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Magnetic properties of immiscible Co–Ag and Ni–Ag thin films prepared by co-sputtering

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Magnetic properties of immiscible Co–Ag and Ni–Ag thin films prepared by co-sputtering have been investigated. Saturation magnetizations of the films decreased linearly with increasing Ag concentration. Although the coercivity of Ni–Ag thin film does not vary with addition of Ag, the coercivity of Co–Ag thin film rises to reach a maximum at 41 % Ag. The coercivity of Co–41 % Ag thin film increases with annealing over 250° C. The thin films all have a fine grain structure. The average grain diameters of Co–Ag thin films and their coercivities increase with annealing. Moreover, it was found that the coercivity and average grain diameter have a linear relation. Therefore, as one reason for a coercivity increase with annealing, it is thought that the phenomenon is caused by the growth of Co grains in the film.

1. Introduction

Recently, various metastable alloys and compounds have been looked at in the hope that they might serve as new materials [1–4]. Immiscible alloys [5] are one such type of material. It is well known that Co–Ag, Ni–Ag, Co–Au and Fe–Ag are immiscible systems containing ferromagnetic elements [6]. The differences in atomic radii for these systems exceeds 10 %. For this reason, metastable phases and amorphous alloys can be proced easily by using splat quenching [7] or vapour deposition, as well as by ion beam mixing [8, 9].

In the present work, Co–Ag and Ni–Ag alloys were studied for the purpose of developing new magnetic alloys. In these alloys, if the ferromagnetic grains are dispersed adequately in a non-magnetic Ag matrix, permanent magnet and semi-hard magnetic materials can be developed. The magnetic properties are described here for co-sputtered thin films and annealed specimens. The relation between the magnetic properties and microstructure, as well as crystallographic relations between the co-sputtered metals are also presented.

2. Experimental details

Mixed thin films were prepared using a conventional r.f. sputtering system. The sputtering targets used were a combination of Co disc with Ag chips on the disc, and Ni disc with Ag chips. The targets were all at 99.99 % purities. Mixed films were co-sputtered from the combined targets.

The substrate was Corning No. 7059 glass, used for measuring magnetic properties, with evaporated carbon thin films, used for observing microstructures. The sputter gas Ar was of 99.9995 vol % purity.

The sputtering system was initially evacuated to 1–2×10^{-6} torr before introduction of the sputtering gas. The sputtering gas pressure and power were 5×10^{-3} torr and 2.2 watt cm^{-2} respectively. Annealing of the film was carried out in a 10^{-6} torr vacuum.

Film composition was analysed using inductively coupled argon plasma spectroscopy. The magnetic properties of the films were measured with a vibrating sample magnetometer. The microstructure of the films was observed using transmission electron microscopy.

3. Results and discussion

3.1. Magnetic properties

Coercivity and saturation magnetization are shown

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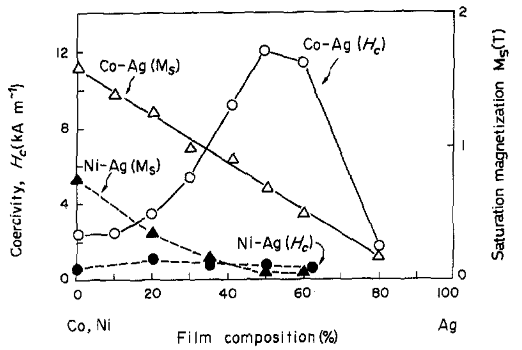

Figure 1 Coercivities and saturation magnetizations for co-sputtered Co–Ag and Ni–Ag thin films.

in Fig. 1 for co-sputtered Co–Ag and Ni–Ag thin films. Film thickness was 80 nm. Saturation magnetization of co-sputtered Co–Ag films decreased with decreasing Co concentration, and became zero at a composition of 15–20 at % Co. The coercivity of the films increased with addition of Ag and showed a maximum at a composition of about 50 at % Ag.

In the case of co-sputtered Ni–Ag films, saturation magnetization decreased with increasing Ag concentration. The coercivity did not become high.

Hysteresis loops are shown for co-sputtered Co–Ag thin films in Fig. 2. The squareness ratio of Co–41 % Ag film was about one. The hysteresis loops collapsed when the Ag content went beyond 50 at %, and the squareness ratio lowered gradually with increasing Ag concentration. The squareness ratio became small when the Ag content was about 80 at %. It is thought that the change in the shape of the hysteresis loop is due to aggregation of Co grains in the films. On the other hand, the hysteresis loops for Ag–Ni films did not depend on the film composition. The squareness ratio decreased slightly with increasing Ag content.

