

# Preface

Crystalline materials are never ideal, perfectly ordered single crystals; rather, they contain lattice defects such as grain boundaries, planar faults, dislocations, disclination, vacancies, and interstitial atoms. The deviation from the perfect single crystalline state is referred to as microstructure of materials. The microstructure is a main factor in determining the physical, chemical, and mechanical properties of materials; therefore, its investigation is unavoidable in materials research. The microstructure of crystalline materials can be investigated by direct methods such as Transmission Electron Microscopy (TEM) or by indirect techniques (e.g. by the analysis of the X-ray diffraction peak shape). Using the microscopy methods, a direct image of the microstructure can be observed; while in the peak shape analysis, only a fingerprint of the microstructure—a diffraction pattern—is obtained, and then the parameters of the defect structure are extracted from the breadth and the shape of the diffraction peak profiles.

X-ray diffraction peak profiles broaden mainly due to the (1) small crystallite size, (2) dislocations, (3) planar defects (e.g. stacking faults and twin boundaries), (4) chemical heterogeneities, and/or (5) surface relaxation in the case of nanoparticles. Some of these effects also cause peak displacement from its ideal position. The procedure of the evaluation of the peak profiles for the microstructure is referred to as X-Ray Line (or Peak) Profile Analysis (XLPA). The term “line” refers to the lines detected on films in powder cameras in the early years of XLPA (in 1920s). These lines are segments of the Debye-Scherrer rings diffracted from powder samples. The scattered intensity distribution in the “line profile” was obtained by scanning the film with microphotometer (Langford, 2004). The phrases “peak profile,” “diffraction profile,” and “line profile” are used equivalently in the relevant literature.

The history of the method of XLPA started in 1918 when Paul Scherrer related the line breadth to the size of noble metal colloidal particles (Langford, 2004). The equation of Scherrer expresses the inverse proportionality between the crystallite size and the breadth of X-ray diffraction peak profiles (Scherrer, 1918). It should be emphasized that this first application of XLPA occurred only six years after the pioneering experiment of X-ray diffraction performed by Friedrich and Knipping.

The latter researchers detected the interference intensity spots scattered from a copper-sulphate single crystal placed in the path of X-rays. Their experiment was based on the calculation of Max von Laue who determined the conditions necessary for diffraction by X-rays.

In the 1920s, XLPAs were mainly restricted to the determination of the size and shape of diffracting crystallites. However, some observed experimental phenomena in XLPAs could not be interpreted in terms of the crystallite size and shape; therefore, the method was further developed by incorporating lattice defects into the evaluation. First, the effects of stacking faults in metals (e.g. in Co) and structural defects in ordered alloys (e.g. in Cu<sub>3</sub>Au) on line profiles were considered in the 1930s (Langford, 2004). The pioneers of this field include, but are not limited to, B. E. Warren, A. J. C. Wilson, and A. R. Stokes (Stokes & Wilson, 1944; Warren, 1959). In the 1940s, the evaluation of X-ray line profiles was improved by E. F. Bertaut, enabling the determination of the crystallite size distribution from the Fourier-transform of the diffraction peak intensity (Bertaut, 1950). Later, the works of J. I. Langford and D. Louer had imperishable merit in the deeper understanding of size-broadening of peak profiles (Louer, Auffredic, Langford, Ciosmak, & Niepce, 1983; Langford & Louer, 1996).

