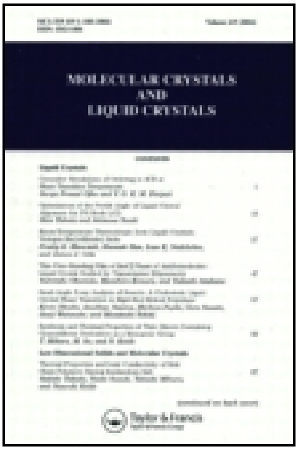

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Exchange-Coupling Effect of $Nd_2Fe_{14}B$/FeCo Nanocomposite by Colloidal Method

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Exchange-coupling effect of $Nd_2Fe_{14}B/FeCo$ nanocomposite by colloidal method is reported. The magnetic hard phase $Nd_{15}Fe_{77}B_8$ alloy was prepared by high energy ball mill process and the magnetic soft phase Fe-Co nanoparticles was synthesized by coprecipitation method, and then were annealed in order to crystallize at the different temperature. The hard phase $Nd_{15}Fe_{77}B_8$ nanoparticles and the soft phase Fe-Co nanoparticles were coated with surfactants such as oleic acid. The hard and soft phase nanoparticles coated by surfactants were mixed by self-assembly with shake-milling process, and then annealed at 650°C for 20 min.

Keywords: coprecipitation; exchange-coupling; high energy ball mill process; self-assembly

INTRODUCTION

A nanocomposite permanent magnet, that is a nano-scale mixture of hard and soft magnetic phase, has become more attractive as a new magnetic material due to their potential for permanent magnet applications and their interesting exchange coupling behavior between both two phases in nano-scale materials [1,2]. A prerequisite for nanocomposite permanent magnetic materials is that the grain sizes of both the soft and hard magnetic phase in nano-scale materials should

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be small enough to be able to do exchange interactions across the interfaces between the two phases [3,4]. Taking advantage of high coercivity (H_c) by hard magnetic and high magnetization (M_s) by the soft magnetic components respectively, possibly results in the high remanence (M_r) and a large maximum energy product ($(BH)_{max}$) if a full exchange coupling exists between the grains of the two phases in nanocomposite magnets. Such systems can exhibit a very high maximum energy product due to the high moment of the soft phase and the large coercivity of the hard phase. However, up to now, the maximum energy products of the rare-earth nanocomposite magnets prepared by means of rapid quenching and mechanical alloying have been much lower than the theoretical expectation, due to difficulties in controlling the nanostructures [5,6].

Chemically synthesized magnetic materials have drawn much attention due to the unique magnetic properties derived from small particle sizes and uniform size distribution, compared with physically prepared magnetic materials [7,8]. Colloidal method using surfactant reported in this study is a comparatively inexpensive and easy way to produce self-assembled nanoparticles with highly controllable size and morphology for exchange coupled permanent magnet. $Nd_2Fe_{14}B$/FeCo nanocomposite was prepared by colloidal method that has a good advantage in dispersibility and so on. This is the first report of $Nd_2Fe_{14}B$/FeCo nanocomposite by colloidal method that will be promising direction.

EXPERIMENTALS

Preparation of FeCo Nanoparticles

In this work, iron chloride tetrahydrate $FeCl_2{\cdot}4H_2O$ (99+%), cobalt chloride hexahydrate $CoCl_2{\cdot}6H_2O$ (98%), and sodium borohydride $NaBH_4$ were purchased from Aldrich. We used high-purity Ar gas (99.999+%) in order to prevent oxidation when distilled water was purged with it. $FeCl_2{\cdot}4H_2O$ (0.008 mol, 1.5261 g) and $CoCl_2{\cdot}6H_2O$ (0.002 mol, 0.7716 g) were dissolved in 50 mL distilled water with vigorous stirring and purged with argon gas for over 30 min. A 50 mL of 0.007 M $NaBH_4$ (0.2632 g) was added to this mixture with vigorous stirring. And reaction was kept to pH 7 and room temperature. As-precipitated powder was washed with deoxygenated water in order to remove reaction residues and with acetone to get rid of water. After drying with Ar gas, the product was annealed for 1 hr at 750°C, under high-purity argon atmosphere.

