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Research Paper

Structural and Magnetic Characterization of Cobalt Nanoparticles Prepared by Chemical Method

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Abstract

In recent years considerable research work has been spent on Co nanoparticles because of their important magnetic and structural properties. In this work we are reporting the preparation and characterization of Co nanoparticles using chemical reduction techniques. Cobalt nanoparticles were prepared by employing the sodium borohydride reduction method at room temperature. The effect of Trioctylphosphine (TOPO) capping on the formation and growth mechanism of cobalt nanoparticles were investigated using powder x-ray diffraction (XRD) and vibrating sample magnetometer (VSM). The as-prepared samples were annealed in water medium at 80˚C for different time durations, it was found that there is increasing crystalline nature and change in crystal structure. Also magnetic behavior of as-prepared and annealed samples shows the significant changes in saturation magnetization, which can be useful for practical technological applications.

Keywords: Co nanoparticles, magnetic materials, chemical method, nanocrystals.

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1 Introduction

Cobalt nanocrystals show size dependent structural, magnetic, electronic and catalytic properties. Critical size for cobalt particle to become single domain is proposed to be below 20 nm [1]. Size effect related to free energy changes may determine crystal structure. Cobalt nanoparticles prepared by high pressure sputtering show size induced phase transition from hcp to fcc below 30 nm [2]. This phase transition from hcp to fcc as a function of size is attributed to lower surface energy of fcc-Co phase [2]. Molecular beam deflection measurements show enhanced magnetic moment per atom in small cobalt clusters compared to bulk cobalt [3]. This result is confirmed by cobalt nanoparticles of 1.8 nm prepared using microemulsion technique [3]. The variation of superparamagnetic blocking temperature (T_B) and anisotropy constant as a function of particle size is studied well in literatures [3, 4]. This paper discusses about the synthesis and characterization of Co nanoparticles and the effect of capping ligands on their structural and magnetic properties. Trioctylphosphine oxide (TOPO) was used as capping agent. The experimental techniques used were X-Ray Diffraction (XRD) for phase identification and average crystallite size measurement and Vibrating Sample Magnetometer (VSM) for magnetic property measurement.

2 Preparation of Cobalt Nanoparticles

The chemical methods have been widely used to prepare nanostructured materials due to its potential to produce large quantity of final product and their control on particle size distribution and shape. Reduction of cobalt salts by strong reducing agents such as polyol [6], thermal decomposition and hydrogenation [7] have been performed. In this work the simple sodium borohydride reduction method was used to prepare cobalt nanoparticles.

Laboratory reagent grade purified $CoCl_2.6H_2O$ (98%) and $NaBH_4$ (97%) were obtained and used without further purification. To prepare Co nanoparticles, 300ml of 0.3 of mol $CoCl_2.6H_2O$ aqueous solution was prepared and stirred to get homogeneous solution. This original solution was pink in color. Then 100 ml aqueous solution of 1 M $NaBH_4$ was prepared and immediately added with the above solution. After addition of $NaBH_4$ solution, the solution color changed from pink color to black color. This color change indicates the reduction of cobalt cation into cobalt. The particles were allowed to precipitate. The precipitated particles were

repeatedly washed using distilled water. Small amount of particles were separated from solution and stored in ethanol medium. The remaining solution was separated into four parts and each part was annealed at 80^0C in water bath for 60 min, 300 min, and 600 min respectively. The collected particles from each part of solution were stored in ethanol medium.

The reduction of cobalt chloride into cobalt in water medium involves following mechanism.

$CoCl_2+2NaBH_4 \rightarrow Co+H_2+B_2H_6+2NaCl$

$B_2H_6+3H_2O \rightarrow B_2O_3+6H_2$

Similarly, cobalt nanoparticles were prepared with concentration of 0.1 mol of $CoCl_2.6H_2O$ in 300 ml water. The particles were annealed at 80^0C for 15 minutes and stored in ethanol medium.

To see the effect of capping ligands on structural and magnetic properties of cobalt nanoparticles, cobalt nanoparticles capped with trioctylphosphine oxide was prepared using same borohydride reduction method. The preparation method involves following steps. Initially 0.5 mol of $CoCl_2.6H_2O$ and 0.01 mol of TOPO were dissolved in 50 ml of ethanol and stirred to get uniform mixture of solution. Ethanol was chosen as a medium due to high solubility of TOPO in ethanol. Then 1M $NaBH_4$ in 50 ml ethanol solution was prepared and added to the above solution. The color change of solution from pink to black was observed. The precipitated particles were washed with ethanol. Particles were annealed at 80^0C in water bath for 30 min, 60 min, and 120 min respectively. The reaction mechanism in ethanol medium is given below.

