

Thermomagnetic studies on chemically prepared amorphous Co nanoparticles

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Abstract

Ultrafine particles of pure amorphous cobalt were chemically synthesized by borohydride reduction of a cobalt salt in aqueous condition. This material were subjected to a controlled annealing in air atmosphere for about an hour at different temperature. Silica coating was carried out using Stöber process. Pure cobalt and Co/SiO₂ samples were annealed at various temperatures. The influence of thermal treatment on the crystallization and magnetic properties of Co particles were examined. The crystallization temperature of amorphous Co particle was found to be 311°C, which also confirmed from thermomagnetic studies by Thermogravimetric analysis. It was observed that crystallization process occurs only in the pure Co particles, which trend is not observed in Co/SiO₂ samples. However magnetization value of pure Co and Co/SiO₂ both are increasing with increase of annealing temperature. The magnetization reach a maximum 35 emu/g for Co/SiO₂ sample, whereas 25 emu/g for pure Co sample. The variation of magnetization and coercivity as a function of temperature were also discussed.

1. Introduction

Nanocomposite powders, consisting of metal nanoparticles buried in host matrix, exhibit a wide variety of interesting solid-state properties and have opened up many possibilities for their use in various technological applications. For instance, nanoparticles of magnetic transition metals (Fe, Co, Ni) encapsulated in either non-magnetic or insulating (eg., Polymer, Al₂O₃ or SiO₂) materials are interesting due to their peculiar electrical, magnetic and magnetotransport properties such as high resistivity, change in coercivity, superparamagnetism, giant magneto resistance and magneto tunneling resistance. These magnetic materials have found applications as inductive components, which are extensively used in high frequency (> 10 MHz) electronic devices [1-7].

Magnetic properties of fine particles are governed by complex interplay between surface and finite size effects, whose importance increases inversely with particle size. However the production of isolated metallic magnetic particles is difficult, as the large surface areas are easily oxidized or otherwise subject to corrosion and chemisorptions of CO. Therefore, it is necessary to develop methods to avoid oxidation, agglomeration and grain growth. Deposition of silica on magnetic particles will be useful for this purpose. However, silica deposition on pure metal particles is complicated because of the lack of OH groups on the metal surface. Recently few authors have reported air stable Co and Fe nanoparticle by formation of a carbon, gold and silica shell on the nanoparticle surface. In this work we concentrate on the synthesis, structural, magnetic and thermal behavior of pure Co and Co-SiO₂ nanocomposites[8-10].

2. Experimental Details

The magnetic Co powders were chemically synthesized by borohydride reduction method. Silica coating of these particles was then achieved using tetra ethyl ortho silicate (TEOS).

2.1 (i) Preparation of Co nanoparticles by borohydride reduction method:

The preparation of colloidal cobalt was performed by addition of 20 ml of 0.4 M CoCl₂.6H₂O in H₂O to 250 ml of 0.04 M NaBH₄ aqueous solution containing 1 ml of 0.001 M ascorbic acid under vigorous mechanical stirring. The formation of cobalt

particle was manifested by block coloration of the dispersion. The Co nanoparticles obtained were precipitated by magnetic decantation after washing with water and ethanol. The precipitate was further washed with acetone and dried in flash heating (60°C). Known portions of the dried material were annealed in air for an hour at temperatures of 200, 300, 400, 500, 600 and 700°C.

2.2 Preparation of Co-SiO₂ nanocomposite:

In order to prepare the Co-SiO₂ nanocomposite, precipitated Co particles were redispersed in 25 ml of 4.2 vol% of ammonia (28% NH₃ in H₂O) in ethanol and immediately 25 ml of 10 vol% TEOS in ethanol was added slowly under vigorous stirring. The stirring was continued for 24 h and the product was then aged for 48 h. The Co-SiO₂ nanocomposite powder was then washed with acetone and dried in flash heating (60°C). This material was also annealed in air for an hour at temperatures 200, 300, 400, 500, 600 and 700°C.

3. Characterization: The samples were characterized by X-ray diffraction, vibrating sample magnetometer (VSM), differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA). X-ray diffraction experiments were performed on a Guinier type diffractometer with CuK_{α1} radiation. The results were used to confirm the phase identification and estimate the grain size of the nanocomposite. The XRD patterns were obtained over the scan range of 10° - 40° (θ) in steps of 0.02° and 1 s dwell time. Room temperature magnetic hysteresis was obtained using a (EG&G PRINCETON MODEL-4500) vibrating sample magnetometer capable of a maximum applied field of 7 kOe. Crystallization temperature was determined on a (Perkin Elmer PC Series DSC-7) differential scanning calorimeter (DSC) employing a constant heating rate of 10°C/ min under Argon atmosphere. A thermogravimetric analyzer (Perkin Elmer PC Series TGA-7) with a permanent magnet system used for thermal study measured in Argon atmosphere.

