

# Effects of the surface tension of the electrolyte on magnetic properties of Co-Ni-Mg electrodeposited thin films

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We investigate in this work the influence of the surface tension of the electrolyte on the magnetic properties of thin electrodeposited Co-Ni alloy films, in order to accurately control their properties for various technological applications. Co-Ni-Mg films containing (75-82) at.% Co, 3-4 at.% Mg, balance Ni, were electrodeposited on aluminium substrates using a complex solution containing ions of Co, Ni and Mg. Sodium laurylsulphate (as surface-active agent), and sodium saccharin (as inhibitor agent) were used to control the surface tension of the solution. The adsorption of some dipoles of these substances on the electrolyte/film interface (studied by square-wave polarography) results in changes in the film morphology (investigated by AFM). Consequently, the magnetic properties (studied by torsion magnetometry and an induction method) are changed as a function of the additive concentrations. The magnetic characteristics are in the range  $H_c = (5 - 70)$  kA/m,  $B_r/B_s = 0.2 - 0.95$ , and  $K_{eff} = -20 \times 10^4$  J/m<sup>3</sup> to  $+40 \times 10^4$  J/m<sup>3</sup>.

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## 1. Introduction

It is known that electrodeposition is capable of producing high quality magnetic films, presenting several advantages by comparison with vacuum techniques (especially low costs, extended surfaces and the possibility of large scale applications). A good control of the electrodeposition parameters assures the reproducibility of the film properties. One of these electrodeposition parameters to be controlled is the surface tension at the electrode/electrolyte interface. Searching of new additives for controlling the surface morphology has been a major objective in the studying of various electroplated metals and alloys in the past years [1 - 4]. But the correlation between the magnetic properties of the films and the kinetics of electrochemical surface processes under the influence of organic additives has not been intensively investigated until now. The organic compounds added to metal plating baths at a small concentration can change the microstructure of the deposits and also the functional properties. In a previous paper [5] we have reported the growth of CoPt superlattices with satisfactory homogeneity and perpendicular anisotropy under precise control of both parameters. The purpose of this study is to investigate the influence of the surface tension of the electrolyte (controlled by organic additives) on the magnetic properties of thin electrodeposited Co-Ni-Mg films, which could be suitable for various technological applications. The films were obtained as a particular case of the electrodeposition of Co-Ni-Mg-N thin films [6 - 9]. There are publications dealing with the electroplating of Co-Mg and Ni-Mg films [10], but we have not found in the literature any study referring to the Co-Ni-Mg films. To our knowledge, the influence of organic additives

(saccharin and sodium laurylsulphate) in the context of electrodeposited Co-Ni-Mg thin films has never been studied until now.

## 2. Experimental

All the films studied in this paper were prepared by electrodeposition on aluminium substrates shaped as disks (surface area: 3.14 cm<sup>2</sup>) with a 50 nm Ni buffer layer, obtained also by electrochemical deposition. The bath composition and the electrodeposition conditions were set accordingly to our previous publications [6-8].

The films were electrodeposited in a complex solution containing: 30 g/l CoSO<sub>4</sub>·7H<sub>2</sub>O, 50 g/l NiSO<sub>4</sub>·7H<sub>2</sub>O, 10 g/l NiCl<sub>2</sub>·6H<sub>2</sub>O, 33 g/l MgSO<sub>4</sub>·7H<sub>2</sub>O, 10 g/l NaCl, 50 g/l Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O, and 30 g/l H<sub>3</sub>BO<sub>3</sub>. Sodium laurylsulphate C<sub>12</sub>H<sub>25</sub>NaO<sub>4</sub>S (labelled L), and sodium saccharin NaC<sub>7</sub>H<sub>4</sub>O<sub>3</sub>NS·2H<sub>2</sub>O (labelled S) were used as additives, with concentrations which ranged from 0.05 to 1.00 g/l. The quantitative chemical composition of the films was determined by EDAX. By controlling the deposition time, the film thickness for all the samples was adjusted to about 450 nm.

The surface tension measurements were performed by using the ring and drop-weight methods for solutions without and with additives. Polarographic analysis of the solutions without and with additives was performed by using a square-wave polarograph OH-104. For all these measurements, the polarograms were obtained with two platinum point electrodes having approximately the same contact area (0.06 mm<sup>2</sup>) with the solution.

