Magnetic properties of electrodeposited Co-W thin films

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Thin films of Co-W, 300–500 Å thick, were electrodeposited at various compositions under a wide range of plating conditions. The saturation magnetization, coercivity, and squareness ratio of the films were derived from the parallel (in-plane) and perpendicular hysteresis loops, measured by using a vibrating sample magnetometer. The magnetic properties of the films are strongly related to their microstructure. The nonmagnetic alloying element (W) affects the saturation magnetization via the dilution mechanism. The in-plane coercivity, which increases with increasing content of the hexagonal phase and with decreasing degree of $[0001]h$ texture, is in the range of 100–600 Oe for the crystalline deposits and decreases to a few oersteds for amorphous deposits. The in-plane squareness ratio increases with the fcc or amorphous phase content and with decreasing degree of $[0001]h$ texture. The magnetic measurements suggest that films that appeared amorphous according to their electron diffraction patterns are actually microcrystalline or at least partially crystallized.

I. INTRODUCTION

The magnetic properties of thin films are determined to a large extent by their microstructure. This is particularly true for cobalt-base alloy electrodeposits. By a proper choice of the deposition variables it is possible to obtain a wide variety of alloy compositions and microstructures, some of which are metastable. The usefulness of these films depends upon their structural stability and behavior in hostile environments and at elevated service temperatures.

Cobalt is readily electrodeposited from aqueous solutions as a pure metal or in the form of various binary, ternary, or even higher alloys. Over 50 such alloys have been reported in the literature,¹ many of these exhibiting interesting magnetic, electrochemical, or mechanical properties. Co-Ni, Co-P, and Co-Ni-P have been the most widely investigated alloy systems, mainly because of their useful magnetic properties.²

Co-W alloy films are of special interest because they combine favorable magnetic properties with wear resistance, wear being a major problem in magnetic recording disks. These alloys possess a high Curie point and display endurance to hostile environments or extreme vacuum conditions, features of value in space technology. Even though Co-W alloy films exhibit a variety of highly useful properties, the amount of information available on this system (and particularly on its magnetic properties) is rather limited.^{2–6}

It has been reported^{3–5} that Co-W alloy films have a medium to high in-plane coercivity (200–600 Oe) and an in-plane squareness ratio of 0.6–0.8.

A systematic study of the microstructure of Co-W alloy thin films, prepared under a wide range of plating conditions, has been reported previously.⁷ The structural features

that were studied are the chemical composition, the grain morphology, the phase composition, the texture, and the defect structure. The dependence of the microstructure on the plating conditions (bath composition, temperature, and pH) was also determined.

The objective of the present investigation was to measure the magnetic properties of Co-W films (those properties that can be inferred from the hysteresis loops), to correlate them to the microstructure, and to show that controlling the deposition process ultimately allows a control of the magnetic properties.

II. EXPERIMENT

Thin Co-W films, 300–500 Å thick, were electrodeposited onto copper-coated microscope slides. Prior to the vacuum deposition of the copper, a thin layer of Formvar was applied to the slides. This was done in order to avoid the peeling off of the film during electrodeposition and to enable the separation of the coating from the slides for the transmission electron microscopy study. The details of the deposition process and techniques involved in the determination of the film composition, thickness, and microstructure are described elsewhere.⁷ The bath composition, temperature, and pH are the process parameters that were varied. Acidic and basic baths were used; the deposits are referred to as “acidic” or “basic” accordingly. The tungsten-ion ratio in the plating solutions, $[W]/([W] + [Co])$, was changed from 0% to 7% in the acidic baths and from 0% to 88% in the basic baths. The plating temperatures were 22, 50, and 90 °C.

The magnetic measurements were carried out by using a Foner-type vibrating sample magnetometer (VSM) at the Twente University of Technology. The samples for the VSM

