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Magnetism and magneto-transport studies in sonochemically prepared amorphous $Co_{100-x}Pt_x$ nano alloys

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Abstract

Bulk amorphous $Co_{(100-x)}Pt_x$ $(0 \le x \le 50)$ nano-alloys have been synthesized using high frequency ultrasound, displaying single domain (4–5 nm) behavior wherein weakly exchange-coupled particles lead to a field-dependent resistivity behavior. Magneto-resistivity is correlated to the order–disorder parameter in these powder compacts. The plot of $\Delta\rho/\rho_0$ as a function of reduced magnetization indicates that all the systems are weakly exchange coupled.

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1. Introduction

Amorphous systems have provided a rich field to study magnetism in disordered systems. Amorphous and more recently nano-crystalline materials have been investigated for applications in magnetic devices requiring magnetically soft materials [1–3]. Specifically, the Co–Pt alloy is one of the candidates for ultrahigh density magnetic recording media because of its high magnetic anisotropy and good chemical stability upon corrosion [4–6]. The demands on bulk soft magnetic materials include higher combined induction and permeability. To achieve such a goal, the alloy chemistry, structure, and ability to tailor micro-structural features become important. Sonochemistry offers a viable route to achieve such features. Sonochemical decomposition of corresponding metal-carbonyl precursors yields $Co_{(100-x)}Pt_x$ $(0 \le x \le 50)$ nano alloys, where the chemical effects of ultrasound does not originate from the direct coupling with molecular vibrations, but from a non-linear phenomenon called sonochemical cavitation: *the nucleation, growth and subsequent implosive collapse* of a bubble in a liquid [7,8]. Acoustic cavitation generates a localized transient hot spot with an effective temperature of 5000 K and a sub-microsecond collapse time. The rapid cavitational cooling rate ($>10^{10}$ K s^{-1}) is much higher than that obtained using conventional melt-spinning techniques (10^5 to 10^6 K s^{-1}) used to prepare amorphous metals. There are important differences in the electrical conduction in amorphous and crystalline alloys. These include enormous differences in the conduction electrons mean free path and magnitude of potential fluctuations. Unlike the bulk magnetic measurements, magneto-resistive effect is less sensitive to domain effects if their size is greater than the mean free path [9]. In this report, we demonstrate the synthesis of Co–Pt nanoalloys, using sonochemistry and show the magnetic and magneto-transport features, peculiar of these amorphous Co–Pt nanoalloys.

2. Experimental

In a typical reaction, nanosized $Co_{100-x}Pt_x$ $(0 \le x \le 50)$ alloys were prepared by irradiating stoichiometric quantities of $Co_2(CO)_8$ and $PtCl_2$ in decalin with a high intensity ultrasonic probe, 20 KHz, 100 W cm^{-2} in Ar atmosphere for 3 h. 1-Propanol was injected into the reaction mixture for

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reduction of $PtCl_2$. The product was centrifuged, washed with dry pentane in an inert glove bag and dried in vacuum. The structural properties were characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD), using Co Kα radiation. Magnetization as a function of field was measured using an Oxford Mag VSM, in the temperature range of 5–300 K up to 30 KOe, for samples heated at 300 °C. Resistance as a function of temperature was carried out employing the four-probe method. Magnetoresistance of the samples was performed at 4.2 and 300 K up to a field of 8 T.

3. Results and discussion

Sonochemically prepared Co–Pt nano alloys are distinctly different from nano-sized Co–Pt alloys reported in the literature using other wet chemical routes [10], wherein alloys prepared by sonochemistry are realized due to high-energy cavitation phenomena. In wet chemical processes, alloy formation occurs from a post-annealing process of intimately mixed metals. TEM images of the 'as-prepared' Co–Pt amorphous alloy are shown in Fig. 1(a) forming a self-assembly of Co–Pt chains with dimensions of ~200 nm. Fig. 1(b) shows monodispersed, nearly spherically particles with an average diameter of 4–5 nm. Electron micro diffraction shows that the Co–Pt alloys are amorphous as initially formed. (Inset to Fig. 1(b), bottom-right). By irradiating the particles with a high-intensity electron beam in the TEM chamber, crystallization was induced presumably from the local heating in the electron beam. In situ crystallization results in the formation of ring pattern, as shown in inset to Fig. 1(b) (top-left).

