

Phase-Controlled Synthesis of Metastable Nanocrystalline Cobalt

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ABSTRACT

Nanocrystalline Cobalt is one of the most important magnetic material due to the phase-dependent magnetic properties exhibited by its allotropic phases. The anisotropic high-coercivity hcp-Co phase is preferred for permanent magnet applications, while the more symmetric low coercivity fcc- and ϵ -Co can be used in soft magnetic applications involving power electronics and magnetic write heads. The present work addresses the synthesis and characterization of nanocrystalline cobalt particles produced through a modified polyol-based approach conducive to the formation of fcc-, hcp-, ϵ -Co, or mixtures of fcc/hcp-Co phases. Magnetic measurements confirmed the strong influence of synthesis conditions on crystal structure and hence, on magnetic properties of nanocrystalline cobalt. The coercivity of the products varied from 148 Oe to 778 Oe depending on the presence of the different cobalt structures.

Keywords: Magnetic nanoparticles, modified polyol process, nanocrystalline Cobalt.

1 INTRODUCTION

Magnetic metallic nanoparticles represent a particularly interesting class of materials for both scientific and technological applications as data storage media, agents for magnetic resonance imaging (MRI) or in hypothermia-based therapies, among others [1–4]. The progress of the applied research involving these magnetic nanostructures is strongly dependent on the development of suitable synthesis approaches. Chemical synthesis has demonstrated to be a powerful and rapid route to obtain large quantities of nanosize building blocks in a single reaction; metallic nanostructures obtained through this route exhibit better crystallinity, and are typically much smaller in size than similar materials produced by physical means [5]. Besides, the particle size and the metal phase can be tuned through varying synthetic conditions. These features of chemical synthesis provide tremendous opportunities to investigate the size- and phase-dependent magnetic behavior of materials from the nanoscale to the bulk level [6].

The basic principle involved with the chemical synthesis of nanostructured materials is to control the rate

of nucleation and growth of the products. This can be achieved by conducting the reactions within a confined environment or controlling the reaction process through a dynamic binding of surface ligands [7]. The polyol process is a flexible route that uses these high-boiling point alcohols to produce elemental metals in organic media without the problems from oxidation presented in aqueous processing [8, 9]. An additional advantage of the polyol route lies on the possibility to control the kinetics of the metal forming reaction, which in turn would lead to the formation of metastable phases. On this basis, we investigated the options to achieve a phase-controlled synthesis of nanocrystalline cobalt using a modified polyol process and different types of polyols to stabilize metastable phases such as hcp-Co or pseudo-cubic ϵ -Co. The rate of the metal forming reaction was accelerated by injecting the cobalt precursor solution to the boiling polyol media in presence of an excess of hydroxyl (OH^-) and a suitable control of the concentration of sodium acetate or sodium oleate to inhibit particle growth.

2 EXPERIMENTAL

2.1 Materials

All chemicals were of chemical grade and were used without any further purification. Trimethylene Glycol, TMEG, (99 %, *bp* 214°C, Alfa Aesar), and Tetraethylene Glycol, TREG, (99 %, *bp* 31°C, Aldrich), were used as the solvent and the reducing medium as well. Co(II) acetate tetrahydrate, (99.995%, Alfa Aesar) was the cobalt precursor whereas sodium hydroxide, NaOH, (99.998%, Aldrich), the source for hydroxyl ions. Sodium oleate (95%, TCI) and sodium acetate (99.5%, EM Science) were used as surfactants.

2.2 Synthesis of Nanocrystalline Powders

A 0.005 M or 0.01M Co-acetate polyol solution was rapidly injected in the boiling polyol-surfactant solution in presence of OH^- ions. Based on our earlier works, the OH^- /Co mole ratio was kept constant at 50 [10]. The alkaline condition provided by the excess of OH^- ions leads to an acceleration of the metal forming reaction due to the enhancement in the solubility of the intermediate

compound; i. e., the faster the re-dissolution of the intermediate cobalt alcoxide, the faster the reduction reaction under boiling polyol condition. An acetate/Co mole ratio of 20, was used when the solids were synthesized from a 0.01M Co solution in TMEG. Another set of experiments were carried out using a 0.005M Co solution in TREG at a acetate/Co mole ratio 20 or oleate/Co mole ratio 5. In all experiments, the reacting solution was refluxed for different reaction times in the so-called 'contact stage'. At the end of this stage, cobalt particles were recovered by centrifugation, washed twice with fresh ethanol and finally stored in this solvent to minimize oxidation.

