Preparation and Magnetic Properties of Anisotropic SmCo₅/Co Composite Particles

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Abstract Anisotropic SmCo₅/Co nanocomposite powders have been prepared by electroless Co deposition on commercial SmCo₅ powders with hydrazine as reducer. The Co particles are mainly in the range of 8–27 nm and form dense/continuous soft magnetic coatings on the surface of SmCo₅ powders. Exchange coupling happened between the coated Co soft magnetic particles and the SmCo₅ hard phase. As a result, SmCo₅/Co nanocomposite powders with remanence of 73.58 emu/g and energy product of 13.74 MGOe were obtained in the optimum condition, as compared with those of 70.52 emu/g and 13.40 MGOe for uncoated SmCo₅ powders. The effects of Co adding amount on Co particle size, coating morphology, and magnetic properties of SmCo₅/Co products were investigated.

KEY WORDS: Nanocomposite; Permanent magnet; Coating; Nanosize; Exchange coupling

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1 Introduction

Nanocomposite permanent magnets, which consist of hard magnetic phases with high coercivity H_{ci} and soft magnetic phases with high saturation magnetization M_s , attract a great deal of attention because of their potential in high energy product and cost-saving application [1–5]. Theoretical calculation predicted that the maximum energy product $(BH)_{max}$ of anisotropic nanocomposite magnets could be above 100 MGOe [6]. However, it remains a great challenge in synthesizing these composite materials. Among the difficulties that hinder the development of these composite materials, the following two issues are mostly concerned: (1) controlling the soft phase below 20 nm and distributing them uniformly around the hard phase in order to obtain effective exchange coupling and (2) forming a strong texture of hard phase in the composite structures [7–10]. At present, most of the nanocomposite magnets are fabricated by the conventional “top-down” methods, such as mechanical milling, melt spinning, and sputtering [11–15]. But the nanocomposite magnets prepared by this conventional route are generally isotropic and therefore have low $(BH)_{max}$. A new “bottom-up” route, by which soft magnetic phases with

desired sizes were firstly assembled around the anisotropic hard phases, is considered more feasible to satisfy the exchange coupling and texture requirements [9, 16, 17]. However, simultaneously controlling the nanosize and distribution of the soft phase is still a challenge work by this “bottom-up” route, and a large size above 20 nm is generally obtained by conventional coating approach. In recent studies, Wang et al. [17] made anisotropic (Sm,Pr)Co₅/Co nanocomposites by reduction of cobalt ions on (Sm,Pr)Co₅ powders. The coated Co particles were sparsely distributed and the Co size was in the range of 20–50 nm, making the hysteresis curve show a serious kink due to decoupling. Poudyal et al. synthesized anisotropic SmCo₅/FeCo core/shell nanocomposite by an electroless coating process, in which higher-saturation-magnetization FeCo phases were introduced onto the SmCo₅ hard phases, and a remanence enhancement of 7–10 emu/g was reported with 12–16 wt% of FeCo soft phase. However, kinks were also observed in all the demagnetization curves due to large size of FeCo particles (20–50 nm as reported) [1, 18]. Wang et al. [19] fabricated anisotropic (Sm,Pr)₁Co₅/Co nanocomposites and observed single-phase-like magnetic behavior by successfully controlling the coated Co particles in nanosize of 9–18 nm. But the (Sm,Pr)₁Co₅ hard phase (~8.6 kOe) still restricts the coercivity enhancement of the composite materials. Therefore, more explorations are needed on the anisotropic hard–soft nanostructured composites for the “bottom-up” route.

In this paper, a simple chemical coating approach is given to make anisotropic SmCo₅/Co composite powders. The selected commercial SmCo₅ hard phase had a high coercivity about 12.16 kOe. The Co particles were yielded by reduction of CoCl₂·6H₂O with hydrazine as reducer in the presence of the SmCo₅ powders and sodium hydroxide. The CoCl₂·6H₂O and NaOH reactants were added into the reaction solution drop by drop. The addition rate of hydrazine was controlled more precisely by a peristaltic pump. In this way, the reduction rate of the cobalt ions was controlled in a low range that makes the Co particles preferably coat on the SmCo₅ powders, stay in nanoscale, and form continuous coating layers on the SmCo₅ hard-phase powders. No obvious kink was observed in the demagnetization curves when the coated Co nanoparticles are below 20 nm.

