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Enhanced phase stabilization of CoPt in the presence of Ag

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We report the synthesis of CoPt and CoPt–Ag nanoparticles by the simultaneous reduction of platinum(II) acetylacetonate (Pt(acac)$_2$), cobalt(II)acetylacetonate (Co(acac)$_2$), and silver nitrate (AgNO$_3$) (for CoPt–Ag) in the presence of poly(N-vinyl-2-pyrrolidone) (PVP). Here the changes in the structural and magnetic properties of these nanoparticles subjected to heat treatment and the effect of adding silver to CoPt in comparison to pure CoPt have been investigated. TEM observations reveal a narrow size distribution with particle diameter of about 2–3 nm. The XRD studies reveal a disordered fcc phase for the as synthesized nanoparticles which after annealing at higher temperatures show peaks corresponding to an ordered $L1_0$ phase. The structural phase transition is also followed by enhanced magnetic properties. The magnetic measurements show the transition of a magnetically soft alloy to a magnetically hard material with a maximum coercivity of $\sim 1$ T after annealing at 700 °C. The addition of silver (Ag) to CoPt alloy induces a reduction in the ordering temperature by 100 °C compared to pure CoPt, with an increased coercivity of 1.2 T. Such thermally stable and structurally ordered hard magnetic nanoparticles are promising candidates for magnetic storage applications. © 2011 American Institute of Physics.

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I. INTRODUCTION

Magnetic nanoparticles have attracted considerable attention in recent years because of their technological applications in areas such as biomedicine, high density data storage, permanent magnets, etc.\textsuperscript{1-8} In particular, the increasing data storage density imposes the need for a material with a size of a few nanometers ($< 10$ nm) along with a high magnetocrystalline anisotropy ($K$) in order to avoid thermal fluctuations that lead to superparamagnetic behavior. Alloyed nanoparticles consisting of equiatomic cobalt or iron in combination with platinum are among the best candidates for these applications due to their high $K$ value ($4-7 \times 10^7$ ergs cm$^{-3}$), as they permit reduction in the size of the particles below 10 nm with simultaneous stability of their magnetization against thermal fluctuations. According to the phase diagram depending on the atomic composition, CoPt exists in different allotropic forms, each exhibiting an order–disorder phase transformation which for equiatomic CoPt occurs at about 825 °C.\textsuperscript{9} In general, the as synthesized alloy possesses a disordered fcc structure with a low coercivity. Formation of a magnetically hard, ordered $L1_0$ phase requires an annealing at high temperatures and the phase diagram shows that the $L1_0$ phase is usually obtained in the temperature range 600–800 °C. Such high temperature treatments may lead to undesirable effects like increase in grain size, deformation of lattice, or even a phase change reverting the hard $L1_0$ to soft fcc structure, etc. Recently, it was found that the addition of a third nonmagnetic element like Au, Ag, Cu, etc., in FePt and CoPt systems results in an appreciable reduction of the ordering temperature, thereby promoting the disordered–ordered transformation. Studies have been carried out by many research groups in order to understand the mechanism of this reduction.\textsuperscript{10-18}

In this paper we report the chemical synthesis of CoPt and CoPt–Ag nanoparticles by Polyol process. The changes observed in the structural and magnetic properties of these nanoparticles as a function of the annealing temperature and the effect of adding silver to CoPt in comparison to pure CoPt has been investigated.

II. EXPERIMENTAL DETAILS

CoPt nanoparticles were synthesized by Polyol process wherein the metal precursors cobalt(II)acetylacetonate (Co(acac)$_2$) and platinum(II) acetylacetonate (Pt(acac)$_2$) were coreduced using poly(N-vinyl-2-pyrrolidone) (PVP) as a capping agent and ethylene glycol as the solvent. Co(acac)$_2$ (97% pure), Pt(acac)$_2$ (97% pure), and PVP (molecular weight 40000) from Sigma Aldrich were used as obtained for the preparation of the CoPt nanoparticles. Co(acac)$_2$ (2 mmol) and Pt(acac)$_2$ (2 mmol) in the presence of PVP were mixed together in ethylene glycol (200 ml). A continuous stirring for 24 h was carried out to obtain a homogeneous solution. Thereafter, the solution was refluxed at a temperature of 200 °C for 4 h with continuous stirring. The coreduction of metallic precursors into metal nanoparticles occurs during refluxing of ethylene glycol, which serves as a reducing agent for the formation of nanoparticles. The change in the color of the solution from light pink to black indicates the completion of reduction and hence the formation of CoPt nanoparticles. Since cobalt ion is readily oxidized, hence there is an oxygen free environment, i.e., an inert (argon) atmosphere is created throughout the experiment. After allowing the solution to cool to room temperature, the black precipitate obtained was isolated by centrifugation (12 000 rpm/10 min) and washed several times with ethanol in order to remove the...
excess of organic surfactants. Finally, it was dried to obtain the powder.

CoPtAg nanoparticles were prepared by modifying the above-mentioned procedure, i.e., the simultaneous polyol reduction of Co(acac)\textsubscript{2} and Pt(acac)\textsubscript{2}, in the presence of silver nitrate, AgNO\textsubscript{3} (as obtained with 99.9% purity, Sigma Aldrich). The mole ratio of AgNO\textsubscript{3} to CoPt salt precursors was taken as 1:1.

To study the changes in structural and magnetic properties, the synthesized powders of CoPt and CoPt–Ag were subjected to different annealing temperatures in argon atmosphere from 500 to 750 °C using a microprocessor controlled high temperature furnace. The crystalline structure of the material was studied by the XRD patterns recorded using a Rigaku Miniflex II diffractometer with Cu K\textalpha\ radiation (\(\lambda = 1.54056\ \text{Å}\)), operated at 30 kV and 15 mA, and at a scanning rate of 0.02° s\textsuperscript{-1}. TEM analysis was performed on sonicated particles dispersed in ethanol on a carbon coated copper grid were used for the TEM measurements. Magnetic measurements were obtained using a vibrating sample magnetometer, MicroSense EV9, with the magnetic field cycling between –2.2 and 2.2 T at room temperature.