2.3 Characterization Techniques

Structural characterization of the solids was carried out in a Siemens D500 x-ray diffractometer (XRD) using the Cu-K α radiation. The average crystallite size of produced powders was estimated by the Scherrer's equation. Scanning electron microscopy (JEOL JSM-5410 LV) was used to determine the morphology and size of produced particles. Fourier Transform Infrared (FTIR) measurements were undertaken in a MIRacle TM ATR FTS 1000 spectrometer in the transmittance mode. Magnetic properties of the powders were measured at room temperature (RT) using a vibrating sample magnetometer (VSM, Lakeshore 7400 Series). The maximum applied field was 22kOe.

3 RESULTS AND DISCUSSION

3.1 XRD Analyses

Figure 1 show the XRD patterns for the powders synthesized in TMEG using sodium acetate as surfactant. Only sharp and well-defined peaks corresponding to the ϵ -Co phase were identified when a acetate/Co mole ratio of 20 was used, (Figure 1-a). The average crystallite size was estimated at 11nm and the lattice parameter at $0.59 \text{ nm} \pm 0.05 \text{ nm}$. This value is in good agreement with the value reported in the literature [11]. The solids produced in the same polyol but with an acetate/Co ratio of 40, consisted exclusively of hcp-Co (Figure 1-b) with a crystallite size averaging 20 nm. The corresponding lattice parameters were ' a ' = $0.2504 \text{ nm} \pm 0.0001 \text{ nm}$ and ' c ' = $0.406 \text{ nm} \pm 0.0001 \text{ nm}$, which concur with reported ' a ' = 0.2505 nm and ' c ' = 0.406 nm values [12a]. The presence of both OH⁻ and acetate ions should have accelerated the intermediate dissolution-cobalt reduction reactions and consequently, promoted the formation of metastable ϵ -Co and hcp-Co nanostructures. The average crystallite size and the lattice parameter were estimated at 10 nm and $0.38 \text{ nm} \pm 0.11 \text{ nm}$, respectively. This lattice parameter is slightly discrepant with the value reported for the bulk (0.35447 nm) [12b].

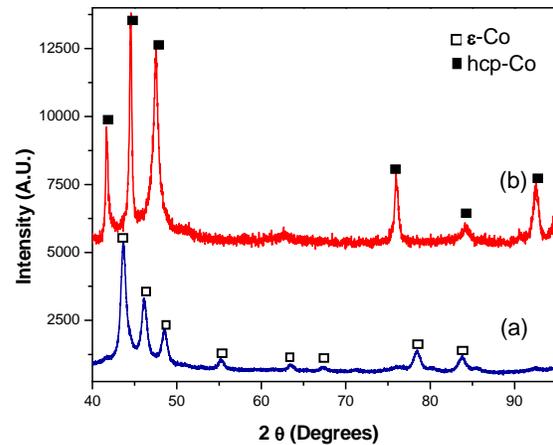


Figure 1: XRD patterns for powders synthesized in TMEG from starting 0.01M Co solutions and 4 hours of reaction. (a) acetate/Co mole ratio 20; (b): acetate/Co mole ratio 40.

The XRD pattern for the solids synthesized in TREG but now in presence of sodium oleate (Figure 2-b and 2-c) revealed the co-existence of both, fcc- and hcp-Co phases. In order to monitor any time-dependent phase change, this later experiment was carried out for 80 minutes and two hours of reaction. The product after 80 minutes of reaction consisted of a mixture of hcp-Co and fcc-Co, but with an evident predominance of the hexagonal phase; also, the pattern showed a broad peak centered on between 57 and 63 degrees that could correspond to an oxidized cobalt compound or residual alcoxide intermediate [12c]. This situation was reverted at the end of 2 hours of reaction; in this case, fcc-Co became the predominant phase. The specific adsorption of oleate species onto particular planes during the formation and growth of cobalt crystals would have inhibited the development of the ϵ -Co structure, favoring instead the stability of hcp- and fcc-Co phases.

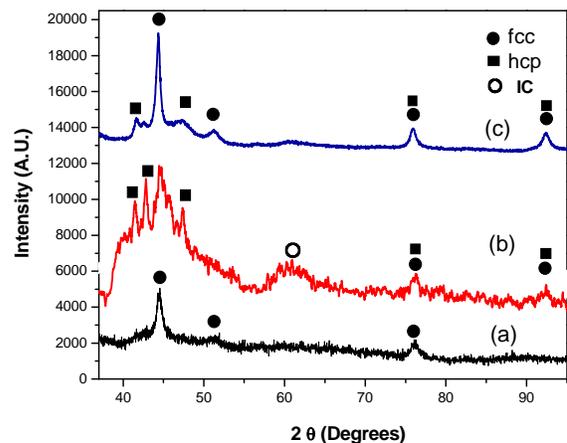


Figure 2: XRD patterns for powders synthesized in TREG from starting 0.005M Co solution. (a) Acetate/Co mole ratio 20, 2 hours of reaction ; (b) oleate/Co mole ratio 5, 80 min, and (c) oleate/Co mole ratio 5, 2 hours.

