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Evidence of Formation of Co_xCu_{1-x} Nanoparticles with Core-Shell Structure

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We have prepared Co_xCu_{1-x} granular alloys with Co contents ($x \approx 0.01-0.30$) by chemical reduction. Samples are characterized by X-ray diffraction and transmission electron microscopy yielding particles of mean diameter 8–20 nm formed in fcc phase. The branching in ZFC/FC magnetization behavior confirm superparamagnetism in the samples, characterized by blocking temperature distributions which represent variations in particle size and inhomogeneities of their chemical compositions. Magnetic field dependence of magnetization show hysteresis loops, and the magnetization at any temperature 4–300 K is a combination of ferromagnetism and superparamagnetism. The saturation moment of Co for the ferromagnetism part increases with the Co content. But the coercive fields (H_C) and magnetic anisotropy of the particles do not vary with Co concentration. Annealed samples exhibit exchange bias in the range 20–150 Oe at 4 K. The results indicate formation of nanoparticles of CoCu alloy in a core-shell type structure with Co being concentrated near the core.

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1. Introduction

The discoveries of superparamagnetism, giant magneto resistance and exchange bias [1, 2] in magnetic granular alloys have generated further interest in the study of binary alloys involving a 3d transition metal and a noble metal. For many years, Co_xCu_{1-x} alloys have been investigated as a model granular system [3, 4] to study the magnetism and transport processes in metallic alloys containing a fine dispersion of nanomagnetic particles. In these studies, the various Co–Cu alloys were prepared by either melt-spinning or electrodeposition on a substrate.

We have reported in this paper the magnetization and exchange bias study in wet chemically prepared CoCu granular alloys with a systematic variation in Co content ≈1–30 wt%.

2. Sample preparation

$CoCl_2$ (Alfa Aesar) and $CuCl_2$ (Merck) mixed in 30 ml aqueous solution with 0.1 mM CTAB (Sigma) as the metal ion concentration in the solution was 0.5 M. A 15 ml 2.8 M aqueous solution of $NaBH_4$ (Merck) was added dropwise from a burette to the salt solution. The solution was continuously stirred by magnetic stirrer in N_2 atmosphere. The black precipitate were washed several times with distilled water and acetone in a glove box in N_2 atmosphere, and finally dried in vacuum at room temperature.

3. Characterization

ICPOES studies give the average composition of Co and Cu in the samples S1–S8 as in Table I. XRD pattern shows (Fig. 1) diffraction peaks coming only from fcc Cu phase and none from the hcp cobalt phase confirming alloy formation. There is a clear broadening in XRD peaks of the samples S1–S8 with respect to Cu bulk indicating formation of nanostructured samples. According to Williamson–Hall method broadening β of peaks in XRD-pattern has two contributions, viz., size broadening, β_D, and, strain broadening, β_ε. These two terms vary differently with the Brag angle (θ):

$$\beta_D = \frac{K\lambda}{D\cos\theta} \tag{1}$$

and

$$\beta_\varepsilon = 4\varepsilon\tan\theta, \tag{2}$$

where D is crystallite size, K — shape factor (0.9), λ — the wavelength of Cu K_α radiation and ε is the strain constant.

The broadening (β), according to Williamson–Hall method can be written [5, 6] as a sum of strain and size broadening, as

TABLE I

The desired (D) and obtained (O) chemical compositions in wt.% for samples S1–S8, and their particle sizes calculated from XRD and TEM studies, strain constant (ε) value from XRD.

Sample	Co-D [wt.%]	Co-O [wt.%]	D^a nm	D^b nm	Strain const. (ε)
S1	1	1.03(1)	12(2)	8	0.0047
S2	3	2.68(1)	13(2)	13	0.0050
S3	5	4.91(1)	14(2)		0.0075
S4	7	7.71(1)	13(2)		0.0069
S5	10	9.69(1)	12(2)	10	0.0049
S6	15	14.03(1)	11(2)	10	0.0047
S7	20	19.97(1)	15(2)	13.5	0.0041
S8	30	31.26(1)	12(2)	18	0.0036

^{1}from XRD; ^{b}from TEM.

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$$\beta^2\cos^2\theta = 16\varepsilon^2\sin^2\theta + \left(\frac{K\lambda}{D}\right)^2. \quad (3)$$

The Williamson–Hall plot of sample S5 is shown in Fig. 2. The particle size D and strain constant, ε, obtained from the above analysis are given in Table I. From the XRD pattern the lattice spacing corresponding three planes (111), (200), and (220) are 0.208, 0.180, and 0.127 nm.

