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Influence of the Cr and Ni concentration in CoCr and CoNi alloys on the structural and magnetic properties

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Abstract

The crystalline and magnetic properties of micron thick magnetron sputtered Co₁₋ₓCrₓ and Co₁₋ₓNiₓ alloy films are analyzed in the view of their implementation as semi-hard magnets. All the tested films crystallize in hcp lattice, at least up to 35 atomic % of alloying elements (Cr or Ni). The structural study shows that the ratio of hcp phase with [0001] axis orientated perpendicular to the film as compared with in-plane orientation increases (resp. decreases), when Ni (resp. Cr) concentration increases independently of the post-annealing temperature. The orientation of the magnetization results from the competition between the demagnetization field which tends to align the magnetization in plane and the crystalline anisotropy which tends to maintain the magnetization along the [0001] axis. Interestingly, we find that, although Co and Ni are very similar atoms, Co₁₋ₓNiₓ alloys crystalline anisotropy can be strongly increased and reach up to twice the anisotropy of the best Co₁₋ₓCrₓ alloy, while maintaining a magnetization at saturation above 1200 kA/m. The thermal stability of the structural and magnetic properties of both alloys is demonstrated for annealing temperature up to 300°C.
1. Introduction

Semi-hard magnetic material is a class of magnets which exhibits intermediate magnetic properties between soft and hard magnets [1]. Their coercivity $H_c$ usually ranges from 50 to 1000 Oe approximately [1]. They exhibit a relatively high magnetization at saturation $M_s$, a medium magnetization at remanence $M_r$ and medium saturation field, so that the energy cost to magnetize the material is much lower than that of hard magnet. Therefore they can be easily magnetized and demagnetized to control the value of the residual magnetization and of the magnetic force which is also proportional to the thickness of the coating. For examples, thick semi-hard magnet films with high magnetic force can be used in magnetic micro-actuators [2] such as magnetic force switch [3], or magnetic microencapsulation [4], in magnetically coupled devices or in magnetic data storage used in magnetic printing [5][6][7]. Among these materials, Co-based alloy with hexagonal close-packed structure is interesting in reason of its high saturation magnetization and of its high uniaxial magneto-crystalline anisotropy. According to the positive magneto-crystalline anisotropy constants ($K_1 = 4,5 \times 10^5$ J m$^{-3}$, and $K_2 = 1,5 \times 10^5$ J m$^{-3}$), the easy axis corresponds to the [0001] c-axis of the hexagonal structure.

Due to this feature, CoNi-based alloys have been especially studied, first as a media for magnetic recording or optical recording, and lately for magnetography and MEMS application. CoNi, CoNiP, CoNiFe alloys have been widely studied since the 1970s. Most of the publications report on the evolution of coercive field as a function of deposition condition [8], concentration [9], film thickness [10][11], grain size [11], post-deposition annealing under field [12], volumic magneto-elastic properties [10][13], and the ratio of hcp and fcc phases [9][12]. Nevertheless the coercive field depends on many parameters which are not intrinsic to the magnetic film and strongly depends on the growth process. There is a lack of reports on the relation between crystalline structure (hcp or fcc) and more intrinsic parameters like magnetization at saturation or anisotropy.

Moreover all the above cited references deal with electrodeposited films with thicknesses ranging from few hundreds of nanometers up to few microns mostly because physical deposition techniques have shown poor magnetic results for a perpendicular magnetic recording application [14][15][16]. Properties of micron thick films grown by magnetron sputtering deposition are
therefore rarely reported. Sputtered films thicker than 500 nm are even rarer although a thickness transition from amorphous to polycrystalline phase [17] and strong thickness dependence of coercivity [18] have been reported and unexplained.

Besides, about at the same time, introduction of Cr (instead of Ni) into Co-based film has been proposed in order to lower the magnetization value and therefore reduce the demagnetizing field below the anisotropy field [19][20][21], in the view of implementation as a media for perpendicular magnetic recording system in the 1970s. Because of its great technological potential, sputtered thin Co-Cr films were largely studied. Reports on the topic mostly focused on microstructure and Cr segregation in a few tens of nanometer thick film microstructure. Only few studies report on Co-Cr films synthesis with a thickness exceeding 1 µm. Among them, as in the case of CoNi, Hc has been studied as a function of various parameters like film thickness [22], temperature [23][24] and stress [25]. But in addition, more attention was paid to characterize the intrinsic parameters of the CoCr layers beyond Hc. Particularly it was demonstrated that both the magnetization and the perpendicular anisotropy constant decreases when the Cr concentration increases [21][26]. Therefore CoCr thick films can be used as a test system for our study of the intrinsic magnetic parameters of micron thick CoNi films.

