Influence of Nd Oxide Phase on the Coercivity of Nd-Fe-B Thin Films

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To understand the coercivity mechanism of Nd-Fe-B sintered magnets, the microstructure of grain boundary composed of Nd2Fe14B and Nd-rich phases has been studied. However, the influence of Nd-rich phase, which contains some amount of oxygen, on microstructure and coercivity has not been clear. In this study, the influence and the interfacial microstructure between the Nd5Fe2B phase and the Nd-rich phase were investigated using Nd-Fe-B thin films. Furthermore, the microstructural change of Nd-oxide (Nd-O) phase was investigated using oxidized Nd thin films. The coercivity (Hc) of the Nd-Fe-B thin films decreased by about 80% from the level of as-deposited film (Hc(as-depo)) after oxidation and annealing at low temperature (~350°C). From TEM observation of the Nd-Fe-B film, some steps along the surface of the Nd2Fe14B phase contacting with the hcp NdOx phase were observed. Investigation of the microstructural change of Nd oxide phase was carried out using Nd thin films. The as-deposited Nd film was composed of the dhcp Nd (α-Nd) phase, and the fcc NdOx phase formed at the surface of α-Nd phase after oxidation. After annealing at 350°C, the hcp NdO2 phase crystallized from the fcc NdOx phase, and it resulted in large roughness at the boundary with the α-Nd phase. From the results described above, the crystallization of hcp NdOx phase causes damage at the surface of Nd2Fe14B phase during the annealing at low temperature, which results in the decrease of coercivity.

Keywords: neodymium-iron-boron thin films, neodymium thin films, neodymium oxide, coercivity, interfacial microstructure

1. Introduction

Nd-Fe-B sintered magnets show the highest energy products and are used in various applications. However, the coercivity of the magnets without additional elements is only about 12% of the anisotropy field of Nd2Fe14B compound, which is the main phase of Nd-Fe-B magnets. In addition, the temperature coefficient of the coercivity is also large. Therefore, the improvement of the coercivity is strongly required for the use at high temperature such as motors in hybrid electric vehicles (HEV).

The coercivity of the Nd-Fe-B sintered magnets is strongly related to their interfacial microstructure between main phase (Nd2Fe14B) and grain boundary phase (Nd-rich). In order to obtain the guiding principles for enhancement of the coercivity, many researchers have observed the interfacial microstructure. Vial et al.1) reported that the optimum annealing after sintering smoothes the interface between the Nd2Fe14B phase and the Nd-rich phase and increases the coercivity. Sagawa et al.2) reported the Nd-rich phase has an fcc structure, and Ramesh et al.3) showed the Nd-rich phase contains oxygen about 20–50 at%. Makita and Yamashita4) showed that the Nd-rich phase forms an fcc NdO with two preferential orientation relationship between the Nd2Fe14B and Nd-rich phases. Fukagawa and Hirose5) reported that the existence of an fcc NdO phase on the Nd2Fe14B grains is necessary for generating coercivity. Shinba et al.6) reported that the Nd-rich phase contains oxygen and the microstructure changes from crystallite to amorphous with decreasing the thickness of Nd-rich phase. According to Mo et al.,7) the crystalline structures of Nd-rich phase change by the amount of oxygen content in the Nd-rich phase. They indicated that the Nd-rich phase with fcc structure can contain a wide range of oxygen (11–43 at%), however that with hcp structure can contain a narrow range of oxygen (55–70 at%). In our previous papers,8,9) we investigated the influence of oxidation state on coercivity and interfacial microstructure by using Nd-Fe-B thin films. However, the relationship between the Nd oxide (Nd-O) phase and coercivity is not clear. In this study, the model interface of Nd2Fe14B/Nd-O and Nd-O thin film were fabricated by sputtering, and the influence of Nd-O phase on the coercivity and interfacial microstructure during annealing at low temperature were investigated.

2. Experimental Procedure

All films were prepared by ultra high vacuum (UHV) magnetron sputtering system with base pressure of 1×10−7 Pa. A Nd-Fe-B layer with the thickness of 100 nm or a Nd layer with the thickness of 40 nm were deposited on Ta buffered MgO (001) substrate, which were annealed at 680 or 450°C for crystallization. The composition of target used for the preparation of Nd-Fe-B layer was Nd18Fe66B16. After deposition of Nd-Fe-B or Nd layer, films were cooled to room temperature and moved to another chamber. The films were kept for 120 min under Ar gas atmosphere to be oxidized. Oxygen content was estimated about 2 vol ppm in the Ar gas atmosphere. After oxidation, the films were annealed at 250–650°C for 60 min in UHV condition (1×10−7 Pa). Finally, a Ta layer with the thickness of 7 nm was deposited on the films for preventing oxidation from air.

Magnetic properties were measured by a vibrating sample magnetometer (VSM) along the direction perpendicular to the film plane after applying a pulsed magnetic field of 6360 kAm−1. Crystalline structure and microstructure were analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM), respectively.

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3. Results and Discussion

3.1 Coercivity and microstructural changes of Nd-Fe-B thin films

Figure 1 shows the annealing temperature dependence of coercivity ratio ($RH_{cJ}$) for Nd-Fe-B thin films. The coercivity ratio is defined by the following formula.

$$RH_{cJ} = \frac{H_{cJ} (as-depo.)}{H_{cJ} (as-depo.)} \times 100$$

The coercivity of Nd-Fe-B thin film decreased to around 40% of the coercivity of as-deposited film after oxidation and showed further decrease to 20% after annealing at low temperature (250–350°C). However, the coercivity recovered to the same value of as-deposited film after annealing at high temperature (550–650°C).

