Determination of the crystallite size and crystal structure of magnesium powder by x-ray diffraction

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Abstract. Magnesium powder has become an important material in the development of science and technology such as alloy and hydrogen storage. In this work, the chemical composition, crystallite size, and crystal structure of the magnesium powder sample have been studied by using x-ray fluorescent and x-ray diffraction. The x-ray diffraction data of the magnesium powder sample was analyzed by using the Rietveld method to obtain the crystal structure. Our results show that the purity of our magnesium powder sample is 93.1%. Our sample has good crystallinity with an average crystallite size of 31 nm. The crystal structure is found to be a hexagonal closed-packed structure with the lattice constants of 3.2100 Å (a and b-axis) and 5.2107 Å (c-axis). Our result revealed that the lattice constant in the c-axis of magnesium powder is influenced by impurities. This finding suggests that the impurity can affect the crystal structure of a material in general.

Keywords: Crystal structure, lattice constant, magnesium powder, x-ray fluorescent, x-ray diffraction.

INTRODUCTION

Magnesium (Mg) was discovered by Joseph Black in 1755. Magnesium is also known as “white stone” or “white earth” [1]. There is abundant magnesium in the universe. In 2018, the production of magnesium worldwide was 996 thousand metric tons. The production increased to 1100 thousand metric tons in 2019 [2]. Magnesium is classified as an alkaline earth metal or divalent metal with the electron arrangement 1s2, 2s2, 2p6, 3s2. Magnesium has two valence electrons and its electronic spectrum is defined by s-p states. Its bulk density of state is nearly free-electron-like; therefore magnesium is considered to be one of the most free-electron-like metals, besides aluminum. For this reason, magnesium is often called as a simple metal [3].

Magnesium has many interesting properties. When magnesium was dopped with Boron with a ratio 1:2, it produced MgB2 having superconductor property below 39 K [4]. The Mg(1010) surface has thermal contraction in the first interlayer [5]. The weight of magnesium is light compared to other materials such as Iron, Nickle, and Copper. However, this metal has good toughness. Scientists have developed magnesium alloys that are a nonferrous material having good corrosion resistance, good strength, light, high ductility [6]. Magnesium can be formed as alloys such as magnesium-aluminum alloy, manganese alloy, magnesium zinc zirconium alloy, etc. [1, 6]. There are some applications of magnesium alloy in industries such as automobiles, aircraft, electronics, etc.

Previous studies showed that nanocrystalline metals can improve the mechanical properties of the material such as increasing the strength, high ductility, and enhanced the chemical properties such as improving hydrogen absorption [7]. Nanocrystalline can be produced by milling the powder material. Hwang et al. milled the magnesium powder to produce the 42 nm magnesium nanocrystalline [8]. Magnesium powder can absorb hydrogen. Therefore, nanocrystalline magnesium can be used for hydrogen storage [7, 9]. Thus, the magnesium powder becomes an important
material for the development of hydrogen storage.

The crystal structure of magnesium metal is already well known in the literature. Its crystal structure is hexagonal closed-packed (hcp). Its bulk lattice constant a=b=3.210 Å and c=5.213 Å, the c/a is 1.624 [3]. However, to our knowledge, the crystal structure of magnesium powder that has some impurities in it has not been available in the literature currently. On the other hand, the information of crystal structure is important since most properties of the material are governed by its crystal structure [10-13]. As discussed previously, the magnesium powder is used for many purposes such as hydrogen storage. Thus, it is important to study the crystal structure of magnesium powder having impurities.

The objective of this work is to determine the crystallite size and crystal structure of magnesium powder that has some impurities in it by using x-ray diffraction.

**METHODOLOGY**

The magnesium powder was manufactured by Aldrich. The magnesium powder sample used in this study was as received from the manufacturer, without any treatment. X-ray fluorescent (XRF) manufactured by PANalytical MiniPal Type 4 was used to identify the compounds and elements contained in the magnesium powder sample. X-ray diffraction (XRD) manufactured by Shimadzu serial D6000 was used to determine the magnesium phase, crystallite size, and crystal structure of the magnesium powder sample. The XRD measurement was performed at room temperature with an x-ray wavelength of 1.5406 Å, continuous scan (2θ) in the range from 10 to 80 degrees with a 0.02-degree step. The crystallite size (D) of magnesium powder was determined by using the equation (1) [14].

\[
D = \frac{k \lambda}{B \cos(\theta)}
\]  

(1)

Where \( \theta \) is the peak position magnesium in the x-ray diffraction pattern in degrees, B is the full width at half maximum of the magnesium peak in radian, \( \lambda \) is 0.15406 nm (the wavelength of x-ray diffraction equipment), and \( k = 0.95 \) (constant).

