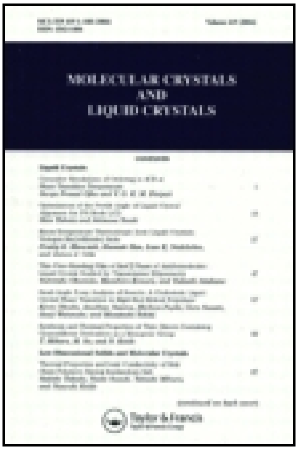

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A Study on the Exchange-Coupling Effect of $Nd_2Fe_{14}B$/CoFe Forming Core/Shell Shape

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We report the core/shell type as the interesting one of the various techniques to prepare exchange-coupled permanent magnet. In this study, the exchange-coupled $Nd_2Fe_{14}B$/CoFe was prepared by ball mill method and chemical reduction. $Nd_{15}Fe_{77}B_8$ powder was prepared by ball milling and the as-milled powder was coated with CoFe nanoparticle by chemical reduction. After annealing, $Nd_2Fe_{14}B$/CoFe forming core/shell shape was identified by using FE-SEM, XRD, TMA, and VSM.

Keywords: chemical reduction; core/shell; exchange-coupling

INTRODUCTION

A nanocomposite permanent magnet has become more attractive as a new magnetic material because of their potential for permanent magnet applications and their interesting exchange coupling behavior between the soft and hard magnetic phase in nanoscale materials [1]. Exchange coupling between both phases causes the magnetization vector of the soft phase to be aligned with that of hard phase. Due to the exchange coupling between both phases, the entire exchange coupling effect inside the material will be enhanced. Also, due to the

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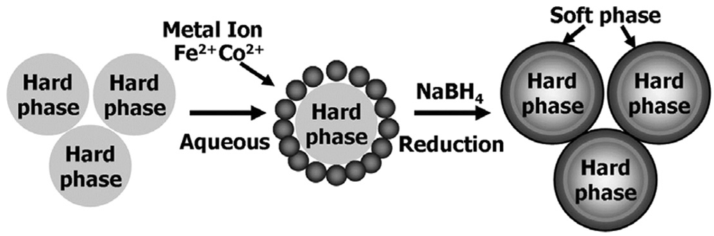

FIGURE 1 The overall scheme for $Nd_2Fe_{14}B$/CoFe forming core/shell.

high saturation magnetization (M_s) of the soft magnetic phase, the magnetostatic coupling between the nanocrystalline grains will be strengthened. Therefore, the nanocomposite magnet can show a remanence (M_r) higher than 1/2 M_s which is obtained in the case of a single hard magnet, and a significant large maximum energy product ($(BH)_{max}$).

Magnetic exchange coupling interactions between the core and shell materials can be obtained if the hard and soft phases are used as the core and the shell, respectively. Other concepts such as increasing anisotropy by magnetic exchange coupling between ferromagnetic and antiferromagnetic materials can also be utilized for the design of core/shell nanoparticles [2]. Core-shell structured nanocrystals which were known to prepare exchange-coupled magnet are interesting because of their unique physical and chemical properties, as well as their technological applications [3]. The core-shell structured nanoparticles have the advantage of tuning and tailoring their physical properties by designing the chemical compositions as well as sizes of core and shell. In this point of view, we report the core/shell type as the interesting one of the various techniques to prepare exchange-coupled permanent magnet. In this study, $Nd_2Fe_{14}B$ prepared by high ball mill process was coated with CoFe nanoparticle by chemical method as you can see Figure 1.

EXPERIMENTALS

Materials

In this work, $CoCl_2 \cdot 6H_2O$ (98%), $FeCl_2 \cdot 4H_2O$ (99 + %), $NaBH_4$ were purchased from Aldrich. High-purity Ar gas (99.999 + %) was used to prevent oxidation during purging the distilled water and drying the synthesized nanoparticles. The as-milled $Nd_{15}Fe_{77}B_8$ as starting materials used in this experiment was obtained as ref. [4]. In the case of the soft magnetic phase, CoFe nanoparticle was obtained in the method of ref. [5].

Preparation of $Nd_2Fe_{14}B$/CoFe Forming Core/Shell

The sample powder of $Nd_{15}Fe_{77}B_8$/CoFe nanoparticles were prepared by chemical reduction of aqueous solutions of $CoCl_2 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$, and as-milled $Nd_{15}Fe_{77}B_8$ powder with $NaBH_4$. $CoCl_2 \cdot 6H_2O$ (0.002 mol, 0.7716 g) and $FeCl_2 \cdot 4H_2O$ (0.008 mol, 1.5261 g) were dissolved in 50 ml distilled water. As-milled $Nd_{15}Fe_{77}B_8$ powder was added to metal ion solution under the vigorous stirring. A 50 mL of 0.007 M $NaBH_4$ (0.2632 g) was dropped to this mixture with vigorous stirring. A drop of aqueous $NaBH_4$ was put into the metal solution at a dropping rate of 5 mL/s at RT. The resulted black precipitate was washed with the purged water. As-prepared powder was annealed at 650°C for 20 min. in a vacuum system with 2×10^{-5} mbar.

