Coercivity of Pulverized ThMn_{12} Compounds with a Limited Amount of α -(Fe,Co) Phase

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We newly prepared the ThMn_{12} compounds $(\text{Sm}_{0.9}\text{Zr}_{0.1})(\text{Fe}_{0.8}\text{Co}_{0.2})_{11.3}\text{Ti}_{0.7}$ (A) and $(\text{Nd}_{0.8}\text{Zr}_{0.2})(\text{Fe}_{0.9}\text{Co}_{0.1})_{11.3}\text{Ti}_{0.7}\text{N}_{1.5}$ (B), which were almost α -(Fe,Co) phase-free. These compounds show magnetic properties superior to those of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase in the high-temperature region (473 K). We also prepared a typical α -(Fe,Co) phase-free compound, $\text{Nd}(\text{Fe}_{0.8}\text{Co}_{0.2})_{11}\text{MoN}_{1.3}$ (C), which has a low saturation polarization, but a high magnetic anisotropy field, and better thermal stability. We examined the effect of pulverization on the coercivity (H_c) of compounds (A)–(C). The critical radii of single-domain particles (R_c) were about 120 nm for (A) and (B), and about 400 nm for (C), and were determined from the measured magnetic domain widths of the most coercive pulverized particles of each sample. As the pulverization time increased, H_c increased to maximum values of 0.10 MA m^{-1} for (A), 0.14 MA m^{-1} for nitrogenated (B), and 0.21 MA m^{-1} for nitrogenated (C). Further pulverization of the samples decreased H_c . The decrease was mainly caused by oxidation in non-nitrogenated (A) and by the accumulation of lattice distortion in (B) and (C). [doi:10.2320/matertrans.M2019038]

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1. Introduction

Magnetic materials with a ThMn_{12} (1–12) structure have attracted interest because of the high Fe concentration in the unit cell, which means that the saturation polarization of these materials is higher than that of 1–5, 1–7, and 2–17 compounds. The ternary and plural alloys of related R-(Fe,Co)-transition metal (TM) (R = Nd, Sm; TM = Ti, Mo, V, Si) structures have been investigated as candidate compounds for permanent magnet materials.^{1,2)} The 1–12 structures require the TM for stability;^{1,2)} therefore, the 1–12 compounds investigated in earlier studies have had compositions of $\text{R}(\text{Fe,Co})_{12-x}\text{TM}_x$ ($x > 1.0$).

In our previous studies, we investigated elemental substitution, including substituting Co into Fe sites and Zr into R sites, in 1–12 compounds based on the atomic size.^{3–7)} We found that the structure can be stabilized even when the Ti content is less than that in earlier studies, such as $\text{-Ti}_{0.5}$. We showed that the nitrogenated compound with R = Nd, $(\text{Nd}_{0.7}\text{Zr}_{0.3})(\text{Fe}_{0.75}\text{Co}_{0.25})_{11.5}\text{Ti}_{0.5}\text{N}_{1.3}$, had good magnetic properties with saturation polarization (J_s) of 1.67 T (excluding α -(Fe,Co) phase contribution) and magnetic anisotropy field (H_a) of 5.25 MA m^{-1} at room temperature.³⁾ The Dy-free and N-free R = Sm alloy, $(\text{Sm}_{0.8}\text{Zr}_{0.2})(\text{Fe}_{0.75}\text{Co}_{0.25})_{11.5}\text{Ti}_{0.5}$, also had $J_s = 1.58 \text{ T}$ and $H_a = 5.90 \text{ MA m}^{-1}$ at room temperature.⁸⁾ The values for the Sm alloy were still $J_s = 1.50 \text{ T}$ and $H_a = 3.70 \text{ MA m}^{-1}$ at 473 K, which were higher than those of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase at this temperature.^{8–10)}

