Electroplating in magnetic field and characterization of NiCoMnP alloy films with permanent magnet

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In the present study, the results of preliminary experiments about electrodeposition in magnetic field of cobalt nickel manganese-phosphorus (CoNiMnP) alloy films on copper substrate are reported. The composition of electrolyte bath was: 26 g/L $CoCl_2.6H_2O$, 24 g/L $NiCl_2.6H_2O$, 3.6 g/L $MnSO_4$, 24 g/L H_3BO_3, 4.6 g/L NaH_2PO_2, 23 g/L NaCl, 0.8 g/L saccharin, 0.2 g/L sodium lauryl sulphate and 0.01 g/L cerium(III) sulphate. The electrodeposition experiments were conducted in the following operating conditions: 3.5-5 pH value, 2-9 mA/cm^2 current density, 2-5 V voltage, room temperature (25^{o}C), magnetic stirring, and 1-15 h electrolysis time. The electrolysis cell was surrounded with a permanent magnet. The CoNiMnP alloy layers showed good appearance and were characterized by uniformity, fine-grained and brightness. The best quality CoNiMnP alloy was a smooth, bright and uniform deposit having about 70 μm thickness, which was obtained working with 5 mA/cm^2 current density during 15 h. The structure, texture, crystallite size and Vickers microhardness were evidenced and measured by SEM and XRD investigations and microhardness tests, respectively. Also, the magnetic characteristics of CoNiMnP films were studied using magnetometry.

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1. Introduction

Electrodeposition of metals and alloys is a useful and inexpensive technique to produce magnetic structures on a substrate having a pre-defined shape. Thin film permanent magnets that contain rare earth metals are commonly used in practice, although they have a high remanence coercitivity and they require a supplementary heat treatment at about 600 ^{o}C to align the magnetic moment by recrystallization, which is inconvenient for post-processing electronics. Another disadvantage is that these films cannot be achieved in defined forms [1].

In addition, rare earth based magnets oxidize and break easily. This has led, as an alternative, to the electrodeposition of magnetic alloys with nickel cobalt films [2-7]. The deposit can be obtained by electrolysis or electroless deposition. The electroless deposition produces more uniform and more resistant to corrosion films; however, this process has very slow deposition rates and the electrolyte is unstable over time. Therefore, regarding the integration of magnetic materials in micro-electro-mechanical systems (MEMS) it is preferred getting films through electrodeposition. The electrodeposition technique is especially interesting due to its low cost, high throughput and high quality of obtained deposit.

Initially, CoP based alloys were prepared in the form of stable and hard magnetic films obtained by electroless deposition [8]. A disadvantage is that these alloys have a high remanence coercivity and unusual magnetic properties on perpendicular direction with respect to the substrate taking into account a significant demagnetizing contribution and the main direction of anisotropy. In general, it is difficult to magnetize a ferromagnetic film along one direction. An example is the relatively harsh electro permanent magnetic materials, such cobalt nickel manganese-phosphorus (CoNiMnP) alloy [9]. A study by Chou *et al.* [10] reported electrodeposition of microcomposite type NiCo / SiC on substrate of stainless steel with the advantages of total absence of internal stress and hardness greater than 600 HV. According to Matsubara *et al.* [11] even high coercivity of CoNiP films decreases from 1000 Oe to 500 Oe, when increasing thickness from 0.2 μm to 0.5 μm.

The galvanostatic deposition, in which a constant current is applied without potential control, is the technique still most commonly used for the electrodeposition of NiCo alloys. The advantage of this method is that it does not require complex equipment, does not need a potentiostat and no reference electrode. It works only with an electrolytic bath, a standard cathode and a DC power supply. An improved version of this method is using pulsed power sources or polarity change. These procedures are used successfully for microcrystalline deposits because sustain nucleation and prevent growth of microcrystals.

The work of Chou and Ahn [12,13] gives more details regarding the optimization of baths content and operating conditions for electrolysis in magnetic field in order to obtain coercivity of NiCoMnP magnetic alloy for microactuators over 200%, compared to what is obtained by electrodeposition without external magnetic field. Thus, the electrolysis bath is surrounded by magnetic tiles (type Ferrimag, manufactured by Adams Magnetic Products,

USA) in an external magnetic field arrangement being applied perpendicular to the substrate surface.

The operating parameters in electrodeposition of NiCoMnP alloys that must be controlled are divided in two categories: (*i*) parameters involved in achieving the metal deposition, as bath parameters (electrolyte, precursor concentration, buffer, additives, pH) and temperature; (*ii*) parameters affecting the uniformity, structure and texture of deposit: current density and application of various current pulses, geometry and configuration of the substrate, stirring of solution, magnetic field during electrolysis.

