

## Research Article

# Preparation and Magnetic Properties of Anisotropic (Sm,Pr)Co<sub>5</sub>/Fe Nanocomposites Particles via Electroless Plating

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Anisotropic (Sm,Pr)Co<sub>5</sub>/Fe nanocomposites particles were prepared by electroless plating iron on the surface of (Sm,Pr)Co<sub>5</sub> nanoflakes after being prepared by ball milling for 4 h. A uniform and continuous coating layer was obtained due to the addition of complexing agent and the particle size of the reduced Fe particles was in the range of 10~20 nm. When the nominal addition of Fe was 15 wt%, the nanocomposites show enhanced remnant and saturation magnetization:  $M_r = 53.35$  emu/g,  $M_s = 73.08$  emu/g compared to the noncoated nanoflakes with  $M_r = 48.52$  emu/g,  $M_s = 60.15$  emu/g, while the coercivity drops from 10.33 kOe to 8.89 kOe. The effect of Fe content on the magnetic properties of the magnets is also discussed.

## 1. Introduction

Nanocomposite magnetic materials have drawn extensive attention since they were reported by Coehoorn et al. [1] in 1988. The theoretical maximum magnetic energy product, (BH)<sub>max</sub>, of anisotropy nanocomposite permanent magnets material can be as high as 1090 kJ/m<sup>3</sup> (137 MGOe) [2], which is much higher than that of any single-phase permanent magnets. However, until now, (BH)<sub>max</sub> of the nanocomposite magnets is still much lower than the theoretical value. An important factor restricting the development of the (BH)<sub>max</sub> is the microstructure of theoretical models which is difficult to control. Generally speaking, an efficient exchange coupling needs to meet two conditions: (i) the size of the soft magnetic phase should be scaled to double domain wall width of the hard magnetic phase and (ii) soft magnetic phase should be uniformly distributed. So far, most of the nanocomposite magnets are fabricated following the conventional top-down routes, for example, high-energy mechanical milling, and melt spinning, but they are all isotropic materials with low (BH)<sub>max</sub> [3–12]. The other “bottom-up” approach has actually attracted more attention, since it allows for the nanoparticles to be distributed uniformly and for the hard phase to be aligned and form an optimum structure so as to ensure efficient exchange coupling. A number of attempts have been

made to synthesize nanocomposite magnetic materials via the bottom-up way. Zeng et al. [13] used simple mechanical blending of Fe nanoparticles with Sm-Co permanent magnet powders, but the magnetic soft phase tended to agglomerate which led to the reduction in exchange coupling. Marinescu et al. [14] reported the use of a chemical deposition method to fabricate Sm-Co/nano-Fe composite, yielding relatively good magnetic properties. Zeng et al. [15] reported the fabrication of FePt-Fe<sub>3</sub>Pt nanocomposites using nanoparticle self-assembly with (BH)<sub>max</sub> of the nanocomposites exceeding the single phase by over 50 percent. However, although the particle size can be reduced to a certain degree, the agglomeration is inevitable.

In this paper, the electroless plating technique was applied to fabricate the (Sm,Pr)Co<sub>5</sub>/Fe nanocomposites materials. The addition of complexing agent can control the deposition rate of the iron to form a continuous and uniform coating layer. The effect of the Fe content on magnetic properties was also investigated.

## 2. Experiment

The (Sm<sub>0.58</sub>Pr<sub>0.42</sub>)Co<sub>5</sub> powders were milled mechanically for 4 h using a SPEX 8000 high-energy ball mill. The initial

