

Magnetic Properties Hard-Soft SmCo₅-FeNi and SmCo₅-FeCo Composites Prepared by Electroless Coating Technique

M. Lamichanne¹, B. K. Rai¹, S. R. Mishra^{1*}, V. V. Nguyen², J. P. Liu²

¹Department of Physics, The University of Memphis, Memphis, USA; ²Department of Physics, The University of Texas, Arlington, USA.

Email: *srmishra@memphis.edu

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ABSTRACT

Composites of SmCo₅-FeNi and SmCo₅-FeCo, hard-soft magnetic materials, have been synthesized via electroless plating of magnetically hard SmCo₅ powder particles with magnetically soft FeNi and FeCo, respectively. The influence of coating thickness of soft magnetic layers on the structure and magnetic properties of the composite has been studied. Overall FeNi coating was found to be less dense compared to FeCo for the same plating duration. Structurally the coating was found to be nodular in morphology. These coating have dramatic effect on the overall magnetic property of the composite. As compared to FeNi coated SmCo₅ composite, two-fold increase in the saturation magnetization has been observed upon coating SmCo₅ ($M_s \sim 28$ emu/g) with FeCo to a value 56 emu/g. The coercivity of composite powder was found to decrease with increasing the coating layer thickness. The absence of exchange spring behavior in the hard-soft composite is attributed to magnetically soft layer thickness exceeding the theoretical length limit for exchange-spring coupling.

Keywords: Electroless Plating; Hard-Soft Composites; Exchange Spring

1. Introduction

Permanent magnetic materials are characterized by their figure of merit, $(BH)_{\max}$ energy product, which is the maximum rectangular area under the second quadrant of the hysteresis loop. The increase in $(BH)_{\max}$ is possible by increasing the coercivity (H_C) and the saturation magnetization (M_s). For materials with high H_C values ($H_C > 2\pi M_s$), the theoretical limit for the energy product is limited only by M_s and is given by $(BH)_{\max} \leq (2\pi M_s)^2$. Methods to overcome this limitation have focused on developing high anisotropy materials with high M_s and Curie temperatures (T_C), materials which are based on rare-earth (RE)-transition metal (TM) intermetallics such as SmCo₅, Sm₂Fe₁₇ and their boride or nitride compounds such as Nd₂Fe₁₄B and Sm₂Fe₁₇N_x [1-3]. In spite of the considerable improvement in the magnetocrystal line anisotropy, these materials still exhibit lower M_s than Co, Fe or Fe₆₅Co₃₅, which have $4\pi M_s$ values of 18, 21, and 24 kG, respectively [1].

The concept of an “Exchange-Spring” or “Exchange-hardened” magnet was proposed by Kneller and Hawig [4] to overcome the limitations outlined above. The

spring magnet is essentially a composite of two ferromagnetic (FM) phases; hard and soft magnetic phases. The soft phase, rich in transition metal, enhances saturation magnetization, while the hard phase provides the required magnetic anisotropy and stabilizes the exchange coupled soft phase from demagnetization. Most of the reported literature on spring magnets is based on Nd₂Fe₁₄B or Sm₂Fe₁₇ (hard)- α -Fe or Fe₃B (soft) [5-7]. Insufficient temperature stability and poor corrosion resistance are main factors limiting applications of Nd₂Fe₁₄B-based magnets. However, the family of samarium based alloys such as SmCo₅ and Sm₂Fe₁₇N_x could be an attractive candidate material since it can be used as the hard phase due to its high magnetization (SmCo₅, $M_s \sim 0.84$ MA m⁻¹, Sm₂Fe₁₇N_x, $M_s \sim 1.22$ MA m⁻¹) and high Curie temperature, T_C , (SmCo₅, $T_C \sim 720^\circ\text{C}$, Sm₂Fe₁₇N_x, $T_C \sim 476^\circ\text{C}$) which are comparable to those of Nd₂Fe₁₄B ($M_s \sim 1.28$ MA m⁻¹, $T_C \sim 312^\circ\text{C}$, $H_C \sim 6.0$ MA m⁻¹) [8].