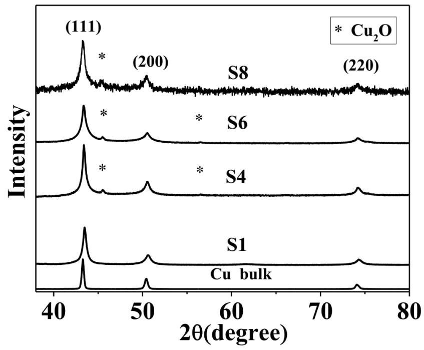

Fig. 1. Room temperature X-ray diffraction patterns of samples S1, S4, S6, S8 and bulk Cu powder.

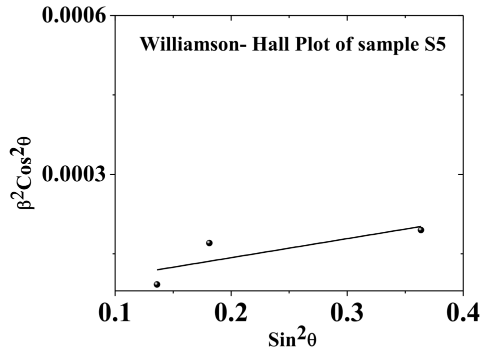

Fig. 2. Williamson–Hall plot from room temperature X-ray diffraction patterns of samples S5.

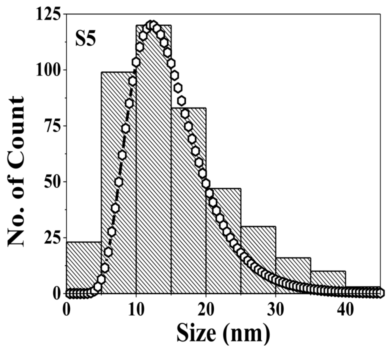

Fig. 3. Histogram of particle size distribution from TEM measurement of sample S5.

TEM studies yielded a particle size of 8–20 nm shown in Table I. Figure 3 shows the particle size histogram of sample S5.

4. Results and discussion

4.1. ZFC/FC magnetization

For zero-field cooled and field cooled (ZFC/FC) magnetization measurements, the experimental data were recorded in the temperature range 4–300 K in presence of 10 mT probing field. ZFC magnetization shows a broad peak at a temperature T_{B}, the so-called blocking temperature, which are centered at 50–100 K for S2–S8 samples. ZFC and FC magnetization curves bifurcate at a certain temperature, T_{P}, higher than $T_{\mathrm{B}}^{\mathrm{expt}}$. For S2–S8, the branching in ZFC-FC behavior are in the range 150–300 K. These samples are superparamagnetic (SPM) above those bifurcation temperatures.

4.2. Hysteresis loops

The behavior of hysteresis loops were studied for all samples at temperatures 4, 100, and 300 K, in ZFC condition in the magnetic field range of 7 T. The data were theoretically fitted using combination of SPM and FM contributions, as the two terms, respectively, in the following sum [7]:

$$M(H) = M_{\mathrm{S}}^{\mathrm{SPM}}\left[\coth\left(\frac{\mu H}{kT}\right) - \left(\frac{\mu H}{kT}\right)^{-1}\right] + \frac{2M_{\mathrm{S}}^{\mathrm{FM}}}{\pi}\tan^{-1}\left(\left(\frac{H \pm H_{\mathrm{C}}}{H_{\mathrm{C}}}\right)\tan\left(\frac{\pi S}{2}\right)\right). \quad (4)$$

$M_{\mathrm{S}}^{\mathrm{FM}}$ and $M_{\mathrm{S}}^{\mathrm{SPM}}$ are the saturation magnetization for FM and SPM parts, in terms of magnetic moment per Co atom. M_{R} is the remanence, H_{C} — the coercivity, and μ — the average magnetic moment of SPM particles or clusters. The values of H_{C} and M_{R} were obtained from experiment. According to the above analysis, sample S1 is superparamagnetic. But S2–S8 have both superparamagnetic and ferromagnetic contributions in the magnetization. The variations of saturation magnetization show that with increase of Co concentration, a larger fraction of Co magnetic moments contribute towards ferromagnetism and less towards superparamagnetism of the particles. The variations in the coercive

