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Microstructure of Crystalline Materials Determined by Whole Powder Pattern X-ray Line Profile Analysis

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Powder diffraction patterns consisting of broadened line profiles are used to evaluate microstructure parameters. The microstructure is modelled in terms of crystallite size and microstrain, where microstrain is assumed to be caused by dislocations, triple junctions corresponding to sinter stresses, and to some extent, by planar defects, especially stacking faults and twin boundaries. Crystallite size needs special interpretation, in the case of ceramic powders it is often identical to the particle or grain size, whereas in the case of bulk materials, especially bulk metals or alloys it is equal to the subgrain size. Electron microscopy strongly facilitates the appropriate interpretation of X-ray crystallite size. The diffraction patterns are evaluated by the method of convolutional multiple whole profile (CMWP) fitting procedure [1,2]. In this procedure strain and size is modelled by dislocations and spherical or ellipsoidal crystallites with log-normal size distributions, respectively. The model generated and the measured diffraction patterns are compared by a nonlinear least squares method, in a similar way as in the whole powder pattern modelling (WPPM) method [3]. The effect of stacking faults and twins on X-ray diffraction patterns has been calculated numerically by using the DIFFaX [4] software for the first 15 Bragg reflections in *fcc* crystals up to 20 % fault densities [5]. It is found that the Bragg reflections consist of 5 types of sub-reflections which are of Lorentzian type. About 15.000 sub-reflections are evaluated and parametrized according to their FWHM and positions relative to the exact Bragg angles. These parameter files are incorporated into the CMWP software for evaluating planar faults together with dislocations and crystallite and/or sub-grain size distributions [5]. In nanocrystalline Cu and Cu-Zn alloys it has been found that twinning becomes a substantial mode of deformation when the grain size is smaller than about 40 and 60 nm, respectively. An unusual behaviour of line broadening in ball milled fluorides has been observed [6]. About twenty diffraction patterns corresponding to different ball milled states of the CaF_2, SrF_2, BaF_2 and CdF_2 fluorides have been analysed in terms of dislocation densities and types, and crystallite size and size distributions by X-ray line profile analysis [6]. The diffraction patterns have been evaluated by the method of convolutional multiple whole profile (CMWP) fitting procedure [2,3]. In about 10 of the 20 patterns the calculated and measured diffraction patterns are in perfect agreement throughout the entire angular range of measurement. However, in the cases of the rest of the patterns the first few measured line profiles appear to be narrower than the calculated profiles based on the model. Nevertheless, also in these latter cases the measured and calculated patterns are in perfect agreement for the higher angular parts of the patterns consisting of 10 to 13 profiles. In the cases where this discrepancy is present, it is interpreted as an X-ray optical interference effect [6] similar to what has been observed by Rafaja et al. [7] in nanocrystalline thin layers. The interference effect has been corrected successfully, either by (i) excluding the affected profiles from the evaluation procedure or by (ii) assuming a diffraction angle dependent apparent bimodal size distribution of crystallites [6].

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Whole Powder Pattern Methods for Nanoparticles characterization

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Due to the specific and tunable size-related properties of Nanoparticles (NPs) and their great technological potentiality, the engineering of nanophase materials has been growing very rapidly in the last decades. Controlling some basic features of NPs, such as well characterized crystalline domains and narrow size/shape distributions, revealed to be a key point for any efficient application and to understand the size reduction effects. In this respect, a combination of different characterization techniques is often required, due to the complexity of the systems under investigation. Among them, modern powder diffraction data analysis methods, so efficient when applied to the even complex task of the structural and microstructural characterization of samples at the micrometre scale, can fail when the particle size reduces to few nanometres. Bragg peaks may be so broadened to be hardly separated; atoms on the surface may play the major role in very small NPs, producing important strain contributions and size-related lattice paramaters [1]; strain fields and size-related effects cannot be easily separated and affect both peak position and width. In the most complex case of some noble metals, non-crystallographic crystal structures can occur. Due to these special features, specifically tuned methods of analysis are needed to extract relevant information like size, strain and structure concentrations from powder diffraction data.
Our work has been specifically addressed to assess potentiality and limits of whole powder pattern fitting techniques to this task. For very small NPs, the Debye function is the correct approach to calculate the diffracted intensity; for larger particles (> 10 nm) a shape-based approach is possible and advisable to save computing time. According to these approaches, Whole Powder Pattern Fitting methods will be presented to deal with data of randomly oriented nanocrystals [2,3]. Applications will be shown for both cases.

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