The exchange-spring magnets have been fabricated by melt-spinning, hot-compaction [9], mechanical alloying [10,11], however these techniques yields nanocomposites with random dispersion and orientation of hard magnetic phase and often having no control on the growth of soft-phase [6,12]. Thus, if the soft phase size could be re-

*Corresponding author.

duced and highly dispersed throughout the magnet, then the interaction between hard-soft phases could be significantly enhanced, leading to significant improvement in $(BH)_{\max}$ energy product. Various techniques such as sputtering, pulse laser deposition (PLD), electrolytic coating, and electroless coating [13] have been explored to increase the interaction between hard-soft phases of the composite.

Majority of electroless coating studies are limited to Nd-Fe-B powder [14-16] and were carried out mainly with a purpose of improving the corrosion resistance of the magnet. However, the use of electroless plating method has not been yet fully explored for the purpose of developing hard-soft exchange-spring magnets [17]. Considering compatible magnetic properties of SmCo₅ to Nd-Fe-B, and high magnetization of FeNi and FeCo as compared to α -Fe, the present study explores the synthesis of hard-soft phase SmCo₅-FeNi/FeCo composites via electroless plating technique. Electroless plating method is known to produce uniform adhesive coating on a wide variety of substrate. In the electroless plating method, the autocatalytic plating baths contain reducing agents ready to react with the substrate in the presence of catalyst, a metal which is to be deposited on the substrate. The property of the coated film depends on time, temperature, and catalyst concentration. In this article, magnetic properties of hard-soft phase composite are studied as a function of thickness of the soft magnetic layer.

2. Experiment

The hard-soft composites, with a choice of SmCo₅ as a hard phase and FeNi and FeCo as soft phase, were prepared using modified electroless plating method [17]. SmCo₅ powder of average grain size ~50 micron and 99.5% purity was obtained from Sigma Aldrich. SmCo₅ was degreased in acetone solution and activated in 0.5 M sodium hypophosphite at 90°C for 10 min. An electroless plating bath was prepared by using 0.09 mol of nickel sulfate (NiSO₄·6H₂O) or cobalt sulfate (CoSO₄·7H₂O), 0.07 mol of iron sulfate (FeSO₄·7H₂O), 0.5 mol of sodium hypophosphite (NaH₂PO₂·H₂O), 0.3 mol of sodium citrate (Na₃C₆H₅·2H₂O), and 0.1 mol of ammonium sulfate ((NH₄)₂SO₄). Activated SmCo₅ powder was introduced into the electroplating bath. The pH value of the plating bath was maintained at 8 - 10 by using sodium hydroxide. The plating was done at temperature 80°C. The electroless plating of FeNi was carried out for the duration of 15, 30, and 60 minutes and for FeCo was carried out for 30, 60, 90, and 120 min. Afterward electroplated SmCo₅ composite powder was rinsed with the de-ionized water and dried in the presence of argon gas at 90°C for three hours. The X-ray diffraction (XRD) patterns of the composite were obtained using Bruker D8 Advance diffractometer using Cu K α radiation. The sur-

face morphology and composition of the composites were studied using scanning electron microscope (SEM) and energy dispersive X-ray (EDX) spectroscopy, respectively. The room temperature magnetic measurements were made by the Alternating Gradient Magnetometer (AGM, Princeton Measurement Corp.) in the maximum field of 14 kOe.

