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Synthesis of nanocrystalline Co–Ni alloys by precursor approach and studies on their magnetic properties

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ABSTRACT

Nanocrystalline Co–Ni alloys with different compositions were prepared by polyol reduction of mixed cobalt nickel hydroxides. The precursors (mixed cobalt nickel hydroxides) were prepared by coprecipitation. Powder X-ray diffraction analysis indicated the formation of *fcc* phase in the alloys and their crystallite size in the range 17–25 nm. Scanning electron microscopy and transmission electron microscopy studies revealed the morphology of the particles as being close to spherical, and the energy dispersive X-ray analysis showed the stoichiometry of the alloys. The magnetization as a function of field and temperature of the alloys, measured using a superconducting quantum interference device, showed superparamagnetic behavior with negligible coercivity and remanence values.

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1. Introduction

Due to their unique physical and chemical characteristics such as small scale and surface effects, nanomaterials are now widely produced and used in different fields. In the recent years, magnetic nanoparticles such as metals, alloys and multi-layers have attracted tremendous interest from researchers in many fields due to their promising applications in the area of ferro-fluids [1], microwave absorbance [2], hyperthermia [3], catalysis [4], magnetic resonance imaging (MRI) and drug delivery system [5], magnetic recording and magnetic based sensors [6,7] and excellent reviews are available on such topics [8,9]. Nanocrystalline magnetic alloys such as Ni-Cu, Co-Ni, Fe-Co and Fe-Co-Cu are promising candidates for hyperthermia and microwave applications because their magnetic transition temperatures and microwave absorbance characteristics vary with composition and grain size. In addition to the polyol reduction, many methods such as hydrogen and hydrothermal reduction [10-13], mechanical alloying [14], sonochemical method [15], thermal decomposition [16,17], sol-gel process [18,19], co-evaporation [20], microemulsion method [21,22], sequential ion implantation [23], electroless

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deposition [24], biomineralization [25] and magnetic field-assisted solvothermal process [26] have been reported in the literature for the synthesis of Co–Ni alloy nanoparticles. In the following section, the literature on the synthesis of Co–Ni nanoparticles by polyol reduction is reviewed.

Monodisperse Co-Ni and Fe-Ni particles have been prepared by Viau et al. [27] by reduction/disproportionation of inorganic compounds in polyols. Oleic acid coated Co-Ni nanoparticles with and without poly-vinyl pyrrolidone (PVP) coating have been synthesized by a polyol process by Jayakumar et al. [28]. Co-Ni particles useful for microwave applications with sub-micron size range have been synthesized by the polyol process by Viau et al. [29]. PVP protected Co-Ni alloy nanoparticles have been prepared by the polyol process by Saravanan et al. [30]. Freshly prepared cobalt (II) and nickel (II) hydroxides have been subjected to reduction in ethylene glycol to obtain Co-Ni powder by Bianco et al. [7]. Co-Ni malonates have been used as precursors during the polyol reduction, without using any protecting agents, to produce sub-micron sized Co-Ni alloy particles [31]. Co-Ni alloy nanoparticles have been synthesized by Luna et al. [32] by the polyol reduction of metallic salts. Spherical and monodisperse Co-Ni fine particles have been prepared by the polyol process by Toneguzzo et al. [33].

Co-Ni alloy particles have been prepared by polyol process coupled with solvothermal treatment [34]. Co-Ni anisotropic particles have been prepared by the polyol reduction of metal acetates by Chakroune et al. [35]. Co-Ni particles with unusual shapes (e.g. dumbbells) have been prepared by the reduction of

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cobalt and nickel acetates in a NaOH solution of 1,2-propanediol [36,37]. Co–Ni nanowires have been prepared by reduction of a mixture of metal salts in NaOH solution of a polyol and the shape was found to depend on NaOH concentration and the Co–Ni composition [6]. A modified polyol method has been reported in which stoichiometric amounts of metal nitrates were mixed with PVP and subjected to ethylene glycol reduction [38]. Sometimes, nucleating agents such as copper (II) acetylacetonate and K₂PtCl₄ have been used to prepare Co–Ni alloy particles [39]. During the preparation of Co–Ni nanowires by the polyol reduction, ruthenium seeds and NaOH have been used to induce heterogeneous nucleation [40]. Heterogeneous nucleation in polyol has been used to prepare Co–Ni nanowires/nanorods [41]. Noble metal nanoparticles such as platinum have also been used as nucleating agent for the preparation of Co–Ni nanoparticles [42].

