Compositional Separation in Co–Cr Based Alloy Films

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Using $^{59}$Co nuclear magnetic resonance and a chemical etching technique, we observed that compositional separation which produces highly Co-rich precipitates occurs in (1) a Co–Cr film which exhibited ultra-high bit density in perpendicular magnetic recording and (2) Co–Cr–X (X = Ta, Pt, Ni) films for longitudinal magnetic recording. It is expected that this kind of separation will enable the compositional microstructure of Co–Cr based alloy films to be changed from a homogeneous structure to a particulate one suitable for either perpendicular or longitudinal high-density recording.

**Key words:** Co–Cr based alloy films, compositional separation, magnetic recording media, nuclear magnetic resonance

1. Introduction

The ultra-high bit density has been realized in perpendicular magnetic recording. This high bit density, which is on the order of 500–680 kFRPI (Flux Reversals Per Inch)$^{11}$, is believed to be primarily due to the existence of a particulate microstructure exhibiting a rotational magnetization reversal in Co–Cr films$^{9}$. In this microstructure, the ferromagnetic regions in the films need to be isolated from each other. In the thin films used in longitudinal magnetic recording, the isolation of the magnetic regions is also considered to be effective in reducing media noise$^9$. Thus, the isolation is an important issue in high-density recording thin films. In this study, we focus on compositional separation in Co–Cr based alloy films, which is thought to be effective in achieving the isolation.

2. Compositional Separation

It has been observed that compositional separation (CS) into Co-rich and Cr-rich components occurs in Co–Cr films with perpendicular magnetic anisotropy when the substrate temperature is increased$^{4,9}$. The CS was observed as a result of the precipitation of a highly Co-rich component, which was detected using thermomagnetic analysis$^{5,7}$, Mössbauer spectroscopy$^{6}$, and nuclear magnetic resonance (NMR)$^{8,9}$. The compositionally separated microstructures, which are referred to as chrysanthemum-like pattern or CP structures, were revealed by chemical etching$^6$. A TEM micrograph of one of these microstructures is shown in Fig. 1. The white stripes in Fig. 1 are thought to correspond to the preferentially dissolved Co-rich regions as a result of passivation occurring at Cr-rich regions$^{10}$.

It is expected that the CS will produce a particulate microstructure suitable for high-density recording. It is worth mentioning that even in longitudinal media, various Co–Cr based alloy films are currently being studied. However, only a few studies$^{11,12}$ have been made from a material point of view to examine the possible occurrence of CS in Co–Cr based alloy films being used for read/write experiments.

In this study, we used NMR and a chemical

![Fig. 1 TEM micrograph of a chemically-etched Co$_{65}$Cr$_{18}$ film (CP structure).](image-url)
etching technique to investigate the possible occurrence of CS in (1) a Co-Cr film which exhibited ultra-high bit density in perpendicular recording\(^6\) and (2) Co-Cr-X (X = Ta, Pt, Ni) films for longitudinal recording.

3. Experimental Procedure

One of the films used in the experiment was an rf-sputtered 100 nm-thick Co\(_{80}\)Cr\(_{20}\) (at\%)/500 nm-thick Permalloy film deposited on a polycrystalline substrate at a substrate temperature of 190°C. The film exhibited a reproduced highest bit density of 680 kFRPI in perpendicular recording\(^7\). The other were 50 nm-thick Co-Cr-X/200 nm-thick Cr films deposited on polycrystalline substrates using an inline dc magnetron sputtering system\(^1\). The Co-Cr-X films were (1) Co\(_{80}\)Cr\(_{12}\)Ta\(_2\), (2) Co\(_{74}\)Cr\(_{13}\)Pt\(_9\), and (3) Co\(_{82}\)Cr\(_{12}\)Ni\(_{38}\) (at\%). The substrate temperature, \(T_s\), defined as the pre-heated substrate temperature prior to film deposition, was set at both 25°C and 150°C.

Spin echo \(^{59}\)Co NMR measurement\(^8,9\) was performed in a zero external field at 4.2K. Powdered samples of an annealed Co\(_{81}\)Cr\(_{19}\) alloy and annealed Co-Cr-Ta, Co-Cr-Pt and Co-Cr-Ni alloys with the same composition as those of the films were prepared as compositionally homogeneous samples. In addition, rf-sputtered Co\(_{80}\)Pt\(_{10}\) and Co\(_{80}\)Ni\(_{35}\) (at\%) films were prepared at substrate temperatures of 40°C and 200°C as samples without the element of Cr. TEM observation of the compositional microstructures of the films was performed using a chemical etching technique similar to that described elsewhere\(^6\).

4. Results and Discussion

4.1 Co-Cr film for perpendicular recording

Figure 2 shows the NMR spectra of (a) the Co-Cr film and (b) the Co\(_{81}\)Cr\(_{19}\) bulk alloy. Though the bulk alloy as a compositionally homogeneous sample showed a broad spectrum with a maximum below 100 MHz, the film spectrum exhibited a strong peak around 215 MHz, indicating the existence of a highly Co-rich component, *i.e.*, the CS occurred; the Co content of the component is estimated to be about 94 ± 1 at\% according to the relation curve between Co content and peak frequency\(^9\).