The analysis of XRD data was conducted using the FullProf program developed for Rietveld analysis to refine the crystal structure [15, 16]. The calculated density for the i\(^{th} \) step was obtained by using equation (2) [17].

\[
Y_{ci} = s \sum_{i} F_{K} L_{K} P_{K} A_{K} \phi(2\theta_i - 2\theta_K) + Y_{bi} \tag{2}
\]

Where s is a scale factor, \( K \) refers to Miller indices for Bragg reflections, \( F_{K} \) is the structure factor, \( L_{K} \) is the Lorentz factor, \( P_{K} \) is orientation function, \( A \) is absorption factor, \( \phi \) is reflection profile function, \( Y_{ci} \) is the background intensity at the i\(^{th} \) step. The residual intensity was calculated using equation (3).

\[
S_y = \sum_{i} w_i (Y_i - Y_{ci})^2
\]  

(3)

Where \( Y_{ci} \) is a calculated intensity at the i\(^{th} \) step from the equation (2), \( Y_i \) is the observed intensity (experimental data) at the i\(^{th} \) step, \( w_i \) is the weight at the i\(^{th} \) step. \( S_y \) is the quantity that will be minimized to obtain a good fit, to obtain the right crystal structure [17].

**RESULTS AND DISCUSSION**

**Chemical Composition**

XRF has been utilized to determine the composition of our magnesium powder sample, the result is listed in Table 1. Our sample contains 93.1% of Mg, 3.1% of P, 1.8% of Ca, and some other impurities (W, Mn, Cr, Cu, Fe, Ni, Zn). So, the purity of our magnesium powder sample is in the range of 90 to 95%.

| Element | Composition (%) |
|---------|-----------------|
| Mg      | 93.1            |
| P       | 3.1             |
| Ca      | 1.8             |
| W       | 0.4             |
| Mn      | 0.3             |
| Cr      | 0.3             |
| Cu      | 0.3             |
| Fe      | 0.2             |
| Ni      | 0.1             |
| Zn      | 0.1             |

**Magnesium Phase**

The XRD data of magnesium powder from this study is shown in Figure 1. There were many peaks observed. The sample is crystallite, no amorphous peak was observed. The magnesium phase was determined by comparing the XRD database for magnesium to our experimental data, as listed in Table 2. There are eleven peaks that can be assigned as magnesium peaks, as shown in Figure 1.
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Figure 1. X-ray diffraction pattern of Mg powder.

Table 2. Comparison of experimental data to the XRD database of magnesium.

| No  | 2θ(degrees) | hkl   |
|-----|-------------|-------|
|     | This study  | Database [18] |
| 1   | 32.33       | 32.18  | 100 |
| 2   | 34.55       | 34.40  | 002 |
| 3   | 36.76       | 36.61  | 101 |
| 4   | 47.95       | 47.81  | 102 |
| 5   | 57.49       | 57.37  | 110 |
| 6   | 63.19       | 63.01  | 103 |
| 7   | 67.62       | 67.32  | 200 |
| 8   | 68.74       | 68.63  | 112 |
| 9   | 70.12       | 70.01  | 201 |
| 10  | 72.64       | 72.51  | 004 |
| 11  | 77.94       | 77.83  | 202 |

The highest intensity of the magnesium phase was observed at the Bragg angle of 36.76 degrees. The second and third highest intensity were observed at the Bragg angles of 34.55 and 32.33 degrees, respectively. Several observed peaks are not magnesium phase, but they are impurities such as the peaks at 18.60, 32.89, 38.05 degrees, etc.

Crystalite Size

To determine the crystallite size of the magnesium powder sample, first, we need to determine the full width at half maximum (B) of the magnesium peak in radian. This can be obtained by fitting the magnesium peak experimental data with the Lorentzian function, as shown in Figure 2. After having B for each peak, then we can calculate the crystallite size by using the equation (1).

