Special Feature: Metallic Materials

Research Report

Consideration of Dy Diffusion Treatment on the Coercivity of NdFeB Sintered Magnets

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ABSTRACT Effects of Dy diffusion treatment on the coercivity of NdFeB sintered magnets were considered by analyses of the Dy distribution and the magnetic domain structure using the XMCD-PEEM technique. Dy diffusing through the grain boundary inhibits the expansion of the magnetic reversed domains, as well as the conventional Dy-doped magnets. Dy diffusion can be classified into 2 steps from the increasing ratio of coercivity. The first step shows a rapid increase in coercivity, where Dy diffuses through the grain boundary, and the second step is a gradual increase, where Dy diffuses inside $Nd_2Fe_{14}B$ grains.

In order to improve the effect of Dy diffusion, microstructural modification has been studied. Diffused Dy reacts with oxygen in NdFeB magnets to form Nd-Dy oxide. The oxidization of Dy would not work for the improvement of the coercivity. Doping fluoride into the NdFeB magnets encourages the diffusion of Dy through the grain boundary because of the formation of NdOF, which resulted in significant improvement of the coercivity.

KEYWORDS NdFeB Sintered Magnet, Dy Diffusion Treatment, Magnetic Domain Structure, Dy Oxide, NdOF

1. Introduction

NdFeB sintered magnets are widely used in various applications, such as voice coil motors (VCMs), hard disk drives (HDDs) and magnetic resonance imaging systems (MRIs), due to their high maximum energy product ($(BH)_{max}$).[1] Recently, the use of NdFeB magnets in motors for hybrid vehicles (HVs) and electric vehicles (EVs) has rapidly expanded. In these applications, high coercivity is desired for NdFeB magnets to suppress the thermal demagnetization at operation temperatures.

The substitution of heavy rare earth elements, such as Dy or Tb, for Nd in NdFeB magnets enhances their coercivity due to an increase in the magnetic anisotropy field.[1] However, the substitution reduce both the saturation magnetization and the energy product due to antiferromagnetic coupling of Dy or Tb with Fe.[1] Moreover, the supply of heavy rare earth elements has become serious problems due to the localized resources. Therefore reduction in the use of these elements is strongly required.[2-4] Recently, a new technique, Dy diffusion treatment, has been studied to solve the risk of Dy supply.[5-12] By adapting this new technique, Dy becomes locating around $Nd_2Fe_{14}B$ grains, resulting in an increase of coercivity with smaller usage of Dy than the Dy-doped magnets. So many studies have been done about Dy-diffused magnets.[13,14]

In this paper, we investigated the relation between the microstructure and coercivity of Dy-diffused sintered magnets, considered with the observation of the magnetic domain structure analyzed using photoelectron emission microscope combined with X-ray magnetic circular dichroism (XMCD-PEEM) technique.[15,16] Furthermore, we tried to improve the effect of Dy diffusion through the trapping the oxygen as impurity in NdFeB magnets, which inhibits the Dy diffusion into the magnet, by forming the oxyfluoride (NdOF).

Table 1 Content of rare earth metals and magnetic properties of NdFeB magnets used in XMCD-PEEM experiments.

	Content of rare earths		Magnetic properties	
	Nd / wt%	Dy / wt%	Coercivity / kOe	Remanent Magnetization / kG
Dy-free magnet	29.2	–	11.6	14.3
Dy-diffused magnet	29.1	0.08	15.0	14.3
Dy-doped magnet	24.0	4.7	24.6	13.1

2. Experimental

2. 1 Preparation of NdFeB Sintered Magnets

NdFeB magnets were prepared from jet-milled powders (mean particle size: 6 μm) with a composition of 31.8Nd-0.98B-0.90Co-0.10Cu-0.15Al-0.05Ga-bal.Fe (wt%). The powders were compacted with 15 MPa under a magnetic field of 1.8 T. The green compacts were sintered at 1293–1353 K for 4 h in a vacuum (< 10^{-2} Pa) and then annealed at 773 K for 1 h. The oxygen content in the sintered magnets was controlled to be 2000 and 5000 ppm, respectively.