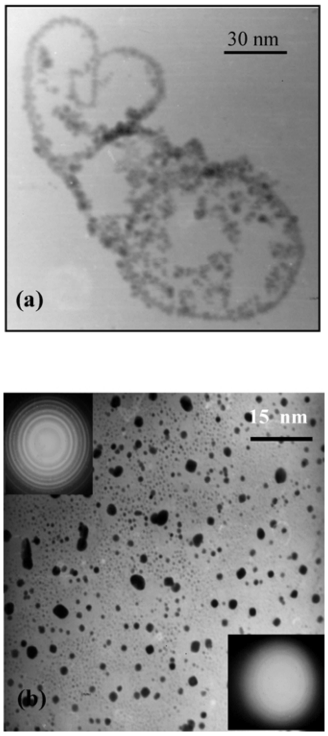

Fig. 1. (a) TEM picture showing self-assembly of the 'as prepared' Co–Pt nano alloys with dimensions ~200 nm length. (b) TEM picture of the dispersed Co–Pt nano-alloys showing nearly spherical, monodispered particles. The inset on bottom-right shows the selected area electron diffraction of the alloys as initially formed. Prolonged exposure to the electron beam induces crystallization as shown in the inset (top-left).

The magnetic size of the particles, $d_{\max}$ estimated from the slope of the magnetization curve employing Eq. (1) ranges from 1.5–2.5 nm [11]. The magnetic dimensions of the nano–alloys are much smaller than the electron mean free path, l (which is about hundreds of Å), allowing domain effects to contribute to the magneto resistive effects.

$$d_{\max} = \left[\frac{18kT(\mathrm{d}M/\mathrm{d}H)_{H=0}}{\pi \rho M_s^2} \right]^{1/3} \tag{1}$$

Differential scanning calorimetric (DSC) curve shows a glass transition at T_1, and a weak crystallization peak at T_2 concurrent with the powder diffraction pattern. The 'as-synthesized' powders are X-ray amorphous. On thermal annealing at 300 °C, the system shows that the *hcp* phase is stabilized for $x = 0$ and 10 compositions. For $x > 10$, the alloys still show amorphous nature as shown as Fig. 2(b). Although it is understood that conventional X-ray diffraction is not a particularly efficient technique in the study of fine nano-structures such as those produced in early stages of crystallization, a clear signature of local ordering is available only for pure Co, heat-treated at 300 °C. Co–Pt

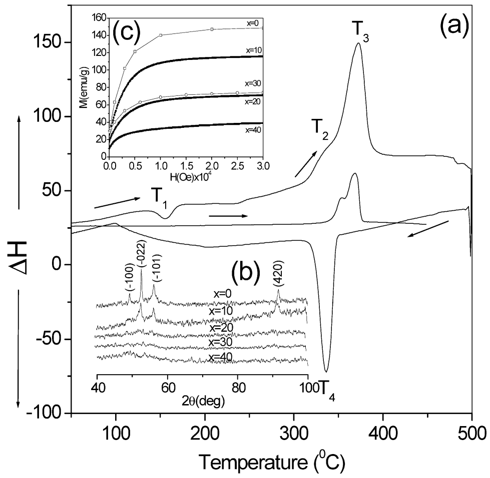

Fig. 2. (a) Shows the DSC curve. T_1 corresponds to the glass transition temperature, T_2 to the crystallization temperature, and $T_3 - T_4$ the reversible phase transformation temperature. Inset (b) shows the X-ray diffraction patterns of the nano alloys heat-treated at 300 °C. Inset (c) shows the demagnetization curves for the amorphous nano alloys exhibiting a typical ferromagnetic behavior.

undergoes a reversible phase transformation from an *fcc* to *fct* phase at T_3 and T_4 in the DSC curve.

In Fig. 3, we show the plot of resistance as a function of field for the Co–Pt nanoalloys, annealed at 300 °C. All the alloy compositions show a negative magneto-resistance ratio ~2% at 4.2 K and 4 T applied magnetic field. We further show the influence of disorder parameter on the electronic transport. According to Nordheim's theory, [12] for the disordered alloys, the residual resistivity ρ_0, which is a good estimate of disorder in the systems depends on the composition x, given by the formula $\rho_0 = \text{const.}\ x(1-x)$. In Fig. 4, we show the variation of ρ_0 as function of x. (ρ_0 increases with Pt concentration showing an oscillatory maximum for the $x = 30$ composition. Another unusual feature in the resistivity curve of amorphous magnetic alloys is the existence of the low temperature resistance minimum, $T_{\min}$ that reflects the local magnetic order in the alloys [13].