2 Experimental Procedure

Commercially available anisotropic SmCo₅ powders with sizes of 0.5–20 μm and coercivity about 12.16 kOe were used as hard phase. CoCl₂·6H₂O was used as a Co precursor. The Co ions were reduced according to the following reaction: N₂H₄ + 2CoCl₂ + 4NaOH → 2Co + N₂ + 4H₂O + 4NaCl. Before coating, the commercial SmCo₅

powders were firstly pretreated in hydrochloric acid solution at 60 °C for 10 min to remove the oxide layer. The pretreated hard powders were then transferred into ethanol solution with polyvinylpyrrolidone as surfactant. Afterward, NaOH (0.5 mol/l), CoCl₂·6H₂O (5.36 mmol/l), and N₂H₄·H₂O (85%) were slowly dropped into the solution under stirring and sonicating at a temperature of 60 °C. Particularly, N₂·H₄·H₂O was more carefully added using a peristaltic pump. All experiments were conducted under an argon atmosphere to protect the materials from oxidization. After coating, the products were collected, washed in ethanol several times, and finally dried in a vacuum chamber for further characterizations. The amount of Co particles was modified by adjusting the CoCl₂·6H₂O weights while keeping the weight of SmCo₅ powders as constant value.

The structure and morphology of SmCo₅/Co powders were characterized by Bruker AXS D8-Advance X-ray diffraction (XRD) with CuK_α radiation and scanning electron microscopy (SEM, Hitachi-S4800). To characterize the powder anisotropy, the products were aligned and immobilized in epoxy resin under a magnetic field of 27 kOe. Magnetic properties of aligned powders were measured at room temperature by a vibrating sample magnetometer (VSM, Lake Shore 7410) with maximum magnetic field of 20 kOe. Characterizations on uncoated SmCo₅ powders were also conducted for comparison.

3 Results and Discussion

Figure 1 shows the XRD patterns of non-aligned and aligned SmCo₅/Co_x powders ($x = 0$ and 15 wt%, x is the weight ratio between the adjusted Co soft phase and the SmCo₅ hard phase). As depicted in Fig. 1a, b, both the uncoated and coated samples have a main SmCo₅ phase with a CaCu₅-type structure (JCPDS No. 27-1122). Additional diffraction peaks corresponding to hcp-Co (JCPDS No. 05-0727) appear in the coated samples, suggesting the formation of SmCo₅/Co composite powders after the coating process. The enhanced (001) and (002) peaks in Fig. 1c demonstrate that the prepared composite powders are strongly textured.

In order to make clear the size and phase distribution of Co particles on the SmCo₅ phases, the morphology of SmCo₅/Co_x ($x = 0, 3, 5, 10$, and 15 wt%) powders was studied by SEM. Figure 2 presents the low- and high-magnification SEM images on the left and right column, respectively. As shown in Fig. 2a, the uncoated SmCo₅ powders are irregularly shaped, having sizes of 0.5–20 μm and fairly smooth surfaces. The sizes of SmCo₅ powders remained unchanged after the coating process, but uniform Co layers appeared on original SmCo₅ surfaces (see Fig. 2b–e). The high-magnification images clearly show that the morphology of the coated Co layers is strongly depended on the Co adding

Fig. 1 XRD patterns of non-aligned and aligned $\text{SmCo}_5/\text{Co}_x$ powders with $x = 0$ and 15 wt%

amount. At $x = 3$ wt%, isolate nanosized Co particles were observed on SmCo_5 surfaces. The gaps between adjacent Co particles are often several nanometers. When the cobalt adding amount rises to $x = 5, 10$, and 15 wt%, both the Co particle number and Co particle size increased monotonously. As a result, the Co particles contacted and merged together in these conditions, forming continuous coating layers on the surface of SmCo_5 powders. It was also found that general single-layer Co coatings with nanosized Co particles were obtained at $x \leq 10$ wt%. Figure 3 plots the size changes of the fine Co particles as a function of the Co adding amount. The Co particles are as fine as ~ 8 nm at a low Co adding amount of $x = 3$ wt%. When the Co adding amount increases to $x = 5, 10$, and 15 wt%, the fine Co particles grow to ~ 14 , ~ 20 , and ~ 27 nm, respectively. Additionally, large particles with sizes of 50–100 nm start to appear on the initial Co thin layers when $x = 10$ wt%. The number of these large Co particles rises sharply when the Co adding amount increases to $x = 15$ wt%, forming additional second-large-particle Co layers on the initial ones. The appearance of the large Co particles and size increase in the fine Co particles are thought highly related to the excessive Co reduction, because merely the amount of Co precursor is changed in all experiments.

