Development and characterization of nanocrystalline cobalt powder prepared via high energy ball milling process

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Abstract. This work investigated the influence of varied milling time and ball-to-powder weight ratio (BPR) at constant milling speed on micron-sized cobalt powder. Stainless steel balls of 2, 3 and 4 mm diameter were used to prevent cold welding of the charged powders and increase the collision energy available. Powder processing was performed in an argon filled chamber to avoid contamination of the powder. Detailed X-ray diffraction (XRD) studies were carried out to evaluate the lattice strain, crystallite size and the planes at different peaks using Williamson-Hall method. The morphologies of the as-received and milled samples were investigated with scanning electron microscope equipped with energy-dispersive spectroscope (SEM/EDS). The results indicated that the lowest crystallite size and highest lattice strain of 9.05 nm and 3.74 % respectively was achieved for powders subjected to 12 hrs milling at constant BPR of 20:1. A constant milling time of 2 hrs and varied BPR also yielded a crystallite size of about 13.73 nm and lattice strain of 0.79 % at BPR of 10:1. The XRD results show the influence of this process on the diffraction width and peaks. Hence, varying the BPR at constant milling time helps to save time, conserve energy and guarantee the economy of the operation.

1. Introduction

Cobalt is viewed as a key raw material and an important metal in areas where high temperature properties, energy storage, process efficiency and environmental benefits are essential requirements. It is used in the fabrication of materials required for diverse applications, ranging from production of magnets, hard metals, superalloys and gas turbine components to the manufacturing of lithium-ion batteries and industrial catalysts [1]. Concerted efforts have been made by researchers to obtain nanoparticle materials from micrometer sized particles through high energy ball milling process [2, 3]. Nanoparticle materials possess enhanced properties which improve the performance of the resultant components in service. During mechanical milling/alloying, ball-powder-ball collision results in cold welding and fracturing of particles, leading to a reduction in crystallite size and introduction of lattice defects [4]. High energy ball milling process can either be mechanical alloying (MA) or mechanical milling (MM). MA is a process which involves milling together of powders of different metals, alloys or compounds. It results in materials transfer and formation of homogeneous alloy whereas MM is conducted on pure metals or powders of uniform composition which does not require material transfer for homogenization to occur [2].
Micron-sized cobalt powder can be reduced to the nano-sized range by mechanical milling with close attention paid to some important process variables which include: milling speed, milling time, BPR, milling vial, milling medium, ball diameter and milling temperature. These parameters influence the powder quality [2, 5]. A nanostructured material is a material consisting of one or more crystallites size measuring in nanometer (10-9 m) range [6]. These materials are important as they exhibit fascinating and novel properties such as electrical, mechanical, optical and magnetic properties which are superior to those found in conventional bulk materials as a result of their quantum-size effect, small-size effect as well as large number of grain boundaries [7]. This made them the desirable materials for many biomedical, technological and industrial applications [3, 6]. In recent years, efforts have been geared towards studying the behaviour of mechanically milled cobalt powder under different operations [8-11]. However, extensive work has not been conducted on the effect of high energy planetary ball milling parameters on the crystallite size and lattice strain of cobalt powder. Therefore, this work investigates the influence of varying milling time and ball-to-powder weight ratio on the crystallite size and lattice strain of nanocrystalline cobalt powder developed through mechanical milling.

2. Experimental Procedure
Commercially available cobalt powder (FlomasterTM metal powder, F.J. Brodmann & Co., ltd., USA) with average particle size < 44 μm (99.9 % Co) was used as the starting material for the milling experiment. The experiment was conducted in two stages (mechanical milling and vacuum drying). Mechanical milling was carried out using the pulverisette planetary ball milling machine. The milling media consisted of stainless steel lined vial and balls of diameter 2, 3 and 4mm. The experiment was carried out in two batches. BPR was kept constant at 20:1 for a milling duration up to 16 hrs at an interval of 4 hrs for the first batch whereas milling duration of 2 hrs was maintained over a varying BPR of 20:1, 15:1, 10:1 and 5:1 for the second batch. A process control agent (PCA), ethanol (3 wt.%) was added to prevent cold welding. Withdrawal of powder from the vial after milling for the desired duration was performed under argon atmosphere in a glove box. The milling speed was maintained at 350 rpm with allowed reverse rotation after 2 hrs and 10 min pause (to avoid overheating during milling) throughout the duration of the experiment. After the milling process, the milled powders were dried at 40 °C in Vacutech drier.

