Analysis of structural properties of X-ray diffraction for composite copper-activated carbon by modified Williamson-Hall and size-strain plotting methods

Heryanto, Hendri, B Abdullah and D Tahir*
Department of Physics, Hasanuddin University, Makassar, 90245 Indonesia

*dtahir@fmipa.unhas.ac.id

Abstract. Structural properties of composite carbon with metal Cu (CCu) were analysis from the X-ray Diffraction (XRD) data by modified Williamson-Hall (W-H) and size-strain plotting methods. The effect of temperature shows influenced to increasing the resistance from 37.3% at room temperature to 66.4% for 600°C. By using the modified equation of Williamson-Hall, we found that the crystallite size about 40.78 nm. Modified Williamson-Hall (W-H) plotting and Gaussian distribution shows good correlation and accuracy for determining the crystallite size from the XRD data in this study.

1. Introduction
Determination crystallite size from XRD data for composite metal and carbon quite rarely reported [1]. A convenient method is needed for determine the crystallite size from XRD data. Several reported for determine crystallite size usually by Scherrer equation but still quite different with result from transmission electron microscope (TEM) [2].

\[ D_s = \frac{k \lambda}{\beta_s \cos(\theta)} \] (1)

where \( D \) is crystallite size, \( k \) is the Scherrer constant (usually 0.98 for nanoparticle), \( \lambda \) is the wavelength (nm), \( \beta_s \) is full width half maximum (FWHM) of the diffraction peak in radian. \( \beta_s \) parameter should be corrected because instrumental effect by using standard sample. According to reference [1-8], the expression for instrumental effect correction \( \beta_s \) [3], where \( \beta_{\text{exp}} \) and \( \beta_{\text{std}} \) are FWHM from the width of sample in this study and width of the standard sample, respectively.

\[ \beta_s = \sqrt{\beta_{\text{exp}}^2 - \beta_{\text{std}}^2} \] (2)

Relation between the crystallite size and microstrain (\( \varepsilon \)) [4] as follows:

\[ \varepsilon = \frac{\beta_s}{4 \sin(\theta)} \] (3)

where \( \beta_s \) is broadening due to microstrain and crystallite size, therefore, we can write as follows:

\[ \beta_s = \frac{k \lambda}{D_s \cos(\theta)} + 4 \varepsilon \tan(\theta) \] (4)
by multiplied cos(θ), equation (4) became:

\[ \beta_s \cos(\theta) = \frac{k\lambda}{D_s} + 4\varepsilon_s \sin(\theta) \] (5)

Equation (5) is called as Williamson-Hall (W-H) equation. The Crystallite size and microstrain are obtained from the intercept and slope value between \( \beta_s \cos(\theta) \) as function of \( 4 \sin(\theta) \), respectively. In this study, we modified the \( \beta_s \) value with interpolation-convolution and Gaussian distribution. We used linear interpolation techniques [5] as follows:

\[ y = y_1 + \frac{(\varphi - \varphi_1)}{(\varphi_2 - \varphi_1)}(y_2 - y_1) \] (6)

The result of interpolation is \( y \), \( (\varphi_1, y_1) \) and \( (\varphi_2, y_2) \) are the bottom and upper limit of a data, respectively. The \( \varphi \) axis as 2theta and intensity as \( y \) axis, interpolated data used for convolution as expressed in equation (7).

\[ y = y_1 + \frac{(\varphi - \varphi_1)}{(\varphi_2 - \varphi_1)}(y_2 - y_1) \] (7)

Symbol \((\cdot)\) is convolution operator and \((\eta)\) is dummy variable. Result convolution is \( h(\varphi), f(\varphi) \) and \( g(\varphi) \) are input data and kernel convolutions, respectively. By convolution, the displacement line broadening \( (\beta_c) \) determined from the standard and instrumental line broadening effect. Gaussian distribution use for calculation the FWHM from the convolution method. According to reference [6] Gaussian formula \( (P(\varphi, \mu, \sigma)) \) expressed in equation (8).

