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Thermal Analysis of Co-Ag Alloy Nanoparticles Synthesized by Chemical Reduction

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Abstract- **Co-Ag nanomaterial has drawn much interest among researchers as it is reported to exhibit greater giant magnetoresistance than other magnetic binary alloy systems. The alloy nanoparticles comprising of immiscible elements Co and Ag were synthesized by chemical reduction method. The efficiency of the method used here has been studied using inductively coupled plasma – optical emission spectra (ICP-OES). The thermal analysis of the particles has been carried out with the differential scanning calorimetry (DSC). Its structure stability and temperature dependent magnetic properties have been investigated from the XRD patterns and the magnetic behavior of the heat treated particles. These results are found to be in correlation with the inferences drawn from the calorimetric studies.**

Keywords- Co-Ag nanoparticles, Thermal analysis, Chemical reduction

I. INTRODUCTION

Heterogeneous nanostructures of Ag-Co exhibit higher giant magnetoresistance compared to various other magnetic binary alloy systems like Co- Cu, Fe-Pt, Fe-Ag, Cu-Ni, Ag-Ni etc., [1]. Xiao et al. have observed GMR values as high as 75% for the Co-Ag system with a low volume fraction of Co synthesized by dc magnetron sputtering [2]. According to the phase diagram of Co- Ag, there is no mutual solubility between the two metals and no stable alloy forms under equilibrium conditions [3]. The two metals have a large positive heat of mixing of 28 kJ/ mol [4]. However, there is a possibility of metastable nanophase alloy formation and the alloy formed has sharp interfaces which enhance giant magnetoresistance Since Ag-Co nanomaterial is a promising candidate for a number of applications several studies have been performed to investigate the magnetic properties and the GMR of heterogeneous structures of Co-Ag synthesized by various methods.

As it is essential to find an efficient method to synthesize a stable alloy before it is used for any application, this work deals with determining the effectiveness of the chemical reduction method used for the synthesis of Co- Ag nanoparticles and investigating the stability of its structure and temperature dependent magnetic properties. The sample $Co_{50}Ag_{50}$ was annealed in a vacuum of 10^{-6} mbar at 300 ^{o}C, 400 ^{o}C and 500 ^{o}C for 1 hour and analyzed in order to study the phase transformation and changes in its magnetic behaviour due to heat treatment.

II. MATERIALS AND METHODS

A. Materials

Samples $Co_{10}Ag_{90}$, $Co_{25}Ag_{75}$, $Co_{50}Ag_{50}$ and $Co_{75}Ag_{25}$ were synthesized by taking precursors containing $CoSO_4$ and $AgNO_3$ in ratios 10:90, 25:75, 50:50 and 75:25 respectively. Sodium borohydride was used as the reducing agent.

B. Method

The synthesis process used for sample preparation has been discussed in detail elsewhere.[5] The reduction mechanism can be given as

$$2AgNO_3 + 2NaBH_4 \rightarrow 2Ag + H_2 + B_2H_6 + 2NaNO_3$$
$$CoSO_4 + 2NaBH_4 \rightarrow Co + H_2 + B_2H_6 + Na_2SO_4$$

III. RESULTS AND DISCUSSION

A. Composition Analysis

The stoichiometry of the alloy samples was determined using Perkin Elmer Optima 5300 DV Inductively coupled plasma optical emission spectroscopy (ICP-OES). As the samples used for this analysis are required to be in the form of a clear solution special care was taken to prepare the same. The results obtained from this analysis are shown in table1. It is evident from the metal contents that the alloy composition in each case is in accordance with the precursor stoichiometry and that sodium borohydride has been an effective reducing agent for reducing both Ag and Co. Hence it indicates that this method can be used for synthesizing Co-Ag alloy of any desired composition.

