Effect of Cu Addition on Coercivity and Interfacial State of Nd-Fe-B/Nd-rich Thin Films

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Abstract. This study provides the effect of Cu addition on coercivity ($H_c$) and interfacial microstructure in Nd-Fe-B/Nd-rich thin films. All films were deposited by using ultra high vacuum (UHV) magnetron sputtering, and the Nd-Fe-B layer was oxidized under several atmospheres with different oxygen content. Then, the films were annealed at 250-550 °C under UHV. The films oxidized in low vacuum ($10^{-2}$-$10^{-3}$ Pa) (under low oxygen state) exhibited the recovery of $H_c$ by the annealing at 450 °C. On the contrary, the $H_c$ of the films oxidized in Ar (under high oxygen state) decreased with increasing annealing temperature. However, the $H_c$
increased drastically at the temperatures above 550 °C. In addition, the Cu added films, which were annealed at temperatures above 350 °C, showed higher coercivities than the films without Cu addition. The XRD analysis suggested the existence of C-Nd$_2$O$_3$ phase in the Cu added films annealed at 550 °C. It can be considered that the Cu addition decreases the eutectic temperature of Nd-rich phase and influences the interfacial state between Nd$_2$Fe$_{14}$B and Nd-rich phase.

1. Introduction

Nd-Fe-B sintered magnets show excellent magnetic properties and used in a wide variety of applications. In these days, heavy rare-earth elements, such as Dy and Tb, are added to the Nd-Fe-B sintered magnets in order to improve their thermal stability. However, the addition of heavy rare-earth elements decreases their energy products and increases the cost of production of the magnets. Therefore, it is strongly required to improve the coercivity at room temperature with decreasing Dy and Tb content.

It is known that the Nd-rich phase in Nd-Fe-B magnets contains some amounts of oxygen and shows several oxidation states [1-8]. Furthermore, some additional elements improve the magnetic properties of Nd-Fe-B sintered magnets. Fidler et. al. [9] reported that Cu addition improves the coercivity and Cu dissolves in the intergranular region. Sakamoto et. al. [10] reported that the addition of Cu improves both coercivity and squareness, and Cu enriches at the surface of Nd$_2$Fe$_{14}$B grains. Li et. al. [11] showed a thin Cu-rich layer forms along the Nd-rich/Nd$_2$Fe$_{14}$B interface from the 3DAP analysis. Thus, some researchers reported Cu addition enhances coercivity. However, the relationships between the oxidation state of Nd-rich phase and effect of Cu addition are not reported.
In this paper, we investigated the effect of Cu addition on coercivity and microstructure in Nd-Fe-B/Nd-rich thin films with different oxidation state.

2. Experimental Procedure

The films were prepared by using ultra high vacuum (UHV) magnetron sputtering system with base pressure of $10^{-7}$ Pa. Ta buffer layers with the thickness of 14 nm were deposited on MgO(001) single crystal substrates at 200 °C, and Nd-Fe-B layers with the thickness of 100 nm were deposited on Ta buffer layers at 680 °C. Hereafter, these as-deposited Nd-Fe-B films were referred as “Sample A”. The composition of target used for the preparation of Nd-Fe-B layers was $\text{Nd}_{18}\text{Fe}_{66}\text{B}_{16}$. After the deposition of Nd-Fe-B layers, the films were cooled to 35 °C and moved to another chamber containing several amounts of oxygen. In order to oxidize, the films were kept in low vacuum ($10^{-2}$-$10^{-5}$ Pa) (oxidized with low oxygen content) or in Ar gas atmosphere (oxidized with high oxygen content) for 120 min (These films are referred as “Sample B$_{\text{(Vac)}}$ or B$_{\text{(Ar)}}$”, respectively). The films were moved back to the UHV chamber and a 1 nm thick of Cu layer was deposited on oxidized Nd-Fe-B layers (These films were referred as “Sample $B_{\text{(Vac)}}^{\text{Cu}}$ and $B_{\text{(Ar)}}^{\text{Cu}}$”, in showing over layers superscript). Then, the films were annealed at 250-550 °C for 60 min in the UHV chamber (“Sample $C_{\text{(Vac)}}$, $C_{\text{(Vac)}}^{\text{Cu}}$, $C_{\text{(Ar)}}$ or $C_{\text{(Ar)}}^{\text{Cu}}$). Finally, a Ta layer was deposited on the top of all films for suppression of oxidation. The series of samples are summarized in Table 1.
Magnetic properties of films were measured along the direction perpendicular to the plane by vibration sample magnetometer (VSM) after applying a pulsed magnetic field of 6360 kAm\(^{-1}\). The coercivity of samples is evaluated as the ratio of coercivity \(RH_c\), which is defined by the following formula.

\[
RH_c = H_c / H_c(\text{as-depo.}) \times 100
\]  

(1)

Crystalline structure and microstructure were analysed by x-ray diffraction (XRD) and transmission electron microscopy (TEM).

