Chapter 5
Influence of Chemical Heterogeneities on Line Profiles

ABSTRACT

The chemical composition fluctuation in a material may cause line broadening due to the variation of the lattice parameter, which yields a distribution of the profile centers scattered from different volumes of the material. The nature of line broadening induced by chemical heterogeneities is similar to a microstrain-like broadening in the sense that the peak width increases with the magnitude of the diffraction vector. However, the dependence of compositional broadening on the orientation of diffraction vector (i.e. the anisotropic nature of this effect) differs very much from other types of strain broadening (e.g. from that caused by dislocations). The anisotropic line broadening caused by composition fluctuation is parameterized for different crystal systems and incorporated into the evaluation procedures of peak profiles. This chapter shows that the composition probability distribution function can be determined from the moments of the experimental line profiles using the Edgeworth series. The concentration fluctuations in decomposed solid solutions can also be determined from the intensity distribution in the splitted diffraction peaks.

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INTRODUCTION

The locally varying composition in a solid solution or an intermetallic compound phase yields a distribution in the interplanar spacings, thereby resulting in microstrain-like broadening of diffraction peaks. The line broadening caused by composition variations in cubic crystals has been analyzed by Mittemeijer and Delhez (1980), revealing that the peak breadth was independent of the reflecting plane orientation (i.e. not depending on the indices of reflection *hkl*). Additionally, the occurrence of anisotropic diffraction line broadening due to compositional inhomogeneities was studied in non-cubic materials, e.g. early transition metal carbide samples (Rempel & Gusev, 2000), $YBa_2Cu_3O_{7-x}$ (David, Moze, Licci, Bolzoni, Cywinski, & Kilconyne, 1989) or $Cu(W_{1-x}Mo_x)O_4$ (Ehrenberg, Theissmann, Gassenbauer, Knapp, Wltschek, Weitzel, Fuess, Herrmannsdörfer, & Sheptyakov, 2002). The evaluation of the compositional inhomogeneities from line profiles is often carried out using the description of anisotropic microstrain broadening proposed by Stephens (1999) and presented in chapter 3. For instance, this method was used to determine compositional inhomogeneities in $Bi_{0.15}Ca_{0.85}MnO_3$ (Llobet, Frontera, García-Munoz, Ritter, & Aranda, 2000). However, it was not proved whether the microstrain model applied for peak profile analysis was compatible with the physical origin of line broadening.

In the first decade of the third millennium, Leineweber and coworkers analyzed the effect of chemical heterogeneities on line profiles in details and elaborated several procedures for the determination of the distribution density function from the shape of the diffraction profiles (Leineweber & Mittemeijer, 2006; Leineweber, 2009). Their procedures are capable to determine concentration variations in cubic and non-cubic crystals from powder diffraction pattern. The methodology developed by Leineweber and coworkers was successfully applied for the evaluation of concentration distribution of nitrogen in hexagonal ε-$FeN_{0.433}$ (Leineweber & Mittemeijer, 2004). The different dependencies of the two hexagonal lattice parameters on the local deviations from the average concentration cause anisotropic line broadening, which allows quantitative determination of the composition variation in the sample. In the following, the concept of compositional microstrain broadening is introduced and several methods for the determination of alloying or impurity element concentration distribution from line profiles are described in details.

THE CONCEPT OF COMPOSITIONAL MICROSTRAIN

Let us assume that the chemical composition in a polycrystalline material varies from crystallite to crystallite. The various composition in the different crystallites yields different lattice parameters and therefore shifts of the centers of peak com-