Courses

MSTRUCT COURSE

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Outline

MStruct is a free computer program for *M*icro-*Struct*ure analysis from powder diffraction data. Purpose of this course is a presentation of current possibilities of the *MStruct* program and a practical demonstration of the program for solution of few problems concerning microstructure analysis by X-ray powder diffraction.

In the first part a short introduction about the program is given. In the second part a solution of few problems using the program is demonstrated:

1) residual stress evaluation in thin TiO_2 anatase films,
2) evaluation of crystallites size distribution in anatase bulk nanopowders,
3) dislocation density determination in an ECAPed Copper sample,
4) complex analysis of TiO_2 anatase-rutile films on ITO glass substrates.

A short insight into the proposed problems 1) – 4) is given in the text. Which particular problems will be presented during the course depends on interest of possible participants.

About the computer program – introduction

MStruct is a free computer program for MicroStructure analysis from powder diffraction data.

- It is practically a typical Rietveld program like many others famous programs: *FullProf* — Rodriguez-Carvajal; *GSAS* —Larson&VonDreele&Toby; *TOPAS* — Kern, *MAUD* — Lutterotti; *BRASS* — Birkenstock; *Jana* — Petříček; etc.
- It includes physically relevant models for peak broadening and shifts like *PM2k* — Leoni&Scardi and *CMWP-fit* — Ribárik&Ungár.
- It accounts for simple residual stress models, thin film absorption correction and asymmetrical diffraction geometry like *MAUD* — Lutterotti.
- *MStruct* program utilizes free GPL projects for Crystallography:
- ObjCryst-FOX — *Free Objects for Crystallography* — Vincent Favre-Nicolin & Radovan Černý
- cctbx — *Computational Crystallography Toolbox* — Grosse-Kunstleve et al.

The program is based on these GPL projects, extending them by routines for microstructure effects modelling. *MStruct* is available for free under the GPL license here: http://xray.cz/mstruct/.

Program still has *no GUI*. Hence it relies on editing input text files in an advanced text editor (Fig. 1) and on using some external plotting utility like gnuplot (Fig. 2) or commercial *MATLAB*.

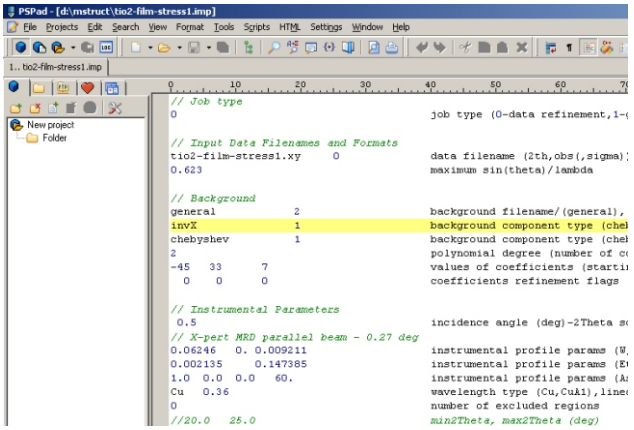

Figure 1. Editing of an input parameter file for *MStruct* in a PSPad freeware code editor with syntax highlighting enabled

Solution of selected problems – practical examples

Tutorial no. 1: Residual stress evaluation in thin TiO_2 anatase films

In this example a powder pattern of TiO_2 anatase thin film on a silicon substrate is analysed. The X-ray pattern was measured as a wide range 2Theta scan in the parallel beam (PB) geometry with low constant incidence angle *Omega* = 0.5°. Additional X-ray residual stress measurements done using an Eulerian cradle and classical $\sin^2$ method showed a presence of residual stress in the films. The aim of this tutorial is an evaluation of a stress value in the film from the single 2Theta scan. A simple stress state is assumed in the film. It is described by an absolute *stress* value and Reuss-Voigt grain interaction *model weight*. An appropriate section has to be inserted into a *MStruct* input parameter file to add an effect (Fig. 3).

In the PB setup used possible *sample displacement* is small – less than few microns – and it has no effect on diffraction lines positions. 2Theta *Zero* value accuracy should also be better than 0.01°. The strongest effect on diffraction lines positions has a *refraction effect* of incidence x-rays on the surface of the film. It causes 2Theta independent diffraction lines shift which is equivalent to the *Zero* shift error for a given material layer and it varies with the incidence angle *Omega*. The program can correct for this effect (Fig. 4). The refinable parameter involved is a relative *film density* n_r which is rather kept constant during refinement on the value determined from reflectivity measurement of an angle of total external reflection of X-rays $_c^{meas}$ and value calculated for the particular film material $_c^{calc}$:

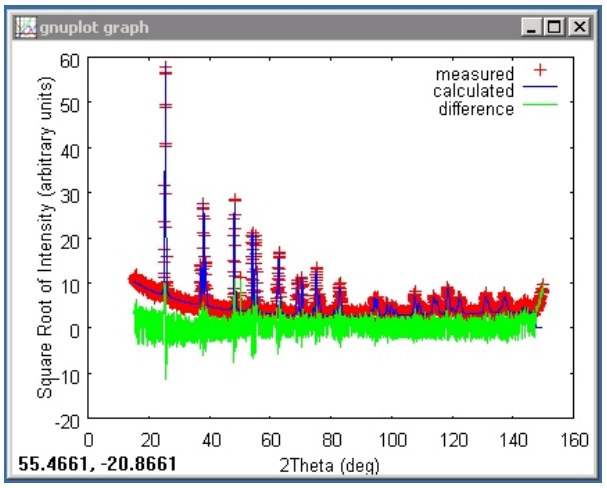

Figure 2. Plotting *MStruct* fitting results using free gnuplot program.

$$n_r \quad \left(\frac{c^{meas}}{c^{calc}} \right)^2 \qquad (1)$$

Beside described residual stress and refraction correction effect this example shows also basic manipulation with line broadening effects, absorption effect and arbitrary texture model. Detailed description can be found on the web: [1] http://xray.cz/mstruct/. Models involved are described in detail in [2-3].

Tutorial no. 2: Evaluation of crystallites size distribution in anatase bulk nanopowders

In this example a nanocrystalline TiO_2 anatase bulk powder prepared by hydrolysis of titanium isopropoxide in solution of hydrogen peroxide is analysed. The sample was measured using a conventional Bragg-Brentano setup. The aim of the example is an analysis of the crystallites size distribution accounting properly for instrumental broadening and possible influence of crystal defects. The analysis is a typical example of the whole powder pattern fitting/modelling method established in [4].

Instrumental resolution is taken from a measurement of LaB_6 standard in the same setup. Line broadening connected with a presence of crystal defects is described by a phenomenological pseudo-Voigt function. Parameters involved are a microdeformation *e*(%) and a parameter determining Gaussian-Lorentzian character of a microstrain part of the diffraction profile. It is assumed in agreement with SEM images that crystallites have spherical shapes. If no sophisticated technique is utilized produced crystallites are usually polydisperse and hence it is appropriate to include some description of grain size distribution into the model. Crystallites size distribution of ceramic particles can usually be well described by the log-normal distribution. This is the first choice used in the example. Refined size distributions for powders prepared from a same metal precursor and calcinated at different temperatures are shown in Fig. 5. The second choice tested is a model [5] using a histogram representation of crystallites size distribution. An example of the refined distribution is depicted in Fig. 6. (The histogram model in *MStruct* is still under development. However, some results can be tested.). The appropriate sections for the above models in a *MStruct* parameter file are depicted in Fig. 7.

```
// the 1st phase - Residual stress reflection position correction - simple stress model
StressSimple   stressCorrAnatase        effect type,effect name,comp=4
Reuss-Voigt     0.                      XECs model, stress (GPa)
// material C11 C12 C13 C33 C44 C66 constants (in GPa) - in the format: C11 value C12 value etc.
C11 320  C12 151  C13 143               // anatase Cij (GPa)
C33 190  C44  54  C66  60               // ref: M.Iuga,Eur.Phys.J.B(2007)58,127-133
0.3                                     model weight (0..Reuss,1..Voigt)
```

Figure 3. Residual stress effect section for anatase phase in an input parameters file.

```
// the 1st phase - Refraction reflection position correction
RefractionCorr   refractionCorrAnatase  effect type,effect name,comp=3
crystal                                 chi0 set directly-value,calculated from-crystal,calculated form chem
1.                                      relative density
```

```
MStruct::RefractionPositionCorr::GetChi0(...): Chi0 and absolute density computed for Crystal: Anatase
        chi0: (-2.3988e-005,-1.2128e-006) (n=1-delata-ii*beta~=1+chi0/2)
        critical angle: 0.28 (deg)
        density:  3.891  (g/cm3)
```

Figure 4. Top: Refraction correction section for anatase phase in an input parameters file. Crystal structure is used to account for the effect. Bottom: Part of a program output showing calculated values of an absolute density and an angle of total external refraction for anatase

