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Preparation and magnetic properties of anisotropic (Sm,Pr)Co₅/Co composite particles

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ABSTRACT

Anisotropic (Sm,Pr)Co₅/Co nanocomposite particles have been fabricated by chemical coating the 2 h ball milled (Sm,Pr)Co₅ 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)Co₅/Co and 66 emu/g for (Sm,Pr)Co₅. 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)Co₅ flakes is discussed.

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1. Introduction

Nanocomposite exchange coupled magnets consisting of a fine mixture of hard- and soft-magnetic phases, e.g., $R_2Fe_{14}B/\alpha$ -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 (001) texture for Nd₂Fe₁₄B 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

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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)Co₅/Co nanocomposites. Using the 2 and 8 h ball milled (Sm,Pr)Co₅ 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-topowder 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:

$$2Co^{2+} + N_2H_4 + 40H^- \to 2Co\downarrow + N_2\uparrow + 4H_2O$$
(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 K α 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)Co₅ flakes with [0 0 1] texture were obtained



Typical SEM images of the (Sm,Pr)Co₅ 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)Co₅ flakes are smooth, and their thicknesses is in the range of 20–100 nm and length is $0.5-5 \,\mu$ m. 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)Co₅ powers reacted with 0.024 g cobalt chloride. From Fig. 2(d) and (e), it can be clearly seen that as-prepared (Sm,Pr)Co₅ 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)Co₅ 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)).

process and another from the residual oleic acid of powders. Obviously, coating processing should be improved to minimize oxygen in future experiments.

Based on the XRD, FESEM and EDS studies, the nanoparticles coated on the surface of the flakes are determined to be Co nanoparticles (Fig. 2). In theory, Eq. (1) is thermodynamically feasible and very exothermic [23]. However, it is still kinetically slow [23,24]. It can be observed that the equilibrium molar ratio of N₂H₄ to Co^{2+} is equal to 0.5. However, the ratio experimented was purposely much larger than 0.5 to accelerate the reaction. We propose that the monodispersed colloidal Co nanoparticles can be the effect of the alkalinity of the reaction solution since it was found that the formation of Co nanoparticles is easier at this condition. In an alkaline medium, a large concentration of hydroxyl ions keeps the Co ions in its active state of $Co(OH)_4^{2-}$, which then promotes the reaction. Thus, to narrow down the size distribution of the particles in the solution, an alkaline environment during the reduction is required. We suggest that the Co nanoparticles are in a disk-like shape using the present method,



Fig. 3. Hysteresis loops of the aligned $(Sm,Pr)Co_5$ flakes ball milled for 2 h and the aligned $(Sm,Pr)Co_5/Co$ composites.

similar results were reported by Gibson and Putzer [23]. The findings, that the Co nanoparticles are distributed uniformly on the surface of the (Sm,Pr)Co₅ flakes, were a bit surprising because ferromagnetic particles tend to form tight aggregates as a result of magnetic attractions between the particles [25]. However, the cobalt nanoclusters are small enough to be strongly influenced by Brownian forces. Because of the shape anisotropy of the Co nanoparticles, these forces result in the rotation of the particles (Brownian rotation). This effect probably inhibits the intimate contact between particles that is necessary for agglomeration [23]. Besides that, PVP has been widely used as a steric stabilizer or capping agent to protect nanoparticles from agglomeration [26]. According to the classical nucleation theory, heterogeneous nucleation is energetically easier than homogeneous nucleation [27]. The liquid/solid interfaces act as anchor sites and consequently make the in situ formed nanoparticles attach on the surface and edges of flakes. Therefore, a high density of uniform Co nanoparticles decorating (Sm,Pr)Co₅ flakes could be obtained.

The hysteresis loops of the aligned (Sm,Pr)Co₅/Co nanocomposite powders and the aligned uncoated powders are shown in Fig. 3, which are measured along the direction parallel to the *c*-axis. As can be seen for the case of Co coating, the saturation magnetization M_s increases distinctly. The (Sm,Pr)Co₅/Co composites show an enhanced remanent magnetization M_r of 72 emu/g with a coercivity H_c of 8.9 kOe as compared with those of (Sm,Pr)Co₅ flakes, M_r =66 emu/g and H_c =10.8 kOe.

Fig. 4 shows the SEM images of the 8 h ball milled (Sm,Pr)Co₅ flakes and the (Sm,Pr)Co₅/Co composite powders after chemical coating for 30 min. It can be seen that most of the powders appear as flakes with thickness about 20 nm and a length of about 1.5 μ m (Fig. 4a and b), much smaller than those of the 2 h ball milled products. Typical SEM images of the (Sm,Pr)Co₅/Co composites are given in Fig. 4c and d. It can be seen that the (Sm,Pr)Co₅ flakes are coated with uniformly distributed nanopartices. Fig. 5 shows XRD patterns of the ball milled (Sm,Pr)Co₅ flakes and (Sm,Pr)Co₅/ Co composites. The diffraction peaks can be indexed as the standard SmCo₅ and hexagonal Co, indicating that the nanoparticles attaching on the surface of (Sm,Pr)Co₅ flakes are soft



Fig. 4. SEM images of the (Sm,Pr)Co₅ flakes. (a, b) typical SEM images of the ball milled (Sm,Pr)Co₅ flakes for 8 h. (c, d) typical SEM images of (Sm,Pr)Co₅/Co composites.



Fig. 5. XRD patterns of (a) 8 h ball milled (Sm,Pr)Co $_5$ powders and (b) (Sm,Pr)Co $_5$ /Co composites.

magnetic Co nanoparticles. The results indicate that the proposed technology can be effectively used to coat the $(Sm,Pr)Co_5$ hard magnetic particles with Co nanoparticles.

