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Magnetic and structural properties of NdFeB thin film prepared by step annealing

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Abstract

The crystallization of the amorphous phase into the tetragonal $Nd_2Fe_{14}B$ (Φ) phase and the corresponding changes in magnetic properties have been examined by step annealing experiment using a 2 μm thick NdFeB film sample. Microstructural and magnetic analysis indicate that the film was magnetically soft as deposited with the coercivity $H_{ci\perp} < 16$ kA m^{-1} and the remnant magnetization $4\pi M_{r\perp} < 0.02$ T. Annealing at a temperature of 550 °C, a coercivity value around 784 kA m^{-1} was developed and diffraction analysis showed evidence of Φ phase 002*l* peaks being aligned perpendicular to the film plane. At an optimum annealing temperature of 575 °C, the remnant magnetization of this anisotropic thin film is around 0.60 T with intrinsic coercivity of ~1340 kA m^{-1}. Annealing the film sample at 200 °C $\leq T_{ann} \leq$ 750 °C showed variations in magnetic properties that were mostly due to the change in the perpendicular anisotropy. Based on $4\pi M_{s\perp}$ values plotted against T_{ann}, a dip in $4\pi M_{s\perp}$ values was observed as T_{ann} increased in the soft-to-hard magnetic characteristics transition region and rose as the hard crystalline phase started to form. The results show that the magnetic properties of the NdFeB film were slightly influenced by the presence of NdO, film surface roughening and the small increase in crystal size as a consequence of repeated heat treatment. At T_{ann} ~300 °C, the nominal saturation magnetization indicated a certain degree of weak perpendicular magnetic anisotropy in the film sample considered to be essential in the enhancement of coercivity in crystallized films.

Keywords: RF sputtering; Anisotropic NdFeB thin film; Vacuum annealing; High coercivity

1. Introduction

The magnetic and structural properties of NdFeB thin films represent a subject of growing scientific interest because of the wide range of applications particularly that of anisotropic and high coercivity permanent magnet materials. The motivation for these investigations has come from the potential use of NdFeB thin film permanent magnet for micro-mechanical systems [1], micro-electronics and micro-magnetic devices [2].

In this paper, we will report on the crystallization behavior of an NdFeB thin film showing the transformation of the magnetic properties in the soft-to-hard magnetic characteristics transition region. In bulk permanent magnet materials, the effect of heat treatments on the hard magnetic properties has been extensively investigated particularly by post sintering heat treatments [3]. The primary effect of heat treatment on permanent magnet materials is on the microstructure, which in turn influences the coercivity. Previously,

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we found that using the typical method of annealing under optimum conditions, film sample of high coercivity characterized by the growth of magnetic grains with the *c*-axis oriented along the film normal is easily produced from as-deposited films [4]. The same kind of as-deposited film sample used in the previous experiment was used in this study.

The motivation of this investigation is based on a challenge to analyze information on the behavior of the magnetic and structural properties of an NdFeB film sample in each stage of the step annealing experiment.

2. Experimental procedure

In this experiment, as-deposited NdFeB film sample prepared by RF sputtering was annealed repeatedly in vacuum at 200 °C $\leq T_{ann} \leq$ 750 °C as depicted in Fig. 1. Each annealing step was done for 30 min after which magnetic and structural characterization was done on the film. The concept of step annealing experiment is related to the idea of post sintering experiments in bulk permanent magnet materials [3]. Improvement of magnetic properties depends on the temperature and duration of heat treatment, which are related directly to the grain growth mechanisms. The thin film form of NdFeB permanent magnet material may exhibit nearly similar magnetic properties compared with the bulk form. It is for this reason that the behavior of its magnetic properties may respond similarly to some of the processing methods in bulk materials like thermal annealing.

