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Preparation and magnetic properties of anisotropic (Sm,Pr)Co_5/Co composite particles

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ABSTRACT

Anisotropic (Sm,Pr)Co_5/Co nanocomposite particles have been fabricated by chemical coating the 2 h ball milled (Sm,Pr)Co_5 flakes with Co nanoparticles. The Co nanoparticles were synthesized with mean particle sizes in the range of 20–50 nm. The nanocomposite particles present [0 0 1] out-of-plane texture and improved magnetic properties, e.g., an enhanced remanent magnetization of 72 emu/g for (Sm,Pr)Co_5/Co and 66 emu/g for (Sm,Pr)Co_5. In addition, by using the 8 h ball milled powders (much smaller than the 2 h ball milled powders) as the starting materials, Co nanoparticles can also be successfully coated on the surface of the flakes. A plausible mechanism for the formation of Co nanoparticles on the surface of (Sm,Pr)Co_5 flakes is discussed.

1. Introduction

Nanocomposite exchange coupled magnets consisting of a fine mixture of hard- and soft-magnetic phases, e.g., $R_2Fe_{14}B$/α-Fe (R=rare earth), have attracted much scientific and technological interests for the development of next generation permanent magnets with a high energy density [1–3]. Theoretical calculations predict that *anisotropic* nanocomposite magnets have the potential to achieve a maximum energy product $(BH)_{max}$ above 100 MGOe [4]. Substantial efforts have been made to manipulate the microstructures of nanocomposite magnets to satisfy the requirements of theoretical models. Unfortunately, at present, most of the nanocomposite magnets fabricated by the conventional top–down methods, e.g., melt spinning and mechanical alloying, are *isotropic* [5–10]. More recently, studies show that the (0 0 l) texture for $Nd_2Fe_{14}B$ nanocrystals can be achieved by a thermo-mechanical processing of amorphous alloys [11,12]. An alternative bottom–up approach is a potential method to fabricate *anisotropic* nanocomposite magnets, where magnetically hard and soft nanoparticles are first prepared, assembled together and then compacted in order to form the nanocomposite magnet [13–17]. Although substantial progress has been made in the synthesis of hard-magnetic particles with crystal texture and an ultrafine and uniform size, the fabrication of *anisotropic* nanocomposite magnets with tailored morphology is still a great challenge [12,18–21]. A number of attempts were made to explore simple mechanical blending of soft magnetic particles with more coarse *anisotropic* hard magnetic powders [14,15]. However, the hard magnetic particles were relatively large and it is extremely difficult to fabricate the soft magnetic phase with controlled morphology. By contrast, coating of hard magnetic particles with a layer of soft magnetic material may enhance the interaction between the soft and hard phases and thus the magnetic performance. One challenge for the powder coating technologies is to disperse the soft phase throughout the magnet, especially for coating the hard magnetic particles produced by a ball milling treatment. Several studies have been performed to explore the powder coating technologies [13,16,17]. Nevertheless, only a few attempts have been made toward coating the ball milled hard magnetic particles with the soft magnetic nanoparticles by chemical reduction [16,17,21].

In this paper, we report a simple chemical coating approach to make anisotropic (Sm,Pr)Co_5/Co nanocomposites. Using the 2 and 8 h ball milled (Sm,Pr)Co_5 flakes as the starting materials, the cobalt soft magnetic nanoparticles can be uniformly deposited on the surface of the flakes using the current method. The nanocomposite particles present [0 0 1] out-of-plane texture and improved magnetic properties.

2. Experimental procedure

The $(Sm_{0.58}Pr_{0.42})Co_5$ flakes were prepared by high-energy ball milling (HEBM) for 2 and 8 h using a SPEX 8000 mill. A ball-to-powder weight ratio of 10:1 was used. Heptane (99.8%) was used as the milling medium and oleic acid (99%) as the surfactant.