The magnetic measurements were carried out at room temperature by torsion magnetometry in fields up to 300 kA·m<sup>-1</sup> and by a Howling type induction method with a system of computerised data acquisition. For the

induction method, the magnetic field (up to  $60 \text{ kA}\cdot\text{m}^{-1}$ ) was applied parallel to the film plane. In the experimental set-up, the winding of the pick-up coil is reversely connected in series with the dummy pick-up coil located at the centre of a coil, which is parallel and identical with the principal coil used for magnetising the sample. The obtained curves represent the derivative of magnetization with respect to time ( $dM/dt$ ) versus the a.c. magnetic field intensity ( $H$ ) with sinusoidal-field excitations (at a frequency of 50 Hz), from which the a.c. susceptibility  $\chi = dM/dH$  versus  $H$  was calculated.

The surface analyses were performed with an atomic force microscope (AFM) at room temperature in tapping mode, using a commercial  $\text{Si}_3\text{N}_4$  tip with a radius of 10 nm.

### 3. Results and discussion

It is known that organic substances added to the electrodeposition bath have different types of effects on the deposited film. Some of these additives (such as saccharin) are inhibitors of crystal growth, leading to the brightening of the deposit, while others are tensio-active agents lowering the film pitting [1, 2]. Sodium laurylsulphate (L) is a surface-active agent (decreasing the surface energy of the air/solution interface), and sodium saccharine (S) is an inhibitor agent, which increases the surface energy [11]. It is presumed that the dipole adsorption on the electrolyte/film interface results in a modification of surface energy and thus of the film morphology. To verify this assumption, we performed the square-wave polarograms of various solutions, without and with additives. We used the following notations: the solution without any additives was labelled A, the solution with an addition of 0.5 g/l L was labelled AL, the solution with addition of 0.5 g/l L and 0.5 g/l S was labelled ALS and a solution with an addition of 0.5 g/l S was labelled AS. Some polarograms were also performed for other concentrations of additives, but they are not included in this study.

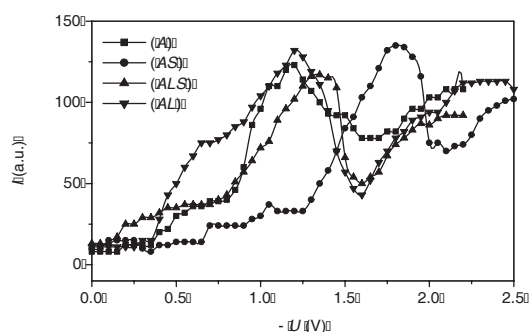


Fig. 1. Forward square-wave polarograms (in the potential range of  $0.00 \div -2.50 \text{ V}$ , with a scan rate of  $0.02\text{V}/1.5 \text{ s}$ , with amplitude of the square-wave of  $0.02 \text{ V}$  and the frequency of  $250 \text{ Hz}$ , without stirring the solution. Notations for the solutions: A - the basic solution without additives, AS - solution A with addition of  $0.5 \text{ g/l}$  saccharine (S), AL - solution A with an addition of  $0.5 \text{ g/l}$  sodium laurylsulphate (L), ALS - basic solution with addition of  $0.5 \text{ g/l}$  L and  $0.5 \text{ g/l}$  S.

Fig. 1 presents forward square-wave polarograms of these solutions performed in the potential range from  $-0.00\text{V}$  to  $-2.50 \text{ V}$ , with a scan rate of  $0.02\text{V}/1.5 \text{ s}$ , with amplitude of the square-wave of  $0.02 \text{ V}$  and the frequency of  $250 \text{ Hz}$ , without stirring of the solution. In this figure, the curve A (obtained from solution A) shows that the reduction of Ni and Co ions is centred on a half-wave potential of  $-1.20 \text{ V}$ . A shift ( $-0.6 \text{ V}$ ) of the reduction wave toward negative potentials is observed for the solution AS. This shift could be explained by the inhibition of the electrochemical process in the presence of S. Some of the solution molecules are temporarily adsorbed on the film surface or in the electrical double layer (in the proximity of cathode) and the reduction of Co and Ni ions takes place at more negative potentials. The experiments in this work were undertaken without stirring of the electrolyte in order to investigate the effects of adsorbed molecules on the electroplating process.

The square-wave polarograms of solutions ALS and AL are represented in Fig. 1 by the curves ALS and, respectively, AL. The peak of the curve AL shifts from the peak of curve A, indicating a slow catalytic effect of sodium laurylsulphate. The peak for the solution ALS appears between the two peaks corresponding to solutions AS and AL and is shifted toward negative potential ( $-0.10 \text{ V}$ ), in comparison with the solution A. The shift of the peaks observed in square-wave polarograms demonstrate the existence of adsorbable substances on the electrode/electrolyte interface or in the electrical double layer situated in the proximity of the electrode. The differences between the curves from Fig. 1 appear because of the different electro-activity of the species adsorbed at the interface (exerting either an inhibitor effect or a catalytic effect on the electrode reaction). However, in our experiments, the presence of impurities was not detected in the electroplated films. One can suppose that the adsorbed molecules are not included in films and that they influence the growth process only by creating voids or sites that slow down nucleation.

