Magnetization and Intrinsic Coercivity for τ-phase Mn$_{54}$Al$_{46}$/α-phase Fe$_{65}$Co$_{35}$ Composite

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We have synthesized ferromagnetic τ-phase Mn$_{54}$Al$_{46}$/α-phase Fe$_{65}$Co$_{35}$ composite by annealing a mixture of paramagnetic ε-phase Mn$_{54}$Al$_{46}$ and ferromagnetic α-phase Fe$_{65}$Co$_{35}$ particles at 650 °C. The volume fraction ($f_h$) of hard τ-phase Mn$_{54}$Al$_{46}$ of the composite was varied from 0 to 1. During the annealing, magnetic phase transformation occurred from paramagnetic ε-phase to ferromagnetic τ-phase Mn$_{54}$Al$_{46}$. The magnetization and coercivity of the composite monotonically decreased and increased, respectively, as the $f_h$ increased. These results are in good agreement with our proposed composition dependent coercivity and modified magnetization equations.

Keywords: permanent magnet, magnetic composites, exchange coupling, Mn-Al, Fe-Co

1. Introduction

A figure of merit for permanent magnets is the maximum energy product ($BH_{\text{max}}$). The ($BH_{\text{max}}$) for Nd$_2$Fe$_{14}$B are theoretically 64 MGOe [1] and experimentally 56 MGOe [2]. However, a low operation temperature and limited availability of rare-earth (RE) elements are potential barriers [2]. However, a low operation temperature and limited availability of rare-earth (RE) elements are potential barriers [2]. Therefore, discovery of RE-free permanent magnets. Soft magnetic phase can be exchange coupled with hard magnetic phase within two times of domain wall thickness (2$\delta_d$) of hard magnetic phase [8]. The exchange coupling makes full use of high coercivity from hard phase and magnetization from soft phase. Therefore, it is possible to achieve large ($BH_{\text{max}}$) of the RE-free permanent magnet by the exchange coupling. Exchange coupled magnets based on hard magnetic phases of Fe-Pt [9-11], Sm-Co [12], and Nd$_2$Fe$_{14}$B [13], have been extensively studied. However, these exchange coupled magnets still contain RE or precious elements, and the exchange coupling effect is not noticeable in Nd$_2$Fe$_{14}$B because there is already a high magnetic moment.

In this paper, we report a unique annealing process synthesizing two-phase hard τ-phase Mn$_{54}$Al$_{46}$/soft α-phase Fe$_{65}$Co$_{35}$ composite magnets, and propose a simple composition dependent coercivity equation to explain experimental coercivity.

2. Experiments

Paramagnetic ε-phase Mn$_{54}$Al$_{46}$ particles were synthesized by gas-atomization. After having dissolved Fe- and Co-salts and dispersed the ε-phase Mn$_{54}$Al$_{46}$ particles in de-ionized water, a NaBH$_4$ solution was added to the solution. Thereby, Fe- and Co-salts were reduced to α-phase Fe$_{65}$Co$_{35}$ metal alloy particles. Then, ε-phase Mn$_{54}$Al$_{46}$/α-phase Fe$_{65}$Co$_{35}$ cakes (0 < $f_h$ < 1) were dried.
at 100 °C, and consequently, annealed at 650 °C for 1 hour under Ar environment. The \( f_h \) is the volume fraction of magnetically hard phase. Both \( \alpha \)-phase Fe\(_{65}\)Co\(_{35} \) (\( f_h = 0 \)) and \( \tau \)-phase Mn\(_{54}\)Al\(_{46} \) (\( f_h = 1 \)) particles were also prepared as reference materials.

The crystalline phases of the Fe\(_{65}\)Co\(_{35} \) and Mn\(_{54}\)Al\(_{46} \) particles and their composites were identified with X-ray diffraction (XRD). A vibrating sample magnetometer (VSM) was used to characterize their magnetic properties. The particle size and size distribution were determined using transmission electron microscopy (TEM) and scanning electron microscope (SEM). Also, we have performed elemental mappings on the composites with scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDS) to observe elemental distribution.