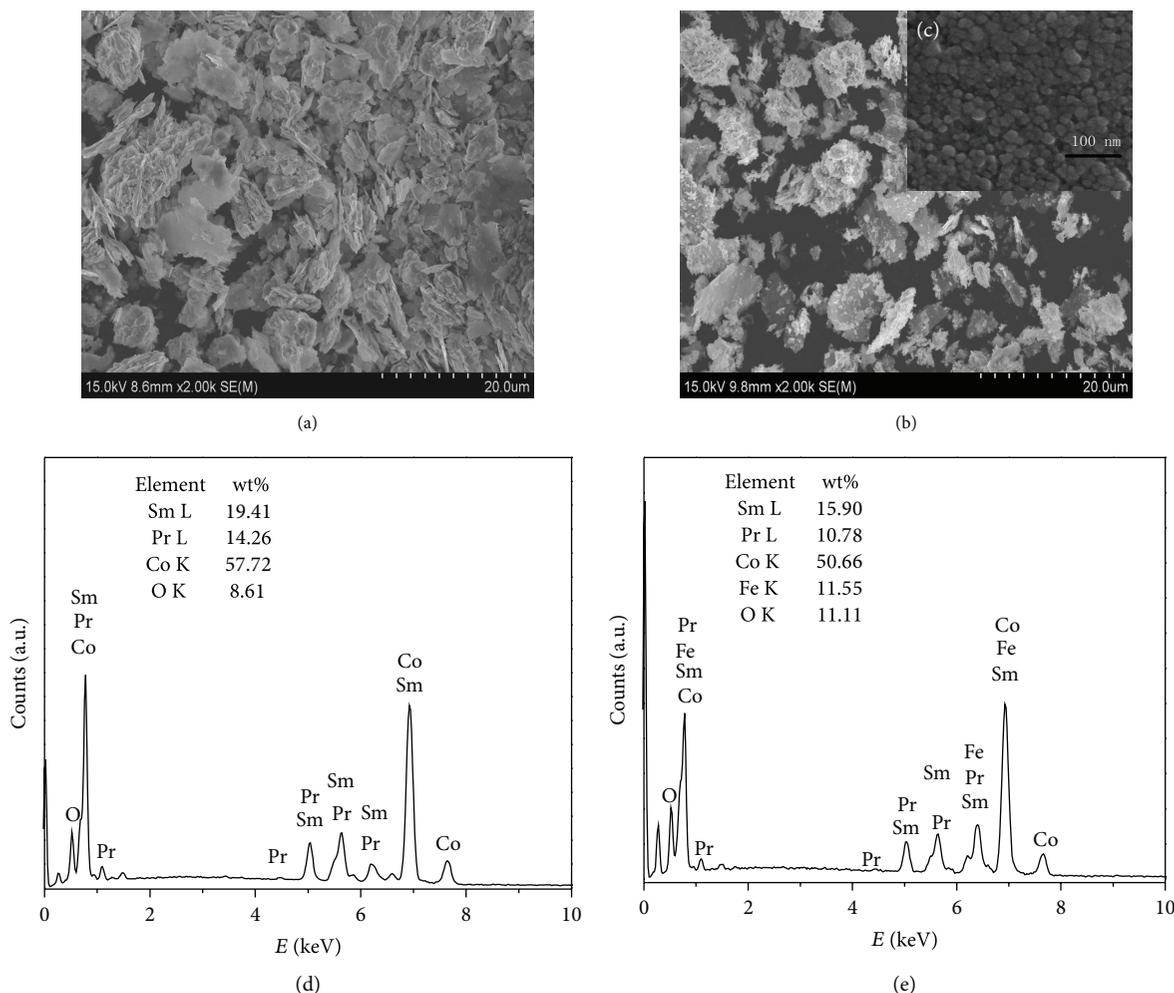
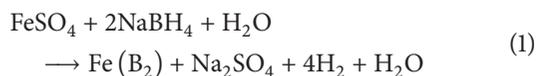


FIGURE 1: SEM micrographs and EDS spectrum of (Sm,Pr)Co<sub>5</sub> powders and (Sm,Pr)Co<sub>5</sub>/Fe nanocomposites. (a) (Sm,Pr)Co<sub>5</sub> powders after ball milling for 4 h; ((b) and (c)) (Sm,Pr)Co<sub>5</sub>/Fe nanocomposites for different magnifications; ((d) and (e)) EDS spectrum of (Sm,Pr)Co<sub>5</sub> and (Sm,Pr)Co<sub>5</sub>/Fe nanocomposites and the element mass percentage.