### III. RESULTS AND DISCUSSIONS

The phase changes induced by temperature were investigated using XRD. The sequence of XRD pattern as a function of annealing temperature varying from 500 to 700 °C for a constant period of 2 h is shown in Figs. 1(a)–1(d). Curve 1(a) shows the diffraction pattern for the as synthesized nanoparticles. The four broad peaks correspond to the disordered fcc CoPt phase with \(hkl\) planes (111), (200), (220), and (311), respectively. The width of the diffraction peaks is considerably broad indicating the formation of particles having small size. An average particle size of 3.7 nm was estimated using Scherrer’s formula.

The fcc phase, with lattice parameters \(a = c = 3.79 \text{ Å}\), is retained at 500 °C as shown in curve 1(b). The appearance of weak superlattice peaks (001) and (110) in the lower angles (2\theta) at 600 °C [curve 1(c)] is indicative of the beginning of a long range ordering with \(c/a\) ratio of 0.978. Ordering parameter, given by \([1 - (c/a)]/[1 - (c/a)_{\text{bulk}}]\), where \((c/a)_{\text{bulk}}\) is the theoretical value, was calculated to be \(S = 0.814\). Further annealing at 700 °C is marked with the splitting of the (200) and (220) peak along with the presence of additional peaks as shown in Fig. 1(d). The splitting observed is the characteristic feature for a complete \(L_1_0\) formation, giving \(c/a = 0.974\) and \(S = 0.963\), which match well with bulk CoPt\textsubscript{2}.\textsuperscript{9} The additional peaks arising are due to the reduction in the crystal symmetry from cubic to tetragonal lattice. The values of lattice parameters calculated for each annealing temperature along with the ordering parameter, \(S\), are given in Table I.

<table>
<thead>
<tr>
<th>Annealing temperature (°C)</th>
<th>Phase</th>
<th>Lattice parameter, (a) (Å)</th>
<th>Lattice parameter, (c) (Å)</th>
<th>Tetragonality ratio, (c/a)</th>
<th>Ordering parameter, (S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unannealed</td>
<td>fcc</td>
<td>3.81</td>
<td>3.81</td>
<td>1</td>
<td>—</td>
</tr>
<tr>
<td>500</td>
<td>fcc</td>
<td>3.79</td>
<td>3.79</td>
<td>1</td>
<td>—</td>
</tr>
<tr>
<td>600</td>
<td>(L_1_0) (beginning)</td>
<td>3.79</td>
<td>3.71</td>
<td>0.978</td>
<td>0.814</td>
</tr>
<tr>
<td>700</td>
<td>(L_1_0) (complete)</td>
<td>3.81</td>
<td>3.71</td>
<td>0.974</td>
<td>0.963</td>
</tr>
</tbody>
</table>

TEM images for the as synthesized nanoparticles are shown in Fig. 2(a). Clusters of 30 nm containing uniformly distributed, spherical CoPt nanoparticles were observed. Figure 2(b) gives the magnified image of Fig. 2(a). The average particle size, calculated by the Gaussian distribution of the corresponding histogram, was 2.7 nm in comparison to 3.7 nm estimated from XRD. The selective area diffraction (SAD) pattern [shown in the inset of image 2(b)] confirms the formation of a disordered fcc CoPt structure. The diffraction rings are diffuse and wide, which is consistent with the small size of particles.

FIG. 1. (Color online) XRD pattern for CoPt nanoparticles (a) as synthesized and annealed at (b) 500 °C, (c) 600 °C, and (d) 700 °C.
SAD pattern with diffraction rings indexed to planes (001), (002), (112), (113), and (203). The outer covering observed on the clusters in image 3(e) may be due to the unavoidable oxygen contamination or the residual carbon from the capping agent, thereby forming a layer on the surface of CoPt nanoparticles. These results match well with the discussion given in XRD pattern.

The hysteresis measurements, recorded up to a field of 2.2 T at 300 K, have been performed on the unannealed and annealed CoPt nanoparticles. Figure 4 shows the hysteresis loop for the unannealed samples and the samples annealed at 500, 600, and 700 °C.

The results show that the as synthesized nanoparticles [curve 4(a)] are magnetically soft with a low coercivity, $H_c$, and magnetization, $M_s$, of 120 Oe and 10 emu/g, respectively. Growth in the hysteresis curve is observed for samples annealed at higher temperatures. The CoPt nanoparticles annealed at 500 and 600 °C [curves 4(b) and 4(c)] saturate well at the maximum applied field (2.2 T); however, a soft magnetic behavior is still observed in these samples. On increasing the annealing temperature to 700 °C [curve 4(d)], there is a sudden increase in the coercivity of about 1 T.
indicating the transformation to a hard magnetic phase. The effect of annealing temperature on the values of coercivity, $H_c$, and magnetization, $M$, at 2.2 T are plotted in Fig. 5.

With increasing annealing temperature, $M$ initially increases, reaches a maximum value at 600 °C, and then decreases. On the other hand, coercivity increases with annealing temperature. The initial increase observed in $M$ and $H_c$ is due to the increase in particle size. At 600 °C, the value of magnetization remains almost constant while the coercivity still increases. This increase indicates the initialization of atomic ordering. However, annealing beyond 600 °C shows a decrease in $M$ and an increase in $H_c$. The reduction in $M$ can be explained due to the ferrimagnetic nature of the ordered $L1_0$ phase\textsuperscript{20} or due to the conversion of fcc to face centered tetragonal (fct) phase.\textsuperscript{21,22} The sudden jump in the value of $H_c$ to 1 T at 700 °C is attributed to the increased volume fraction of magnetically hard $L1_0$ phase. All these results are in accordance with the XRD profile shown in Fig. 1. The squareness factor ($S = M_r/M_s$) increases with annealing temperature, reaching a maximum of 0.70 at 700 °C. The shoulder observed in the hysteresis loop obtained at 700 °C may be due to the coexistence of soft fcc (e.g., CoPt\textsubscript{3} or CoPt) and hard $L1_0$ phase, i.e., the presence of a mixed phase\textsuperscript{23,24} or due to the presence of a nonmagnetic shell on the surface of the alloy particle [image 3(e)], although none of these phases were detected in the XRD spectra (Fig. 1).

