Characterization Of Size Dependent Thermal Properties In Strained Nanocrystalline Powder Using Williamson–Hall Method

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Abstract. In this present investigation Williamson–Hall technique has been used for the size dependent thermal properties are crystallite size, effect of strain on the Debye Waller factors, root mean square amplitudes of vibrations and Debye temperatures of nickel nanoparticles. The ball milled nanopowders has been characterized by X-ray diffraction method. The values of the crystallite size and strain obtained from the Williamson-Hall method to the experimental data were reasonable. The ball milling time increased with decreasing particle size, Debye temperature, vacancy formation energy and increasing strain, mean square amplitudes of vibrations and Debye-Waller factor for the nickel sample. The change in lattice strain particle size of the samples was explained by Williamson-Hall method. All the thermal properties of nickel nanoparticles were explained more precisely using Williamson-Hall plots, and also milling time versus thermal properties plots. The results calculated were approximately similar with the standard values.

1. Introduction
Due to their appealing electronic, optical, and thermal properties; metal nanoparticles have developed with incredible enthusiasm, just as reactant properties, in the fields of material science, science, science, medication, material science and some interdisciplinary fields. Gold is delicate, pliable and the most pliant of metals, Ag is somewhat harder than gold and is bendable and moldable. An exact estimation of grain size/crystallite size becomes fundamental when such materials are created with their crystallite size of the request for under 100 nm. Despite the fact that Transmission Electron Microscope (TEM) is one of the incredible procedures for crystallite size estimation, it has certain confinements. Since TEM pictures speak to just a nearby area, numerous examples and pictures are required to give a normal data to the whole example. Not just this, the TEM test readiness strategy is an included and tedious one. The XRD procedure is liberated from these constraints. X-beam diffraction is, then again, a straightforward and easier approach for assurance of crystallite size of powder tests. Nanocrystalline precious materials with crystallite size of a couple of nanometers have been the enthusiasm of prior researchers [1, 3]. Nanocrystalline nickel has pulled in much consideration because of its business significance and specific properties [4, 5]. There are various strategies for creating nanocrystallite materials. High-vitality mechanical processing is one of these.
methods. In this procedure, nanometer estimated grain structures can be gotten in metals, composites and earthenware production, after adequate processing time [6,8]. The result of processing and arrangement system rely upon different boundaries especially substance organization and kind of powders [9]. In this paper, Ni nanocrystallite powder was incorporated by ball processing and the impact of cross section strain on the Debye-Waller factor was examined. There is impressive X-beam chip away at the Debye-Waller variables of Ni [10], yet it is fascinating to consider the impact of cross section strains on the Debye-Waller elements of this metal. The fragility of tungsten may prompt helpless warm stun obstruction when presented to incredibly high cyclic warming. Influence of Tool Revolving on Mechanical Properties of certain metals and combinations [11, 12] had been created as cutting edge designing creation and with some warm and mechanical properties and building applications [13,14]. In this investigation Williamson–Hall procedure has been utilized for the size ward warm properties of molecule size, impact of cross section strain on the Debye Waller components and Debye temperatures of nickel nanoparticles.

2. Experimental Procedures
Fine powder samples were acquired by delicately documenting profoundly unadulterated nickel metal ingots using jeweller’s files; it was utilized as the underlying example it was taken zero hours. The rest of the powder was exposed to processing in a high-vitality ball mill (Model: Retsch, PM 100) for ball milling time 4, 8, 12, 16, 20, 24, 28 and 32 hours to deliver strains and lessening the crystallite/particle size in a ball plant steel chamber utilizing zirconium and tungsten carbide balls/wads of 10 and 3 mm Φ ball estimates separately. The XRD patters of nickel samples/tests, the diffractograms were recorded by using Philips CWU X-ray powder diffractometer in the 2θ territory 20 - 120° utilizing sifted CuKα. The XRD patterns of nickel diffractograms were given in Figure1. By utilizing the strategy for Chipman and Paskin [15] method and the watched incorporated powers have been rectified for thermal diffuse dispersing.