In the samples in our previous studies, the α -(Fe,Co) phase content of $(\text{Nd}_{0.7}\text{Zr}_{0.3})(\text{Fe}_{0.75}\text{Co}_{0.25})_{11.5}\text{Ti}_{0.5}\text{N}_{1.3}$ was comparatively high at about 16.7 vol%.³⁾ It is expected that

eliminating the contribution of the α -(Fe,Co) phase from the main 1–12 phase sample will provide better magnetic properties for permanent magnet materials. In this study, we more precisely optimized the Ti, Zr, and Co contents in the compounds ($\text{-Ti}_{0.7}$ for R = Sm and Nd compounds) and prepared almost α -(Fe,Co) phase-free 1–12 compounds. The magnetic properties of these compounds (R = Sm and Nd) are nearly the same as or slightly better than those of the $\text{-Ti}_{0.5}$ compounds in our previous studies. We also prepared the nitrogenated α -(Fe,Co) phase-free alloy, $\text{Nd}(\text{Fe}_{0.8}\text{Co}_{0.2})_{11}\text{MoN}_{1.3}$, as a reference sample typical of earlier studies, which has good thermal stability up to about 1000 K and comparatively high H_a , even though J_s was slightly lower than the compounds with TM = $\text{Ti}_{0.5}$ and $\text{Ti}_{0.7}$, and R = Sm.¹¹⁾ We prepared pulverized powders of the α -(Fe,Co) phase-free compounds with $\text{-Ti}_{0.7}$ by ball-milling and examined the appearance of high coercivity with single-domain particle sizes (R_c). We also analyzed the origins of the reduction of H_c in the samples with a longer pulverization time after the appearance of the maximum H_c values.

2. Experimental Methods and Results

2.1 Sample preparation

The strip-cast method was used to prepare the starting alloy. These alloys were annealed in an Ar atmosphere at 1373 K for 4 h, and the homogeneous elemental distributions in the samples were confirmed by electron probe micro-analyzer (EPMA-1720H, Shimadzu Co. Ltd., Japan). The samples were pulverized by a cutter mill, and the particles were classified as $<32 \mu\text{m}$ for samples (A) and (C) and $<20 \mu\text{m}$ for sample (B). The following three alloys with a ThMn_{12} structure without the precipitation of the α -(Fe,Co) phase were prepared with the method described above: (A) $(\text{Sm}_{0.9}\text{Zr}_{0.1})(\text{Fe}_{0.8}\text{Co}_{0.2})_{11.3}\text{Ti}_{0.7}$, (B-st) $(\text{Nd}_{0.8}\text{Zr}_{0.2})(\text{Fe}_{0.9}\text{Co}_{0.1})_{11.3}\text{Ti}_{0.7}$, and (C-st) $\text{Nd}(\text{Fe}_{0.8}\text{Co}_{0.2})_{11}\text{Mo}$.

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Table 1 Sample compositions (a) and the precipitated α -(Fe,Co) phase (vol%), magnetic properties, and $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase at room temperature (b).

(a)				
Sample	Composition formula			
(A)	$(\text{Sm}_{0.9}\text{Zr}_{0.1})(\text{Fe}_{0.8}\text{Co}_{0.2})_{11.3}\text{Ti}_{0.7}$			
(B)	$(\text{Nd}_{0.8}\text{Zr}_{0.2})(\text{Fe}_{0.9}\text{Co}_{0.1})_{11.3}\text{Ti}_{0.7}\text{N}_{1.5}$			
(C)	$\text{Nd}(\text{Fe}_{0.8}\text{Co}_{0.2})_{11}\text{MoN}_{1.3}$			
(b)				
	Sample			
	(A)	(B)	(C)	$\text{Nd}_2\text{Fe}_{14}\text{B}^{(6,7)}$
Saturation polarization				
J_s / T	1.56	1.72	1.41	1.61
M_s / emug^{-1}	161	182	138	-
Magnetic anisotropy				
H_a / MAM^{-1}	7.7	9.0	9.1	6.1
Curie point				
T_C / K	973	953	1008	585
$\alpha(\text{Fe,Co}) / \text{vol \%}$	1.2	2.7	0.0	-

The $<32 \mu\text{m}$ powder of the $(\text{Sm}_{0.9}\text{Zr}_{0.1})(\text{Fe}_{0.8}\text{Co}_{0.2})_{11.3}\text{Ti}_{0.7}$ compound is referred to as sample (A). The R = Nd compounds were nitrogenated further. Sample (B-st) (-Ti_{0.7} compound) powder ($<20 \mu\text{m}$) was nitrided at 673 K for 24 h in an N_2 - H_2 mixed gas atmosphere to obtain sample (B). Sample (C-st) (-Mo compound) powder ($<32 \mu\text{m}$) was also nitrogenated at 873 K for 4 h in an N_2 gas atmosphere to obtain sample (C). The nitrogenation conditions for each sample were optimized in preliminary experiments. The N content in the treated samples was calculated from the weight gain after nitrogenation, and the final sample compositions are shown in Table 1(a).