This paper presents preliminary experiments of obtaining CoNiMnP alloys with permanent magnet electrodeposited on Cu substrate in order to establish and evaluate the conditions of deposition and physical and chemical properties of these alloys.

2. Experimental

The following optimal electrolyte composition was chosen as: 26 g/L $CoCl_2.6H_2O$, 24 g/L $NiCl_2.6H_2O$, 3.6 g/L $MnSO_4$, 24 g/L H_3BO_3, 4.6 g/L NaH_2PO_2, 23 g/L NaCl, 0.8 g/L saccharin, 0.2 g/L sodium lauryl sulphate and 0.01 g/L cerium(III) sulphate. The pH values (measured using a Inolab electrometric pH-meter) were adjusted within 3.5 - 5 range with amidosulfonic acid as additive. All reagents were purchased from Merck. Copper substrate of 99% purity was in shape of sheets.

A two-electrode cell was used, containing the copper substrate as cathode and both Ni and Co plates with large surface area as soluble anodes. The surface of copper electrode prior to film electrodeposition was polished gradually with 800 to 2000 grit silicon carbide paper, degreased with acetone, rinsed successively with HNO_3 (1:1) aqueous solution, running water followed by distilled water and dried. The electrodeposition experiments were conducted in the following operating conditions: 1.5 - 9.5 mA/cm^2 current density, 2 - 5 V voltage, room temperature, 5 - 15 h electrolysis time. Electrolyte magnetic stirring was performed for avoiding diffusive control of mass transfer at cathode and for working with an increased current density. The electrolysis cell was surrounded with a permanent magnet in order to obtain magnetic films with good performances. After electrolysis, the cathode was removed from the cell and NiCoMnP deposit was thoroughly washed with water and dried.

The cathodic current efficiency was calculated from the weight gained by the cathode following after electrolysis, taking into account the Faraday's law and using the number of transferred electrons, z = 2. The layer thickness was determined by knowing the density of pure Ni and Co, ρ_{Ni} = 8.908 $g \cdot cm^{-3}$, ρ_{Co} = 8.72 $g \cdot cm^{-3}$ and measuring the surface area of NiCoMnP deposit.

SEM micrographs of NiCoMnP alloy films were obtained using a FESEM-FIB Auriga (Carl Zeiss) SEM microscope. X-ray diffractometry measurements (XRD) were carried out using Bruker AXS D8 ADVANCE diffractometer with Cu anode and k_α Ni filter. For hardness examination, a Vickers FM 700 type, XMO 195 equipment was employed together with a MP NRW 173430.1007 sample as a hardness etalon. Magnetic measurements on the CoNiMnP alloy films were performed using the vibrating sample magnetometer (LakeShore type).

3. Results and discussion

During the experiments we proved that the electrolytic bath containing cobalt chloride and nickel chloride possesses the required good throwing power, buffer capacity and stability for the electrodeposition of nanocrystalline and smooth NiCoMnP films. A selection of optimal bath composition and operating conditions was done, as it was indicated in the Experimental Part.

Table 1 shows the appearrances and thicknesses of some good quality NiCoMnP deposits obtained in the cell placed in the magnetic field. Values of 90 - 92% current efficiencies were determined gravimetrically.

Table 1. Operation conditions and appearances of NiCoMnP deposits onto copper substrate obtained in magnetic field.

No.	Temperature (^oC)	Current density, (mA/cm^2)	Time (min.)	Layer thickness (μm)	Deposit appearence
1	25	2.2	360	26.2	Adherent, uniform deposit
2	25	2.3	420	33	Glossy, adherent and uniform deposit
3	**25**	**5**	**900**	**70**	**Shiny, adherent and uniform deposit**
4	25	7	300	31	Adherent, uniform deposit but dull
5	25	9.5	300	49	Shiny and uniform deposit but with few spots on surface

Deposits obtained onto copper substrates are uniform, adherent, and shiny with a light gray color. From experiments performed onto copper substrate it can be seen that the thickness of the deposited layer increases with increasing current density and deposition time. For instance, a smooth, bright and uniform deposit of CoNiMnP alloy having about 70 μm thickness was obtained working with 5mA/cm^2 current density during 15 h (sample 3).