The unmilled and milled powders were subjected to X-ray diffraction studies with the aid of PW1710 Philips X-ray diffractometer utilizing Cu Kα radiation at 40 kV and 40 mA to determine the phases present in the milled powder. Diffraction patterns were obtained over a range of 2θ between 5 and 90°, with a step size of 0.02. A search-match routine was carried out to compare the data obtained with the data base of the equipment using XPert High Score Plus software for identification of phases. The crystallite size and lattice strain of the analysed samples were calculated from the XRD pattern by applying the Williamson-Hall (W-H) method. The applicable equation is as follows:

$$\beta \cos (\theta) = \frac{k \lambda}{D} + \eta \sin (\theta)$$

where $\theta$ is the Bragg diffraction angle, $k$ is the Scherrer constant (0.91), $\lambda$ the radiation wavelength (0.15406 nm), $D$ the crystallite size, $\beta$ the diffraction peak at half maximum intensity and $\eta$ is the lattice strain. By plotting $\beta \cos(\theta)$ versus $\sin(\theta)$, the slope of the straight line graph gives the estimated average lattice strain and the point at which $\sin(\theta) = 0$ gives the estimated average crystallite size of the analysed powder. The morphology of the ball milled powders was investigated using scanning electron microscope (JOEL FE-SEM JSM- 7600F). The energy-dispersive X-ray spectroscopy (EDS) incorporated with SEM was employed for compositional analysis of the milled powder.
3. Result and discussion

The morphology of the unmilled cobalt powder is shown in Figure 1a. The SEM image revealed clusters of irregularly shaped particles. The particles flatten out into sheet-like shapes due to heavy deformation during cold milling operation as shown by the SEM images in Figures 1b-1d. It was observed from Figure 2 that milling over varied times reduced the crystallite size of the cobalt powder from 64.8 nm to 9.05 nm and lattice strain of 3.74 % which represented about 3.44 % increase over the unmilled (0.3 %) at 12 hrs was obtained. This can be attributed to the influence of lattice defects such as stacking faults, dislocation and other imperfections introduced as the powder particles undergone severe plastic deformation due to interaction of the powder particle with the stainless steel balls and the wall of the vial. [4, 12]. Continued milling (16 hrs), caused an increase in the crystallite size and reduction in lattice strain (Figure 2) due to cold welding and subsequent agglomeration of the particles (Figure 1d).

Milling at a constant time of 2 hrs and varied ball-to-powder weight ratio (BPR) also yielded a reduction in the crystallite size and an increase in the lattice strain of the cobalt powder. The lowest crystallite size of about 13.73 nm and highest lattice strain of 0.79 % was achieved for this set of powders at an optimum BPR of 10:1 after, which cold welding and agglomeration resulted in increasing crystallite size and reducing lattice strain as shown in Figure 3. Crystallite size reduction introduces strains into the lattice of the material as a result of an increase in the volume of particles per unit area. According to Bhatt et al. [6], introduction of lattice strain into nanostructured materials has been found to be a beneficial and economical method of altering the band structure and enhance the performance of energy devices.

The EDS analysis results (not shown here) indicated that there was no contamination of the powder either during handling or with any interstitial element as a result of milling operation.

Figure 1. SEM images of cobalt powder (a) unmilled (b) milled for 12 h at constant BPR (c) milled at BPR of 10:1 for constant milling time of 2 h (d) milled for 16 h at constant BPR.
Figure 2. Variation of milling time with crystallite size and lattice strain of the milled cobalt powder.

Figure 3. Variation of BPR with crystallite size and lattice strain of the milled cobalt powder.

XRD patterns shown in Figures 4 and 5 were obtained at different stages and processing parameters. In Figure 4, three pronounced peaks of (100), (002), (101) and one weak (110) planes were noticed in the unmilled Co powder. These diffraction peaks were suppressed leaving only the peak of (002) plane which was shifted towards left as the milling time increased. This can be attributed to the formation of amorphous phase in the milled cobalt powder [8, 9]. The intensity of the (002) plane does not really change because the crystals in this plane were not significantly affected by the milling operation [13]. During mechanical milling, fragmentation of the particles occurred, this leads to variation in strain from point to point of the irradiated area of the samples, thereby causing the line broadening observed in Figure 4. This observation is in agreement with the previous findings of Ravi et al.[5].

Figure 4. XRD patterns of cobalt powder milled over varied time.

Diffraction patterns of powders subjected to varying BPR and constant milling time of 2 hrs is presented in Figure 5. The least diffraction peak was observed in powders milled at BPR of 10:1.
Amorphization was not observed in the milled cobalt. This might be due to insufficient available milling energy which is a function of milling speed, milling time and ball-to-powder weight ratio [14]. Nonetheless, broadening in diffraction peaks and movement in position of the diffraction maxima due to varying BPR at constant milling time resulted in reduction of crystallite size and increase in the developed strain within the material. The observed peak at BPR of 10:1 correlated with the lowest crystallite size observed in Figure 3.

Figure 5. XRD patterns of milled cobalt powder with varied BPR.

4. Conclusions
Development and characterization of nanocrystalline cobalt powder prepared through high energy ball milling process was investigated. The important findings in this study are summarized as follows:
1. High energy ball milling process was found to reduce crystallite size and increased lattice strain until the right combination of parameters which yielded optimum result(s) were attained under the different conditions investigated.
2. A shorter milling time of 2 hrs at BPR of 10:1 yielded better results which could positively affect the efficiency of the operation since less energy was used.
3. High energy ball milling resulted in the development of nanocrystalline cobalt with increased lattice strain. Increasing the lattice strain of nanostructured materials is an economic way of enhancing their utilization in energy devices. Hence, this process aids in the production of nanostructured cobalt utilized in energy devices.

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