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The synthesis of (Sm,Pr)Co_5/Co particles was carried out by employing mixtures of cobalt chloride ($CoCl_2 \cdot 6H_2O$) and the ball milled (Sm,Pr)Co_5 flakes in the desired Co:(Sm,Pr)Co_5 weight ratio in ethanol solution. The mixture was dispersed into the solution under continuous ultrasonic mixing at 50–70 °C for ~5 min. Poly(vinylpyrrolidone) (K30) (1 g) was added as capping agent and dispersant to protect the particles from oxidation and avoid their aggregation. Then another solution consisting of 1.5 g NaOH and 6 ml hydrazine monohydrate liquid (80%) was added. The process of the reaction can be described as below:

$$2Co^{2+} + N_2H_4 + 4OH^- \rightarrow 2Co\downarrow + N_2\uparrow + 4H_2O \quad (1)$$

After strong stirring under ultrasonic for 30 min, the black magnetic powders were recovered by centrifugation and rinsed in ethanol.

The surface morphology and composition of the products were investigated by field emission scanning microscopy (FESEM) equipped with energy dispersion X-ray spectrometer (EDS). The microstructures of the products were investigated by employing an x-ray diffraction (XRD) with Cu Kα radiation. Magnetic measurements were performed using a vibrating sample magnetometer (VSM) with an applied field of up to 9 T at room temperature. The alignment of the flakes was done by applying a 4 kOe field and immobilizing the flakes with epoxy resin or wax for XRD and VSM measurements, respectively.

3. Results and discussion

XRD patterns of the as-prepared magnetically non-aligned and aligned flakes are presented in Fig. 1(a). It can be seen that after magnetic alignment (see the inset in Fig. 1(a)) crystallographically anisotropic (Sm,Pr)Co_5 flakes with [0 0 1] texture were obtained by ball milling for 2 h in heptane and oleic acid, which is in agreement with the report of Cui et al. [22]. Fig. 1(b) and (c) shows the XRD patterns of the magnetically non-aligned and aligned nanocomposite particles. The diffraction peaks can be indexed as the standard $SmCo_5$ (JCPDS NO. 35-1400) and hexagonal Co (JCPDS NO. 05-0727). In Fig. 1(c), the (0 0 2) peak of (Sm,Pr)Co_5 hard phase becomes the dominant reflection, indicating a strong *c*-axis crystallographic alignment of (Sm,Pr)Co_5 phase in the nanocomposite particles.

Typical SEM images of the (Sm,Pr)Co_5 flakes milled for 2 h and the composite powders are presented in Fig. 2. In this figure, (a) and (b) show the magnetic powders with flaky-like morphology at different magnifications. It can be seen that the surface of the as-prepared (Sm,Pr)Co_5 flakes are smooth, and their thicknesses is in the range of 20–100 nm and length is 0.5–5 μm. Fig. 2(d) and the corresponding high-magnification SEM image (see Fig. 2(e)) exhibit the feature of nanocomposite flakes when 0.03 g (Sm,Pr)Co_5 powers reacted with 0.024 g cobalt chloride. From Fig. 2(d) and (e), it can be clearly seen that as-prepared (Sm,Pr)Co_5 flakes are decorated by uniform nanoparticles in the range of 20–50 nm in diameter. The energy dispersive X-ray spectroscopy performed on the surface of particles showed the atomic ratio of the samples at different stages of reaction (Fig. 2(c) and (f)). The loss of a small amount of Sm and Pr from the as-prepared (Sm,Pr)Co_5 may be mainly due to the minor oxidation of Sm and Pr during the HEBM processes. The composition of this heterostructure is confirmed by the EDS studies, which reveals the presence of Sm, Pr, Co and O element. In Fig. 2(f), a relatively high content of cobalt element was detected. It can also be seen from Fig. 2(c) and (f) that the concentration of oxygen is relatively high. The oxygen likely came from two sources, one from the oxidation of Sm and Pr during the HEBM

