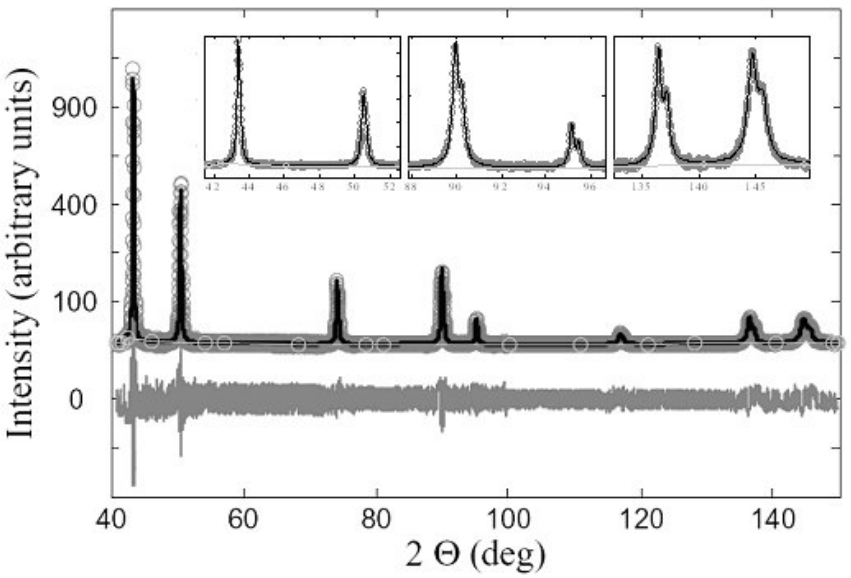

Figure 2. Result of the FOX LSQ-refinement of the deformed Cu sample – BB geometry, phenomenological approach – (hkl) specific broadening, intensities as free params. not constrained by the crystal structure model.

fixed by the crystal structure. It was not necessary to apply any texture correction.

In the second example the program ability to fit strongly anisotropic line broadening is demonstrated on the sample of deformed Cu (Fig. 2). This problem can be solved using physically relevant dislocation broadening model [3, 4, 5] or one can start a preliminary analysis with a phenomenological model. One of the program extensions enables to add an additional broadening described by the pseudo-Voigt function to the arbitrary selected peaks. The width and shape of this function can be refined. Moreover, it is possible to add refinable peak position correction. In this way, the diffraction pattern can be fitted at the beginning without proper knowledge of the microstructure model. Obtained peak position corrections can be used e.g. for stress analysis and the physical profile widths for the Williamson-Hall plot. In cases of complicated texture or if the texture is not of main interest it is possible to treat intensities of selected/all peaks as free independent refinable parameters (the so called "Arbitrary texture" in Maud [7]).

As the last example, results for sputtered TiO_2 thin films (thickness ~ 2 m) are shown (Fig. 3). The samples were nanocrystalline (10–100 nm). Small crystallites together with the strong microstrain broadening cause large peak overlap. As the deposition process was not cyllindrically symmetric, it introduced non-fibre texture (see below). Analysis of such samples is more complicated than in the previous examples. For profile modelling, the same approach as in the first case of TiO_2 powders was used. Unfortunately, it was not possible to refine properly the shape/width of crystallite size distribution. Although it is possible to measure pole figures for two diffractions and get some idea of preferred orientation, no appropriate model describing peak intensities was found and peak intensities had to be refined as free independent model parameters. This way may be quite reasonable (Fig. 4). Diffraction line width and shape are continuous slowly varying functions of the diffraction angle (broadening anisotropy is neglected). In quite a good approximation all the diffractions in the picture could be considered as they would have the same width. Their positions are determined by the crystal structure. With all these constrains on peak position and shape, the peak intensities of five diffractions

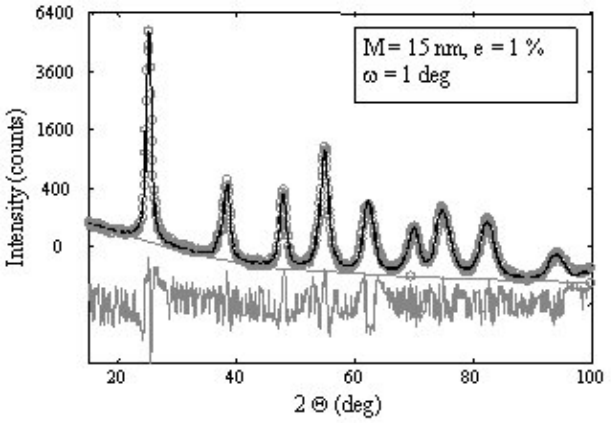

Figure 3. Result of the FOX LSQ-refinement of a TiO2 film – PB geometry, WPPFitting, intensities were free refineable parameters.