![Figure 1. The XRD patterns of Ni powder of for different (0, 4, 8, 12, 16, 20, 24, 28 and 32 hours) milling times.](image-url)
3. Analysis of Data

Nickel element belongs to face-centered cubic structure. The observed intensity $I_0$ is

$$I_0 = CLJF^2$$  \(1\)

Where: $L$ - Lorentz-polarization factor, $J$ - multiplicity factor, $F_T$ - structure factor and $C$ - Constant. The structure factor $F_T$ is given by

$$F_T = Fe^M$$  \(2\)

Where $F$ is the structure factor for the static lattice

We may also write Eq. (1) as

$$I_0 = I_c e^{-2B \left( \frac{\sin \theta}{\lambda} \right)^2}$$  \(3\)

The intensity $I_c$ corresponding to the static lattice is

$$I_c = LpJF^2$$  \(4\)

For crystals with face-centered cubic structure, the structure factor $F$ is

$$F = 4f$$  \(5\)

Where, $f$ - atomic scattering factor

According to Equation (3) it has been observed that $\log \left(\frac{I_0}{I_c}\right)$ is linearly connected to $\left(\sin \frac{\theta}{\lambda}\right)^2$.

By utilizing a least square treatment of the given data, Debye-Waller factor have been measured.

According to Debye-Waller theory $B$ is

$$B = \left( \frac{8\pi^2}{3} \right) <u^2>$$  \(6\)

We can be observed here, $<u^2>$ : mean-square amplitude of vibration and $<u>$ : root mean-square amplitude of vibration.

Further, $B$, can also be articulated as

$$B = \left( \frac{6h^2}{mk_BT} \right) W(x)$$  \(7\)

The function $W(x)$ is written as

$$W(x) = \left[ \frac{\phi(x)}{x^2 + \frac{1}{4x}} \right]$$  \(8\)

Where, $\phi(x)$ being the Debye function and $x = \theta_M/T$, $\theta_M$ is the Debye temperature. The Debye temperature is

$$\theta_M = xT$$  \(9\)

4. Results and discussion

The evaluation of crystallite size has been made after Hall-Williamson technique. In the current work, the crystallite size has been dictated by estimating the incorporated widths of the diffraction tops instead of half-widths. In the wake of dispensing with the instrumental widening impacts, crystallite/grain size ($D$) and strain ($J$) have been resolved utilizing the accompanying conditions,

$$B_r = \frac{k\lambda}{D\cos\theta} + J \tan\theta$$  \(10\)

which can be written as

$$B_r \cos\theta = \frac{k\lambda}{D} + J \sin\theta$$  \(11\)
Where, $B_r$ is peak broadening because of crystallite size, strain and $k$ is the shape factor typically taken as 1.0 and $D$ the crystallite size in nanometers. The crystallite size has additionally been evaluated by Scherer condition. Typical Williamson-Hall plot has been appeared in Figure 2.

\[ B_r \cos \theta / \lambda \text{ versus } \sin \theta / \lambda \]

Figure 2. Williamson-Hall plot of $B_r \cos \theta / \lambda$ versus $\sin \theta / \lambda$ for Ni after milling for 24 hours.

The vacancy formation energy is

\[ E_f = A(k/\hbar)^2 M \theta^2 a^2 \]  \hspace{1cm} (12)

Where, $a$ being the interatomic spacing, the constant $A = 1.17 \times 10^{-2}$.

Since, in the current work, the Ni strained nanoparticles have been set up by high-vitality ball processing, the plastic disfigurement delivered by processing offers ascend to changes in the molecule size of nano-powders. It has determined and seen that the estimations of molecule size in all the distinctive processing time are less from Scherrer condition than the qualities got from Williamson-Hall technique. It is because of the way that the Scherrer condition doesn't consider the impacts of cross section strain. This prompts underestimation of crystallite size. Henceforth, in the entirety of our further computations the molecule size qualities got from Williamson-Hall technique have been measured. The estimations of impact of cross section strain ($D$) on the Debye-Waller factor ($B$), Debye temperature ($\theta_M$), mean square amplitudes of vibration ($<u^2>$) and vitality of arrangement ($E_f$) of Ni with various crystallite sizes got in the current work are summed up in Table 1.