adding amount of the (Sm<sub>0.58</sub>Pr<sub>0.42</sub>)Co<sub>5</sub> powders was 2 g and the ball to powder ratio was 10:1 and the diameter of the steel ball is about 12 mm. During the process, heptane was used as the solvent with oleic acid used as the surfactant; the content in total mass was 10 wt.% and 55 wt.%, respectively. The synthesis of (Sm,Pr)Co<sub>5</sub>/Fe nanoparticles was carried out under Argon atmosphere in a three-necked bottle. The following chemicals were used to synthesize the composite nanoparticle: (Sm,Pr)Co<sub>5</sub> (0.12 g), FeSO<sub>4</sub>·7H<sub>2</sub>O (0.1 g), C<sub>6</sub>H<sub>5</sub>Na<sub>3</sub>O<sub>7</sub>·2H<sub>2</sub>O (0.6 g), and NaBH<sub>4</sub> (0.0625 g). In the first step, all the reagents except the reducing agent (NaBH<sub>4</sub>) were dissolved in deionizer water and then diluted to 100 mL inside the container. Polyvinylpyrrolidone was added as surfactant to protect the particles from oxidation and avoid the soft magnetic phase aggregation [16]. In the end, NaBH<sub>4</sub> was dissolved in the deionizer water and then poured into the bottle slowly under the condition of continuous ultrason and mechanical stirring. The final chemical equation can be described as follows:



After reacting for 40 min, the powders were collected via magnetic separation and were washed by ethanol for several times. The composite powders were dried in a vacuum environment for further investigation.

The coating morphology and composition of the powders were characterized by scanning electron microscopy (SEM) equipped with an energy dispersion X-ray spectrometer (EDS). The crystal structure was determined by X-ray diffraction (XRD) using the Cu K $\alpha$  radiation, with the diffraction angular range from  $2\theta = 25^\circ$  to  $90^\circ$ . The magnetic properties were investigated by a vibrating sample magnetometer (VSM). The powders were aligned under a 4 kOe field and solidified with epoxy resin for the VSM and XRD measurements.

### 3. Results and Discussion

SEM images of noncoated powders and coated nanocomposites are shown in Figure 1. The typical SEM image of (Sm,Pr)Co<sub>5</sub> powders is presented in Figure 1(a). It can be seen that after ball milling for 4 h, powders' agglomeration

