Electrodeposition of Hard Magnetic Layers of CoPtW

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Introduction

The wide range of applications of permanent magnets drives the researches to find simple methods for their manufacture. Electrodeposited CoPt alloys have received a growing interest in the past years because of their possible use to obtain permanent micromagnets [1,2]. Addition of sodium tungstate in the electrolyte gives CoPtW alloys, reducing the Pt content, and increasing the magnetic properties at high thickness.

Experimentals

Deposits were prepared on brass substrates from a bath whose composition is reported in Table1. Temperature of deposition was in the range 40÷60°C and current density 5÷20 mA/cm^2. Deposits compositions were measured with EDS analysis; thickness and morphology with a laser profilometer and SEM. Structure was controlled by XRD patterns. Magnetic measurements were made with a VSM at room and higher T.

Table1. Electrolyte composition

Cobalt sulphamate [$Co(NH_2SO_3)_2$]	0.1M
Platinum p salt [$Pt(NH_2)_2(NO_2)_2$]	0.01M
Ammonium citrate [$(NH_4)_2C_6H_6O_7$]	0.1M
Glycine [NH_2CH_2COOH]	0.1M
Sodium tungstate [$Na_2WO_4 \cdot 2H_2O$]	0.27M
Sodium hypophosphite [NaH_2PO_2]	0.055M

Results

CoPtW alloys with W content from 4%at to 6%at and Pt content from 9%at to 13%at were electrodeposited.
Increasing hypophosphite bath concentration phosphorus content in the deposit increases and correspondingly tungsten content decreases. The W content can be controlled with ammonia addition. Deposits showed a strong [00.1] preferred orientation. Table2 reports the composition of the samples obtained under identical conditions (V = 250 ml; T = 60°C; j = 10 mA cm^{-2}) in order to test the repeatability of the results.

Table 1. Properties of ECD CoPtW alloys.

Sample	$d_{(00.2)}$ *(Å)*	$I_{(00.2)}$ *(cps)*	*Co (%at)*	*Pt (%at)*	*W (%at)*
CFA 2	2.086	1974	85	9	6
CFA 3	2.079	2511	85	10	5
CFA 4	2.077	920	83	11	6
CFA 5	2.084	1408	83	13	4

Experimental values of saturation magnetization are in good agreement with those calculated ($M_{s,t}$) as a weighted sum of the saturation moment of the two binary systems - CoPt and CoW respectively - using the formula

$$M_{s,t} = 1.4 \cdot 1.13 x_{Pt} + 0.74 x_W \quad \text{emu/mm}^3$$ [3,4].

Figure 1 shows the typical hysteresis loop for the electrodeposited samples. Reasonably good saturation magnetisation moments and coercitivities in both perpendicular and parallel magnetic field are obtainable, while the demagnetisation field effect is stronger in the perpendicular direction than in the parallel direction.

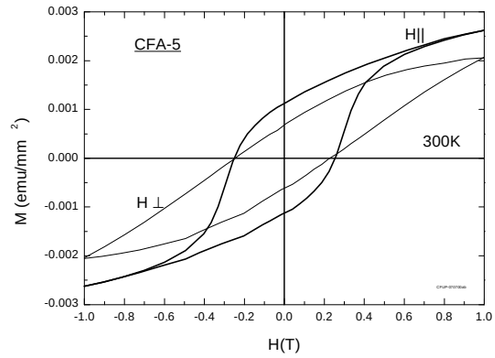

Figure 1– Hysteresis cycles (T=298K) of CoPtW films in the field applied parallel (H ||) and perpendicular (H⊥) to the surface of the film.

The temperature dependence of sample magnetic properties (in plane and perpendicular coercivity, remanent magnetisation and saturation magnetisation) was investigated. Results for the sample CFA3 are summarized in Table 3.

Table 3. Change in hysteresis cycle parameters with temperature.

Magnetic property	*345 K*	*390 K*	*436 K*	*485 K*
H_c ‖	-7.5	-15.0	-24.3	-30.5
M_r ‖	-1.1	-2.4	-3.8	-5.5
M(1T) ‖	1.5	2.1	3.3	3.3
H_c ⊥	-2.9	-7.4	-16.2	-24.5
M_r ⊥	-3.9	-7.3	-12.7	-22.1
M(1T) ⊥	1.9	3.8	5.6	7.1

Samples saturated at room temperature in a field H > 2.2T were investigated to determine the time dependence of the remanent perpendicular magnetization at 400 K, as shown in Table 4 (CFA4). After a first decrease the value remained quite constant.

Table 4. Time dependence of perpendicular magnetization.

t (min)	30	60	120	300	360
CFA4	7.5	8.2	8.8	9.7	9.9

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