

MAGNETIC PROPERTIES AND MORPHOLOGY OF ELECTRODEPOSITED Co-Ni-Mg-N THIN FILMS

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The influence of the nitrogen content on the magnetic properties and thin film morphology is investigated in Co-Ni-Mg-base thin films. The thin films are electrolytically prepared from an original complex bath containing sulphate electrolytes and additional substances. Co-Ni-Mg-N thin films (450 nm) in the composition range 0 - 16 at. % N, 82 - 66 at. % Co, 4 at. % Mg (balance Ni) were electrodeposited onto an aluminium substrate covered with a Ni buffer layer (50 nm). The effect of the nitrogen content, C_N , on the magnetic characteristics (B_s , H_c , B_r/B_s) of Co-Ni-Mg-N thin films is studied. The dependence of the magnetic behaviour of thin films on nitrogen content is explained by the changes both in the phase composition and in the surface morphology of the samples.

(Received February 5, 2002; accepted May 15, 2002)

Keywords: Magnetic thin films; Metallic films; Atomic force microscopy.

1. Introduction

Recently, many studies have focused on preparation by inexpensive methods of thin films from 3d transition metals-base alloys with P or N as impurities, with a view to use them for applications, especially magnetic recording media and magnetic sensors [1-4]. In our previous papers we reported on preparation and magnetic properties of some Co-Ni thin films with Mg and N as impurities [5, 6]. It is known that the extrinsic magnetic properties of thin films (coercive field, magnetic susceptibility, induced anisotropy, squareness of the B-H hysteresis loop) are influenced particularly by the thin film microstructure (grain morphology, texture, phase content, etc). The purpose of this paper is to investigate the influence of the nitrogen content, C_N , on the Co-Ni-Mg thin films morphology and magnetic properties.

2. Experimental

The thin films were electroplated from a complex bath containing: $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ with a total metallic ion content of 20 g/l. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, NaCl, $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$, H_3BO_3 , sodium citrate, sodium lauryl-sulphate, sodium saccharine, and NaNO_3 (0 - 3.5 g/l) were used as additional substances. The concentration of the substances in solution and the deposition parameters were set according to our previous results [5, 6]. The increase of the NaNO_3 percentage in the above-mentioned ranges results into a nitrogen content, C_N , in the deposited thin films ranging from 0 to 16 at %. The film substrate was aluminium disk-shaped (23 mm in diameter) covered with a Ni buffer layer (50 nm). The thin films composition was determined polarographically and by using electron probe X-ray microanalysis [5]. The nitrogen content from Co-Ni-Mg-base thin films was determined by Auger spectroscopy. A linear dependence of C_N on the NaNO_3 concentration in the bath was considered in the case of the thin films with very low nitrogen content. The crystal structure of the thin films was determined previously by X-ray diffraction (Bragg-Brentano and grazing incidence angle) using $\text{Co-K}\alpha$ radiation [5]. Magnetic properties at room temperature were investigated by two procedures: an AC induction method with computerized data acquisition system (in a maximum applied field of 60 kA/m and a frequency of 50 Hz), and by torque magnetometry in fields up to 300 kA/m.

3. Results and discussion

A set of samples having 0 - 16 at. % N, 82 - 66 at. % Co, 4 at. % Mg (balance Ni) was prepared by using solutions with different contents of NaNO_3 , all the other deposition parameters being maintained at constant values. The thin films composition (in atomic percentage) varies between 82 % Co, 14 % Ni, 4 % Mg and 66 % Co, 14 % Ni, 4 % Mg, 16 % N as the result of the increase of the nitrogen content (C_N). The film thickness was maintained to about 450 nm for all the studied thin films.

X-ray diffraction measurements show that the film structure changes from amorphous ($C_N = 0$) to polycrystalline ($C_N > 0$), depending on the nitrogen content. Nitrogen adsorbed in the deposited thin films influences their structure and morphology. The thin films consist in an hcp crystalline phase mixed with amorphous phase for $2 < C_N < 10$ at. %. For thin films containing more than 10 at. % N, a small amount of fcc phase mixes with the hcp phase. Our results are in relative agreement with the results reported in the literature on the effect of nitrogen on the structure of 70 at. % Co - 30 at. % Ni thin films prepared by r.f. sputtering in an Ar- N_2 atmosphere [2].

The precipitation mode and the morphology of the thin films are also changing as the result of the nitrogen absorption. AFM measurements in phase contrast mode were used to investigate some samples with different C_N . Fig. 1 shows the phase images recorded for thin films containing (a) 0, (b) 4, (c) 8, and (d) 16 at. % N. All scans are $20 \mu\text{m} \times 10 \mu\text{m}$. It is known that the phase images reflect differences in the properties of the individual components of the heterogeneous materials.