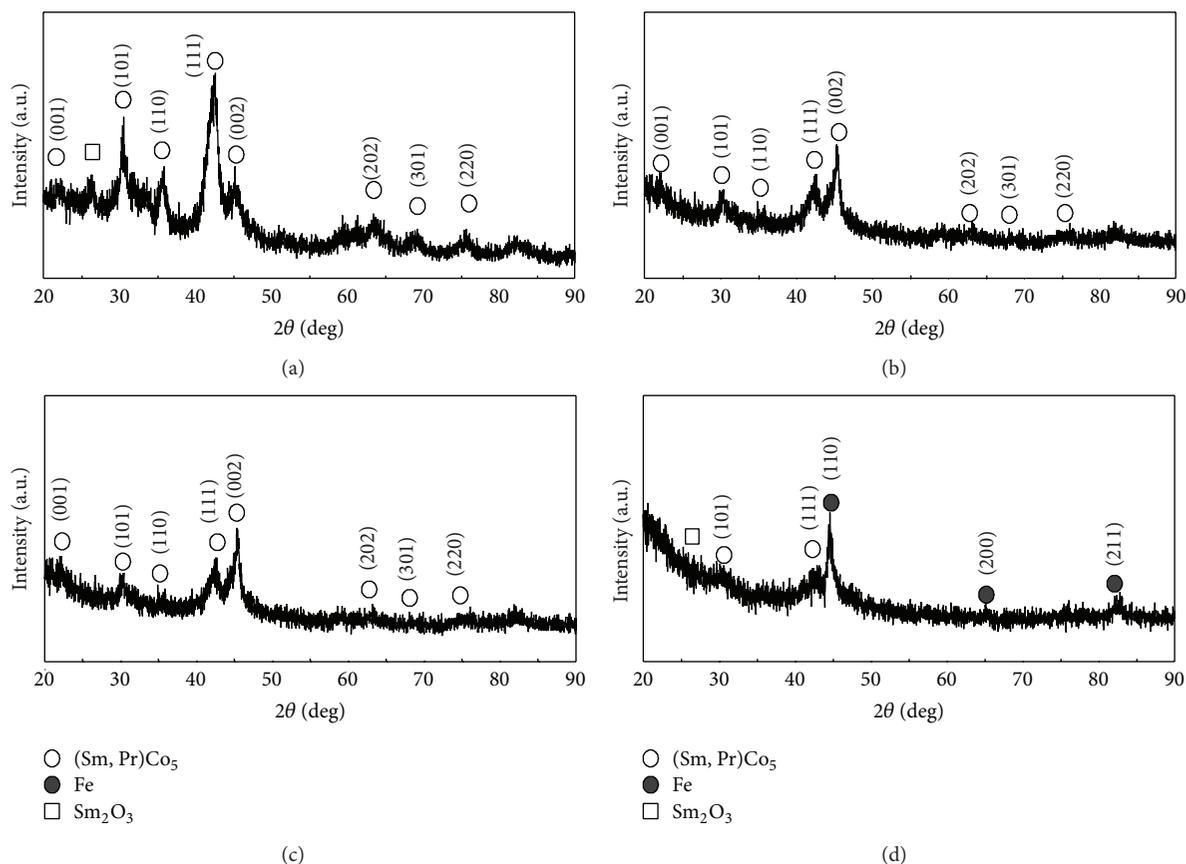


FIGURE 2: XRD patterns of (Sm,Pr)Co<sub>5</sub> nanoflakes: (a) nonaligned; (b) magnetically aligned; (c) (Sm,Pr)Co<sub>5</sub>/Fe nanocomposites magnetically aligned; (d) (Sm,Pr)Co<sub>5</sub>/Fe nanocomposites annealed at 450°C.

is still obvious and the particles have a flaky-like structure. The thickness of the nanoflakes is about 50–100 nm, with the length range from 0.5 to 8  $\mu\text{m}$ . The nanoflakes provide a large specific surface area for further coating. Figures 1(b) and 1(c) show the SEM micrographs of the (Sm,Pr)Co<sub>5</sub>/Fe nanocomposites at different magnifications. From Figure 1(b), the flakes are coated with a large amount of nanoparticles, but a few of the nanoparticles are also aggregated separately. The inset Figure 1(c) shows the much greater magnification of nanocomposites; a layer of continuous nanoparticles is coated on the surface and the particles' size is about 10–20 nm. The iron layer distributes uniformly and not simply stacks together. The elemental composition and mass fraction of the nanocomposites are revealed by the energy dispersive X-ray spectroscopy. Figures 1(d) and 1(e) show the energy spectrum of (Sm,Pr)Co<sub>5</sub> and (Sm,Pr)Co<sub>5</sub>/Fe, respectively. The mass fraction of iron is 11.5%, which indicates that the nanocomposites have a relatively high content of soft phase. However, the iron coating content relative to the composite powder stoichiometry was 15% in mass. The content is still lower than the nominal content we initially added, which implies that the iron particles are not fully deposited on the surface of (Sm,Pr)Co<sub>5</sub> and fewer iron particles nucleate and grow directly in the solution. It is worth mentioning that the oxidation is inevitable during the process of ball milling

and electroless plating, which would lead to a decrease in magnetic properties.