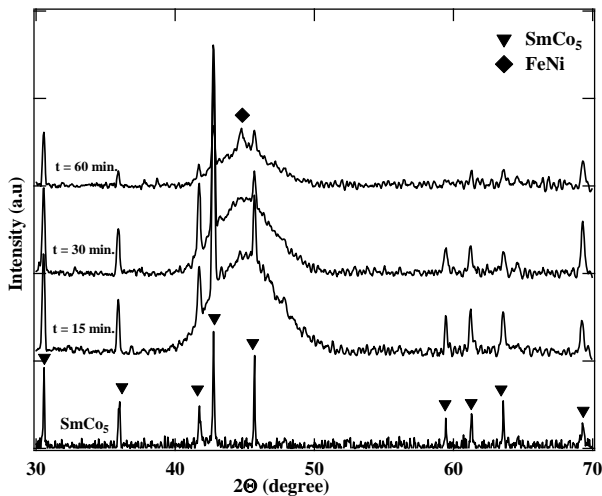
3. Results and Discussion

X-ray diffraction pattern of SmCo₅ powder electroplated with FeNi and FeCo is shown in **Figures 1(a)** and **(b)**, respectively. Presence of strong FeNi and FeCo peaks is recorded. With the electroless plating time, the peak intensity of FeNi and FeCo increases and correspondingly the peak intensity of SmCo₅ decreases. Difference in the growth of FeNi and FeCo is also evident. The presence of broad FeNi peaks shows that initially FeNi layers are amorphous. Furthermore, the presence of SmCo₅ peaks even after 60 minute of plating time shows the formation of thin layer of FeNi. However, the full-width-at-half-maximum (FWHM) of FeNi peak decreases with the plating time. This decrease of FWHM of FeNi peaks indicate a crystalline growth of FeNi, a growth which results upon thickening of FeNi layers. On the other hand, even for short plating duration ~15 min, thick and crystalline FeCo layers are formed as evident from the presence of sharp FeCo diffraction peaks. Furthermore, gradual reduction in SmCo₅ peaks is noticed with the plating time; which clearly indicates the thickening of FeCo layers over SmCo₅ particles.

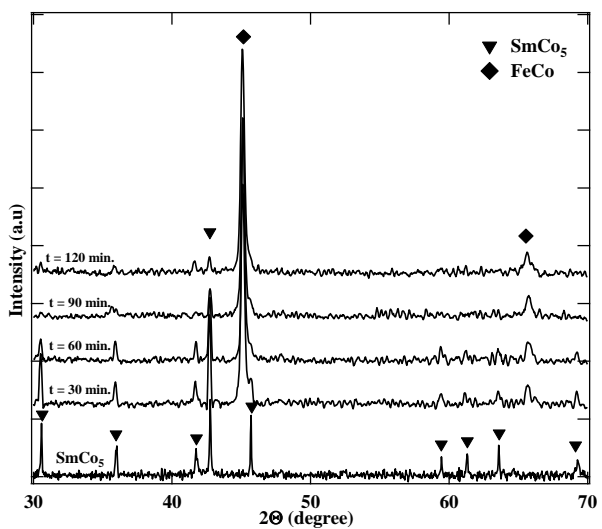
Figures 2 and **3** show SEM images of FeNi and FeCo coated SmCo₅ composite powders, respectively. These SEM images show that in all cases the coated layer is neither smooth nor uniform. A nodule like coating structure appears. The EDX elemental analysis confirms that both FeNi and FeCo are in 30:70 weight ratios. This is further confirmed by the X-ray diffraction peaks indexed by ICDD data base. The ICDD index number 71-8326 and 50-0795, for FeNi and FeCo, respectively show that soft layers are iron deficient. Presence of trace amount of phosphorous is also detected in EDX.

Figures 4(a) and **(b)** show the room temperature hysteresis loops of SmCo₅-FeNi and SmCo₅-FeCo composites, respectively. The hysteresis loops of electroless plated SmCo₅ particles are also compared with SmCo₅ particles. As it can be seen from these plots, that FeNi and FeCo both have different influence on the overall magnetic properties of these composites. **Table 1** lists the room temperature magnetic parameters extracted from the hysteresis loop of these composites.

The observed decrease in magnetization of FeNi coated SmCo₅ composite (15 minute sample) may result partly from the increased weight of the sample and amorphousness of the FeNi layer. With the increase in the



(a)

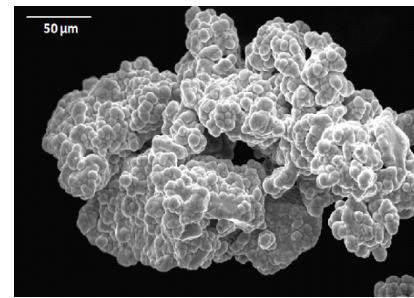


(b)

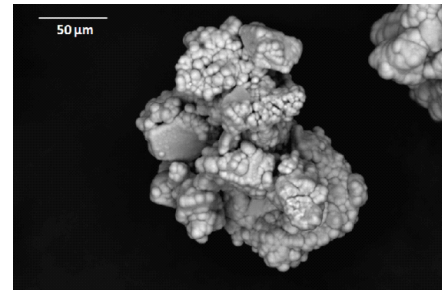
Figure 1. (a) X-ray diffraction pattern of SmCo_5 powder coated with FeNi as a function of electroless plating time; (b) X-ray diffraction pattern of SmCo_5 powder coated with FeCo as a function of electroless plating time.

plating time, the magnetization seems to increase because of the growth of FeNi crystals. This is also evident from monitoring the FeNi peaks in the XRD results. On the contrary, in case of $\text{SmCo}_5\text{-FeCo}$ composites, highly crystalline FeCo coating enhances the saturation magnetization of the composite by almost a factor of two. This is because FeCo has higher magnetization than FeNi.