It is known that the surface morphology of the electrodeposits is affected by both bath temperature and current density. Therefore, the electrolysis parameters were maintained at the same values for all experiments, to make a precise study on the influence of only organic additives on the magnetic properties of deposits. Electroplating without and with additives was performed for all the samples in this work at the same current density of  $120 \text{ mA}/\text{cm}^2$  and at the same temperature ( $30 \pm 0.5$ )  $^\circ\text{C}$ , without stirring the electrolyte. Film thickness for all the samples was adjusted, by controlling the deposition time, to about  $450 \text{ nm}$ . The films were obtained with compositions in the range (75 - 73) at.% Co, 4 at.% Mg, balance Ni.

The surface morphology of the films (shape and size of crystallites) changes as a result of these additives. AFM images are shown in Fig. 2 for three samples prepared from the solutions: A (Fig. 2a), AL (2b) and ALS (2c). The films prepared in the solution AS have not a satisfactory substrate adherence.

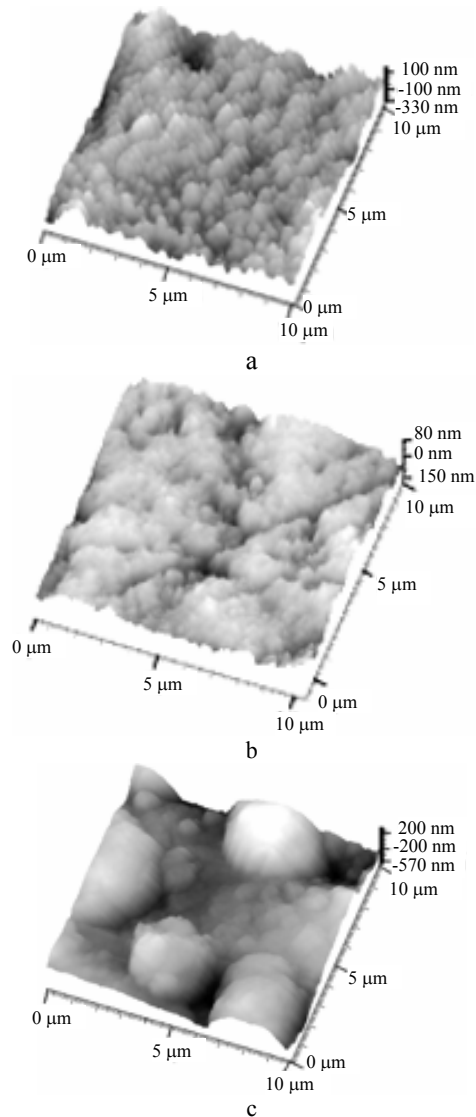


Fig. 2. AFM images for three typical samples prepared from the solutions: A (a), AL (b) and ASL (c).

The surface morphology (shape and size of the crystallites) is different in the three typical samples. As it can be seen in Fig. 2, the anionic surfactant  $L$  exhibits a strong influence on the morphology of the film. The addition of sodium laurylsulphate in solution enhances the formation of a smooth surface and the creation of elongated crystallites, which are parallel to the film plane. A significant change in morphology (Fig. 2c) also appears as a result of the presence of  $S$  in the electrolytic bath  $AL$ . The saccharin molecules adsorbed at the surface create disorder in the incorporation of adatoms into the lattice or inhibits the surface diffusion of adatoms towards growing centers. This is an evidence of the inhomogeneous growth of the crystallites on different nucleation sites and of the modification of the morphological shape of the crystallites. The mean square roughness of the three samples (calculated from the  $10 \mu\text{m} \times 10 \mu\text{m}$  AFM topography scan) has the following values: (A) 84.7 nm, (AL) 29.7 nm and (ASL) 214.27 nm. At the same time, the crystallite sizes and shapes are different between these samples. In

other words, the film nucleation and growth process is modified as an effect of additives in the electroplating solution.

The XRD analyses indicate that our samples are constituted from a Co-Ni solid solution with a polycrystalline fcc structure [7,9]. The relative diffraction intensity of the plane (111) is enhanced in films deposited in solution  $AL$ . The effect of  $L$  on the film morphology could be explained in a similar way with the effect of this additive in the gold plating solutions [3]. We suppose that the laurylsulphate tends to be adsorbed on the surface, rather than on the edge of grains, and thus gives rise to a flake-like structure (elongated crystallites), with the (111) facets being the major facets of the films obtained in the presence of  $L$ .