were prepared by cutting the coated slides into 1-cm² squares. For each sample the parallel (in-plane) and perpendicular hysteresis loops were obtained at fields ranging from 0 to 10 kOe. The in-plane coercivity $H_c(\parallel)$, the saturation magnetic moment m_s , and the in-plane remanent magnetic moment $m_r(\parallel)$ were derived from the parallel loops (Fig. 1). The squareness ratio, $R(\parallel) = m_r(\parallel)/m_s$, was thus obtained. The saturation magnetization M_s (i.e., the saturation magnetic moment per unit volume) was calculated from the amount of shearing of the perpendicular hysteresis loops (Fig. 1), caused by the demagnetizing fields (Fig. 2). For a perpendicular hysteresis loop of an infinite thin film, the applied field H_{ex} is lowered by the opposing demagnetizing field, $H_d = N_\perp M \leq 4\pi M$, where $N_\perp$ is the demagnetizing factor and M the magnetization. This results in a sheared hysteresis loop obtained formally by the transformation $H \rightarrow H - 4\pi M$ [Fig. 2(b)]. M_s is readily derived from the sheared loop. For comparison, M_s was also determined directly by using the relation $M_s = m_s/V = m_s/Sd$, where S is the area of the sample and d its thickness, measured by multiple-beam interferometry. The magnetic volume of the sample was assumed to be equal to its actual volume.

The minimum detectability limit of the magnetometer was below 1×10^{-4} emu, this being the equivalent to the magnetic moment of $1 \text{ cm}^2 \times 5$ atomic layers of pure cobalt. In most cases the measured magnetic moment was one to two orders of magnitude higher than this value.

III. RESULTS

Typical parallel and perpendicular hysteresis loops are shown in Fig. 1. The negative slope of the curves at saturation, indicating a diamagnetic susceptibility, $\chi_D = -0.5 \times 10^{-6} \text{ emu}/(\text{Oe cm}^3)$, is due to the diamagnetic contribution of the copper-coated glass substrate. The loops have been corrected for this effect prior to the measurement of M_s . The difference between the saturation values of the two loops is a result of the different sensitivities of the detection coils of the VSM for the two positions of the specimen.

FIG. 1. Typical parallel (in-plane) and perpendicular hysteresis loops for Co-W thin films. The difference in the saturation values of the two loops is a result of the different sensitivities of the VSM for the two positions of the specimen.

FIG. 2. Perpendicular hysteresis loop (schematic) (a) without and (b) with the influence of the demagnetizing field.

A. Saturation magnetization

Values of the saturation magnetization M_s , calculated from the amount of shear of the perpendicular loops along with those measured directly as m_s/Sd , are given in Table I. Fair agreement between the two sets of values can be observed. The discrepancies (e.g., sample c) can be accounted for by the inherent inaccuracy of the method and the possibility that the measured thickness of the samples may be larger than their "magnetic thickness" because of porosity and the presence of hydroxides.

Figure 3 is a plot of M_s as a function of the W concentration in the basic Co-W alloy deposits. It shows that M_s decreases linearly as the W concentration increases. The extrapolation value of M_s at zero percent W is 1420 emu/cm^3 , corresponding to that of pure bulk cobalt. In Fig. 3 only results for samples with W contents below its saturation value were included. It was shown⁷ that the saturation values are 27, 34, and 30 wt. % for samples deposited at 22, 50, and 90 °C, respectively. The corresponding W-ion ratios, $[W]/([W] + [Co])$, in the plating solutions were 45%, 65%, and 70%. An increase of the W-ion ratio beyond these values resulted in a further decrease of M_s , although the W content in the deposits did not increase (e.g., samples e and f in Table I).

B. In-plane coercivity and squareness ratio

The coercivity $H_c(\parallel)$ and the squareness ratio $R(\parallel)$ as a function of the deposition variables are shown in Figs. 4 and 5, respectively. For the basic deposits, the bath pH was kept constant, while the W-ion ratio and the bath temperature were varied. For acidic coatings the bath pH and temperature were changed at constant W-ion ratio. In all cases the schematic "phase diagrams," discussed in detail in Ref. 7, are also presented to illustrate the correlation between the magnetic properties and microstructure. This correlation will be discussed in Sec. IV.

IV. DISCUSSION

The magnetic properties of the Co-W films are strongly related to their microstructure. The microstructure of the deposits has been the subject of a separate investigation.⁷

TABLE I. Saturation magnetization M_s for basic deposits ($pH = 8.5$) derived from (a) the amplitude of the in-plane loops and the dimensions of the samples and (b) the shear of the perpendicular loops. The relative error in (a) and (b) is 20%.