A characterization of morphology is performed by SEM micrographs, some examples being given in Figs. 1 and 2. As the SEM images show, a coherent, uniform NiCoMnP deposit with a compact structure is obtained by electroplating procedure for both analysed samples. This good quality morphology indicates the important role as wetting and brightener agents of additives introduced in bath, namely saccharin and sodium lauryl sulphate, as well as the selection of their appropriate concentration.

A relatively high purity of deposited NiCoMnP may be considered from information provided by EDX spectra presented also in Figs. 1 and 2.

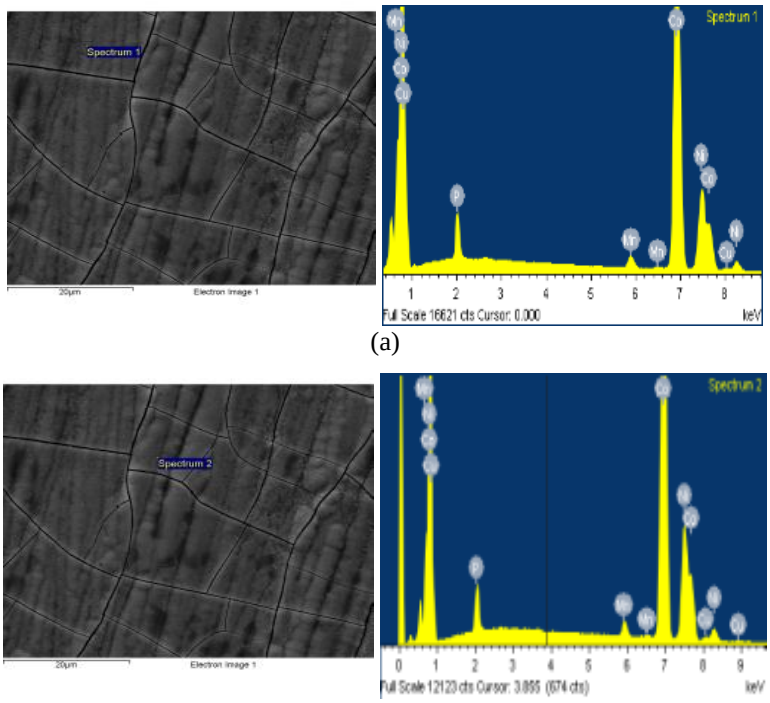

Fig. 1. SEM micrograph for sample 2 (see Table 1) and the corresponding EDX spectra in two locations denoted as spectrum 1 (a) and spectrum 2 (b).

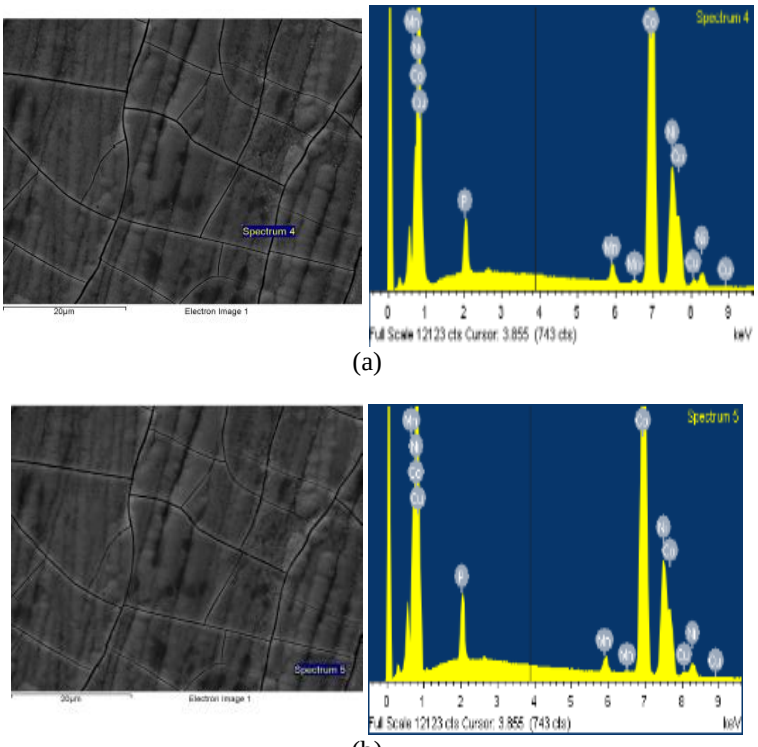

Fig. 2. SEM micrographs for sample 3 and the corresponding EDX spectra in two locations denoted as spectrum 4 (a) and spectrum 5 (b).