4. Results and Discussion:

4.1 Colloid Synthesis: Several synthetic procedures were tried for obtaining colloids of the metal nanoparticles and it was found that the borohydride reduction technique was

most suitable for the Co particles. The preparation conditions were optimized for the production of stable colloids after trials.

4.2 Structural and magnetic properties:

The XRD result for pure Co sample is shown in Figure 1. As-prepared sample was mostly amorphous. Annealing at 500° C and above oxidizes the samples of pure Co and Co-SiO₂ as revealed by the Co₃O₄ peaks at 36.57° (not shown). Figure 2 shows the differential scanning calorimeter (DSC) curve obtained for the as-prepared amorphous Co and as-prepared Co-SiO₂ powders, at a heating rate of 10°C/min in the flow of Ar gas. In DSC endothermic peak at 311°C may correspond to the desorption's of the dissolved H and O in the metal cluster of the pure Co, and exothermic peak at 500°C corresponds to the crystallization temperature for fcc phase. In the previous reports of Co nanoparticles, it was found that amorphous cobalt crystallizes to fcc phase in normal annealing process. Also some research report shows that amorphous cobalt crystallizes to hcp phase. There are required systematic studies of annealing procedure followed by X-ray diffraction pattern to understand the crystallization mechanism. TGA (fig 3.) plot shows the

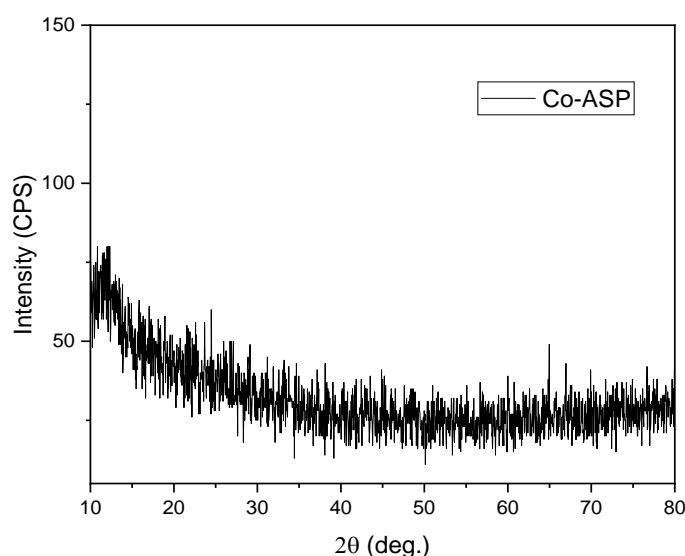


Figure 1 XRD pattern of as-prepared Co particles (before annealed 80° C for 15 min)

thermomagnetic behaviour of as-prepared samples. In TGA 311°C corresponds to the curie temperature of amorphous Co simultaneous crystallization shows the increasing magnetic moment. In the case of Co-SiO₂-as prepared sample shows the

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exothermic peak at 490°C corresponds to crystallization temperature of Co in Co-SiO₂ nanocomposite.

Magnetic Characterization was performed at room temperature for all the as-prepared and annealed samples. Figure 4 (a & b) shows the $M-H$ loops of five pure Co samples, which are annealed in air atmosphere in order to form Co/CoO or Co₃O₄ core shell nanoparticle. In the figure it can be observed that magnetization saturated relatively at low applied field for as-prepared sample and increases for annealed samples. Saturation magnetization (M_s) of pure Co nanoparticles increases upto 300°C annealing temperature and above that temperature decreases drastically, probably due to oxidation. This indicates the pure cobalt particles are no longer stable in air atmosphere.

