

# Electrodeposited nanocrystalline and amorphous co-rich alloys for recording heads

S. A. CIUREANU

University “Politehnica” of Bucharest, Splaiul Independentei 313, RO-060042, Romania

This work is a comparative study of two magnetic materials: Co-rich nanocrystalline films and amorphous films of the same compositions, obtained by electroplating at different current density. The  $(\text{Co}_{1-x}\text{Fe}_x)_y(\text{MP})_{1-y}$  amorphous alloys, formed by electroplating at  $200 \text{ mA/cm}^2$ , are investigated. At the composition  $\text{Co}_{86}\text{Fe}_{10}\text{P}_{10}$ , the amorphous layer is zero-magnetostrictive and show high saturation magnetic induction and high permeability. These properties are suitable for the inductive thin film heads useful in high density magnetic recording. The electrodeposited Co-rich alloys formed at  $20\text{-}30 \text{ mA/cm}^2$  are nanocrystalline and have the same magnetic behaviour and a good stability. The aim of this work is a structural modulation of Co-rich films.

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## 1. Introduction

Upon designing a magnetic head, one intends to obtain certain performances, some of them being dependent on the properties of those materials constituting the core. Therefore, the spatial distribution of the air-gap dispersion field [1] of the magnetic circuit depends on its geometry as well as on the electric permeability and conductivity of the material of polar pieces.

The amorphous alloys have a series of properties unusual for crystalline metals such as: *high magnetic permeability* accompanied by *high electrical resistivity*, qualities which are maintained up to frequencies of about 100 MHz. This is why, in recent years, the development of magnetic registration techniques is correlated with the progress made in order to obtain such materials among which the most competitive ones are the cobalt-rich amorphous alloys [2,3]. The magnetic properties of Co-rich thin films depend greatly on the methods and conditions of preparation. They are affected significantly by structural parameters such as crystallographic structure, particle size, texture, surface roughness etc. The structure of electrodeposited thin films is primarily determined by the current density. At great current density ( $>200 \text{ mA/cm}^2$ ) the formation rate of film is great and the film is amorphous. But at very small current density ( $20\text{-}40 \text{ A/cm}^2$ ) the electrodeposited films are crystalline.

In this work we report on an analysis of the evolution of the structural and magnetic properties of the Co-rich thin films with the current density of the electroplating. The Co-rich alloys investigated are  $(\text{Co}_x\text{Fe}_{1-x})_y(\text{MP})_{1-y}$ , with  $x > 80$ . Phosphorous was incorporated to the alloys for

higher resistivity. The addition of a metal M, as Sn or Cr, improves the corrosion resistance and the stability.

## 2. Experimental procedures

The CoFeP alloys were obtained through the cathodic deposition, using galvanic direct current (dc), at high current densities ( $>200 \text{ mA/cm}^2$ ) and at small current densities ( $<30 \text{ A/cm}^2$ ), with temperatures of about  $50^\circ \text{ C}$ , in solutions with compositions given in table 1. Test samples were electrodeposited from freshly prepared solutions, using mechanical agitation, in open atmosphere, on Cu substrates. The concentrations and compositions of the electrolyte baths and of the alloys were determined by energy dispersive X-ray spectrometry (EDS) and by chemical methods. The film thickness was measured using a stylus profilometer (Dektak). Films with different thickness were obtained by varying the deposition time. The crystallographic structure of the films was studied by X-ray diffraction (XRD) using  $\text{CuK}_\alpha$  radiation. The crystallite size was estimated using the Scherrer formula. The hysteresis loops were characterized by a vibrating sample magnetometer Lake Shore model 7304.

## 3. Results and discussion

The concentrations and compositions of the electrolyte baths establish the alloys compositions (Tab.1). In very acid bath ( $\text{pH}=1$ ) a strong preferential electrodeposition of Co make difficult the control of alloys compositions. At  $\text{pH}=2,5$  this effect is lower.

Table 1. The dependence of the alloys compositions on the bath composition.

