

# Microstructural Characterization of Nickel Nanoparticles Synthesized using Mechanical Milling

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## ABSTRACT

This paper presents microstructural characterization of nickel nano-particles synthesized by mechanical milling under wet environment. The structure and morphology of nickel powder were characterized by XRD and SEM. An attempt was made to approximate the milling time to obtain nano-sized nickel particles from the feedstock micron-sized nickel powder. The milling was done at 300 rpm, ball-to-powder ratio of 10:1 and running time-to-pause time ratio as 30:15. The crystallite size and internal strain were evaluated from XRD using Scherrer and Williamson-Hall methods. The particle size of synthesized powder was evaluated using particle size analyser. It was found that with the increase in milling time crystallite size decreased. After 60 hours of milling particle size was found to be 67 nm.

**Keywords:** Mechanical milling, nano-particles, ball-to-powder ratio, particle size.

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## 1. INTRODUCTION

Nickel nanoparticles has attracted an increasing interest in the field of nanotechnology because of its unique properties like wear, erosion and corrosion resistance, low coefficient of friction, high hardness and good thermal conductivity. Due to these properties nickel finds numerous applications in material processing. As a matter of fact, nickel is one of the most widely used elements in alloy manufacture. Micron-sized nickel powders are frequently considered for surface engineering applications such as corrosion resistance and wear resistance. It is established that the attractive properties of nickel powders can be enhanced tremendously if they can be used in nano-size particle size distribution, instead of micron-size. However the synthesis of nickel in nano-size is a challenge, especially with regard to its demand in bulk amounts.

Mechanical milling has been widely used for the synthesis of micron-sized, as well as, nano-sized powders of a wide range of metals, alloys and compounds [1-3]. Several studies have shown that various milling parameters such as milling speed, running time, pause time, milling speed and media like dry, wet or inert have strong influence on the final crystal size of the feed stock without any phase transformations [4-7]. The nano-particles are formed in a wet environment using high speed ball mills in which energy is imparted to a coarse-grained material through impact force to reduce the particle size. The unique feature of mechanical milling is that “top down” approach is followed while milling larger crystal size particles to smaller ones [8-12]. The particles themselves, which normally possess a distribution of sizes, can be “nano-particles” if their average crystal size is less than 100 nm [13]. In this work, the nickel nano-particles were synthesized in bulk using mechanical milling. Subsequently, the crystallite size and internal strain analysis of particles was carried out using Williamson-Hall and Scherrer methods. Further morphology studies were done and particle size was found using particle size analyzer.

## 2. EXPERIMENTAL

### 2.1 Sample preparation

The nano-particles of nickel were prepared from a commercial nickel powder (99.9%) purchased from Sigma Aldrich (USA). A 10 g of nickel powder was taken in the tungsten carbide bowl of Fritsch, P-7 (premium line) planetary ball mill.

The balls made of tungsten carbide having diameter 5 mm were then mixed in the bowl maintaining ball-to-powder ratio of 10:1 by weight. Toluene (S-d fine chemicals, India) was then added to the bowl in a quantity so as to just wet the powder. Toluene acts as a process control agent which stops the agglomeration of the particles with each other. The speed of ball mill was fixed at 300 rpm and running time-to-pause time ratio as 30:15 minutes [14-24].

## 2.2 Structural characterization

The powder was characterized by X-ray diffraction (XRD) analysis using PANalytical X'Pert-Pro machine, equipped with Cu-K $\alpha$  radiation ( $\lambda=1.5418 \text{ \AA}$ ), by taking small amount of powder after every 5 hour upto 60 hours of milling time so as to approximate the particle size from the broadening of X-ray peaks [25-29]. In order to obtain crystallite size and internal strains (which contribute in peak broadening as the milling time was increased), the Williamson-Hall and Scherrer's formulae were used [30]. The Williamson-Hall method consists of two steps:

**Step 1:** The width ( $B_o$ ) of each peak was measured as the observed width. The width due to instrumental effects ( $B_i$ ) was determined from the Si source. The remaining peak width  $B_r$  is calculated according to the Gaussian profile.

$$B_r^2 = B_o^2 - B_i^2$$

**Step 2:** The width  $B_r$  of the diffraction peak after subtracting the instrumental effect can now be considered as the sum of widths due to small crystallite sizes and lattice strains:

$$B_r = B_{crystallite} + B_{strain}$$

$$B_{crystallite} = k \lambda / L \cos \theta \quad (\text{from Scherrer's formula})$$

$$B_{strain} = \eta \tan \theta$$

where  $k$  – constant whose value is 0.9 ;  $\lambda$  – wavelength corresponding to Cu source used in XRD, value is 1.54  $\text{\AA}$ ;  
 $L$  – crystallite size;  $\eta$  – strain;  $\theta$  – angle corresponding to particular peak.