The 2 μm film sample was deposited on a 0.1 mm Mo substrate using Nd, B rich and Fe poor target with composition $Nd_{20}Fe_{64}B_{16}$ compared with the stoichiometric composition $Nd_{12}Fe_{82}B_6$. A thin Ti coating with thickness around 700 Å was deposited in order to minimize oxidation on the surface of the NdFeB film. Sputtering deposition power used was 350 W with a deposition rate of around 260 Å min^{-1} in a constant supply of Argon gas at a vacuum pressure of 6.7×10^{-1} Pa. The substrate is thermally insulated from the water-cooled substrate holder with a 1.0 mm glass and held at a substrate-target distance of 5.0 cm. The purpose of the glass insulation between the Mo substrate and the copper holder is to obtain weak perpendicular anisotropy in the as deposited film as reported in [4]. Diffraction patterns of the film sample were analyzed by an X-ray diffractometer (Philips X'pert-MPD) using Cu–Kα radiation. Minor hysteresis loops were plotted using a vibrating sample magnetometer (VSM) with a maximum applied field of 1600 kA m^{-1}, which is not enough to record the full hysteresis loops of crystallized films.

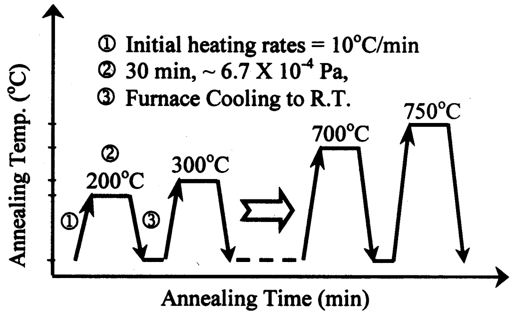

Fig. 1. Schematic diagram of the step annealing procedure performed on the film sample.

3. Results and discussion

3.1. X-ray diffraction patterns

Fig. 2 shows XRD patterns of the initial heat treatments up to T_{ann} = 500 °C indicating that the

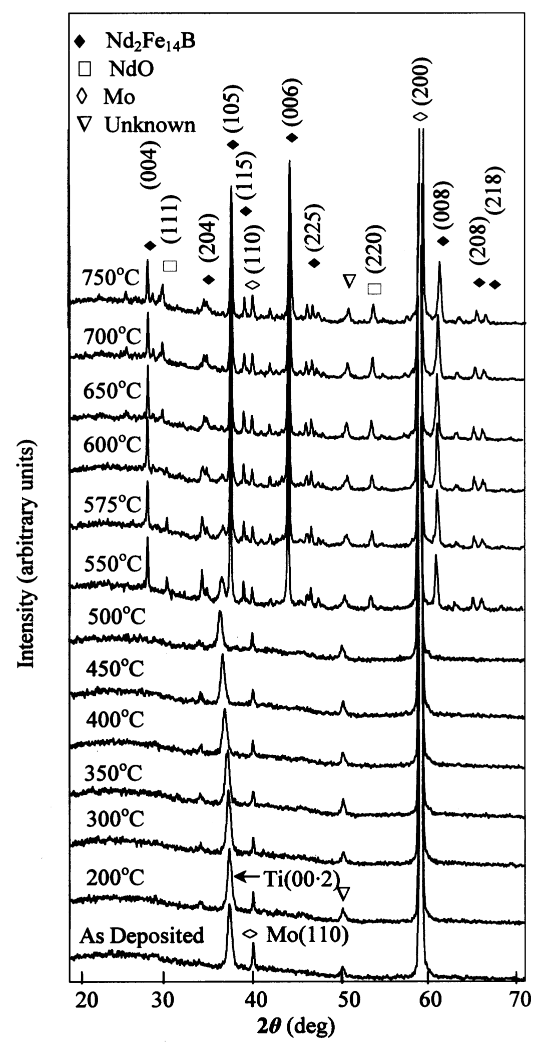

Fig. 2. X-ray diffraction patterns of annealed film plotted in increasing order of the annealing temperature.

film remains in its amorphous structure. The patterns exhibit broad halo pattern suggesting existence of an amorphous phase with a prominent Ti 00•2 peak from the surface coating material and other peaks from the Mo substrate. It also shows a small broadening and slight line shift towards smaller 2θ of the Ti 00•2 peak reflection. It can be attributed to the presence of a non-uniform strain in the amorphous film. Annealing at $T_{ann} \geq 550$ °C, the film undergoes a structural transformation to Φ phase as the major component with distinct preferential alignment of the magnetically easy direction (tetragonal c axes) normal to the film plane. It can also be observed that the diffraction patterns of the film annealed at higher temperatures ≥650 °C showed the existence of some neodymium oxide. Similar observations were made by Gasgnier et al. [5].