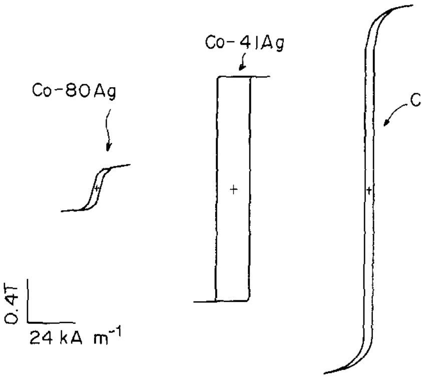

Figure 2 Hysteresis loops for co-sputtered Co–Ag thin films.

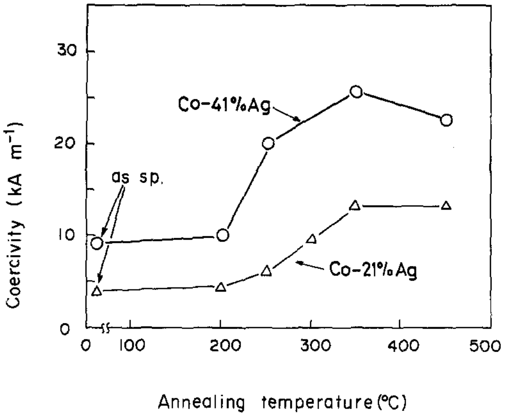

Figure 3 Coercivity change of co-sputtered Co–Ag thin films in response to vacuum annealing.

3.2. Annealing behaviour

Fig. 3 shows the coercivity change of co-sputtered Co–Ag thin film in response to differing vacuum annealing conditions. Although Co–21 at % Ag thin film coercivity increase slightly with increasing annealing temperature, the coercivity values were not sufficient for a permanent magnet. During the annealing of Co–41 at % Ag thin films, however, the coercivity increased above an annealing temperature of 250° C and reached a maximum when the annealing temperature was 350° C. The maximum coercivity of the film was 25.6 kA m^{-1} (320 Oe). Therefore, it can be thought that Co–41 at % Ag thin film having such a value qualifies as a permanent magnet. Beyond this point, coercivity decreased with increasing annealing temperature.

The coercivity of Co–50 at % Ag also rose high with annealing. However, the maximum coercivity was only about 18 kA m^{-1} (225 Oe), the coercivity value did not reach that of a permanent magnet.

In the case of Ni–Ag thin films, scarcely no coercivity increase was observed during annealing.

3.3. Relation between coercivity and microstructure

Transmission electron micrographs of co-sputtered Ni–Ag films are shown in Fig. 4. Crystal grains of Ni–25 at % Ag film were very small, as can be seen in Fig. 4a, and thus each grain could not be identified. Since Ag and Ni rings could be obtained from the electron diffraction pattern, it can be assumed that Ni and Ag grains existed independently. The broadened diffraction ring may indicate that the

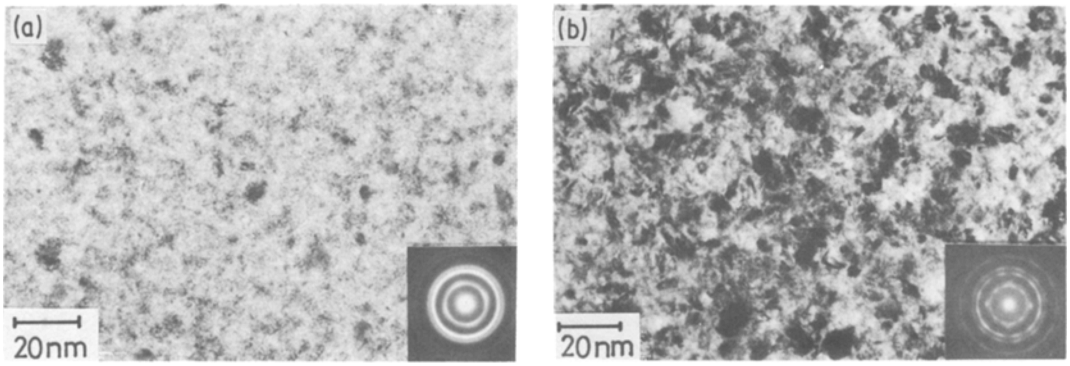

Figure 4 Transmission electron micrographs of co-sputtered Ni–Ag thin films: (a) Ni–21 % Ag, (b)Ni–50 % Ag.

crystal grains were very small or that high internal stress existed in the film.