$$B_r = k \lambda / L \cos \theta + \eta \tan \theta$$

$$B_r \cos \theta = k \lambda / L + \eta \sin \theta \text{ is known as Williamson-Hall equation.}$$

Table 1 shows the calculated values  $B_r \cos \theta$  and  $\sin \theta$  for the given samples.

**Table 1. List of spectral width of different Bragg peaks of nickel after 60 hours of ball milling**

Peak	Peak position ( $2\theta$ )	Width due to instrumental effect ( $B_i$ )	Observed width ( $B_o$ )	$B_r = \sqrt{B_o^2 - B_i^2}$	$B_r$ (rad.)	$B_r \cos \theta$ (rad.)	$\sin \theta$
1	44.05°	0.0757°	0.96°	0.8843°	0.01543	0.01430	0.37
2	51.25°	0.0819°	1.42°	1.3381°	0.02335	0.02335	0.43
3	75.60°	0.0940°	1.69°	1.5960°	0.02785	0.02785	0.61
4	91.81°	0.1170°	2.20°	2.0830°	0.03635	0.03635	0.72

Morphology changes in the particles were studied using scanning electron microscopy (Make JEOL, Model JSM-6610LV). After 60 hours of milling the powder was characterized using particle size analyser (Make Nikkiso, Model Nanotract Ultra).

## 3. RESULTS AND DISCUSSION

### 3.1 XRD analysis of nickel powder

Continuous efforts to study the formation of nano-particles using planetary ball mill were made by analyzing the XRD patterns after different milling hours (0, 20, 40, 60 h). The corresponding XRD profiles are shown in Fig. 1. It is clear from the analysis that no oxidation of the nickel took place during the milling process, which is a positive attribute. It can also be easily seen that the diffraction peaks of nickel decrease, as well as, broaden with the increase in milling time. It is well known phenomenon that peak broadening with increasing milling time is due to reduction in crystallite size and increase in lattice strain. The physical broadening of the peaks of milled samples at 0, 20, 40, 60 h are presented in Fig. 2, whereas the variation of crystallite size with milling time is plotted in Fig 3. Four peaks were used for broadening analysis in the scan

range of 40 - 100°. The Williamson-Hall plot for the sample after 60 h of milling is shown in Fig. 4. The crystallite size was found using Scherrer method and the lattice strain (<1%) found using Williamson-Hall method. The crystallite size was found to be 8.92 nm after 60 h of milling and the particle size was found to be 67 nm which is well qualified to be designated as a nanoparticle.

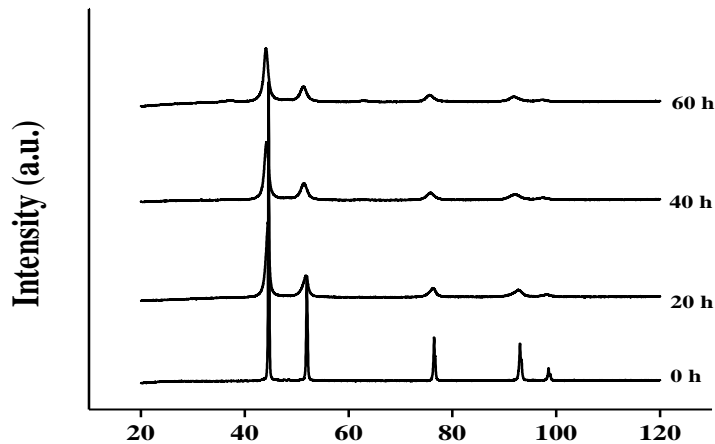


Fig. 1 X-ray diffraction of nickel particles after different hours of wet ball milling