Most of the literature methods discussed above use either nucleating agents or protecting agents. The main goal of the present work is to prepare Co–Ni nanocrystalline alloys by reducing chemically mixed $Co_xNi_{1-x}(OH)_2$ precursors, prepared by co-precipitation, in ethylene glycol–NaOH and to investigate the effect of composition on the magnetic properties. The present synthesis approach is a simple and low cost process to prepare superparamagnetic Co–Ni alloys without using any nucleating or protecting agent.

Materials and methods

1.1. Reagents

All the chemicals were used without further purification. Nickel chloride hexahydrate (NiCl₂ · $6H_2O$, 97% pure) was received from Fisher Scientific[®], cobalt chloride hexahydrate (CoCl₂ · $6H_2O$, 97% pure) from Loba Chemicals[®], sodium hydroxide pellets (NaOH, 98% pure) from Qualigens[®] and ethylene glycol (98% pure) from Rankem[®]. Millipore[®] water was used for the preparation of aqueous solutions.

1.2. Synthesis

Co–Ni alloy particles were synthesized by polyol reduction of $Co_xNi_{1-x}(OH)_2$. In a typical synthesis, the mixed cobalt nickel hydroxide was prepared by co-precipitation as follows [43,44]. In a 250 ml beaker, nickel chloride hexahydrate and cobalt chloride hexahydrate in appropriate molar ratios (see Table 1) were dissolved in 60 ml de-ionized water. To this, 60 ml aqueous solution of sodium hydroxide (6 mmol) was added dropwise at room temperature for about 35 min. During the precipitation, green precipitates were formed in all the cases. The precipitates were filtered, washed with de-ionized water many times followed with ethanol and then dried at room temperature in air. The dried hydroxide powders were ground using a ceramic mortar and pestle. The yield of precursors varied from about 0.2 to 0.4 g. The

Table 1

Composition of reagents used during the synthesis, yield and stoichiometry of the precursors.

Yield (g) Precursor Composition of regents used Ni and Co salts Composition of the molar ratio [Ni]:[Co] precursors NiCl₂ · 6H₂O (mmol) CoCl₂ · 6H₂O (mmol) NaOH (mmol) P1 6 0 1:0 Ni(OH)₂ 0.164 6 Co41Ni59(OH)2 P2 6 6 6 1:1 0 368 P3 12 6 1:2 Co54Ni46(OH)2 0.374 6 P4 6 18 6 1:3 Co63Ni37(OH)2 0.385 P5 0 6 0:1 $Co(OH)_{2}$ 0.195 6

polyol reduction of the mixed hydroxides was carried out as follows.

About 0.25 g of the precursors (mixed metal hydroxides) was heated at 115 °C for 4 h to remove the physically adsorbed water molecules. Then, the precursor powders were refluxed at 180 °C for 6–14 h in about 20 ml ethylene glycol–NaOH (1 g) system to yield the nanocrystalline alloys. The powders turned black within 2–4 h, in all the cases, indicating the reduction process. The alloy powders were filtered, washed with acetone many times and then dried at room temperature in air. More details on the precursors and the alloy powders, obtained after the polyol reduction, are given in Table 1 and Table 2, respectively.

1.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded using a Bruker AXS D8 Advance powder diffractometer operating with Cu K α radiation (40 kV, 45 mA, λ =1.5418 Å) at a scan speed 2°/min with a 2θ step of 0.02° . Field emission scanning electron microscopy (SEM) images and energy dispersive X-ray analysis (EDXA) were obtained on a FEI Quanta 200F electron microscope operating at 20 kV. Transmission electron microscopy (TEM) images were recorded using a IEOL IEM 2100F electron microscope operating at 200 kV. Sample preparation for the TEM analysis involved sonication of a small amount of the alloy powder in ethanol for about 20 min and then using a few drops of the dispersion to be dried in air on a carbon coated Cu grid. Magnetic measurements using a superconducting quantum interference device (SQUID) were done on a Quantum Design MPMS XL magnetometer with temperature varying from 300 K to 5 K at an applied maximum field of 10 kOe. For the field cooled (FC) measurements, an applied field of 400 Oe was used.

2. Results and discussion

2.1. Structural analysis

The XRD patterns of the precursors are shown in Fig. 1 and the XRD patterns were indexed using the JCPDS data base. The XRD pattern of pure cobalt hydroxide (P5) is similar to that of cobalt

Table 2

Average crystallite size, stoichiometry and lattice parameters of the alloys obtained by the polyol reduction of precursors.