In order to investigate this behavior the sample was further annealed at 750 °C. Higher temperature annealing decomposes the alloy into Pt and CoO as shown in Fig. 6(a). The presence of weak CoPt\textsubscript{3} peaks are also observed at $2\theta = 40.7, 47.2, 69, \text{and} 83.2$.\textsuperscript{25} The occurrence of this phase might be due to the distortion of atomic arrangement in the alloy at higher temperatures. This result is also confirmed by the magnetic measurements performed at room temperature [Fig. 6(b)] which correspond to a magnetically soft phase with values of $H_c$ and $M_s$ being 130 Oe and 1 emu/g, respectively. The remaining percent of $L1_0$ CoPt or the presence of CoPt\textsubscript{3} may be the reason for ferromagnetism in the dealloyed system.

The results show that CoPt nanoparticles with ordered $L1_0$ phase were achieved after annealing at 700 °C. However, annealing at higher temperatures results in the loss of the position ordering and hence particle interdiffusion. In order to see any probability of phase stabilization or lowering of ordering temperature, an attempt was made by the addition of silver in CoPt nanoparticles.

A. Effect of Ag addition to CoPt

In order to investigate the effect of Ag, a systematic study of CoPt-Ag (1:1 mol ratio) nanoparticles as a function of annealing temperature from 500 to 750 °C was performed. Figure 7 show the XRD pattern for CoPt–Ag as a function of annealing temperature.

The XRD pattern for the as synthesized alloy shows the clear formation of CoPt in its fcc phase with the presence of Ag peaks (marked by closed black squares).\textsuperscript{26} The observation that Ag peak does not show any marked variation is indicative of the fact that Ag neither forms any alloy nor does not form a separate phase.
it get oxidized. However, an expansion in the (111) lattice spacing to 2.24 Å by the addition of Ag relative to 2.22 Å for pure CoPt was observed. Such type of lattice expansion has been reported previously on FePt–Ag by other research groups. Due to the large ionic radii of silver, the probability for it to occupy the interstitial sites is low. The other possibilities might be the substitution of silver in the lattice or it may be precipitated as silver atoms localized at the surface of the alloy. The diffraction pattern at 600 °C is marked with the appearance of superlattice peaks and the splitting of (200) and (220) peaks, hence indicating a complete L10 formation with c/a = 0.974 and S = 0.963. Occurrence of well-resolved and distinguishable peaks has been observed on further annealing. The spectra show that the as synthesized disordered fcc nanoparticles transform to the L10 phase at an annealing temperature of 600 °C. A comparison of XRD spectra with and without Ag suggests that the addition of Ag to the CoPt nanoparticles reduces the ordering temperature by 100 °C.

The ratio of the intensity of the (002) peak to that of the (200) peak, i.e., I(002)/I(200), is an indication of texture. The larger the ratio, the better the material texture. It is observed that in the case of CoPt–Ag, with increasing annealing temperature the value of I(002)/I(200) increases from 0.27 to 0.49 at 600 and 700 °C, respectively. Also, the I(002)/I(200) ratio corresponding to CoPt–Ag annealed at 700 °C is larger than that obtained for CoPt I(002)/I(200) = 0.23], indicating an improvement in the texture on addition of silver.

A homogeneous distribution of the as synthesized CoPt–Ag nanoparticles can be seen in the TEM image of Fig. 8(a), with an average particle size of 2 nm. The inset is the SAD pattern which shows diffraction rings corresponding to pure fcc CoPt phase and no plane corresponds to Ag. However, annealing at a higher temperature (700 °C) shows the presence of a (111) plane for Ag [Fig. 8(b)] despite that there is no direct evidence of the formation of separate Ag particles in TEM images.

Figure 9 shows the hysteresis loop recorded up to a field of 2.2 T for CoPt–Ag nanoparticles at 300 K, as a function of annealing temperature varying from 500 to 700 °C. The results show that the as synthesized nanoparticles [curve 9(a)] are soft magnetic materials with a low coercivity of 470 Oe. An increase in the coercivity with annealing temperature is observed up to 600 °C, where it jumps to a value of 0.9 T [curve 9(c)]. This sudden increase, attributed to the formation of L10 phase for CoPt, is observed at a temperature 100 °C less than that for pure CoPt. This implies that the presence of Ag promotes the formation of L10 phase by reducing the ordering temperature (consistent with XRD results, Fig. 7). On further annealing at 700 °C, the loop shows no tendency to saturate, indicating the presence of a large anisotropy with a maximum coercivity of 1.2 T. The shoulder observed in the hysteresis loop at 600 °C is attributed to the strain produced by the presence of Ag or due to the mixed phase.

For comparison, the coercivity of CoPt and CoPt–Ag nanoparticles as a function of annealing temperature is shown in Fig. 10. It is seen that there is no increase in the coercivity of CoPt annealed up to 600 °C. This differs for

FIG. 7. (Color online) XRD pattern for CoPt–Ag nanoparticles (a) as synthesized and annealed at (b) 500 °C, (c) 600 °C, and (d) 700 °C.

FIG. 8. (Color online) TEM image of CoPt–Ag nanoparticles (a) as synthesized and (b) annealed at 700 °C.
CoPt–Ag, which shows a coercivity of 0.9 T at 600°C. With further increase in temperature, although the coercivity of both CoPt and CoPt–Ag increases to 1 and 1.2 T, respectively, the maximum value obtained for CoPt is lower than that for CoPt–Ag. Table II gives the comparative magnetic parameters for CoPt in the absence and presence of Ag, hence reflecting the effect of Ag on the magnetic properties.

The presence of Ag in CoPt lowers the transition temperature and enhances the coercivity. Also, the value of saturation magnetization for CoPt–Ag was half of those obtained for pure CoPt since the composite contained 50% of Ag. Subsequent to these results, Sun et al. showed, using chemically prepared CoPt–Ag nanoparticles, that the addition of Ag has no effect on the phase transformation temperature.

TABLE II. Magnetic parameters for CoPt in the absence and presence of Ag.