Electrolytic bath composition:					
Co(SO <sub>3</sub> NH <sub>2</sub> ) <sub>2</sub>	.....4H <sub>2</sub> O, 0,3mol/l				
Fe(SO <sub>3</sub> NH <sub>2</sub> ) <sub>2</sub>	.....nH <sub>2</sub> O, 0,03mol/l				
NaH <sub>2</sub> PO <sub>2</sub> H <sub>2</sub> O	.....0,07mol/l				
NH <sub>4</sub> OSO <sub>2</sub> NH <sub>2</sub>	.....0,09mol/l				
NH <sub>2</sub> CONH <sub>2</sub>	.....0,33mol/l				
pH	.....2,5				
Components molar fractions					
Solution			Alloy		
X <sub>Co</sub>	X <sub>Fe</sub>	X <sub>P</sub>	X <sub>Co</sub>	X <sub>Fe</sub>	X <sub>P</sub>
0,77	0,05	0,18	0,81	0,02	0,17
0,73	0,10	0,17	0,78	0,04	0,18

The nanocrystalline films were obtained by electroplating at current density of 30mA/cm<sup>2</sup> and the amorphous films at 200 mA/cm<sup>2</sup>. As can be seen in table 2, the composition of electrodeposited alloys is weakly dependent on the current density, for current densities larger than 20mA/cm<sup>2</sup>. At high and

at lower current density the amorphous and the nanocrystalline films can have the same composition.

Phosphorous incorporated in the alloys increases the resistivity but increases also the coercivity and decreases the magnetization saturation. For recording heads, the main requirements are: high magnetization saturation, low coercivity and high resistivity. Because the phosphorous concentration given in table 1 is too high, we have investigated the influence of P on the magnetic propriety of Co-rich films, crystalline and amorphous. For better properties the P concentration must be lower (~10%)

Table 2. The dependence of the alloy's composition on plating current density for electrodeposited CoFeP films.

.Current density (mA/cm <sup>2</sup> )	10	20	40	60	80	100	120
Co(at%)	78	81	82	84	83	83	82
Fe(at%)	4	5	4	5	4	6	6
P(at%)	18	14	14	11	13	11	12

In the crystalline alloys the crystallite size decreases on the thickness of film. For the thin films obtained, the structure is nanocrystalline (Fig. 1).

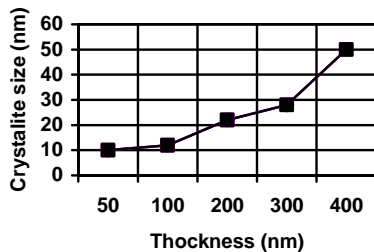


Fig. 1. The dependence of the crystallites size on the thickness of films.

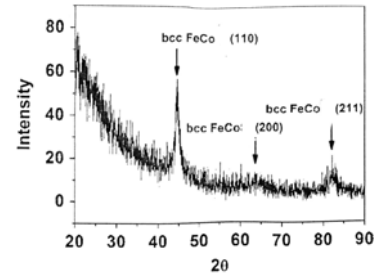


Fig. 2. X-ray diffraction spectra for the crystalline Co<sub>86</sub>Fe<sub>4</sub>P<sub>10</sub> films.

The structural properties of the electrodeposited films are different. In fig.1 an evidence of crystallization is shown by the diffraction line at 45° assigned as a diffraction from body-centered-cube, bcc(110). Fig. 2 shows an amorphization when the content of phosphorous is greater than 10%. The high current densities eliminate the face-centered cubic (fcc) phase.

The replacement of crystalline permalloys with Co-rich amorphous films presents only one difficulty: the Co-alloys have a lower saturation magnetization than the Fe-alloys. Cobalt, having a smaller number of uncompensated spins than iron, has a lower magnetic moment. The correction of this disadvantage is made by addition of iron or of rare metals of high magnetic moment (Dy or Gd). In the Co-alloys obtained in the framework of this paper, the allying with Fe is limited by the growth of magnetostriction which, for magnetic heads, must be practically null. On the other hand, the metalloids, necessary for amorphization, lessen the magnetic moment. That is why the optimal concentration in phosphorus was looked for; that is the lowest concentration at which the amorphization is still produced. The X-ray diffraction analysis shows that, under 10%P, the amorphization capacity decreases very much.

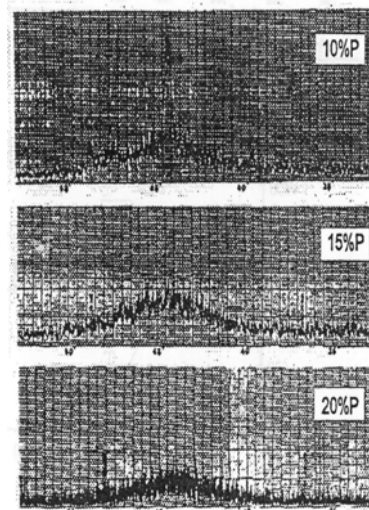


Fig. 3. X-ray diffraction spectra for amorphous CoFeP films.

