Study on the Surface Oxidation of Co-Cr Films (Co-Cr合金膜の表面酸化に関する研究)

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STUDY ON THE SURFACE OXIDATION OF Co-Cr FILMS

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Abstract-The tribological properties of a Co-Cr thin film were greatly improved by surface oxidation. Accord -ing to surface analyses, it was found that a Cr-rich oxidized region in which Cr is oxidized to Cr_2O_3 was formed near the surface of the film by the above treat-ment. This Cr-rich oxidized region mainly composed of Cr_2O_3 plays an important role in improving its tribolo-gical properties.

INTRODUCTION

It is essential to improve the mechanical durability of a Co-Cr perpendicular recording medium for practical use. Recently, surface oxidation treatment of a Co-Cr tape was proposed to improve its tribological proper-ties, such as friction coefficient and still life [1]. However, there was little knowledge on the mechanism of the improvement of the tribological properties by the above treatment. In this report, we will discuss the mechanisms of the surface oxidation of the Co-Cr film and the improvement of the tribological properties.

EXPERIMENTAL PROCEDURE

Samples were prepared by a vacuum evaporation method. Substrates used in this experiment were polyimide films. They were first baked in a vacuum ($1x10^{-5}$Torr) and then Co-Cr were deposited upon them. Substrate tem -perature and pressure in the chamber during deposition were about 150C and $1x10^{-6}$Torr, respectively. Surface oxidation of the Co-Cr films were performed in the at-mosphere. The tribological properties of Co-Cr films were evaluated by a sliding test in which a steel ball slider (1/4 inch in diameter) pressed on the films slides on it repeatedly. The load applied to the slider was 5 gf, and average sliding velocity was 2 m/min.

RESULTS AND DISCUSSION

The structures of surface-oxidized Co-Cr films

Table 1 shows the dependence of the durabilities of Co -Cr films on the conditions of surface oxidation. In the case of an as-prepared film,severe wear was observed on its surface just after a steel ball began to slide on it. On the other hand, its durability remarkably im -proved by the surface oxidation at high temperature.

Table 1 The durability of surface-oxidized Co-Cr films

Temperature (C)	Time (sec.)	Durability (passes)
25	—	1
200	40	100 - 2000
250	40	800 - 2300
300	40	3500 - 10000
300	20	3500 - 8500
300	40	3500 - 10000
300	60	3500 - 10000
300	90	5000
sputtered carbon film (20 nm)		3500 - 10000

In particular, when the temperature of surface oxida-tion was set at 300C, the durability reached 3500 - 10000 passes, which was comparable to that of 20 nm thick sputtered carbon protective layer. It can be also recognized that the durability already reaches maximum value even when oxidation period is relatively short. As mentioned above, surface oxidation treatment greatly improves the anti-wear properties of Co-Cr films. In order to investigate the cause of this improvement, we performed AES to analyze compositional depth profiles of surface oxidized Co-Cr films. The results are shown in Fig.1. According to these results, it is found that oxygen penetrates into the film and a high Cr ratio(Cr /(Co+Cr)) region is formed near the surface by the surface oxidation. Comparing these results with those in Table 1, it can be recognized that high durability can be realized by existence of the high Cr ratio region near the surface. Fig.2 shows XPS depth profiles of an as-prepared Co-Cr film(Cr content:27at.%) and its surface-oxidized one (315C, 30sec.). In the case of the as-prepared one, only Cr is partially oxidized to Cr_2O_3 although Co remains at metallic state. On the other hand, in the case of the surface oxidized one, Co and Cr is oxidized to CoO and Cr_2O_3 at the surface, re-spectively. At depth of 5 nm, Cr is still oxidized to Cr_2O_3 although Co is almost metallic. At depth of 10nm, both Co and Cr become metallic. Reffering to the peak intensities of Co and Cr, Cr_2O_3 peak is relatively stronger than that of Co in the depth of 1 - 5 nm. This region corresponds to the high Cr ratio region observed in the AES analyses, in which Cr is almost oxidized to Cr_2O_3. Judging from these results, the surface-oxidized Co-Cr film is different from the as-prepared one as follows. First is that Co near the surface is almost oxidized to CoO. Second is that a relatively Cr-rich oxidized region in which Cr is oxidized to Cr_2O_3 are formed just below the film surface. It is considered that these two defferences made the surface-oxidized Co-Cr film to be durable. As will be discussed later,