Tables 2 and 3 show the results of the elemental chemical analysis obtained from EDX spectra. It may be noticed that the content in copper provided by substrate is less than 2 wt.% for both analysed samples, which is a reasonable layer purity from technical point of view.

Table 2. Results of EDX chemical analysis of NiCoMnP deposit as sample 2.

Element	Wt. %		At. %	
	Spectrum 1	Spectrum 2	Spectrum 1	Spectrum 2
P (K)	3.49	2.48	6.43	4.61
Mn (K)	1.39	1.31	1.44	1.37
Co (K)	74.36	75.25	72.02	73.55
Ni (K)	19.71	19.76	19.16	19.39
Cu (K)	1.05	1.20	0.95	1.08
Total	100.00	100.00	100.00	100.00

Table 3. Results of EDX chemical analysis of NiCoMnP deposit as sample 3.

Element	Wt. %		At. %	
	Spectrum 4	Spectrum 5	Spectrum 4	Spectrum 5
P (K)	2,83	3.51	5.26	6.42
Mn (K)	1.39	1.29	1.46	1.33
Co (K)	74.19	74.29	72,32	71.96
Ni (K)	19.70	19.27	19.26	19.12
Cu (K)	1.88	1.64	1.70	1.17
Total	100.00	100.00	100.00	100.00

XRD spectra were recorded to get information on the deposit crystalline structure. An example of X-ray diffraction pattern for sample 3 (see Table 1) is presented in Fig. 3. The shape of this spectrum with narrow peaks suggests a very crystalline deposit. The nickel cobalt phase has electrocrystallised in *fcc* (face centered cubic) crystallographic system.

The collection of main peaks consists in characteristic peaks; three of them, at $2\theta = 45^o$, 52^o and 77^o, were attributed to NiCo species and the other three peaks (at 37^o, 42^o and 63^o) may be attributed to nickel cobalt oxide.

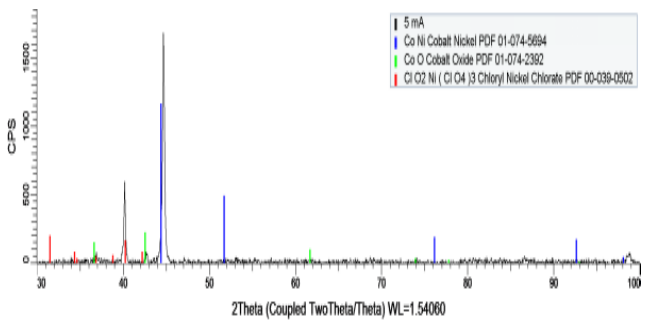

Fig. 3. XRD pattern for sample 3 (see Table 1) of Ni CoMn P layer deposited in magnetic field.

By processing the XRD data, the average size of crystallites was calculated using the Debye-Scherrer equation:

$$D = \frac{0.9\lambda}{B\cos\theta} \quad (1)$$

where λ is the wavelength of the X-rays, $\lambda = 0.154056$ nm in our case; B is the full width at half maximum (FWHM) and θ is the half diffraction angle of crystal orientation peak. Table 4 contains the obtained structural data, including the parameters of elementary cell. The crystallite size was found 353.8 Å as an average.

Table 4. Crystallographic parameters of elementary cell and crystallite dimensions of a typical NiCoMnP deposit (sample 3, Table 1).

System of Ni crystalline phase	Crystallo-graphic plane (hkl)	Interplanar distance d (Å)		Parameters of elementary cell (Å)		Mean value of crystal size, D_{hkl} (Å)
		theore-tical	experi-mental	theore-tical	experi-mental	
Face centered cubic (fcc)	(111)	2.03400	2.03376	3.521	3.522	353.8

The characterization of mechanical properties of NiCoMnP layers was performed by determination of Vickers microhardness (HV) for sample 3 (Table 1). The indentation tests were performed with a constant load of 0.3 kgf, at 10 s time duration, room temperature and 27% relative air humidity. The results of HV measurements for surface of NiCoMnP alloy films are presented in Table 5.

In this Table, the examples of the individual hardness values, H1...H5 (on different sites on the indentation area) are listed together with the arithmetical mean value of hardness. However, it may note that for the majority of samples, these values of Vickers hardness for NiCoMnP deposit are slightly lower, comparatively to those of samples with large areas that may have even a hardness of about 530 kgf/mm^2 (5.3 GPa), as literature reports [14].

Table 5. Vickers microhardness values (kgfmm^{-2}) of NiCoMnP deposits in magnetic field.