Between the 1960s and 1990s, several researchers (e.g. M. A. Krivoglaz, K. P. Ryaboshapka, M. Wilkens, T. Ungár, P. Klimanek, R. Kuzel, G. Groma, and A. Borbély) contributed to the development of XLPAs in order to determine the type, density, and arrangement of dislocations (Krivoglaz & Ryaboshapka, 1963; Krivoglaz, 1969; Wilkens, 1970; Groma, Ungár, & Wilkens, 1988; Kuzel & Klimanek, 1988; Ungár & Borbély, 1996). Dislocations are important lattice defects in crystalline materials as they play a unique role in plastic deformation, especially in metals and alloys. However, besides dislocations, other lattice defects, such as planar faults, also yield characteristic broadening of X-ray line profiles. Although the basic relationships between the line breadth and the planar fault probability were established in the 1950s (Warren, 1959), sophisticated methods for the evaluation of stacking fault and twin boundary probabilities from peak profiles were developed in the 2000s by E. Estevez-Rams, E. Velterop, L. Balogh, and their coworkers (Velterop, Delhez, de Keijser, Mittemeijer, & Reefman, 2000; Estevez-Rams, Leoni, Scardi, Aragon-Fernandez, & Fuess, 2003; Balogh, Ribárik, & Ungár, 2006; Balogh, Tichy, & Ungár, 2009). In addition to lattice defects, the variation of alloying element concentration in a solid solution or an intermetallic compound phase also results in microstrain-like broadening of diffraction peaks. The theory of the effect of chemical heterogeneities on line profiles was elaborated by A. Leineweber, E. Mittemeijer, and R. Delhez, and they have also proposed some procedures for the evaluation of composition distribution from diffraction peaks (Mittemeijer & Delhez, 1980; Leineweber & Mittemeijer, 2004; Leineweber, 2009). The microstrains caused by surface relaxation

in nanoparticles were introduced into the line profile evaluation by M. Leoni and P. Scardi (Leoni & Scardi, 2004).

In the 2000s, a revolution in XLPA started by elaborating sophisticated diffraction-pattern-fitting methods in which microstructure-based theoretical functions were fitted to the whole experimental diffractogram. An incomplete list of researchers who contributed to this field includes M. Leoni, G. Ribárik, and P. Scardi (Ribárik, Ungár, & Gubicza, 2001; Scardi & Leoni, 2002; Ribárik, 2009). This progress in XLPA was enabled by the increase of the power of computers in terms of memory capacity and calculation speed. Concurrently with the development of the methodology, the instruments (e.g. X-ray sources and detectors) used for the measurement of line profiles were also improved (Levine, Larson, Yang, Kassner, Tischler, Delos-Reyes, Fields, & Liu, 2006). Currently, the parameters of the microstructure in XLPA are usually determined by fitting theoretical functions on the measured peak profiles. These functions are calculated on the basis of a model of the microstructure. For the construction and control of realistic models, simultaneous direct investigations of the microstructure by Transmission Electron Microscopy (TEM) are suggested.

XLPA and TEM may be either alternative or complementary procedures in materials science. Comparing the two methods, the most important advantage of TEM is that the microstructure can be investigated directly, while a model of the microstructure is necessary to evaluate X-ray line profiles. Furthermore, the instrumental broadening in XLPA yields upper and lower detection limits for the crystallite size and the dislocation density, respectively. These limits are 200-800 nm for the crystallite size and  $10^{12}$ - $10^{13}$  m<sup>-2</sup> for the dislocation density, depending on the instrumental effects. At the same time, XLPA gives the parameters of the defect structure with a better statistics since X-ray diffraction usually examines  $10^3$ - $10^5$  larger sample volume than that studied by TEM. Additionally, XLPA is a non-destructive method with a much easier sample preparation process, as compared to TEM. Moreover, for materials containing very high densities of lattice defects (e.g. nanostructured materials), XLPA has no competitive methods in the determination of dislocation density in a reliable manner. High-Resolution TEM (HRTEM) can provide the local dislocation density even for its very large values, but with a much worse statistics compared to XLPA. Furthermore, the local dislocation density may strongly deviate from the value averaged for a larger volume. However, in most cases, the methods of XLPA and TEM are suggested to be used to as complementary procedures in the investigation of the microstructure of materials, as they provide different aspects of the microstructure. For instance, in severely deformed metals and alloys, the crystallite size obtained by XLPA corresponds rather to the subgrain size; therefore, its value is 2-10 times smaller than the grain size determined by TEM.