Figure 3 shows a TEM micrograph of the chemically-etched structure of the film. The bit density of 680 kFRPI corresponds to a bit size of about 40 nm, which is comparable to a grain diameter. A clear-defined CP structure is observable and there is no strong grain boundary Cr segregation. It is inferred that a Co-rich wall-like structure\(^6\) within grains is effective in producing a particulate microstructure suitable for recording bits as small as grains.

4.2 Co-Cr-X films for longitudinal recording

Figure 4 shows the NMR spectra of (a) the Co-Cr-Ta, (b) the Co-Cr-Pt and (c) the Co-Cr-Ni films at \(T_s\) of both 25°C and 150°C. The figure also shows the NMR spectra of the bulk alloys as compositionally homogeneous sam-

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Fig. 2 NMR spectra of (a) Co\(_{80}\)Cr\(_{20}\) film and (b) Co\(_{81}\)Cr\(_{19}\) bulk alloy. The contribution of the Permalloy underlayer was subtracted in (a).

Fig. 3 TEM micrograph of a chemically-etched Co\(_{80}\)Cr\(_{20}\) film.
Fig. 4 NMR spectra of (a) Co–Cr–Ta, (b) Co–Cr–Pt and (c) Co–Cr–Ni films at $T_s = 25^\circ $C and 150$^\circ $C. The spectra in the bottom frames are those of bulk alloys.

Samples in the bottom frames. In all the Co–Cr–X films, it is observed that as $T_s$ is increased from 25$^\circ $C to 150$^\circ $C, the intensity of the peak around 200–220 MHz becomes stronger, indicating the precipitation of a highly Cr-rich component, i.e., the CS occurred. For example, although the Co–Cr–Ta film at $T_s = 25^\circ $C showed a broad spectrum similar to that of the bulk alloy, it is clear that the echo intensity around 205 MHz became stronger. At $T_s = 150^\circ $C, the intensity increased dramatically and the spectrum became similar to that of a highly Cr-rich alloy such as a Co$_{90}$Cr$_5$ bulk alloy.

We then examined the possible occurrence of the CS in Co alloy films without the element of Cr. Figure 5 shows the NMR spectra of (a) Co$_{90}$Pt$_{10}$ and (b) Co$_{90}$Ni$_{15}$ films deposited at substrate temperatures of 40$^\circ $C and 200$^\circ $C. Neither film showed any drastic spectrum change as the substrate temperature was increased, which suggested that the CS did not occur. Thus, it can be concluded that the element of Cr is effective in causing CS.

Recently, Suzuki et al.$^{12}$ succeeded in using SEM to observe chemically-etched structures in Co–Cr–Pt films. Figure 6 shows TEM micrographs of the chemically-etched structures in (a) the Co–Cr–Ta and (b) the Co–Cr–Ni films at $T_s = 150^\circ $C. The both films showed a chemically-etched structure which suggests a slight Cr segregation at grain boundaries (as indicated by the arrows in the figures) and in-grain compositional separation. Taking into account of the fact that no grain boundary Cr segregation has been observed in Co–Cr bulk alloys$^4$ and that grain boundaries have remained Cr-rich throughout the CS process$^4$, the possibility that the CS enhances Cr segregation to grain boundaries cannot be discounted.

One possible origin of CS is a two-phase separation occurring as a result of magnetic effects, which would hardly occur at all in a bulk state due to sluggish diffusion$^9$. The CS inherently produces highly Cr-rich precipitates surrounded by nonmagnetic or weakly ferromagnetic Co-poor regions and probably enhances Cr-enrichment at grain boundaries. As the CS proceeds, the microstructural change would increase wall-pinning and eventually form a particulate structure. The increase in coercivity which occurs as $T_s$ is increased (see Fig. 4), may be due to this increase in wall pinning. The authors$^{11}$ observed that media noise in Co–Cr–Ta/Cr films tended to decrease as $T_s$ was increased. This tendency was recently confirmed by Lu et al.$^{15}$, who attributed the origin to a weakening of the intergranular exchange coupling.

Although the relationship between CS and read/write characteristics has just begun to be

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References


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5. Summary

Using NMR and a chemical etching method, it was observed that compositional separation uniformly occurred in Co–Cr based alloy films such as a Co–Cr film for ultra-high bit density perpendicular recording and Co–Cr–X (X=Ta, Pt, Ni) films for longitudinal recording. The element of Cr is effective in causing the compositional separation. As the compositional separation inherently produces highly Co-rich precipitates, it is expected that the separation will enable the microstructure of Co–Cr based alloy films to be changed from a homogeneous structure to a particulate one suitable for either perpendicular or longitudinal high-density recording.