



Research article

Anisotropic SmCo₅/FeCo core/shell nanocomposite chips prepared via electroless coating

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Abstract: We report the preparation of anisotropic SmCo₅/FeCo core/shell nanocomposite chip-like particles via an electroless coating process. The anisotropic SmCo₅ nanoscale chips were first prepared by surfactant-assisted ball milling then coated with soft magnetic FeCo using cobalt sulfate (CoSO₄·7H₂O) and iron sulfate (FeSO₄·7H₂O) as metal precursors in presence of complexing agents. The influence of the soft-phase coating on the magnetic properties of the nanocomposite particles has been studied. The saturation magnetization of the composite particles increases with increasing coating while the coercivity decreases. The FeCo coated chips have an enhanced remanence ($M_r = 44.5$ emu/g with 16 wt % of FeCo) compared to the uncoated chips ($M_r = 36.7$ emu/g), indicating exchange coupling between the hard and soft phases for the optimal soft-phase coating. Results of magnetic field alignment show the strong anisotropy of SmCo₅/FeCo core/shell nanocomposite particles which can be used as building blocks of high-strength anisotropic magnets.

Keywords: core/shell nanoparticles; anisotropic magnetic nanoparticles; hard magnetic nanoparticles; nanocomposite magnets; electroless coating

1. Introduction

Nanocomposite magnets consisting of exchange-coupled hard and soft phases have potential applications as advanced permanent magnets with high energy product [1–3]. Possible application for nanocomposite permanent magnets are fully dense bulk or bonded magnets used in consumer electronic applications, electrical vehicles and wind turbines. Our recent experimental work has shown a remarkable enhancement on maximum energy product $(BH)_{\max}$ of the exchanged-coupled isotropic hard/soft nanocomposite (FePt/Fe₃Pt and Sm-Co/Fe(Co)) bulk magnets compared to the

single phase counterpart [4–8]. The nanocomposite magnets are also commercially important as they have significantly lower materials cost compared to their single-phase counterpart magnets [9].

The values of remanence and maximum energy product $(BH)_{\max}$ will be significantly enhanced if the crystallographic c -axis of the hard-phase grains or particles of the nanocomposite materials are aligned to form anisotropic nanocomposite magnets [10]. It is still a great challenge to fabricate nanostructured bulk magnets with texture. One of the possible approaches to producing anisotropic bulk nanocomposite magnets is to fabricate anisotropic hard/soft core/shell nanocomposite particles so that anisotropic bulk magnets can be made from the particles [11]. Bimagnetic nanoparticles with core/shell structures with tailored hard and soft dimensions can be ideal building blocks for fabrication of advanced permanent magnetic materials because the intimate contact between the hard and soft magnetic phases in the nanoparticles can lead to effective interphase exchange coupling [12]. Our previous experimental studies have demonstrated that the surfactant-assisted ball milling is a promising technique for producing single-phase anisotropic hard magnetic (Sm-Co and $\text{Nd}_2\text{Fe}_{14}\text{B}$) and soft magnetic (Co, Fe and FeCo) nanoparticles, submicron particles and anisotropic bonded magnets [13–17]. In recent years electroless coatings have been applied to hard magnetic SmCo micron-sized powder particles with soft phase layers [18–19]. In this paper, we report the preparation of anisotropic $\text{SmCo}_5/\text{FeCo}$ core/shell nanocomposite chip-like particles via an electroless coating process and the effect of the soft phase coating on the magnetic properties of the nanocomposite particles.

2. Materials and Method

The anisotropic hard/soft $\text{SmCo}_5/\text{FeCo}$ core/shell nanocomposite chip-like particles were prepared via a two-step process: 1. Preparation of anisotropic hard magnetic SmCo_5 nanochip-like particles by surfactant-assisted high energy ball milling [17], and 2. Electroless coating of FeCo soft magnetic phase on the SmCo_5 nano-chips [19].