The composition dependence of the saturation induction is done in the Fig. 4. We may conclude that the obtained experimental data check the linear relationship which gives the composition dependence of the magnetic moment of the transition metals alloys. The relationship is established on the grounds of the rigid band pattern, supposing that the metalloid atoms contribute with some of their electrons *s* and *p* to the completion of *d*-band of the transition metal. The amorphization has a reduced influence over this behaviour and, practically, no significant differences are to be seen between the saturation magnetization of amorphous alloys and that of the crystalline alloys of similar composition obtained in the same conditions of electroplating..

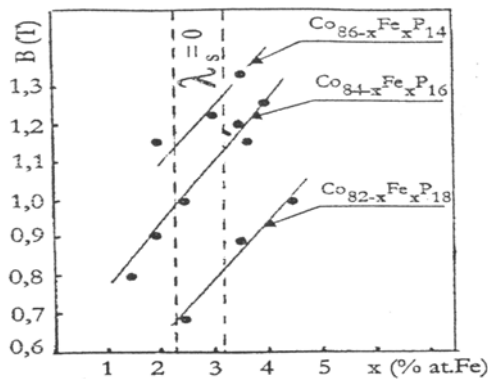


Fig. 4. The dependence of the saturation induction on the concentration of Fe, for the CoFeP alloys.

The effect of the alloying with iron, in the domain in which the magnetostriction is low, is obvious from Fig. 4. The straight lines have the same slope, mainly determined by the magnetic moment of cobalt.

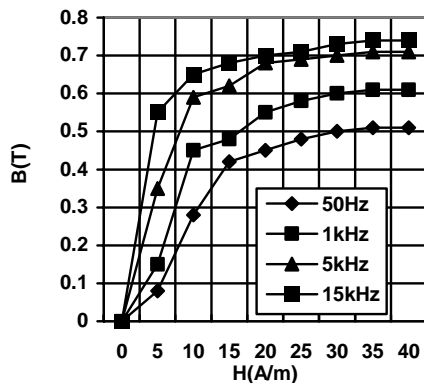


Fig. 6. The variation of the induction on the field at different frequencies, for an electrodeposited amorphous film with a composition  $Co_{80}Fe_2P_{18}$ .

Therefore, in order to get the highest possible value for the saturation magnetization, the amorphous alloys studied  $Co_yFe_xP_z$  must have compositions that satisfy the following requirements:  $10 < z < 20$  ;  $(y/x) \approx 24$  ;  $2 < x < 6$ . However these domains are restrained by the requirements connected with the steadiness and with the

behaviour at high frequency. For the crystalline alloys, there is the same problem because the magnetostriction is primarily determined by the composition of films. In the films obtained at  $30 \text{ ma/cm}^2$  the concentration of P is about 10%at

The amorphous electrodeposited films with a low content of iron which have, at 50 Hz, the saturation induction,  $B_s$ , smaller than 0,7 T become inadequate at high frequency (Fig. 4) but the value of saturation induction for the Co-rich obtained films with different additions (Sn, Mo, Dy, Gd) can be 1,1-1,3T

The diminution of the saturation magnetization with the temperature, determined by means of a vibrating sample magnetometer that records the temperature dependence of the magnetic moment measured in emu, is linear within the interval 300-400 K, and indicates greater values with the increase of the iron content. The results not confirm the law  $T^{3/2}$  but approach more the relation:

$$\Delta M_s(T) = T \exp\left(-\frac{W_{\text{aniz}}}{kT}\right) \quad (1)$$

when  $W_{\text{aniz}} \ll kT$ , the relation (1) is practically linear.

For amorphous alloys, the diminution takes place more abruptly and at lower temperature than for the crystalline ones, as the Curie temperatures are diminished as well. In the studied case, the Curie temperatures lessen with the content in cobalt, while the temperatures of phase transition grow (Fig. 5).

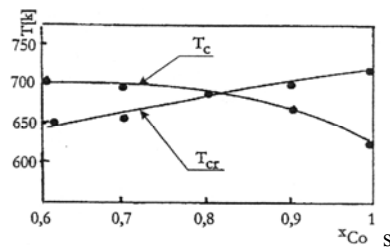


Fig. 5. The Curie ( $T_c$ ) temperatures and those of crystallisation, ( $T_{cr}$ ), function of the content in Co at the amorphous alloys CoFeP.

The coercivity field ( $H_c$ ) of Co-rich alloys has little values and that is the main quality of these materials. Fujimori [4] established that the principal contribution at  $H_c$  results from the fluctuations of the anisotropy due to the magnetostriction. The alloys obtained in the frame of this work have practically null magnetostriction, therefore they present low  $H_c$  and can be used for magnetic heads.  $H_c$  decreases with increasing of cobalt concentration for all the alloys, amorphous or crystalline (Fig. 7). Fe and P increase the coercivity.