### 3. Results and Discussion

The gas-atomized Mn\(_{54}\)Al\(_{46} \) is paramagnetic \( \varepsilon \)-phase, and its shape is spherical (7-70 \( \mu \)m in diameter), while the as-synthesized Fe\(_{65}\)Co\(_{35} \) is ferromagnetic \( \alpha \)-phase spherical chain (40 nm in average diameter). These were confirmed by XRD, SEM, and TEM, which are not shown in this paper. We have synthesized \( \varepsilon \)-phase Mn\(_{54}\)Al\(_{46} \)/\( \alpha \)-phase Fe\(_{65}\)Co\(_{35} \) composites with various volume fractions of hard phase, i.e. \( f_h = 0.327, 0.500, 0.694, 0.773, \) and 0.819. As described in the experimental section, the synthesized composite was annealed at 650 °C to convert the paramagnetic \( \varepsilon \)-phase Mn\(_{54}\)Al\(_{46} \) to ferromagnetic \( \tau \)-phase Mn\(_{54}\)Al\(_{46} \). The prolonged annealing causes paramagnetic \( \beta \) or \( \gamma \)-phase Mn\(_{54}\)Al\(_{46} \) to nucleate. Therefore, we have optimized annealing time of one hour. Ferromagnetic \( \alpha \)-phase Fe\(_{65}\)Co\(_{35} \) (\( f_h = 0.000 \)) and paramagnetic \( \varepsilon \)-phase Mn\(_{54}\)Al\(_{46} \) (\( f_h = 1.000 \)) particles were annealed, separately, under the same annealing conditions as those used for annealing of \( \varepsilon \)-phase Mn\(_{54}\)Al\(_{46} \)/\( \alpha \)-phase Fe\(_{65}\)Co\(_{35} \) composites. This is because we wanted to compare magnetic properties of annealed single phase \( \tau \)-phase Mn\(_{54}\)Al\(_{46} \) and \( \alpha \)-phase Fe\(_{65}\)Co\(_{35} \) to those of \( \tau \)-phase Mn\(_{54}\)Al\(_{46} \)/\( \alpha \)-phase Fe\(_{65}\)Co\(_{35} \) composite.

Figure 1 shows elemental mapping image of ferromagnetic \( \tau \)-phase Mn\(_{54}\)Al\(_{46} \)/\( \alpha \)-phase Fe\(_{65}\)Co\(_{35} \) composite (\( f_h = 0.819 \)). It can be seen that Mn, Al, Fe, and Co elements are well distributed, and Fe and Co elements are more concentrated on the Mn\(_{54}\)Al\(_{46} \) particles’ surface than Mn and Al elements. This indicates that Mn\(_{54}\)Al\(_{46} \) particles are well covered with Fe\(_{65}\)Co\(_{35} \) particles during the reducing and annealing processes.

Figure 2 shows XRD patterns and magnetic hysteresis loops of the \( \tau \)-phase Mn\(_{54}\)Al\(_{46} \), \( \alpha \)-phase Fe\(_{65}\)Co\(_{35} \), and composite with \( f_h = 0.819 \). All the \( \tau \)-phase Mn\(_{54}\)Al\(_{46} \), \( \alpha \)-phase Fe\(_{65}\)Co\(_{35} \), and composite (\( f_h = 0.819 \)) are well crystallized. The \( \tau \)-phase Mn\(_{54}\)Al\(_{46} \) shows the saturation
magnetization of 53 emu/g and intrinsic coercivity ($H_{ci}$) of 3093 Oe, and $\alpha$-phase Fe$_{35}$Co$_{35}$ shows 131 emu/g and 75 Oe as shown in Fig. 2(b). It is noted that the magnetization of $\alpha$-phase Fe$_{35}$Co$_{35}$ powder is lower than 240 emu/g of its bulk value [14]. This is due to the thermal agitation of magnetization, slight oxidation of Fe$_{65}$Co$_{35}$ particle or incomplete reduction of Fe- and Co-salts. After converting a mixture of paramagnetic $\varepsilon$-phase Mn$_{54}$Al$_{46}$ and ferromagnetic $\alpha$-phase Fe$_{65}$Co$_{35}$ particles to ferromagnetic $\tau$-phase Mn$_{54}$Al$_{46}$/soft $\alpha$-phase Fe$_{65}$Co$_{35}$ composite ($f_h = 0.819$), the saturation magnetization increased to 69 emu/g from 53 emu/g in Fig. 2(b). On the other hand, the $H_{ci}$ decreased to 1926 Oe from 3093 Oe. No kink was observed from hysteresis loops of $\tau$-phase Mn$_{54}$Al$_{46}$/$\alpha$-phase Fe$_{65}$Co$_{35}$ composites with $0 \leq f_h \leq 1$. However, the remanent magnetization of the composite was lower than that of the hard phase. The exchange coupling between hard and soft phases occurs only if the thickness of soft phase is thinner than two times of the hard phase’s domain wall thickness ($2\delta_h$) [8]. The experimental $\delta_h$ of Mn-Al is 15 nm [15]. The diameter of the synthesized $\alpha$-phase Fe$_{65}$Co$_{35}$ particle is 40 nm in average, which is greater than $2\delta_h$ (30 nm) of $\tau$-phase Mn$_{54}$Al$_{46}$. Therefore, it can be assumed that the soft $\alpha$-phase Fe$_{65}$Co$_{35}$ particles are partially involved in exchange coupling.