The morphology investigations are also supported by the magnetic measurements. We present in Fig. 3 (a, b and c) the susceptibility curves for the same three samples from Fig. 2. The shape of an M-H loop is a very sensitive function of the sample microstructure. The small changes in the shape of the susceptibility loops reflect changes in the switching properties of films. The shape of the curve in Fig. 3b points to a preference for in-plane magnetization, with lower coercive field and preponderance of wall displacements process. On the other side, the curve in Fig. 3c indicates a preference for the rotational magnetization process in the case of samples with out of plane magnetic anisotropy.

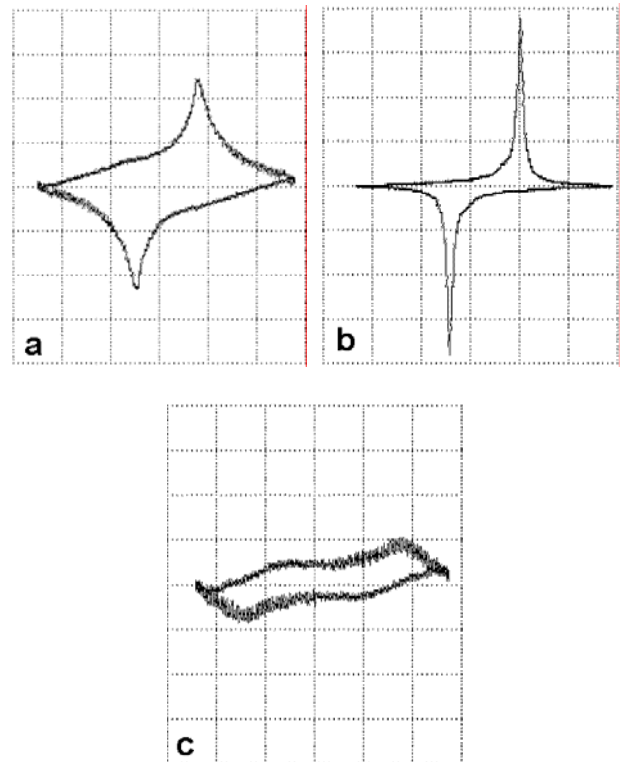


Fig. 3. Curves  $\chi = dM/dH$  vs.  $H$  or susceptibility curves for the three samples whose AFM images were presented in Fig. 2: a) solution A, b) solution AL, c) solution ALS.

Scalation: ( $H_{\text{max}} = 60 \text{ kA m}^{-1}$ ),  $\chi$  in arbitrary units.

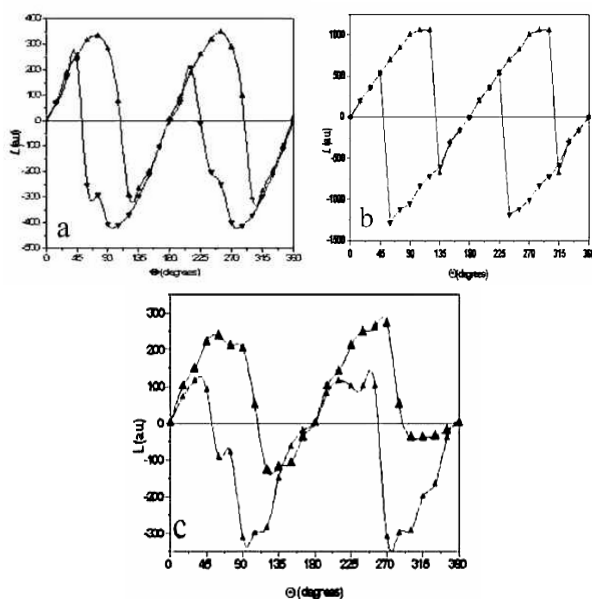


Fig. 4. Torsion magnetometry for the films deposited in: solution A – (Fig. 4a), solution AL – (Fig. 4b), solution ALS – (Fig. 4c).