2.2 Magnetic properties of starting compounds

Because the starting particles of 1–12 compounds in this study were composed of primary particles several micrometers in diameter and secondary particles 20–30 μm in diameter, the samples were magnetically isotropic.^{3,11} Therefore, the law of approach to ferromagnetic saturation (LAFS)^{12–17} was used to measure the magnetic properties based on eq. (1), and J_s and H_a of the samples were determined.

$$J = J_s(1 - b/H^2 + \dots) + \chi_0 \quad (1)$$

Fig. 1 XRD patterns of the samples, including non-nitrogenated starting powders.

Here, b is $1/15H_a^2$. The magnetization curves of the isotropic sample powders were measured up to a high magnetic field of 7.2–11.9 MAm^{-1} . The Curie temperature (T_c) was estimated from the thermal demagnetization curve measured under an applied field of 11.9 MAm^{-1} up to 870 K.

The magnetic properties of the samples were measured with vibrating sample magnetometers (5T-VSM, Shizuoka Institute of Science and Technology, TOEI Industry Co. Ltd., Japan and 15T-VSM High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University). The samples generally had higher magnetic properties than the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase (Table 1(b)). That is, these samples may be more suitable for magnets used at higher temperatures, such as $>473 \text{ K}$,^{3,8} than Nd-Fe-B magnets.^{10,18,19}

Figure 1 shows the XRD patterns (SmartLab, Rigaku Co. Ltd., Japan) of the samples, including the non-nitrogenated starting powders. The X-ray source was Cu-K α for the measurements. The XRD pattern of $\text{SmFe}_{11}\text{Ti}$ (ICDD No. 03-065-5363) is shown at the bottom of Fig. 1 with diffraction peaks displayed as vertical lines. $\text{SmFe}_{11}\text{Ti}$ is the standard compound for sample (A). $\text{NdFe}_{11}\text{Ti}$ and $\text{NdFe}_{10}\text{Mo}_2$, which were standard compounds for samples (B) and (C), respectively, showed XRD patterns similar to that of $\text{SmFe}_{11}\text{Ti}$, except for slight differences in diffraction angles and peak intensities. The amount of the α -(Fe,Co) phase was calculated from the intensity ratio of the main diffraction peak of the α -(Fe,Co) phase at $2\theta \approx 44.5^\circ$ (Cu-K α) to the strongest peak of the 1–12 phase of (321) ($2\theta \approx 42.3^\circ$)³ and is shown in Table 1(b).

Because the peak shift to the lower angle originated from the lattice expansion caused by nitrogenation, the (330) peak in the nitrogenated samples overlapped with the main peak of the α -(Fe,Co) phase at $2\theta \approx 44.5^\circ$. Therefore, it was difficult to evaluate the amount of precipitated α -(Fe,Co) phase

accurately. The electron backscatter diffraction (JSM-7000F, JEOL, Japan) analysis³⁾ revealed that the amount of the $\alpha\text{-(Fe,Co)}$ phase in the nitrogenated samples was the same as that in the non-nitrogenated starting powders; thus, the amount of precipitated $\alpha\text{-(Fe,Co)}$ phase in each sample was small, and the maximum amount was estimated to be about 2.7 vol% in sample (B) (Table 1(b)).

2.3 Preparation of fine particles

The sample powders were pulverized by ball-milling. The sample powder (~ 1 g) was added to a glass bottle of $\varnothing 40\text{ mm} \times 75\text{ mm}$ containing stainless steel balls ($\varnothing 3\text{ mm}$) occupying about 1/3 of the bottle volume, and the bottle was filled with cyclohexane. Ball-milling (ANZ-505, Nitto Kagaku Co., Ltd., Japan) was performed at a rotational speed of 180–300 rpm for 0–48 h. The milled sample was dried in a glass laboratory dish, and collected after volatilization of cyclohexane in a glove box (Ar atmosphere).