3.2 SEM Analyses

SEM images of synthesized cobalt powders are presented in Figures 3 (a)-(e). These images evidence the remarkable effect of the synthesis conditions on the morphological features of the solids. The solids produced in TMG and an acetate/Co mole ratio 20 (Figure 3-a), consisted of spherical particles in the sub-micrometric range; the particles were more polydisperse and irregular in shape when an acetate/Co ratio 40 was used (Figure 3-b). Careful observation of these images will show that each particle consists of tiny individuals that should have been irreversibly aggregated in order to decrease the total surface energy of the system. Apparently, the electrostatic repulsive interactions generated by the adsorbed acetate species would have not been strong enough to prevent nanocrystal aggregation. Figures 3-d and 3-e show the morphology of the particles produced in TREG, and an oleate/Co ratio 5. Oleate species were used as an attempt to inhibit particle growth; the formation of sub-micrometric particles can be explained in terms of the combined effect of a faster metal formation in TREG and the growth-inhibition effect due to the adsorption of oleate species onto the forming cobalt particles.

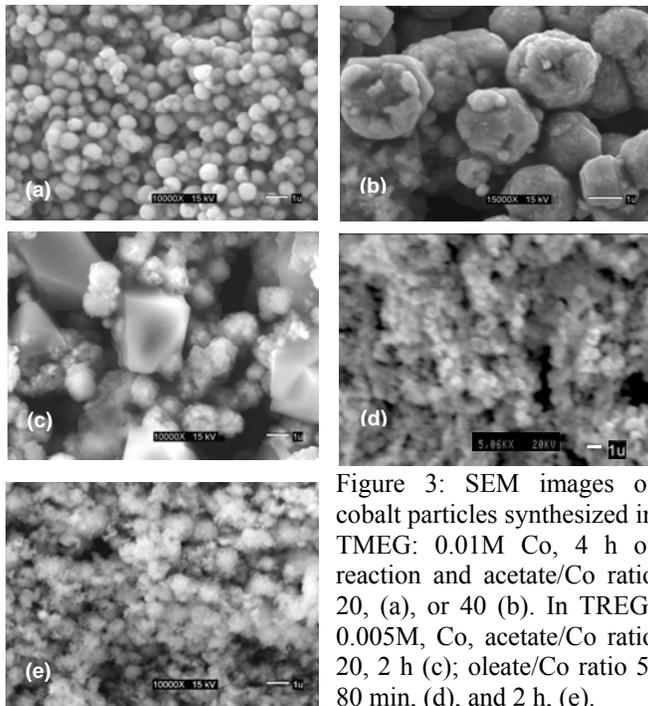


Figure 3: SEM images of cobalt particles synthesized in TMEG: 0.01M Co, 4 h of reaction and acetate/Co ratio 20, (a), or 40 (b). In TREG: 0.005M, Co, acetate/Co ratio 20, 2 h (c); oleate/Co ratio 5, 80 min, (d), and 2 h, (e).

3.3 FT-IR Measurements

The FT-IR spectra of cobalt powders produced in TREG in presence of oleate at different reaction times, Figure 4, shows two signature bands at 1600 cm^{-1} and 1400 cm^{-1} that were assigned to the $\nu_s(\text{C}=\text{O})$ and $\nu_a(\text{C}=\text{O})$ stretching modes

in the oleate structure. The fact that these bands were detected even after intensive washing of the solids would indicate the adsorption of oleate species onto the metal. It surface. It has been suggested that surfactants, such as oleate, can be adsorbed on the surface of metallic nanoparticles via ionic bonding [13]. All other bands below 1200 cm^{-1} can be caused by $\nu(\text{C}-\text{C})$ stretch, $\nu(\text{C}-\text{O})$ stretches, CH_2 deformations and other motions that are too complex to assign [14]; however, they match pretty well with those bands of sodium oleate spectrum. The presence of these adsorbed oleate species supports our previous considerations regarding the inhibition of particle growth in synthesized cobalt particles.

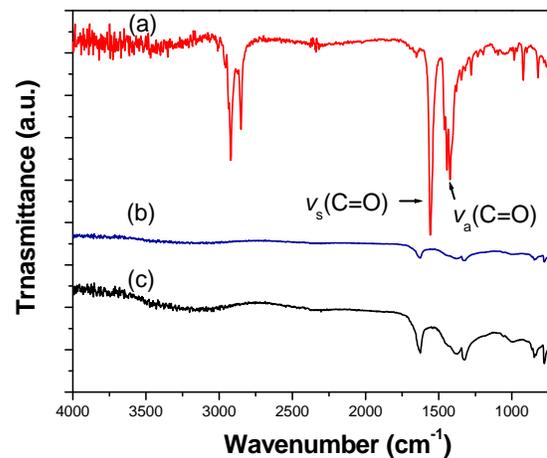


Figure 4: FT-IR spectra of pure sodium oleate, (a), and cobalt particles synthesized in 0.005M Co solution in TREG after 80 minutes, (b), and 2 hours, (c), of reaction.