The correlation between  $H_c$  values and the magnetostriction can justify the soft magnetic properties of the materials with a little number of inclusions and defaults. In these cases the magnetization processes near the coercivity point occurs predominantly with the motion of the domain boundaries and can be explained in terms of

the tension theory. When the internal mechanic tensions are predominant in the superficial density of the fluctuations in the domain walls ( $\sigma$ ), the critical field ( $H_0$ ) which produces the motion of the domain is:

$$H_0 = a_0 \frac{\lambda(\Delta\sigma)}{\mu_0 M_s} \quad (2)$$

where: ( $\Delta\sigma$ ) is the average value of tension fluctuations;  $a_0$  is a number dependent on the thickness of the frontier walls and on the wavelength of tension dispersion;  $\mu_0$  is the wide permeability,  $M_s$  is the saturation magnetization.

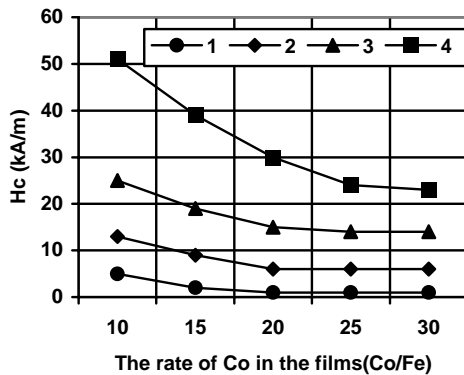


Fig. 7. Dependences of  $H_c$  on composition of the amorphous electrodeposited CoFeP alloys; 1 -  $P_{10}$ ,  $1\mu\text{m}$ ; 2 -  $P_{16}$ ,  $1\mu\text{m}$ ; 3 -  $P_{20}$ ,  $1\mu\text{m}$ ; 4 -  $P_{10}$ ,  $2\mu\text{m}$ .

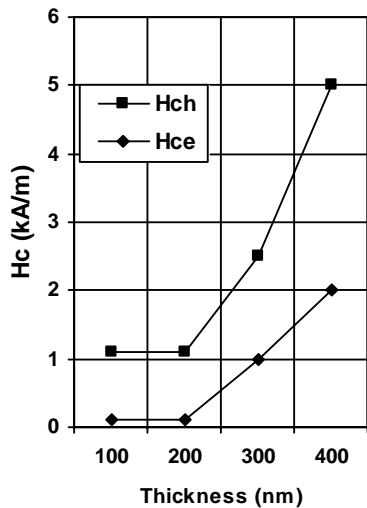


Fig. 8. Dependence of  $H_c$  on the crystalline films thickness ( $H_{ce}$ , coercitive field easy-axis,  $H_{ch}$ , coercitive field hard-axis).

The relation (2) shows that, in materials with little number of inclusions and defaults,  $H_0$  depend on the internal strains and is great when the tension dispersion become comparable with the thickness of domain walls. Because  $H_c \geq H_0$ , its dependence on magnetostriction proves that these materials are homogeneous, with a little number of inclusions and defaults. Their magnetic

properties are predominantly determined by the internal strains.

The Fig. 8 shows the influence of the film thickness on the coercivity, for the crystalline alloys.  $H_c$  change slightly when the thickness increases. Therefore is difficult to obtain an experimental evidence for the very thin films. For the amorphous films with 1- 40  $\mu\text{m}$  thickness,  $H_c$  increases more. The coercivity is affected significantly by structural parameters such as particle size, texture, surface roughness and crystallographic structure, hence by the preparation conditions. Some authors detected a sharp increase of the coercivity on the thickness of Co thin films [ 5 ]. Another authors [ 6 ] found two distinct types of behaviour of the coercivity and magnetostriction depending on thickness of Co films when all the films had the same structure independent of the thickness.

We strictly assured the same conditions of the electroplating, only the time of electrodeposition was varied, and found that the coercivity increases slightly on the thickness. This is related to the physical microstructure of the films and particularly to the grain size which has been controlled [7,8]. The crystallographic data and the grain size data indicate that for films of thickness greater than 10nm a multiplicity of layers of small grains occur in these samples rather than columnar growth. This structure provides an enormous number of pinning sites for Néel walls that will form in these films. In very thick films it is even possible that same crosstie walls might form.