B. Structure Analysis

The structure of the samples was determined using the X-ray diffraction patterns obtained at room temperature using Rich Seifert 3000 X-ray diffractometer with Cu $K\alpha_1$ (λ= 0.15406 nm) radiation. The XRD patterns of the as prepared Co-Ag materials exhibit fcc structure peaks (111), (200), (220) and (311) that match with the fcc phase of silver as per JCPDS card no.893722. These well defined fcc structure peaks indicate the tendency of the alloy to have a preferential orientation of Ag fcc phase. Chandra et al. have observed similar peaks for the Co-Ag alloy samples [6]. Reports on observance of similar fcc structure peaks in the case of Ag-Ni and Ag-Fe alloy nanomaterials, owing to the substitution of Ni and Fe atoms in Ag lattices, are also found in literature [7,8].

The XRD patterns of the as prepared and the annealed $Co_{50}Ag_{50}$ sample show that there is no significant change in the alloy structure after annealing at 300 °C for 1 hour (fig. 1). However segregation of the metal contents is initiated when the sample is heat treated at 500 °C. A small hump seems to appear at 2θ of 44.22° due to the reflections from the (111) plane of fcc Co phase (JCPDS card no. 897093). As the segregated Co content is very less, no other fcc Co structure peak than Co(111) could be observed in XRD. Hence heating the samples beyond 500°C leads to further segregation of the metals. The crystallite sizes of the annealed samples at these two temperatures are determined to be 34 nm and 39 nm. This shows the growth of the crystallites on annealing from 24nm for the as prepared sample.

C. Thermodynamical Analysis

The thermograms recorded in DSC analyzer from the analyses of $Co_{25}Ag_{75,}$ $Co_{50}Ag_{50}$ and $Co_{75}Ag_{25}$ samples by heating them at a constant rate of 10 °C in nitrogen atmosphere, depict a broad exothermic peak in each case as shown in figure 2 a-c. The peaks include three successive processes viz. order – disorder transition in fcc nanocrystals and grain growth which is followed by phase segregation. Similar broad exothermic peak has been observed in the case of Co-Ag alloy samples prepared by RF sputtering [9]. The enthalpy changes reported for the immiscible systems such as Ag-Ni, and Fe-Cu have the trend of increasing with increase in the magnetic component and reaching a maximum for about 50 at.% and then decreasing with further increase in the magnetic metal content [10,11]. The same trend is observed in the case of these Co-Ag samples. However, the heat of mixing for all compositions of Co-Ag is comparatively higher than that for Ag-Ni and Ag-Fe alloys prepared by chemical reduction method[12]. From the theoretical calculations, Kong et al. have predicted a higher heat of formation for various structures of Ag-Co alloys [13].

The heat of mixing was calculated by resolving the broad peak into three components representing the different processes (shown in fig. 3. a-c). The values determined from the first peak above 450 °C are 31.0, 49. 9 and 43.3 kJ/mol for Co contents of 19.4, 44.2 and 73.9 at.%, respectively. The second peak centred around 600 °C is mainly attributed to growth in grain size upon annealing [14,15]. There is overlapping of the third deconvoluted peak which denotes precipitation and crystallization of the metals. This peak starting from about 500 °C, is centred around 775 °C and extends upto 900 °C. The changes in enthalpy during this process for the samples were obtained as 38.5, 42.6 and 32.7 kJ/mol. This indicates that phase segregation is initiated around 500 °C and continues up to 900 °C. A sharp endothermic peak symbolising melting of silver at 962 °C is speculated in all the three graphs.

