Preparation and Characterization of Cadmium Metal Nanoparticle-by X-Ray Study

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Abstract: Crystallite size and lattice strains in cadmium (Cd) powders produced by milling have been analyzed by X-ray powder diffraction. The lattice strain (ε) and Debye-Waller factor (B) are determined from the half-widths and integrated intensities of the Bragg reflections. In Cd the Debye-Waller factor is found to increase with the lattice strain. Cadmium powder was ball milled in an argon inert atmosphere. The milled powders were characterized by X-ray diffraction. The high-energy ball milling of Cd after 25 hours resulted in particle size of 21 nm. Lattice strains in Cd powder produced by milling have been analyzed by X-ray powder diffraction. The lattice strain (ε) and Debye-Waller factor (B) are determined from the half-widths and integrated intensities of the Bragg reflections. Debye-Waller factor is found to increase with the lattice strain. From the correlation between the strain and effective Debye-Waller factors have been estimated for Cd. The variation of energy of vacancy formation as a function of lattice strain has been studied.

Keywords: Ball Milling, X-ray Diffraction, Particle Size, Lattice Strain, Debye-Waller Factor, Vacancy Formation Energy

1. Introduction

Chemists, physicists and materials scientists have shown great interest in the development of new methods for the synthesis of nanomaterials.

Influence of Tool Revolving on Mechanical Properties of some metals and alloy had been developed as next generation engineering production [1, 2] and with some thermal and mechanical properties and engineering applications [3, 4]. Physical and chemical properties of these materials are highly size dependent. Therefore, it is important to develop novel techniques for the synthesis of nanomaterials.

The Debye-Waller factor is an important lattice dynamical property. There is considerable X-ray work on the Debye-Waller factors of Cd [5-6]. But it is interesting to study the effect of particle size and lattice strains on the Debye-Waller factors of these metals. Inagaki *et al* [7, 8] showed that in several non-metallic powders, the strains produced during grinding have a significant effect on the Debye-Waller factors measured from X-ray diffraction intensities. Sirdeshmukh *et al* [9] observed the effect of lattice strains on the Debye-Waller factors in semiconductor powder materials. Gopi

Krishna and Sirdeshmukh [10] studied the effect of lattice strains on the Debye-Waller factor of ytterbium metal. Gopi Krishna et al [11] studied the effect of lattice strains on the Debye-Waller factor of Mg, Zn and Cd for slow grinding in an agate mortar. In the present investigation the results of a systematic study of the effect of particle size and lattice strains on the Debye-Waller factors of hexagonal Cd metal powder is reported using ball mill.

2. Experimental

The powder samples were obtained by gently filing highly pure Mg metal ingots with a jeweller's file. A part of this powder was used to prepare the initial sample. The remaining powder was subjected to milling in a high emerged ball mill for 2, 4, 6 and 10 hours to produce strains and decrease particle size. X-ray diffractograms were recorded with the initial sample and with samples prepared after each spell of milling. The diffractograms were obtained with a Philips CWU 3710 X-ray powder diffractometer in the 2θ range 20 - 120° using filtered CuK$_\alpha$ at a goniometer speed of 0.5° per minute and a chart speed of 20 mm/min. All measurements were made at room temperature.

Figure 1: The X-Ray Diffraction patern of Cd powder is given in Figure 1 for initial sample. The observed integrated intensities have been corrected for thermal diffuse scattering using the method of Chipman and Paskin [12].

3. Analysis of Data

The procedure for the determination of directional mean-square amplitudes of vibration $< u_{\parallel}^2 >$ and $< u_{\perp}^2 >$ from the intensity data and the estimation of associated errors is as discussed by Gopi Krishna et al [13]. The average mean square amplitude $<u_{av}^2>$ can be obtained from the relation,

$$< u_{av}^2 > = 1/3 (< u_{\parallel}^2 > + 2 < u_{\perp}^2 >) \quad (1)$$

And the directional Debye-Waller factors $B_{\perp}$ and $B_{\parallel}$ were obtained from the equations

$$\left. \begin{array}{l} B_{\perp} = 8\pi^2 < u_{\perp}^2 > \\ B_{\parallel} = 8\pi^2 < u_{\parallel}^2 > \end{array} \right\} \quad (2)$$