<table>
<thead>
<tr>
<th>Annealing temperature (°C)</th>
<th>CoPt without Ag</th>
<th>CoPt with Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M (at 2.2 T) (emu/g)</td>
<td>Hc (T)</td>
</tr>
<tr>
<td>Unannealed</td>
<td>9.7</td>
<td>0.01</td>
</tr>
<tr>
<td>500</td>
<td>39.5</td>
<td>0.12</td>
</tr>
<tr>
<td>600</td>
<td>39.7</td>
<td>0.18</td>
</tr>
<tr>
<td>700</td>
<td>25</td>
<td>1.00</td>
</tr>
</tbody>
</table>

A further annealing at 750°C resulted in the dealloying of the material. The XRD pattern and the hysteresis curve corresponding to CoPt–Ag annealed at 750°C are shown in Figs. 11(a) and 11(b), respectively. Higher temperature annealing decomposes the alloy into Pt and CoO and CoPt3.
peaks as shown in Fig. 11(a). The hysteresis loop in Fig. 11(b) shows the contribution of the magnetically soft CoPt$_3$ phase with values of $H_c$ and $M_s$ being 210 Oe and 4 emu/g, respectively.

IV. CONCLUSIONS

CoPt and CoPt–Ag nanoparticles of 2–3 nm were prepared using polyol process. CoPt undergoes a structural phase transformation from disordered fcc to ordered Li$_2$ phase at 700°C. The structural phase transition results in a soft to hard magnetic material with a maximum coercivity of 1 T. The addition of Ag to CoPt nanoparticles significantly reduces the annealing temperature required for chemical ordering. Also, the coercivity was greater than that achieved in pure CoPt, reaching a maximum value 1.2 T. Further annealing resulted in the debiloying of the material for both cases. The mechanism by which this additive induces an enhanced phase transformation is still not clear. However a systematic variation of Ag concentration would help us to understand the mechanism further and the work is in progress.

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Ag assisted evolution of ordered L1₀ CoPt alloy nanoparticles

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CoPt–Ag nanoparticles were successfully prepared by the simultaneous polyol reduction of the corresponding metal precursors in the presence of poly(N-vinyl-2-pyrrolidone) (PVP). This study details the influence of Ag additive on the structural and magnetic properties of CoPt as a function of Ag concentration. Despite a slight tetragonal distortion, the XRD studies reveal the maximum degree of transformation from fcc to L1₀ phase, for CoPt–Ag nanoparticles containing the highest Ag percent (i.e. 70%) on annealing at 700 °C for 2 h. The Ag particles are clearly observed to be in contact with the surface of the annealed CoPt thus imparting surface strain to these nanoparticles. A magnetic phase transformation is observed after heat treatment showing an evolution of a hard magnetic material from the initially synthesized soft CoPt–Ag nanoparticles. The measure of magnetic hardness increases with increasing Ag content. Consistent with XRD, magnetic measurements show the most remarkable increase in coercivity for the maximum Ag content attaining a value of 1.5 T. The interesting feature of tunability between chemical ordering and coercivity may be useful for data storage devices.

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1. Introduction

Magnetic nano-materials have drawn a lot of attention because of their wide range of technological applications in permanent magnets, high density data storage [1–5], biomedicine [6,7], etc. The interest to further improve the storage density has been a primary focus of research these days. The key point while making progress toward this direction is the processing of nano-magnetic materials with high magnetocrystalline anisotropy and a well oriented growth [8]. The L1₀ materials, e.g. FePt and CoPt, etc., which possess a natural multilayered structure, are being recently investigated for this application. Their high magnetocrystalline anisotropy value (4–7 × 10⁶ ergs cm⁻³) permits stability of magnetization against thermal fluctuations. However, the necessary heat treatment required for its formation leads to unavoidable effects like grain growth, etc. hence limiting its practical utility. A significant reduction in the temperature required for L1₀ phase formation of CoPt and FePt can be obtained by the addition of a third element (e.g. Ag, Au, Cu, etc.) [9–14]. Besides this assistance, a complementary enhancement in the magnetic properties has also been observed in such systems [15–19] thereby promoting its applicative approach. Encouraged by the results obtained in our previous communication on the stabilization of L1₀ CoPt in the presence of Ag [20], lead us to examine the possible mechanism of this effect.

In the present communication we report a systematic study on the effect of Ag on the magnetic behavior of CoPt nanoparticles with varying Ag content.

2. Experimental

2.1. Synthesis of CoPt–Ag nanoparticles

CoPt–Ag nanoparticles with varying concentration of Ag were synthesized by the simultaneous polyol reduction of platinum(II)acetylacetonate (Pt(acac)₂), cobalt(II)acetylacetonate (Co(acac)₂) and silver nitrate (AgNO₃) using PVP as a capping agent and ethylene glycol as the solvent and reducing agent. Detailed synthesis process for the preparation of CoPt–Ag nanoparticles has been described in our previous report [20]. The concentration of Ag in CoPt could easily be varied by varying the mole ratio of CoPt to AgNO₃ salt precursors added during the particle synthesis. To study the role of Ag additive in the structural and magnetic ordering of L1₀ CoPt phase, CoPt–Ag nanoparticles with mole ratio ranging from 2:0.5 to 2:4 were prepared. These nanoparticles are further referred according to their mole percentage of Ag, i.e. 20%, 40% and 70% Ag content.

The as synthesized powders of CoPt–Ag with different concentrations of Ag were subjected to a heat treatment in Ar + 5%H₂ atmosphere at 700 °C for 2 h using a microprocessor controlled temperature furnace. Heat treatment at 700 °C was chosen as the temperature of interest due to preliminary studies that showed a formation of L1₀ phase at 600 °C and a significant enhancement in the magnetic properties on further annealing [20].

2.2. Characterizations

The crystalline structure was studied by the XRD patterns recorded using a Rigaku Miniflex II diffractometer with Cu Kr radiation (λ = 1.54056 Å), operated at 30 kV and 15 mA. TEM analysis was performed on the powders using a 300 kV FEI Tecnai G² 30 Model. Room temperature magnetic measurements were performed using a Vibrating Sample Magnetometer, Micro Sense EV9 with a maximum magnetic field of 2 T.
3. Results and discussion

The effect on the structural ordering of CoPt induced by the presence of Ag was investigated using X-ray diffraction (XRD). Fig. 1 compares the XRD patterns corresponding to the as synthesized CoPt–Ag nanoparticles containing different percentages of Ag.