Reduced precursor	Co and Ni atomic composition in the alloys	Average crystallite size (nm)	Lattice parameter (Å)
RP1	Ni	32	3.5180
RP2	Co40Ni60	17	3.5341
RP3	C053Ni47	18	3.5343
RP4	C063Ni37	25	3.5358
RP5	Со	10	3.5367



Fig. 1. XRD patterns of the precursors obtained by co-precipitation using nickel and cobalt chloride salts.



Fig. 2. XRD patterns of pure cobalt, pure nickel and cobalt–nickel alloys obtained after reducing the corresponding precursors in an ethylene glycol–NaOH system.

nitrate hydroxide (α -cobalt hydroxide, JCPDS file # 46-0605) with an interplanar distance of 7.98 Å, calculated using the (0 0 3) reflection [45]. Pure nickel hydroxide (P1) shows the pattern similar to that of β -nickel hydroxide (JCPDS file # 01-1047, Ni(OH)₂) with an interplanar spacing of 4.37 Å, calculated using the (0 0 1) reflection [46]. All the mixed cobalt nickel hydroxide precursors (P2–P4) show XRD patterns similar to that of α -cobalt hydroxide.

The pure cobalt and nickel hydroxide precursors, on polyol reduction, yield the corresponding metals (Fig. 2) with fcc structure (JCPDS file # 15-0806 for pure Co and # 01-1258 for pure Ni). The mixed metal hydroxides $(Co_xNi_{1-x}(OH)_2)$ on reduction yield nanocrystalline alloys. All the Co-Ni alloys show the familiar three peaks representative of the *fcc* structure at 2θ values of about 44.5°, 51.3° and 76.4° with the corresponding reflections (111), (200) and (220), respectively. The peak broadening in the patterns is attributed to smaller crystallites, stress gradient and/or chemical heterogeneities. Additionally, peak asymmetries have been attributed to long range internal stresses or planar faults such as stacking faults/twinning [47]. The structures of cobalt-nickel alloys, reported in the literature, are either amorphous or crystalline with fcc or hcp and fcc mixed structures [15,38,48]. The average crystallite size, calculated using the Debye Scherrer formula for the alloy samples, was found to be in the range 17-25 nm.



Fig. 3. XRD patterns of cobalt–nickel alloys (RP2–RP4), which were physically mixed with electrolytic grade Cu powder for internal calibration.

2.2. Proof of alloy formation

The alloy formation is confirmed from the shift of XRD peak positions (Fig. 3) with respect to those of the constituent pure phases. When an alloy is formed of two elements with similar crystal structure (isomorphous system), the lattice parameter is different from those of pure metals and the shift is a measure of the amount of the elements present [49]. As the XRD peak positions are representative of the crystal structure and lattice parameters, a quantitative analysis can be carried out. The challenge is to separate the instrumental shift due to misalignment and other extraneous effects from the peak shifts due to crystal lattice distortion. Without proper instrumental calibration. it is practically impossible to detect the shifts solely due to changes in the lattice parameters. In the present work, this problem was overcome using pure electrolytic grade Cu powder as an internal calibrant during the XRD measurements to accurately measure the peak positions of the alloys. This is a standard practice to nullify the extraneous instrumental effects as the exact peak positions of the alloy are measured with reference to the peak positions of the calibrant, which is mixed with the alloy powder. The instrumental peak shifts in pure Cu (1 1 1) reflection and in alloy (111) reflections will be the same. The lattice parameter 'a' for all the Co-Ni alloys was calculated from the corrected 2θ values after eliminating the instrumental peak shift. The lattice parameter calculated from the XRD data for pure cobalt is 3.5367 Å, in agreement with that of fcc Co 3.5305 Å [13] and for nickel it is 3.5180 Å, in agreement of 3.526 Å [50]. The lattice parameter of the alloys (RP2-RP4) lies between the values of pure cobalt and pure nickel and shifts towards pure cobalt value with increasing Co concentration in the alloys (Table 2), as expected.