2. 2 Dy Diffusion Treatment

Dy diffusion treatment to the NdFeB magnets was carried out by heating both the Dy metal and magnets in same tray at temperature from 1053 to 1113 K for 16–128 h in a vacuum (< 10^{-4} Pa).

The content of Dy was evaluated using inductively coupled plasma spectroscopy (ICP) analysis. The magnetic properties were measured using a pulsed magnetometer. Elemental distributions were measured with an electron probe microanalyzer (EPMA).

2. 3 Magnetic Domain Structure Analyses by XMCD-PEEM

The contents of the rare-earth elements and the magnetic properties of the samples are listed in **Table 1**. The samples with a size of 2 × 2 × 2 mm^3 were magnetized using a magnetic field of 10 T in the direction parallel to the *c*-axis of the $Nd_2Fe_{14}B$ before the observation of the magnetic domain structures. The samples were then attached to an iron yoke to prevent the leakage of the magnetic fields, as shown in **Fig. 1**.

Observation of the magnetic domain structures was carried out by XMCD-PEEM measurements at the

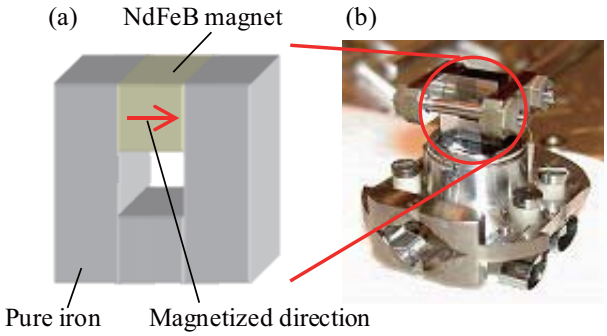

Fig. 1 (a) Schematic illustration of the yoke system. (b) XMCD-PEEM sample holder with the yoke.

beamline BL17SU with soft X-rays in SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (Hyogo, Japan). Also the observation was done to the surfaces parallel to the *c*-axis of the $Nd_2Fe_{14}B$ using the Fe L_3 (i.e. $2p_{3/2} \rightarrow 3d$) photoabsorption edge of Fe for Dy-free, Dy-diffused, and Dy-doped magnets. The elemental maps of Fe, Nd and Dy were measured at the Fe L_3, Nd M_4 (i.e. $3d_{3/2} \rightarrow 4f$) and Dy M_5 (i.e. $3d_{5/2} \rightarrow 4f$) edges, respectively.

3. Results and Discussion

3. 1 Effect of Dy Diffusion Treatment on Magnetic Domain Structure

Figure 2 shows (a) the elemental map of Nd and (b) magnetic domain image for the Dy-free magnet. The magnetized direction is also marked as an arrow. The image contrasts colored from dark to bright in the elemental map (Fig. 2(a)) indicate the Nd content. That is, dark and bright regions correspond to the $Nd_2Fe_{14}B$ matrix and Nd-rich regions, respectively. The magnetic domain image (Fig. 2(b)) shows the spin directions as dark and bright colors. The spin directions in the

brighter area indicate parallel to the magnetized direction. And those in the darker regions indicate antiparallel to the magnetized direction, which mean magnetic reversed regions. Polishing damages were also observed in this image. From the above observations, a schematic illustration of the magnetic domain image and grain boundary for the Dy-free sample is drawn in Fig. 2(c). The magnetic reversed domains exist extending across several $Nd_2Fe_{14}B$ grains to the direction of the *c*-axis.

Figure 3 shows a magnetic domain image of the Dy-doped magnet, in which the grain boundary is also drawn with white line. In case of the Dy-doped magnet, the magnetic reversed domains (darker regions) were observed smaller size than that for the Dy-free magnet. This means that Dy doping into NdFeB magnets prevents the expansion of magnetic reversed regions.