The sharp peaks (solid squares) observed are signatures of the presence of Ag and the broad humps correspond to the disordered fcc CoPt phase (solid circles) with hkl planes (1 1 1), (2 0 0) and (2 2 0), respectively. The relatively high percentage of Ag compared to CoPt leads to a suppression of the humps as clearly observed for 70% concentration (curve 1c). The width of the humps corresponding to CoPt is considerably broad indicating the formation of small size particles. An average particle size of 2–3 nm was estimated from the full width at half maxima for the (1 1 1) peak of CoPt for each Ag concentration using Scherrer’s formula. A shift in the most intense peak of CoPt (1 1 1) is observed suggesting a lattice expansion [9,21]. This expansion maybe due to the strain induced in the system on account of the difference in the lattice parameters of CoPt and Ag. The increasing amount of Ag atoms substituted in the lattice, causes a corresponding increase in the d_{111}-spacing’s [18] ranging from 2.22 Å to 2.27 Å for 0% to 70% Ag, respectively. Fig. 2 shows the change in the CoPt unit cell dimensions, i.e. the variation in the d-spacing (calculated from the position of CoPt (1 1 1) peak) with increasing content of Ag. The plot includes a data point corresponding to 0% and 50% Ag content which is in accordance to the previously reported results [20].

In order to obtain the chemically ordered L10 phase, CoPt–Ag nanoparticles with different Ag contents were annealed at 700 °C for 2 h under the same annealing conditions. The CoPt broad humps evolved as relatively sharp peaks at 700 °C as observed in Fig. 3. Evidence of the formation of an ordered L10 phase at this temperature was indicated by the presence of the superlattice peaks (0 0 1) and (1 1 0) at low 2θ values (24° and 33°, respectively) and the splitting of the (2 0 0) hump into two distinguishable peaks, i.e. (2 0 0) and (0 0 2) for each concentration of Ag [22]. Strain in the annealed samples was analyzed using Williamson’s–Hall plot [23]. A continuous increase in the strain ranging from 0.3% to 3% has been observed with increasing Ag content.

Since Ag has a low surface energy [24], after annealing, the Ag atoms tend to segregate from CoPt hence assisting CoPt to achieve the ordered phase. The CoPt–Ag sample with 70% additive attains a value, d = 2.19 Å which is close to that of bulk L10 CoPt (d = 2.17 Å). In all concentrations, as clearly observed, the greatest degree of transformation from fcc to L10 phase, is seen in the diffraction pattern corresponding to the highest percentage of Ag, i.e. 70% (curve 3c) with a tetragonality ratio, c/a = 0.976 and ordering parameter, S = 0.89. For 50% Ag content we had however obtained a c/a ratio of value = 0.973 and a better ordering of S = 0.96 [20]. From these analyses it is clear that there may be an optimum percentage of Ag which helps in the chemical ordering, beyond which, there is a possible tetragonal distortion in the unit cell due to the excessive strain in the system.

An attempt to determine the location of the Ag additive, pre and post heat treatment was made by HRTEM analysis. Fig. 4a shows the TEM image of as synthesized CoPt–Ag nanoparticles with 20% Ag additive.

The TEM micrograph shows a spherical morphology for the nanoparticles. The corresponding particle size histogram (inset) follows a Gaussian distribution with an average particle size of 2.6 nm. Inset shows the HRTEM image of an individual nanosphere with a d-spacing of 0.133 nm which closely matches the (2 2 0) plane of fcc CoPt hence confirming its formation. The formation of a disordered fcc CoPt phase is further confirmed by the indexed selected area diffraction (SAD) pattern given in Fig. 4b. The diffused nature of the diffraction rings is consistent with the formation of particles with small size. The existence of Ag was however remains unnoticed in the TEM image and the SAD pattern as well showed no plane corresponding to Ag.

![Fig. 1. X-ray diffraction pattern for the as synthesized CoPt–Ag nanoparticles with (a) 20%, (b) 40% and (c) 70% Ag content.](image1)

![Fig. 2. Variation of d-spacing with increasing content of Ag.](image2)

![Fig. 3. X-ray diffraction pattern for CoPt–Ag nanoparticles annealed at 700 °C with (a) 20%, (b) 40% and (c) 70% Ag content.](image3)
The HRTEM image of these nanoparticles, subsequent to annealing, has been shown in Fig. 5a. The presence of two distinct planes with different \(d\)-spacings values are observed. The distance between the lattice fringes \(0.213\,\text{nm}\) and \(0.135\,\text{nm}\) closely match to the \(L1_0\) CoPt planes (1 1 1) and (2 2 0), respectively, while the \(d\)-spacing \(0.239\,\text{nm}\) corresponds to (1 1 1) plane of Ag \([25]\). The arrangement of Ag atoms in the \(L1_0\) CoPt–Ag nanoparticles was found to be in contact with the surface region surrounding and overlapping the CoPt nanoparticles.

Using ESCA technique, Iskandar et al. \([26]\) also reported an arrangement of Ag atoms on the surface region of annealed FePt nanoparticles. The corresponding SAD pattern (Fig. 5b) show rings indexed to planes prominently matching with \(L1_0\) CoPt phase. The suppression of any ring related to Ag planes may be due to the relatively less percent of Ag in the sample. Interestingly, the annealed sample containing 70% Ag content shows a distribution of two particles (Fig. 6a).

It is observed that small size particles are overlapped by particles of comparatively large size. These big particles may correspond to Ag atoms which overlap the small CoPt nanoparticles. This statement is supported by the corresponding SAD pattern (Fig. 6b) which shows Ag planes, i.e. (1 1 1), (2 0 0) and (2 2 0) dominate over CoPt whose presence is justified by the appearance of a minor reflection of (1 1 0) superlattice plane.