2.3. Morphological analysis

The morphology of all the alloy samples and the precursors was investigated by FE-SEM and TEM studies. Figs. 4 and 5 show the FE-SEM images of the precursors (P1–P5) and alloys, respectively. It can be clearly seen that the hydroxide precursors consist of lumps of aggregated particles. The nanocrystalline Co–Ni alloy particles show close to spherical shaped aggregated particles with a few hundreds of nanometer in diameter. The strong magnetic interaction between the Co–Ni alloy particles causes agglomeration [28]. The Co–Ni alloy particles exhibit narrow size distribution and the mean particle size in the sub-micrometer range. Typical histograms (Fig. 6) of size distribution were





 $\textbf{Fig. 4.} \ FE-SEM \ images \ of \ precursors. \ P1: \ Ni(OH)_2, \ P2: \ Co_{41}Ni_{59}(OH)_2, \ P3: \ Co_{54}Ni_{46}(OH)_2, \ P4: \ Co_{63}Ni_{37}(OH)_2 \ and \ P5: \ Co(OH)_2. \ P4: \ Co_{63}Ni_{37}(OH)_2 \ and \ P5: \ Co(OH)_2. \ P4: \ Co_{63}Ni_{64}(OH)_2 \ P4: \ Co_{64}Ni_{64}(OH)_2 \ P4: \ P4:$

obtained by picking unagglomerated particles from the SEM images of the Co–Ni alloy samples. The mean particle size of the Co–Ni alloy samples RP2, RP3 and RP4 are $145\pm68,175\pm37$ and

 299 ± 13 nm, respectively. Pure nickel sample (RP1) consists of agglomerated spherical particles but in the case of pure cobalt (RP5) sample small rod-like structures are observed. During the



89 400

HV 20.0 kV Mag 100000x

Fig. 5. FE-SEM images of reduced precursors. RP1: pure Ni, RP2: Co₄₀Ni₆₀, RP3: Co₅₃Ni₄₇, RP4: Co₆₃Ni₃₇ and RP5: pure Co.

HFW 1.49 um

WD Det 10.0 mm ETD -500.0n IIT Ro-



Fig. 6. Histograms of size distribution for the nanocrystalline Co-Ni alloys obtained from the FE-SEM images. Solid lines indicate the mean size of the alloy particles.

polyol reduction, sodium hydroxide present in ethylene glycol is known to control the shape of cobalt and cobalt–nickel alloys [36,51]. Fig. 7 shows the TEM images and the corresponding selected area electron diffraction (SAED) patterns of the Co–Ni alloys. TEM images also indicate that the Co–Ni alloy particles are close to spherical shape, in agreement with the FE-SEM results. The presence of concentric bright rings in the SAED patterns is indicative of polycrystalline nature of the alloys.

2.4. EDX analysis

Energy dispersive X-ray (EDX) analysis was performed on both unreduced and reduced precursors by scanning different zones of the SEM images. It was found that the composition of cobalt and nickel remains homogeneous throughout the alloy samples. The stoichiometry was calculated as Co₄₀Ni₆₀, Co₅₃Ni₄₇ and Co₆₃Ni₃₇ corresponding to the alloys RP2, RP3 and RP4, respectively. The error in the stoichiometric calculation was about 1.5 at % which is comparable to the instrumental error. The unreduced precursors show the stoichiometries of cobalt and nickel to be about the same as those of the corresponding alloys with negligible differences (see Tables 1 and 2). The presence of chlorine in the cobalt containing precursors is attributed to the chloride ions intercalated between the hydroxide layers, while in the case of β -Ni(OH)₂ the presence of chlorine is attributed to the ions adsorbed within the crystal lattice [52]. Negligible amount of silicon was present in all the reduced samples, which is attributed to the etching of borosilicate glass by NaOH [53].

2.5. Magnetic measurements

The magnetization versus applied magnetic field (M-H) plots for the nanocrystalline Co-Ni alloys measured at 5 and 300 K under a maximum applied field of 10 kOe are shown in Fig. 8. The precursors were found to be paramagnetic in nature. All the alloy samples, presented in this work, exhibit superparamagnetic behavior with negligible coercivity and remanence values at both 5 and 300 K. A similar behavior has been reported for the Co₅₀Ni₅₀ alloy nanoparticles prepared by the polyol method [28]. Pure Ni sample (RP1) exhibits soft ferromagnetism and pure cobalt (RP5) is superparamagnetic at room temperature. In general, the saturation magnetization of all the Co-Ni alloys at 5 K is larger compared to that at room temperature (Table 3). This is attributed to magnetic moments being blocked along the applied field direction and the blocked magnetic moments start disappearing with increasing temperature due to thermal activation [54]. The saturation magnetization (M_s) tends to decrease from bulk to nano size [55]. The saturation magnetization of the Co-Ni nanoalloys falls in between that of pure bulk nickel and cobalt which are 54.4 emu/g [55] and 162 emu/g [56], respectively. The saturation magnetizations of Co-Ni alloys are known to vary with the concentration of cobalt, in Co–Ni alloy particles [30]. The M_s values of the alloys in the present study are higher than that of pure nanocrystalline nickel. This is due to the fact that bulk cobalt has higher magnetic moment than bulk nickel.

