RAPID PUBLICATION

Observation of Microstructures and Magnetic Domains of Sm-Co Based Permanent Magnets by High-Voltage Electron Microscopy

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Microstructures and magnetic domains of precipitation hardened $\text{Sm}(\text{Co}_{0.653}\text{Fe}_{0.257}\text{Cu}_{0.066}\text{Zr}_{0.024})_{7.3}$ permanent magnets were investigated using a high-voltage electron microscope. The cellular microstructures controlled by step aging were clearly observed on atomic scale by high-voltage HREM. It was found that the cell interior phases of as-sintered magnets contained microtwins but those of step aged magnets contained the Z phase on the basal plane with disappearance of the twins. Also, Lorentz electron microscope images showed that the domain wall pinning at the cell boundary phases of the SmCo_5 structure was increased by the step aging. Furthermore, the intensity distributions of Lorentz electron microscope images obtained by imaging plates were compared with the calculated intensity distribution, and the domain wall width was evaluated to be 10 nm.

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I. Introduction

Precipitation hardened Sm-Co permanent magnets having a large coercive force and high energy product by step aging after sintering consist of the rhombohedral $\text{Sm}_2\text{Co}_{17}$ structure of $\text{Th}_2\text{Zn}_{17}$ type (space group $R\bar{3}m$) and the hexagonal SmCo_5 structure of CaCu_5 type ($P6_3/mmm$). Some elements such as Fe, Cu, etc. added to increase magnetic properties modify composition of $\text{Sm}_2\text{Co}_{17}$ or SmCo_5 , and their phases are generally labelled as 2:17 phases of cell interior and 1:5 phases of cell boundary, respectively⁽¹⁾⁻⁽⁴⁾.

$\text{Sm}_2\text{Co}_{17}$ is generated from SmCo_5 by replacing one third of Sm atoms with pairs of Co atoms. Thus, the $\text{Sm}_2\text{Co}_{17}$ structure results in stacking of three SmCo_5 unit cells along the [0001] direction and has $\cdots\text{ABCAB-CABC}\cdots$ type stacking sequence. Occasionally, the 2:17 phases are twinned because the reverse in this stacking, $\cdots\text{ABCABACBA}\cdots$ type is possible. A third phase of thin coherent plates, which has been named as the Z phase because it is enriched with Zr with respect to the matrix, is also observed. The Z phase lies on the basal plane of the matrix with the cellular microstructures⁽⁵⁾⁻⁽⁷⁾. The large coercive force of these alloys is controlled by the domain wall pinning in the cell boundary phases. HREM study⁽⁸⁾⁽⁹⁾ of the cellular microstructures and Lorentz electron microscope study⁽⁴⁾⁽⁶⁾⁽⁷⁾ on the domain wall pinning have been carried out so far, but the details of the Z phase and the domain wall pinning changed by step aging have not yet been clarified. In order to make clear internal structure of Sm-Co permanent magnetic al-

loys on atomic scale, we made high-voltage HREM study on Sm(Co, Fe, Cu, Zr)-based magnets. We also carried out Lorentz electron microscopy with a high-voltage electron microscope on the domain wall pinning controlled by step aging. Moreover, in order to analyze the intensity distributions of Lorentz electron microscope images accurately, we utilized imaging plates, which have good linearity and a wide dynamic range for electron intensity as compared with conventional electron microscope films⁽¹⁰⁾⁽¹¹⁾ and have been applied to quantitative analysis of HREM images⁽¹²⁾ and electron diffraction patterns⁽¹³⁾. We will compare the intensity distributions of the domain wall images obtained by imaging plates with the calculated intensity distributions and evaluate the domain wall width.