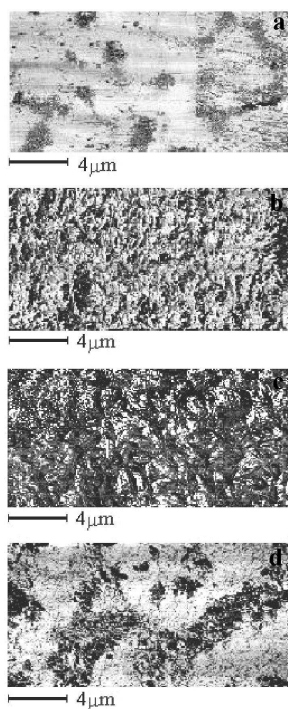


Fig. 1. AFM phase images obtained for Co-Ni-Mg-N thin films with different nitrogen contents (at. %): (a) $C_N = 0$, (b) $C_N = 4$, (c) $C_N = 8$, and (d) $C_N = 16$

The phase profiles corresponding to the images from Fig. 1 (along the x-y line marked by triangle in Fig. 1) are shown in Fig. 2. Cross section analysis (Fig. 2) show that the increase of the thin films nitrogen content result in the phase profiles with step-like increasing changes (for $0 < C_N < 10$ at %), which differentiate regions corresponding to different phases. The largest phase difference was found for $C_N = 8$, where the height difference between regions is maximal. XRD measurements reveal a mixture of hcp and fcc phases of solid solution of Co-Ni with Mg and N as impurities for the sample presented in Fig. 2c. We suppose that an amorphous mixture with an excess of nitrogen agglomerates on the surface. This tendency is better evidenced for the sample containing 16 at % N (Fig. 2d). The

thin films containing large amounts of nitrogen become fragile and show internal stresses and fractures.

Fig. 3 shows topographic profiles taken along the same x - y line on the surface as in the phase images (marked by triangle in Fig. 1) for thin films containing: (a) 0, (b) 4, (c) 8, and (d) 16 at. % N. The mean square roughness of these samples (calculated from the $20\ \mu\text{m} \times 20\ \mu\text{m}$ AFM topography scan) is 35.68 nm, 88.65 nm, 130.70 nm and 77.77 nm, for the samples with $C_N = 0$; 4; 8 and 16, respectively. Topographic images, which evidence the roughness and the granulation of the surface, are very different in comparison with the phase profiles that reflect the difference in the energy dissipated on the different components on the surface. These points are still matters of debate.

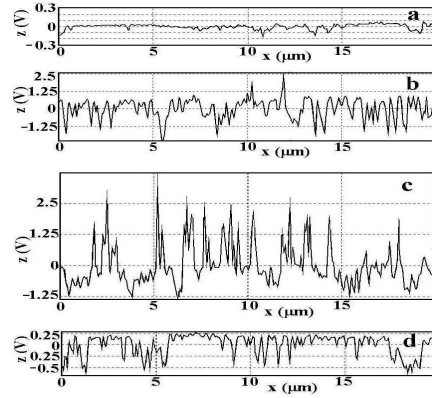


Fig. 2. Phase profiles of the images shown in figure 1 (taken along the x - y line marked with triangle), for Co-Ni-Mn-base thin films with different C_N : (a) 0, (b) 4, (c) 8, and (d) 16 at. %.

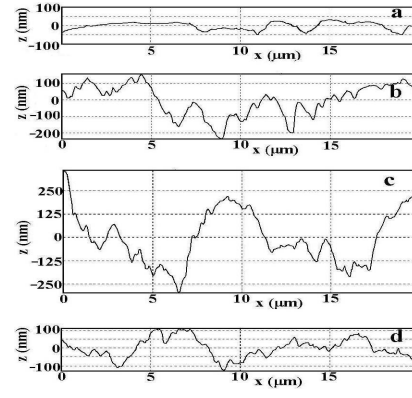


Fig. 3. Cross-section topographic profile of the images presented in Fig. 1 (taken along the x - y line marked with triangle), for thin films with different C_N : (a) 0, (b) 4, (c) 8, and (d) 16 at. %.

Magnetic characteristics of the thin films vary with the nitrogen content, as we shown in one of our previous paper [5]. The saturation magnetic induction, B_s , attains a maximum around $C_N = 1.5$ and then decreases with the increase of C_N . The dependence of B_s on C_N reflects the variation of the local electronic structure of Co or Ni atoms. The modification of nitrogen coordination number around magnetic atoms, by including N as interstitial in the crystalline lattice of the Co-Ni solid solution, results in the modification of the exchange interactions between magnetic atoms from ferromagnetic to antiferromagnetic ones. Consequently, B_s depends on C_N . The samples become antiferromagnetic at room temperature (in the experimental limit of our experiments) for $C_N > 15.3$ at. %.