Fig. 9 shows the magnetization as a function of temperature measured for all the Co–Ni nanocrystalline alloys with an applied field of 400 Oe under field cooled (FC) and zero field cooled (ZFC) conditions. The blocking temperature (T_B) of all the nanocrystalline



Fig. 7. TEM images and the corresponding SAED patterns of the Co-Ni nanocrystalline alloys.

alloys is observed to be close to 300 K (Table 3). The ZFC curves bifurcate the FC curves around the blocking temperature, which corresponds to the "ferromagnetic–superparamagnetic" transition. This transition is observed when thermal energy becomes greater than the barrier height for the magnetization reversal [57].

2.6. Mechanism of alloy formation

The proposed mechanism involved in the formation of mixed cobalt nickel hydroxides $(Co_xNi_{1-x}(OH)_2)$ is as follows.

$$CoCl_2 + NiCl_2 + 2NaOH \rightarrow Co_x Ni_{1-x}(OH)_2 + 2NaCl$$
(1)

The by-product (NaCl) is easily removable by washing with deionized water.

The mechanism involved in the reduction of mixed cobalt nickel hydroxides by hot ethylene glycol is due to the degradation of ethylene glycol in two steps [58]. The first one is the dehydration (Eq. (2)) giving rise to the formation of acetaldehyde:

$$2CH_2OH-CH_2OH \rightarrow 2CH_3CHO + 2H_2O \tag{2}$$

The second step is the oxidation of acetaldehyde with the formation of diacetyl:

$$2CH_3CHO + M_xN_{1-x}(OH)_2 \rightarrow CH_3COCOCH_3 + M^o \text{ or}$$

$$N^o (M = Co, N = Ni) + 2H_2O$$
(3)



Fig. 8. Magnetization versus field plots measured at 5 and 300 K for the Co-Ni alloys. RP1: pure Ni, RP2: Co₄₀Ni₆₀, RP3: Co₅₃Ni₄₇, RP4: Co₆₃Ni₃₇ and RP5: pure Co.

Table 3Magnetic properties of nanocrystalline Co-Ni alloys.

Sample	Magnetic parameters	c parameters		
	<i>M</i> _s at 300 K (emu/g)	<i>M</i> _s at 5 K (emu/g)	<i>T</i> _B (K)	
RP1	42	45	> 300	
RP2	63	78	~ 300	
RP3	72	81	~ 298	
RP4	90	93	~ 300	
RP5	109	121	$\sim \! 297$	

At the same time cobalt and nickel atoms are generated *in situ*, which will be available for the nucleation and growth process. The mixed metal hydroxide, after early reduction, serves not only as a reactant to form Co–Ni alloy but also acts as a catalyst to induce the reduction of remaining Ni(OH)₂ and Co(OH)₂ species

[59]. The role of hydroxyl ions (OH⁻) during the reduction is to increase the reduction rate via acceleration of formation of acetaldehyde from ethylene glycol [60].

3. Conclusions

Nanocrystalline Co–Ni alloys with *fcc* phase were prepared by poyol reduction of mixed cobalt–nickel hydroxides. This method is a simple and reproducible route without any requirement for nucleating agent or protective agent for the preparation of nanocrystalline Co–Ni alloys with controlled composition. The composition of elements in the alloys can be controlled during the precursor (mixed metal hydroxide) synthesis. The morphology of the nanocrystalline alloy particles is close to spherical, as observed by SEM and TEM studies. All the nanocrystalline alloys exhibit superparamagnetic behavior with negligible coercivity and remanence values at 300 K and their magnetic properties



Fig. 9. Magnetization versus temperature plots measured at an applied field of 400 Oe for the alloys. RP1: pure Ni, RP2: Co₄₀Ni₆₀, RP3: Co₅₃Ni₄₇, RP4: Co₆₃Ni₃₇ and RP5: pure Co.

are influenced by the cobalt concentration; the saturation magnetization increases with increasing cobalt percentage in the alloys. The present synthesis method may be extended to other bimetallic and ternary alloys such as Co-Cu, Ni-Cu, Co-Ni-Cu, etc.

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