Co-W sample	W-ion ratio (%) [W]/([W] + [Co])	W in deposit (wt. %)	T (°C)	m_s (10^{-3} emu)	d (Å)	S (cm ²)	(a) m_s/dS (emu/cm ³)	(b) M_s (emu/cm ³)
a	0	0	50°	3.2	390	1.03	800	830
b	22	28	50°	1.6	410	1.01	390	420
c	46	32	50°	1.2	430	1.00	280	360
d	66	34	50°	0.9	350	1.03	250	250
e	88	34	50°	0.7	490	0.92	155	150
f	88	30	90°	0.7	420	1.04	160	160

The main structural features that bear upon the magnetic properties will be reviewed briefly.

Tungsten has a significant influence on the film structure. It codeposits as a substitutional solid solution in cobalt. Films containing up to 35 wt. % (15 at. %) W were obtained. No intermediate compounds or any free W could be detected. The deposits were either amorphous (in the sense that they yielded diffuse electron diffraction patterns) or crystalline, depending on the plating conditions. The crystalline coatings consisted of a dispersion of large grains (a few thousand angstroms in diameter) in a background of small grains (a few hundred angstroms in diameter). The latter were hcp, fcc, or mixed, the hcp grains showing a varying degree of $[0001]_h$ texture (namely, the c axis being perpendicular to the film plane). An azimuthal symmetry prevailed within the film plane. The large grains comprised alternate hcp and fcc platelets, displaying a definite orientation relationship. Analysis of the occluded hydrogen and oxygen showed that hydroxides tend to codeposit within the films, particularly at high pH values.

A. Saturation magnetization

Table I indicates that there is an agreement between the values of the saturation magnetization derived by the direct

measurements and those derived by using the indirect "shearing" method. It should be noted that the use of the latter method is based on the implicit assumption that the magnetization may have any intermediate value between $+M_s$ and $-M_s$.⁸ This occurs in polycrystalline materials or where a multidomain structure can develop, such as in the electroplated Co-W films.

The presence of W, a nonmagnetic alloying element, affects the saturation magnetization by means of a dilution mechanism. The linear decrease of M_s with the W concentration in the deposits supports this mechanism and is in close agreement with the behavior observed by Luborsky.² However, the continuous decrease of M_s even beyond the W-ion ratio in the bath, corresponding to the saturation concentration of W in the deposit, implies that in the high W-ion-ratio range a mechanism other than the dilution mechanism takes place.

The azimuthal symmetry that prevails within the film plane, inferred from the azimuthal uniformity of the large-area electron diffraction patterns,⁷ is supported by the invariance of the in-plane loops under sample rotation.

B. Correlation between $H_c(//)$, $R(//)$, and the microstructure

The phase composition and texture exert a strong influence on the coercivity and squareness ratio of the deposits, as seen in Figs. 4 and 5. Because of the complexity of the electrodeposition process and the synergistic effects associated with the various deposition parameters, it is not possible to isolate the influence of any single structural feature on the magnetic properties. Nevertheless, the magnetic behavior can be related to the microstructure, and the following conclusions can be enounced:

(1) Electrodeposited Co-W thin films have a medium to high coercivity that ranges between 100–600 Oe in the crystalline films and decreases to a few oersted in the amorphous films. These values are in agreement with those quoted in the literature.^{1–6}

(2) The mean size of the small grains in the crystalline deposits, obtained in the present study (100–400 Å), lies in the transition range between the dimension of grains that favor the formation of multidomains and that in which a single-domain structure is stable. Actually, the highest coercivity is associated with that intermediate grain size.⁹

(3) The coercivity has its lowest values for films with an

FIG. 3. Dependence of the saturation magnetization on the W concentration in the basic deposits.

FIG. 4. Dependence of the in-plane coercivity (upper diagrams) and the phase composition (Ref. 7) (lower diagrams) on the plating conditions in (a) basic and (b) acidic deposits. The pH is constant ($= 8.5$) in (a) and the W-ion ratio is constant ($= 6.6\%$) in (b). Dots, fcc; bars, hcp; shaded area, amorphous; and small dots, nonmagnetic. The $[0001]_h$ texture (the c axis of the hexagonal crystallites being perpendicular to the film plane) is illustrated by the degree of alignment of the bars.

amorphous structure. It increases to higher values, albeit still low, for films containing a high proportion of fcc crystallites. H_c reaches much higher values with increasing content of the hcp phase. This behavior stems from the variation of the magnetocrystalline anisotropy, which is the highest in

the hexagonal phase, low in the cubic phase, and zero in the amorphous phase. The nonzero value of H_c in the amorphous films indicates either the presence of impurities or microprecipitates not discernable in the electron diffraction patterns (e.g., hydroxides) or that these films are microcrys-

FIG. 5. Dependence of the in-plane squareness ratio (upper diagrams) and the phase composition (Ref. 7) (lower diagrams) on the plating conditions in (a) basic and (b) acidic deposits (for symbols, see caption to Fig. 4).

talline rather than amorphous, possibly in the superparamagnetic state.