Preparation of $Nd_2Fe_{14}B$/FeCo Nanocomposite

The as-milled $Nd_{15}Fe_{77}B_8$ as starting materials used in this experiment was obtained as ref 9. The bulk $Nd_{15}Fe_{77}B_8$ alloy was milled by high energy shaker-mill for 20 hrs with 12 mm diameter hardened steel ball. And then, the as-milled Nd-Fe-B powder (2 g), FeCo nanoparticles (0.5 g) annealed for 1 hr at 750°C, and oleic acid were placed into a steel vial along with 12 mm diameter hardened steel ball. As-milled mixtures were annealed in a vacuum furnace under vacuum ($\sim 10^{-5}$ Torr) at 650°C for 20 min in order to be crystallized. All the process were worked in the glovebox in order to keep from oxidizing.

Analysis

To identify properties of the prepared FeCo nanoparticles, Nd-Fe-B alloy and $Nd_2Fe_{14}B$/FeCo nanocomposite, we did various experiments. Elemental analyses of them were conducted by using energy dispersive X-ray microanalysis (EDX) with JEOL JEM2010 TEM operated under an acceleration voltage of 200 kV. The crystal structure of the prepared nanoparticles was identified by using X-ray powder diffraction (XRD) with a Philips X'Pert-MPD System with a Cu- K_α radiation source ($\lambda = 0.154056$ nm). The size and shape of nanoparticles were obtained by transmission electron microscopy (TEM). TEM measurements were carried out on a HITACHI H-7500 low resolution TEM. Samples for TEM samples were prepared on 300 mesh copper grids coated with carbon. The magnetization curves were characterized with Lake Shore 7300 vibrating sample magnetometer (VSM). The crystallization kinetics of the nanocomposite was observed by measurements of thermo-magnetic analysis (TMA).

RESULTS AND DISCUSSION

The chemical method of coprecipitation has good advantage such as the uniform size and spherical shape of the nanoparticles [10]. The reaction was taken place at room temperature. Moreover it is easy to control contents of the materials [11,12].

Figure 1 shows TEM image (a) and EDX spectrum (b) of FeCo alloy synthesized by coprecipitation. As can be seen TEM image (a) and EDX spectrum (b) of as-precipitated FeCo alloy in Figure 1, alloy prepared by coprecipitation method is the particle with ultrafine size and has pure content without impurities such as surfactant in comparison with langmuir-blogett technique [13] or polyol process [14]. In addition the ratio of metal can be controlled as exactly as reqired. The ratio of

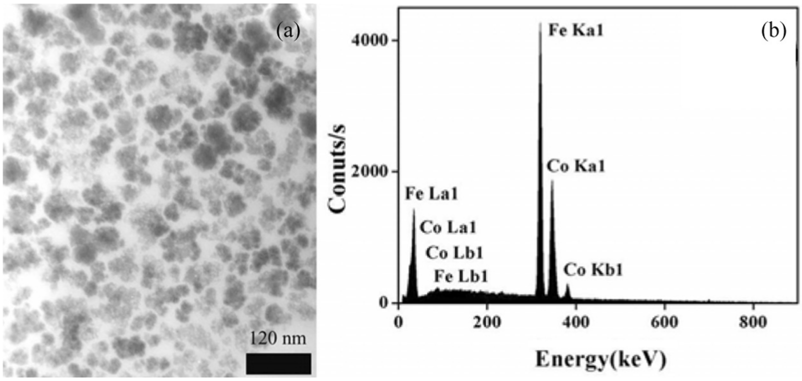

FIGURE 1 TEM image (a) and EDX spectrum (b) of FeCo nanoparticle.

Fe to Co is around 7:3 in the prepared precipitate. The prepared sample was annealed for 1 hr at 750°C in order to crystallize. TEM image (a) in Figure 2 shows that the size of FeCo nanoparticle annealed for 1 hr at 750°C determined as 10 nm–15 nm and the shape of FeCo nanoparticles was generally spherical. XRD result (b) shows that the discernible peaks can be indexed to (110), (200), (211) planes of a cubic unit cell, which corresponds to cubic structure of Co_3Fe_7 (JCPDS card, no. 48-1816). Accordingly, it can be seen that content of $Fe_{70}Co_{30}$ can be controlled. Generally TMA and XRD can be used to investigation phase and crystallization temperature of a sample. Figure 3 shows TMA (a) and XRD result (b) of $Nd_2Fe_{14}B$/FeCo nanocomposite prepared by shaker-milled with oleic acid. In TMA result (a), the