$CoCl_2+2NaBH_4 \rightarrow Co+H_2+B_2H_6+2NaCl$

$B_2H_6+6CH_3CH_2OH \rightarrow 2B(OCH_2CH_3)_3+6H_2$

3 Characterization

3.1 X-Ray Diffraction

X-ray diffraction patterns were recorded using Cu-$K_{\alpha 1}$ radiation (λ = 1.5406A^0). The patterns were obtained in 20-90^0 2θ range. To identify the phase, the peak positions and relative peak intensities were compared with JCPDS data. The XRD pattern matched with card number 897373 which represents cobalt crystallized into hexagonal structure. M. A. Short et al had derived a method to measure the relative amount of hexagonal and cubic phases in the mixture of hexagonal and cubic stacking at both atomic and macroscopic level [8]. This method gives,

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$$\frac{I(10.0)}{I(00.2/111)} = \frac{\alpha H}{4-3H} \text{ ---------- (1)}$$

Where, α - Standard value of I(10.0)/I(00.2) in pure hcp phase.

H – Volume fraction of hcp phase.

The above relation was used to determine the volume fraction of hcp and fcc phases for samples crystallized into mixed phases.

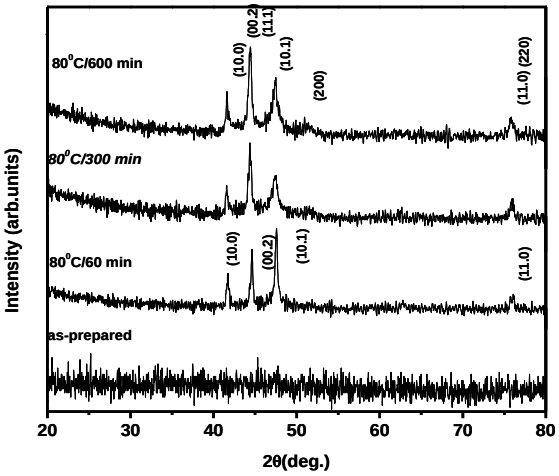

Fig. 4.1 XRD pattern of cobalt nanoparticles annealed for various durations

The full width at half maximum value was determined for all reflection planes. To calculate the average crystallite size these values were corrected for instrumental broadening value using the following equation.

$$\beta = (\beta_{obs}{}^2 - \beta_{Si}{}^2)^{0.5} \text{ ----------(2)}$$

Where, β_{Si} (= 0.0964 deg) – FWHM value of standard silica peak.

The average crystallite was measured using scherrer equation [4],

$$D = \frac{0.94\lambda}{\beta \cos\theta} \text{ ---------- (3)}$$

Where, β - Full width at half maximum value in radians.

3.2 Magnetic Measurement

The room temperature magnetic measurements were taken using EG&G PARC, 4500 model vibrating sample magnetometer. The sample was taken in the form of powder compacted in a known mass of aluminium foil and it was weighed to determine the mass of the sample. Then the sample was put into sample holder which is connected to slender rod and placed between two magnetic pole pieces. The magnetic field was increased gradually from 0 kOe to 7 kOe in both forward and reverse directions in order to observe the hysteresis behavior of the sample. From the hysteresis loop, the saturation magnetization (M_s), remenant magnetization (M_r), and coercivity values (H_c) were determined. Initially the instrument was calibrated using standard nickel specimen. In a similar way, the saturation magnetization (M_s), remenant magnetization (M_r), and coercivity values (H_c) of all samples were determined.

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4 Results and Discussion

4.1 Cobalt Nanoparticles

Figure 1 shows x-ray diffraction patterns of cobalt prepared by borohydride reduction method. The XRD pattern of as prepared sample shows it is amorphous. The diffraction peaks observed for samples annealed at 80^0C show their crystalline nature. The diffraction angle (2θ), FWHM value, and relative intensities of (10.0), (00.2), and (10.1) reflections for cobalt samples annealed at 80^0C for 60 min, 300 min, and 600 min are tabulated and analysed respectively. The relative intensity values of cobalt particles annealed at 80^0C for 60 min shows; it is crystallized into hexagonal structure. For cobalt particles annealed at 80^0C for 300min and 600min, the raise in (00.2) reflection peak intensity, may be due to the presence of both hcp and fcc phases. Table 1 shows the comparison of ratio of intensity values of all annealed samples with JCPDS data (Card number: 897373). The deviation of intensity ratios of cobalt annealed for 60 min from JCPDS data may be attributed to preferred orientation along (00.2) direction. For samples annealed for 300 min and 600 min, I(10.0)/I(00.2) values are same as JCPDS data whereas, I(10.0)/I(00.2) values are small and I(00.2)/I(10.1) values are large compared to JCPDS data. This indicates the presence of mixture of hcp and fcc phases. The volume fraction of each phases were calculated using equation (1) by putting α= 0.96 from JCPDS data. These values are tabulated in Table 2. The average crystallite size was calculated for hexagonal phase from the FWHM value of (10.0) reflection peak. These FWHM values were subtracted from instrumental broadening using equation (2).