The mean Debye-Waller factor B is given by

$$B = (2B_{\perp} + B_{\parallel}) /3$$

The directional Debye temperatures $\theta_{\perp}$, $\theta_{\parallel}$ and mean Debye temperature θ_M were obtained from $B_{\perp}$, $B_{\parallel}$ and B, respectively using the Debye-Waller theory [14] relation,

$$\left. \begin{array}{l} B = (6h^2 /M k_B \theta_M) W(X) \\ B_{\perp} = (6h^2 /M k_B \theta_{\perp}) W(X) \\ B = (6h^2 /M k_B \theta_{\parallel}) W(X) \end{array} \right\} \quad (3)$$

Where h is the Planck's constant, k_B the Boltzmann constant, M the atomic weight. The function W(X) is given by

$$W(X) = [\phi(X)/X + (1/4)] \quad (4)$$

where $X= \theta_M/T$, T is the temperature of the crystal and $\phi(X)$ is the Debye function. The values of W(X) for a wide range of X can be obtained from standard tables [15].

Lattice strain and Particle size determination

When the size of the individual crystals is less than about 100nm the term "particle size" is usually used. When the crystallites of a material are smaller than 100nm, they have too small a number of parallel diffraction planes and so they produce broadened diffraction peaks instead of a sharp peak. Lattice strain present in the sample is another cause of broadening of Bragg diffraction peaks. In addition to this, there are instrumental factors such as unresolved α_1 and α_2 peaks, imperfect focusing which lead to the line broadening. There are various methods in practice to estimate the particle size. X-ray diffraction is a simpler and easier approach for the determination of precise particle size and the lattice strain in powder samples. The principle involved in the X-ray diffraction approach is precise quantification of the broadening of the Bragg diffraction peaks. Scherrer equation, Hall-Williamson method and Warren-Averbach method are some of the techniques based on this principle. Of the above methods, Scherrer equation method for the estimation of particle size does not take into account the broadening due to lattice strain present in the sample. As such in the present investigation, the lattice strains have been estimated using Hall-Williamson method. Recently, Bharati et al [16] have used this method to estimate the lattice strain and particle sizes of silver nano particles and composite silver nano particles. In this method the integral breadth of the diffraction peak is determined. The integral breadth is given by the integrated intensity divided by the maximum intensity. Thus, the observed peak broadening B_o may be represented as

$$B_o = B_i + B_r \quad (5)$$

where B_o is the observed peak broadening in radians, B_i is the instrumental broadening in radians and B_r is the broadening due to the small particle size and lattice strain. The instrumental broadening has been estimated using a pure strain-free fine sodium chloride powder sample subjected to XRD under identical conditions as those for the strained metallic powders. Eq. (5) holds good if the diffraction peaks exhibit purely Cauchy profile. However, when the diffraction peaks are partly Cauchy and partly Gaussian for profiles, the following relation between B_o, B_i and B_r holds good, Bharati et al [16].

$$B_r = [(B_o - B_i) (B_o^2 - B_i^2)^{1/2}]^{1/2} \quad (6)$$

Now, according to Scherrer equation, the broadening due to small particle size may be expressed as

$$B_c = \frac{k\lambda}{t} \cos\theta \quad (7)$$

where B_c is the broadening solely due to small crystallite size, K a constant whose value depends on particle shape and usually taken as unity, t the crystallite size in nanometers, θ the Bragg angle and λ is the wavelength of incident X-ray beam in nanometers. Similarly, according to Wilson [17], the broadening due to lattice strain may be expressed by the relation,

$$B_s = \varepsilon \tan\theta \quad (8)$$

where B_s is the peak broadening due to lattice strain and ε the strain distribution within the material and θ is the Bragg angle. Based on Eqs. (7) and (8) the total peak broadening B_r may be expressed as,