\[ P(\varphi, \mu, \sigma) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{(\varphi - \mu)^2}{2\sigma^2}} \] (8)

The mean is \( \mu \) and the variance is \( \sigma \). According to the derivative of Gaussian distribution the FWHM is about 2.35\( \sigma \). Knowledge of crystallite size of composite metal is essential for search which suitable in the characteristic material for different applications. In this study, we focus our attention for calculation of crystallite size by using the modified W-H ploiting from the x-ray diffraction data. We applied several method to determine the \( \beta_s \), \( \beta_c \), and FWHM by Gaussian methods \( (\beta_g) \) for accurate crystallite size.

2. Preparation and Instrumentation

In this study, composite (C-Cu) was prepared by mixing Cu powder (CAT 2703) with activated carbon (AC) 10% by Retsch MM for 30 minutes at frequency 10 Hz, which was controlled by XRF. The final mass of the sample is 15 grams and annealing in the free oxygen environment at 600°C for 30 minutes. The sample was measured by using X-ray diffraction (XRD) Shimadzu X-RD 7000. X-RD instrument with CuK\( \alpha \) radiation using qualitative analysis and report of \( \beta \) values FWHM at 20 values with the voltage input 40kV and current input 30 mA. Observation angle from are 20° to 80° with step size 0.02°/minutes. We compared our data with standard data from the Joint Committee Diffraction Standar (JCPDS: 96-901-1605) [7] to identify the crystal orientations of the main peaks ([111], [200] and [202]).

3. Method and Analysis

Result of interpolation are density data then we convolute the diffraction data between standard Cu CAT 2703 and (CCu). FWHM determine from the Gaussian distribution but relatives larger compare with result from convolution \( (\beta_c) \) and Scherrer equations \( (\beta_s) \). By using Williamson Hall (W-H) plots by using uniform deformation model (UDM) for explains distortion of the strain and imperfections of crystal induced broadening from the equation (3) [8]. The addition of the Scherrer equation after equation (3) we will get an equation (4). We modified \( \beta_s \) value in equation (4) with \( \beta_g \) and \( \beta_c \). FWHM modified \( (\beta_m) \) is in between \( \beta_s \), \( \beta_k \) and \( \beta_c \) as:
\[ \beta_m \cos(\theta) = \frac{k D_m}{m} + 4 \varepsilon_m \sin(\theta_m) \]  

\( D_m \) is crystalline size from W-H modified and \( \varepsilon_m \) is strain with modified which was determine from the intercept fitted data. We obtain \( D_m \) component and \( \varepsilon_m \) component by plotting \( \beta_m \cos(\theta) \) versus \( 4\sin(\theta) \). In this study, We applied W-H plots UDM method [4][8].

4. Result

X-RD spectra are shown in Figure 1 for Cu, Cu\(_2\)O and CuO. We determine the diffraction peaks of Cu for determining the crystallite size. We compared between Cu and composite Cu with 10% C in figure 1. Carbon effective to increase the resistance of Cu by thermal treatment, from 37.3% to 66.4%. Composite of Cu at 600\(^\circ\)C allows us to estimate crystallite size only for the peaks [111], [200] and [202].

![Figure 1. X-ray diffractogram pattern of Cu.](image)

Figure 2 and figure 3 are convolution proces and calculation FWHM by Gaussian method. \( \beta_c \) value is in between \( \beta_s \) and \( \beta_c \) indicated that the weakness of the Gaussian distribution method due to assumption is broadening peak is ideal.

![Figure 2. (a) is Cu CAT Standard data, (b) Carbon 10% and Cu 90%, and (c) result of convolution.](image)

![Figure 3. Comparison of the peak diffraction and Gaussian distribution in determine FWHM value.](image)
Figure 4 shows the slope (b=0.0006) and intercept (a=0.0037) by modified W-H plotting. Figure 5 shows the slope (b=0.0011) and intercept (a=0.0026) by W-H plotting (without modification).

