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## Annealing of amorphous $\text{Fe}_x\text{Co}_{100-x}$ nanoparticles synthesized by a modified aqueous reduction using $\text{NaBH}_4$

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$\text{Fe}_x\text{Co}_{100-x}$  nanoparticles were synthesized by aqueous reduction in iron (II) sulfate and cobalt (II) sulfate using sodium borohydride and sodium citrate. The initial concentrations of iron and cobalt were varied while maintaining an overall metal concentration of 4.60 mM. Increasing the cobalt content from 0 to 100 at. % decreased the magnetization saturation from 152 to 48 emu/g, as determined by room temperature vibrating sample magnetometry. Annealing the samples at 450 and 600 °C showed an increase in crystallite size. Powder x-ray diffraction and transmission electron microscopy was performed to determine the phases and morphology of the materials. © 2010 American Institute of Physics. [doi:10.1063/1.3334172]

The design, synthesis, characterization, and implementation of novel ferromagnetic nanoparticles and their alloys have been of significant interest over the past decade. FeCo based alloys have specifically gained interest due to elevated magnetization along with a high Curie temperature.<sup>1,2</sup> These ferromagnetic alloys have been prepared several ways, including thermal decomposition, sonochemical reduction, and aqueous reduction by borohydride derivatives.<sup>3-7</sup> Aqueous reduction by borohydride provides the greatest commercial potential but requires surface capping agents, which makes it difficult to get alloy formation without high temperature annealing. Chelating agents such as sodium citrate can be used as low cost surfactant capping agents which help to produce  $\text{Fe}_x\text{Co}_{100-x}$  nanoparticles. Various metal ratios were synthesized and heat treated to study the resulting crystallization. Several characterization techniques were used to elucidate the compositional changes as a function of heat treatments.

The synthesis of  $\text{Fe}_x\text{Co}_{100-x}$  nanoparticles was carried out under ambient conditions. Several ratios of cobalt and iron were analyzed. Throughout the trials a borohydride to metal ratio and a metal to citrate ratio were kept at 2:1 and 10:1, respectively. In a typical experiment X mM iron(II) sulfate heptahydrate, Y mM cobalt(II) sulfate tetrahydrate (such that, X+Y=4.60 mM), and 0.460 mM trisodium citrate dihydrate were mixed vigorously using a magnetic stir-bar in 2 L of DI- $\text{H}_2\text{O}$  to ensure total dissolution. Sodium borohydride (8.80 mM) was added to the mixture and allowed to react for 10 min. The particles were magnetically separated and washed several times with ethanol. After washing, the particles were placed in a vacuum oven to dry overnight prior to analysis. Annealing was performed on the dried nanoparticles using a Q200 TA instruments differential scanning calorimeter (DSC) under forming gas.

The dried alloyed nanoparticles were characterized by x-ray photoelectron spectroscopy (XPS), x-ray diffraction, transmission electron microscopy (TEM), and vibrating sample magnetometry (VSM) for determination of phase, morphology, and temperature dependent magnetic properties. Elemental compositions for all alloys were confirmed by using a Varian Vista-MPX charge coupled device (CCD) and inductively coupled plasma-optical emission spectrometer.

Annealing temperatures of 450 and 600 °C were chosen from DSC to represent the before and after crystallization events of the samples. Prior to annealing, the powders were pressed into 3 mm sized pellets and placed in a DSC aluminum pan. The powders were pressed to ensure uniform heating. The samples were then annealed at a ramp rate of 5 °C/min and held at the final temperature for 10 min.

Room temperature magnetometry was performed on a Lakeshore Cryotronics Inc. model 7300 VSM. Field cooled and zero field cooled temperature dependence of magnetization measurements were performed by using Quantum design MPMS XL-5 superconducting quantum interference device (SQUID) magnetometer. The SQUID magnetometer has sensitivity of  $10^{-8}$  emu, where samples were placed in an EverCool Dewar for the measurements in the temperature ranges in between 10 and 400 K with applied dc magnetic field of 100 Oe. Room temperature hysteresis loop curves were conducted on the as-prepared powders at room temperature (see Fig. 1). Variations in the room temperature magnetization saturation with Co content in the alloyed nanoparticles are shown in Fig. 1. Table I lists the magnetization saturation and coercivity results with different heat treatments for all samples. The magnetization saturation ( $M_s$ ) decreases with increasing Co content for the as-prepared alloys. For example, the  $M_s$  decreases from 152 to 48 emu/g as the Co content increases from 0 to 100 at. %. A field cooled/zero field cooled (FC/ZFC) plot of M versus T [Fig. 1, inset (A)] of the as-prepared 50 at. % Co content sample shows