Sample	Individual value of HV 0.3/10, H1...5, kgf/mm^2	Mean value of HV 0.3/10, $\overline{H}$
Sample 3 (see table 1)	208.6	**206.7** kgf/mm^2 (**2.067** GPa) (arithmetical mean value)
	203.1	
	201.8	
	210.0	
	210.0	

The magnetic characterization of the prepared samples was performed using the vibrating sample magnetometer. The sample anisotropy was emphasized, plotting two hysteresis loops at different angles: 0^{o}C and 90^{o}C (see Fig. 4). The main magnetic characteristics of the prepared NiCoMnP films, determined from the hysteresis loops, are: remanence, B_r = 119 kA/m (1.5 kGs), coercivity, H_c = 56 kA/m (700 Oe) and maximum energy product, $(BH)_{max}$ = 1.5 kJ/m^3.

From Fig. 4, can be easily observed the magnetic anisotropy of the sample, evidenced by the hysteresis curve shape.

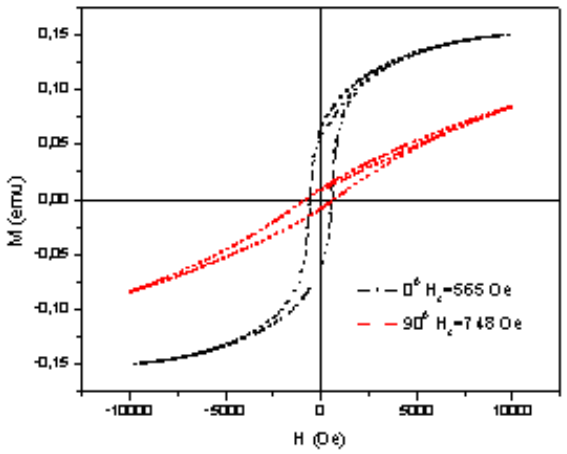

Fig. 4. The hysteresis loops of CoNiMnP alloy sample 3 deposited onto copper substrate in presence of an external magnetic field of 0.2 T for 0^o and 90^o angles.

The sample 3 realized through NiCoMnP alloy deposition in the presence of external magnetic field (H_{ext} = 0.2 T) was also studied by plotting the FORC diagrams (FORC - ***F**irst **O**rder **R**eversal **C**urve*). These diagrams provide a detailed characterization of the hysteresis behaviour for the magnetic materials, as thin or thick films, and can be efficient tools in the studies of these materials.

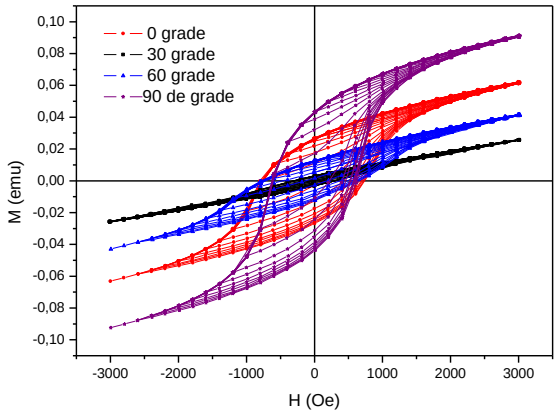

Fig. 5. Comparison of the FORC diagrams, realized for angles of 0, 30, 60 respectively 90^o, on the sample based of NiCoMnP alloy, deposited in the presence of the external magnetic field of 0.2 T.

In Fig. 5 it is represented the hysteresis loops family obtained for the NiCoMnP alloy film, deposited in presence of external magnetic field for different angles: 0^o, 30^o, 60^o, respectively 90^o. This figure shows that the films are ferromagnetic and present an anisotropy out-of plane.

4. Conclusions

The use of electrolytic bath containing cobalt chloride and nickel chloride that possesses the required good throwing power, buffer capacity and stability for the electrodeposition of nanocrystalline and smooth NiCoMnP films was proposed. A selection of optimum operating conditions was also done.

Better appearance was for relatively thin NiCoMnP layers, which were uniform, adherent and in general fine-grained and bright. The nanometric crystallite size was evidenced by optical and SEM microscopy, as well as by XRD spectra. A relatively high Vickers microhardness value (around 200 - 210 kgf/mm^2 or 2 – 2.1 GPa) was also measured.

The main magnetic characteristics, obtained for the NiCoMnP alloy films, deposited in the presence of 0.2 T external field on the cooper substrate, were: remanence, B_r = 119 kA/m (1.5 kGs), coercivity, H_c = 56 kA/m (700 Oe) and maximum energy product, $(BH)_{max}$ = 1.5 kJ/m^3.

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