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Novel analytical model for the determination of grain size distributions in nanocrystalline materials with low lattice microstrains by X-ray diffractometry

F. Sánchez-Bajo [a], A.L. Ortiz [a,*], F.L. Cumbrera [b]

[a] *Departamento de Electrónica e Ingeniería Electromecánica, Escuela de Ingenierías Industriales, Universidad de Extremadura, Avda. de Elvas S/N, Badajoz 06071, Spain*
[b] *Departamento de Física, Facultad de Ciencias, Universidad de Extremadura, Badajoz 06071, Spain*

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Abstract

We have developed a novel, analytical model for the determination of grain size distributions in nanocrystalline (nc) materials with low internal stresses by X-ray diffractometry (XRD). The model assumes explicitly that the XRD peaks are pseudo-Voigtian and that the grain size distributions are lognormal, both of which are assumptions amply supported by the experimental evidence. It was found analytically that the grain size dispersion depends on the shape of the XRD peaks only, whereas the grain size median depends on both the shape and width of the XRD peaks. In addition, the theoretical predictions resulting from the model were validated using standard XRD peaks obtained by computer simulation from first principles. Particular emphasis is given to the discussion of the validity limits of the model, and to the analysis of the influence of the characteristics of the grain size distributions on the nature of the XRD peaks. We then show how to calculate the average and apparent grain sizes from the grain size distribution determined with the model, and how this compares with the Scherrer method. Implications for the characterization of (undistorted and distorted) nc-materials are indicated, and a case study of an nc-powder of cubic ZrO_2 is presented. The application of the model itself is simple, involving only the fit of a pseudo-Voigt function to a single XRD peak followed by the use of two equations. This suggests that the model may have an important role to play in the characterization of nc-materials.
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1. Introduction

Nanocrystalline (nc) materials are those formed by polycrystals with grain sizes of the order of nanometers (nanograins; grain size $\leqslant$100 nm). Because of the small grain sizes and the large volume fraction of atoms at the grain boundaries, nc-materials exhibit some novel properties of considerable interest for a wide variety of structural and functional applications [1]. In this context, the determination of grain sizes is almost mandatory in any technical paper concerning nc-materials. However, despite the interest, only the average grain size (not the grain size distribution) is routinely reported.

Determination of the grain sizes of nc-materials is generally carried out by X-ray diffractometry (XRD), although they are later independently corroborated by transmission electron microscopy (TEM). XRD is used because, according to line-broadening theory, the diffraction peaks are broadened when the grain sizes are in the nanometer or submicrometer ranges [2–5], and the smaller the grain sizes the broader the peaks. Several methods are currently available to determine the average size of the nanograins from the characteristics of the XRD peaks. These include methods based on the width [6], integral breadth [7,8], variance

* Corresponding author. Tel.: +34 924 289600x6726; fax: +34 924 289601.
E-mail address: alortiz@unex.es (A.L. Ortiz).

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[9–11], and Fourier coefficients/transform [3,12,13] of the XRD peaks. There also exist methods to determine the grain size distribution. These include methods that calculate these distributions either indirectly from the Fourier coefficients/transforms of the XRD peaks [12] or directly from the XRD peaks by procedures based on Monte Carlo [14,15], maximum entropy [5,16,17], and statistical regularization [18,19] methods. Unfortunately, the grain size distributions are not often evaluated because the mathematical complexity associated with the calculation outweighs the gain in understanding the microstructure. In sum, there is thus a need for novel, simple models of exhaustive line-broadening analysis in nc-materials.