Figure 4 shows the elemental maps of (a) Nd and (b) Dy, and (c) a magnetic domain image for the Dy-diffused magnet. A schematic illustration of the magnetic domain image and grain boundary for the Dy-diffused magnet is also drawn in Fig. 4(d). In case of the Dy-diffused magnet, Dy exists in the grain boundary. Then, the magnetic reversed domains were observed only in limited regions, as well as that for the Dy-doped magnet.

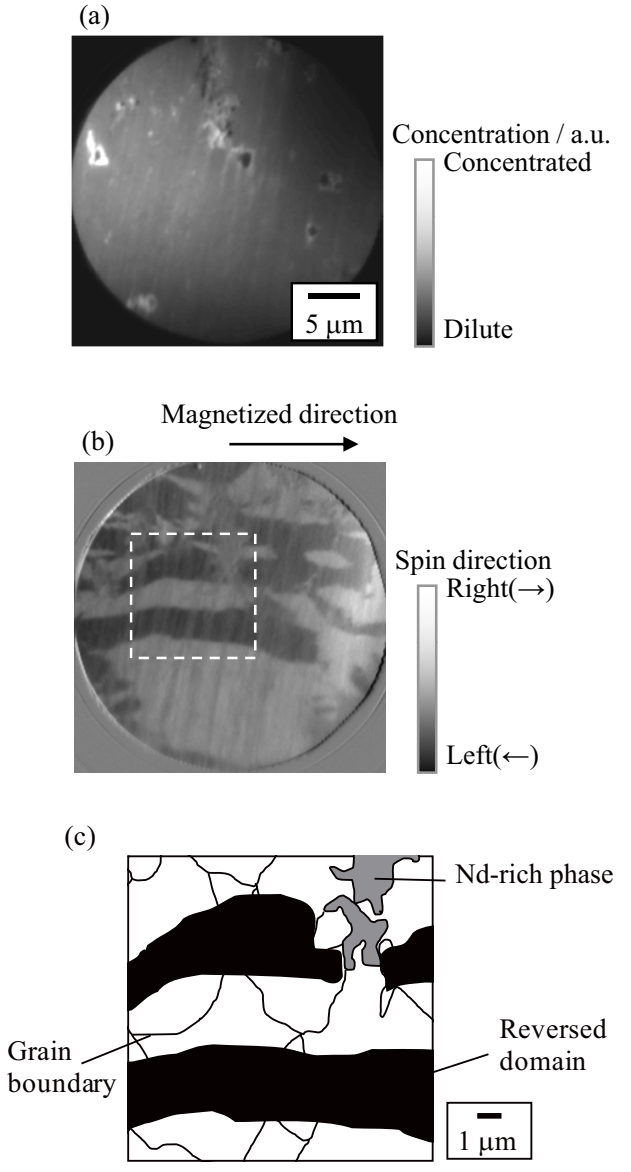

Fig. 2 (a) The elemental map of Nd and (b) magnetic domain image of the Dy-free sample. (c) Schematic illustration of the magnetic domain image and grain boundary region surrounded by the dotted lines in Fig. 2(b).

3. 2 Influence of the Distribution of Dy in NdFeB Magnets on Their Coercivity

Dy diffusion treatments were carried out with various heating conditions for the magnets with oxygen content of 5000 ppm in order to investigate the influence of the distribution of Dy in NdFeB magnets on their coercivity. **Figure 5** shows the variation of coercivity of Dy-diffused magnets with changing the conditions of Dy diffusion treatments. The coercivity increases with raising temperature and holding time.

Figure 6 shows the analytical result from Fig. 5 by replotting as a function of Dy content. The coercivity shows 2 step increase with Dy content: (1) A rapid increase in coercivity at less than 0.2 wt% of Dy content. (2) A gradual increase at more than 0.2 wt% of Dy content.