Figure 2. The best fit of the Lorentzian function (solid line) to XRD magnesium powder data (unfilled circles).

The summary of results is shown in Table 3. Based on the highest peak intensity, the crystallite size of the sample is 38.56 nm (386 Å). The average crystallite size is 30.83 nm (=31 nm).

Table 3. The crystallite size of the magnesium powder sample.

| Peak | 2θ (degrees) | β (rad) | Crystallite size (nm) |
|------|--------------|---------|-----------------------|
| 1    | 32.33        | 0.004   | 38.10                 |
| 2    | 34.55        | 0.004   | 38.32                 |
| 3    | 36.76        | 0.004   | 38.56                 |
| 4    | 47.95        | 0.005   | 32.04                 |
| 5    | 57.49        | 0.005   | 33.39                 |
| 6    | 63.19        | 0.006   | 28.64                 |
| 7    | 67.62        | 0.007   | 25.16                 |
| 8    | 68.74        | 0.007   | 25.33                 |
| 9    | 70.12        | 0.007   | 25.54                 |
| 10   | 72.64        | 0.008   | 22.71                 |
| 11   | 77.94        | 0.006   | 31.37                 |

The average crystallite size (nm) 30.83

In the previous study by Hwang et al., the crystallite size of magnesium powder was found to be 42 nm [8]. The crystallite size of our magnesium powder is slightly smaller than that of the study by Hwang [8]. A recent study by Sutapa found that the crystallite size of MgO was 10 nm [19], which is smaller than that of the present study. The crystallite size of magnesium nanoparticles studied by Rather et al. was found to be 26 – 71 nm [20]. The
crystallite size obtained from our study is in this range of values. Thus, based on the crystallite size, our magnesium powder sample has good crystalline.

**Crystal Structure**

The XRD data of magnesium powder has been analyzed by the Rietveld method using equation (2) and (3). The results of the fit are shown in Table 4. The lowest goodness of fit (GoF) is 5.1% with the lattice constant a=b=3.2100 Å and c=5.2107 Å. This is the best fit obtained for magnesium powder data. The comparison between the calculated intensity of the best fit and measured intensity is shown in Figure 3.

| No. | a=b (Å)  | c (Å)  | GoF (%) |
|-----|----------|-------|---------|
| 1   | 2.8091   | 4.8109| 10.1    |
| 2   | 3.0090   | 5.0106| 9.9     |
| 3   | 3.2100   | 5.2107| 5.1     |
| 4   | 3.4091   | 5.4105| 10.0    |
| 5   | 3.6098   | 5.6102| 10.3    |

**Table 4.** The GoF for several fits to the magnesium powder sample.

The space group of magnesium powder is P6_3/mmc. The crystal structure is hexagonal closed-packed (hcp). The first m in the space group refers to the mirror plane perpendicular to the c-axis, the second m refers to the mirror plane parallel to the c-axis, and c in the space group refer to the glide plane. The unit cell of magnesium powder is shown in Figure 4. The angle between the a and c axes is 90 degrees, the angle between the b and c axes is 90 degrees, the angle between the a and b axes is 120 degrees. There are two atoms in the unit cell located at (1/3; 2/3; 1/4) and (2/3; 1/3; 3/4).

The lattice constant (a and b) of our sample is 3.2100 Å that is the same as the value reported in the literature [3]. However, the lattice constant (c) of our sample is found to be 5.2107 Å that is smaller than the available in the literature, i.e. c=5.2130 Å. The discrepancy is due to some impurities in our sample, i.e. the purity of our sample is about 93%. This implies that the crystal structure of magnesium powder is significantly affected by the impurities. This behavior was also observed in previous studies [11-12]. Wachowicz et al. observed the influence of impurities on the structure in Fe [11]. Bruno et al. also observed that magnesium impurities affected the structure of calcite [12]. Thus, we are sure that the impurities affect the crystal structure of material generally.

**CONCLUSION**

The crystallite size of magnesium powder is about 31 nm that indicates that our magnesium powder sample has a good crystallinity. There was no amorphous peak observed in our XRD data. The crystal structure of magnesium powder is found to be the hexagonal closed-packed structure with the lattice constants a=b=3.2100 Å and c=5.2107 Å. Our result showed that the lattice constant in the c-axis of magnesium powder is affected by the impurity.
This finding indicates that the impurity affects the lattice constant of crystal of a material.

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