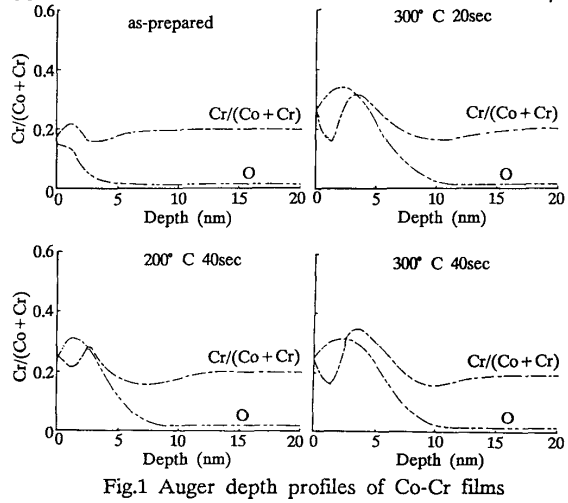

Fig.1 Auger depth profiles of Co-Cr films

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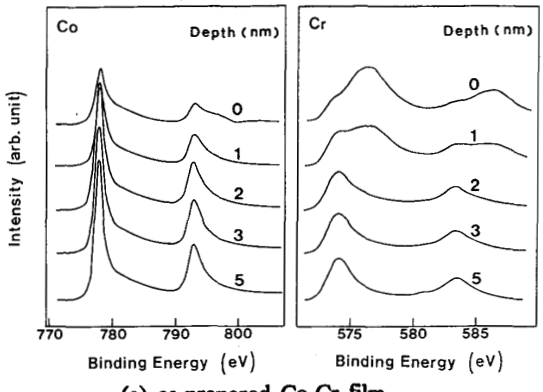
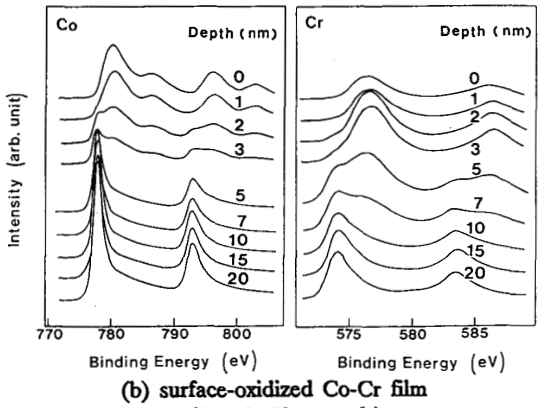
existence of the relatively Cr-rich oxidized region is especially important to improve the durability of the Co-Cr film.

The mechanism of the surface oxidation of Co-Cr films

In this section, we will discuss the mechanism of the surface oxidation of Co-Cr films. When a Co-Cr film is oxidized, an apparent triple layer structure is formed, in which relatively Co-rich oxidized region, Cr-rich oxidized region and Co-Cr alloy region are successively formed from the surface to the substrate as can be seen in Figs.1 and 2. It can be explained by Wood's theory on high temperature oxidation of alloys why such a structure was formed by oxidation [3]. At first, since a Co-Cr film is oxidized in the atmosphere in this experiment, the partial pressure of oxygen is far beyond the equilibrium dissociation pressure of Co and Cr oxides [4]. So, at the initial stage of oxidation, Co and Cr at the film surface are rapidly oxidized to CoO and Cr_2O_3 as shown in Fig. 3(a). At the next stage, since oxygen pressure in Co oxide is higher than the equilibrium dissociation pressure of Cr oxide, metallic Cr existing on the border of Co oxide and Co-Cr alloy are preferably oxidized. At the same time, since the diffusion constant of Co is rather larger than that of Cr in the oxides, Co easily diffuse outward and become the oxide by combining with oxygen at the surface (Fig. 3(b))[5][6]. When oxidation is carried out more intensively, Co-rich oxidized region,Cr-rich oxidized region and Co-Cr alloy region are successively formed from the top to the bottom.