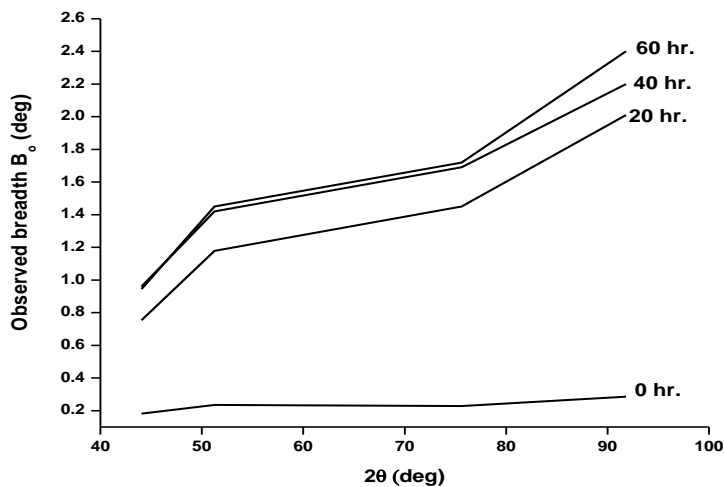


Fig. 2 Change in observed breadth of samples milled at different milling time

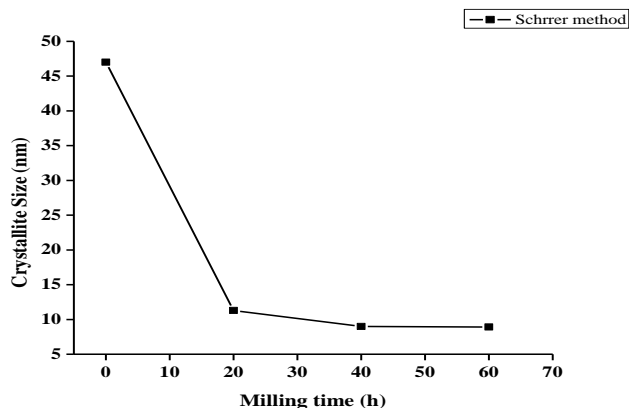