A good estimate of the onset of crystallization of the sample in this experiment can be based on a plot of compositional dependence of crystallization temperature of NdFeB glasses formed by melt spinning which may take place at around 550 °C [6]. Optimum vacuum annealing conditions in our previous experiment give us the best possible magnetic properties at 650 °C for 30 min [4,9]. And in fact, enhanced coercivities in sintered and melt spun NdFeB magnets are attained after heat treatment at around 650 °C [7].

The gradual discoloration of the reflecting surface of the as-deposited film to a faded surface after the entire annealing process was also observed. It can be considered to be a change in the surface roughness of the film, which resulted from the formation of Φ phase during crystallization wherein the c-axis is oriented along the film normal. Usually, randomly oriented film is characterized by a shiny flat surface.

The sharp peaks of the polycrystalline film show the good crystalline quality composed of magnetic grains with diameters between 433 and 454 Å estimated by X-ray line broadening analysis [8] using the Φ phase 006 peak. Considering that some of the individual grains in film material are under non-uniform strain, this estimation is still subject to further experiments. At present, accurate determination of the origin of the observed broadening needs to be confirmed. In contrast with cast materials, the crystal size indicated a small increase during annealing up to $T_{ann} = 750$ °C. These results may have specific influence on the magnetic property of the film sample.

3.2. Magnetic hysteresis loops

Fig. 3 shows the magnetic hysteresis loops measured at room temperature with applied field normal and parallel to the film plane of as deposited film in the stages of step annealing at 200 °C ≤ T_{ann} ≤ 750 °C. For $T_{ann} < 550$ °C, M–H loops are quite similar and indicate soft magnetic properties with coercivities less

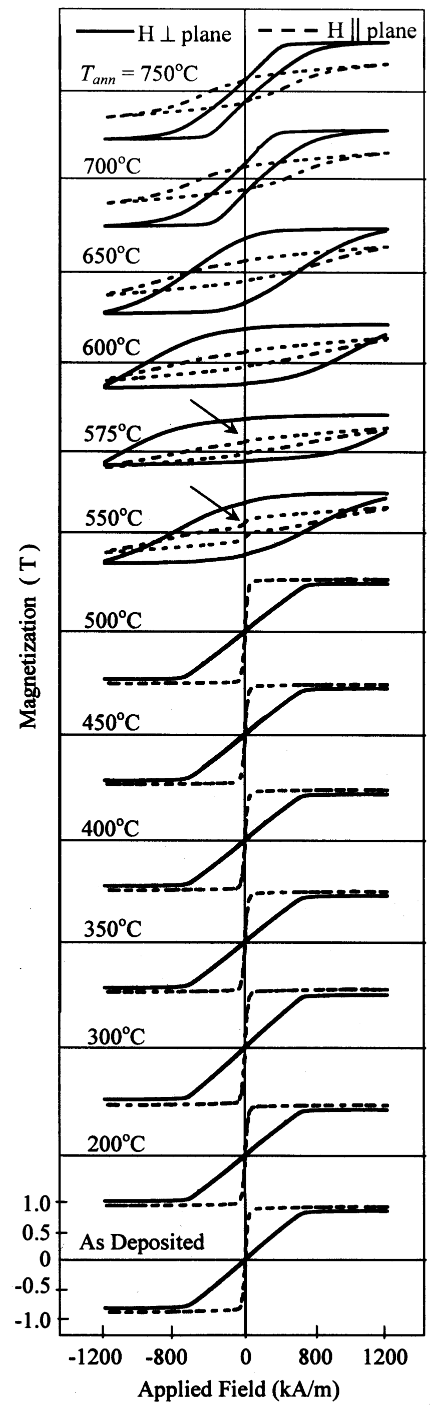

Fig. 3. Room temperature hysteresis loops as measured perpendicular to plane and in-plane parallel to the maximum applied field of 1600 kA m^{-1}.

than 16 kA m^{-1}. No significant difference in coercivity and magnetization values was observed. On the other hand, magnetic properties of films annealed at $T_{ann} \geq 550$ °C varied significantly with the coercivity values $(H_{ci\perp}) = 132–1340$ kA m^{-1} and $4\pi M_{r\perp} = 0.2–0.6$ T.