4. Conclusion

We have shown the fabrication of anisotropic (Sm,Pr)Co₅/Co nanoocomposite flakes by a simply chemical reduction method. The nanocomposite particles present [0 0 1] out-of-plane texture and improved magnetic properties. The (Sm,Pr)Co₅/Co composites show an enhanced remanent magnetization of 72 emu/g (66 emu/g for (Sm,Pr)Co₅) with a H_c of 8.9 kOe (10.8 kOe for (Sm,Pr)Co₅). Using the current synthetic strategy, the smaller hard magnetic flakes (with a thickness of 10–20 nm and a length of 0.5–1.5 µm) can also be coated with Co nanoparticles. However, the squareness and coercivity of the composites decrease slightly compared with those of the (Sm,Pr)Co₅ flakes. The study of improving the magnetic exchange coupling of the composites and performing the powder compaction is underway.

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References

- R. Coehoorn, D.B. Mooji, C. De Waard, Journal of Magnetism and Magnetic Materials 80 (1989) 101.
- [2] E.F. Kneller, R. Hawig, IEEE Transactions on Magnetics 27 (1991) 3588.
- [3] T. Schrefl, J. Fidler, H. Kronmüller, Physical Review B 49 (1994) 6100.
- [4] R. Skomski, J.M.D. Coey, Physical Review B 48 (1993) 15812.
- [5] R. Fischer, T. Schrefl, H. Kronmüller, J. Fidler, Journal of Magnetism and Magnetic Materials 150 (1995) 329.
- [6] D. Goll, M. Seeger, H. Kronmüller, Journal of Magnetism and Magnetic Materials 185 (1998) 49.
- [7] P.G. McCormick, W.F. Maio, P.A.I. Smith, J. Ding, R. Street, Journal of Applied Physics 83 (1998) 6256.
- [8] J. Zhang, S.Y. Zhang, H.W. Zhang, B.G. Shen, Journal of Applied Physics 89 (2001) 5601.
- [9] W. Li, L.L. Li, Y. Nan, X.H. Li, X.Y. Zhang, D.V. Gunderov, V.V. Stolyarov, A.G. Popov, Applied Physics Letters 91 (2007) 062509.
- [10] C. Rong, Y. Zhang, N. Poudyal, I. Szlufarska, R.J. Hebert, M.J. Kramer, J.P. Liu, Journal of Materials Science 46 (2011) 6065.
- [11] Y.G. Liu, L. Xu, Q.F. Wang, W. Li, X.Y. Zhang, Applied Physics Letters 94 (2009) 172502.
- [12] L. Xu, Y.G. Liu, D.F. Guo, L.P. Zhou, F.Q. Wang, H.T. Zhang, X.Y. Zhang, Journal of Physics D: Applied Physics 44 (2011) 355002.
- [13] Q. Zeng, Y. Zhang, M.J. Bonder, G.C. Hadjipanayis, Journal of Applied Physics 93 (2003) 6498.
- [14] Q. Zeng, Y. Zhang, M.J. Bonder, G.C. Hadjipanayis, R. Radhakrishnan, IEEE Transactions on Magnetics 39 (2003) 2974.
- [15] S. Chu, S.A. Majetich, M. Huang, R.T. Fingers, Journal of Applied Physics 93 (2003) 8146.
- [16] S. Liu, A. Higgins, E. Shin, S. Bauser, C. Chen, D. Lee, Y. Shen, Y. He, M.Q. Huang, IEEE Transactions on Magnetics 42 (2006) 2912.
- [17] M. Marinescu, J.F. Liu, M.J. Bonder, G.C. Hadjipanayis, Journal of Applied Physics 103 (2008) 07E120.
- [18] M.Q. Huang, Z. Turgut, B. Wheeler, D. Lee, S. Liu, B.M. Ma, Y.G. Peng, S.Y. Chu, D.E. Laughlin, J.C. Horwath, R.T. Fingers, Journal of Applied Physics 97 (2005) 10H104.
- [19] C.B. Rong, V. Nandwana, N. Poudyal, J.P. Liu, M.E. Kozlov, R.H. Baughman, Y. Ding, Z.L. Wang, Journal of Applied Physics 101 (2007) 023908.
- [20] C. Rong, Y. Zhang, M.J. Kramer, J.P. Liu, Physics Letters A. 375 (2011) 1329.
- Y. Hou, S. Sun, C.B. Rong, J.P. Liu, Applied Physics Letters 91 (2007) 153117.
 B. Cui, A. Gabay, W. Li, M. Marinescu, J. Liu, G.C. Hadjipanayis, Journal of
- [22] B. Cui, A. Gabay, W. Li, M. Marinescu, J. Liu, G.C. Hadjipanayis, Journal of Applied Physics 107 (2010) 09A721.
- [23] C.P. Gibson, K.J. Putzer, Science 267 (1995) 1338.
- [24] D.M. Littrell, D.H. Bowers, B.J. Tatarchuk, Journal of the Chemical Society, Faraday Transactions I 83 (1987) 3271.
- [25] P.C. Scholten, Journal of Magnetism and Magnetic Materials 39 (1988) 99.
 [26] X.H. Liu, R. Yi, Y.T. Wang, G.Z. Qiu, N. Zhang, X.G. Li, Journal of Physical
- Chemistry C 111 (2007) 163.
- [27] D. Turnbull, J.C. Fisher, Journal of Chemical Physics 17 (1949) 71.