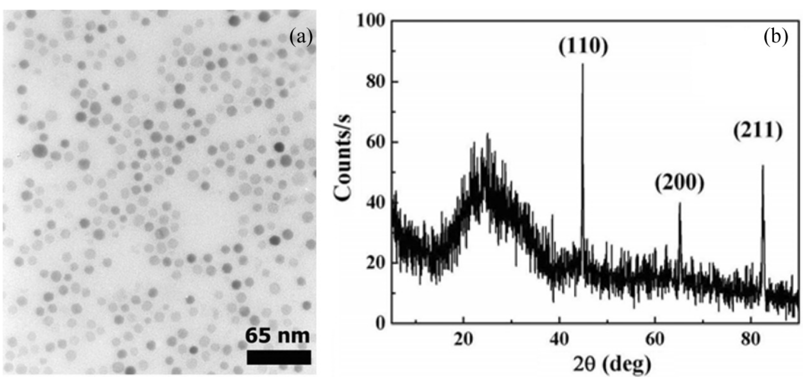

FIGURE 2 TEM image (a) and XRD spectrum (b) of as-annealed FeCo nanoparticle.

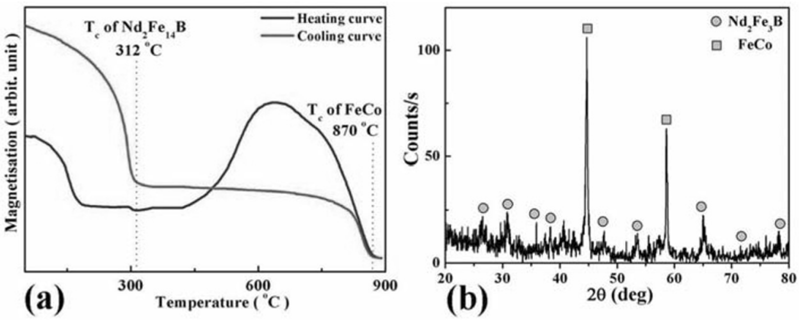

FIGURE 3 TMA curve (a) and XRD spectrum (b) of $Nd_2Fe_{14}B$/FeCo nanocomposite.

magnetization inflections at around 870 and 312°C correspond to the Curie temperature (T_c) of FeCo and $Nd_2Fe_{14}B$ phase, respectively. In addition XRD spectra (b) shows the hard phase of $Nd_2Fe_{14}B$ and the soft phase FeCo are also existing in the prepared nanocomposite annealed at 650°C for 20 min. Figure 4 shows that FeCo nanoparticles and $Nd_2Fe_{14}B$ phase were mixed homogeneously after shaker-milled

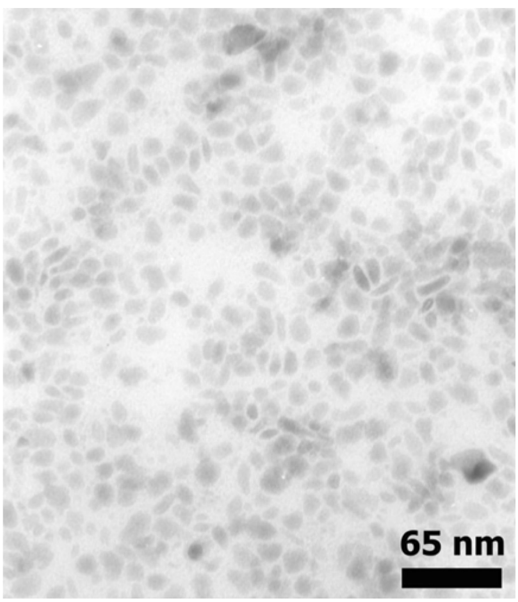

FIGURE 4 TEM image of $Nd_2Fe_{14}B$/FeCo nanocomposite.

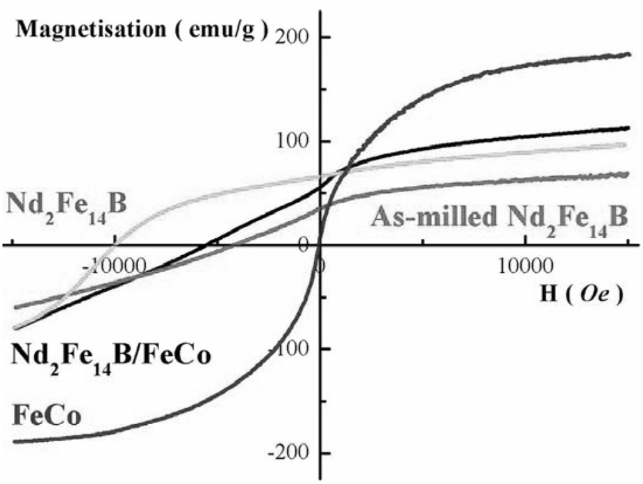

FIGURE 5 VSM curve of $Nd_2Fe_{14}B$/FeCo nanocomposite.