Minor hysteresis loops of the films measured with applied field parallel and perpendicular to the film plane

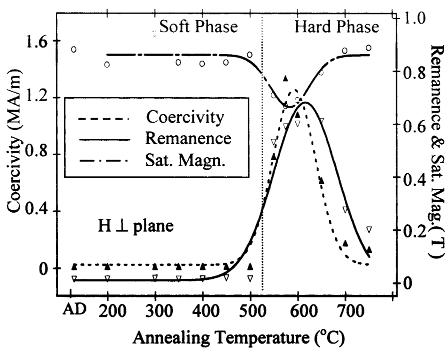

Fig. 4. Annealing temperature dependence of the coercivity, remnant magnetization and saturation magnetization measured with applied field perpendicular to the film plane. The data points were curve fitted to aid visual analysis only.

revealed the presence of the soft and hard phase in the film before and after crystallization at around 550 °C, respectively. The magnetically soft phase present in the film annealed at $T_{ann} \leq 500$ °C showed weak perpendicular anisotropy that was deduced from the saturation magnetic field of the hysteresis curves [9].

Fig. 4 is a summary of the magnetic properties plotted in Fig. 3. It shows the dependence of coercivity (H_{ci}), remanent magnetization ($4\pi M_{r\perp}$) and saturation magnetization ($4\pi M_{s\perp}$) on the annealing temperature. The data points were approximately curve fitted but the minimum and maximum peaks in the curves do not necessarily coincide with the low and high data points of the magnetic properties. These H_{ci}, $4\pi M_{r\perp}$ and $4\pi M_{s\perp}$ values were obtained from the minor hysteresis loops measured with a maximum applied field (H) of 1600 kA m^{-1} perpendicular to the film plane.

Dependence of $4\pi M_{s\perp}$ on T_{ann} is almost constant up to 500 °C. For $T_{ann} > 500$ °C, $4\pi M_{s\perp}$ decreases as a consequence of the formation of the crystalline phase with higher coercivity. Since the crystalline Φ phase is thought to be completely formed at $T_{ann} = 575$ °C, $4\pi M_{s\perp}$ value is at a minimum around 0.67 T while coercivity is at a maximum value of 1340 kA m^{-1} maintaining the high energy density of the film at this annealing temperature. Increasing T_{ann} further, a different behavior is observed where both H_{ci} and $4\pi M_{r\perp}$ decrease together with the increase in $4\pi M_{s\perp}$. In this transition region, a dip in the $4\pi M_{s\perp}$ plot is evidently indicating transformation of the soft magnetic phase to the hard magnetic phase. It is in this transition region that change in crystal structure occurs and brings a corresponding change in the magnetization of the film sample. Around 550 °C of annealing temperature, soft amorphous phase was brought to either partial or full crystalline state associated with the increase in H_{ci}. Therefore, the combination of soft and hard phases in the film resulted to changes in the perpendicular magnetic anisotropy. This behavior has been previously obtained on permanent magnet materials without rare earths [10,11]. Gu et al. demonstrated similar results on a series of sputtered NdFeB thin films annealed at 550 °C $\leq T_{ann} \leq$ 850 °C [12].

At the onset of crystallization (500 °C $\leq T_{ann} \leq$ 550 °C), existence of a soft magnetic phase is indicated by a small bend which is pointed by an arrow in Fig. 3, in the magnetization curve of the in-plane hysteresis loop around $H = 0$ kA m^{-1}. In-plane loops of films annealed at $T_{ann} = 550$ °C and 575 °C, are shown indicating presence of small amount of soft magnetic phase. Above $T_{ann} = 575$ °C, no more evidence of the existence of soft magnetic phase like an amorphous phase or Fe is observed. Behavior of the $4\pi M_{s\perp}$ curve at $T_{ann} \geq 550$ °C, shows that the only ferromagnetic phase with Curie temperature (T_c) higher than room temperature is the Φ phase. Saturation magnetization of as deposited film is nearly equal to the saturation magnetization measured after annealing at $T_{ann} > 700$ °C.