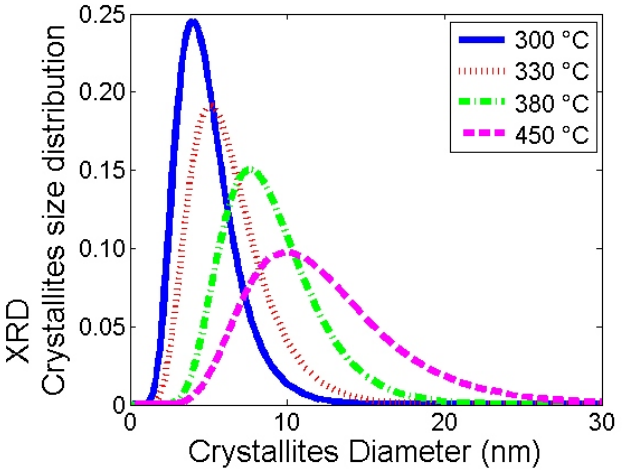

Figure 5. Crystallites size distribution of anatase nanopowders prepared from a same precursor and calcinated at different temper-

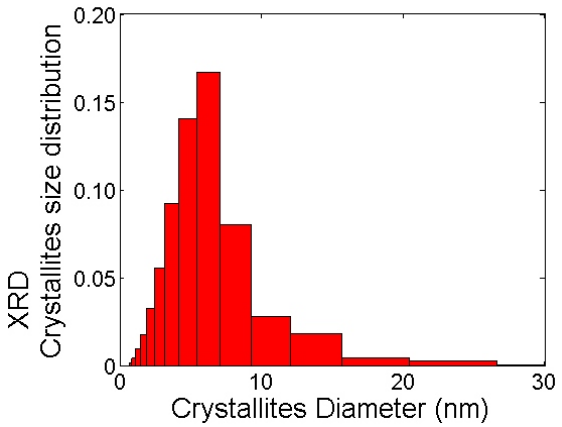

Figure 6. Crystallites size distribution represented by histogram.

```
// the 1st phase - Size broadening - lognormal distribution of crystals diameter (median - M, shape - Sigma)
SizeLn          sizeProfAnatase          broadening component type (pVoigt(A),SizeLn,dislocSLvB,HKLpVoigtA),effect name
5.0     0.3                              M(nm),sigma

// the 1st phase - Size broadening - refinable Size Distribution model
SizeDistrib       sProfA               broadening component type (pVoigt(A),SizeLn,SizeDistrib,dislocSLvB,HKLpVoigtA),effect name
create          1.e2                   distribution type/source (file/create), LSQ constraint scale factor
log   0.5   100.    20                 histogram spacing type (linear/log/sqrt), Dmin(nm), Dmax(nm), nb. of intervals
deriv           1.e+6                  LSQ regularization method type (none/derivative/curvature) LSQ weight factor
```

Figure 7. Sections in input parameters files for a size broadening models for anatase crystalline phase. Top: Log-normal size distribution. Bottom: Histogram representation.

Tutorial no. 3: Dislocation density determination in an ECAPed Copper sample

In this example a Copper sample treated by ECAP is analysed. The sample was measured in the conventional Brag-Brentano setup with variable slits and PSD detector to enhance data statistics of high angle reflections. In metal samples treated by ECAP a high amount of defects is generated. Diffraction line broadening is usually induced mainly by presence of dislocations, by small size of coherently diffracting domains and by twin faults. The whole powder pattern modelling [4, 6] is a method which can estimate e.g. dislocation density values in such materials. In this example a simple model describing [4, 6,7] these effects will be used to determine coherently diffracting domains size, twinning probability, edge-screw character of dislocations, dislocations density and Wilkens characteristic parameter of their arrangement. An appropriate part describing the effects is depicted in Fig. 8 and a typical pattern fit is shown in Fig. 9.

Tutorial no. 4: Complex analysis of TiO_2 anatase-rutile films on ITO glass substrates

In this example a sol-gel TiO_2 film on ITO glass substrate is studied. Film has thickness of about 200 nm and it was measured in parallel beam (PB) geometry with low incidence angle. Electron density of ITO is higher than el. density of TiO_2. This helps to suppress ITO signal in PB setup. The film was calcinated at a relatively high temperature and it contains both anatase and rutile. The aim of this study is to roughly estimate crystallite size and relative anatase and rutile fractions. This tutorial employs refraction and stress corrections described in tutorial no. 1, peak broadening corrections used in tutorial no. 2 and if scale factors and absorption correction are further examined also some information about film thickness can be deduced from diffraction experiments.