Figure 2 shows TEM images of the interface between Nd$_2$Fe$_{14}$B and Nd-rich phases and a SAD pattern taken from the Nd-rich phase, in the as-deposited Nd-Fe-B thin film. As shown in Fig. 2(a), there are Nd$_2$Fe$_{14}$B and Nd-rich phases in the Nd-Fe-B layer because of using Nd and B riched Nd-Fe-B ternary alloy as a sputtering target. The SAD pattern of the Nd-rich phase shown in Fig. 2(c) is identified as the patterns of the $\alpha$-Nd taken from [001] direction (Fig. 2(d)). Figure 2(b) reveals that the interface between the Nd$_2$Fe$_{14}$B and $\alpha$-Nd phases is flat in the as-deposited Nd-Fe-B thin film.

Figure 3 shows bright field (BF) TEM (a) and HRTEM (b) images at the Nd$_2$Fe$_{14}$B/$\alpha$-Nd interface in a Nd-Fe-B thin film, which was oxidized and then annealed at 350°C. A SAD pattern taken from the Nd-rich phase is shown in Fig. 3(c). It reveals that the Nd-rich phase is indexed as hcp Nd$_2$O$_3$ phase (Fig. 3(d)), and the hcp Nd$_2$O$_3$ phase is polycrystalline. The HRTEM image (Fig. 3(b)) shows that there are some steps at the surface of the Nd$_2$Fe$_{14}$B phase contacted with the hcp Nd$_2$O$_3$ phase. The depth of these surface steps is estimated at 1~3 lattice fringes of (002) plane of the Nd$_2$Fe$_{14}$B.

3.2 Nd-O Phase in Nd thin films

The results described above suggest that the Nd-O phase influences the coercivity and the microstructure of Nd-Fe-B thin films. Therefore, microstructural change of Nd-O was investigated by using Nd thin films in this study.

Figure 4 shows XRD patterns of the Nd thin films after oxidation (b) and subsequent annealing at 350°C (c), 550°C (d) and 650°C (e) in comparison with that of as-deposited film (a), respectively. The (111) peak of fcc NdO$_x$ phase with the lattice parameter of $a = 0.547$ nm, which seems to be the same structure with that is reported by some researchers, appeared after oxidation, and it decreased with increasing annealing temperature. On the contrary, the (002) peak of hcp Nd$_2$O$_3$ was identified after annealing at 350°C, and it increased with increasing annealing temperature. These results indicate that the fcc NdO$_x$ phase changes to the hcp Nd$_2$O$_3$ phase during annealing. Then, microstructural change of the Nd-O phase was investigated by TEM.

TEM images and SAD patterns of the as-deposited and the as-oxidized Nd thin films were shown in Fig. 5(a) and (b), respectively. The SAD patterns shown in both of Fig. 5(a) and (b) can be indexed as $\alpha$-Nd [111] and [121], respectively. It means that the $\alpha$-Nd phase existed mainly in the as-deposited and the as-oxidized Nd thin films. From the TEM image shown in Fig. 5(b), a continuous phase with different...
contrast was observed along the surface of the \(\alpha\)-Nd phase in the as-oxidized film. The spacing of the lattice fringe contrast to the film plane, is estimated as 0.32 nm. In Nd-O compounds, the (111) plane of NdO\(_x\) \((a \approx 0.547\,\text{nm})\) and (222) of C-Nd\(_2\)O\(_3\) \((a \approx 1.107\,\text{nm})\) have a spacing of around 0.32 nm. Though the (111) peak of fcc NdO\(_x\) phase was observed in the XRD profile, the (222) peak of C-Nd\(_2\)O\(_3\) phase was not observed, as shown in Fig. 4(b). Therefore, it is considered that the phase with dark contrast shown in Fig. 5(b) is the fcc NdO\(_x\).

Figure 6 shows TEM images and a SAD pattern of the Nd thin film, which was oxidized and then annealed at 350°C. The SAD pattern reveals that main phase of this film is the \(\alpha\)-Nd. In low magnification TEM image shown in Fig. 6(a), there were some regions with different dark contrast at the surface of the \(\alpha\)-Nd phase. The lattice spacing calculated from the lattice fringes in the HRTEM image shown in Fig. 6(b), reveals that these regions are the hcp Nd\(_2\)O\(_3\) phase. Therefore, it is considered that the hcp Nd\(_2\)O\(_3\) phase precipitates discontinuously from the fcc NdO\(_x\) phase. Since the fcc NdO\(_x\) phase is metastable, one possibility is transformation from the fcc NdO\(_x\) phase into the hcp Nd\(_2\)O\(_3\) and the \(\alpha\)-Nd phases below 863°C,\(^{10}\) and the roughness at the interface with \(\alpha\)-Nd phase becomes large.

### 3.3 Relationship between coercivity and interfacial microstructural changes in Nd-Fe-B thin films

From the present study, the decline of the coercivity of oxidized Nd-Fe-B thin films (Fig. 1) can be explained as being due to the microstructural changes of Nd-O described above. The Nd-Fe-B thin film in as-deposited state has a flat
interface of Nd$_2$Fe$_{14}$B/α-Nd phases. After oxidation and subsequent annealing at low temperature, the hcp Nd$_2$O$_3$ phase crystallizes (Fig. 6(b)) and induces damages to the surface of the Nd$_2$Fe$_{14}$B phase (Fig. 3(b)). As a result, coercivity decreases to around 20% of that in as-deposited film.

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