In this article, the magnetic behavior of 1 µm-thick film of CoNi and CoCr alloys deposited by sputtering technique is reported. We focus on the influence of Ni or Cr concentration, as well as annealing temperature, on their structural and magnetic properties. Our results on CoCr are coherent with the literature and gives credit to our results and conclusions on thick CoNi alloys.

2. Experimental details

2.1 Co alloys films preparation

The sputtering device consists in a 45 L stainless steel vessel (Alcatel SCM 450). A base pressure of less than $10^{-4}$ Pa is obtained with a turbomolecular pump unit. Co target is sputtered with a pulsed Advanced Energy Pinnacle Plus+ power supply. The current density set at 68 A m$^{-2}$. Cr or Ni targets are sputtered with a DC Advanced Energy MDX 500. The substrates used are 6x6 mm$^2$ Al squares. They were fixed at equal distance from the center of the rotating substrate-holder to prevent any microstructural modification linked to the impingement angle variation. The
substrate-holder is located at 70 mm from the metallic targets. Ar gas flow rates are controlled with MKS flowmeters, and MKS Baratron gauge measured the total pressure. Coatings were post-annealed from 200°C to 400°C in Ar inert atmosphere.

2.2 Co-based alloys films characterization

The thickness of the deposited films on glass substrate was determined by the step method with an Altysurf profilometer equipped with a tungsten micro force inductive probe allowing an accuracy of about 20 nm. The structural features of the coatings deposited on Al substrates were performed in using a Bruker D8 focus diffractometer (Co K\textsubscript{α} radiation) equipped with the LynxEye linear detector in Bragg Brentano configuration. The morphology of the coatings was characterized by means of a Field Emission Scanning Electron Microscope (FE-SEM JEOL JSM-7800F). The chemical composition of the film deposited on Al substrates was estimated by energy dispersive spectroscopy (Quantax Bruker with XFLASH 6|30 detector) coupled with a Field Emission Scanning Electron Microscope (FE-SEM JEOL JSM-7800 F). Magnetometry measurements were performed by vibrating sample magnetometer (Micro-sense) at room temperature with magnetic field (up to 2T) applied in the plane of the films.

3. Results and discussion

3.1 Synthesis of the Co alloys thick films by cosputtering

Co alloy films have been prepared by cosputtering from pure metallic targets. The chemical content was controlled through the current density $I_d$ dissipated in the addition element target. Indeed as shown in Figure 1 the target voltages, the deposition rates and the atomic content in Co\textsubscript{1-x}Cr\textsubscript{x} and Co\textsubscript{1-x}Ni\textsubscript{x} sputtered films depend on $I_d$. The atomic content of the addition element linearly increases with $I_d$. For a fixed current density, the Ni atomic content in Co\textsubscript{1-x}Ni\textsubscript{x} is higher than that of Cr content in Co\textsubscript{1-x}Cr\textsubscript{x} films. This difference is ascribed to a higher sputtering yield of Ni than that of Cr ($S_{Ni} = 0.95$ and $S_{Cr} = 0.87$ for a bombarding Ar\textsuperscript{+} ion energy of 300 eV) [27][28], but also to the slightly higher Ni voltage and lower Co voltage with Ni addition element. Despite the difference in chemical composition, it is worth noting that the deposition rates are identical. Ferromagnetic target being sensitive to the magnetron effect, the thickness of the target was adjusted to 1 mm accelerating the aging of the target. Voltage of Co target in the
presence of Ni is lower than that of the voltage of Co with Cr because of the aging of the Co target. This effect compensates the higher Ni sputtering yield leading to identical deposition rates.