2.1. Preparation of anisotropic SmCo_5 nano-chips

SmCo_5 nano-chips were first prepared by surfactant-assisted high energy ball milling method using starting commercial SmCo_5 powder of particle size $\sim 45 \mu\text{m}$. Heptane with 99.8% purity was used as solvent and oleic acid with 90% purity was used as surfactant. The amount of surfactant used was 50% by weight of the starting powder. The mixture of SmCo_5 powder, surfactant and solvent was sealed in an argon gas environment inside a glove box. The mixture was milled for 1 h with balls made of hardened steel by using a Spex 8000 M high-energy ball milling machine with a powder to ball weight ratio of 1:10. Handling of the starting materials and as-milled products was carried out in an argon gas environment inside a glove box to protect the particles from oxidation during processing.

2.2. Preparation of $\text{SmCo}_5/\text{FeCo}$ core/shell nanocomposite nano-chips

$\text{SmCo}_5/\text{FeCo}$ core/shell nanocomposite nano-chips were prepared by coating FeCo soft magnetic phase on SmCo_5 nanochips by an electroless coating process. As prepared SmCo_5 nano-chips were first washed in an acetone then activated in 0.5 M sodium hypophosphite at 90°C

for 20 min. An electroless plating bath was prepared by using 0.09 mol of cobalt sulfate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$), 0.07 mol of iron sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), 0.5 mol of sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$), 0.3 mol of sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$), and 0.1 mol of ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$). Then 0.5 g of activated SmCo_5 nanochips were put into the electroplating bath. The pH value of the plating bath was maintained between 9–11 by using sodium hydroxide. The electroless plating of FeCo was carried out at a temperature of 80 °C for 60 minutes. The content of FeCo in the final product was controlled by varying the initial molar concentration of the electroless plating bath while keeping the SmCo_5 particle amount constant. The $\text{SmCo}_5/\text{FeCo}$ composite particles obtained after electroless plating was purified by washing with the de-ionized water then dried in a glove box in an inert argon gas environment.

To characterize the anisotropic magnetic properties, the nanoscale chips were mixed with epoxy and aligned in a magnetic field of 2 Tesla. The magnetic properties of randomly oriented and aligned samples were measured by a superconducting quantum interference device (SQUID) magnetometer with a maximum applied field of 7 Tesla. Structural characterizations were performed using x-ray diffraction (XRD) (Rigaku Ultima IV diffractometer operating with $\text{Cu K}\alpha$ radiation). The wt % of FeCo in the $\text{SmCo}_5/\text{FeCo}$ nanocomposites samples was estimated from a Rietveld refinement procedure of the XRD patterns using JADE-9 software. Morphological and compositional characterizations were performed using scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) analysis. A Hitachi S-3000N VP-SEM microscope attached with an EDAX EDX system was used for SEM/EDX analysis at the accelerating voltage of 25 kV. Samples for both SEM and EDX analyses were placed on the sample holders supported by silicon substrates without sputter coating

3. Results and Discussion

Figure 1 shows the XRD patterns of randomly oriented as-prepared SmCo_5 nano-chips and nano-chips after the electroless coating process. It can be seen from the XRD patterns that the coated samples give two sets of peaks with one set matching to the SmCo 1:5 hard magnetic phase (International Center for Diffraction Data (ICDD) PDF # 00-027-1122) and the other to bcc-FeCo phase (ICDD PDF # 00-048-1818), indicating the deposition of a FeCo soft phase on the SmCo_5 surface resulting in the formation of a nanocomposite. It is also observed that the relative intensity of the FeCo peaks increases compared to the SmCo peaks with increasing FeCo content on the coated samples, as the coating proceeded. The coated FeCo content on the hard SmCo_5 particles was controlled by varying the ratio of electroless bath molar concentrations to the mass of SmCo_5 particles. For example, when the ratio was varied as 1:1, 1:3 and 1:4 the wt % of FeCo estimated from a Rietveld refinement procedure of the XRD patterns was 16%, 32% and 48%, respectively.