**Table 1. Thermal properties values of strained Nickel nano powders.**

| Material | Ball milling time (in Hours) | Lattice strain $D \times 10^3$ | Particle size $J$(nm) | $<u^2>$($\AA^2$) | $B$(Å$^2$) | $\theta_M$(K) | $E_f$(eV) |
|----------|-----------------------------|-------------------------------|-----------------------|-----------------|-----------|-------------|-----------|
| Ni       | 0                           | 1.106                         | 245.3                 | 0.0051(6)       | 0.41(2)   | 385(8)     | 2.31      |
|          | 4                           | 1.889                         | 194.4                 | 0.0056(5)       | 0.45(4)   | 371(6)     | 2.12      |
|          | 8                           | 2.276                         | 73.5                  | 0.0061(3)       | 0.47(1)   | 355(3)     | 1.93      |
|          | 12                          | 2.849                         | 46.2                  | 0.0065(8)       | 0.50(4)   | 346(7)     | 1.82      |
|          | 16                          | 3.417                         | 37.4                  | 0.0070(9)       | 0.56(3)   | 331(6)     | 1.69      |
|          | 20                          | 4.056                         | 35.3                  | 0.0075(6)       | 0.58(7)   | 322(8)     | 1.58      |
|          | 24                          | 4.112                         | 34.8                  | 0.0077(5)       | 0.59(2)   | 321(6)     | 1.49      |
Where D: lattice strain, J: crystallite size, B: Debye-Waller factor, \( <u^2> \): mean square amplitudes of vibration, \( \theta_M \): Debye temperature and \( E_f \): energy of vacancy formation.

It can be observed from Table 1 that the particle size progressively decreases in every case with increasing ball mill time. The distinction of crystallite size with ball milling time has been given in Figure 4 and observed from Table 1 that the characteristic Debye temperature decreases as the particle size decreases. Consider the spherical shape for the particles. Ball milling time increases, Lattice strain (D), root mean square amplitudes of vibration (\( <u^2> \)), Debye-Waller factor increases [6, 8] and particle size (J), Debye temperature (\( \theta_M \)), vacancy formation energy (\( E_f \)) decreases.

The Debye-Waller factors and the Debye temperatures of several crystals belonging to different structures have been determined from a measurement of the X-ray diffraction intensities. A bibliography of the reports on the determination of the Debye-Waller factors, Debye temperatures and amplitudes of vibration by the X-ray method is compiled in Table 2 for Ni metal with the face-centered cubic structure. The results from these reports have been included wherever possible. The data pertain mostly to room temperature results. Reports which were not explicitly aimed at the determination of the Debye-Waller factors or Debye temperatures, but, in which such information is obtained as byproduct have also been included. While an effort has been made to make a comprehensive survey of the available reports, no claim is made regarding the completeness of this bibliography. Bibliography on the determination of the Debye-Waller factors and Debye temperatures of face-centered cubic structure of Nickel (Ni) metal for different methods has been summarized in Table 2.

**Table 2. Bibliography on the determination of the Debye-Waller factors and Debye temperatures of face-centered cubic structure Nickel (Ni) metal**

| Element | Method | B (Å\(^2\)) | \( \theta \) (K) | Reference |
|---------|--------|-------------|----------------|-----------|
| Ni      | X-ray diffraction | 0.41 | 380 | Brindley and Spiers [16] (1935) |
|         | X-ray diffraction | 0.41 | - | Brindley [17] (1936) |
|         | X-ray diffraction | 0.40 | 390 | Ageev and Guseva [18] (1948) |
|         | Powder X-ray diffraction | - | 350 | Ilyina and Kristskaya [19] (1955) |
|         | Powder X-ray diffraction | - | 431 | Zhuravlev and Katsnel’son [20] (1959) |
|         | Powder X-ray diffraction | - | 405 | Simerska [21] (1962) |
|         | X-ray diffraction | 0.41 | - | Inkinen and Suortti [22] (1964) |
|         | Single Crystal X-ray diffraction (SCX) | - | 410 | Wilson et al [23] (1966) |
|         | Powder Neutron diffraction (PN) | 0.42 | - | Cooper and Taylor [24] (1969) |
|         | Electron diffraction | 0.42 | 390 | Arii and Uyeda [25] (1973) |
|         | Powder X-ray diffraction (PX) | - | 397 | Paakkari [26] (1974) |
|         | Powder Neutron diffraction (PN) | 0.34 | - | Windsor and Sinclair [27] (1976) |
The Present work Debye-Waller factor $B = 0.41 \, \text{Å}^2$ and Debye temperature $\theta_M = 385 \, \text{K}$ values have been agreed well with the previous values [16 - 23] and other methods [24 - 39]. High vitality ball milling process is a perceived strategy for creating nanocrystalline metal powders. During the technique for Ball processing, because of the plastic twisting of the powder particles, huge grid strains are likewise brought into the powder particles. The variety of cross section strain with processing time for Ni in diagrams. These grid strains in nanopowders cause static uprooting of molecules in the cross section offering ascend to static part of the Debye-Waller factor. The static part of the Debye-Waller factor increments with processing time. Therefore, the deliberate estimations of Debye-Waller components of particles arranged by ball processing increment quicker than the relating strain free particles as the molecule size abatements. Processing time bit by bit expands the variety of cross section strain, molecule size, root mean square sufficiency of vibrations, Debye-Waller factor, Debye temperature and vitality of opportunity arrangement bends have been appeared in Figure 3.