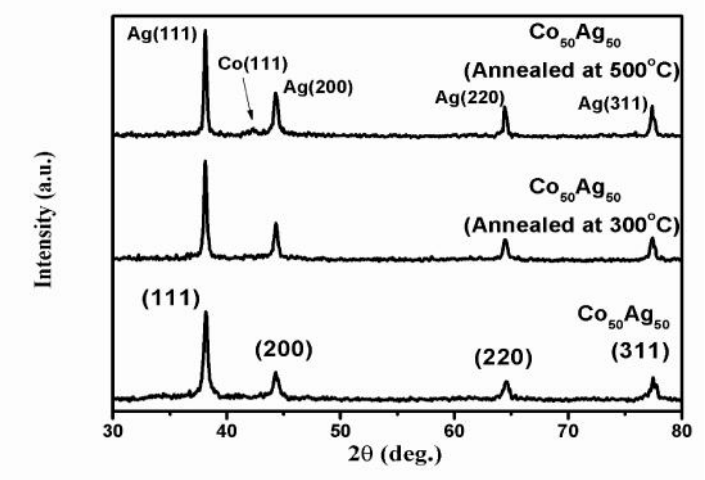

Figure 1. XRD patterns of $Co_{50}Ag_{50}$ sample annealed at 300 °C and 500 °C

Table 1. Composition of Ag and Co in Co-Ag alloy samples as obtained from ICP-OES

Sample	**$CoSO_4$:$AgNO_3$ molar ratio in precursor**	**Co : Ag ratio in alloy**
$Co_{10}Ag_{90}$	10:90	05.6 : 94.4
$Co_{25}Ag_{75}$	25:75	19.4 : 80.6
$Co_{50}Ag_{50}$	50:50	44.2 : 55.8
$Co_{75}Ag_{25}$	75:25	73.9 : 26.1