The morphology of SmCo nanochips before and after coating was observed by SEM. The figure 2(a) shows the SEM image of SmCo_5 chips with a high aspect ratio obtained after 1 h milling with a diameter in the range 5–10 μm and thickness in the range 20–150 nm (determined by HRSEM analysis, not shown here). Figure 2(b) shows the SEM image of the SmCo_5 nanochips obtained after the electroless coating. An analysis of the SEM images shows that there is no considerable difference in the size of the as-prepared particles compared with those obtained after the electroless coating. However, it can be clearly seen that the surface of the particles after electroless process appears to be smoother than that of the as-prepared particles, suggesting a layer of FeCo on the SmCo surface. A

clear contrast difference around the edge of particle and the rest of a single FeCo coated SmCo particle further confirms the formation of core/shell morphology (figure 2(c)). Figure 3(a) shows a SEM image and figure 3(b)–3(d) show EDX elemental maps of Co, Sm, and Fe on an FeCo coated single chip. The EDX elemental maps of Co and Fe in figure 3(b) and 3(c) reveal a homogeneous distribution of the Co and Fe that suggest uniform coating of FeCo on the hard-phase particles.

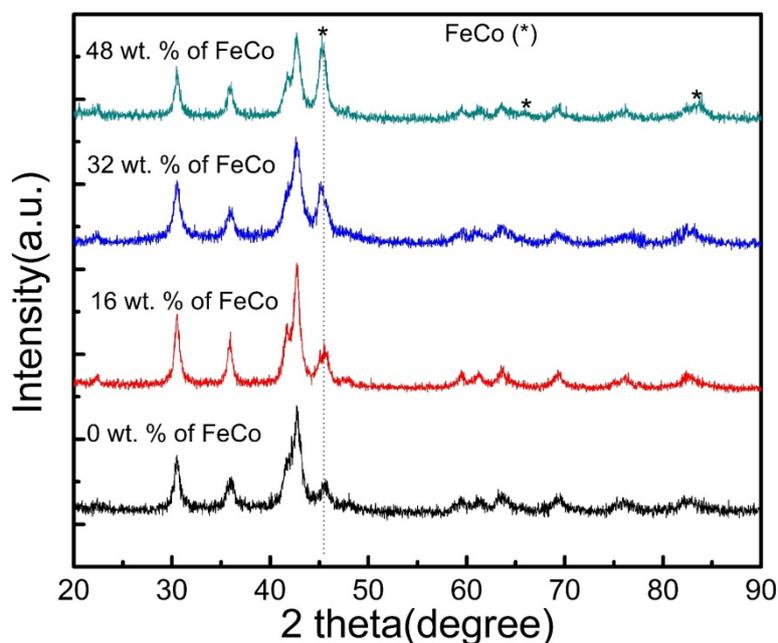


Figure 1. XRD pattern of FeCo coated SmCo₅ nanoflakes with different content of FeCo coating (wt % estimated from XRD analysis).

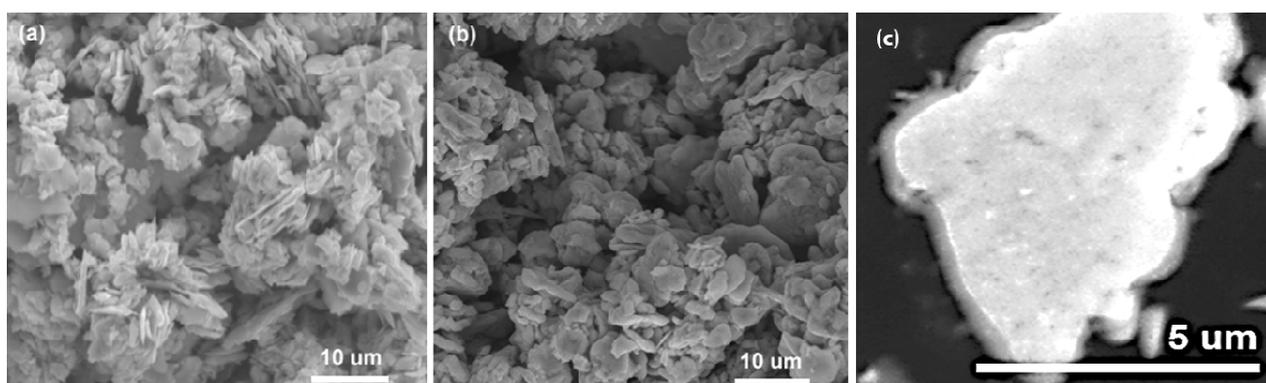


Figure 2. SEM images of (a) as prepared SmCo₅ nano-chips, (b) SmCo₅/FeCo core/shell nano-chips and (c) a single SmCo₅/FeCo core/shell chip.