(a) as-prepared Co-Cr film



(b) surface-oxidized Co-Cr film
(315 C, 30 seconds)

Fig.2 XPS depth profiles of Co-Cr films

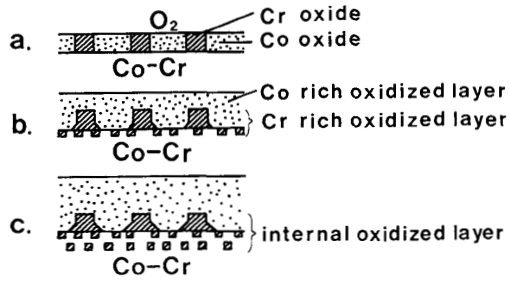


Fig.3 The mechanism of surface-oxidation

Influence of Cr-rich oxidized region on the tribologi -cal properties of Co-Cr films

As mentioned above, it is considered that existence of the Cr-rich oxidized region near the surface remarkably influenced the durability of a Co-Cr film. In this section, we will examine the above speculation experimentally. Fig.4 shows the dependenceof the mechanical durability of surface-oxidized Co-Cr films on their Cr contents. Two samples were used in this experiment. One is a Cr-rich Co-Cr film (Cr content:27 at.%), the other is a Co-rich one(Cr:15at.%). They were surface-oxidized at 315C for 30 seconds. In this experiment,load applied to a steel-ball slider was increased from 5 g to 10 g since a surface-oxidized Co-Cr film is very durable. As can be seen in this figure, the friction coefficient of the Cr-rich one is more stable than that of the Co-rich one. Figs. 5(a) and (b) are the photographs of their surfaces after the durability tests. In the case of the Cr-rich one, any damage cannot be found on its surface after 5000 passes. On the other hand, severe damage was found in the Co-rich one even after 500 passes. Fig.6 is their compositional depth profiles measured by AES. It can be recognized that a region of high Cr ratio of 0.4 is formed near the surface of the Cr-rich film by oxidation. As mentioned above, the more the Cr content of a Co-Cr film increases, the more the durability of its surface oxidized one improves because of the existence of the Cr-rich oxidized region near the surface. This result indicates that the existence of the Cr-rich oxidized region plays an impor-

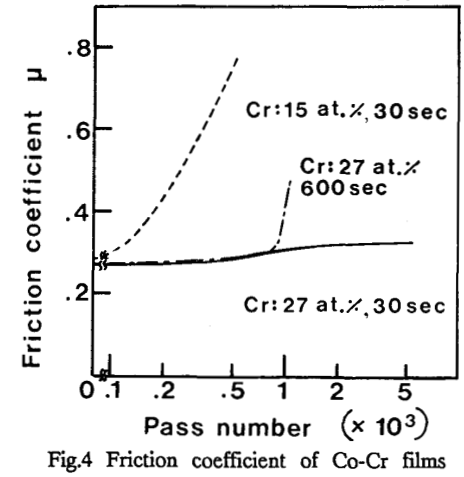
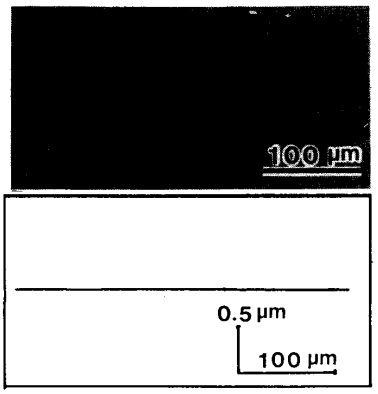
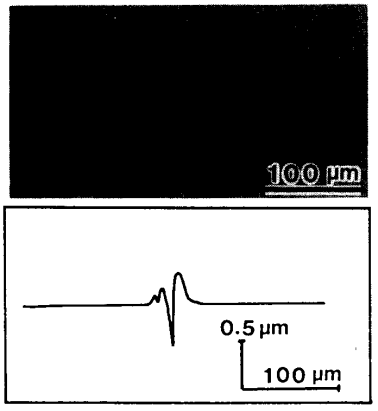