Many moiré patterns were observed in co-sputtered Ni–50 at % Ag film (Fig. 4b), however, it is difficult to identify Ag and Ni grains. Most of these moiré patterns have intervals of between 0.8 to 1.5 nm. It can be assumed that the moiré patterns originated in an overlap between the Ag and Ni crystal planes.

A transmission electron micrograph for Co–21 at % Ag thin film is shown in Fig. 5a. The crystal grains were observed more clearly here than

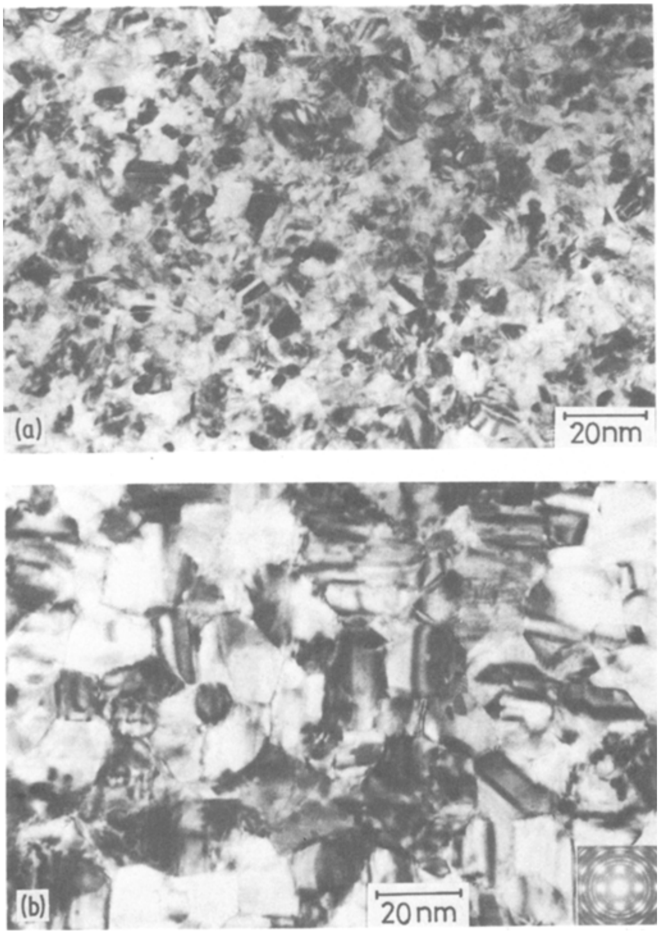

Figure 5 Transmission electron micrographs of co-sputtered Co–Ag thin films: (a) Co–21 % Ag, (b) Co–51 % Ag.