Residual error by fit line is shows in equation (10).

\[ r_i^2 = \sum_{i=1}^{n} (y_i - (a + b\varphi_i))^2 \]  

For n data points (\(\varphi_i, y_i\)) the slope and intercept shows in equation (11).

\[ b = \frac{\left(\sum_{i=1}^{n} \varphi_i y_i\right) - n(\overline{\varphi y})}{\sum_{i=1}^{n} \varphi_i^2 - n(\overline{\varphi})^2} \quad \text{and} \quad a = \frac{\overline{\varphi y} - b(\sum_{i=1}^{n} \varphi_i)}{\sum_{i=1}^{n} \varphi_i^2 - n(\overline{\varphi})^2} \]  

Algebra form of equation (11) can be written by equation (12).

\[ na + b \sum_{i=1}^{n} \varphi_i = \sum_{i=1}^{n} y_i \quad \text{and} \quad a \sum_{i=1}^{n} \varphi_i + b \sum_{i=1}^{n} \varphi_i^2 = \sum_{i=1}^{n} \varphi_i y_i \]  

Where \(y\) and \(\overline{\varphi}\) the average values of the \(y_i\) and \(\varphi_i\). If we compute for both equations can be written in matrix form (equation (13)).

\[ \begin{bmatrix} \sum_{i=1}^{n} \varphi_i \\ \sum_{i=1}^{n} \varphi_i^2 \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} = \begin{bmatrix} \sum_{i=1}^{n} y_i \\ \sum_{i=1}^{n} \varphi_i y_i \end{bmatrix} \]  

Equation (13) used for extracting crystalline size from intercept and microstrain extracted from slope value. Table 1 shows the crystalline size by Scherrer equation, interpolation-convolution, Gaussian distribution and modified Williamson-Hall plots.

| Hkl | Scherrer equation (nm) | Scherrer with interpolation-convolution (nm) | Scherrer with Gaussian Distribution (nm) | Williamson Hall with modification (nm) | Williamson Hall without modification (nm) |
|-----|------------------------|--------------------------------------------|------------------------------------------|-------------------------------|-----------------------------------------|
| [111] | 32.5                   | 37.2                                       | 25.89                                    | 40.78                         | 58.04                                   |
| [200] | 34.2                   | 32.9                                       | 23.11                                    |                               |                                         |
| [202] | 39.7                   | 29.3                                       | 20.76                                    |                               |                                         |
5. Conclusion
We successful analysis the crystallite size for composites CCu with several methods from the X-RD spectra shows is effective way to increase the thermal resistance from 37.3% to 66.4%. In this study shows effective and efficient method for determine crystallite size from Interpolation-convolution, Gaussian distribution and modified W-H plots.

Acknowledgments
We would like to thanks to the Hasanuddin University, Indonesia by PKLN-UH 2018 program for financial support of this research

References
[1] Wijaya S R, Tjandrawinata R and Parangtopo 1996 Prosiding Pertemuan Ilmiah Sains Materi. (Indonesia: PPSM)
[2] Monshi A, Foroughi M R and Monshi M R 2012 World Journal of Nano Science and Engineering 2 154
[3] Goncalves N S, Carvalho J A, Lima Z M, Sasaki J M 2012 Materials Letter 72 26
[4] Mote V D, Purushotham Y and Dole B N 2012 Journal of Theoritical and Applied Physics 6:6
[5] Stoyan G 1978. Applied Mathematical Science 27 in Journal of Applied Mathematics and Mechanics Springer-Verlag XXIV392 S DM 32.50
[6] Ribeiro M I 2004 Gaussian Probability Density Function: Properties and Error Characterzatio (Lisboa Portugal : Institute for System and Robotics Instituto Superior Tcnico 1049-001)
[7] Davey W P 1925 Physical Review 25 753
[8] Prabhu Y T, Rao K V, Kumar V S S, Kumari B S 2014 India. World Journal of Nano Science and Engineering 4 21