Figure 4 shows the demagnetization curves of the aligned SmCo_5/Co powders. The curves were measured parallel to the aligned magnetic field. It can be found that the demagnetization curves show a near-single-phase behavior when the Co adding amount is lower than 10 wt%, at which the cobalt particles are no bigger than 20 nm. But when the Co

Fig. 2 SEM images of $\text{SmCo}_5/\text{Co}_x$ composite particles with cobalt adding amounts of: **a** $x = 0$; **b** $x = 3$; **c** $x = 5$; **d** $x = 10$; **e** $x = 15$ wt%. The right column shows enlarged images for typical areas in the corresponding left panels

adding amount increases to $x = 15$ wt%, at which the coated Co particles are about 27 nm, a kink appears in the demagnetization curve. The kink, which implies the existence of decoupling effect between the coated Co particles and SmCo_5 hard phases, is caused by the large particle size or over-thickness of the soft-phase coatings. From theoretical work, the domain wall thickness for SmCo_5 alloy is about 3.7 nm [20, 21], and the twice of it is about 7.4 nm. In this work, the critical size of soft-phase Co for effectively exchange coupling with SmCo_5 hard phase is around 20 nm, which is larger than twice of the expected size.

Figure 5 summarizes the changes of magnetic properties (i.e., maximum magnetic energy product $(BH)_{\text{max}}$, the

Fig. 3 Size of Co particles as a function of Co adding amount

Fig. 4 Demagnetization curves of aligned SmCo₅/Co _{x} ($x = 0, 3, 5, 10$, and 15 wt%) powders. The curves were measured parallel to the aligned magnetic field

magnetization M_{2T} , the remanence M_r , and intrinsic coercivity H_{ci}) as a function of the Co adding amount. The inset in Fig. 5d shows the changes of intrinsic coercivity as a function of the size of coated Co particles. With the Co amount increases, the M_{2T} monotonically increases from 72.43 emu/g for uncoated SmCo₅ powders to 85.78 emu/g for the SmCo₅/Co _{x} composite powders with $x = 15$ wt%, while the coercivity decreases sharply from 12.16 to 6.63 kOe correspondingly. Both remanence and energy product first increase, peak at a maximum value, and then decrease. An optimum magnetic performance with $M_r = 73.58$ emu/g and $(BH)_{\max} = 13.74$ MGOe, which has an obvious increase as compared with those of 70.52 emu/g and 13.40 MGOe for uncoated SmCo₅ hard phase, was obtained for the sample with $x = 10$ wt% and Co particle size of ~ 20 nm. The increase in M_{2T} results from the higher magnetization moment for Co particles (160 emu/g in bulk magnets). The enhancement of remanence and energy product in the composite powders confirms the existence of exchange coupling

Fig. 5 Maximum magnetic energy product $(BH)_{\max}$, magnetization M_{2T} at the magnetic field of 2T, remanence M_r , and intrinsic coercivity H_{ci} of the SmCo₅/Co composites as a function of Co adding amount. The inset in d shows the changes of intrinsic coercivity as a function of the size of coated Co particles

between the coated soft-phase cobalt particles and the hard-phase SmCo₅ particles. Partial decoupling effects, which are demonstrated in Fig. 6, are thought reasons for the decrease in M_r and $(BH)_{\max}$ at the large Co adding amount of $x = 15$ wt%. The rises of coated Co amount, the size increase in the soft-phase particles, as well as the exchange coupling effect between the soft and hard phases, are possible reasons for the monotonous decrease in coercivity [22–25].

For a more detailed understanding of the demagnetization behavior, the normalized demagnetization susceptibility (dM/dH) was obtained by differentiating each hysteresis loop [26, 27]. Typical curves for $x = 0, 10$, and 15 wt% are shown in Fig. 6. For $x = 10$ wt% at which the

Fig. 6 dM/dH curves for aligned $\text{SmCo}_5/\text{Co}_x$ powders with $x = 0$, 10, and 15 wt%. The curves were obtained by taking first-order derivative of the demagnetization curves measured parallel to the aligning direction

coated Co particles are 20 nm, the dM/dH curve shows similar single-peak profile but higher peak intensity as compared with that of the uncoated SmCo_5 particles, confirming the effective exchange coupling between the small-sized soft Co particles and hard SmCo_5 phase. For $x = 15$ wt%, when Co particles are mainly ~ 27 nm, however, a second peak at low field appears in the dM/dH curve, demonstrating magnetic decoupling between the over-sized Co particles and SmCo_5 hard phase [28–30]. These exchange coupling and decoupling effects are consistent with the results obtained from Fig. 4.

4 Conclusion

In summary, anisotropic SmCo_5/Co composite particles have been prepared by electroless cobalt coating on commercial SmCo_5 powders. The Co particles form dense coatings on the SmCo_5 powders, and the Co particle size increases from ~ 8 to ~ 27 nm when the Co adding amount is increased from $x = 3$ to $x = 15$ wt%. The SmCo_5/Co composite powders show enhanced remanence and energy product as compared with the uncoated SmCo_5 particles, confirming the existence of exchange coupling in the coated two-phase composites. The present anisotropic SmCo_5/Co composite powders with tailored soft-phase size and distribution can serve as promising building blocks for making high-strength exchanged-coupled anisotropic composite magnets via bottom-up approach.

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