In the last decades, there is a growing demand for the application of XLPA in materials science. This can be explained by the recognition of the effectiveness of this

method in studying the defect structure in advanced materials. In the last decade of the second millennium, nanomaterials have become a focal point of materials science due to their unique physical, chemical, and mechanical properties that destine these materials to novel and promising applications. The small dimension of the grains or particles in nanomaterials and their specific processing methods affect their defect structure (vacancies, dislocations, planar defects, and grain boundaries) that has a significant influence on the properties of these materials. The knowledge of the relationships between the production methods, the lattice defects, and the physical properties of nanomaterials is very important not only in order to understand the specific phenomena occurring when the grain size is very small but also from the point of view of practical applications of these materials. XLPAs can be used effectively for the study of defect structure in nanomaterials since the high defect density and the small crystallite size in these materials yield large peak broadening, thereby increasing the reliability of the results obtained by this non-destructive method. The large interest in this topic is indicated by the two very successful international training courses on the theory and application of XLPAs, which were organized in Eötvös Loránd University, Hungary.

Although, instruments for measuring X-ray line profiles are available in the majority of research laboratories in either the industrial or the academic sector, the "know-how" for determining the microstructure parameters from X-ray diffraction line profiles is often missing. Therefore, this book aims to synthesize the knowledge of the theory, the methodology, and the application of XLPAs. The book is written with a very strong theoretical background; at the same time, it presents numerous examples for practical applications. Therefore, the book serves as a basic reference for materials scientists and also a practical guide for engineers. In the first section, the theory of diffraction line broadening caused by the finite crystallite size, the different lattice defects (e.g. dislocations and planar faults), and the chemical heterogeneities is presented. Then, the evaluation methods of line profiles are introduced on the basis of theoretical considerations. Several suggestions for the practical applications of the methods and instruments are also given. The capability and the limits of XLPAs in comparison with other methods are presented. The information in this book is organized and presented in the form that is hopefully beneficial for a wide audience: materials scientists, engineers, as well as lecturers and students at universities.

The book gives a comprehensive introduction to XLPAs and a coherent overview from the basics to the applications that is missing from the literature of this field. Using this book, the mechanical engineers and the materials scientists can learn how to apply the most sophisticated methods of XLPAs in the study of microstructures of materials. Therefore, this book may contribute to the development of novel materials and the better understanding of the correlation between their microstructures

and physical/chemical properties. This publication may improve the engineering and materials sciences, as well as all fields connected to materials (e.g. medicine). Additionally, this book is also useful for scholars and their students at universities; therefore, it may promote the education of the next generation of engineers and materials scientists.

## ORGANIZATION OF THE BOOK

The book is organized into nine chapters. In the following, a brief description of each chapter is given.

Chapter one reviews the basic concepts and equations of the kinematical X-ray scattering in order to better understand the theory of line profile analysis. The correlation between the crystal structure and the diffracted intensity distribution is shown. The concept of the reciprocal lattice is introduced, and the correspondence between the reciprocal lattice vectors and the lattice planes is also presented. The angles between the directions of the diffracted maxima and the incident beam are calculated from the wavelength of X-rays and the interplanar spacings using the Bragg's law. The Ewald construction is presented for the graphical representation of the condition for the diffraction intensity maxima.

In chapter two, the X-ray peak profile broadening caused by the finite size of scattering crystallites is studied in detail. It is shown that the Fourier transform of the line profile with indices  $hkl$  at a variable value  $L$  can be obtained as the volume of the common of the scattering crystallite and its "ghost" shifted by  $L$  perpendicular to planes ( $hkl$ ). Additionally, it is revealed that the  $hkl$  line profile is the same as the sum of the intensities scattered incoherently from the columns building up the crystallites normal to the ( $hkl$ ) reflecting planes (Bertaut's theorem). The effect of median and variance of crystallite size distribution on the shape of line profiles is also discussed. The line shapes for different crystallite size distribution functions (e.g. lognormal, Poisson, and York distributions) are given. It is shown that for spherical crystallites the peak broadening does not depend on the indices of reflections. The dependence of line profiles on the indices  $hkl$  is presented for various anisotropic shapes of crystallites (e.g. octahedron, cube, and tetrahedron).

In chapter three, the line shape caused by lattice distortions in a crystal is reviewed. It is revealed that the broadening of a diffraction peak with indices  $hkl$  is related to the mean-square-strain perpendicular to the reflecting ( $hkl$ ) lattice planes. The strain broadening of line profiles depends on the order of diffraction. The line profiles for a crystal in which the lattice distortions are caused by dislocations are described in detail. It is revealed that due to the anisotropic strain field of dislocations and the elastic anisotropy of crystals, the peak broadening of dislocations