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LINE BROADENING CORRECTION IN X-RAY DIFFRACTION ANALYSIS FOR NANOMATERIALS CHARACTERIZATION USING CALCINED YTTRIUM OXIDE POWDER AS A STANDARD MATERIAL

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Abstract

X-ray diffraction-line broadening correction for several instruments has been done using annealed yttrium oxide (Y_2O_3) powders. This investigation was to determine the instrumental broadening of three diffractometers, i.e. Philips X-Pert MPD in LPPM – ITS (X1), X-Pert MPD in the Department of Materials Engineering ITS (X2), and Rigaku MiniFlex 2 in the Microstructure Laboratory of UNM Makassar (X3). The yttrium oxide powder as the standard material was prepared by annealing the as-received powder at 1100°C for 1h. The XRD line broadening determination was performed using *Match! 2* for single line and *Rietica* for the Rietveld method. This investigation showed that the XRD FWHMs of this material were minimum as compared to those of other powders. Therefore, these broadening characteristics can be implemented in size-strain determination including in *MAUD* software for each instrument. To ensure the reliability of the implementation we measured XRD data from spinel nanomaterial samples. This investigation confirmed that XRD data for these nanomaterials gave an average crystallite size at above 95% similarity measured by the above three different instruments.

Key words: XRD line broadening, yttrium oxide, nanomaterials, instrumental broadening correction

INTRODUCTION

X - ray diffraction is one of characterization techniques are frequently used in various research of materials engineering [1], [2]. Powder diffraction measurements with x-ray diffractometer willl 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 can provide three important 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 instrumen profile g and specimen profile f [3]. 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 [4] as it relates to the evaluation of the properties of nanomaterials that have been made such as optical, electrical, and chemical properties[5]. There were elaborating theories for crystallite size assesment 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 to the microscopic sizes [4]. Determination of specimen profile *f* is done by extracting specimen profile *f* from a measured diffraction profile *h*, called deconvolution.

$$h\ 2\theta\ = g\ 2\theta\ \otimes f(2\theta) \qquad (1)$$

where ⊗ denotes convolution. 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) [6].

Obtaining an accurate powder diffraction size-strain analysis requires some knowledge about peak shape profiles derived from the instrument (profile *g*). 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 modelling the instrumental fundamental parameters or by measuring diffraction data using a standard specimen. This paper focused in the second approach. A specimen could be an instrument broadening correction when exhibits minimum measurable specimen broadening.

Development of a standard material to determine the profile of this istrument has previously been done in some places i.e. at Curtin University which uses standard material LaB_6 and MgO [7] and ITS Surabaya uses Yttria (Y_2O_3) standard material [8]. This article will further report corrections of XRD peak broadening for three instruments in three places (i.e. LPPM – ITS, Department of Materials Engineering ITS and Microstructure Laboratory of UNM Makassar). These broadening characteristics will be imported into the software MAUD so it can be used for more accurate nanomaterials characterization for these instruments.

METHOD

The raw materials used in this investigation were Y_2O_3 powders (Unical Molycorp, USA). The yttria powder was calcined at 1100°C for 1 hours with rate 10°C per minute to avoid thermal residual strain during the cooling process. XRD data were collected in several instrument to determine the profile broadening of each instrument. Diffraction data were collected in LPPM ITS using Philips X-Pert Bragg Brentano diffractometer with Cu tube ($K\alpha$ = 1.5418 Angstrom) operating at 30 kV and 40 mA. The data measured with scan speed 0,02 °2θ/s. Diffraction data were collected in Department of Materials Engineering ITS using Philips X-Pert Pro MPD diffractometer with Cu tube operating with step size 0.017° 2θ/s. At the same time, diffraction data were collected in Microstructure Laboratory Department of Physics UNM Makassar using Rigaku MiniFlex 2 diffractometer with monochromator (activated at 26,57 °2θ). All data measured with range 10-130° with Bragg-Brentano geometry.

Diffraction data have been obtained were analyzed by using a single line method and whole pattern using *Match!* program [9]. Pseudo Voigt and Voigt functions were selected as profile shape functions to fit the peak profiles which were performed using the *Fityk 0.9.1* program for single-line [10]. The pseudo-Voigt function is simply a linear combination of Lorentzian and Gaussian components in the ratio $\eta/(1-\eta)$, where η is the pseudo-Voigt mixing parameter. This appear to describe the symmetrical part of an X-ray diffraction peak quite well [11]. The peak shape can be varied accross the pattern by application of the mixing parameter function [12]:

$$\gamma = \gamma_1 + \gamma_2 2\theta + \gamma_2 \; 2\theta^{\;2} \tag{2}$$

On the other hand, the variation of peak FWHM is defined by the Cagliotti expression [12]:

$$FWHM = U\,tan^2\theta + V \tan\theta + W \tag{3}$$

In this study, Rietveld analysis was done using a pseudo-Voigt function to acquire the peak broadening parameters *U*, *V*, and *W*. Rietveld analysis was performed using software *Rietica* [12]. Rietveld refinement involved background parameters and sample displacement as global parameters, peak profile parameters, scale factor, lattice parameters, atomic positions, thermal factors and asymmetry effect. Rietveld refinement performed to the collected XRD patterns was successfull indicated by *Figures-of-Merit (FoMs)*. According to Kisi (1994), all FoMs are acceptable if *goodness-of-fit* is less than 4% and R_{wp} less than 20% [13]. Crystallography data for yttria, spinel and periclase were taken from ICSD Collection Code 23811 [14], 7900 [15] and 9863 [16]. Therefore, these broadening characteristics can be implemented in size-strain determination including in *MAUD* [17] software for each instrument. To ensure that the characteristics of the instrument are accurate, we measured XRD data from a tested spinel nanomaterial which was produced using a *dissolved metal method* [18] and compare the anayslsis results.

RESULTS AND DISCUSSION

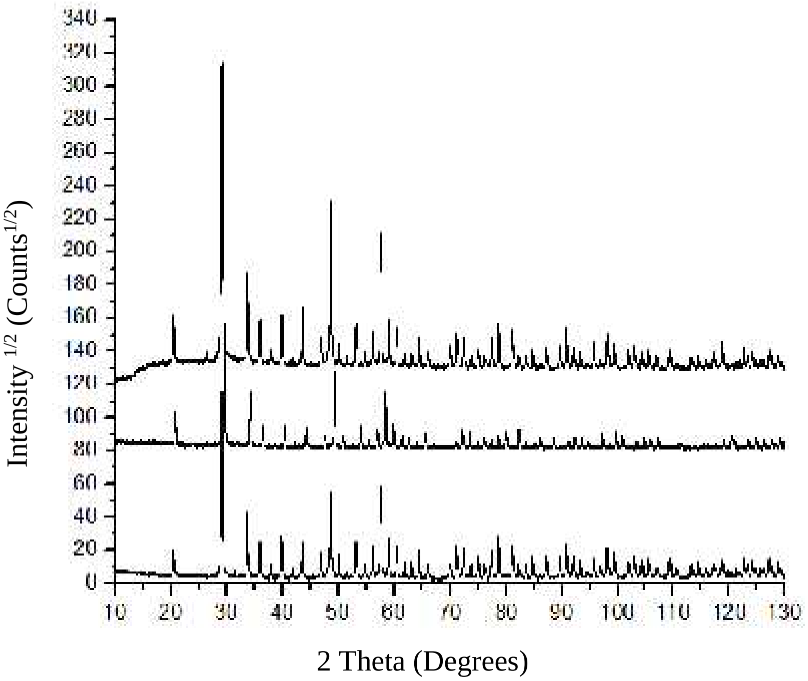

Figure 1 XRD patterns (CuKα radiation) for an yttria powder calcined at 1100˚C for 1 hour collected at LPPM ITS (X1), Materials Engineering ITS (X2) and UNM Makassar (X3)

Fig. 1 shows diffraction patterns for yttria powder calcined at 1100°C for 1 hour, collected using three difractometers i.e. Philips X-Pert MPD (X1), Philips X-Pert Pro (X2) and Rigaku Miniflex 2 (X3). It can seen that the material has sharp XRD peaks and is therefore polycrystalline. According to the crystallography data is known that the sample consists of single phase corresponding to the ICSD code 23811. Previously mentioned in Eq. 1 that a measurable diffraction peak are the convolution product of those with peak broadening caused by the instrument and specimen profiles. Contribution of instrument profile on the measured diffraction peaks will produce systematic errors in the analysis results so that the information obtained is not accurate therefore requires a its removal. Instead of a mathematical deconvolution, we chose to construct a *g* profile from a standard material and used it as a part of the profile fitting. The calcined yttria powder was selected as the standard material since its showed the narrowest peak width among other candidates [8].The peak broadening effect is now assumed to only influenced by the instrument profile. The diffraction data from the standard material were analyzed using Rietveld and single line methods.