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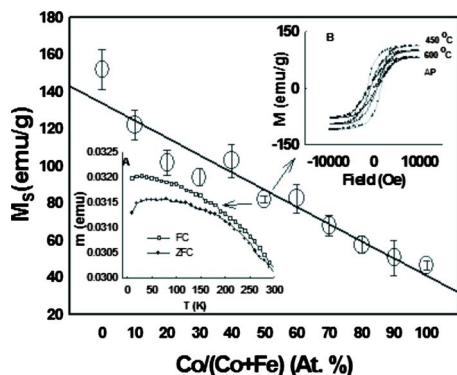


FIG. 1. (Color online) Room temperature VSM and SQUID data of the as-prepared samples. A linear decrease in magnetization saturation is shown as the amount of cobalt is increased. Inset A is the FC/ZFC plot of 50 at. % Co nanoparticles and shows ferromagnetic ordering and with a Curie temperature of 940 K.

ferromagnetic magnetic ordering with a Curie temperature of 940 K. Due to a lack of long range order or crystallinity in the as-prepared samples an overall decrease in the saturation magnetization is expected compared to crystalline Fe–Co samples.<sup>7</sup> Hysteresis curves were conducted on heat treated samples as well. For example, Fig. 1 shows how the temperature affects the hysteresis loops for 50 at. % Co content particles. An increase in both magnetization saturation and coercivity is seen for the 450 °C sample as compared to the as-prepared samples. The 600 °C sample shows an increase in magnetization saturation relative to the as-prepared, however, it is lower than the 450 °C sample. Also the coercivity decreases back to the same coercivity as the as-prepared sample.

X-ray powder diffraction (XRD) was taken on a PANalytical X'pert pro diffractometer at a scanning step of 0.500°, in a  $2\theta$  range from 20°–110° with monochromated Cu  $K\alpha$  radiation ( $\lambda=0.51418$  nm). The diffraction patterns were analyzed to determine the phases present in each of the samples (see Fig. 2). All dried powders were analyzed as-synthesized and after each annealing cycle. Figure 2 shows the diffraction patterns for the Fe<sub>30</sub>Co<sub>70</sub> nanoparticles at various annealing temperatures. The Bragg diffraction peaks are labeled and referenced from the Joint Committee for Powder

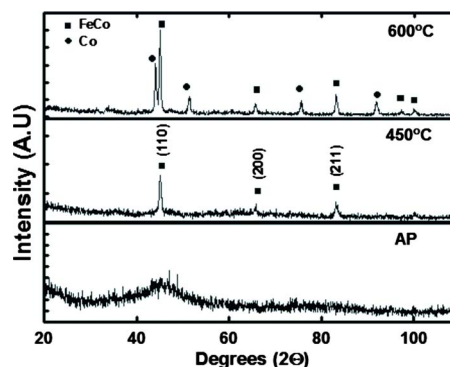


FIG. 2. (Color online) XRD patterns of 50 at. % Co nanoparticles at various annealing temperatures. An increase in crystallinity can be seen as the annealing temperature increases to 600 °C.

Diffraction Standard (JCPDS) reference powder diffraction files from Fe<sub>30</sub>Co<sub>70</sub> (50–0795) and Co (25–0806). The other alloys match similarly to the JCPDS reference powder diffraction files, however, with different alloy compositions.

The powders were characterized using a JEOL JEM-1230 TEM at 150 kV with a Gatan Ultra Scan 4000 SP 4 K×4 K CCD camera. Samples for TEM were prepared by dispersing a drop of nanoparticle loaded liquid suspension onto a carbon film supported by copper mesh (400 grid mesh) followed by evaporation of the liquid medium. Figure 3 depicts TEM images. The TEMs show a morphological transition from spherical to cubic as the cobalt is increased (see Fig. 2). The 50 at. % Co nanoparticles show core/shell character with a large size distribution. The nanoparticles show slight aggregation which can be due to the TEM sample preparation techniques or also it could be due to citrate ions adsorbed onto the surface of the particles causing aggregation.

