3.6. WHOLE POWDER PATTERN MODELLING

with the definitions of surface-weighted domain size and column-length distribution function' (Balzar & Popović, 1996): integral breadth methods are therefore intrinsically limited for the microstructure analysis of real materials. This is in stark contrast to the fact that equation (3.6.2) is used, for example, by a large number of Rietveld refinement codes to describe the observed trend in line-profile broadening (and to perform a rough micro-structure analysis). This situation can be improved a little by properly considering at least the anisotropic broadening component, as performed, for example, in the modified Williamson–Hall method (MWH; Ungár & Borbély, 1996; Ungár, 2001; Scardi *et al.*, 2004). The results are more accurate and related to some physical quantities (a dislocation density and a stacking fault probability), but they are still tightly bound to a Voigtian profile approximation.

An alternative to the integral breadth methods was developed by Warren & Averbach (1950, 1952) almost simultaneously with the idea of Williamson and Hall, but took longer to be fully employed owing to the lack of fast computing tools. It is based on the extensive use of Fourier transforms and represents the starting point of modern line-profile analysis techniques. The whole profile carries information on the microstructure, as each point in reciprocal space is related to the Fourier transform of real space (and thus to the size and shape of the domains and also the deviation from perfect three-dimensional periodicity). Each profile also contributes to a better picture of the microstructure, as it samples along a different direction in space.

For decades, these Fourier methods were only used in a very small number of scientific areas; the availability of fast computers and the fast Fourier transform has contributed greatly to their further diffusion. It is, however, only in recent years that the full power of the Fourier approach has been unveiled, with the development of whole-pattern methods and the extension of most models to a wider range of materials.

3.6.2. Fourier methods

3.6.2.1. *Definitions*

In the following, the diffraction peaks for a powder will be described in reciprocal space with reference to the Bragg position $d^*_{\{hkl\}}$ expected for the $\{hkl\}$ reflection family in the absence of any type of defect. The coordinate s, where

$$s = d^* - d^*_{\{hkl\}} = \frac{2}{\lambda}\left(\sin\theta - \sin\theta_{\{hkl\}}\right), \quad (3.6.3)$$

will be employed. Moving from reciprocal to diffraction space ('2θ space') involves a trivial but nonlinear change of variables: peaks that are symmetrical in reciprocal space will become asymmetrical in 2θ space and *vice versa*.

3.6.2.2. *Peak profile and the convolution theorem*

Each peak profile $h(s)$ in a powder diffraction pattern can be described as the convolution of an instrumental profile $g(s)$ with a function $f(s)$ accounting for sample-related effects (microstructure; see, for example, Jones, 1938; Alexander, 1954; Klug & Alexander, 1974; and references therein):

$$h(s) = \int_{-\infty}^{\infty} f(y)g(s-y)\,dy = f \otimes g(s). \quad (3.6.4)$$

The calculation of the integral in equation (3.6.4) can be simplified through the use of a Fourier transform (FT). In fact,

the convolution theorem states that the FT of a convolution is the product of the Fourier transforms of the functions to be folded:

$$\mathcal{C}(L) = \mathrm{FT}[h(s)] = \mathrm{FT}[f(s)] \times \mathrm{FT}[g(s)]. \quad (3.6.5)$$

In this equation, L is the (real) Fourier variable conjugate to s. The properties of the Fourier transform allow equation (3.6.4) to be rewritten as

$$h(s) = \mathrm{FT}^{-1}[\mathcal{C}(L)] = \mathrm{FT}^{-1}\big[\mathrm{FT}[h(s)]\big] = \mathrm{FT}^{-1}\big[\mathrm{FT}[f(s)]\mathrm{FT}[g(s)]\big]. \quad (3.6.6)$$

This equation is the basis of the Warren–Averbach approach and also of all modern LPA methods.

3.6.2.3. *The Warren–Averbach method and its variations*

The convolution theorem can be employed to disentangle the specimen-related broadening contributions described by $f(s)$. In fact, let us suppose, as in the Williamson–Hall method, that size and microstrain are the only two sources of specimen-related broadening. We call the Fourier transform of the profiles broadened by size and distortion effects only $A^S_{hkl}(L)$ and $A^D_{hkl}(L)$, respectively. As the size and distortion profiles are folded into $f(s)$, the following holds:

$$A(L) = \mathrm{FT}[f(s)] = \mathrm{FT}[h(s)]/\mathrm{FT}[g(s)] = A^S_{hkl}(L)A^D_{hkl}(L). \quad (3.6.7)$$

The separation of the size and distortion terms is straightforward for spherical domains: the size effects for a sphere are independent of the reflection order, whereas those related to distortions (causing the change in the slope of the Williamson–Hall plot) are order-dependent. To describe the distortion term it is convenient to follow the idea of Bertaut (1949a,b, 1950), considering the specimen as made of columns of cells along the **c** direction. The profile due to distortions is calculated by taking the average phase shift along the column due to the presence of defects. The analytical formula for the distortion term is thus of the type $A^D_{hkl}(L) = \langle\exp(2\pi iLn\varepsilon_L)\rangle$, where $\varepsilon_L = \Delta L/L$ is the average strain along **c** calculated for a correlation distance (*i.e.* Fourier length) L.

