

3. METHODOLOGY

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)

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

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

$$I_{\{hkl\}}(s) = k(d^*) \sum_{hkl} w_{hkl} I_{hkl}(s_{hkl}) = k(d^*) \sum_{hkl} w_{hkl} I_{hkl}(s - \delta_{hkl}), \quad (3.6.12)$$

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,

$$\mathcal{C}(L) = T^{\text{IP}}(L) A_{hkl}^{\text{S}}(L) \langle \exp[2\pi i \psi_{hkl}(L)] \rangle \langle \exp[2\pi i \varphi_{hkl}(L)] \rangle \dots, \quad (3.6.13)$$

where $T^{\text{IP}}(L)$ and $A_{hkl}^{\text{S}}(L)$ 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,

2005; Leoni & Scardi, 2004; Leineweber & Mittemeijer, 2004; van Berkum, 1994; Cheary & Coelho, 1992).

The approach is strictly valid when the broadening sources can be considered as diluted and independent (*i.e.* uncorrelated defects). If this does not apply, then cross-terms should be considered and the whole approach revised. In fact, here we assume that the structure factor can be factored and the lattice is fully periodic in three dimensions: under these conditions, structure (peak intensity) and microstructure (peak shape) can be decoupled as the peak positions can be determined in a straightforward way. Extended defects (*e.g.* faults) cause the appearance of diffuse effects and the displacement of the Bragg peaks: in order to calculate the diffraction pattern, the structure and the microstructure must be simultaneously known (see, for example, Drits & Tchoubar, 1990).

3.6.2.6. Broadening components

A brief account is given of the main sources of broadening that can be encountered in practice. An accent will be placed on X-rays, but extension to electrons and neutrons is in most cases straightforward. Concerning electron diffraction, precession data can be used in a straightforward way, whereas for traditional data, containing dynamical effects, further calculations, for example of the intensity, are in principle needed.

3.6.2.6.1. Instrument

Each of the components of the diffraction instrument (*i.e.* source, optics, specimen stage, measurement geometry and detector) can have a dramatic impact both on the position and the broadening of the peaks. Axial divergence, for instance, introduces both an asymmetric broadening and an apparent shift of the low-angle peaks. When microstructure (*i.e.* specimen-related effects) is the focus of the analysis, the primary recommendation is to try to limit the instrumental influence. Alternatively, it is preferred to have an instrumental profile (no matter how complex) that can be well described and properly simulated: for instance the profile of an instrument with a $K\alpha_1$ primary monochromator (apparently advantageous) might be hard to model if the $K\alpha_2$ removal is not perfect. This becomes more and more important when the instrumental effects are of the same order of magnitude as the specimen-related broadening.

Two possible paths can be followed when dealing with the instrumental contribution: modelling using the fundamental parameters approach (see, for example, Cheary & Coelho, 1992; Kern & Coelho, 1998) or parameterization of the pattern of an ideal specimen. In the fundamental parameters approach, the geometry of the instrument and the effects of each optical component on the peak profile are described mathematically in 2θ . Most of the formulae for the various optical elements can be found, for example, in the work of Wilson (1963), Klug & Alexander (1974) and Cheary & Coelho (1992, 1994, 1998*a,b*). The aberration profiles are folded into the (X-ray) source emission profile (Hölzer *et al.*, 1997; Deutsch *et al.*, 2004) to generate a combined instrumental profile.

When no information on the instrument is available, it is possible to predict the instrumental profile just by using the nominal data for the optical components. It is however advised, whenever possible, to tune the instrumental parameters using the pattern of a line-profile standard [*e.g.* NIST LaB₆ SRM 660(*x*) series; Cline *et al.*, 2010] showing negligible specimen effects. These instrument-only parameters must then be kept fixed for any subsequent microstructure refinement. It is of paramount

importance that all instrumental features are well reproduced when dealing with microstructure effects. Provided that this condition is met, we can therefore employ any arbitrary function to describe the instrumental profile. Thus, as an alternative to FPA, we can either ‘learn’ the instrumental profile from a standard (Bergmann & Kleeberg, 2001) or use a Voigtian to model it. The Voigtian is particularly convenient as it can be defined directly in L space and thus directly enter the Fourier product of equation (3.6.13).

3.6.2.6.2. Source emission profile

For X-rays, the source emission profile at an energy E_l can be well described by a Lorentzian of energy width Γ_l (Hölzer *et al.*, 1997; Deutsch *et al.*, 2004),

$$I_l(E) = \frac{2}{\Gamma_l \pi} \left[1 + 4 \left(\frac{E - E_l}{\Gamma_l} \right)^2 \right]^{-1}. \quad (3.6.14)$$

As $dE/E = d\lambda/\lambda = ds/s$, the function can also be represented as a function of s :

$$I_{hkl,l}^{\text{IP}}(s, d_{hkl}^*) = \frac{2}{\pi} \frac{E_l}{d_{hkl}^* \Gamma_l} \left[1 + 4 \left(\frac{s_{hkl}}{d_{hkl}^* \Gamma_l / E_l} \right)^2 \right]^{-1}. \quad (3.6.15)$$

For a laboratory tube emitting simultaneously a set of N_λ wavelengths, we have

$$I_{hkl}^{\text{IP}}(s, d_{hkl}^*) = \sum_{l=1}^{N_\lambda} w_l I_{hkl,l}^{\text{IP}}(s, d_{hkl}^*), \quad (3.6.16)$$

where w_l is the relative intensity of the l th wavelength component (referred, for example, to $w_l = 1$). The corresponding Fourier transform entering (3.6.13) can be written as

$$\begin{aligned} T^{\text{IP}}(L) &= \sum_{l=1}^{N_\lambda} \exp \left[2\pi i d_{hkl}^* \left(1 - \frac{\Gamma_l}{E_l} \right) L \right] \exp \left(-2\pi s_{hkl} \frac{\Gamma_l}{E_l} L \right) \\ &= \sum_{l=1}^{N_\lambda} \left\{ \cos \left[2\pi d_{hkl}^* \left(1 - \frac{\Gamma_l}{E_l} \right) L \right] + i \sin \left[2\pi d_{hkl}^* \left(1 - \frac{\Gamma_l}{E_l} \right) L \right] \right\} \\ &\quad \times \exp \left(-2\pi s_{hkl} \frac{\Gamma_l}{E_l} L \right). \end{aligned} \quad (3.6.17)$$

The complex term in (3.6.17) accounts for the shift of each emission component with respect to the reference one. For more flexibility (for example to consider the non-ideal behaviour of the instrument), we can use a pseudo-Voigt (pV) in place of the Lorentzian in equation (3.6.14).

3.6.2.6.3. Optical elements

The equation of Caglioti *et al.* (1958), modified by Rietveld (1969) and originally developed for constant-wavelength neutron diffraction, is frequently employed for parameterization of the instrumental profile. The FWHM and the pV mixing parameter η (replacing the Lorentzian and Gaussian widths of the Voigt) are then parameterized according to functions in $\tan(\theta)$ and θ , respectively (Caglioti *et al.*, 1958; Leoni *et al.*, 1998; Scardi & Leoni, 1999),

$$\text{FWHM}^2 = U \tan^2 \theta + V \tan \theta + W, \quad (3.6.18)$$

$$\eta = a + b\theta + c\theta^2. \quad (3.6.19)$$

The parameters of the Fourier transform of a Voigt or pseudo-Voigt are then constrained to those of equations (3.6.18) and