High resolution photoelectron spectra were recorded using an ESCALAB 250 spectrometer. The 180° hemispherical analyzer and monochromated Al  $K\alpha$  x-ray excitation (Al anode, 12 Kv, 20 mA, and  $h\nu=1486.6$  eV) were applied. The instrument was operated with a magnetic lens in the large area XL-mode with a pass energy of 15 eV. Binding energies are given relative to the binding energy of C1s peak (Eb

TABLE I. Table of magnetization and coercivity data at various heat treatment temperatures.

Sample Co/(Co+Fe) (at. %)	AP		450 °C		600 °C	
	M <sub>s</sub> (emu/g)	H <sub>c</sub> (kOe)	M <sub>s</sub> (emu/g)	H <sub>c</sub> (kOe)	M <sub>s</sub> (emu/g)	H <sub>c</sub> (kOe)
0	151.88	0.55	152.508	0.611	N/A	N/A
10	121.99	0.65	112.501	0.993	69.78	0.73
20	101.59	0.67	59.62	0.837	34.56	0.84
30	93.85	0.7	67.51	0.874	53.66	0.82
40	102.78	0.81	114.28	1.323	106.44	0.77
50	82.18	0.83	112.98	1.496	65.59	0.71
60	82.59	0.66	98.86	1.338	103.14	0.71
70	67.82	0.62	83.13	1.286	108.18	0.77
80	57.52	0.55	113.86	1.102	122.26	0.72
90	50.47	0.51	116.47	0.914	89.71	0.84
100	46.21	0.49	97.46	0.783	92.54	0.82

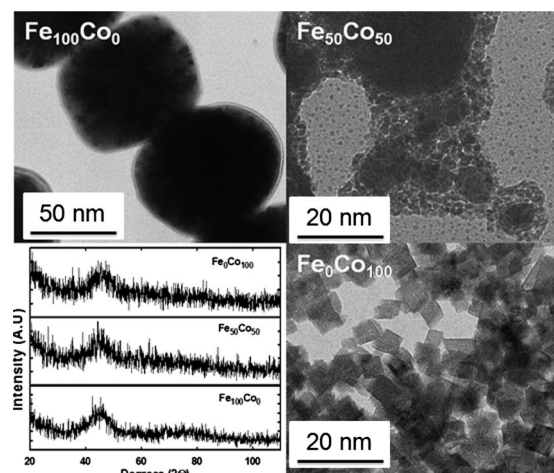


FIG. 3. Transmission electron micrographs of the as-synthesized nanoparticles. It can be seen that the particle morphology changes from spherical to cubic for the pure metals. The 50 at. % Co produced core/shell Fe/Co nanoparticles with a relatively wide size distribution.

(=384.6 eV). An Ar<sup>+</sup> ion flood gun was used for charge compensation. XPS survey scans were used to determine elemental surface chemistry. The scans revealed Na, Co, Fe, O, and C on the surface for all samples (see Fig. 4). Figure 4 is a representative survey scan of the as-prepared nanoparticles and no deviations were seen with the various ratios. The C1s spectrum has three peaks which is consistent with sodium citrate on the surface. The peaks can be attributed to carboxyl carbons, carbon-carbon bonds, and carbon single bond oxygen from the hydroxyl group.

Fe<sub>x</sub>Co<sub>100-x</sub> nanoparticles were synthesized by an aqueous reduction in Fe<sup>2+</sup> and Co<sup>2+</sup> with sodium borohydride and sodium citrate. The as-prepared amorphous nanoparticles produced unexpected trends in the magnetic behavior. The saturation magnetization decreased with an increase in Co content from 152 to 48 emu/g. Although the as-prepared samples exhibit poor magnetic properties due to the lack of

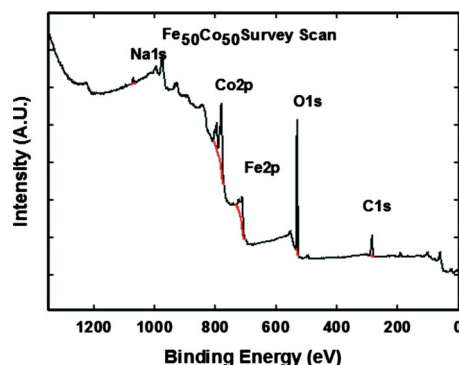


FIG. 4. (Color online) XPS survey scan of as-prepared 50 at. % Co nanoparticles. From the scan it can be concluded that Na, Co, Fe, O, and C are present on the surface of the particles.

crystallinity, the magnetic properties can be improved by annealing at 450 °C under forming gas.

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