As a first-order approximation, the distortion terms give no profile asymmetry; $A^D_{hkl}(L)$ is just a cosine Fourier transform. We can thus expand it as (Warren, 1990)

$$A^D_{hkl}(L) = \langle\cos(2\pi Ln\varepsilon_L)\rangle = 1 - 2\pi^2 L^2 n^2 \langle\varepsilon_L^2\rangle. \quad (3.6.8)$$

If we now rewrite equation (3.6.7) on a log scale, taking equation (3.6.8) into account, we obtain

$$
\begin{aligned}
\ln[A_{hkl}(L)] &= \ln[A^S_{hkl}(L)] + \ln[A^D_{hkl}(L)] \\
&= \ln[A^S_{hkl}(L)] + \ln[1 - 2\pi 2L^2 n^2 \langle\varepsilon_L^2\rangle] \\
&= \ln[A^S_{hkl}(L)] - 2\pi^2 L^2 n^2 \langle\varepsilon_L^2\rangle.
\end{aligned} \quad (3.6.9)
$$

Equation (3.6.9) represents a line in the variable n^2: the intercepts at increasing L values provide the logarithm of the Fourier size term, whereas the slopes give the microstrain directly (Warren, 1990). From the size coefficients, we can obtain an average size, again following the idea of Bertaut (1949a, 1950), related to the properties of the Fourier transform:

$$\langle D\rangle = \left[-\frac{\partial A^S_{hkl}(L)}{\partial L}\bigg|_{L=0}\right]^{-1}. \quad (3.6.10)$$

This average size is thus related to the initial slope of the Fourier coefficients [assuming that they are well behaved, *i.e.* that the tangent is always below the $A^S_{hkl}(L)$ curve].

A long chain of operations is needed to obtain the size and the strain contributions; there is thus a risk that the final result will no longer be compatible with the experimental data. Only a few years after the introduction of this method, Garrod *et al.* (1954) wrote

> Hence, in any attempt to distinguish between particle size or strain broadening from a particular material, the use of the one or the other of these functions [Gaussian and Lorentzian] (together with the appropriate relationship between *B*, *b*, and *β*) involves an intrinsic initial assumption about the cause of the broadening, when the object of the investigation is to discover the cause. Such an assumption must inevitably weight the experimental results, partially at least, in favour of one or the other of the two effects. In this connexion it is therefore perhaps significant that in most previous work on the cause of line broadening from cold-worked metals, those investigators who have used the Warren relationship between *B*, *b*, and *β* have concluded that lattice distortion was the predominant factor, whilst those who have employed the Scherrer correction found that particle size was the main cause. The best procedure in such work therefore is to make no assumptions at all about the shape of the experimental line profiles...

This is owing to the fact that a direct connection between the experimental data and the final microstructural result does not really exist in those methods and that the whole information contained in the pattern is not exploited.

3.6.2.4. *Beyond the Warren–Averbach method*

The work of Alexander (see, for example, Alexander, 1954; Klug & Alexander, 1974; and references therein) was definitely pioneering here. Alexander proposed a set of formulae for the synthesis of the instrumental profile, with the aim of obtaining a correction curve to subtract the instrumental contribution to the measured breadth of the profiles (thus improving the accuracy of the size determination). The true power of this idea was not fully exploited, as the Scherrer formula was still used for microstructure analysis. A few decades later, Adler, Houska and Smith (Adler & Houska, 1979; Houska & Smith, 1981) proposed the use of simplified analytical functions to describe the instrument, size and strain broadening and to perform the convolution of the equation numerically *via* Gauss–Legendre quadrature. Rao & Houska (1986) improved the procedure by carrying out part of the integration analytically (for monodisperse spheres). The microstructure parameters are directly obtained from a fit of this numerical peak to the experimental data. The fit partly solves the problem of peak overlap: in traditional methods it is in fact impossible to establish the extent of overlap between the peaks and therefore to correctly extract the area or maximum intensity. The method is a major step forward, but is still related to the Warren–Averbach approach, as just two multiple-order peaks are considered.