(4) The coercivity decreases with increasing perfection of the $[0001]h$ texture of the hexagonal grains. This occurs in films deposited from basic baths at high temperatures and W-ion ratio over 40%, and in W-containing films deposited from acidic baths at $pH = 6$ when the bath temperature increases from 50 to 90 °C.

(5) The addition of tungsten to the hot basic solutions results in an increase of H_c , which reaches a maximum at 20% W-ion ratio. In basic solution at room temperature the addition of tungsten yields a decreasing H_c , caused by the formation of the amorphous (or microcrystalline) phase. In hot acidic solutions the addition of tungsten causes an increase in H_c , while for room temperature solutions H_c decreases because of the formation of the fcc phase.

(6) The squareness ratio increases in deposits containing a higher fraction of fcc phase and reaches values as high as 0.9. This can be attributed to the existence of four possible directions associated with the $\langle 111 \rangle$ easy axis of magnetization in the fcc Co crystallites, in contrast to the single direction associated with the $[0001]$ easy axis in the hcp Co crystallites. Upon removal of the external field there is a higher probability for the magnetization vector to be able to shift into an easy direction close to the field direction, thus resulting in a higher R . A simple theory, based on geometrical considerations,^{10,11} predicts R values of 0.866 and 0.5 for randomly oriented fcc and hcp cobalt, respectively. According to the same model, the type of texture within the hcp phase, present in the films, should yield $0 < R < 0.5$ for the hcp phase alone; the higher the degree of alignment of the individual crystallites with their c axis perpendicular to the film plane, the lower the value of R . Indeed, a decrease in R is observed with increasing texture perfection.

(7) The squareness ratio is high in the amorphous films. This is to be expected since the magnetocrystalline anisotropy vanishes in noncrystalline structures. However, R being less than unity indicates some degree of crystallinity or, alternatively, the existence of a short-range order, as suggested by Omi *et al.*¹² This supports the previous conclusion, namely, that the amorphous deposits may be actually microcrystalline. In this connection preliminary differential scanning calorimetry measurements on thick deposits, obtained under the conditions corresponding to the formation of so-called "amorphous" structure, were carried out. No exothermal peaks characteristic of a crystallization process were observed. This further supports the tentative conclusion that these films are actually microcrystalline to begin with.

(8) In a system of particles for which the mutual magnetic interaction is vanishingly small and the magnetocrystalline anisotropy is the only source of coercivity, the coercivity passes through a maximum for a grain size corresponding to single-domain particles.⁹ H_c decreases at higher grain sizes where a multidomain structure may develop and at lower grain sizes where superparamagnetism prevails. Unfortunately, in the present case the thin films contained a spread of particle sizes around two values, the so-called "large" and "small" grains. This made it difficult

to derive a systematic trend of H_c with respect to grain size.

(9) The magnetic properties of thin films are known to be thickness dependent and so is the microstructure. A correlation between magnetic properties and microstructure was shown to exist in the range of film thicknesses that was studied. It is only reasonable to assume that similar correlations exist for other film thickness ranges.

V. SUMMARY

The magnetic properties of electrodeposited Co-W thin films are strongly related to their microstructure. The saturation magnetization decreases linearly with increasing content of tungsten in the deposits, presumably by a dilution mechanism. The coercivity increases with increasing W concentration and hcp phase content, and with decreasing degree of $[0001]h$ texture or amount of large grains present. The squareness ratio increases with the fcc phase or the amorphous (microcrystalline) phase content and with decreasing degree of $[0001]h$ texture.

The magnetic measurements suggest that films yielding diffuse large-area electron diffraction patterns may be actually microcrystalline rather than amorphous.

Because of the complexity of the electrodeposition process, it was not possible to isolate the influence of a single deposition variable on the microstructure or the effect of a single structural feature on the magnetic properties. Nevertheless, a choice of the proper combination of deposition parameters ultimately allows control of the magnetic properties of Co-W films.

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