The hysteresis measurements, recorded up to a field of 2.2 T at 300 K, have been performed on the CoPt–Ag nanoparticles with varying concentration of Ag, both pre and post annealed. The as synthesized nanoparticles exhibit a magnetically soft behavior with a low coercivity, \(H_c\) as shown in Fig. 7. The relative value of saturation magnetization, \(M_s\) for the different Ag percent nanoparticles match well according to the concentration of Ag.

The effect of Ag additive as a function of increasing concentration on the magnetic behavior of CoPt–Ag nanoparticles subsequent to heat treatment at 700 °C is shown in Fig. 8. According to these results, there is a strong increase in the magnetic anisotropy with increasing Ag concentration. The most prominent increase was observed in the sample with 70% of Ag giving a maximum coercivity of 1.5 T.

As clearly observed, the hysteresis loop corresponding to each sample has a shoulder close to the zero field. Such a curvature suggests a mixture of nanoparticles with different magnetic phases, i.e. soft and hard phase \([27,28]\). The shoulder in these nanoparticles reduces with increase in the Ag content thus indicating an improvement in the \(L1_0\) phase formation. These results are
consistent with XRD where the highest degree of transformation to the L1\textsubscript{0} phase was observed for 70% Ag content.

4. Conclusions

The role of Ag additive in influencing the L1\textsubscript{0} ordering and in magnetic anisotropy enhancement, as a function of varying Ag content, can hence be understood by the correlating the XRD, TEM and VSM results. The XRD studies reveal that on annealing the CoPt–Ag nanoparticles, due to maximum lattice expansion, the sample with highest Ag content will create more vacant sites on segregation. Therefore the relative percent of Co and Pt atoms able to arrange themselves in an ordered manner will be more, resulting in a relatively higher volume fraction of L1\textsubscript{0} grains than the disordered fcc phase. This is supported by the VSM analysis which shows an improved coercivity and better degree of transformation (less shoulder) for the sample with maximum Ag. Despite the improved coercivity, the $c/a$ ratio for the 70% Ag is less with respect to that of 50% Ag \[20\] implying a tetragonal distortion. Thus, it is clear that merely the concept of chemical ordering is not the only reason for the enhancement in the magnetic properties. The enhancement in coercivity may quite possibly be related to the contribution of strain to the magnetic anisotropy. As observed by the TEM images it is clear that Ag particles are in contact around the surface of CoPt nanoparticles. This pinning of Ag to the surface may perhaps introduce a strain in the surface and hence impart an additional contribution to the magnetic anisotropy reflected by the improved coercivity value. In addition to magnetocrystalline anisotropy of the L1\textsubscript{0} CoPt phase, the strain anisotropy contributed due to the presence of Ag results in an appreciable enhancement of magnetic anisotropy. This enhanced coercivity is effective in stabilizing magnetization, a main property required for magnetic data storage devices. Thus the interesting feature of tunability between chemical ordering and coercivity may be useful for practical applications.

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Correlation of interlayer diffusion with the stoichiometric composition of RF sputtered Pt/Co/Pt sandwiched structures

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Abstract Sandwiched structures comprising Pt/Co/Pt layers with varying cobalt deposition time was studied and its importance on the alloy composition, by correlating the effective interlayer diffusion with the atomic stoichiometry, has been presented. A structural phase transition from ordered L1\textsubscript{2}CoPt\textsubscript{3} \rightarrow L1\textsubscript{0}CoPt \rightarrow L1\textsubscript{2}Co\textsubscript{3}Pt was observed with increasing Co deposition time after annealing at 700 °C. The cross-sectional SEM image of the as-deposited film clearly shows a cobalt layer sandwiched between platinum layers. Rutherford back scattering (RBS) analysis shows a multi-peak signature for the as-deposited films. A detailed RBS investigation on the extent of interatomic diffusion reveals an equiatomic composition for 20 and 30 min deposition time after annealing. The equiatomic CoPt phase shows a magnetically hard behaviour with a maximum coercivity of 15000 Oe. The reported dependence of \( (BH)_{\text{max}} \) on coercivity concludes that by tailoring an additional parameter of deposition time, diverse combinations of structural and magnetic properties can be achieved for appropriate practical applications.

Introduction

Interest in high density recording media has led to intensive research in the area of hard magnetic materials whose properties can be controlled at smaller size scales. The study of CoPt and FePt alloy films and multilayers have recently found much interest for basic as well as technological research due to their exceptional magnetic and magneto-optical behaviour linked with the presence of long range chemical ordering [1, 2]. According to the phase diagram [3] depending on the relative atomic composition, CoPt alloy exists in several ordered phases: face centred cubic (fcc) L1\textsubscript{2} structure for CoPt\textsubscript{3} and Co\textsubscript{3}Pt, and face centred tetragonal (fct) L1\textsubscript{0} structure for CoPt. The equiatomic CoPt alloy compositions gain their prominence mainly because of their high magneto-crystalline anisotropy (\( \sim 4 \times 10^7 \) ergs/cc), a key property required for ultra high density recording materials [4–8]. Large numbers of studies have been conducted on the investigation of structural and magnetic phase transitions of such L1\textsubscript{0} binary alloys e.g. CoPt and FePt [9–11]. Sputtering is one of the common techniques to deposit alloy or layered structures of desired system. The properties of alloy films is well known to be dependent on the sputtering conditions e.g. sputtering power, base pressure, deposition temperature, choice of substrate etc. [12–14]. However, a heat treatment in these layered structures is necessary to synthesize the L1\textsubscript{0} binary alloy. Yet many unsolved questions on interdiffusion of layered structures and phase formation remain, and the detailed study of thin films L1\textsubscript{0} phase formation due to the diffusion of atoms during annealing is in its infancy. To the best of our knowledge, the challenge of acquiring a reduction in the high temperature treatment (mandatory for the formation of L1\textsubscript{0} alloys) so as to avoid the undesirable effects of grain growth etc. has currently been the area of interest [15–20]. Furthermore, up to date very little has been done in the area of developing Co\textsubscript{3}Pt or CoPt\textsubscript{3} alloys using multilayer structures as a means of varying the thickness of the layers. In order to have a better understanding of magnetic properties in CoPt system of varying compositions, we need to prepare films consisting
of different atomic fractions and need to optimise the annealing conditions to get the desired phases of the alloy.