To quantify the efficiency of Dy for the coercivity,

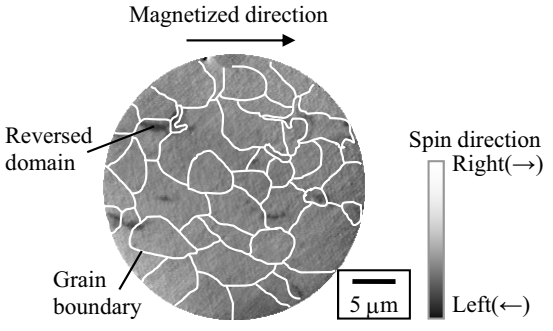

Fig. 3 Magnetic domain image of the Dy-doped sample. Grain boundary are drawn with white lines.

the increase ratio (f) of coercivity by Dy content is defined as;

$$f\,(\mathrm{kOe}\,/\,\mathrm{wt\%}) = \Delta H\,/\,w \cdots\cdots\cdots\cdots\cdots\cdots (1)$$

ΔH: increase in coercivity by Dy diffusion treatment (kOe)

w: Dy content (wt%)

Figure 7 shows the variation of f with w. In case of $w < 0.2$ wt% (step (1) in Fig. 7), f shows more than 30. On the other hand, in case of $w > 0.2$ wt% (step (2) in Fig. 7), f rapidly decreases to less than 10 with increasing w.

Figure 8 shows the elemental maps of Dy in the samples (a) and (b) shown in Fig. 7. The sample (a) reveals that Dy diffused mainly from the surface to

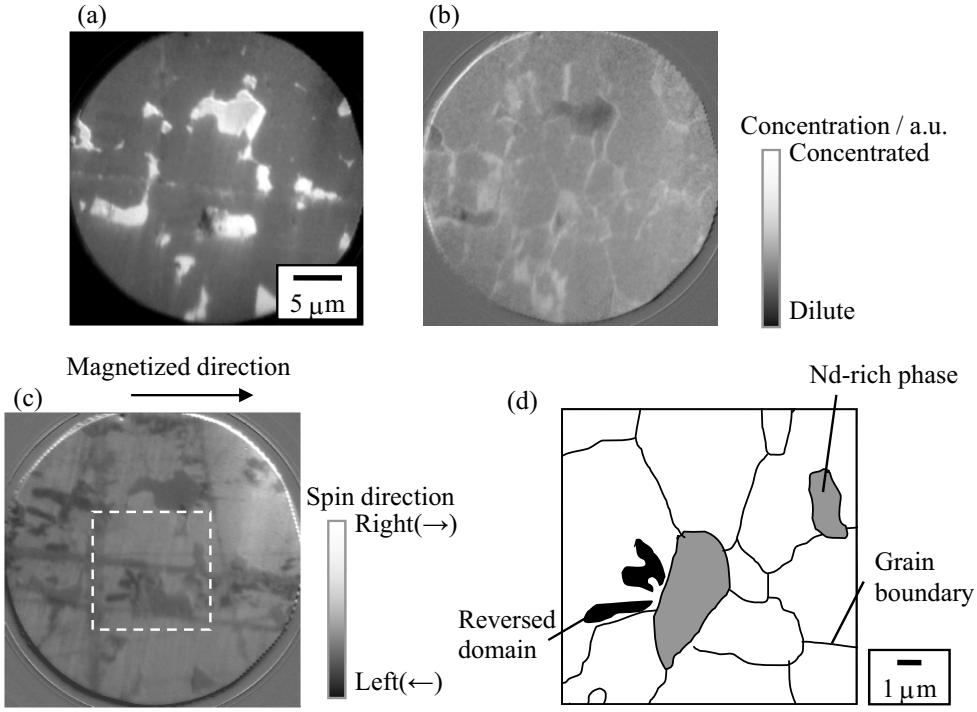

Fig. 4 The elemental maps of (a) Nd and (b) Dy, and (c) magnetic domain image for the Dy-diffused sample. (d) Schematic illustration of the magnetic domain image and grain boundary region surrounded by dotted lines in Fig. 4(c).