II. Experimental Procedure

Samples were produced with several steps as follows. The powders having the nominal composition of $\text{Sm}(\text{Co}_{0.653}\text{Fe}_{0.257}\text{Cu}_{0.066}\text{Zr}_{0.024})_{7.3}$ were pressed under a magnet field of 1.2 T. The pressed samples were sintered for 0.5 h at 1443 K, solution treated at 1423 K and furnace cooled in Ar atmosphere. The sintered samples were step aged: cooled until 673 K through 10 h after 2 h holding at 1098 K and furnace cooled after 6 h holding. Thin foils for TEM observation were prepared by combining mechanical polishing and ion milling. In addition to conventional electron microscopy at relatively low magnification with a 200 kV electron microscope (JEM-2000EX), HREM study was carried out by using a high-voltage electron microscope (JEM-ARM1250) with an accelerating

voltage of 1250 kV. Since the objective lens of the high-voltage electron microscope has magnetic leakage below 0.5 mT, it was also used for Lorentz electron microscopy with a specific sample holder. Lorentz electron microscope images were recorded not only on conventional EM films but also on imaging plates of $25\ \mu\text{m}/\text{pixel}$. The images obtained by imaging plates were converted into digital data and the intensity profiles of those data were investigated in the image processing system (FDL5000/PIXsysTEM II).

III. Results and Discussion

1. HREM of cellular microstructures changed by step aging

Figure 1 shows a dark field image and an HREM image of an as-sintered magnet having a low coercive force of 137 kA/m. In Fig. 1(b), the 1:5 phases indicated by arrows and microtwins in the cell interiors of the 2:17 phases are clearly observed. Alternate bright and dark bands perpendicular to c -axis in Fig. 1(a) correspond to these microtwins. Due to existence of the microtwins, diffraction spots corresponding to the 2:17 phases indicated by arrows in the electron diffraction pattern of Fig. 1(a) are elongated along the c -axis. Figure 2 shows a dark field image and an HREM image of a step aged magnet having a large coercive force of 840 kA/m. In Fig. 2(b), the Z phases in the cell microstructures are observed on

atomic scale. These Z phases are also observed as thin dark lines in Fig. 2(a). It is noted that very few microtwins are observed in Fig. 2(a). The Z phase is identified as the SmCo_3 structure having space group $R\bar{3}m$ from diffraction pattern obtained by Fourier transforming the HREM image of Fig. 2(b). In the insets of Fig. 2(b), an upper diffractogram corresponds to the 2:17 phases while a lower diffractogram corresponds to the 2:17 phases including the Z phases. In the lower diffractogram, the diffraction spot indicated by an arrow corresponds to (0002) plane of SmCo_3 . The result is in consistence with the previous work⁽⁵⁾. The electron diffraction pattern of Fig. 2(a) shows the orientation relations between the Z phase and the matrix. Weak spots indicated by arrows seem to be caused by double diffraction. Also, diffuse streaks parallel to the c -axis in the electron diffraction pattern are attributed to the Z phase thin plates. It is considered that Zr preferentially goes into twin planes of 2:17 phases resulting in the disappearance of microtwins during step aging, and eventually, the Z phases are originated on basal planes in the cellular microstructure. The lattice spacing of the Z phase along the c -axis are about twice as large as that of the $\text{Sm}_2\text{Co}_{17}$ structure. Therefore, the Z phases can behave as high diffusion path for addition elements, such as Cu, Fe etc. Actually, the previous X-ray fluorescent microanalysis⁽⁵⁾ and ALCHEMI⁽¹⁴⁾ of overaged magnets showed that Cu goes to the 1:5

Fig. 1 Dark field image (a) and a high-voltage HREM image (b) of an as-sintered magnet. The incident electron beam was parallel to the $[1\bar{1}00]_{1:5}$ direction.

Fig. 2 Dark field image (a) and a high-voltage HREM image (b) of a step aged magnet. The incident electron beam was parallel to the $[1\bar{1}00]_{1:5}$ direction. In the insets of (b), an upper diffractogram corresponds to the 2:17 phases while a lower diffractogram corresponds to the 2:17 phases including the Z phases.

phases and Fe to the 2:17 phases during aging. Thus, the formation of the Z phases by step aging facilitates the chemical partitioning of the transition metals between the 1:5 phases and the 2:17 phases as reported previously⁽¹⁵⁾⁽¹⁶⁾. The chemical partitioning of the transition metals may contribute to the lattice mismatch between the 1:5 phases and the 2:17 phases. This may be the reason why the 1:5 phases in Fig. 2 are more clear than those of Fig. 1.