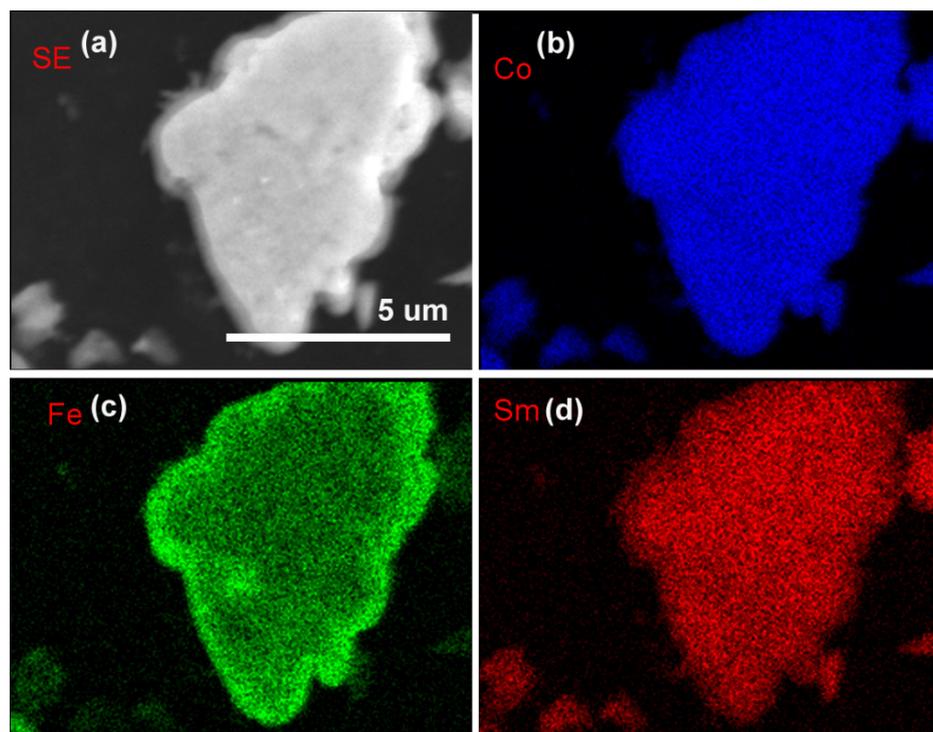


Figure 3. (a) SEM image of a single $\text{SmCo}_5/\text{FeCo}$ core/shell chip, and EDX element maps of the single $\text{SmCo}_5/\text{FeCo}$ core/shell chip for (b) Co, (c) Fe and (d) Sm.

Figure 4 shows the demagnetization curves of randomly oriented $\text{SmCo}_5/\text{FeCo}$ nanocomposites chips with different wt % of FeCo estimated by XRD. It can be seen that the single-phase SmCo_5 chips have the highest coercivity but the lowest magnetization. As expected, an increase in the soft-phase content reduces the coercivity while it leads to an increase in saturation magnetization. Figure 5 summarizes the effects of the soft-phase content on the saturation magnetization (M_s), remanence (M_r) and coercivity (H_c) of isotropic samples at room temperature. It can obviously be seen that the M_s increased with the soft magnetic FeCo content as one would expect since FeCo has a larger moment than SmCo_5 . The saturation magnetization increased from 57 to 82 emu/g monotonically with increasing soft phase content (from 0 to 48 wt % of FeCo) while the coercivity decreased rapidly from 19 to 4 kOe. The FeCo coated chips have an enhanced remanence ($M_r = 44.5$ emu/g with 16 wt % of FeCo) compared to the uncoated SmCo_5 chips ($M_r = 36.7$ emu/g), indicating exchange coupling between the hard and soft phases for optimal soft phase coating. With further increasing soft phase coating (wt %) the remanence decreases because of a rapid drop in coercivity. The enhanced remanence in nanocomposite for optimal coating further confirmed the intergranular exchange interaction among those hard magnetic SmCo_5 particles and coated soft magnetic FeCo phases. Nevertheless, kinks are observed in all the demagnetization curves, implying the decoupling behavior caused by an over-size of the hard phase and possible inhomogeneity of the soft phase. For effective exchange coupling in a hard/soft nanocomposite, the layer of the soft phase coating should not exceed the critical length which is dependent on both the hard and soft phase properties.[11] Magnetic properties of core/shell hard/soft magnetic nanocomposite particles can be further tailored by controlling the core and shell dimensions.

