Fundamental Parameter Method Applied to X-Ray Line Profile Analysis

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BulletinUASVM Horticulture 73(2) / 2016

Print ISSN 1843-5254, Electronic ISSN 1843-5394

DOI:10.15835/buasvmcn-hort:11954

Abstract

Crystallite size strain effect the mechanical, electric, magnetic and optical properties of many kind of the nanomaterials. The effects of the finite crystallite size and lattice strain can be very well observed as the deformation in the shape of the X-ray line profile (XRLP). In this contribution we have used the fundamental parameter method (FP) (Arfken and Weber, 2000, Bot *et al.*, 2015) to evaluate the nanostructure materials assuming a theoretical model of experimental XRLP. In this contribution we have used various distribution functions such as normal, lognormal, Gumbel, Maxwell and Student. The best values of the crystallite size of nanostructured materials are chosen by analysis of root mean squares of residuals and by correlation matrix of the fit parameters. The entire procedure was implemented in the GnuPlot script.

Keywords: *crystallite size, distribution functions, fundamental parameter method*

INTRODUCTION

The XRLP analysis includes the peak profile analysis and is important to provide a quick overview of the theory from behind of peak profile analysis. X-ray diffraction is one of characterization techniques are frequently used in various researches of materials engineering (Himeda, 2012) and (Langford and Wilson, 1978). Powder diffraction measurements with X-ray diffractometer will generate data in the form of a diffraction pattern that will provide an overview of diffraction peaks at certain angles according to the characteristics of material observed. A diffraction pattern provides three important aspects of information i.e. position, height (intensity) and peak shape. Information that has been obtained can be analyzed and used to identify the phase composition, crystallite size, crystal structure, effect of strain and some other common uses that will be very helpful in the analysis of the

performance of an engineered material. A measured diffraction profile of material symbolized as h is assumed as the convolution product between instrumental profile g and specimen profile f , (Bot *et al.*, 2015). Two parameters that contribute to the specimen profile function (f) are crystallite size and non-uniform strain. Analysis of the crystallite size and strain effects are very important in engineering nanomaterial (Pratapa *et al.*, 2010) as it relates to the evaluation of the properties of nanomaterials that have been made such as optical, electrical, and chemical properties (Sivasankaran *et al.*, 2011) There were elaborating theories for crystallite size assessment from XRD data, where at least four aspects emerged, namely (1) the important of correction for instrument broadening effect, (2) pattern fitting by making use of mathematical and physical models, (3) effect of size distribution on XRD peak broadening and (4) comparability of diffraction based crystallite sizes

Fig. 1 Theoretical X-ray profile of nickel (111) line for progressive numbers of unit cells

to the microscopic sizes (Pratapa *et al.*, 2010). Determination of specimen profile I is done by extracting specimen profile I from a measured diffraction profile h , called deconvolution.

$$h(s) = \int_{-\infty}^{\infty} g(x-s)I(x)dx \quad (1)$$

There are two methods of deconvolution that can be done by conventional methods such as Fourier analysis of the diffraction peak profile or a more modern method with a computerized system that is commonly used in this era i.e. the diffraction pattern fitting with the peak profile function (model) (Arfken and Weber, 2000).

Obtaining an accurate powder diffraction size-strain analysis requires some knowledge about peak shape profiles derived from the instrument (profile g). The profile g derived from the optical effects of diffraction and the wavelength distribution of the radiation that causes peak broadening by the instrument, allowing the existence of differences between the characteristics of the instrument with other. There are two ways that can be done to determine profile g , i.e. by modeling the instrumental fundamental parameters or by measuring diffraction data using a standard specimen.

MATERIALS AND METHODES

This paper is based on consideration that instrumental broadening g is described by a Dirac distribution (Arfken and Weber, 2000) or

a specimen could be an instrument broadening correction when exhibits minimum measurable specimen broadening.

X-Ray peak broadening h can be analyzed as a deviation from the ideal crystalline lattice. Laue equation was used to emphasize the intensity of the diffracted peaks from the ideal parallelepiped crystal. The ideal crystal has perfectly ordered crystalline array and it is infinitely large. In the domain of X ray infinitely large means a few microns. Any small changes from the ideal generate peak broadening and it is assumed that the nanocrystallite is not infinitely, imperfect ordering of the crystallite array and the defects distributed as non-uniform interplanar spacing disorder. Based on these assumption Laue equations have the following form,