2.4 Particle sizes of pulverized particles

Figure 2 shows scanning electron microscope (SEM; JSM-5610LV, JEOL, Japan) images of particles of sample (A) obtained after different milling times (0, 12, and 30 h). Because the particles in samples (B) and (C) looked similar, only the images for sample (A) are shown as a representative example. Particle sizes of about 3 and 1 μm were observed for the powders milled for 12 and 30 h, respectively.

Figure 3 shows the effect of milling time on the average particle sizes. The particle size was calculated from the polished surface of about 50 powder particles in each sample, and the average value was taken as the average particle diameter. The above average particle diameters were expected to be slightly smaller than the actual diameters because the average diameters were calculated based on the polished surface images of the particles. The average particle diameter was about 20 μm before milling, decreased to about 1.5 μm after a milling time of 30 h, and remained the same after a milling time of 48 h.

2.5 Magnetic properties of milled powders

Figure 4(a) shows the magnetization curves of the sample powders after different milling times (0, 12, 30, and 48 h). Sample densities are calculated using lattice constants of each sample. The shapes of the magnetization curves were changed by milling. The polarization (J) under the maximum applied field of 7.2 MA m^{-1} decreased after long milling times of 30 and 48 h, and the polarizations were almost saturated under high applied fields in those samples. Therefore, J_s and H_a decreased as milling time increased. Using the LAFS (eq. (1)), the magnetic properties were measured from the magnetization curves shown in Fig. 4(a). Figures 4(b) and (c) show that J_s and H_a in all samples decreased as pulverization progressed.

The coercivity of the samples was measured from the hysteresis curves in which the maximum applied magnetic field was 4 MA m^{-1} . Figure 5(a) shows the magnetization curves of non-milled and milled samples of sample (A). The full-magnetization curves of all samples were similar, except for the magnetization value. In Fig. 5(b), the second quadrants of the demagnetization curves are enlarged.

(a) Starting powder

— 5 μm

(b) Milling time 12 h

— 5 μm

(c) Milling time 30 h

— 5 μm

Fig. 2 SEM images of particles of sample (A) after milling times of 0 (a), 12 (b), and 30 h (c).

Sample densities are calculated using lattice constants of each sample. The H_a values of the starting samples were 7.7, 9.0, and 9.1 MA m^{-1} (Table 1(b)) for samples (A)–(C), respectively, but there were large differences in the H_c values.

Fig. 3 Variation of particle size with milling time (0–48 h).

Figure 6(a) shows the variation of coercivity with milling time, and the relationship between the coercivity and the particle size is shown in Fig. 6(b). The H_c of samples for different milling times reached maximum values of 0.10 MA m^{-1} for sample (A) (12 h), 0.14 MA m^{-1} for sample (B) (30 h), and 0.21 MA m^{-1} for sample (C) (30 h). Every sample reached maximum H_c ($H_{c\text{-max}}$) at a particle size of about $2 \mu\text{m}$. These results revealed that H_c of each sample increased as the powder particle size decreased, but after the particle size reached about $2 \mu\text{m}$, H_c decreased with further milling.

It is important to explain the appearance of the $H_{c\text{-max}}$ in each sample and the differences in $H_{c\text{-max}}$ between the samples despite the similar particle sizes of about $2 \mu\text{m}$. The reason for this will be discussed in the following sections.

2.6 Detailed analyses of powder samples

2.6.1 Effect of pulverization on magnetic domain structure

To consider the mechanism of the appearance of coercivity in the samples in this study, it is important to confirm whether

Fig. 4 Magnetization curves (a), J_s (b), and H_a (c) of samples for milling times of 0, 12, 30, and 48 h.

Fig. 5 Magnetization curves of non-milled and milled samples of sample (A) (a) and the second quadrant of the demagnetization curves of the samples (b).

single-domain particles were prepared by pulverizing the samples. Therefore, the magnetic domain structure of the milled powder of maximum coercivity ($H_c\text{-max}$) was examined for each sample.