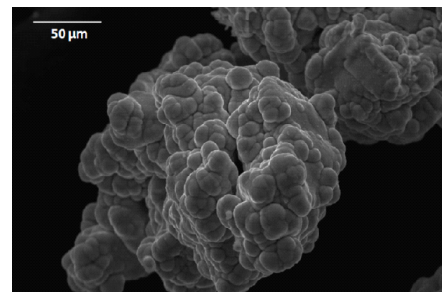
The coercivity of composites was observed to decrease upon coating as depicted in inset **Figure 4** and **Table 1**. The observed decrease in coercivity in $\text{SmCo}_5\text{-FeCo}$ is more than that of $\text{SmCo}_5\text{-FeNi}$. The decrease in coercivity is schematically explained in **Figure 5**. Assuming SmCo_5 as a spherical particle coated with thick and magnetically soft phase layer of FeCo or FeNi. Under the



(a)



(b)



(c)

Figure 2. SEM images of $\text{SmCo}_5\text{-FeNi}$ composites electroless plated for (a) 15; (b) 30; and (c) 60 minutes.

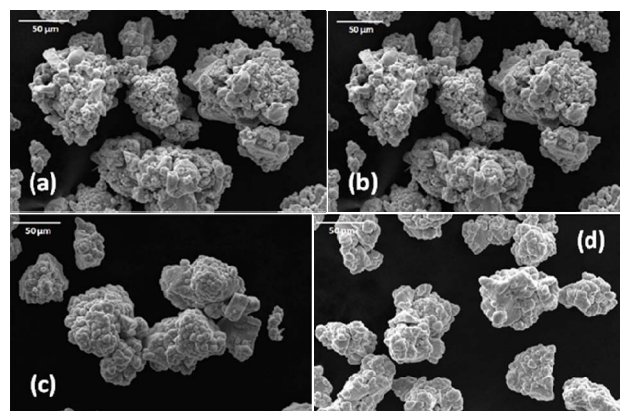
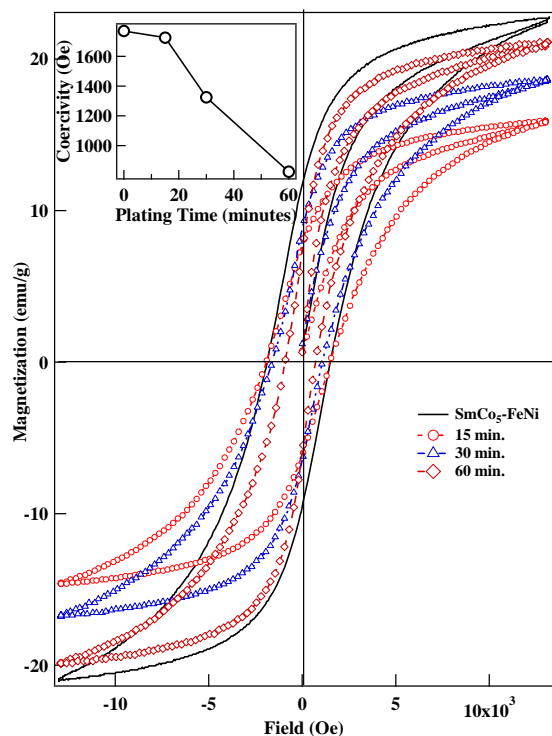
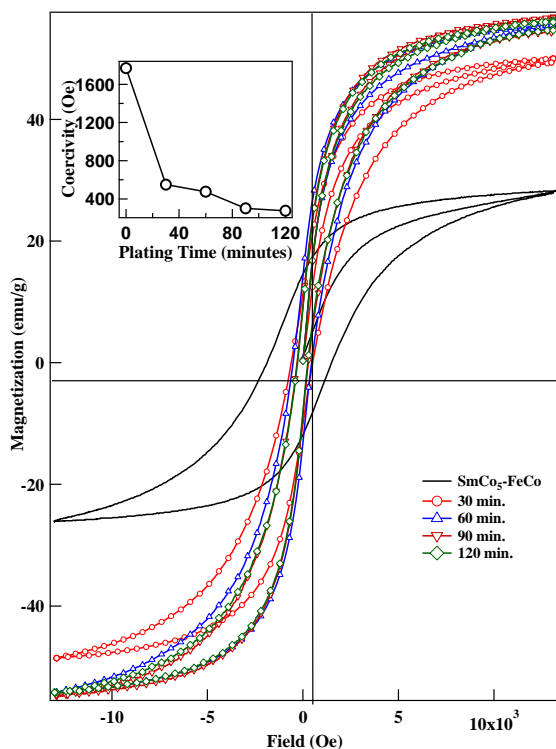