Figures 2(a) and 2(b) show the XRD patterns of the sample of (Sm,Pr)Co<sub>5</sub> nanoflakes nonaligned and aligned, respectively. The diffraction peaks can be indexed as the standard SmCo<sub>5</sub> (JCPDS NO.35-1400). After magnetic alignment, the (002) peak becomes dominant, indicating a strong *c*-axis crystallographic alignment [16]. The results are consistent with the report of Cui et al. [17, 18]. But there are no obvious diffraction peaks of iron in the XRD pattern of (Sm,Pr)Co<sub>5</sub>/Fe nanoflakes (Figure 2(c)). The possible reason was that the iron grain was too small or partly crystallized, so the intensity of the iron diffraction peak was weak and partly covered by the (Sm,Pr)Co<sub>5</sub> peaks. Therefore, (Sm,Pr)Co<sub>5</sub>/Fe nanocomposites were annealed by vacuum at 450°C for 10 minutes. Figure 2(d) shows the XRD pattern of (Sm,Pr)Co<sub>5</sub>/Fe nanocomposites after annealing treatment. The iron diffraction peaks could be indexed (JCPDS NO.06-0696), which proved the existence of iron. Oxidation of (Sm,Pr)Co<sub>5</sub> occurred during the annealing process due to the remain surfactant being removed incompletely. Moreover, the main diffraction peaks of Fe-B compounds cannot be indexed which proves the nonexistence of the Fe-B compounds and the particle layer is Fe nanoparticle coated on the (Sm,Pr)Co<sub>5</sub> surface.

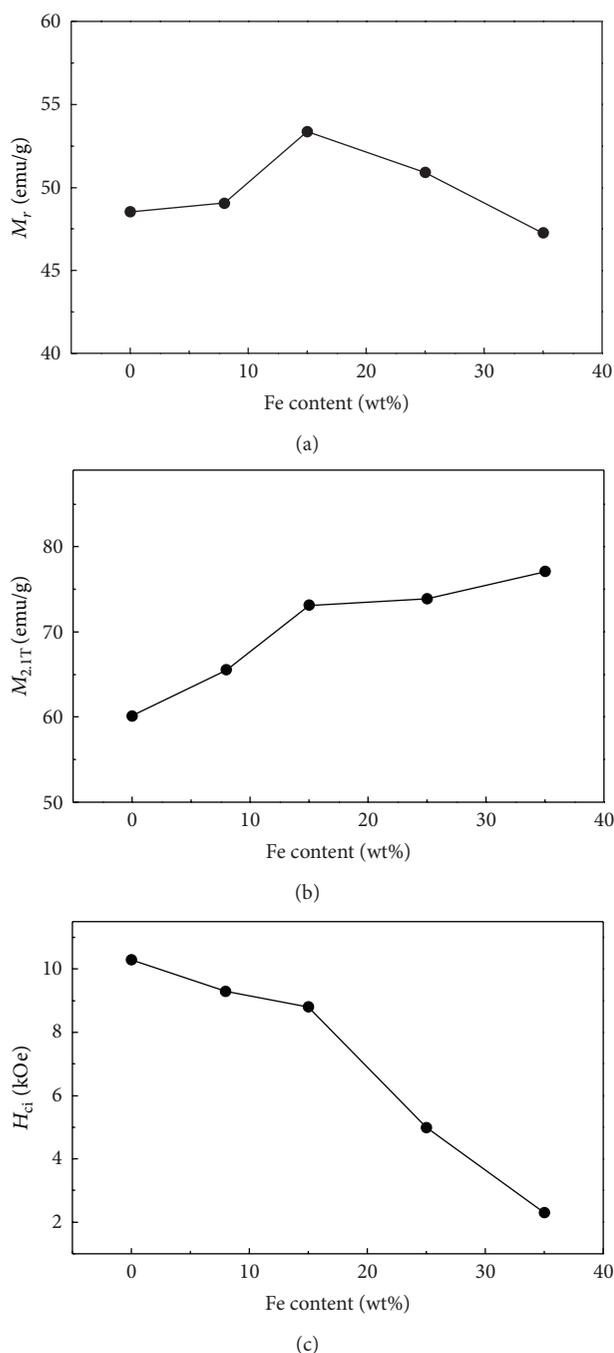


FIGURE 3: Magnetic properties of (Sm,Pr)Co<sub>5</sub>/Fe nanocomposites with different Fe contents.