References

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2. Z. Matěj, L. Nichtová, R. Kužel, *Mater. Struct. Chem., Biol., Phys. Technol.,* http://xray.cz/ms, **15** (1), (2008), 46.
3. Z. Matěj, R. Kužel, L. Nichtová, *Powder Diffr.*, **25** (2), (2010), in press [DOI: 10.1154/1.3392371].
4. P. Scardi, M. Leoni, *Acta Crystallogr.*, **A58**, (2002), 190.
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6. G. Ribárik, T. Ungár, J. Gubicza, *J. Appl. Crystallogr.*, **34**, (2001), 669.
7. L. Velterop, R. Delhez, Th. H. de Keijser, E. J. Mittemeijer, D. Reefman, *J. Appl. Crystallogr.*, **33**, (2000), 296.

```
// the 1st phase - Dislocation Strain broadening (Scardi&Leoni&van Berkum)
dislocSLvB+          strainProfCu       broadening component type (pVoigt(A),SizeLn,dislocSLvB,HKLpVoigtA),effect name
   1       1                           use MWilk instead of Re (0-No,1-Yes), use full Wilkens formula (0-No,1-Yes)
 1.0       0.002                       MWilk,rou(1/nm^2)
0.30     -2.1    0.                    Cg0,q1,q2


// the 1st phase - Stacking Faults - Warren, Velterop2000, Scardi, Leoni
faultsVfcc           faultsProfCu     broadening component type (pVoigt(A),SizeLn,dislocSLvB,HKLpVoigtA,faultsVfcc),effect name
0.0     0.00                         alpha, beta(twins)
```

Figure 8. Sections in input parameters files for broadening effects connected with defects in ECAP Copper. Top: Dislocation broadening – Wilkens model – Scardi&Leoni&vanBerkum function [4]. Bottom: Faulting defects in fcc materials – Waren&Velterop model [7].

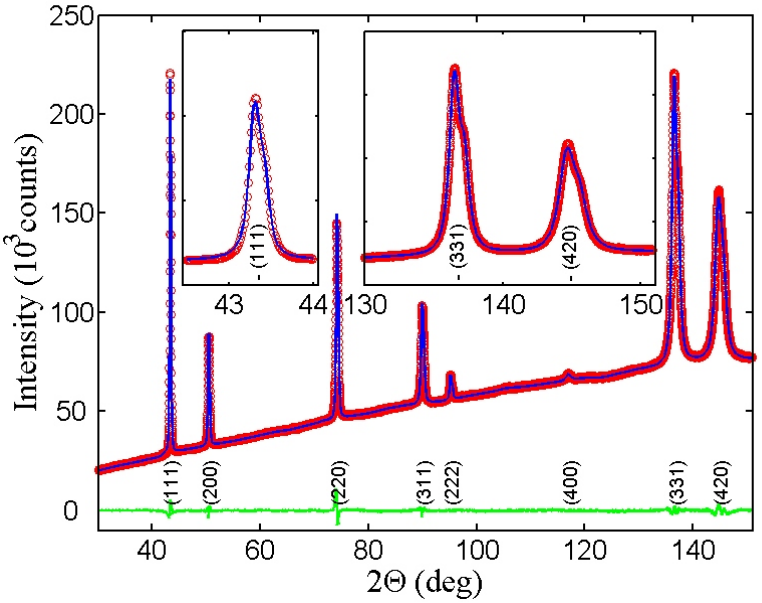

Figure 9. Powder pattern fit of an ECAPed (1 pass) Copper.

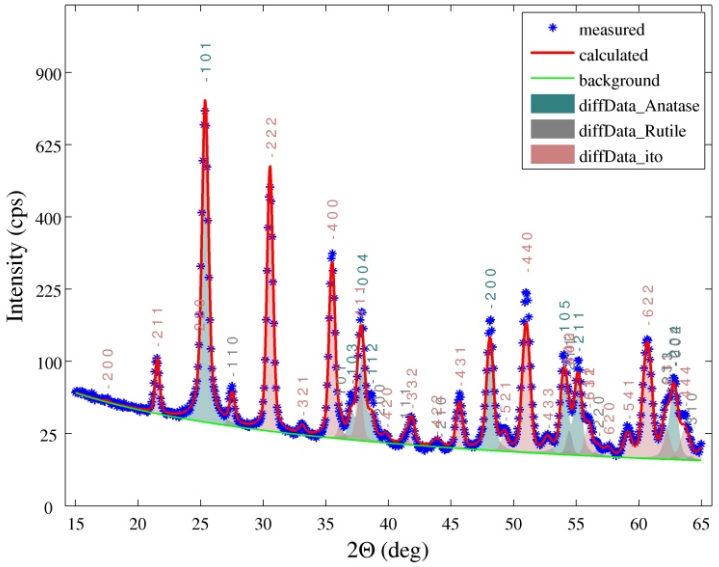

Figure 10. Powder pattern fit of a TiO_2 sol-gel film on an ITO glass substrate.

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