In the present letter, by systematically varying the Co deposition time, we extend our investigation over a wide range of alloy composition: CoPt3, CoPt and Co3Pt. An effort to achieve a highly ordered, equiatomic CoPt film was performed by sputtering Pt/Co/Pt sandwiched layers. Based on the detailed RBS analysis, an attempt to understand the effect of interface atomic diffusion on the structural and magnetic properties of the equiatomic alloy compositions has been presented.

### Experimental

Pt/Co/Pt sandwiched layers were fabricated by RF magnetron sputtering at ambient temperature on Si (100) wafers with a base pressure of $\sim 1 \times 10^{-5}$ mbar. A power of 100 W was maintained with an argon flow initially set at 0.03 mbar for these depositions. The multilayers were deposited by moving the substrate over two elemental sources: Cobalt (Co) and Platinum (Pt) [99.9 % purity, Alfa Aesar]. By keeping the Pt deposition time constant, of 1 and 2 min for the under and over layer, respectively, a series of films were prepared with varying Co deposition time, $t_{\text{co}}$ (in minutes): Sample S1 with $t_{\text{co}} = 10$; Sample S2 with $t_{\text{co}} = 20$; Sample S3 with $t_{\text{co}} = 30$ and Sample S4 with $t_{\text{co}} = 40$. To achieve a structural ordering in the multilayers, the films were further annealed at 700 °C for 6 h under an Ar + 5 % H2 atmosphere. The temperature and duration of heat treatment was chosen so as to allow the occurrence of a complete interlayer diffusion.

The structural phase analysis was performed using a Bruker (D8) X-ray diffractometer (XRD) with Cu Kα ($\lambda = 1.54056$ Å) radiation. The film cross section and surface morphology was viewed using a ZEISS Field emission scanning electron microscopy (FE-SEM) at SSPL, DRDO, New Delhi. Rutherford Backscattering technique (RBS) was performed with a 2 MeV alpha particle beam at scattering angle of 165° at IUAC, Delhi. The magnetic behaviour at room temperature was studied using a Micro Sense EV9 Vibrating Sample Magnetometer (VSM) with the film plane perpendicular to the magnetic field.

### Results and discussions

#### Structure and morphology: XRD and SEM

Figure 1a shows the XRD pattern recorded for the as-deposited S1, S2, S3 and S4 series. All samples show peaks at 41.8° and 48.4°. These peaks are assigned to Pt(111) and Pt(200) planes and are represented by hollow squares in Fig. 1a. It is observed that in Co/Pt multilayer samples, the position of the Pt peak gets shifted to higher angle due to the stress induced by neighbouring atom Co [21, 22]. It is observed that with the increasing cobalt content, the peaks in the XRD pattern become sharper. This clearly indicates an increase in the crystalline nature of the CoPt alloy. This feature may arise as an effect of increasing layer thickness or grain size of film.

The structural phase transitions induced in the multilayers after providing a heat treatment are shown in Fig. 1b. Figure 1b, i represents the annealed phase of S1. Marked by solid circles, the peaks correspond to L12 CoPt3 phase. The super lattice peak intensities i.e. (001) and (110) are weak or almost disappearing, suggesting a weak ordering at such a high temperature. This is in accordance with the phase diagram which illustrates a high temperature phase transformation to disordered phase at 750 °C for L12 CoPt3 [23].

However, the presence of sharp super lattice peaks observed for S2 and S3 suggests an effective structural ordering induced upon annealing (shown in Fig. 1b, ii and iii, respectively). Along with this, the presence of split reflections indexed as (200) and (002) indicates a structural phase transition from fcc to fct phase, a characteristic feature of the L12 CoPt phase [24]. This phase has been represented by indexed planes in Fig. 1b. The degree of ordering, given by $1 - (c/a)/(1 - (c/a)th)$, where, a and c are the lattice parameters and $(c/a)th$ is the theoretical value of L12 CoPt, was estimated to be 0.69 and 0.92 for the annealed S2 and S3 films, respectively. The increased extent of ordering obtained for the film with higher Co content is indicative of the corresponding increase in the volume fraction of fct CoPt grains. Accompanying the ordering parameter, the crystallographic orientation of the film also appears to improve with enhanced fct phase as indicated by the amplified (001) peak with respect to (111) in Fig. 1b, iii. The degree of (001) orientation as measured by the peak intensity ratio $I_{\text{001}}/I_{\text{111}}$ [25] shows an improvement of 44 to 68 % from annealed S2 to S3 films, indicating a gradual development of perpendicular orientation i.e. along the c-axis, in the L12 ordered CoPt film. Further increase in the cobalt content results in the disturbance of atomic arrangement at 700 °C, leading to the formation of a weakly ordered L12 Co3Pt phase (namely S4), marked by solid squares in Fig. 1b, iv. Hence, analysis of the recorded XRD spectra reveals a systematic variation in the atomic composition of the alloy as a function of Co deposition time, transforming from ordered L12 CoPt3 $\rightarrow$ L12 CoPt $\rightarrow$ L12 CoPt alloy phase.

Formation of the structure Pt/Co/Pt with Co sandwiched between Pt layers was evidenced by the cross-sectional SEM image of the as-deposited S2 multilayer as shown in
The FE-SEM image of the as-deposited S2 multilayer shows uniformly distributed granular structures; (Fig. 2b–d) show the cross-sectional and FE-SEM image of the corresponding film annealed at 700 °C, respectively. The cross-sectional SEM image shows a layer of non uniform granular structures. No individual layers could be distinguished confirming an interlayer mixing on annealing. A thickness of about 103 nm was measured for the granular layer. The agglomeration of the grains, consequent to annealing results in the formation of non uniform and big granular like structures as shown in image 2d.

