Modeling of diffraction patterns based on microstructural properties

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Contents

1 Introduction

Most of the physical properties of crystalline materials are fundamentally determined by the microstructure. Electron microscopy is one of the most straightforward methods for the characterization of microstructures, since we get a visual picture of the different components and types of lattice features. The most important fundamental microstructural properties are the type, density and distribution of crystal defects and the grain or crystallite structure. X-ray line profile analysis (XLPA) is one of the most important and powerful alternative methods besides electron microscopy for the characterization of microstructures. This method gives information about the following basic microstructural properties: (i) the size and distribution of crystallites, (ii) the shape anisotropy of crystallites, (iii) the density, character and distribution of dislocations and (iv) the density and type of stacking faults and twin boundaries. Since electron microscopy and XLPA are two fundamentally different methods it is evident that they give different kind of information about the various aspects of the microstructure. One of these differences is that while the micrographs provided by electron microscopy give information about domains of about a micrometer or even smaller in diameter, the method of XLPA gives information about considerably larger volumes with diameters of mm or even larger. It should be noted, however, that at the same time, by using the method of microdiffraction the size of the investigated domain can be diminished down to the magnitude of micrometers.

The goal of the dissertation is double. On the one hand, new methods of XLPA are developed, which are based on the modelling of the physical properties of the different crystal defects. By comparing the so obtained model based line profiles with the measured ones the methods give the microstructural parameters of the investigated materials. On the other hand, by applying these methods the microstructural properties of several different materials or groups of materials are determined and these properties are examined as a function of several mechanical or thermal treatments.

2   Applied methods

In accordance with the goals of the dissertation, the applied methods require (a) theoretical considerations, (b) the application of modern and efficient numerical methods and (c) the usage of high resolution laboratory and synchrotron X-ray measurements. During the theoretical work, according to the literature, the previously used microstructural models have been explored. The applicability of these models in XLPA has been examined [S4, S6, S14]. By revealing the deficiencies of the previous models, the theory has been further elaborated, especially if it was necessary [S4, S5, S6, S8, S17].

The efficiency of the numerical methods depends basically on the application of as fast as possible numerical algorithms. For this reason the theoretical models have been further developed, e.g. the Fourier transform of the size profile has been determined. The nonlinear least squares algorithm has fundamental significance for the extraction of microstructural parameters from the experimental measurements. For this purpose, the nonlinear Marquardt-Levenberg algorithm of the freely available `gnuplot` program package has been used [S4, S6, S14]. By using high resolution laboratory and synchrotron measurements and applying the newly developed methods, the crystallite size and size distribution and the several parameters of the dislocation structure have been determined for several different materials or groups of materials. These parameters have been correlated with other physical properties of the investigated materials [S1–S22].

3   New scientific results

1. I have determined the size profile [S1] and the size Fourier transform of coherently scattering domains with spherical or ellipsoidal crystallite shape and lognormal size distribution [S4, S5, S6, S8]. The expression of the Fourier transform supports the fast numerical evaluation.

2. I elaborated the method for applying the strain profile for XLPA based on the Wilkens model of dislocations and the model of average contrast factors [S4, S6, S14].

3. I developed two new methods by using the theoretical size and strain profiles for the extraction of microstructural parameters from X-ray measurements:

   3a. by fitting simultaneously the whole Fourier transforms or intensity profiles obtained by separation and instrumental deconvolution, (the method Multiple Whole Profile Fitting: MWP) [S4, S6], and

   3b. by the convolutional fitting (with the inclusion of the instrumental effect) of the whole diffraction spectrum, (the method of Convolutional Multiple Whole Profile Fitting: CMWP) [S14].

4. I worked out a software package for the methods described in 3. which is publicly available [S4, S6, S14] through the web: `http://www.renyi.hu/mwp` and `http://www.renyi.hu/cmwp`.

5. By using the MWP method I have shown that:

   5a. the dislocation density has the average value of $10^{16}m^{-2}$ in severely deformed Ti, which is in accordance with electron microscopy investigations; and in this deformation stage mainly the slip systems <a> and <c+a> are activated [S11, S12, S22],

   5b. by applying ball milling and heat treatment of PbS (galena) samples, a systematic set of samples has been produced and by evaluating the X-ray line profiles of these samples using the MWP method a map of microstrucure has been obtained. By comparing the microstrucural parameters of samples from ancient cosmetics fabricated in the Egyptian Kingdom 3500 b.c. with the parameters of the systematically prepared samples I have shown that only gentle crushing and no heat treatment or heat treatment at a temperature of less than 300 ^{o}C was applied [S9] for the fabrication of the archaelogical cosmetics.

6. By using the CMWP method I have shown that:

   6a. in ball milled Al-Mg alloys the dislocation density as well as the average crystallite size shows a saturation after 2h of ball milling and the

results obtained by the MWP and CMWP methods have been compared [S13, S16, S14],

6b. in ball milled fluorides (MF_2, M=Ca,Ba,Cd,Sr) the presence of an X-ray optical interference effect can be observed which is present primarily if the average crystallite size of a larger portion of crystallites is about 5-10 nm or smaller [S17]. The X-ray optical interference effect means that the first few reflection profiles becomes narrower than what would correspond to the domain size.

7. I have shown that if the method of XLPA is carried out correctly, which means that the experiments are done with a high enough angular resolution and that the evaluation is based on correct microstructural models, then good correlation is observed between TEM and XLPA parameters. For example, in the case of nanocrystalline Si_3N_4 particles the size distribution determined either by TEM or XLPA are in excellent agreement, cf. [S1]. In a large number of cases very good correlation was found between the microstructural parameters, especially the subgrain size, and size distribution, the dislocation density and dislocation types determined either by TEM or XLPA [S1–S22].

4   Conclusions

As the results of my work, a coherent set of methods has been developed which is suitable for the characterization of the microstructure of most different crystalline materials, e.g. metals, alloys, ceramic materials, minerals or polimers, in terms of the size and size distribution of crystallites or grains, the density, the distribution and character of dislocations and the density and type of planar defects.

Own Publications

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