Figure 3(a) and (b) show $f_h$ dependence of magnetization $\sigma(f_h)$ and intrinsic coercivity $H_{ci}(f_h)$ for ferromagnetic $\tau$-phase Mn$_{54}$Al$_{46}$/$\alpha$-phase Fe$_{65}$Co$_{35}$ composites. The magnetization monotonically decreases as the $f_h$ increases, while the intrinsic coercivity increases. We now analyze $\sigma(f_h)$ and $H_{ci}(f_h)$ for ferromagnetic $\tau$-phase Mn$_{54}$Al$_{46}$/$\alpha$-phase Fe$_{65}$Co$_{35}$ composites. According to theoretical studies on two-phase composite magnet, the saturation magnetization [8] and anisotropy constant [16] of composite can be expressed as:

$$\sigma = \frac{\sigma_h \rho_h f_h + \sigma_s \rho_s f_s}{\rho_h f_h + \rho_s f_s}$$  \hspace{1cm} (1)$$

$$K = (1 - f_h)K_s + f_h K_h,$$  \hspace{1cm} (2)

where $\sigma$ is the saturation magnetization, $K$ is the magnetocrystalline anisotropy constant, and $\rho$ is the density, $h$ and $s$ in the subscript denote hard and soft phase, respectively. Because of the experimental difficulty of obtaining $K$, we have developed an expression for $H_{ci}$ of two-phase magnetic composite using experimentally accessible $H_{ci}$ for both hard and soft phases. $H_{ci}$ due to magnetocrystalline anisotropy [17] is

$$H_{ci} = \frac{\alpha K}{\sigma \rho},$$  \hspace{1cm} (3)

where $\alpha$ is a constant depending on the crystal structure and degree of alignment. For aligned particles, $\alpha$ is 2; for unaligned (random) particles, $\alpha$ is 0.64 for cubic crystals and 0.96 for uniaxial crystals. Then, $H_{ci}$ of the two-phase magnetic composite can be modified to equation (4) by combining Eqs. (2) and (3):

$$H_{ci} = \frac{(1 - f_h)K_s + f_h K_h}{(1 - f_h)\sigma \rho_s + f_h \sigma \rho_h}.$$  \hspace{1cm} (4)

By replacing $K$ in Eq. (4) with $H_{ci}$ in Eqs. (3), Eq. (4) becomes Eq. (5).

$$H_{ci} = \frac{\sigma_h \rho_h H_s(1 - f_h) + \sigma_s \rho_s H_h f_h}{\sigma_h \rho_h (1 - f_h) + \sigma_s \rho_s f_h}.$$  \hspace{1cm} (5)

Equation (5) suggests that the coercivity of a composite
can be estimated by experimental \( H_{ci} \) of hard and soft phase materials instead of \( K \) of each material.

The \( \sigma \) and \( H_{ci} \) of single phase \( \tau \)-phase Mn\(_{54}\)Al\(_{46} \) (\( \sigma_\theta = 53 \) emu/g and \( H_\theta = 3093 \) Oe) and \( \alpha \)-phase Fe\(_{65}\)Co\(_{35} \) (\( \sigma_\alpha = 131 \) emu/g and \( H_\alpha = 75 \) Oe) were used as input parameters in Eqs. (1) and (5) to calculate \( \sigma(f_\theta) \) and \( H_{ci}(f_\theta) \). The calculated \( \sigma(f_\theta) \) and \( H_{ci}(f_\theta) \) are shown in Fig. 3, and are in good agreement with the experimental results. Therefore, our developed coercivity equation, i.e. Eq. (5), serves as guidance to predict \( H_{ci} \) for two-phase magnetic composite.

4. Conclusion

Ferromagnetic \( \tau \)-phase Mn\(_{54}\)Al\(_{46} \) (\( f_\theta = 1.000 \)), \( \alpha \)-phase Fe\(_{65}\)Co\(_{35} \) (\( f_\alpha = 0.000 \)), and \( \tau \)-phase Mn\(_{54}\)Al\(_{46}/\alpha \)-phase Fe\(_{65}\)Co\(_{35} \) composites (\( 0 < f_\theta < 1 \)) were synthesized. The magnetization and intrinsic coercivity of single phase \( \tau \)-phase Mn\(_{54}\)Al\(_{46} \) were 53 emu/g and 3090 Oe, and those of single phase \( \alpha \)-phase Fe\(_{65}\)Co\(_{35} \) were 131 emu/g and 75 Oe, respectively. The magnetization and intrinsic coercivity of two-phase magnetic composite monotonically decreased and increased, respectively, as the \( f_\theta \) increased. The experimental intrinsic coercivity and magnetization of the composite with various \( f_\theta \) are in good agreement with the proposed coercivity and modified magnetization equations, respectively.

References