Fig. 3 Variation of crystallite size with milling time using Scherrer method

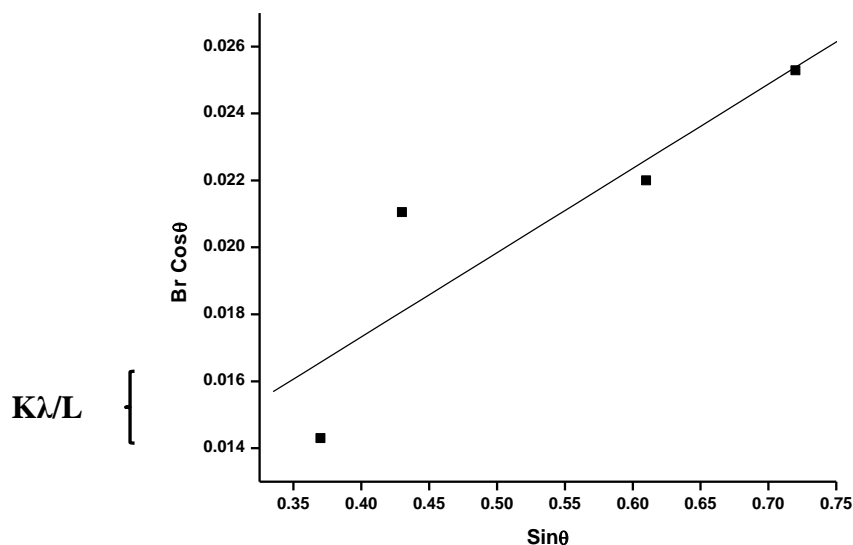
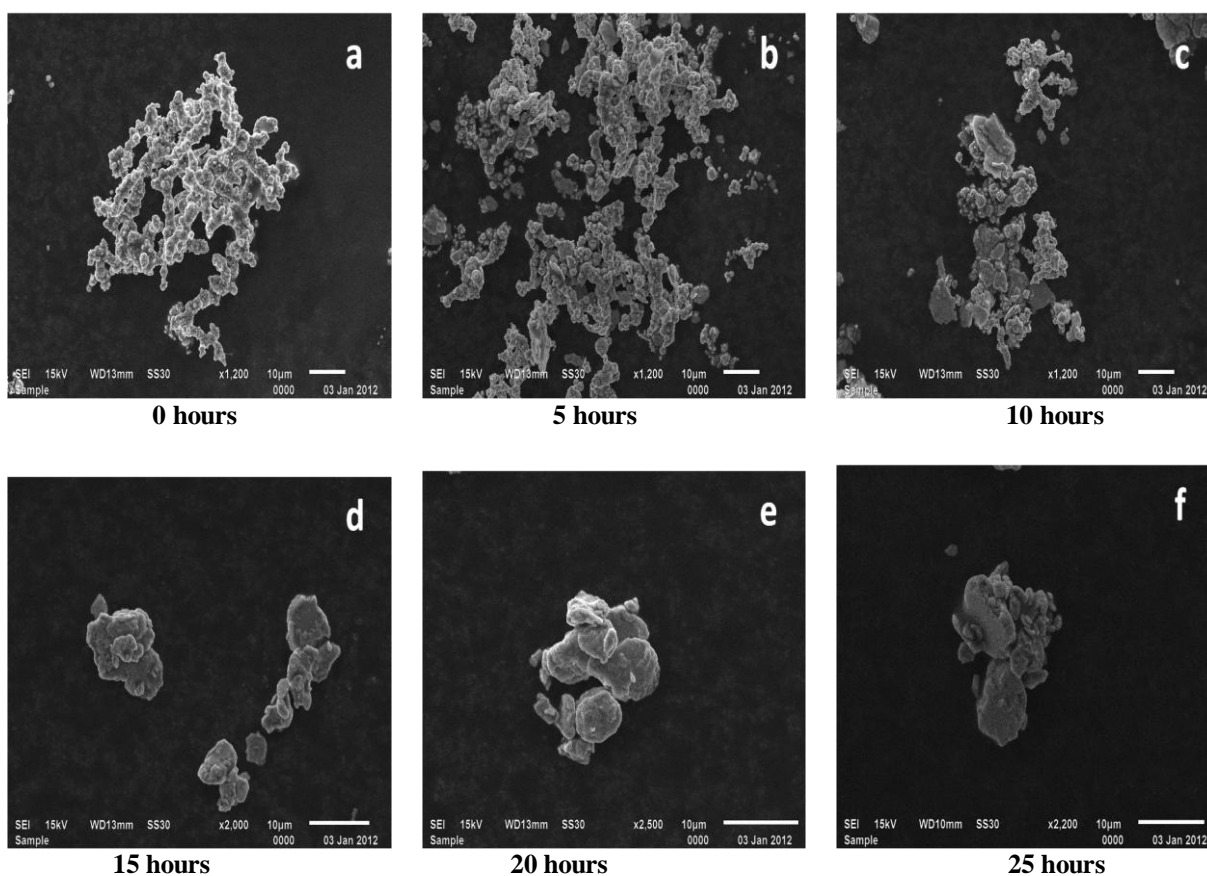
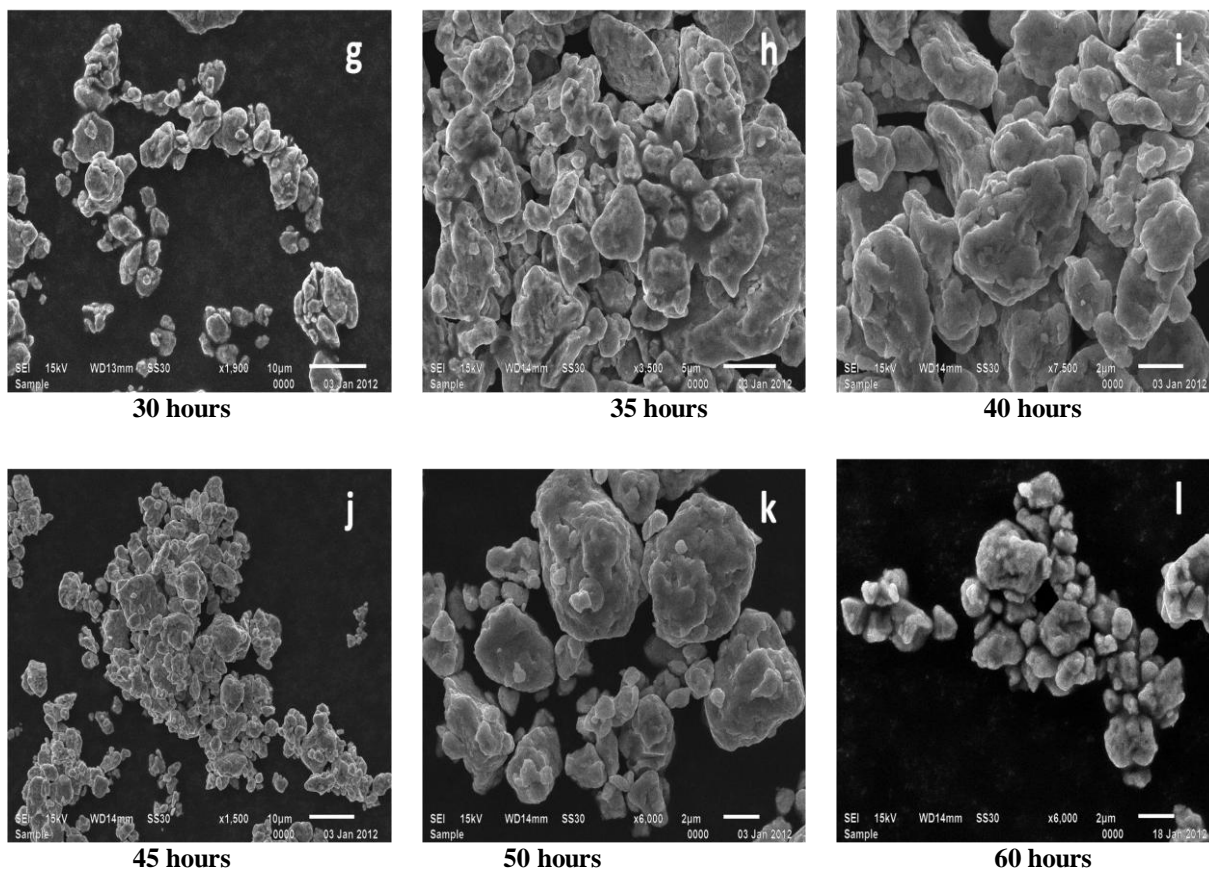