RESULTS AND DISCUSSION

In order to obtain efficiently exchange-coupling effect, the grain size of soft phase should be smaller than 20 nm [6] and the interaction between the hard and soft magnetic grains can not be obtained efficiently in the presence of impurities such as a stabilizer. In this point of view, chemical method such as coprecipitation can be very useful [7]. Figure 2 shows the particle size of starting materials as hard and soft phases. The sizes of as-milled $Nd_{15}Fe_{77}B_8$ and CoFe nanoparticle were determined as 1–2 μm, and 30 nm, respectively. As you can see in Figure 3, FE-SEM image shows the size and shape of $Nd_{15}Fe_{77}B_8$/FeCo forming core/shell. It indicates that the surface of as-milled $Nd_{15}Fe_{77}B_8$ was coated with CoFe nanoparticle. As-made $Nd_{15}Fe_{77}B_8$/CoFe forming core/shell was subjected to the TMA in order to check the existence of magnetic phase. The TMA curve showing the dependence of the magnetization on the temperature is shown

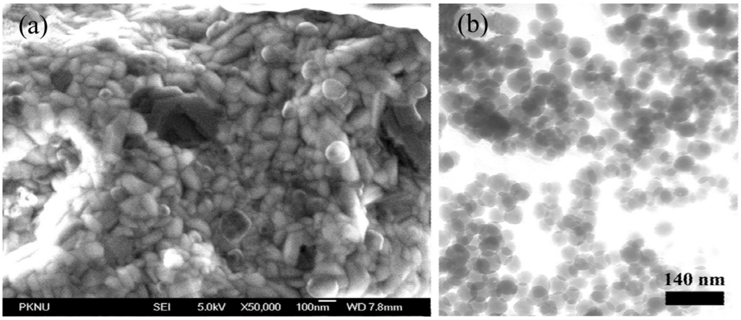

FIGURE 2 The images of starting materials; (a) FE-SEM image of $Nd_{15}Fe_{77}B_8$ and TEM image of (b) as-synthesized CoFe nanoparticle.

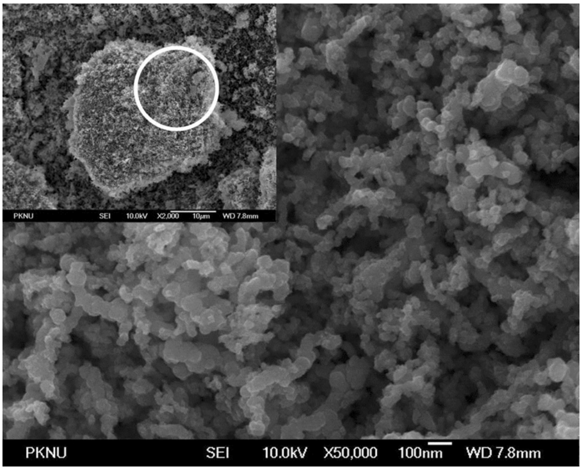

FIGURE 3 FE-SEM image of $Nd_{15}Fe_{77}B_8$/CoFe forming core/shell.

in Figure 4. As can be seen, there are two magnetization reductions at around 324 and above 820°C in the course of heating. For the cooling curve, the magnetization inflection appearing at around 324°C in the heating curve disappeared, and instead a magnetization rise is observed at around 324°C. The magnetization inflections at around above 820 and 324°C correspond to the Curie temperatures (T_c) of CoFe and $Nd_2Fe_{14}B$ phase, respectively. This means that $Nd_2Fe_{14}B$ and CoFe as magnetic phase with nanosized particle exist in the as-made powder. After as-made $Nd_{15}Fe_{77}B_8$/CoFe forming core/shell

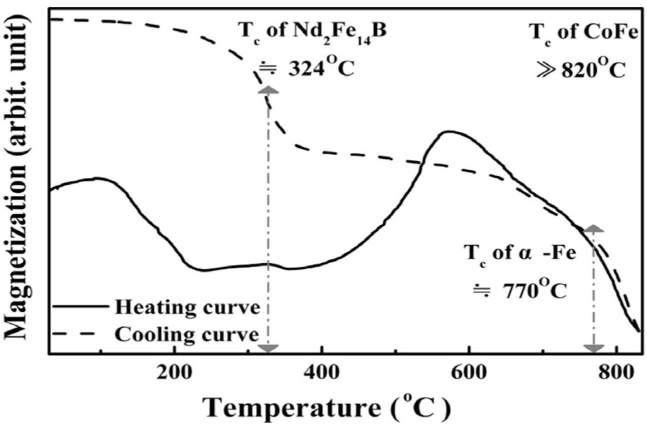

FIGURE 4 TMA curve of $Nd_2Fe_{14}B$/CoFe forming core/shell.