$$B_r = \frac{k\lambda}{t\cos\theta} + \varepsilon \tan\theta \quad (9)$$

which can be written as

$$B_r\cos\theta = \frac{k\lambda}{t} + \varepsilon \sin\theta \quad (10)$$

Figure 2: The plot of $B_r \cos\theta/\lambda$ versus $\sin\theta/\lambda$ is a straight line with slope equal to ε and hence the particle size 't' can be estimated from the intercept. Typical Hall-Williamson plot between $B_r\cos\theta/\lambda$ and $\sin\theta/\lambda$ is shown in Figure 2.
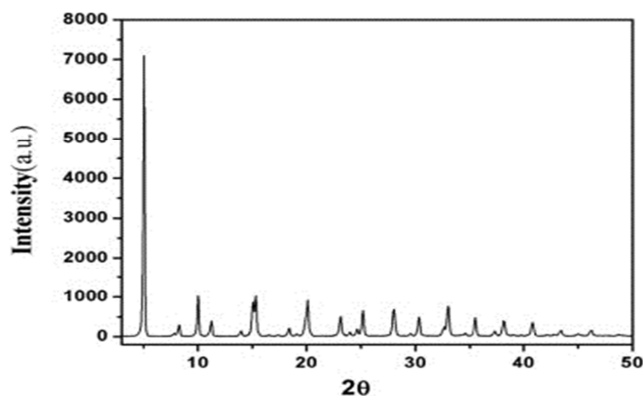
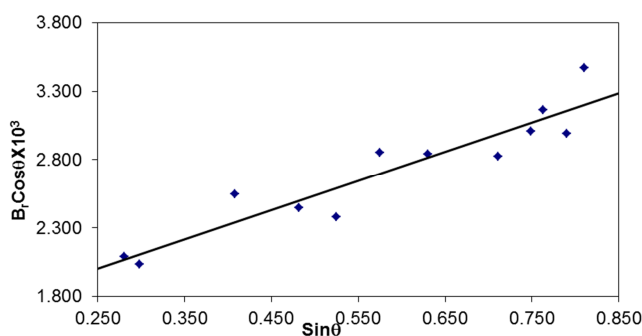**Figure 1.** *The X- Ray Diffraction patern of* Cd *powder for initial sample.*

Figure 2. *Plot of $B_r cos\theta/\lambda$ Vs $sin\theta/\lambda$ for Cd after milling for 10 hours.*

The lattice strains were determined from the plot of $B_r cos\theta/\lambda$ against $sin\theta/\lambda$ following standard procedures [18]. The measured half-widths were corrected for instrumental broadening with reference to a pure strain-free silicon powder. The variation of particle size with milling time is within the limits of experimental errors. This shows that while the milling is enough to create strains, it affect the particle size to a measurable extent. A typical Hall-Williamson plot is shown in Figure 2 for Cd after milling for 20 hours.

4. Results and Discussion

Table 1: The values of the particle size, lattice strain, root mean square amplitude of vibrations, Debye-Waller factor and Debye temperature of Cd powders, ground for different durations, obtained in the present study are given in Table 1. Although, values of Deby-Waller factor, amplitude of vibration and Debye temperature in the 'a' and 'c' directions have been determined separately, the average values of these quantities are given in Table 1. as the objective of the present work is to investigate the strain dependence of Debye-Waller factors. Debye-Waller factor Cd powder sample carries an effect due to lattice strain. While comparing the Debye-Waller factors calculated from the lattice dynamical models with experimental results Vetelino et al [19] have attributed the difference to inaccuracies in the experimental values caused by neglecting the TDS corrections. The repeated milling of the powder sample leads to lattice distortion which gives rise to microstrains in the lattice. These microstrains increase the contribution of static component of Debye-

Waller factor. Thus both lattice strain and the observed Debye-Waller factor, which is the sum of static and thermal components, increase with grinding time. Thus, whenever Debye-Waller factors are determined from X-ray intensities on powder samples, it is desirable, to make an estimate of the lattice strain and if the strain is large, a suitable correction is to be made as in the present study.

Glyde [20] derived the following relation between the energy of vacancy formation (E_f) and the Debye temperature (θ) of a solid. The relation is

$$E_f = A(k/\hbar)2 \ M\theta 2 a 2 \qquad (11)$$

where a is the interatomic spacing, A a constant shown to be equal to 1.17×10^{-2}, M the molecular weight and h and k are the Plank's and the Boltzmann's constants, respectively. Glyde recommended the use of X-ray based values in eq. (11). The validity of eq. (11) was verified for a number of fcc, bcc and hcp metals [21]. Therefore, the X-ray Debye temperatures obtained in the present work have been used to study the variation of vacancy formation energy as a function of lattice strain in Mg. The values of vacancy formation energies are also included in Table 1.

Table 1. *Values of particle size (t), lattice strain (ε), mean Debye-Waller factor (B), root mean square amplitudes of vibration <uav> and mean Debye temperature (θM) of strained nzno Cd powder.*

Metal	Milling time(hrs)	$\varepsilon \times 10^3$	t(nm)	u_{av}(Å)	B_{av}(Å²)	θ_M(K)
Cd	0	1.19	190	0.150	1.80	144
	2	1.45	160	0.122	1.81	142
	4	1.72	130	0.144	1.84	140
	6	2.00	69	0.171	2.21	126
	10	2.99	60	0.164	1.91	136

5. Conclusion

Cd powder was strained by milling for 25 hours. From a study of X-ray diffractograms recorded at different stages of milling, it is observed that milling for 25 hours has systematic effect on the particle size. However, the milling produces lattice strain and also enhances the effective Debye-Waller factor.

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