RBS analysis

To conduct a detailed investigation on the sandwiched structures observed in cross-sectional SEM (Fig. 2a), a RBS measurement was performed on the series of the as-deposited multilayers as shown in Fig. 3a. The signature of multilayer peak configuration is clear in the as-deposited samples. Though the high energy edge of Pt over layer matches accurately, a shift in the high energy edge of Pt under layer, towards the lower energy regime, has been observed. This result is in accordance with the varying cobalt thickness and authenticates that the multilayers are not equispaced in the film series. The valley between Pt
peaks quantifies the sequential increase in the thickness of Co layer which is also indicated by the widening of Co signal. In spite of the constant deposition time for Pt overlayer, the variation observed in its thickness maybe due to the oxygen contamination as a result of atmospheric exposure to the film surface [26].

The Rutherford Universal Manipulation Program (RUMP) simulation code [27] was used for the analysis of RBS spectra and generation of the depth profiles, consequently determining the thickness and stoichiometry of the films. The average thickness for Pt under and overlayer were estimated to be 24 and 40 nm, respectively, while the thickness for cobalt layer varied from 20 to 115 nm with increasing Co deposition time. Figure 3b shows a typical simulated spectra corresponding to the as-deposited S2 multilayer for reference.

Since the atomic composition is of utmost importance, a RBS analysis of the annealed S2 and S3 films (which by XRD analysis has been confirmed to exhibit an ordered CoPt alloy) was performed in order to extract the stoichiometry and understand the undergoing diffusion process. The RBS spectra for the annealed S2 and S3 films are shown in Fig. 4a. The most noticeable feature is the reduction in the peak intensities, for the S3 spectrum, possibly due to the surface oxygen contamination. The evidence of interlayer diffusion occurring upon annealing arises from the following observations: (1) the merging of Pt over and under layer signals into an individual Pt peak and (2) the tailing of the low energy edges of Co peak. The tailing of the low and high energy edges of over and under Pt layer peaks, respectively, are not visible due to the unification of peaks; however, the tailing nature of Co gives quantitative information about the diffusion process.

The step at the lower energy edge of Co is sharper for S2 or in other words inclined for S3 indicating that the Co diffusion in S3 occurs over a larger range than that for S2. The tailing of Pt lower energy edge and the step observed at the substrate interface signifies a diffusion of atoms into the substrate [28–30] which is more prominent for S3.

Figure 4b, c shows the simulated RBS spectra (indicated by a solid line) for annealed S2 and S3 films wherein the stars (*) represent the experimentally obtained spectrum. The atomic composition of CoPt alloy has been elucidated in the depth profile and shown in Fig. 5 for the corresponding simulated spectrums. The depth profile analysis shows that although there is an interdiffusion, the mixing between the layers is not uniform leading to a variation in the alloy composition and hence a discontinuity in the

![Fig. 3 The RBS spectra for a the as-deposited multilayers (i) S1, (ii) S2, (iii) S3 and (iv) S4 and b simulated spectrum for the as-deposited S2 multilayer](image)

![Fig. 4 a RBS spectra for annealed (i) S2 and (ii) S3 films with the corresponding simulated spectra's b S2 and c S3](image)
As observed in the depth profile, in accordance to the varying Co deposition times, S2 contains a slight excess of Pt with respect to Co; however, for S3, a nearly equiatomic composition is maintained throughout. As predictable, the atomic contribution from oxygen is confined to the surface layer; however, due to the high affinity of Co oxidation, the extent of oxygen diffusion is more in S3. This result is in good agreement with the reduced peak intensities as shown in Fig. 4a.

Magnetic measurements

The magnetic anisotropy in an alloy system depends on the atomic environment and hence very sensitive to the alloy composition. The hysteresis loop for the as-deposited multilayers reveals a soft ferromagnetic behaviour (as shown in Fig. 6a). The magnetisation value increases with increasing cobalt content with, however, no significant variation in the coercivity (inset of Fig. 6a).

The effectiveness of varying the Co deposition time, leading to different atomic compositions and thus influencing the magnetic properties, is clearly viewed by the hysteresis loop recorded for the multilayers after heat treatment. The L1_0 CoPt phase exhibited by annealed S2 and S3 films is accompanied by drastic changes in the magnetic properties. Figure 6b shows the hysteresis loop for the annealed S1, S2, S3 and S4 films. The annealed S2 film exhibits a magnetically hard
behaviour with a coercivity of 11500 Oe. The shape of the loop indicates an almost perfect square with $M_r \sim M_i$ and the energy product, $(BH)_{max}$, is estimated to be 11.2 MGOe. As tabulated in Table 1, the atomic composition of S2 film shows an insignificant off stoichiometric ratio with a slight excess of Pt, however, the contribution of additional Co atoms in the annealed S3 film improves the diffusion with Pt layers to an extended range hence resulting in an equiatomic composition. This formation of equiatomic fct CoPt phase results in an enhanced magnetic anisotropy as clearly indicated by the improved coercive value of 15000 Oe. Though there is an increase in the coercivity, the value for energy product is limited by saturation magnetisation giving a maximum of 5.2 MGOe. Hence for practical applications, like magnetic data storage and permanent magnets, optimised magnetic properties have to be attained with a high coercivity and maximised value of energy product, $(BH)_{max}$.

Conclusion

An understanding on the role of varying deposition time in influencing the structural and magnetic properties of CoPt films has been achieved by correlating the XRD, RBS and VSM measurements. As a function of Co deposition time, the structural transition between the ordered CoPt phases had been observed by XRD analysis. For the 30 min deposition time, a maximum of 68 % orientation and 92 % ordering was achieved for CoPt alloy. The diffusion of Co and Pt atoms within the deposition time range played a crucial role in adjusting the composition of CoPt film. A successful formation of $Co_{50}Pt_{50}$ composition was accomplished at 30 min deposition for the S3 sample with coercivity and $BH_{max}$ of 15000 Oe and 5.2 MGOe, respectively. Although slightly off stoichiometric, the 20 min deposited film also exhibited a hard phase of 11500 Oe coercivity with a better $BH_{max}$ value of 11.2 MGOe. Therefore, by tailoring the composition of the alloy multilayers by controlling the deposition time, we can mould the structural configuration and magnetic parameters of the alloy. This interplay of alloy composition and their magnetic properties can be well tuned for various and accordingly suited, practical applications.

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