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Synthesis and magnetic properties of flower-like FeCo particles through a one pot polyol process

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ABSTRACT

FeCo alloys of various compositions with flower-like morphology were synthesized using a unique one pot polyol process. The morphology of Fe particles was cubic, whereas the FeCo particles showed flower-like morphology, with more petals for the Co rich FeCo. The average particle size varied from 120 to 155 nm depending on the composition of the alloy. The Curie temperature as determined by thermomagnetic analysis was 985 °C for $Fe_{67}Co_{33}$ and 939 °C for the $Fe_{36}Co_{64}$ samples. Their corresponding bcc to fcc phase transformation temperatures were 985 and 825 °C, respectively. Coercivity up to 511 Oe was observed due to the shape anisotropy arising out of the flower-like morphology compared to the usual cubic or spherical morphologies. Post-annealing studies showed that $Fe_{67}Co_{33}$ is more stable compared to other compositions.

1. Introduction

FeCo alloys are used in variety of applications such as targeted drug delivery, cancer therapy [1,2], high-frequency power applications [3], magnetic-resonance imaging [4], electromagnetic EM-wave absorption [5,6], and magnetoelastic soft actuators [7]. The synthesis of FeCo through chemical synthesis techniques has been a subject of interest and attempted through sol–gel method [8], hydrogen reduction (CSM-HR) [9], thermal decomposition [10,11], thermolysis [12,13], borohydride reduction [14], co-precipitation [15], and alkalide reduction [16]. However, most of these methods have limitations like prolonged synthesis duration [15,17], use of environmentally hazardous chemicals [18], undesirable oxide formation in the final product [19], complex synthesis setups [20], and too many reaction dependent parameters [9]. As compared to these synthesis methods, polyol process is a simple, eco-friendly, and cost effective route to synthesize metal and alloy particles [21–23]. Polyols act as reducing agent and also overcome the problem of oxidation of metal particles in solution compared to other chemical methods. Although Au and Ag were synthesized using polyol process, the synthesis of Fe and its alloys has been found to be a challenge due to the limited reduction potential of polyols [24]. Later on, by enhancing the reduction potential of polyols using appropriate concentration of NaOH, Fe [25,26] and FeCo of varying compositions were successfully synthesized [27,28]. Furthermore, Huba et al. [29] prepared FeCo particles by slightly modifying the synthesis procedure; but the final particles showed irregular morphology and agglomeration compared to the previous reports. The physical properties of metals and their alloys are influenced not only by the size but also on the morphology of the nanoparticles [30–34]. Metals such as Au and Ag which are highly reducible and alloys such as CoNi could be synthesized with various morphologies like wires, cubes, spheres, plates, flowers, rice, and dumbbells using additives by polyol process [35–39]. Since the synthesis of FeCo by co-reduction of Fe and Co from its precursors depends on the experimental conditions such as temperature, type of precursor, NaOH concentration and the scheme of introducing the precursors into the solvent, morphology control is a challenge. The morphology of FeCo particles synthesized through polyol process was reported to be either spherical or cubic so far [27–29]. Moreover, properties of the FeCo particles such as the Curie temperature and bcc to fcc phase transition temperature were not discussed. In this paper, we report the synthesis of flower-like FeCo alloy particles by a simple one pot polyol process without any morphology controlling surfactants and report their compositional dependent properties.

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2. Experimental

For the synthesis of FeCo particles, a one pot one-step procedure was designed which is schematically represented in Fig. 1. In a typical synthesis procedure, 100 mL of ethylene glycol (EG) was heated in a reaction vessel up to a set temperature of 180 °C in a heater plate. The total metal salts concentration was fixed at 0.1 mol/L and the Fe/Co molar ratio was varied according to the anticipated final alloy composition. The precursor salts, Fe(II) chloride tetrahydrate, and cobalt acetate tetrahydrate were weighed, physically mixed thoroughly, and added to this heated solution (at time t). After 5 s (at time $t + \Delta t$), 2 M of NaOH pellets were also added to it followed by mechanical stirring at around 300 rpm. Immediately, the solution starts bubbling, and the formation of alloy was indicated by the gray color supernatant solution. The heater was then turned off and stirring was continued while the solution cooled slowly. The recovery of the particles from the solution is easier at a temperature slightly higher than room temperature due to the lower viscosity of the solvent. The solution was centrifuged, washed several times with methanol, and the black colored FeCo particles were magnetically separated and stored in methanol.

The synthesized FeCo particles were characterized by X-ray diffraction (XRD), thermomagnetic analysis (TMA), vibrating sample magnetometer (VSM), Energy Dispersive Spectroscopy (EDS), and transmission electron microscope (TEM). XRD patterns were obtained using a Rigaku Ultima III X-ray diffractometer with Cu Kα radiation. The elemental composition of the samples was determined using an EDAX detector fitted to a PHILIPS XL30 SEM operated at 20 kV. Thermomagnetic analysis (TMA) was performed using an EXSTAR 6200 Thermo-Gravimetric Analyzer/Differential Thermal Analyzer (TG/DTA) under N_2 atmosphere with a flow rate of 500 mL/min in the temperature range from ambient to 1000 °C. Room temperature hysteresis loop was recorded in a vibrating sample magnetometer (VSM) (Model 7404, Lakeshore, USA). The morphology of the particles was determined using a FEI make 300 kV TEM.