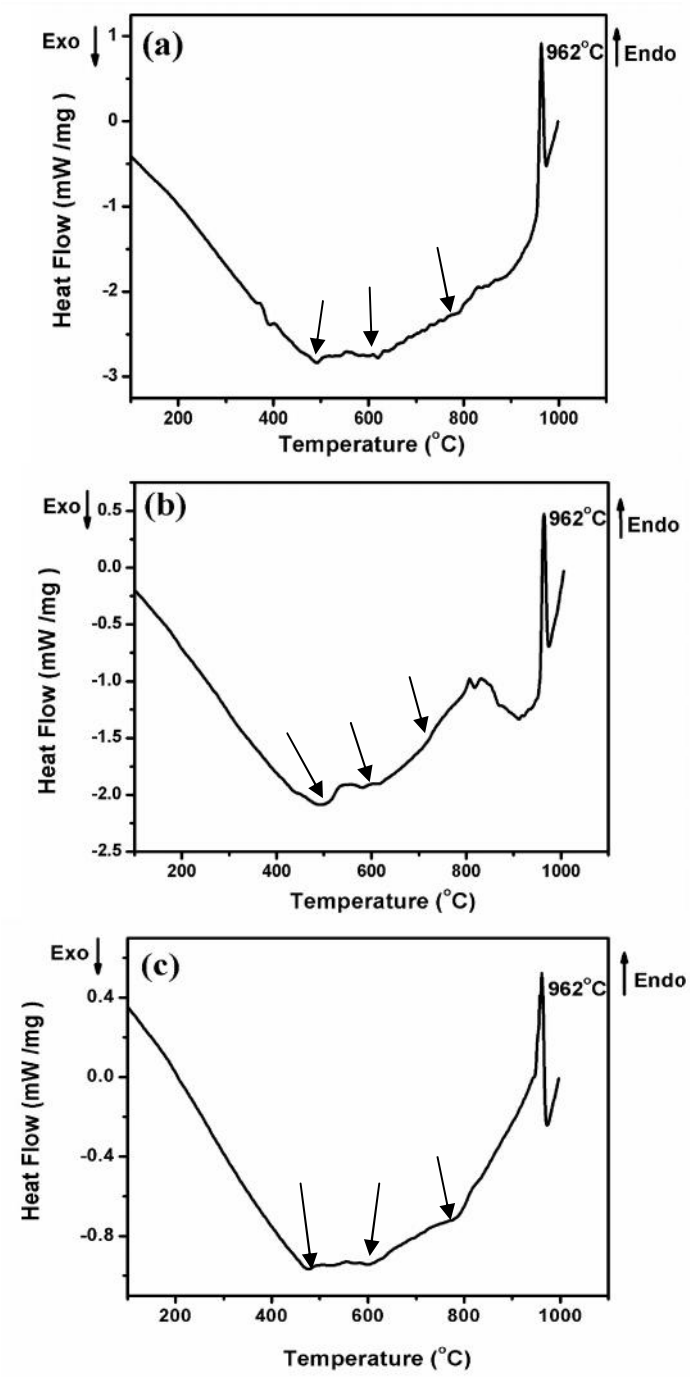

Figure 2. DSC plots of a) $Co_{25}Ag_{75}$ b) $Co_{50}Ag_{50}$ and c) $Co_{75}Ag_{25}$ samples.

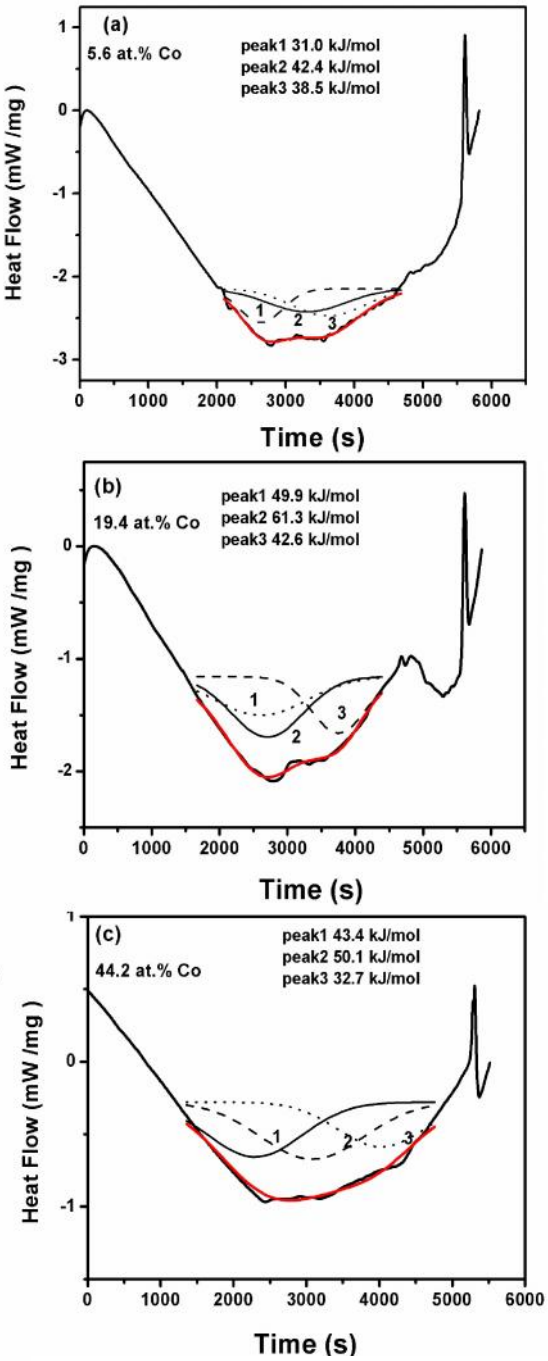

Figure 3. DSC traces resolved into 3 peaks representing the three processes

Table 2. Magnetic data of the as prepared and the annealed Co-Ag alloy samples

Sample	Co content (atom. %)	Saturation Magnetization(σ_s) A-m^2/kg	Coercivity (H_c) kA/m	Remanence (M_R) A-m^2/kg
$Co_{50}Ag_{50}$(as prepared)	44.20	04.62	07.20	01.39
$Co_{50}Ag_{50}$ (T_A=300°C)	44.20	07.07	17.12	02.38
$Co_{50}Ag_{50}$ (T_A=400°C)	44.20	12.05	19.91	03.09
$Co_{50}Ag_{50}$ (T_A=500°C)	44.20	22.34	47.50	09.38