Table 1 shows line broadening characteristics of three diffractometer after analysis of the XRD data from the calcined yttria as a standard materials. It shows that average FWHM of the standard material is 0.138 °2θ, lower than that of an MgO ceramic standard material reported previosly, i.e. 0.167 °2θ [8]. These analysis results also showed differences in the peak broadening

Table 1 Line broadening characteristics for each instruments estimated by Rietveld refinement using MAUD

Instruments	Average FWHM (˚2θ)	Caglioti Value			Gaussian Value	
		U	V	W	0	1
X1	0.138	0.007	-0.005	0.02	0.5	0.005
X2	0.146	0.043	-0.175	0.24	0.3	0.005
X3	0.130	0.030	-0.030	0.03	0.6	0.001

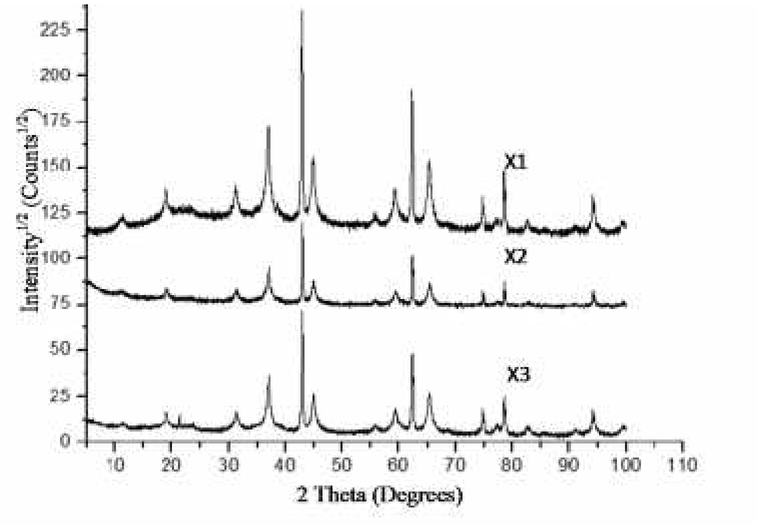

Figure 2. XRD full patterns (CuKα radiation) for the tested nanomaterial collected at LPPM ITS (X1), Materials Engineering ITS (X2) and UNM Makassar (X3)

characteristics in each instrument. These differences come from the optical effects of diffractometer and the wavelength distribution of radiation, leading to the necessity of instrument characterization prior to the use of line broadening information for microstructural analysis. It further causes the possibility of differences in the line broadening characteristics of each instrument.

Table 1 shows the line broadening characteristics of each instrument estimated by Rietveld refinement using MAUD, where Cagliotti value 0, 1 & 2 are the parameters U, V & W in the Cagliotti expression shown in Eq. 3. On the other hand, Gaussian value in table 1 refers to mixing parameter shown in the Eq. 2. Gaussian parameter values in Table 1 indicate that instrument X3 has a broader peak characters than the other two instruments. Similarly, Fig.2 shows the diffraction

Table 2. Estimated crystallite size and non-uniform microstrain for the spinel tested material performed using MAUD software [17]. Estimated standard deviations for the least significant digit are given in the parantheses.

Instruments	Crystallite Size (nm)	Strain ($\times 10^{-4}$)
X1	11(1)	1.7 (0)
X2	10(1)	1.0 (0)
X3	10 (1)	1.6 (0)

pattern of the tested nanomaterial measured using three instruments. It appears that the diffraction pattern produced by instrument X3 has a broader peak and also a considerable background as compared to the other instrument.

The line broadening characteristics for each instrument was then introduced to MAUD software [17] for estimating the crystallite size and microstrain. Reliability test was performed to ensure that the instrument characterization was correct and the analysis results were accurate. As shown in Fig.2, the tested material is composed of two phases, namely spinel $MgAl_2O_4$ (according to ICSD code 7900) and periclase (ICSD code 9863) with phase content of, respectively, 58.6(2) and 41.4 (1) wt%.

The crystallite size estimation and the non-uniform strain of the spinel in the tested materials obtained from the instruments are shown in Table 2. The size-strain analyses were done after eliminating the instrument profile that has been imported into MAUD. By doing so, the peak broadening of the sample is only affected by the specimen profile. In principle, relation between the diffraction peak broadening (*B*) with crystallite size (*D*) is described by the Scherrer's equation [19]

$$D \approx \frac{\lambda}{B \cos \theta} \qquad (2)$$

where ª is the wavelength of the radiation used in Å and 2θ is the Bragg angle. Note, however, that the peak broadening in Eq.(2) should be (a) instrumentally corrected and (b) free from strain effects.

Data in Table 2 shows that the estimated average crystallite size from the instruments are in about 95% agreement. This indicates that the peak broadening characteristics of each instrument which has been introduced to MAUD are reliable. Table 2 also presents the non-uniform strain values for the tested material which maybe resulted from the sample processing. These values, however, are minute and quite similar, emphasizing that the instrument profile corrections are satisfactory.

CONCLUSIONS

It can be concluded from this study that:

1. The average XRD FWHMs from yttria powders calcined at temperatures 1100°C lower than that of the MgO standard ceramic material. This result accentuates that the powder has fulfilled the requirement for its use as a standard material for XRD line broadening correction.
2. Each XRD instrument used in this study exhibits a specific line broadening characteristics but further analysis to the tested material shows that the estimated crystallite size and non-uniform microstrain are very similar at a value of approximately ±10 nm and of around a diminutive value of $1{,}3\times10^{-4}$ respectively

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