Figure 7 shows the SEM images and the magnetic domain structures obtained by magnetic-force microscopy (MFM) of non-milled ((a) and (b)) and milled sample (A) (milling time of 12 h, (c) and (d)) in the thermally demagnetized state. The magnetic domain structure was observed by MFM (Nano Navi II/E-sweep, Hitachi High-Tech Science, Japan). The image of sample (A) is shown as a representative example, but the image analysis method was the same for all samples.

In the figure, the non-milled samples with a particle diameter (D) of about $15 \mu\text{m}$ had a magnetic domain width (d) of about $1.3 \mu\text{m}$ (Fig. 7(b)). However, the milled sample (12 h) with D of about $2 \mu\text{m}$ (Fig. 7(c)) had d of about $0.2 \mu\text{m}$ (Fig. 7(e)). These results showed that d decreased with the particle diameter, and clarified the magnetic domain structure of the milled powder of the $H_c\text{-max}$ sample (Figs. 7(c)–(e)). In the thermally demagnetized state, the powders were in a multi-domain state (Fig. 7). The coercivity of the sample reached 0.13MAm^{-1} after magnetization in a field of 4MAm^{-1} . Therefore, we estimated that applying a

Fig. 6 Variation of H_c with milling time (0–48 h) (a) and variation of H_c with particle size (b).

4MAm^{-1} field converted the multi-domain particles in the milled powder to single-domain particles, resulting in the measured H_c .

The critical single-domain size, R_c , was calculated with the following calculation method based on the domain structure observations.²⁰⁾ Initially, the domain wall energy (γ) of the sample can be determined using the following equation.

$$\gamma = (J_s^2 / 9\mu_0 D) d^2 \quad (2)$$

Here, J_s is the saturated polarization (experimental value) and μ_0 is the vacuum permeability ($4\pi \times 10^{-7} \text{Hm}^{-1}$). The experimental values of d^2 and D give the domain wall energy as the average value for the particles. The value of D and the magnetic domain width in the magnetic domain structure on the c -plane were measured with the MFM images.

For each sample, 10–15 particles of different diameters and around 50 domain widths in the particles were measured. It is important to measure the domain widths on the c -plane of the particles; thus, we carefully selected the candidate particles (at least 10–15 particles) for measuring the pattern of the domain structure in each particle. The parallel stripes on the c -plane were ideal for these observations. The details of the

Fig. 7 SEM images and magnetic domain structures obtained by MFM in non-milled (a) and (b), and milled sample (A) (milling time of 12 h) (c), (d), and (e).

method for determining the domain wall energy and the critical size of the single-domain sizes of the samples in this study are reported in Ref. 21). The domain wall energies were 6.6, 6.9, and 20 mJm^{-2} for samples (A), (B), and (C), respectively. In connection to this, the energy (γ) in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ sintered magnet was reported as 25 mJm^{-2} .

The critical radius for a single-domain particle, R_c , can be obtained from eq. (3) by using these domain wall energies.²⁰⁾

$$R_c = 18\mu_0\gamma/J_s^2 \quad (3)$$

The values of R_c were about 120, 120, and 400 nm for samples (A), (B), and (C), respectively. The R_c values of samples (A) and (B) were close to that of Nd-Fe-B magnets, whereas that of sample (C) was about 4 times larger. In addition, the critical size for single-domain particles of the Mo compound (sample (C)) was much larger than those of the other samples. The values are all for the pulverized

Fig. 8 Variation of H_c with oxygen content in the milled samples (0–48 h).

particles in which J_s and H_a were both decreased by oxidation and lowering of the crystallinity (ref. Fig. 4).

The R_c measurements were consistent with the results in Fig. 6. It should be easiest to prepare the single-domain particles in sample (C) by ball-milling because it has the largest R_c of 400 nm. The observed coercivity (H_c -max) was the largest in sample (C), even though the absolute values were small.

2.6.2 Effect of oxidation during pulverization on coercivity

The particles in the single-domain state prepared by pulverization were expected to show the H_c -max. For sample (A), the average particle size for a milling time of 12 h was 2–3 μm (Fig. 2), and the maximum coercivity was 0.10 MAm^{-1} . However, in the sample milled for 30 h, the coercivity decreased, even though the particle size decreased to about 1 μm . Therefore, decreasing the particle size does not always increase the coercivity.