The magnetic properties of composite (Sm,Pr)Co<sub>5</sub>/Fe nanoflakes with different iron contents are shown in Figure 3. The nanocomposites were measured in the direction parallel to the  $c$ -axis. It can be seen that the remnant magnetization shows a trend of first increasing then decreasing with the content of iron increases and reaches the maximum value when the iron content is 15% in weight. Although the saturation magnetization increases gradually with the increase of iron content as we expect, the coercivity drops

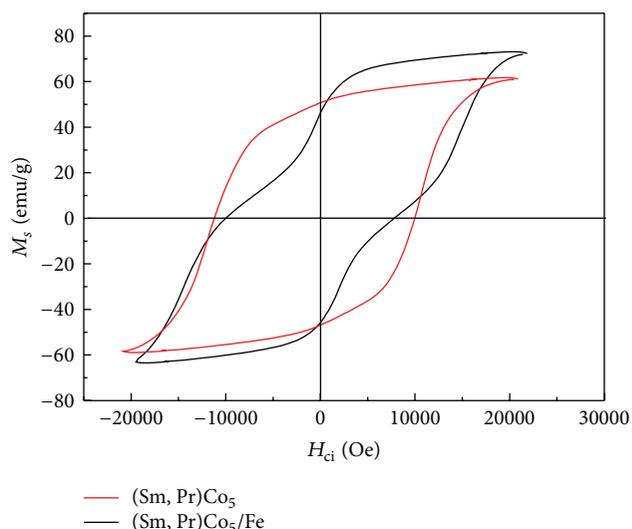


FIGURE 4: Magnetic hysteresis loops of aligned (Sm,Pr)Co<sub>5</sub> nanoflakes and (Sm,Pr)Co<sub>5</sub>/Fe nanocomposites.

dramatically. Figure 4 shows the magnetic hysteresis loops of the (Sm,Pr)Co<sub>5</sub> nanoflakes and the (Sm,Pr)Co<sub>5</sub>/Fe nanocomposites with 15 wt.% Fe content. The magnetic properties of (Sm,Pr)Co<sub>5</sub>/Fe nanocomposites nonannealing are shown below:  $M_r = 53.35$  emu/g,  $M_s = 73.08$  emu/g, and  $H_{ci} = 8.89$  kOe; the magnetic properties of (Sm,Pr)Co<sub>5</sub> nanoflakes are presented as a reference:  $M_r = 48.52$  emu/g,  $M_s = 60.15$  emu/g, and  $H_{ci} = 10.33$  kOe. However, the magnetic hysteresis loop of (Sm,Pr)Co<sub>5</sub>/Fe is not smooth and there is an obvious collapse in the second quadrant, which indicates that the exchange coupling effect between the magnetically soft and hard phase is not strong. The possible reasons for this may be that the particle size and the distribution of the soft phase are not precise enough to achieve the requirements of the theory.

#### 4. Conclusion

In summary, we prepared (Sm,Pr)Co<sub>5</sub>/Fe nanocomposites via electroless plating. The addition of a complexing agent effectively controls the coating morphology, to obtain a continuous and uniform Fe layer. The nanocomposites show enhanced magnetic properties when the nominal addition of Fe was 15 wt.%,  $M_r = 53.35$  emu/g,  $M_s = 73.08$  emu/g, and  $H_{ci} = 8.89$  kOe compared to the properties of uncoated nanoflakes  $M_r = 48.52$  emu/g,  $M_s = 60.15$  emu/g, and  $H_{ci} = 10.33$  kOe. The coercivity drops dramatically with the increase of Fe content, and also the magnetic hysteresis loop of the nanocomposite shows an obvious collapse in the second quadrant.

#### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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