with oleic acid. The size of the hard phase was determined as 20 nm–30 nm and the size of soft phase was determined as 10 nm–15 nm on the shaker milling process. Figure 5 shows VSM result of $Nd_2Fe_{14}B$/FeCo nanocomposite. In the Figure 5, the value of M_s of FeCo is over 180 emu/g and this value is that the highest value of M_s of the powder prepared by coprecipitation method. This means that the prepared FeCo powder has good magnetic property of soft phase. The value of M_r of $Nd_2Fe_{14}B$ used for hard phase is 70 emu/g. The value of M_s of $Nd_2Fe_{14}B$/FeCo nanocomposite is 120 emu/g, and this value is higher than that of $Nd_2Fe_{14}B$. The value of M_r of $Nd_2Fe_{14}B$/FeCo nanocomposite is 56 emu/g, and this value is higher than that of as-milled $Nd_2Fe_{14}B$. Moreover the value of coercivity of $Nd_2Fe_{14}B$/FeCo nanocomposite is over 5.5 kO_e in comparable with that of as-milled Nd-Fe-B. Judging from this point of view, the prepared $Nd_2Fe_{14}B$/FeCo nanocomposite has 25% of the amount of the soft phase, the coercivity of over 5.5 kO_e of prepared nanocomposite means that it has exchange coupling effect.

CONCLUSIONS

Among many methods to synthesize nano-meter materials, the chemical method of coprecipitation used in the present study is good and easy to get uniform and spherical nanosized powder without component change. In addition the property of the FeCo prepared by coprecipitation has the highest value of M_s among the powders prepared by chemical method. This means that the prepared FeCo powder has good magnetic property of soft phase and the prepared FeCo by coprecipitation can be used in the many fields, such as many kinds of sensor, MRI and so on. It was confirmed from XRD spectra, TMA data that hard phase and soft phase are co-existing in the prepared $Nd_2Fe_{14}B$/FeCo nanocomposite. Moreover, it is observed that exchange coupling effect takes place in the prepared $Nd_2Fe_{14}B$/FeCo nanocomposite in VSM data.

REFERENCES

[1] Kneller, E. F. & Hawig, R. (1991). *IEEE Trans. Magn.*, *27*, 3588.
[2] Hadjipanayis, G. C. (1999). *J. Magn. Magn. Mater.*, *200*, 373.
[3] McCormick, P. G., Miao, W. F., Smith, P. A. I., Ding, J., & Street, R. (1998). *J. Appl. Phys.*, *83*, 6256.
[4] Skomski, R. & Coey. J. M. D. (1993). *Phys. Rev. B*, *48*, 15812.
[5] David, S. & Givord, D. (1998). *J. Alloys Compd.*, *281*, 6.
[6] Goll, D., Seeger, M., & Kronmuller, H., (1998). *J. Magn. Magn. Mater.*, *185*, 4.
[7] Eckert, D., Müller, K. H., & Handstein, A. (1990). *IEEE Trans. Magn.*, *26*, 1834.
[8] Sun, S., Murray, C. B., Weller, D., Folks, L., & Moser, A. (2002). *A. Science*, *287*, 1989.
[9] Kwon, H. W. & Jeong, I. C. (2004). *Phys. Stat. Sol. (a)*, *201*, 1921.
[10] Zheng, Q., Zhang, Y., Wang, H. L., Papaefthymiou, V., & Hadjipanayis, G. C. (2004). *J. Magn. Magn. Mater.*, *272*, E122.
[11] Kim, C. W., Kim, Y. H., Lee, D. K., Jeong, I. C., Kwon, H. W., & Kang, Y. S. (2006). *J. Nanosci. Nanotechnol.*, in press.
[12] Kim, C. W. & Kang, Y. S. (2006). *Solid state phenomena*, in press.
[13] Lee, D. K., Kim, Y. H., Kang, Y. S., & Stroeve, P. (2005). *J. Phys. Chem. B.*, *109*, 14939.
[14] Shin, S. J., Lee, D. K., Kim, Y. H., & Kang, Y. S. (2006). *Curr. Appl. Phys.*, in press.