The samples with smaller particle sizes should contain a higher volume fraction of single-domain particles, even though J_s and H_a decreased with the milling time (Fig. 4). We speculated that the pulverized particles were oxidized by residual oxygen in the cyclohexane used for the ball-milling and by atmospheric oxygen during the sample preparation for measurements, and this degraded the magnetic properties. Thus, the oxygen content in the milled samples was measured by gas analysis (M-101QA-TDM, Canon Anelva Corp., Japan).

Figure 8 shows the relationship between the oxygen contents measured by gas analysis and H_c in the milled samples (Fig. 6). For the H_c -max samples, the oxygen content was 1.5 wt% for sample (A), whereas it was 3.0–4.0 wt% for samples (B) and (C). The oxygen content in the H_c -max samples was in the order sample (A) < sample (B) < sample (C).

For sample (A), the oxygen content of the particles milled for 30 h was about 4.0 wt%, which was higher than that of the H_c -max sample (~ 1.5 wt%). H_c of the particles milled for 30 h decreased to near of that of the non-milled powder, even

when the average particle size was decreased to half ($\sim 1.5 \mu\text{m}$) of that of the particles milled for 3 h of $\sim 3.0 \mu\text{m}$ (Fig. 6(b)). The thermal stability of sample (A) was studied in our previous paper,²² and sample (A) was more easily oxidized than samples (B) and (C) in this study. Therefore, at least for sample (A), the oxidation played an important role in the decrease in H_c .

The increases in the oxygen content ($\Delta W(\text{oxy.})$) from the H_c -max particles (30 h milling time) to the particles milled for 48 h that decreased H_c by half (Fig. 8) were only 1.0 wt% for sample (B) and 0.2 wt% for sample (C). The abrupt decrease in H_c in the samples without a substantial increase in oxygen content is therefore not fully explained by the oxidation of sample particles.

2.6.3 Effect of pulverization on the crystallinity

The XRD patterns of the samples with different milling times were measured to determine whether lattice distortion occurred during ball milling due to mechanical stress (Fig. 9). The XRD peak broadening in the samples with long milling times originated from the lattice distortion and the decrease in crystallite size. The lattice distortion is reflected in the crystallinity of the particles, and the crystallite size corresponds to the size of a perfect single-crystal region.

Initially, the full-widths at half-maximum (FWHMs) of each XRD peak for each milling time were measured. Figure 9 shows the XRD patterns of non-milled (0 h) and milled samples (12, 30, and 48 h for samples (B) and (C)) on the left-hand side, and the enlarged (301) peak in the samples as an example on the right-hand side. The peak is independent from other peaks and has a sufficient intensity for the analysis, even in the milled samples.

The following Williamson-Hall method (eq. (4)) and the Scherrer equation (eq. (5)) were applied to the measured values.

$$\beta \cos \theta = \lambda / D + 2\eta \sin \theta \quad (4)$$

$$D_{\text{hkl}} = K\lambda / \beta \cos \theta \quad (5)$$

In eq. (4), θ is the XRD angle, β is the FWHM of each peak, and λ is the X-ray wavelength (Cu-K α ; 0.154 nm). The inhomogeneous distortion (η) and the crystallite diameter (D) are important terms. In eq. (5), K is the Scherrer constant (~ 0.94).

For the accurate measurement of the FWHM, the following processing was applied to each peak. On the higher-angle side of each XRD peak, there is a shoulder from the Cu-K α_2 radiation (Fig. 9, right-hand side). Therefore, the half (angle) width from the center of the peak to the edge of the lower angle side of the peak was measured first, and the width was doubled to give the FWHM of the peak (β in eqs. (4) and (5)). The FWHMs of almost all the diffraction peaks could be measured in the non-milled starting powders (0 h patterns in Fig. 9). However, the only two clear peaks were (301) and (310) in the milled samples. These peaks were analyzed with eqs. (4) and (5).

Figure 10 shows the Williamson-Hall plots using eq. (4) of the non-milled samples. The $\beta \cos \theta$ values on the vertical axis of non-milled samples (A) and (C) were similar, and the crystallite diameters (D) calculated from Scherrer eq. (5) were 90.4 and 114.6 nm for samples (A) and (C), respectively. In contrast, the values for non-milled sample

Fig. 9 XRD patterns of the samples at each milling time.