Cheary & Coelho (1992, 1994, 1998*a*,*b*) pushed the idea forward with the fundamental parameters approach (FPA). The FPA is based on the intuition of Alexander (1954) and the general idea of the Rietveld (1969) method: the calculation speed is greatly improved to facilitate widespread use. The convolution is performed directly in 2θ space, where instrumental aberrations, which were extensively explored by these researchers, occur. Very simplistic models were employed to describe the broadening due to the specimen; the whole pattern (and therefore all of the measured information) is considered in place of one or more peaks and of the extracted information. For structural analysis and for the Rietveld method, the FPA is a huge step forward, as it allows a more accurate determination of lattice parameters and integrated intensities. Moreover, it enables some line-profile analysis on low-quality patterns or on data affected by strong peak asymmetry.

3.6.2.5. *Whole powder pattern modelling (WPPM)*

The techniques briefly illustrated in the previous section, as well as other alternatives appearing in the literature before the beginning of this century, lack full completeness for quantitative microstructure analysis. The whole powder pattern modelling method attempted to fill this gap. Starting with the same ideas as in Section 3.6.2.1 (*i.e.* peaks as convolution), it uses equations (3.6.5) and (3.6.6) to generate the peaks within a fully convolutional approach. The peak profiles are therefore generated from the Fourier transform of each broadening component; the resulting $h(x)$ function accounts just for the shape of the profile, which in turn can be represented as (Scardi & Leoni, 2002)

$$I_{\{hkl\}}(s) = k(d^*)h(s) = k(d^*) \int_{-\infty}^{\infty} \mathcal{C}(L)\exp(2\pi iLs)\,\mathrm{d}L, \quad (3.6.11)$$

where $k(d^*)$ includes all constant or known functions of d^* (*e.g.* structure factor, Lorentz–polarization factor *etc.*), whereas $\mathcal{C}(L)$ is the Fourier transform of the peak profile. The term k is a function of d^*; it is not necessarily a function of s, as the peak is actually centred in $d^*_{\{hkl\}}$.

Equation (3.6.11) assumes that the broadening sources act on the entire family of symmetry-equivalent reflections $\{hkl\}$ and therefore that a multiplicity term [included in $k(d^*)$] can be used: however, certain types of defects (*e.g.* faults) can act independently on each of the symmetry-equivalent reflections. Equation (3.6.11) then becomes more correctly

$$I_{\{hkl\}}(s) = k(d^*)\sum_{hkl} w_{hkl}I_{hkl}(s_{hkl}) = k(d^*)\sum_{hkl} w_{hkl}I_{hkl}(s - \delta_{hkl}),$$

$$(3.6.12)$$

where w_{hkl} is a weight function depending on the lattice symmetry and actual broadening source, $s_{hkl} = d^* - (d^*_{\{hkl\}} + \delta_{hkl})$ $= s - \delta_{hkl}$ is the distance, in reciprocal space, from the centroid of the peak hkl, and δ_{hkl} is the shift from $d^*_{\{hkl\}}$, the Bragg position in the absence of defects. The sum is over independent profile subcomponents selected on the basis of the specific defects (*e.g.* two for the $\{111\}$ family in f.c.c. when faults are present; selection is based on the value of $|L_0| = |h + k + l|$, *i.e.* 3 or 1).

According to equation (3.6.5), the function $\mathcal{C}(L)$ is the product of the Fourier transforms of the broadening contributions. In a real material, broadening is mostly due to the specific nature of the instrument, to the finite size of the coherently diffracting domain (size effect) and to the presence of defects such as, for example, dislocations and faults (Cheary & Coelho, 1992; van Berkum, 1994; Scardi & Leoni, 2002). Taking these into account,

$$\mathcal{C}(L) = T^{\mathrm{IP}}(L)A^S_{hkl}(L)\langle\exp[2\pi i\psi_{hkl}(L)]\rangle\langle\exp[2\pi i\varphi_{hkl}(L)]\rangle\ldots,$$

$$(3.6.13)$$

where $T^{\mathrm{IP}}(L)$ and $A^S_{hkl}(L)$ are the FTs of the instrumental and domain-size components, respectively, whereas the terms in angle brackets $\langle\rangle$ are average phase factors related to lattice distortions (ψ_{hkl}) and faulting (φ_{hkl}).

Equation (3.6.13) is the core of the WPPM method: as indicated by the ellipsis, any other broadening source can easily be considered by including the corresponding (complex) Fourier transform (*i.e.* the corresponding average phase factor) in equation (3.6.13). Expressions are known for several cases of practical interest (see, for example, Scardi & Leoni, 2002, 2004,