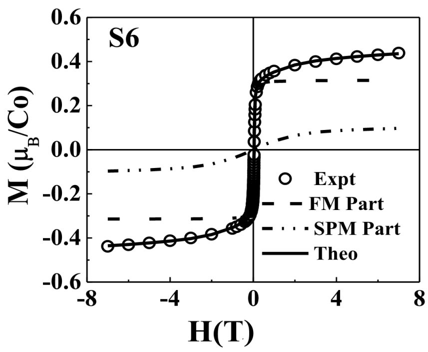

Fig. 4. Magnetization vs. magnetic fields obtained at 4 K for S6. Experimental data are shown as open circles, and the fitted FM (dash), the SPM (dash, dot and dot), components and their sum (continuous line) also shown in this figure.

field are independent of Co concentration. The experimental data and theoretically fitted data for M vs. H for sample S8 are shown in Fig. 4. The magnetic anisotropy constant, K_{A}, of a SPM particle of volume V is given by the Néel–Arrhenius relation, $K_{\mathrm{A}}V = 25k_{\mathrm{B}}T_{\mathrm{B}}$. The values obtained from the above formula for K_{A} are given in Table II. The values are two orders of magnitude larger than that of bulk Co, due to the increased surface effect and stress of nanosized fcc Co clusters. It also shows that Co clusters are almost identical in composition irrespective of Co content in samples.

TABLE II

Ferromagnetic and superparamagnetic saturation magnetizations, $M_{\mathrm{S}}^{\mathrm{FM}}$ and $M_{\mathrm{S}}^{\mathrm{SPM}}$, anisotropy constant, K_{A} (at 300 K), and coercive field, $\mathrm{H_C}$ of S1–S8 samples from analysis of magnetization data at 4 K.

Sample	$M_{\mathrm{S}}^{\mathrm{FM}}$ $[\mu_{\mathrm{B}}/\mathrm{Co}]^a$	$M_{\mathrm{S}}^{\mathrm{SPM}}$ $[\mu_{\mathrm{B}}/\mathrm{Co}]$	K_{A} [erg/cm^3]	H_{C} [Oe]
S1	–	1.310(5)	–	–
S2	0.07(1)	0.480(1)	4.2×10^8	390(10)
S3	0.08(1)	0.450(1)	4.7×10^8	420(20)
S4	0.08(1)	0.380(1)	2.4×10^8	330(10)
S5	0.13(1)	0.225(5)	3.4×10^8	410(20)
S6	0.12(1)	0.225(5)	2.7×10^8	420(20)
S7	0.20(1)	0.360(5)	3.2×10^8	340(10)
S8	0.18(1)	0.200(5)	3.1×10^8	320(10)

Bohr magneton per Co atom.

4.3. Exchange bias

The samples annealed at 200 °C for 1 h yielded exchange bias ranging in between 20–150 Oe at 4 K. The existence of exchange bias shows that in a particle there is a magnetically hard region that is Co-rich and FM, adjacent to a magnetically soft SPM region, probably in a core-shell type structure. Shift of hysteresis loop due to exchange bias for sample S6 is shown in Fig. 5.

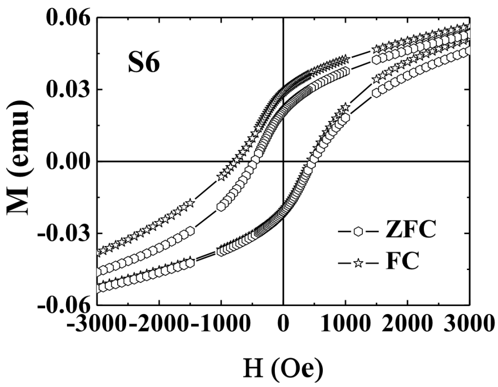

Fig. 5. Shift of hysteresis loop showing exchange bias in S6.

5. Conclusions

At low Co concentration of ≈1%, CoCu alloy is entirely SPM. At higher Co concentrations the magnetization is a combination of SPM and FM at all temperatures 4–300 K, with a blocking temperature distribution. Study of hysteresis loops shows that coercivity do not vary as the Co content. Co atoms participating in ferromagnetism tend to increase and those in superparamagnetism decrease with increase in Co content. The above observations indicate that for S2–S8 samples, there is a cobalt rich part where ferromagnetism is favored, and another part low in cobalt that is superparamagnetic. Annealed samples show exchange bias indicating well-defined FM and SPM regions in the particles. It is reasonable to conclude that Co_xCu_{1-x} alloy particles are formed in a core-shell type structure. The core is progressively rich in cobalt. Moving away from core, Co moments are more and more diluted with Cu. With increase in Co concentration only the size of the core increases in relation to the shell. With decrease in temperature, an increased volume fraction of core becomes FM, and the remaining part behave as SPM.

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