3. Results and discussions

3.1. Reaction process

For the formation of FeCo alloy, co-reduction of Fe and Co has to be achieved which can be explained based on the following reactions [21,24,26]:

$$C_2H_6O_2 \xrightarrow[-H_2O]{\Delta} CH_3CHO \quad (1)$$

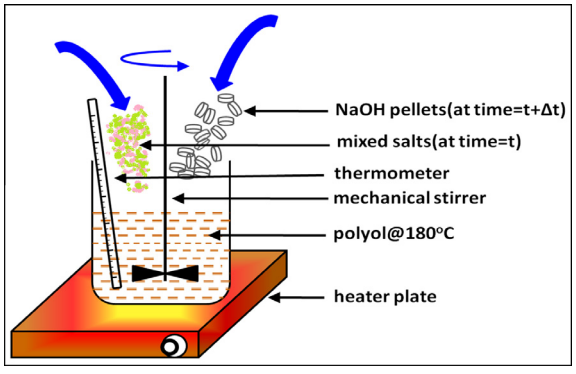

Fig. 1. Schematic representation for the synthesis of FeCo particles by one pot polyol process.

$$2CH_3CHO + FeCl_2 \xrightarrow[-2NaCl]{\text{Excess NaOH}} CH_3COCOCH_3 + 2H_2O + Fe^0 \quad (2)$$

$$CH_3CHO + Co(C_2H_4O_2) \longrightarrow CH_3COCOCH_3 + H_2O + Co^0 \quad (3)$$

In the above Eq. (2), the experimental condition must be controlled in such a way that Fe^{2+} ions directly reduces to Fe without forming $Fe(OH)_2$. This condition can be met by adding the precursor salt at the reaction temperature directly. The high concentration of [OH^-] ions enhances the continuous dehydration of polyol and formation of acetaldehyde by facilitating the electron transfer from polyol to the ionic species thereby resulting in the reduction of Fe. In the case of Co as per Eq. (3), the reduction is preceded by the formation of alkoxide and dissolution. The presence of [OH^-] ions accelerates the above reduction process. However, the presence of [OH^-] ions is more critical for the reduction of Fe compared to Co since the standard reduction potential (SRP) of Fe is lower than the polyol reduction limit.

The proposed synthesis procedure in this paper overcomes some of the possible difficulties in the earlier reports for the polyol synthesis of FeCo alloy. As per the procedure adopted by Kodama et al. [27], the EG/metal salts/NaOH system was heated to the required temperature, refluxed for 1 h in the presence of PVP, and cooled to room temperature. Also, the reaction was carried out at a lower temperature of 130 °C, at which Co is not easily reducible as of Fe and also would result in obtaining unreacted final products or agglomerated particles even with a slight variation in the optimized reaction parameters. Later on, Huba et al. [29] introduced metal precursors to the EG/NaOH solution at an elevated temperature of 195 °C. At this temperature very close to the boiling point of EG (~198 °C), it is difficult to maintain the solvent concentration, and slight thermal fluctuations would affect the composition drastically. Moreover, reduction of Co is more favoured than Fe at higher temperatures [27]. However, the co-reduction of Co and Fe, a prerequisite for the alloy formation, is possible only if the reaction medium is subjected to a very high concentration of precursor salts and NaOH within a short span of time at the elevated temperature. This is feasible only if both the metal salts and the NaOH are incorporated into the solvent at the elevated temperature, and NaOH is added as pellets instead of aqueous form which could be justified on the basis of collision theory of chemical reactions. According to collision theory [40], chemical reaction occurs when the reactant molecules collide with each other with sufficient energy (activation energy) to break the pre-existing bonds and form new bonds. Higher the concentration of the reactants more is the probability for successful collisions, thus increasing the rate of reaction. Also, when a catalyst is involved, less energy is required for the chemical change to take place, and hence, more collisions have sufficient energy for reaction to occur. The reaction rate therefore increases. Moreover, the introduction of NaOH pellets supplies the required enthalpy by the sudden exothermic dissolution of NaOH at elevated temperature and enhances the reduction of Fe and Co. The exothermic energy should be available at the same instant when the metal precursors are introduced. If the NaOH is dissolved first, the dissolution of all the NaOH occurs in a wide range of temperature, and therefore, sufficient exothermic energy may not be available to reduce Fe. The slow reaction would also result in the formation of Fe hydroxides.

The synthesis of FeCo has been attempted at different temperatures such as 130 °C, 160 °C, and 180 °C in this work. Samples prepared at temperatures other than 180 °C showed agglomeration or lack of composition control under the present experimental conditions. Therefore, 180 °C was chosen as the appropriate temperature for further synthesis of the samples. Table 1 shows the initial and final composition of the FeCo alloys synthesized at 180 °C. The final composition is in close agreement for Fe rich samples, whereas it