2. Lorentz electron microscopy carried with imaging plates

Figures 3(a) and (c) show Lorentz electron microscope images of an as-sintered magnet observed by Fresnel mode and Foucault mode, respectively. 180° magnetic domain walls parallel to the *c*-axis are clearly observed. Figures 3(b) and (d) are Lorentz electron microscope images of a step aged magnet. In Figs. 3(b) and (d), the serrated domain walls corresponding to the cell boundaries are observed. These Lorentz electron microscope images clearly show that the domain wall pinning at the cell boundary phases is increased by step aging. It is considered that the domain wall pinning increased by step aging is due to not only the growth of the cell boundary phases but also the increase of the lattice mismatch in the *a* direction and domain wall energy gradient by the segregation of Cu to the 1:5 phases facilitated by the formation of the Z phases during step aging. Therefore, coercive force of step aged magnets can be increased several

times larger than that of as-sintered magnets. However, Fig. 3(d) indicates that the thin Z phase plates perpendicular to *c*-axis do not affect the domain wall pinning directly.

Figure 4 shows the comparison of the intensity distributions of the domain wall images in an as-sintered magnet observed by Fresnel mode with the calculated intensity distributions considered spin distribution in the domain wall. The equation⁽¹⁷⁾ of the theoretical intensity distribution of the domain wall images based on geometric optics is given by

$$I(U)/I_0 = |1 \pm R \operatorname{sech}^2 u|^{-1}, \quad U = u \pm R \tanh u \quad (1)$$

where $u = x/a$, $U = X/a$, and $R = z\Phi/a$. x and X are the coordinates normal to the wall direction in the specimen plane and the image plane, respectively. $2a$ is the wall width, z the defocus distance, and Φ deflection due to saturation magnetization. The plus and minus signs in the eq. (1) refer to divergent and convergent cases, respectively. In Fig. 4, the experimental intensity profiles at a defocus distance 0.63 mm were best fitted with the calculated intensity profiles of divergent and convergent cases at $R=0.3$. The wall width $2a$ is defined by the slope of a function of $dB_y(x)/dx$ at the wall center, whereas W_0 is given as the width at half maximum of the function of $dB_y(x)/dx$ where B_y is the component of the magnetic induction along the direction parallel to the wall. A linear extrapolation of the width W_z at half maximum of divergent wall image to $z=0$ directly gives the experimental

Fig. 3 Lorentz electron microscope images of an as-sintered magnet ((a), (c)) and a step aged magnet ((b), (d)). (a) and (b) are images observed by Fresnel mode while (c) and (d) are images observed by Foucault mode.

Fig. 4 Comparison of theoretical intensity distributions with intensity distributions of Fresnel images obtained by imaging plates. In the graphs, solid lines and dots indicate the theoretical and observed intensity distributions, respectively. (a) Divergent case, (b) Convergent case. Defocus distance z is equal to 0.63 mm.

wall width $W_0^{(18)(19)}$. In this study, widths W_z at half maximum were measured from the intensity profiles of divergent wall images obtained by imaging plates. These intensity profiles were obtained in the narrowest areas of divergent wall images to avoid overestimation of the wall width due to tilting of the magnetic domain wall against the electron beam. In Fig. 5, the widths W_z at half maximum plotted against defocus distances z are on a straight line. By the extrapolation, the wall width of a as-sintered magnet is evaluated to be about 10 nm. In the previous reports⁽²⁾⁽⁶⁾, the coercive force of Sm-Co based magnets has been calculated using the relation of $H_c = (\gamma' - \gamma) / 2M_s W_0$ where H_c is coercive force, γ' the wall energy in the 1:5 phase, γ the wall energy in the 2:17 phase, M_s the magnetization per unit volume and W_0 the wall width. In their calculation, the wall width was assumed to be 10 nm. The wall width measured by the extrapolation in this study agrees well with the assumed value.

High-voltage HREM is very useful for observation on atomic scale of a lattice strained area which is difficult to resolve with a low voltage electron microscope because of the dark contrast of the localized strain field. Moreover, observation of domain wall images by imaging plates is convenient for digitization of the images and the digital

Fig. 5 Width W_z at half maximum of divergent wall image as a function of defocus distance z .

data is very useful for measurement of the intensity distributions of the images. It is expected that interaction of magnetic domain walls and pinning centers can be investigated in detail by image processing of the digital image data. Detailed investigation on the intensity distributions and image processing of Lorentz electron microscope images obtained by imaging plates is under progress. The results will be published elsewhere.

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