Fig. 5 shows the dependence of the nominal saturation points (M_{NS}) on the annealing temperature. M_{NS} is assumed to be a point where the rotation of the magnetic moments commences towards the direction of the applied field, which will eventually lead to saturation [9]. Amorphous films prepared at 340 °C by Lileev et al. [13] were found to have weak perpendicular anisotropy, which led to high coercivity after thermal annealing. At temperatures below 340 °C, isotropic and lower coercivity films were produced. Deposition at temperatures above 340 °C resulted in anisotropic and low coercivity films. These amorphous films prepared on heated substrates at 340 °C may have acquired the right amount of ferromagnetic substructure characterized by weak perpendicular anisotropy, which contributed to the enhancement of coercivity in the film sample after thermal annealing.

The curve in Fig. 5 is plotted as a measure of weak perpendicular anisotropy in the film in each annealing step. M_{NS} varied as a consequence of accumulated heat treatment showing a peak at 300 °C.

The peak suggests that a sufficient amount of ferromagnetic substructure is also present and ready to

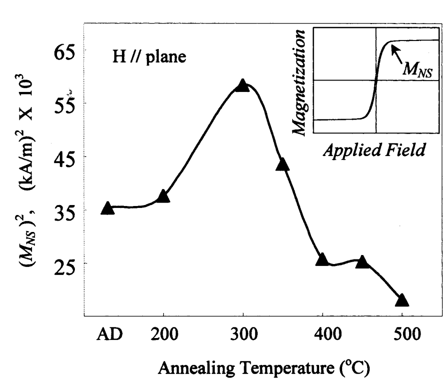

Fig. 5. Dependence of nominal saturation field (M_{NS}) on the annealing temperature (T_{ann}).

be transformed to Φ phase if annealed at optimum conditions. Below 300 °C, the start of the formation of the substructure can be estimated by the extent of nominal saturation value in the figure. Step annealing at temperatures higher than 300 °C, M_{NS} decreased corresponding to the reduction of weak perpendicular anisotropy and less possibility of getting high coercivity if annealed under optimum conditions. The correlation of these data and those from [13], is justifiable because of the fact that in previous experiments [4,9] higher M_{NS} value is desired for the as-deposited films. Although there is slight difference in processing routes, the effect of temperature that focused on the internal structure of amorphous phase turned out to be remarkably interesting based on the aforementioned findings. It is, therefore, worthy to note that amorphous films can be prepared under specific conditions for the purpose of reproducing thermally crystallized NdFeB films with excellent magnetic properties.

As a final point, the optimum properties of this ferromagnetic thin film depend on the extent of heat treatment. Since the film sample possesses both the crystallographic texture and perpendicular anisotropy, it is reasonably preferable to simultaneously control both during heat treatment to obtain a perpendicularly oriented and high energy product thin film material.

4. Conclusions

We have demonstrated the effect of successive vacuum annealing of as-deposited NdFeB film sample at 200 °C $\leq T_{ann} \leq$ 750 °C. The transformation of the soft amorphous phase to the hard magnetic phase is carried out through a crystallization process characterized by a significant change in the structural and magnetic properties of the film. The results showed the crystallization behavior of the film with an optimum $T_{ann} \sim 575$ °C from which H_{ci} and $4\pi M_{s\perp}$ are nearly of optimal value. Magnetization varied considerably according to the material phase developed while T_{ann} is increased. H_{ci} and $4\pi M_{r\perp}$ varied significantly with respect to the change in T_{ann} from 550 to 750 °C, which can be attributed to the changes in the microstructure of the film. On the other hand, $4\pi M_{s\perp}$ appears to be constant except for a dip during the soft-to-hard phase transition region where a change in the crystal structure occurred. The step annealing technique provided valuable information on the behavior of an NdFeB thin film under different annealing temperature conditions. Of particular interest are the properties of the amorphous phase, which show signs of perpendicular anisotropy based on the nominal saturation magnetization. The findings in this work are very important in an effort to finally establish a correlation between the magnetic properties of amorphous and crystallized film.

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