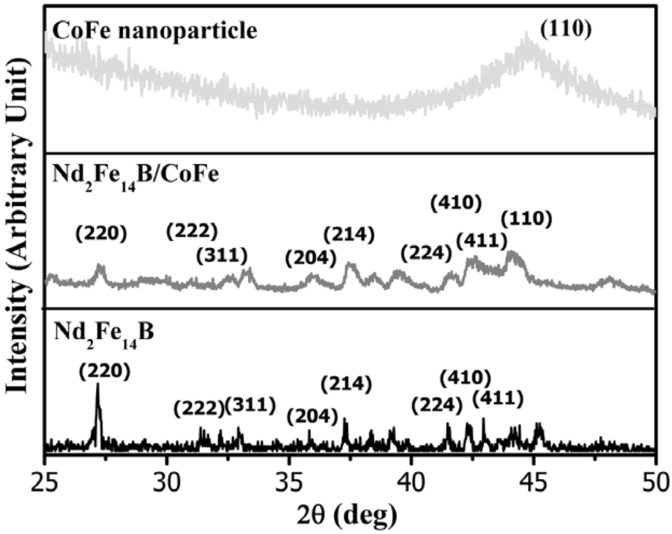

FIGURE 5 XRD spectrum of $Nd_2Fe_{14}B$/CoFe forming core/shell.

was annealed at 650°C under a vacuum of 10^{-6} mbar for 20 min., as-annealed powder was analyzed with XRD in order to distinguish the crystal structure of core/shell. In Figure 5, the XRD spectrum shows the peak of as-annealed $Nd_2Fe_{14}B$/CoFe forming core/shell

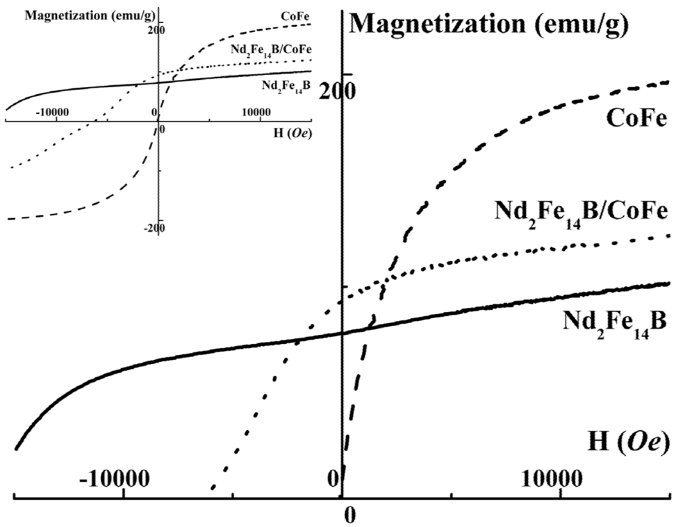

FIGURE 6 Magnetization curve of $Nd_2Fe_{14}B$/CoFe forming core/shell.

compared to that of CoFe (upper) and $Nd_2Fe_{14}B$ (lower). We can see that the material consists of the $Nd_2Fe_{14}B$ phase and CoFe phase, as the same of the result of TMA in Figure 4. Figure 6 shows the magnetization curve of $Nd_2Fe_{14}B$/CoFe forming core/shell to characterize magnetic properties at RT. M of magnetic nanoparticle have determined by using VSM with maximum applied field of 15 kOe. The values of M of $Nd_2Fe_{14}B$, CoFe nanoparticle, and $Nd_2Fe_{14}B$/CoFe forming core/shell were around 101 emu/g, 196 emu/g and 125 emu/g, respectively. The value of M_r and H_c of $Nd_2Fe_{14}B$/CoFe forming core/shell were 94 emu/g, and around 6.3 kOe. This results indicate that the values of M and M_r are increased but the value of H_c is reduced as amount of CoFe nanoparticle is increasing by exchange-coupling effect.

CONCLUSIONS

In our work, $Nd_2Fe_{14}B$/CoFe forming core/shell was prepared by high ball mill processing and chemical reduction. We can see that ball milled $Nd_{15}Fe_{77}B_8$ was surrounded with CoFe nanoparticle in FE-SEM images. In TMA curves and XRD spectrum, prepared $Nd_2Fe_{14}B$/CoFe with core/shell has $Nd_2Fe_{14}B$ phase and CoFe phase as hard and soft phases, respectively. In the magnetization curve of $Nd_2Fe_{14}B$/CoFe with core/shell because curves did not have kink, and M, M_r, and H_c of core/shell are increased to 125 emu/g, 94 emu/g, and 6.3 kOe, respectively, we can see that $Nd_2Fe_{14}B$/CoFe with core/shell prepared by high ball mill processing and coprecipitation method has exchage-coupling effect.

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