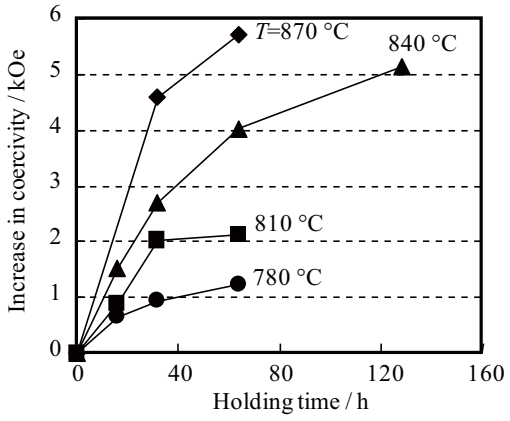

Fig. 5 The variation of coercivity of Dy-diffused magnets with changing the conditions of Dy diffusion treatment. (T: holding temperature)

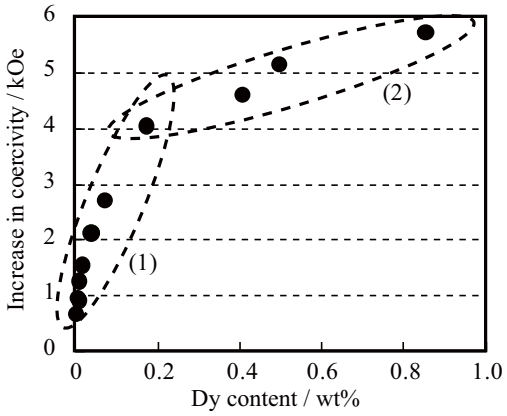

Fig. 6 The analytical result from Fig. 5 by replotting Dy content.

500 μm, while, for sample (b), the wide distribution of Dy was observed even at 1000 μm. In case of the 500 μm-region from the Dy-diffused surface, Dy is located around $Nd_2Fe_{14}B$ grains for sample (a). In contrast, Dy diffuses inside $Nd_2Fe_{14}B$ grains for sample (b).

As a result, at the first step, Dy diffuses through grain boundary, resulting in a rapid increase in coercivity. Then, at the second step, Dy diffuses inside NdFeB grains, resulting in a gradual increase in coercivity. The localization of Dy at grain boundary is effective for reduction of Dy usage.

3. 3 Influence of Oxygen in NdFeB Magnets on the Dy Diffusion

In order to improve the effect of Dy diffusion, microstructural modification has been studied.

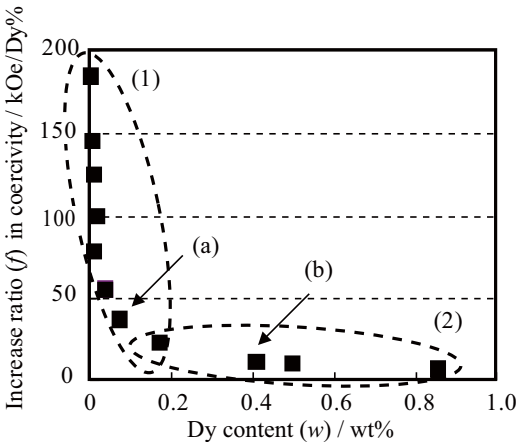

Fig. 7 The variation of the increase ratio (*f*) of coercivity as a function of Dy content (*w*).