Although the amorphous alloys have not crystalline anisotropy, all the authors detected in the thin films an anisotropy perpendicular on the film plan. This anisotropy, which increases the coercivity fields and decreases the magnetisation, can be explained by the microcrystals formed in the amorphous material (a little distance order) or by internal strains. In the electrodeposited films, the mechanical tensions are insignificant but the inclusions of hydrogen are present in the alloys obtained at great current density. The crystalline films have crystalline anisotropy but at low current density the structure is fine or ultra fine, thus the anisotropy became lower. Hence we have the possibility of choice the electroplating conditions, and we can obtain the films with the same magnetic properties at different current densities. The figures 7 and 8 show that the amorphous films, at great concentrations of Co and at thickness  $1\mu\text{m}$ , and the crystalline films at thickness lower than 100nm, have the same  $H_c$  ( $\sim 1\text{A/m}$ ).

The relative magnetic permeability,  $\mu_r = \mu_r' + j\mu_r''$ , has two components: a real part, ( $\mu_r'$ ), which is associated with no dissipative processes, and a complex part ( $\mu_r''$ ) which represents irreversible processes as dissipation via Joule effect and/or radiofrequency radiation. We utilised the  $\mu_r'$  to characterize the response of the electrodeposited films to an alternating magnetic field.

For the amorphous films,  $\mu_r'$  increases with the concentration of Co and decreases with the film thickness. (Fig.-9). The dependence of  $\mu_r'$  on the inductor field (Fig. - 10) shows that the permeability is constant at lower values than a critical value of field, when the magnetisation is due at the rotation processes. After this

critical field,  $\mu_r'$  increases by the intervention of the walls motion. The thin nanocrystalline films present, at same concentration of components, an approach relative permeability. The thickness of very thin films influences more the permeability values.

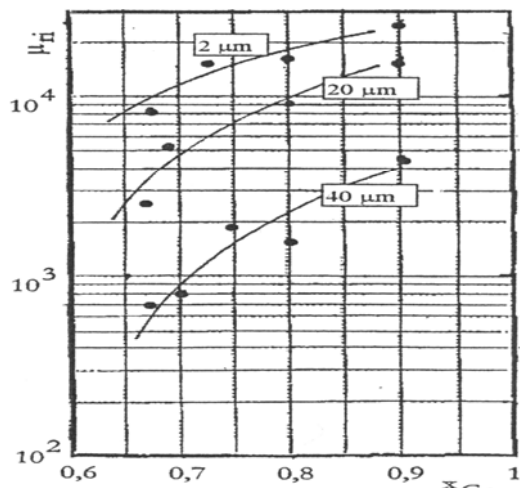


Fig. 9. The initial relative permeability dependence on the Co concentrations.

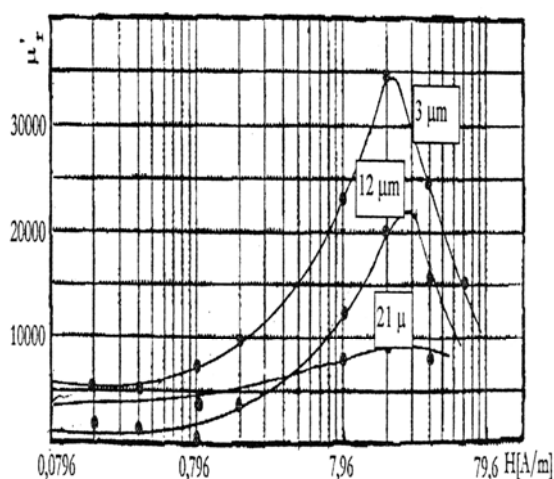


Fig. 10. The relative permeability dependence on the inductor field, at frequency 10 kHz, for the amorphous electrodeposited  $\text{Co}_{86}\text{Fe}_4\text{P}_{10}$  films.

#### 4. Conclusions

The comparative study of nanocrystalline and amorphous Co-rich films shows that these materials have approach soft magnetic properties. Both alloys can be obtained by electroplating at little ( $30 \text{ mA/cm}^2$ ) and large ( $200 \text{ mA/cm}^2$ ) current density from the same electrolytic bath. The films can have the same composition but structurally differ. The soft magnetic properties which are strongly dependent of composition have very approach values. At zero magnetostrictive composition and equal

thickness, the coercivity is  $1 - 4 \text{ kA/m}$  and the saturation induction is  $0.7 - 1 \text{ T}$ . The permeability is more affected by the structure and the preparation conditions but has values about  $10^3 - 10^4$  which not much differ. The resistivity is of the order of  $10^{-5}$  hence the losses by eddy current are reduced. The nanocrystalline films have an advantage: a better stability. The method permits the use of an electroplating installation with pulse tension power, which can obtain alternatively the two current density, for the electrodeposition of multilayers amorphous/nanocrystalline. This structural modulation confers the possibility to obtain a large spectrum of soft magnetic properties for recording heads.

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\*Corresponding author: sciureanu@yahoo.com