(B) were distributed, and D was estimated to be 55.2 nm. This D value was calculated as an average value of $\beta \cos \theta$ for all observed peaks.

In eq. (4), when the values of $\beta \cos \theta$ for $\sin \theta$ are constant, as in samples (A) and (C) in Fig. 10, the lattice distortion plays a minor role in the state of crystal lattice, and $\eta \approx 0$. In contrast, when the $\beta \cos \theta$ values vary with the $\sin \theta$ values, as in sample (B), $\eta > 0$, the lattice distortion must be considered.

If we compare the nitrogenated samples (B) and (C) (Fig. 1), the XRD peaks of the ThMn₁₂ structure in non-milled sample (C) were sharp and clearly separated. However, those for non-milled sample (B) were blurred and the FWHMs were wide. Therefore, based on our

Fig. 10 Williamson-Hall analysis for the non-milled samples.

Fig. 11 Dependence of crystallite diameter (\$D\$) on particle size.

experimental observations above, sample (C) with $\text{-N}_{1.3}$ should be a more stable nitrogenated compound than sample (B) with $\text{-N}_{1.5}$.

This difference in XRD patterns was consistent with the D values in Fig. 10, where D is 115 and 55 nm for samples (C) and (B), respectively. The crystallite size in eqs. (4) and (5) for sample (C) was double that for sample (B); thus, the crystallinity of sample (C) was estimated to be higher than that of sample (B).

Figure 11 shows the dependence of D on the particle size. In sample (B), the D value was already about 50 nm, even in the particles with an average size of 17 μm , and was almost the same in the 3 μm particles (Fig. 3). The value decreased slightly to about 40 nm in the finer particles. In contrast, in samples (A) and (C), the D values decreased from those in the starting non-milled samples of 90.4 and 114.6 nm, respectively, to about 40 nm for sample (A) and 20 nm for sample (C). Furthermore, when the particles sizes decreased more than the H_c -max samples, for example in sample (A), from the sample milled for 12 h to that milled for 30 h (Fig. 6), D increased slightly. This behavior was also observed in samples (B) and (C). These results were explained as follows.

Solving eq. (4) for D gives a negative term including lattice distortion (η) in the denominator, as shown in eq. (6).

$$D = \lambda / (\beta \cos \theta - 2\eta \sin \theta) \quad (6)$$

The value of D calculated using eq. (6) should be larger than that when only the $\lambda / \beta \cos \theta$ term is considered, because of the decrease in the denominator. Therefore, the slight increase in D with the pulverization in Fig. 11 in the minimum grain sizes samples should indicate the accumulation of lattice distortion (appearance of $2\eta \sin \theta$ term in eq. (6)). The increase in lattice distortion means the increase of defects in the structure. Therefore, the magnetic polarization and anisotropy of the sample should be partially degraded by the distortion.

3. Discussion

3.1 Coercivity generation by pulverizing particles

Because H_c of each sample reached the maximum value after a certain milling time, we initially discuss the cause of the increase of H_c by pulverization.

The coercivity is defined as the applied magnetic field necessary for reversing the magnetization, and some magnetization reversal mechanisms have been proposed. The simplest mechanism is the Stoner-Wohlfarth model,^{23,24)} in which the value of H_c for generating magnetization reversal, namely the coercivity, is expressed by the following equation.²⁴⁾

$$H_c = 2K_u / J_s \quad (7)$$

Here, K_u is the uniaxial magnetic anisotropy constant. The model assumes that the sample is a single-domain particle and that the magnetic field is applied in the opposite direction to the magnetic anisotropy (N-S poles) direction of the specimen, which is the c -axis. In the model, the theoretical coercivity is $2K_u / J_s$, namely, the magnetic anisotropy field (H_a) of the sample. Based on eq. (7), single-domain particles of rare earth compounds with high K_u should show high coercivity. H_c -max samples (A)–(C) still had high H_a values of 5.0, 4.8, and 6.0 MAm^{-1} , respectively (Fig. 4), and were expected to show high coercivities of nearly or more than 5.0 MAm^{-1} after pulverization to single-domain particles. However, H_c in these samples was only about 2–3% of the expected value (Fig. 6(a)). The particle sizes of the H_c -max samples were about 2 μm (Fig. 6(b)), which was sufficiently small to be single-domain particles after magnetization. (ref. Fig. 8)