Figure 9 shows the elemental maps of the Dy-diffused magnet with an oxygen content of 5000 ppm. Focusing to the triple junctions, Dy, Nd, and also oxygen are co-existing there. This result indicates that diffused Dy may react with oxygen to form Nd-Dy oxide according to reaction (2). The oxidization of Dy would not work for the improvement of the coercivity.

$$NdO_x + Dy \rightarrow (Nd, Dy)O_x + Nd \quad \cdots\cdots\cdots (2)$$

So, in order to clarify the influence of oxygen in the NdFeB magnets on the Dy diffusion, the distribution of Dy in the magnets with different oxygen content was analyzed. **Figure 10** shows the elemental maps of Dy, Nd and oxygen for the samples with oxygen content of (a) 5000 and (b) 2000 ppm, respectively. Dy contents after diffusion treatment show 0.17 and 0.45 wt%, respectively, even at the same treated condition. In case of the oxygen content of 2000 ppm, the contrast of Dy does not fit to that of oxygen, then distributes widely along the grain boundary. These results indicate that the reduction of oxygen content in the NdFeB magnet is effective to diffuse Dy through the grain boundary.

New technique to prevent from the oxidization of Dy was studied, in which the rare earth fluorides were doped into the NdFeB magnets. **Figure 11** shows the elemental maps of the magnets with doping (a) NdF_3 and (b) DyF_3 powders. In either case, fluorine is localized at the triple junctions with Nd and oxygen, indicating the formation of oxyfluoride (NdOF) according to reactions (3) and (4).[17,18]

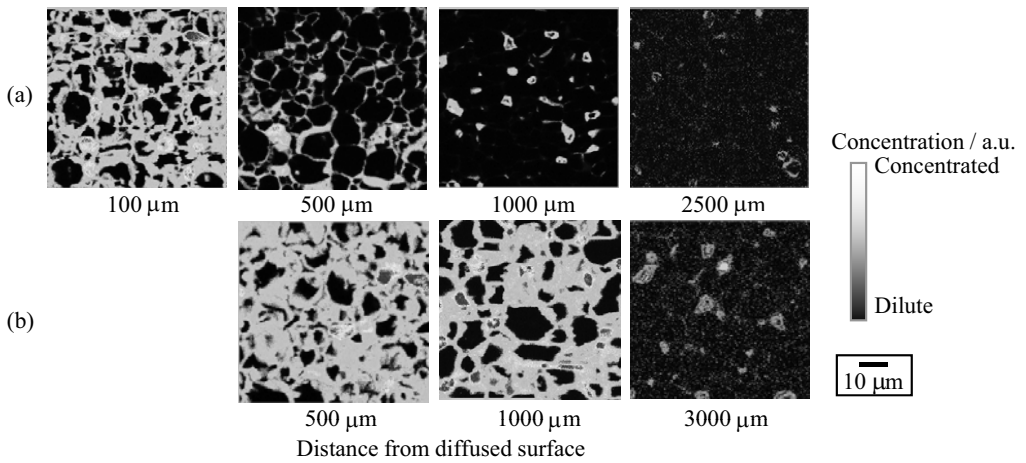

Fig. 8 The elemental maps of Dy in the samples (a) and (b) shown in Fig. 7.

$$NdO_x + NdF_3 \rightarrow NdOF \quad \cdots\cdots\cdots\cdots\cdots (3)$$

$$NdO_x + DyF_3 + Nd \rightarrow NdOF + Dy \quad \cdots\cdots\cdots (4)$$

Even if DyF_3 is doped, the reactive product is only NdOF as shown in Fig. 11(b), because NdOF is stable in the magnet compared from Nd-Dy oxide.

This new technique was applied to the magnet with oxygen content of 5000 ppm, and Dy diffusion treatment was carried out. The oxygen exists only as NdOF and Dy smoothly diffuses through the grain boundary without the oxidation as shown in **Fig. 12**.

Figure 13 shows the variation of coercivity as a function of Dy content for the several samples: the samples with oxygen contents of (a) 5000 and (b) 2000 ppm, and (c) NdF_3-doped samples with oxygen content of 5000 ppm. The coercivity increases by reducing the oxygen content from 5000 (Fig. 13(a)) to 2000 ppm (Fig. 13(b)). Furthermore, the coercivity of the NdF_3-doped magnet (Fig. 13(c)) increased more significantly than that of the magnet with oxygen content of 2000 ppm.