Figure 3. SEM images of $\text{SmCo}_5\text{-FeCo}$ composites electroless plated for (a) 30; (b) 60; (c) 90; and (d) 120 minutes.

external field the soft layer is magnetized quickly. If this soft phase layer (shell) is thick and coats entirely the hard phase sphere (core) then the core cannot see the external field but only see the field created by the magnetization



(a)



(b)

Figure 4. (a) Room temperature hysteresis loops of $\text{SmCo}_5\text{-FeNi}$ composites. Coercivity of composites as a function of plating time is shown in the inset; (b) Room temperature hysteresis loops of $\text{SmCo}_5\text{-FeCo}$ composites. Coercivity of composites as a function of plating time is shown in the inset.

Table 1. Magnetic parameters obtained from hysteresis loop measured at room temperature.

	Coating Time (min)	M_s (emu/g)	H_c (Oe)	M_r (emu/g)	M_r/M_s
SmCo_5	--	27.99	1770	10.48	0.37
$\text{SmCo}_5\text{-FeNi}$	15	15.83	1725	6.93	0.43
	30	18.49	1325	7.60	0.41
	60	20.96	825	6.70	0.31
$\text{SmCo}_5\text{-FeCo}$	30	49.98	550	10.68	0.21
	60	55.38	475	13.66	0.24
	90	56.71	301	8.98	0.15
	120	55.97	275	8.82	0.15

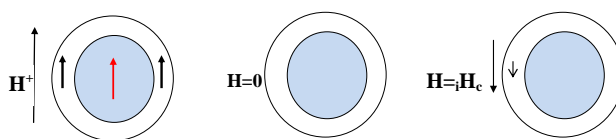


Figure 5. A model of the magnetic behavior of the hard phase sphere coated by the thick soft phase layer.

vector of the soft phase layer. When the H_{ext} is applied, the magnetization in the soft phase shell is saturated first; the magnetization in the hard phase core has some moderate value dependent on the M_s of the shell. When the H_{ext} is being reduced to zero, the M inside the shell is rapidly approaches zero but the M inside the core decreases to some value. Next assume H_{ext} goes on to the value iH_c which corresponds to the zero averaged value of magnetization. Since in this case the M inside the core is not zero (arrow in the core, right picture of **Figure 5**, that means that this value iH_c must be smaller than the value of the coercivity of the core hard phase when no shell covers it. Thus, thicker shell the smaller the iH_c .

Overall exchange-spring hardening is not observed in these composites. The absence of exchange spring phenomenon in $\text{SmCo}_5\text{-FeNi/FeCo}$ composites may be attributed to large thickness/grain size of soft FeNi and FeCo layers, which are much larger than the domain wall width of SmCo_5 ($\delta_B \sim 3 - 6$ nm) [18-20]. This cannot guarantee that the entire volume of FeNi or FeCo is exchange hardened by the SmCo_5 phase because the exchange coupling requires grain sizes of the order of $\delta_B \sim 8$ nm.

4. Conclusion

In summary we have successfully coated hard SmCo_5 particles with soft-magnetic FeNi and FeCo via electroless plating technique. The electroless coating resulted in a thick uniform coating more so for FeCo than FeNi for similar plating duration. Adding magnetically soft phase into the $\text{SmCo}_5\text{-FeNi/FeCo}$ composite enhances its magnetization but decreases its coercivity. This coercivity

ity reduction is explained on the bases of increased amount of magnetic softness of the coated layer. An independently tuning the size and composition of the individual building blocks of the composite is necessary in order to enhance exchange coupling between hard-soft phases of the composite. It is expected that composite magnets of SmCo₅-FeNi or FeCo could be obtained with core-particles' coercivity exceeding 10 kOe, which can be attained either via ball milling technique [21-23] or wet-chemical method [24]. It is also evident from the present study that the growth rate of soft magnetic layer needs to be better controlled in order to form a fine uniform coating of a few nanometer thicknesses on core particles to meet the theoretical exchanges spring interaction length limit.

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