3.2 Origins of decrease in coercivity

Kronmüller²⁵⁾ and Sugimoto and Kato²⁶⁾ expressed the coercivity of a permanent magnet, such as a Nd-Fe-B magnet, as

$$H_c = \alpha(2K_u / J_s) - N_{\text{eff}}(J_s / \mu_0) \quad (8)$$

where α and N_{eff} are the various factors that represent H_c in actual permanent magnets. They showed that this equation can be phenomenologically applied to both nucleation and pinning magnets. The α factor should be decreased by the existence of inhomogeneous magnetic regions in the sample. The N_{eff} factor initially shows variation in the local

demagnetization field in the sample, and simply corresponds to the shape of the local unit, such as edges or corners, in the samples. Depending on these factors, the α and N_{eff} coefficients should be changed and H_c should become lower than H_a .

We revealed that the observed coercivities in the H_c -max samples were only about 2–3% of the anisotropy fields ($H_a = 2K_u/J_s$). The particle sizes of the samples were 1.5–2.0 μm (Fig. 6(b)), and R_c was about 120 nm for samples (A) and (B) and about 400 nm for sample (C) (see Section 2.6.1). In contrast, the crystallite sizes that corresponded to single crystals were about 100 nm for samples (A) and (C), and 55 nm for sample (B) in non-milled samples. Therefore, the H_c -max samples were pulverized secondary (isotropic) particles 1.5–2.0 μm in size, consisting of agglomerated single-domain grains (Fig. 7). Therefore, the particle size did not explain the decrease in anisotropy field.

The contribution of the second term ($N_{\text{eff}}(J_s/\mu_0)$) for H_c should physically correspond to the oxidation of samples, as discussed in Section 2.6.2, and also to the changing of crystallite sizes and lattice distortion, as discussed in Section 2.6.3. Oxidation deteriorated the coercivity, especially in sample (A) ($R = \text{Sm}$). The oxidation reaction mainly forms Sm and Zr oxides on the surface of the particles.²⁷⁾ The reaction changes the local demagnetizing field by forming oxides and precipitating Fe- and Ti-containing phases, and the change corresponds exactly to the second term in eq. (8).

The anisotropy fields are affected by changes in crystallite sizes and lattice distortion. The disordering of the lattice should reduce H_a of the samples. Therefore, the first term of eq. (8) should become small with the decrease of crystallite sizes and the appearance of lattice distortion (ref. Fig. 11). Those changes may also increase the local demagnetization field, expressed by the second term in eq. (8). The physical separation of these phenomena mentioned above is difficult at present stage of research.

4. Conclusion

The almost α -(Fe,Co) phase-free ThMn₁₂ samples (A)–(C) in this study have magnetic properties superior to those of the Nd₂Fe₁₄B phase in the high-temperature region (about 500 K). The pulverized samples showed maximum coercivities of 0.10 MA m⁻¹ for sample (A), 0.14 MA m⁻¹ for sample (B), and 0.21 MA m⁻¹ for sample (C). However, H_c decreased as the milling time increased.

The magnetic critical radius of single-domain particle (R_c) was determined from the observed magnetic domain widths, from which the domain wall energies of the samples were calculated. R_c was 120 nm for samples (A) and (B), and 400 nm for sample (C). The results suggested that sample (C) should show higher H_c for a similar particle size, and this was also observed experimentally.

The samples were pulverized after the appearance of H_c -max and showed a decrease in H_c . H_c decreased in sample (A) mainly because of the oxidation of the powder. In contrast, in samples (B) and (C), the decrease in H_c was also caused by the increase in lattice distortion that was partially reflected in the decrease in crystallite diameter (D)

by pulverization, as shown by the Williamson-Hall plots. D reached minimum values for samples (B) and (C) after a milling time of 30 h, and the D values and oxygen contents were almost the same for all milled powders after 48 h, after which H_c had decreased by more than 60%. Therefore, the accumulation of lattice distortion is also an important factor in the decrease in H_c in the samples. In future work, we will investigate the formation of single-domain particles in which both oxidation and lattice distortion are suppressed to increase H_c .

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