These results indicate that doping fluoride into the NdFeB magnets encourages the diffusion of Dy through the grain boundary because of the formation of NdOF, resulting in significant improvement of the coercivity.

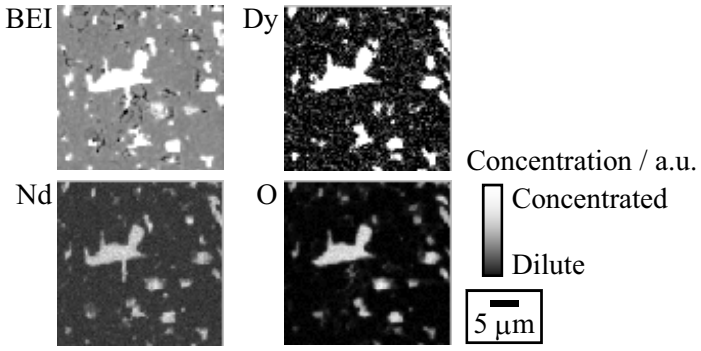

Fig. 9 Backscattered electron image (BEI) and the elemental maps for Dy, Nd and O in the Dy-diffused magnet.

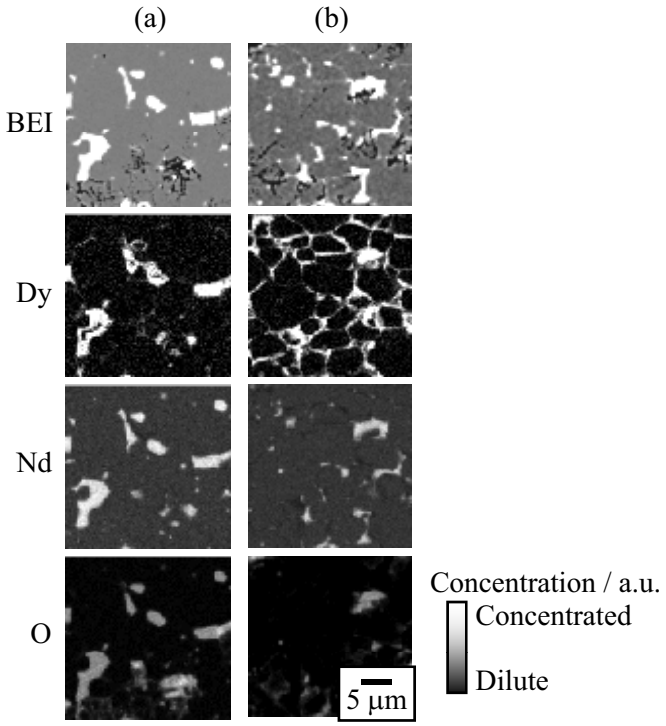

Fig. 10 Backscattered electron images (BEI) and the elemental maps for Dy, Nd and O in the Dy-diffused magnets. The oxygen contents in these samples were (a) 5000 and (b) 2000 ppm, respectively.

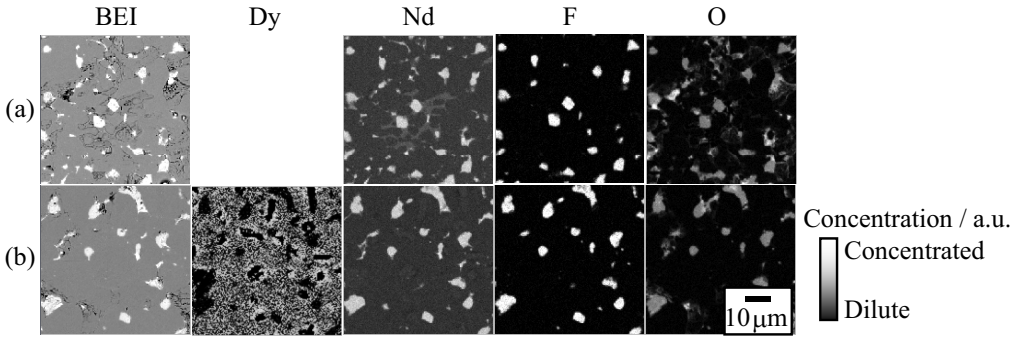

Fig. 11 Backscattered electron images (BEI) and the elemental maps for Dy, Nd, F and O in (a) NdF_3- and (b) DyF_3-doped magnets.