Fig.4 Friction coefficient of Co-Cr films



(a) Surface-oxidized Cr-rich film (27 at.%) after 5000 passes



(b) Surface-oxidized Co-rich film (15 at.%) after 500 passes

Fig.5 Co-Cr surfaces after durability test

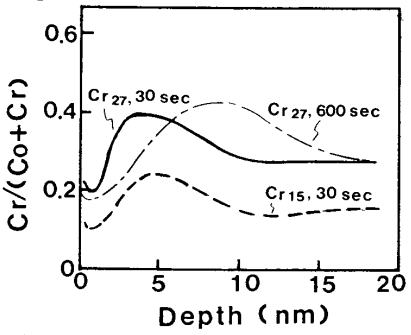


Fig.6 Auger depth profiles of Co-Cr films

tant role in improving the durability.

Next,we investigated the influence of oxidation period on the durability. The results are shown in Figs.4 and 7. When the Co-Cr film (Cr:27at.%) was oxidized for 600 seconds, its durability noticeably deteriorated compared with that of short-period oxidation (30 sec.). Fig.6 also shows the AES depth profiles of these samples. As predicted by Wood's theory, it is found that the thickness of a Co-rich oxidized region on a Cr -rich region becomes thick as oxidation proceeds too much. According to these results, the Cr-rich oxidized

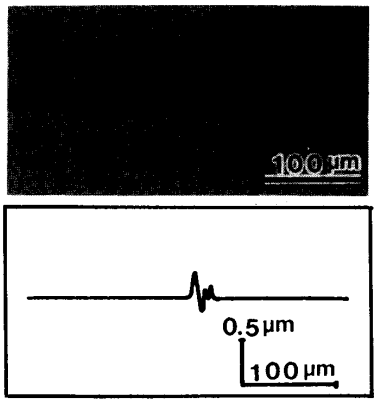


Fig.7 Co-Cr surface after durability test

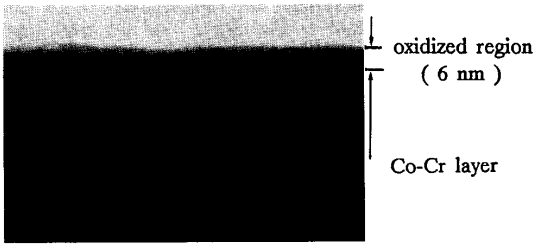


Fig.8 Cross-sectional TEM image of a surface-oxidized Co-Cr film

region should exist near the surface to improve the durability. Fig.8 is the cross-sectional TEM micrograph of the Co-Cr film which was oxidized at 315 C for 30 seconds. It can be seen that very thin (6 nm) oxidized region is formed at the surface, and this corresponds to the oxidized region formed by outward diffusion of Co and Cr.

As mentioned above,a Cr-rich oxidized region composed of Cr_2O_3 is formed near the surface by the surface oxidation of a Co-Cr film. Such a region plays an important role in improving the mechanical durability of the film. However, when the oxidation is carried out for a long time, a Co-rich oxidized region grows thick on a Cr-rich oxidized one. As a result, the durability again deteriorates.

REFERENCES

[1] K.Honda,R.Sugita and Y.Sakamoto, "Surface oxidation of Co-Cr evaporated films", IEEE Trans. Magn., Vol.24, pp.2664-2666, 1988.

[2] M.Futamoto, Y.Honda, H.Kakibayashi,T.Shimotsu and Y.Uesaka, "Microstructure of CoCr thin films prepared by sputtering", Jpn. J. Appl. Phys., Vol.24, pp.L460-462, 1985.

[3] G.C.Wood,"High-temperature oxidation of alloys ", Oxid. Metals, Vol.2, pp.11-57, 1970.

[4] K.Nii, " High-temperature oxidation of alloys ", Boushoku Gijutsu, Vol.26, pp.389-400, 1977.

[5] M.G.C.Cox, B.McEnaney and V.D.Scott, " A chemical diffusion model for partitioning of transition elements in oxide scales on alloys", Phils. Mag., Vol.26, pp.839 -851, 1972.

[6] P.Kofstad,"Nonstoichiometry, diffusion and electrical conductivity in binary metal oxides", Wiley Interscience, 1972.