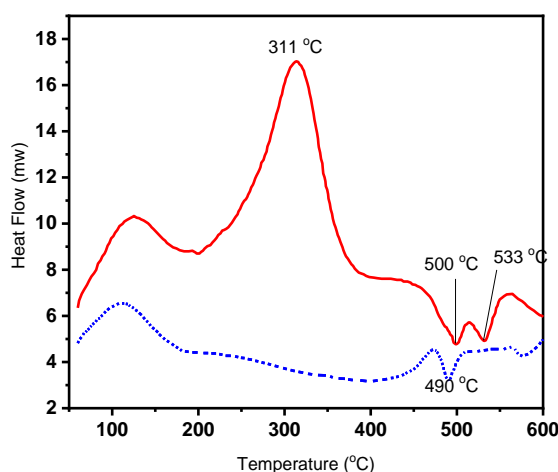


Fig. 2. DSC plot for pure Co nanoparticles of as-prepared (solid line) and Co-SiO₂ of

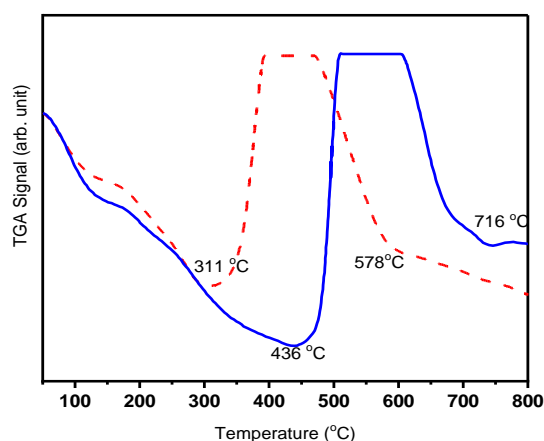


Fig. 3 TGA plot for Co-SiO₂ nanocomposite of as-prepared (solid line) and annealed at 500 °C for an hour (dotted line)

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In Co-SiO₂ sample also magnetization is saturated at relatively low applied magnetic fields for as-prepared sample but magnetization increases with annealing temperature up to 500°C and then decreases. The maximum saturation magnetization of 33 and 27 emu/g was obtained for 400 and 500°C annealed samples respectively. This shows that Co-SiO₂ nanocomposite particles are stable up to 400°C with Co surface free from oxidation.

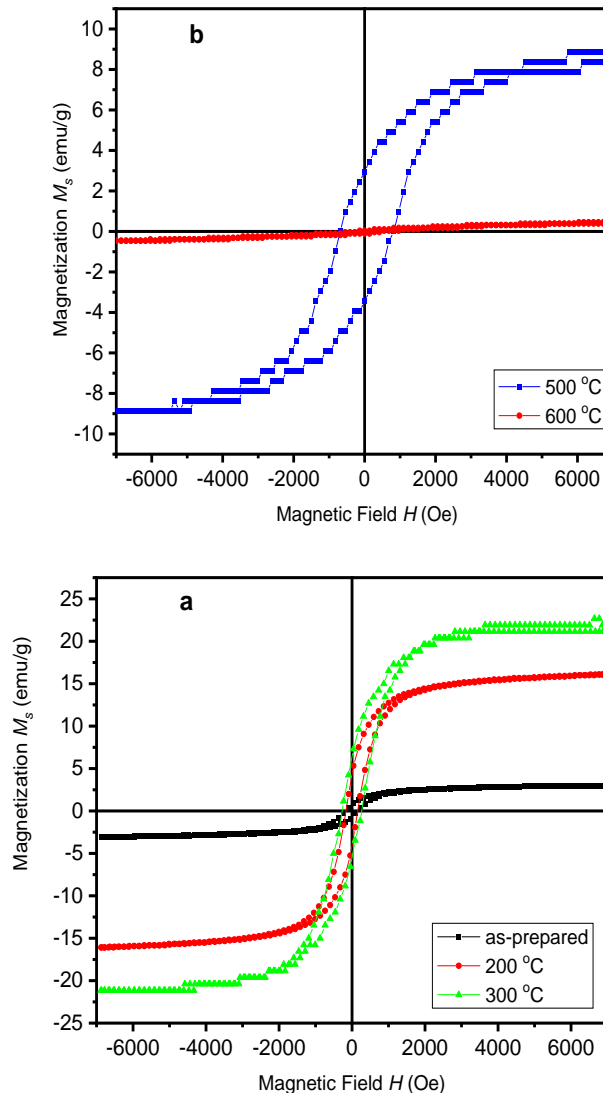


Fig. 5. (a & b) M-H Plot at 300 K for Co nanoparticles as-prepared and annealed at various temperature for an hour

Conclusions

Cobalt nanoparticles were prepared using sodium borohydride reduction method. The magnetization value at 7 kOe was small compared with bulk value. The cobalt nanoparticles capped with SiO₂ shows unusual structural and magnetic properties which may be due to more chemical stability. In future, further work has to be done to predict proper reasons for this result.

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