3. Results and Discussion

3.1 Effect of Cu addition on the magnetic properties of films oxidized in low vacuum (under low oxygen state)

Figure 1 shows changes of \(RH_c\) of Samples A, \(B_{(\text{Vac})}\), \(B_{(\text{Vac})\text{Cu}}\), \(B_{(\text{Ar})}\), \(B_{(\text{Ar})\text{Cu}}\), \(C_{(\text{Vac})}\), \(C_{(\text{Vac})\text{Cu}}\), \(C_{(\text{Ar})}\) and \(C_{(\text{Ar})\text{Cu}}\). As shown in figure 1, the Nd-Fe-B films oxidized in low vacuum (Sample \(B_{(\text{Vac})}\)) show \(RH_c\) of 65\%, and their \(RH_c\) values recover to the same value of Sample A after annealing at 450 °C (Sample \(C_{(\text{Vac})}\)). In these samples, we reported that an amorphous phase was observed at the interface between Nd\(_2\)Fe\(_{14}\)B and A-Nd\(_2\)O\(_3\) (hcp Nd\(_2\)O\(_3\)) phases. The amorphous phase seems to remove the influences of oxidation and recover the coercivity [8]. However, the \(RH_c\) values do not show remarkable increase after annealing at 550 °C.

### Table 1 The series of samples studied in this investigation.

| Sample     | Nd-Fe-B layer (nm) | Oxidation state | Cu layer (nm) | Annealing temp. (°C) |
|------------|--------------------|-----------------|---------------|----------------------|
| A          | 100                | ---             | ---           | ---                  |
| B\(_{(\text{Vac})}\) | 100             | Low             | 1             | 250-550              |
| B\(_{(\text{Vac})\text{Cu}}\) | 100             | Low             | 1             | 250-550              |
| B\(_{(\text{Ar})}\) | 100             | High            | ---           | 250-550              |
| B\(_{(\text{Ar})\text{Cu}}\) | 100             | High            | ---           | 250-550              |
| C\(_{(\text{Vac})}\) | 100             | High            | ---           | 250-550              |
| C\(_{(\text{Vac})\text{Cu}}\) | 100             | High            | ---           | 250-550              |
| C\(_{(\text{Ar})}\) | 100             | High            | ---           | 250-550              |
| C\(_{(\text{Ar})\text{Cu}}\) | 100             | High            | ---           | 250-550              |
On the contrary, the $RH_{d,3}$ of film with Cu layer (Sample $C_{(Vac)}^{Cu}$) recovers to the same value of Sample A at 350 °C, which is 100 °C lower than temperature in the case of films without Cu layer. The film also shows a drastic increase in $RH_{d,3}$ by annealing at temperature above 450 °C and the $RH_{d,3}$ reaches to the value around 150% after annealing at 550 °C.

Figure 2 shows the XRD patterns of Sample A, Sample $B_{(Vac)}$ and Sample $C_{(Vac)}$, which were annealed at 350 °C ($C_{(Vac)}(350 °C)$) or 550 °C ($C_{(Vac)}(550 °C)$). In figure 2 (b), the corresponding XRD patterns of films with Cu layer, such as Sample $B_{(Vac)}^{Cu}$ and Sample $C_{(Vac)}^{Cu}$ annealed at 350 °C ($C_{(Vac)}^{Cu}(350 °C)$) or 550 °C ($C_{(Vac)}^{Cu}(550 °C)$) are also shown.
In the Samples B\(_{(\text{Vac})}\) and B\(_{(\text{Vac})}\)\(\text{Cu}\), the XRD peak of fcc NdO\(_x\) is observed. However, the intensity of the peak decreases after annealing at 350 °C. In our previous study [8], we reported that a phase transformation from fcc NdO\(_x\) to A-Nd\(_2\)O\(_3\) occurs and an amorphous phase forms at the interface between Nd\(_3\)Fe\(_{14}\)B and A-Nd\(_2\)O\(_3\) during the annealing at 350 °C. We also reported that the amorphous phase plays an important role for the recovery of coercivity. Comparing figure 2 (a) with figure 2 (b), the phase transformation can be considered to occur in the films with Cu layer (C\(_{(\text{Vac})}\)\(\text{Cu}\) 350 °C)). However, the X-ray intensity of A-Nd\(_2\)O\(_3\) peak in the Sample C\(_{(\text{Vac})}\)\(\text{Cu}\) 350 °C) shown in figure 2 (b) is lower than that of Sample C\(_{(\text{Vac})}\) 350 °C) shown in figure 2 (a). On the contrary, after annealing at 550 °C...
°C, the X-ray intensity of A-Nd₂O₃ peak in the Sample Cₜ(Vac)Cu (550 °C) is higher than that in the Sample Cₜ(Vac) (550 °C). In addition, the (222) peak of C-type Nd₂O₃ phase with space group Ia̅3 and lattice parameter of a=1.107 nm [12] appears in the Sample Cₜ(Vac)Cu (550 °C).