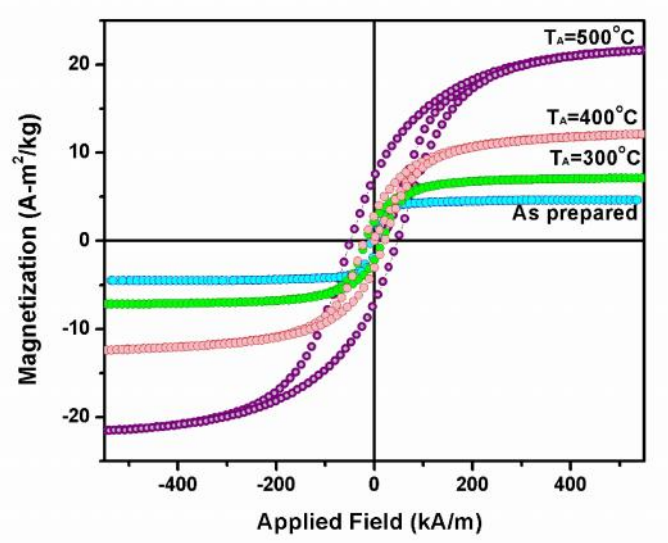

Figure 4. Magnetic behaviour of annealed $Co_{50}Ag_{50}$ sample

D. Magnetic Properties after treatment

The magnetisation behaviour of the sample $Co_{50}Ag_{50}$ annealed at 300 °C, 400 °C and 500 °C was studied (fig.4) using the vibrating sample magnetometer and the data obtained are shown in table 2. It is found that with increase in annealing temperature the saturation magnetization and the coercivity values increase as shown in the table 2. As the samples are heated, initially the fine magnetic particles which are too small to crystallize contribute to the increase in the magnetic moment. On further heating to higher temperatures, the metal components in the alloy which is metastable begin to segregate. As a result of this, the grain size of the magnetic component increases and the magnetic interactions become stronger. As precipitation advances, due to the formation of separate magnetic islands in the non magnetic matrix, the saturation magnetization values further increase. This is also supported by the thermomagnetic behaviour of the material when analyzed by heating the samples in the vibrating sample magnetometer applying a constant magnetic field of 100 Oe.

As reported by the authors elsewhere [5] the Curie transition of the sample annealed at 300 ^oC, occurs at a single temperature of 561 ^oC which is higher than that of the as prepared sample. This signifies that the sample still remains in the same single fcc phase even after annealing it at 300 ^oC for 1 hour. The behaviour of the sample annealed at 400 ^oC was similar to that annealed at 300 ^oC. The graph obtained with the sample annealed at 500 ^oC

has two step Curie transition at 421 ^{o}C (T_{C1}) and 615 ^{o}C (T_{C2}) confirming that phase segregation has been induced by annealing [5]. These two temperatures may correspond to the Ag rich and the Co rich fcc phases with T_{C1} shifting towards the lower temperatures and T_{C2} shifting towards the higher temperature side. The results obtained from the high temperature VSM studies for this sample, is indicative that phase segregation has begun at 500 ^{o}C.

IV. CONCLUSION

The borohydride reduction technique is found to be an effective method for synthesizing Co-Ag alloy samples at normal conditions, as evidenced from the composition of the alloy samples. The structure analysis of the as prepared materials exhibit single fcc structure peaks similar to the fcc phase of Ag where as that of the sample annealed at 500 °C shows an additional fcc Co(111) phase. The broad exotherms obtained from the DSC traces help to understand the thermodynamics of alloy formation in the as prepared state and phase segregation with increase in temperature. The samples are ferromagnetic at room temperature. They exhibit stronger ferromagnetic behaviour with higher magneization values after annealing. The thermomagnetic analysis also confirms that the samples are in a single phase in their as prepared form and even after annealing at 300 °C, exhibiting a single Curie transition. Heating the sample to 500 °C induces precipitation which is eveident from the observsnce of two Curie temperatures .

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