Fig. 4 shows the in-plane coercive field (H_c) and the squareness of the B-H hysteresis loop ($S = B_r/B_s$) as a function of the N content (C_N). An increase of C_N up to 8 at. % causes the increase of the coercive field and squareness of the B-H loop, whereas for $8 < C_N < 15$ both H_c and S reach a plateau.

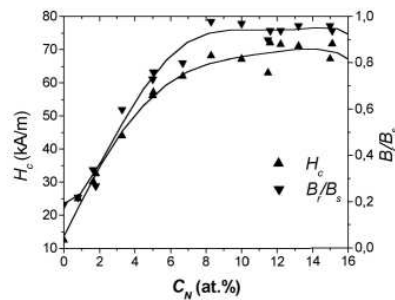


Fig. 4. The dependence of the coercive field (H_c) and squareness (B_r/B_s) of the hysteresis loop on the nitrogen content C_N for Co-based thin films and the polynomial fit of the data.

A good agreement for the experimental data for H_c is obtained by the polynomial fit of the equation

$$H_c = H_{ca} + A_1(c_N) + A_2(c_N)^2 + A_3(c_N)^3, \quad (1)$$

where $H_{ca} = (13.50 \pm 1.49)$ kA/m, $A_1 = (12.32 \pm 0.93)$ kA/m, $A_2 = -(0.88 \pm 0.14)$ kA/m and $A_3 = (0.021 \pm 0.006)$ kA/m.

The same kind of experimental data analysis for $S = B_r/B_s$ was performed by polynomial fit of the equation

$$S = S_a + B_1(c_N) + B_2(c_N)^2 + B_3(c_N)^3, \quad (2)$$

where $S_a = 0.11 \pm 0.013$, $B_1 = 0.170 \pm 0.002$, $B_2 = -(0.010 \pm 0.003)$, and $B_3 = (2.0 \pm 0.5) \cdot 10^{-4}$.

In these equations we assumed that H_{ca} and S_a are the values of the coercive field and squareness, respectively, for Co-Ni-Mg amorphous samples. The increase of both H_c and S with C_N is almost linear for low nitrogen content (A_1 and B_1 are the dominant coefficients). We will specify the significance of the other coefficients after we will present some details about the sample morphology and microstructure.

From the specific shape of the magnetization curve [6] we have found for Co-Ni-Mg-N thin films the following types of magnetic behaviour: (a) ferromagnetism with easy plane of magnetization in plane for thin films with C_N less than 3 at. %, (b) ferromagnetism with inclined to the plane easy axis for $3 < C_N < 8$ at. %, (c) spin-flopping behaviour with in-plane easy magnetization axis in the case of thin films with C_N over 8 at. %.

The crystallographic structure and the morphology of the thin films determine the magnetic behaviour of the samples. Thin films electrodeposited in bath without nitrogen addition ($C_N = 0$) contain an amorphous phase. The hcp phase with c-axis perpendicular to the thin film plane and small magnetocrystalline anisotropy was evidenced for thin films deposited in the bath with 2 to 10 at. % N, while for $C_N > 10$ at. % thin films consist in a mixture of hcp and fcc phases with columnar growth [5]. From AFM images (Fig. 1), one see that the samples are composed of insular grains grown on different nucleation centers. The size of the crystalline grains decreases by increasing C_N over 8 at. %. The nature of the grains and of the interface between grains influences exchange interactions between the grains that play an important role in determining the coercive field and squareness of the hysteresis loop. This effect is important in the thin films with a large content of nitrogen, because the nature, size and texture of the grains depend on the nitrogen content. The appearance of the antiferromagnetic phase in thin films with a larger amount of nitrogen could explain the dominance of the A_1 and B_1 coefficients in equations (1) and (2), respectively. The negative values of A_2 and B_2 , could be correlated with the existence of a small amount of soft ferromagnetic fcc phase. The increase of the number of the magnetization pinning sites on the grain surface for high N contents could explain the significance of the coefficients A_3 and B_3 . The large values of H_c and S are related to the magnetic spins compensation in the antiferromagnetic structure. The nitrogen concentration at which the thin films become antiferromagnetic is about 15.3 at. %, at room temperature.

4. Conclusion

Co-Ni-Mg-N thin films (450 nm) in the range of compositions 0 - 16 at. % N, 82 - 66 at. % Co, 4 at. % Mg (balance Ni) were prepared by electrodeposition. The effect of the nitrogen content of the thin films on the magnetic characteristics (B_s , H_c and B_r/B_s) were studied (with C_N varying in the range 0 - 16 at. % N). The dependence of the magnetic characteristics on C_N was explained by the phase content (hcp, fcc) and the surface morphology of the samples studied by AFM (phase imaging and topography).

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