Fig. 4 shows the torsion magnetometer curves of the films deposited in the following solutions: A – Fig. 4a, AL – Fig. 4b, and ALS – Fig. 4c. The film plane was oriented perpendicular to the field-rotation plane; e. g. the torque was measured around an arbitrary axis parallel to the film plane. The torque curves were initiated with the applied field in the plane of the sample. In the torque experiment a magnetic field is rotated from the film plane ( $\theta = 0$ ) to the normal of the film ( $\theta = \pi/2$ ) and the magnetization  $M$  follows at an angle  $\varphi$  with respect to the film plane. An equilibrium orientation for the magnetization is reached when the torques on  $M$  due to  $H$  and to the total uniaxial anisotropy  $K_{eff}$  cancel. This could be described by

$$MHV \sin(\theta - \varphi) = L = K_{eff} \sin(2\varphi), \quad (1)$$

where  $V$  is the magnetic volume of the film [10]. At high fields, when the magnetization is saturated ( $\theta = \varphi$ ),  $K_{eff}$  can be determined directly from the equation (1). This type of anisotropy is called two-fold anisotropy.

As it can be seen in Fig. 4, the experimental torque curves exhibit mainly a two-fold periodicity. For the sample deposited from the solution ALS, a significant four-fold periodicity (i. e. the presence of an anisotropy energy term  $K_2 \sin 4\varphi$ ) can be observed in Fig. 4c. This four-fold periodicity can be explained by the simultaneous existence of regions with positive and negative  $K_{eff}$ , therefore by inhomogeneity of  $K_{eff}$  in different crystallites. The curves in Figs. 3 and 4 indicate that the easy axis of magnetization for the three cases is out of plane for the sample (A), in plane for the sample (AL) and perpendicular to the plane of the film for (ALS). The most probable source of out of plane anisotropy in these films is the columnar irregular shape of the grains [11].

The variation of the magnetic properties (coercive

field  $H_c$ , magnetic anisotropy constant  $K_{eff}$ , squareness of the hysteresis cycle  $B_r/B_s$  and rotational hysteresis loss) was also studied as a function of the additive concentration. The values of these characteristics varied in the range  $H_c = (5 - 70)$  kA/m,  $B_r/B_s = 0.2 - 0.95$ , and  $K_{eff} = -20 \times 10^4$  J/m<sup>3</sup> to  $+40 \times 10^4$  J/m<sup>3</sup>.

## 4. Conclusions

Co-Ni films containing 75 at % Co, 21 % Ni, and 4 at % Mg were electrodeposited on aluminium substrates using a solution containing sodium laurylsulphate and sodium saccharine as surface-active and, respectively, inhibitor agent, in order to modify the film morphology and the magnetic anisotropy of the films.

The presence of sodium laurylsulphate and saccharin in the electroplating solution causes a considerable shift of the polarisation curve towards more negative potentials in comparison with the curve determined for the electrolyte without additives. The adsorption of dipoles of the addition substances on the electrolyte/film interface results in morphology changes in the thin films. The magnetic characteristics and the morphology of the electrodeposited Co-Ni-Mg films were found to strongly depend on the additive concentration of the electrolytic bath. The easy axis of magnetization is oriented out of plane for the samples deposited from the solution A, in plane for the samples deposited in the solution (AL) and perpendicular to the film plane in the case of deposition from solution (ALS). From our experiments, we conclude that the surface tension of the solution is an important parameter for controlling the magnetic anisotropy, the coercivity and the morphology of electrodeposited films.

## References

- [1] L. Burzyńska, E. Rudnik, Hydrometallurgy **54**, 133 (2000).
- [2] M. Troyon, L. Wang, Applied Surface Science **103**, 517 (1996).
- [3] K.-Lin, W. -Ch. Liu, M. H. M. Lin, Y. W. Hu, J. Electrochem. Soc. **138**, 3276 (1991).
- [4] P. F. J. de Leon, E. V. Albano, R. C. Salvarezza, H. G. Solari, Physical Review E **66**, 042601 (2002).
- [5] V. Georgescu, M. Daub, J. Optoelectron. Adv. Mater. **7**(2), 853 (2005).
- [6] V. Georgescu, Materials Science and Engineering **B27**, 17 (1994).
- [7] V. Georgescu, V. Mazur, M. Georgescu, B. Pushcashu, Balkan Physics Letters **5**, 944 (1997).
- [8] V. Georgescu, M. Georgescu, J. Magn. Magn. Materials, Vol **242-245**, Part 1, 416 (2002).
- [9] M. Georgescu, V. Georgescu, N. Apetroaei, J. Optoelectron. Adv. Mater. **4**(2), 353 (2002).
- [10] A. Riesenkauf, Z. Fura, Arch. Hutn. **20**, 3 (1975).
- [11] J. T. Davies, E. K. Rideal, Interfacial Phenomena, 2nd ed. (Academic Press, New York and London, 1963).