As ball milling time increases,

- Lattice strain also increases from $1.106 \times 10^3$ to $4.346 \times 10^3$ for zero and 32 hours respectively as shown in figure 4 (Milling time versus lattice strain with non-linear curve).

- Particle size, decreases from $J = 245.3 \, \text{nm}$ to $30.4 \, \text{nm}$ for zero and 32 hours respectively.

- RMS amplitudes of vibration increases from $\langle u^2 \rangle = 0.0051 \, \text{Å}^2$ to $0.0079 \, \text{Å}^2$ and Debye-Waller factor also increases from $B = 0.41 \, \text{Å}^2$ to $0.61 \, \text{Å}^2$ for zero and 32 hours respectively as shown in figure 4.

- Debye temperature and energy of vacancy formation decreases from $\theta_M = 385 \, \text{K}$ to $319 \, \text{K}$ and $E_f = 2.31 \, \text{eV}$ to $1.41 \, \text{eV}$ for zero and 32 hours respectively as shown in figure 4.
Figure 3. Milling time versus lattice strain, particle size, rms amplitude of vibrations, Debye-Waller factor, Debye temperature and energy of vacancy formation curves for nickel (Ni).

The variation of lattice strain with respect to particle size, Debye-Waller factor, rms amplitude of vibrations and Debye temperature for nickel element have been shown in Figure 4. The variation of particle size with respect to rms amplitude of vibrations, Debye-Waller factor and Debye temperature for nickel element has been shown in Figure 6. From the following curves, article size versus RMS amplitudes of vibration and Debye-Waller factor have been observed that both the curves are similar curves with different values, the main reason is that the effect of RMS amplitudes of vibration and Debye—Waller factor in both the graphs are gradually increases with gradual decrease of particle size. But the effect of Debye temperature and energy of vacancy formation in both the graphs are gradually decreases with gradual decrease of particle size in Particle size versus Debye temperature and energy of vacancy formation for nickel (Ni).

Figure 4. Lattice strain versus particle size, Debye-Waller factor, rms amplitude of vibrations and Debye temperature for nickel (Ni)
The increase in the estimation of Debye-Waller factor causes an abatement in the estimation of Debye temperature and henceforth, in the current works the decrease in the estimations of Debye temperature as appeared in Figure 5.

Figure 5. Particle size versus rms amplitude of vibrations, Debye-Waller factor, Debye temperature and energy of vacancy formation for nickel (Ni).

4. Conclusion
The ball milling process is a perceived strategy for delivering nanocrystalline metal powders. During the strategy for Ball milling process, because of the plastic disfigurement of the strained nanoparticles, huge cross section strains are likewise brought into the powder nanoparticles. The lattice strains in strained nanopowder cause static uprooting of iotas in the grid offering ascend to static part of the Debye-Waller factor. The static segment of the Debye-Waller factor increase with increase of ball mill time. Therefore, the deliberate estimations of Debye-Waller variables of particles arranged by ball processing increment quicker than the relating strain free particles as the molecule size abatements. The expansion in the estimation of Debye-Waller factor causes an abatement in the estimation of Debye temperature. The lower esteems for $s$ in the current work additionally appear to be because of the nearness of huge strains in the nanoparticles delivered by ball plant. Nickel powder has been set up by ball processing for 32 hours, it has been seen that ball milling process for 32 hours has likewise methodical impact of strain on the Debye-Waller factor, Debye temperature and mean amplitudes of vibration and vitality of opportunity development has been gotten and read for Ni metal.

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