3.2 Effects of Cu addition on the magnetic properties of oxidized films in Ar (under high oxygen state)

Figure 3 shows the annealing temperature dependence of RHₜ of Samples Cₜ(Ar) and Cₜ(Ar)Cu, which were oxidized in Ar (under high oxygen state).

In the as-oxidized films such as Samples Bₜ(Ar) and Bₜ(Ar)Cu, the RHₜ values were around 40%, which are about 20% lower than the values in the case of oxidation in low vacuum. The RHₜ values decrease more 20% by annealing at 250 °C. However, the values increase by annealing at 350-450 °C. From HRTEM observation, the amorphous phase is not observed in these films. These temperature dependences of coercivity are almost the same between the films with and without Cu layer (Samples Cₜ(Ar) and Cₜ(Ar)Cu). After annealing at temperatures above 450 °C, the RHₜ of Samples Cₜ(Ar) and Cₜ(Ar)Cu increase drastically. Furthermore, the remarkable increase in coercivity is observed in the film with Cu
layer (Sample $C_{(Ar)}^{Cu}$) annealed at 550 °C. The $RH_{j}$ values corresponds to the value of Sample $C_{(Vac)}^{Cu}$ shown in figure 1.

The crystalline structure were analysed by XRD and the XRD patterns of Sample A, $B_{(Ar)}^{Cu}$, $C_{(Ar)}$, and $C_{(Ar)}^{Cu}$, which were annealed at 250 °C ($C_{(Ar)}^{Cu}(250 °C)$ and $C_{(Ar)}^{Cu}(250 °C)$), 350 °C ($C_{(Ar)}^{Cu}(350 °C)$ and $C_{(Ar)}^{Cu}(350 °C)$) and 550 °C ($C_{(Ar)}^{Cu}(550 °C)$ and $C_{(Ar)}^{Cu}(550 °C)$), are shown in figure 4. Namely, the XRD patterns of films without or with Cu layer are shown in figure 4 (a) or figure 4 (b), respectively.
In XRD patterns of the Sample B in figure 4 (a) and the Sample B(Cu) in figure 4 (b), the peaks of fcc NdO$_x$(111) are observed. However, the fcc NdO$_x$ peaks disappear and the peaks of A-Nd$_2$O$_3$ (002) are observed after annealing at 250-350 °C, as shown in the Samples C(Ar)(250 °C) and C(Ar)(350 °C) of figure 4 (a) and the Samples C(Ar)(Cu)(250 °C) and C(Ar)(Cu)(350 °C) of figure 4 (b). In comparison with figure 2, as the films oxidized in Ar contain large amount of oxygen, they show higher intensity of A-Nd$_2$O$_3$ peak and lower coercivity. In addition, a obvious difference caused by Cu addition is found by comparing the XRD patterns of Sample C(Ar)(550 °C) in figure 4 (a) and Sample C(Ar)(Cu)(550 °C) in figure 4 (b). After annealing at 550 °C, the peak intensity of A-Nd$_2$O$_3$ is higher in the sample with Cu layer and the remarkable peak of C-Nd$_2$O$_3$(222) is observed.

3.3 Discussion

From the results of this study, it is considered that the effect of Cu addition depends on the oxidation state of films. In the case of films oxidized in low vacuum (under low oxygen state), the decrease in coercivity by oxidation is small and the recovery of coercivity is observed after annealing at low temperatures. The Cu addition is also effective for the decrease in annealing temperature, at which the coercivity can recover. This recovery of coercivity is thought to be caused by the formation of
amorphous phase at the Nd₂Fe₁₄B/Nd-rich interface. Therefore, the Cu addition seems to promote the formation of amorphous phase.

The annealing at high temperature around 550 °C increases coercivity in both films with Cu oxidized in low vacuum and Ar (under low and high oxygen states). In these films, the C-Nd₂O₃ phase is present and the phase has a possibility to be related to the increase in coercivity. Another possibility is the existence of liquid phase, which cleans the surface of Nd₂Fe₁₄B grains to decrease the number of nucleation site of reverse domain. In the Nd-Cu binary phase diagram [13], the eutectic temperature is existed at 520 °C, which is lower than the annealing temperature. Therefore, it is considered that liquid Nd-rich phase appears during annealing at 550 °C and it cleans the surface of Nd₂Fe₁₄B.

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