A plot of $T_{\min}$ observed in the resistivity curve at low temperature, shows a similar behavior as that of ρ_0-dependence of Pt concentration. The maxima in both $T_{\min}$ and ρ_0 match well with the oscillatory dependence of negative magneto-resistance. Although the MR ratio is fairly low for all the compositions, the maxima for $x = 30$ composition (having lowest (−)% MR) can be argued based on the structural and magnetic disorder suggesting that the magneto-resistance behavior in amorphous nano alloys depends both on the structural disorder and the weak exchange coupling. The plot of $\Delta\rho/\rho_0$ curves of Co–Pt as a function of $m = M/M_s$ shows a flat-top parabola, [14] which suggests weakly correlated magnetic moments. Magneto-resistance studies made at 300 K, however, show a positive MR of ~3% for $x = 30$ composition only, while all other compositions show a negative MR ~1%. This is attributed to the thermal scattering at room temperature besides the short-range disorder effects.

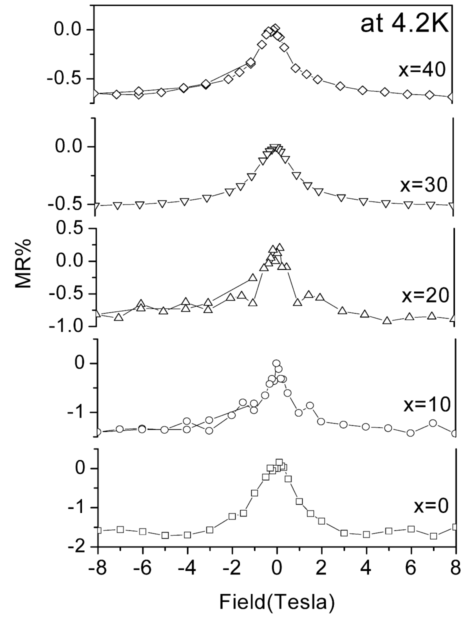

Fig. 3. Resistance as a function of field up to 8 T measured at 4.2 K for $Co_{100-x}Pt_x$ nano alloys heat-treated at 300 °C showing a negative magneto-resistance ratio of ~ 2% is noted up to $x = 40$ percent.

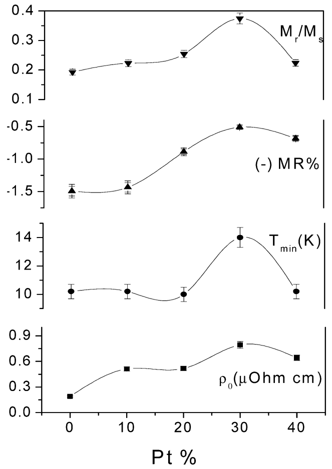

Fig. 4. Plot of remenance magnetization, B_r; negative magneto-resistance, MR%; $T_{\min}$ and residual resistivity, ρ_0 as a function of Pt content showing an oscillatory dependence due to structural disorder effects and weak-magnetic correlation.

We finally show the remenance ratio M_r/M_s as a function of x with values <0.5, suggesting the existence of weak exchange coupling. We observe a similar trend showing a monotonic increase with increasing Pt concentration, with a very sharp increase for $x = 30$ composition. The evolution of H_c and M_r/M_s with x is the result of the transition from an assembly of almost independent particles to a network of connected magnetic particles. The increasing coalescence of magnetic particles could also contribute to the scattering effect due to random ordering. A corresponding decrease in H_c coinciding with the peak in MR% is also seen, because both GMR and H_c are sensitive to multi domain or cluster formation.

4. Conclusions

In summary, we have studied the structural, magnetic and magneto-transport properties of sonochemically prepared $Co_{100-x}Pt_x$ nano alloys. The weak oscillatory dependence of MR seems to agree well with the structural disorder and weak exchange coupling. The study of amorphous alloys leads to striking and yet fairly understood differences from the better-known crystalline systems. These results suggest that $Co_{100-x}Pt_x$ nano-alloys could prove a model system for understanding the fundamental relation between magnetism and magneto-transport in nano particles.

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