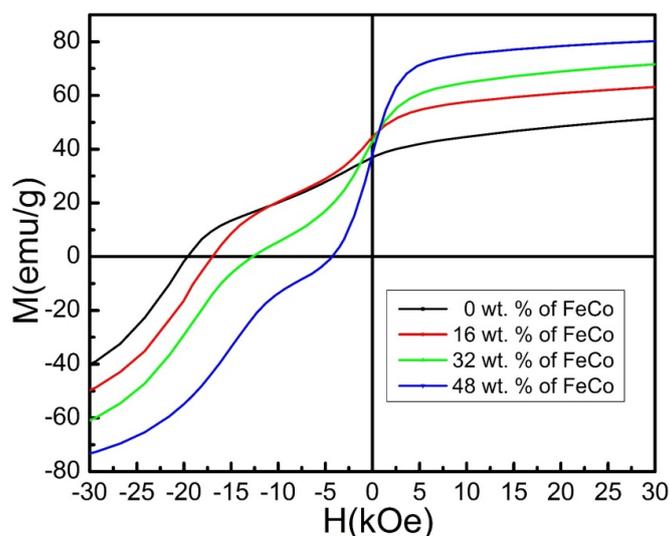


Figure 4. Demagnetization curves of FeCo coated SmCo₅ nano-chips with different content of FeCo coating (wt % estimated from XRD analysis).

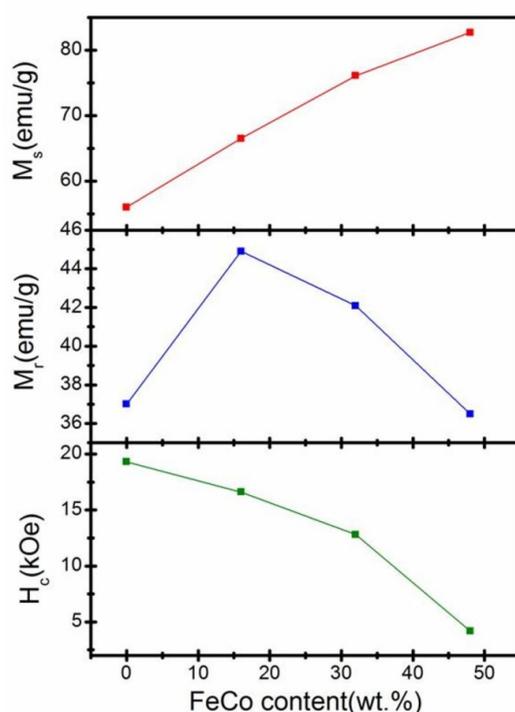


Figure 5. Dependence of M_s , M_r and H_c on content of FeCo on SmCo₅/FeCo nanocomposite chips.

Figure 6 shows the typical XRD patterns of the aligned and randomly oriented SmCo₅/FeCo nanocomposite particles in the epoxy. The samples were aligned in 2 Tesla magnetic field. Compared with the randomly oriented samples, the intensities of (002) of SmCo₅ diffraction peaks of the aligned samples are enhanced significantly, while other peaks largely disappear, suggesting a (00l)

out-of-plane alignment (of the c-axis). Figure 7 shows the demagnetization curves of the corresponding aligned sample in figure 6. The demagnetization curves with substantial difference measured in parallel and perpendicular to the aligned field direction confirm the strong anisotropy resulting from the grain alignment along the c-axis in the $\text{SmCo}_5/\text{FeCo}$ nanocomposite chips.