Additional FT-IR measurements on samples synthesized in presence of sodium acetate did not show any band corresponding to acetate species. These species should have been completely removed after intensive washing of the particles.

3.4 Magnetic Properties

M-H measurements confirmed the phase-dependence of magnetic properties in nanocrystalline cobalt. The magnetization and coercivity of the ϵ -Co phase were 88 emu/g and 338 Oe, respectively (Figure 5-a). The low coercivity for this sample is attributed to the well known soft magnetic behavior of the ϵ -phase [12, 15]. In turn, the hcp-Co solids exhibited a magnetization of 141 emu/g and coercivity of 148 Oe (Figure 5-b). Despite of the exclusive presence of the hcp-Co phase in this sample, the coercivity is even lower than the 338 Oe exhibited by the soft ϵ -Co phase. The average crystallite size estimated for the hcp-Co sample was 20 nm, which is very close to the single domain limit in Co [16]. Therefore, the presence of Co crystals with a size within the magnetic multi-domain region could explain the low coercivity in this sample. Although the

coercivity for this particular sample can be considered only moderate, it is still far above the bulk value of 10 Oe [17]. When nanocrystalline fcc-Co was the only phase (Figure 5-c), the saturation magnetization and coercivity were 60emu/g and 357 Oe, respectively. M-H loops of Figures 5-d and 5-e correspond to cobalt particles synthesized in presence of oleate species. The coercivity values were 778Oe and 550Oe when the reaction time was increased from 80 minutes to 2 hours, respectively. The relatively high coercivity exhibited by these two samples can be explained by the probable pinning of the magnetic domains in these particles or the confirmed presence of nanocrystalline hcp-Co, which is expected to exhibit high magneto-crystalline anisotropy [18].

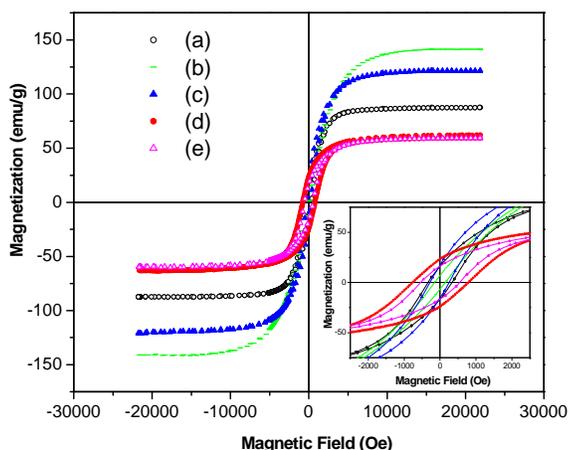


Figure 5: M-H loops at 300K for nanocrystalline Cobalt particles exhibiting different structures. Table 1 summarizes the corresponding coercivity (H_c) and saturation magnetization (M_s) values.

4 CONCLUDING REMARKS

Nanocrystalline cobalt particles exhibiting different structures have been successfully synthesized by a modified polyol method. XRD characterization evidenced the influence of the synthesis conditions on the formation of crystalline metastable ϵ -Co and hcp-Co as well as fcc-Co phases. The use of oleate species inhibited particle growth and favored the development of mixtures of hcp and fcc phases. The presence of nanocrystalline hcp-Co explained the attained high coercivity values in these samples.

5 ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation under NSF-PREM Grant No. 0351449 at UPRM.

Sample	Synthesis Conditions	Phase(s)	H_c (Oe)	M_s (emu/g)
(a)	TMEG, 0.01M Co, 4 hours of reaction, acetate/Co mole ratio 20	ϵ -Co	338	88
(b)	TMG, 0.01M Co, 4 hours of reaction, acetate/Co mole ratio 40	hcp-Co	148	141
(c)	TREG, 0.005M Co, 2 hours reaction, acetate/Co mole ratio 20	fcc>> hcp	357	121
(d)	TREG, 0.005M Co, 80 minutes of reaction, oleate/Co mole ratio 5	hcp>>fcc	778	63
(e)	TREG, 0.005M Co, 2 hours of reaction, oleate/Co mole ratio 5	fcc>hcp	550	60

Table 1. Room-temperature saturation magnetization, M_s , and coercivity, H_c , of cobalt particles synthesized in various polyol solutions.

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