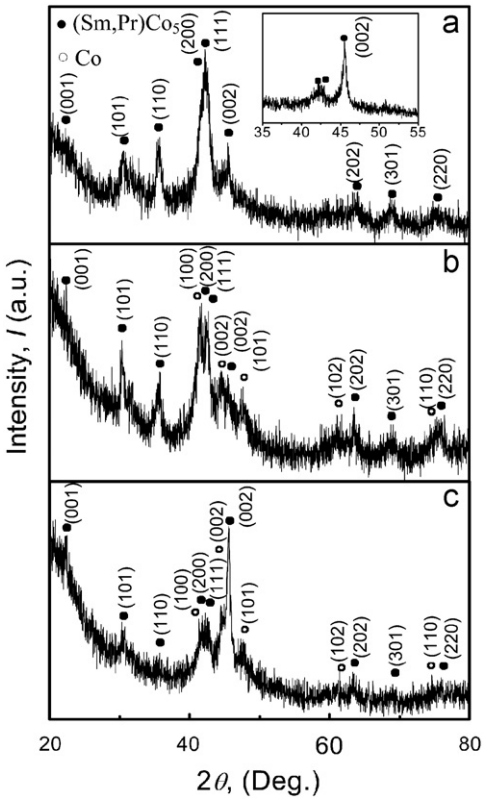

Fig. 1. XRD patterns of nonaligned (a) and magnetically aligned (inset in (a)) (Sm,Pr)Co_5 flakes, nonaligned (b) and magnetically aligned (c) (Sm,Pr)Co_5/Co composites fixed in epoxy resin.

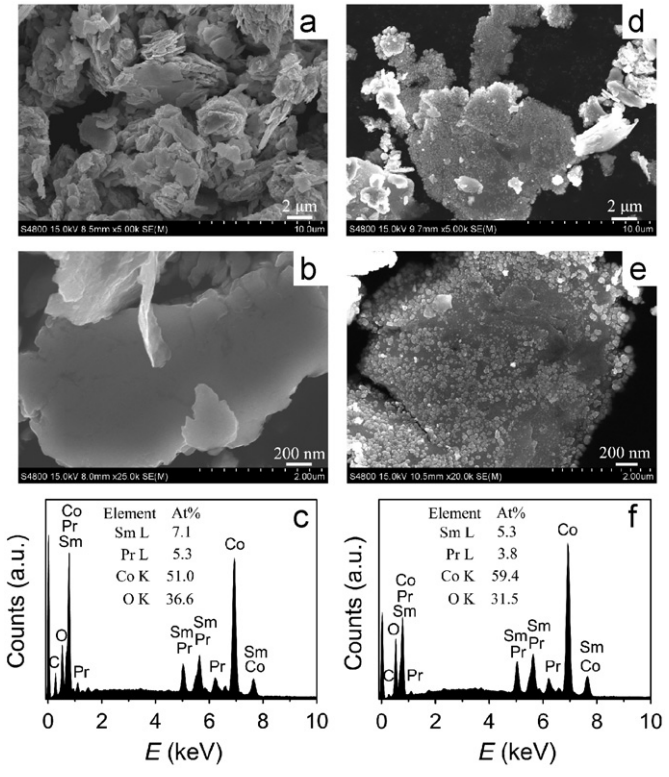

Fig. 2. SEM images and EDS spectrums of the (Sm,Pr)Co_5 flakes and (Sm,Pr)Co_5/Co composites. (a, b) typical SEM images of the ball milled (Sm,Pr)Co_5 flakes for 2 h. (c) Typical EDS spectrum of the (Sm,Pr)Co_5 flakes and the atomic ratio (inset in (c)). (d, e) typical SEM images of (Sm,Pr)Co_5/Co composites. (f) Typical EDS spectrum of the (Sm,Pr)Co_5/Co composites and the atomic ratio (inset in (f)).