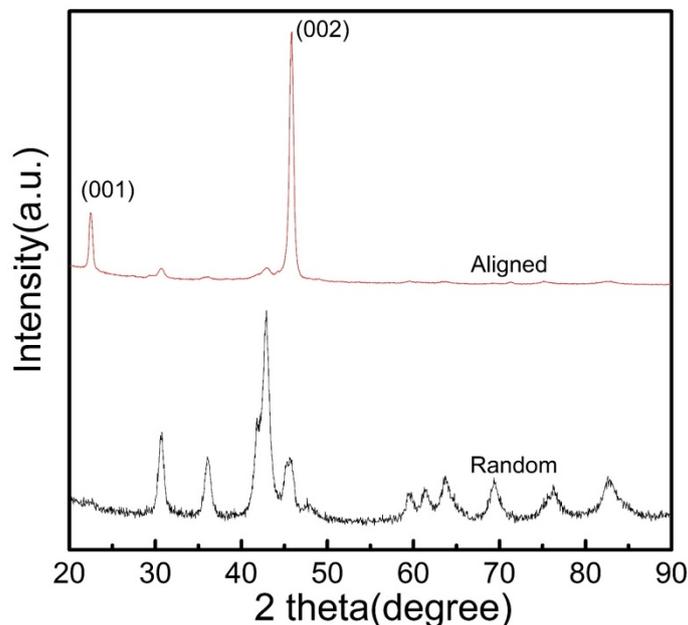


Figure 6. XRD patterns of randomly oriented $\text{SmCo}_5/\text{FeCo}$ nanocomposite and aligned $\text{SmCo}_5/\text{FeCo}$ nanocomposite chips in 2 Tesla magnetic field hardening in epoxy during alignment.

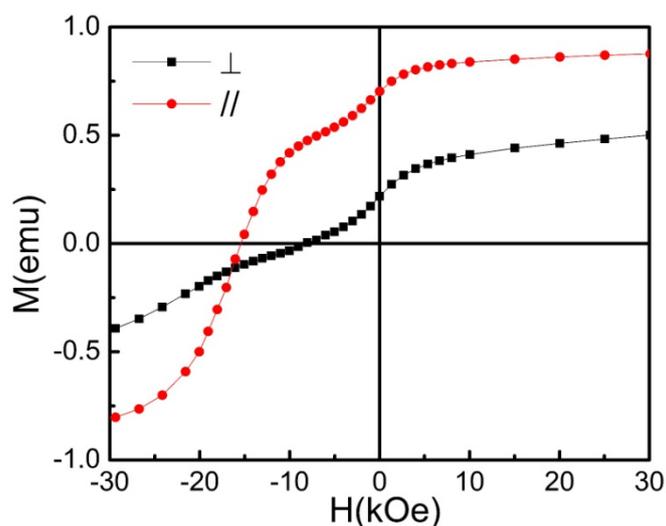


Figure 7. Demagnetization curves of $\text{SmCo}_5/\text{FeCo}$ nanocomposite chips sample measured parallel and perpendicular to aligned field direction. The sample was aligned in magnetic field of 2 Tesla and was hardened in epoxy during alignment.

4. Conclusion

In summary anisotropic SmCo₅/FeCo core/shell nanocomposite chip-like particles have been prepared via an electroless coating process. The influence of the soft-phase coating on the magnetic properties of the nanocomposite particles has been studied. The saturation magnetization of SmCo₅/FeCo core/shell nanocomposite particles increases while the coercivity decreases with increasing coating of the soft phase. An enhanced remanence of the FeCo coated SmCo₅ nano-chips compared to the uncoated SmCo₅ nano-chips indicates exchange coupling between the hard and soft phases for proper soft phase coating. The results show that the anisotropic SmCo₅/FeCo core/shell magnetic nanocomposite particles with tailored dimensions can serve as promising building blocks for high-strength anisotropic bonded or fully dense nanocomposite bulk magnets via this bottom-up approach.

Acknowledgments

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Conflict of Interest

All authors declare no conflicts of interest in this paper.

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