$$I(s; s_0, N_1, N_2, N_3, a_1, a_2, a_3) = NF_{h,k,l}^2 \frac{\sin^2\left(\frac{\pi(s-s_0)}{\lambda}\right)_{a_1}}{\sin^2\left(\frac{\pi(s-s_0)}{\lambda}\right)_{a_1}} \frac{\sin^2\left(\frac{\pi(s-s_0)}{\lambda}\right)_{a_2}}{\sin^2\left(\frac{\pi(s-s_0)}{\lambda}\right)_{a_2}} \frac{\sin^2\left(\frac{\pi(s-s_0)}{\lambda}\right)_{a_3}}{\sin^2\left(\frac{\pi(s-s_0)}{\lambda}\right)_{a_3}} \quad (2)$$

where N_1, N_2, N_3 are the number of unit cells along the a_1, a_2 and a_3 directions, $s = 2\sin \theta/\lambda$ and s_0 gives gravity center of X ray line profile(XRLP).

The calculated peak is narrow when N is a large number and if when N is small the diffraction peaks become broader. So the ideal crystal is an infinitely large and perfectly ordered crystalline array. A nanocrystalline phase has a small number of unit cells. In Fig. 1 and Fig. 2 are graphical presentations of these mathematical considerations for (111) XRLP of nickel crystallites.

Fig. 2 Experimental (111) XRLP obtained by synchrotron radiation

Fig. 3 Experimental (111) XRLP and its background correction

XRD measurements on nickel crystallites were made in the 4W1C beamlines in Beijing Synchrotron Radiation Facilities operating at 50–80 mA and 2.2 GeV at room temperature. The beamline 4W1C is a time-shared branch with beamline 4W1B. The photon beam is deflected by a bent triangle crystal and led into beamline 4W1C. The bent triangle crystal with size $40\text{ V}\times 120(\text{H})\times 1\text{ mm}^2$ monochromatizes and focuses radiation in the horizontal direction. A cylindrical mirror focuses the photons beam in the vertical direction. A focal spot size of $1.5\text{ H}\times 1.0\text{ V}\times 1\text{ mm}^2$ thick was expected at 18.665 m from light source. The energy resolution is 0.5 eV at 0.154 nm . A $\text{NaI}(\text{Tl})$ detector was used, signals were amplified and fed to a single channel analyzer (ORTEC 850)

and read out by a computer. A silicon powder was used as standard sample for calibration and instrumental correction. The scanning scale, 2θ , ranges from 28° to 70° .

RESULTS AND DISCUSSION

Starting from Eq. (2) for a spherical shape of XRLP (Himeda, 2012) was developed a new relation given by

$$I(s, D) = \frac{N}{(2\pi D(s-s_0))^2} \left(\left(1 - \frac{2}{2\pi D(s-s_0)} \right) \sin(2\pi D(s-s_0)) + \frac{4}{(2\pi D(s-s_0))^2} \sin\left(\frac{2\pi D(s-s_0)}{2}\right)^2 \right) \quad (3)$$

where N is normalization factor and D represents the average crystallite diameter. The last

Fig.4 Fundamental parameters method using direct formula

Fig. 5 Fundamental parameters method using normal distribution in relation (4)

Tab. 1. Average crystallites size of (111) line and their standard deviation

No distribution	Normal distribution		Lognormal distribution		Gumbel distribution	
117 Å	134 Å	46 Å	147 Å	70 Å	142 Å	62 Å

relation can be generalized by following relation if we take in consideration various statistical distributions denoted by $p(D, D_{av}, \sigma)$.

$$I(s)_{average} = \int_{D_{min}}^{D_{max}} I(s, D) p(D, D_{av}, \sigma) dD$$

(4)

where D_{av} is moment of the first order of distributions and σ is standard deviation. In Fig 2 it is drawn experimental (111) XRLP.

The background correction for experimental (111) XRLP by polynomial approximation implemented in the Gnuplot software.

The Fig. 4 displays application of Eq. (3) using fundamental parameters method in crystallite size determination for nickel crystallites.

The Fig. 5 displays application of Eq. (4) using fundamental parameters method in crystallite size determination for nickel crystallites when was considered the normal distribution. The crystallite

size and the standard deviation were finding for lognormal distributions and Gumbel distribution.

Table 1 gives the crystallite size and standard deviation values using fundamental parameters method. We can see small differences values for crystallite size; it is due to distribution function used. Validity of these values can be correlated with root mean squares between experimental and calculated data and other spectroscopic method such as high electronic transmission microscopy (HRTEM).

CONCLUSIONS

The fundamental parameter method can be considered one of the best algorithms for crystallites size determination because it can use a large variety of probability distribution functions and its results are more reliable in comparison with Scherrer method (Langford and Wilson, 1978). The whole numerical application was developed in Gnuplot script and Maple

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