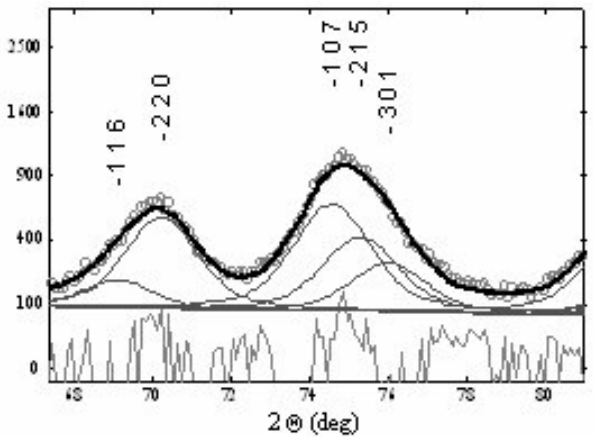

Figure 4. Thin film TiO2 sample – peak intensities are free params., peaks positions, width and shape are determined by the model.

in Fig. 4 are the only free parameters that have to be determined by the LSQ-fitting. This problem has in many cases (the diffractions are not to much close together) unique solution. Program contains an object that is able to calculate projection of the ODF function in any direction. This opens the possibility of pole figure simulation. Pole figures were measured only for selected samples. For the chosen sample, the texture can have simple interpretation of preferred orientation of crystallites with (100) planes almost parallel to the surface and normal to the (001) crystallite plane parallel with one side of the sample (Fig. 5 – measured, Fig. 6 – simulated).

Conclusions

The fitting of the whole powder diffraction pattern can be often cumbersome technique because the knowledge of correct microstructural model is necessary. On the other hand, constraints induced by the model can help to overcome some difficulties such as strong peak overlap in the case of lower-symmetry nanopowders. In addition to this, a possibility for breaking crystallographic restrictions were implemented as well in order to allow the user to achieve a good fit without too high demands on the specificity of the chosen/starting model.

The program FOX was extended in such a way, that it is suitable for analysis of microstructure of materials. In next step, a graphical user interface should be written and more effort is also necessary to find an appropriate model/approach for texture correction of investigated TiO_2 samples. All the presented problems can be in some way solved by using of already existing programs (Pm2k, Maud, FullProf). However, the usage of existing crystallographic computing libraries ([2], [9], [10]) has often advantages. In the present case, for example the implementation of a general algorithm for generation of symmetrically equivalent diffractions (from [2] and [9]) was also utilized for pole figure simulation.

The LSQ-algorithm was used for the microstructure refinement from powder diffraction data because it is a well-established and tested way in all the Rietveld programs. ObjCryst++ library contains also global optimization algorithms based on the Monte-Carlo methods used by the original FOX program, but these algorithms are not

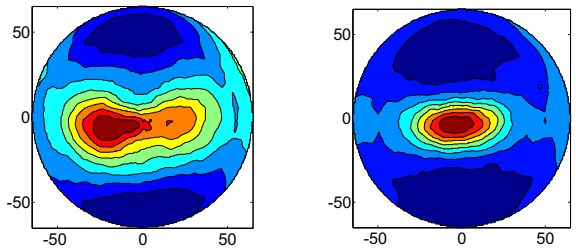

Figure 5. TiO_2 thin film sample: measured pole figures of (101) diffraction (left) and (200) diffraction (right).

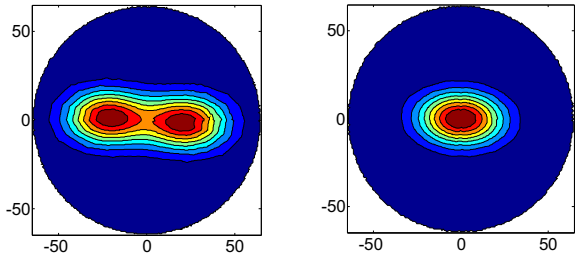

Figure 6. TiO2 thin film sample: simulated pole figures of (101) diffraction (left) and (200) diffraction (right).

generally suitable for fast optimization of small deviations of a choosen mirostructure model and other parameters (instrumental, lattice parameters). However the global optimization algorithms could be applied in the cases when the LSQ-algorithm fails: such as the global search of a correct texture model or determination of some special parameters as e. g. free refinable symmetry non-constrained intensities of almost overlapping diffractions.

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References

1. V. Favre-Nicolin, R. Černý, *J. Appl. Cryst*., **35** (2002) 734-743.
2. V. Favre-Nicolin: http://objcryst.sourceforge.net/Fox.
3. P. Scardi, M. Leoni, *Acta Cryst.,* **A58** (2002) 190-200.
4. R. Kuzel, P. Klimanek, *J. Appl. Cryst*., **22** (1989) 229-307.
5. T. Ungar, J. Gubicza, G. Ribarik, A. Borbely, *J. Appl. Cryst*., **34** (2001) 669-676.
6. A. Borbely, J. Dragomir-Cernatescu, G. Ribarik, T. Ungar, *J. Appl. Cryst*., **36** (2003) 160-162.
7. L. Lutterotti: http://www.ing.unitn.it/~maud/.
8. H. J. Bunge: Texture Analysis in *Defect and Microstructure Analysis*, Oxford Uni. Press 1999.
9. R. W. Grosse-Kunstleve, N.K.Sauter, N.W.Moriarty, P.D.Adams, *J. Appl. Cryst*., **35** (2002) 126-136.
10. J. Rodriguez-Carvajal, J. Gonzalez-Platas (CrysFML): http://www.ill.fr/dif/Soft/fp/.