Fig. 4 Williamson-Hall plot showing X-ray peak broadening (B) as a function of Bragg angle ( $\theta$ ) for the sample milled at 60 h

### 3.2 SEM analysis of nickel powder

Scanning electron micrographs of the nickel powder after different time intervals of milling show changes in the morphology and size of the nickel particles, as is clear from Fig. 5 a - f. The SEM image of Fig. 5(a) reveals an angular morphology for the pure nickel (99.9%) having particle size 5  $\mu\text{m}$ . After 35 hours of milling (Fig.3 b-h) the average particle size of 2  $\mu\text{m}$  is obtained. On further milling upto 60 hours, Fig. 5(f), average particle size less than 100 nm is achieved.

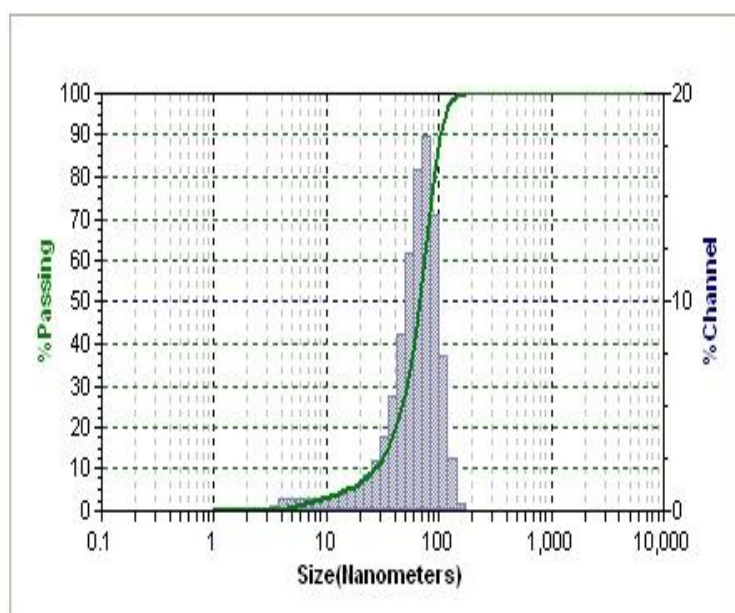




**Fig. 5 SEM micrographs of nickel particles after different hours of wet ball milling**

### 3.3 Particle size analyser

Finally the particle size distribution of nickel particles was calculated using particle size analyser based on the dynamic light scattering principle, after 60 h of milling, which shows the average particle size of 67 nm as shown in Fig. 6.



**Fig. 6 Particle size distribution of nickel nanoparticles**

## CONCLUSIONS

Mechanical milling was proved to be an effective, low cost and simple technique to produce nickel nano-particles. The influence of milling time to decrease crystallite size is calculated by Scherrer method and found to be 8.92 nm. The lattice strain was calculated using Williamson-Hall method. The particle size of nickel powder found to be 67 nm after 60 hours of milling, which was validated by particle size analyser.

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