4. Conclusion

We investigated the relation between the microstructure and coercivity of Dy-diffused magnets, considered with the observation of the magnetic domain structure analyzed using XMCD-PEEM technique. Furthermore, we tried to improve the effect of Dy diffusion through the trapping the oxide by forming the oxyfluoride. The following conclusions were made:

(1) Dy diffusing through the grain boundary inhibits the expansion of magnetic reversed domains in NdFeB magnets, as well as the conventional Dy-doping magnets.

(2) Dy diffusion can be classified into 2 steps from the increasing ratio of coercivity. The first step is a rapid increase in coercivity, where Dy diffuses through grain boundary, and the second step is a gradual increase, where Dy diffuses inside $Nd_2Fe_{14}B$ grains.

(3) The oxygen in the NdFeB magnets reacts with Dy to form Nd-Dy oxide. The oxidation of Dy would not work for the improvement for the coercivity. The reduction of oxygen content in the NdFeB magnet is effective to diffuse of Dy through the grain boundary.

(4) Doping fluoride into the NdFeB magnets induced the formation of NdOF and encourages the diffusion of Dy through the grain boundary, which results in significant improvement of the coercivity.

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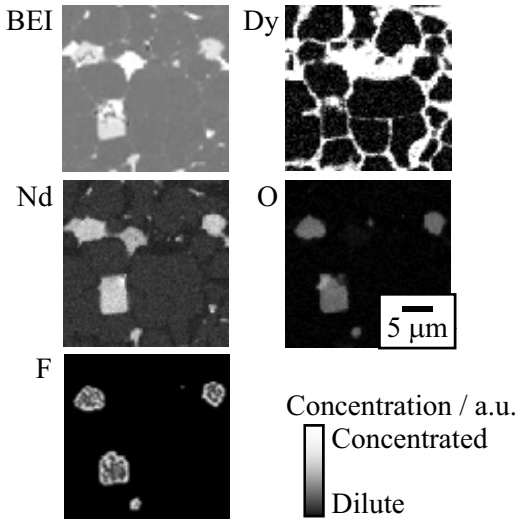

Fig. 12 Backscattered electron images (BEI) and the elemental maps for Dy, Nd, F and O in the NdF_3-doped NdFeB sample after Dy diffusion treatment.

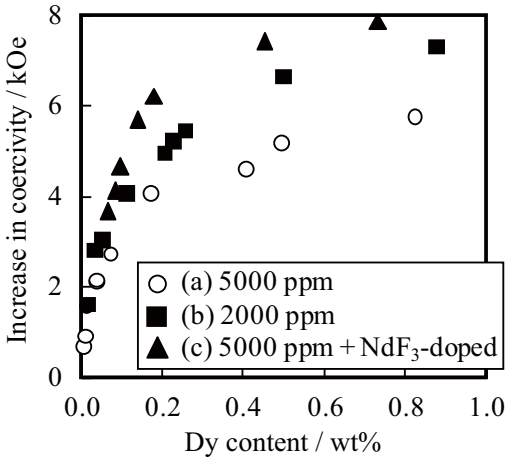

Fig. 13 The variation of coercivity as a function of the Dy content of the NdFeB magnets with oxygen contents of (a) 5000 and (b) 2000 ppm, and (c) the NdF_3-doped NdFeB magnets with oxygen content of 5000 ppm.

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