Sample	**I(10.0)/I(00.2)**	**I(10.0)/I(10.1)**	**I(00.2)/I(10.1)**
JCPDS Data (Card No:897373)	0.96	0.27	0.28
Co–80^0C/ 60 min	0.72	0.41	0.57
Co–80^0C/ 300 min	0.24	0.27	1.11
Co–80^0C/ 600 min	0.20	0.27	1.35

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Table 2 Calculated volume fraction of hcp and fcc phases for annealed samples

Sample	I(10.0)/I(00.2+111)	Volume fraction of hcp phase	Volume fraction of fcc Phase
Co-80^{0}C /300 min	0.24	0.57	0.43
Co-80^{0}C / 600 min	0.20	0.5	0.5

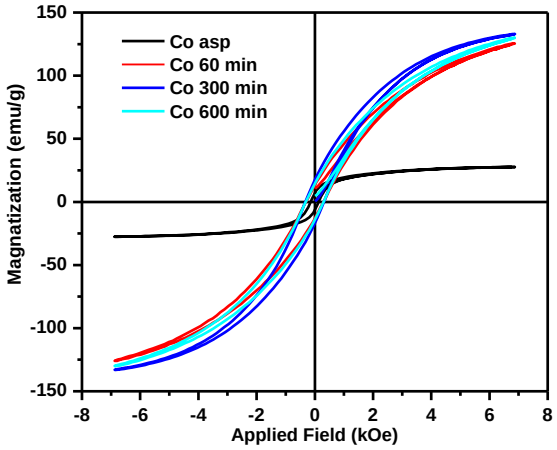

Fig. 2 Hysteresis loops of cobalt nanoparticles annealed at 80°C for various durations

These values are tabulated in Table 3. Figure 2 shows magnetization hysteresis loops of cobalt nanoparticles.

The as prepared cobalt particles are amorphous and hence they have saturated quickly. The hysteresis loop of annealed cobalt nanoparticles shows unsaturated magnetization up to 7 kOe. Saturation magnetization value of bulk cobalt particle is 168 emu/g. Cobalt annealed at 80^{0}C for 300 min shows high magnetization value of 133.1 emu/g at 7 kOe which is less than the bulk value.

5 Conclusions

Cobalt nanoparticles were prepared using sodium borohydride reduction method. The particles annealed for shorter duration shows preferred orientation along (00.2) direction. The particles annealed at 80^{0}C for 300 min and 600 min have mixture of both hcp and fcc phases. The volume fraction of fcc phase was found to increase by 7 % as the annealing duration increases from 300 min to 600 min. The magnetization value at 7 kOe was small compared with bulk value. The cobalt nanoparticles capped with TOPO shows unusual structural and magnetic properties which may be due to some chemical changes. In future, further work has to be done to predict proper reasons for this result.

References

1) W.Gong, H.Zhao, and J.Chen, J.Appl. Phys. 69 (1991) 5119.

2) O.Kitakami, H.Sato, Y.Shimada, F.Sato, and M.Tanaka, Phys. Rev. B. 56 (1998) 13849.

3) I. M.L.Billas, A.Chatelain, and W. A. de Heer, Science. 265 (1994) 1682.

4) J.P.Chen, C.M.Sorensen, K.J.Klabunde, and G.C.Hadjipanayis, Phys.Rev.B. 51 (1995) 11527.

5) S.Ram, J. Mater. Sci. 35 (2000) 3561.

6.) N. Chakroune, G. Viau, C. Ricolleau, F. F. Vincent and F. Fievet, J. Mater. Chem. 13 (2003) 312.

7) V.F.Puntes, D.Zanchet, C.K.Erdonmez, and A.P.Alivisatos, J.Am.Chem.Soc. 124 (2002) 12874.

8) M.A. Short, and E.G.Steward, The American Mineralogist, 44 (1959) 189.

9) B.E. Warren, X-ray diffraction, Dover Pubs. (1968).

10) D. P. Dinega, and M.G.Bawendi, Angew. Chem. Int.Ed. 38 (1999) 1788