Steady progress has been made over recent years in elucidating the influence of the grain size distributions on the characteristics of the XRD peaks. For example, Langford et al. [20] assumed pseudo-Voigtian forms for the XRD peaks and Gaussian or lognormal grain size distributions, and found empirically that the XRD peaks tend to sharpen and become more Lorentzian as the dispersion in grain sizes increases. Rao and Houska [21] observed that the XRD peaks depend on the shape, mean size, and size distribution of grains, and that the influence of the grain shape diminishes as the grain size dispersion increases. Ungár et al. [22] established an analytical relationship between the Fourier coefficients of the size-broadened peaks (no assumption about the peak shape is involved) and the parameters of lognormal size distributions of spherical grains. Scardi and Leoni [23] extended the work of Ungár et al. to spherical, cubic, tetrahedral, and octahedral grains, considering lognormal and Poisson grain size distributions. More recently, Popa and Balzar [24] found analytical approximations to the size-broadened peaks induced by lognormal and γ distributions of spherical grains; also, they concluded that the XRD peaks become more Lorentzian for broad grain size distributions. Furthermore, Ida et al. [25] gave an efficient algorithm to evaluate the theoretical XRD peaks caused by spherical grains with lognormal size distributions, and reported an increase in the peaks' Lorentzian character with increasing dispersion of the grain sizes.

While analytical studies have established the connection between the Fourier coefficients of the XRD peaks calculated from first principles and the grain size distributions described by mathematical functions, as an alternative one could also assume a mathematical function for the XRD peaks, and then search for the analytical relationships (if any) between the parameters of these two functions. This appears to be important for the XRD characterization of nc-materials, since in these cases the Bragg reflections overlap severely and have to be resolved prior to the determination of the grain sizes. To the best of the authors' knowledge, no studies have been reported in the literature on such methods. We hence present a theoretical, analytical model to relate lognormal grain size distributions of spherical nanograins with pseudo-Voigtian XRD peaks, in the absence of lattice microstrains and instrumental broadening. The analytical expressions derived from the theoretical model are subsequently validated using standard XRD peaks obtained by computer simulation from first principles, and the implications for the characterization of nc-materials are discussed. Finally, an nc-powder of cubic ZrO_2 is used as an illustrative case study, with the intention of comparing the grain size distributions determined via TEM and XRD (through our model).

2. Definition of the analytical model

In the absence of lattice microstrains and instrumental broadening, the XRD peaks in real space ($f = f(2\theta)$) can be written as [2]:

$$f(2\theta) = \int_0^\infty \phi(2\theta, L) p_a(L)\, dL, \tag{1}$$

where θ is the diffraction angle, L the column length orthogonal to the diffracting planes, $\phi = \phi(2\theta, L)$ the interference function, and $p_a = p_a(L)$ the surface-weighted column-length distribution. The interference function, which defines the intensity diffracted by a column of length L, is given by [3]:

$$\phi(2\theta, L) = \frac{\sin^2[(2\pi/\lambda)(\sin\theta - \sin\theta_0)L]}{\sin^2[(2\pi/\lambda)(\sin\theta - \sin\theta_0)]}, \tag{2}$$

θ_0 and λ being the Bragg angle and the wavelength of the X-ray incident radiation, respectively. The surface-weighted column-length distribution is given by [2,3]:

$$p_a(L) = \int_{D_0(L)}^\infty G(L, D) P(D)\, dD, \tag{3}$$

where D is the grain size, $P = P(D)$ the grain size distribution, $G = G(L,D)$ the shape kernel defining how the distribution of grain sizes is mapped onto the column-length distribution, and $D_0(L)$ the smallest value of D. Substitution of Eqs. (2) and (3) into Eq. (1) leads directly to:

$$f(2\theta) = \int_0^\infty \int_{D_0(L)}^\infty \frac{\sin^2[(2\pi/\lambda)(\sin\theta - \sin\theta_0)L]}{\sin^2[(2\pi/\lambda)(\sin\theta - \sin\theta_0)]} G(L, D) P(D)\, dD\, dL, \tag{4}$$

which expresses how the XRD peaks are influenced by the grain size distributions and the grain shapes. Two important equations can now be formulated from Eq. (4). The first is the expression [26]:

$$\beta = \frac{180\lambda}{\pi\cos\theta_0} \frac{\bar{L}}{\overline{L^2}}, \tag{5}$$

that relates in real space the integral breadth of the XRD peak (β; expressed in degrees), the average surface-weighted column length ($\bar{L}$), and the average surface-weighted squared column length ($\overline{L^2}$). The second is the expression [27]:

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