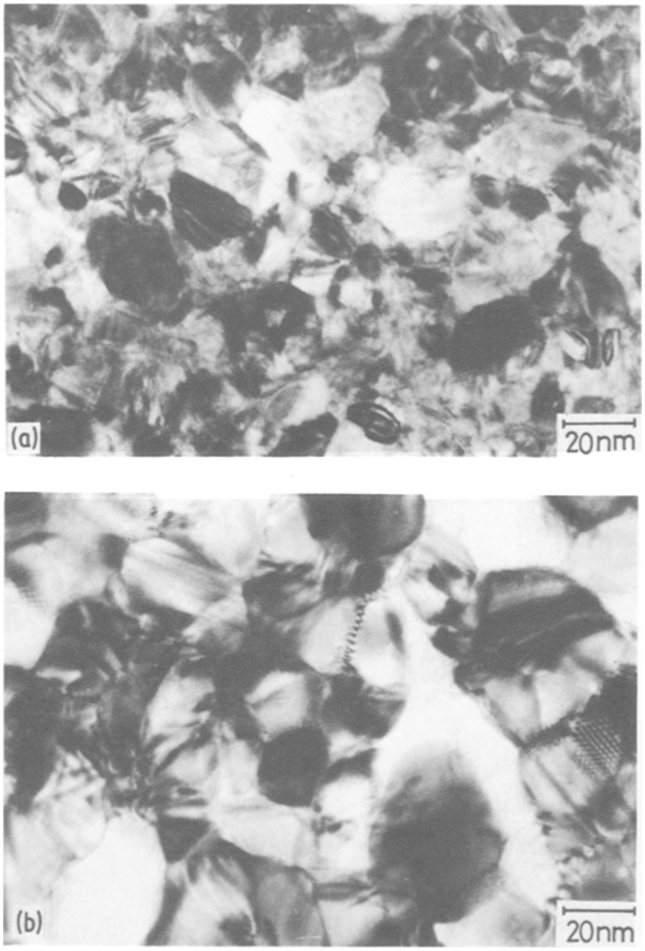

Figure 6 Transmission electron micrographs of annealed Co–41% Ag thin films: annealing temperatures T_a are (a) 250° C and (b) 350° C.

in the Ni–Ag thin film. Each grain of Co and Ag could not be separated, however, the average grain diameter was about 10 nm.

Electron micrograph and electron diffraction pattern for Co–41 at% Ag thin film are shown in Fig. 5b. The crystal grains demonstrate a strong anisotropy in the film. As shown in Fig. 2, the squareness of co-sputtered Co–Ag thin film first became high with increasing Ag concentration. This effect may have originated in the formation of the above mentioned film texture. On the other hand, the average grain diameters of co-sputtered Co–Ag thin films increased with increasing Ag concentration, and the coercivities of the films increased with increasing Ag concentration. This relation suggests that the coercivity increase originated in the grain growth of Co in the film. In the sputtered Co–Re [10], Co–Pt [11], and Co–Ir [12] thin films, those coercivities increased with increasing Co grain diameter over a range of 20 to 60 nm. Therefore, it is thought that the coercivity increase is due to Co grain growth.

The Co–Ag thin films became magnetically hard with annealing, as is shown in Fig. 3. Transmission electron micrographs of the annealed Co–41 at% Ag thin films can be seen in Fig. 6. The average grain diameter of the films was increased by annealing, however, the texture observed in as-sputtered specimens was no longer existent.

Fig. 7 shows the relation between the average grain diameter and the coercivity for Co–Ag thin film. The coercivity depended on the average grain diameter of the film. However, the average grain diameter that showed a maximum coercivity was larger than Co–Pt [11] and Co–Ir [12] thin films. This is one reason that the measured grain diameter has been the average of Co and Ag grains. On the other hand, the squareness decreased due to disappearing of the film texture observed in the as-

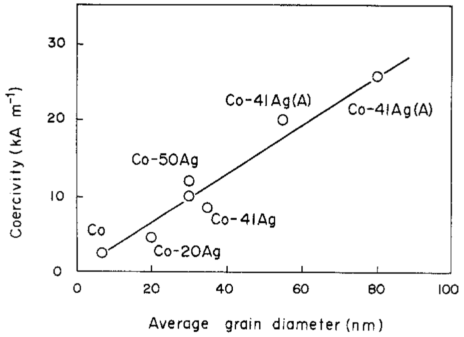

Figure 7 Coercivity versus average grain diameter for co-sputtered Co–Ag thin films. (A) indicates annealed specimens.

sputtered specimen. This phenomenon originated in the spherodization of Co grains, as shown in the electron micrograph.

Since the Co–Ag system is an immiscible one, the mutual solubilities may be very small. Thus, grain growth by grain boundary migration occurs easily for Co grains neighbouring each other. However, it is assumed that the growth of Co grains imbedded in the Ag grains was very difficult. Therefore, it is thought that Co grain growth was controlled by short-circuit diffusion, for example through grain boundaries and crystal surfaces.

In the case of Co–41 at% Ag annealed at 350° C, the average grain diameter became about 3 to 4 times that for in the as-sputtered condition. The activation energy was about 0.4 eV for grain growth obtained from average grain diameter measurement. The value was very small. Consequently, it is concluded that the grain growth of Co–41 at% Ag thin film was controlled by short-circuit diffusion.

4. Conclusions

Saturation magnetization for Co–Ag and Ni–Ag thin films decreased with increasing Ag concentration. On the other hand, the coercivity of Co–Ag thin film showed a maximum with addition of Ag, and it also increased with annealing. The obtained maximum coercivity was about 26 kA m^{-1}; this falls within the values for a permanent magnet. Nevertheless, the coercivity for the Ni–Ag thin film was very small.

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