2.1 Structure of the CoCr and CoNi alloy films

Figure 2 shows X-ray diffractograms of cosputtered Co$_{1-x}$Cr$_x$ and Co$_{1-x}$Ni$_x$ coatings after annealing at different temperatures in Ar atmosphere. All films crystallised in hcp lattice (P6$_3$/mmc space group) along the [0002] direction, which corresponds to the easy axis of magnetization (c-axis). Presence of Co fcc lattice, which is the stable phase of pure Co for temperature higher than 417°C, is detected in Co$_{1-x}$Ni$_x$ films for x larger than 20% after annealing at 400°C. Ni enrichment induces a growth along the [111] easy axis of the fcc phase. To qualitatively investigate the degree of the [0002] preferential orientation in the hcp lattice, i.e. to determine if the easy c-axis lays in-plane or out-of-plane, the Lotgering factor has been calculated [29][30]. These calculations have been performed on (0002) peaks which correspond to the hcp c-axis perpendicular to the film (see Figure 3) and on (1010) peaks which correspond to other directions of the c-axis in the plane of the film. Note that the (1011) peak is barely detectable for all alloys. Co$_{1-x}$Cr$_x$ films exhibit a strong [0002] preferential orientation for a Cr content lower than 12.4 at. %. Further increase of the Cr content degrades the degree of the [0002] preferential orientation. Co$_{1-x}$Cr$_x$ crystalline structure has good thermal stability since annealing does not affect the Lotgering factor of [0002] peak (see Figure 3). By contrast, the [0002] preferential orientation in Co$_{1-x}$Ni$_x$ films is only favoured by increasing the Ni content, up to 0.9 for 30 at. % of Ni. At 400°C, we note that the increase of Ni content also leads to the growth of a [111] textured fcc phase.

2.2 Magnetic properties of the CoCr and CoNi alloys films

The magnetization hysteresis loops were measured with a magnetic field applied in the film plane as shown in Figure 4. The orientation of the magnetic field in plane does not affect the magnetic response which allows us to conclude that there is no significant anisotropy in-plane. However there is a clear difference between the hysteresis loops measured in-plane and out-of-
plane (see Figure 4). In Figure 5, the main magnetic features are presented (magnetization at saturation (a), anisotropy constant (b), squareness (c) and coercive field (d)) as a function of the Cr or Ni content. In Figure 5(a), magnetization at saturation (Mₛ) is shown to decrease progressively with increasing Cr content in Co₁₋ₓCrₓ alloy, according to the Slater-Pauling rule [1][31]. As expected, the saturation magnetization of Co₁₋ₓNiₓ films slightly decreases as the Ni content is modified since the Ni magnetization is lower than Co magnetization [14][32]. The presence of the fcc phase in the 400°C-annealed Co₁₋ₓNiₓ samples does not seem to affect their magnetic properties.

The magnetization orientation results from the competition between the demagnetization field (4πMₛ) which tends to maintain the magnetization in the film plane and the magneto-crystalline anisotropy which tends to align the magnetization along the direction perpendicular to the film [33][34]. In Figure 5(b), we present the crystalline anisotropy constant (Kᵥ) of Co₁₋ₓCrₓ and Co₁₋ₓNiₓ alloys. Kᵥ is calculated from the saturation field (Hₖ_eff) measured when applying the magnetic field perpendicularly to the films and defined as Hₖ_eff = 4πMₛ - (2Kᵥ/Mₛ). A positive Kᵥ value is extracted for all tested hcp Co-based alloys. Since we found the same value within the error bar for all annealing temperature, we plot only one point per concentration. For low concentration of Cr and Ni, Kᵥ is similar for both alloys and is around 2 × 10⁵ J m⁻³. Such value is typical of the reported values for pure hcp Cobalt [35][36][37]. Nevertheless, its amplitude varies differently for the two alloys when increasing the Cr and Ni content respectively. Increasing Cr content (resp. Ni), decreases (resp. increases) Kᵥ. Similar results for CoCr films have been reported [21][26], but not for CoNi. From our study, it is clear that both evolutions can be directly correlated to the quality of hcp crystal orientation (Figure 3). Kᵥ increases when the degree of orientation of hcp c-axis along the direction perpendicular to the film is improved.

The squareness of the in-plane field hysteresis loop is defined as the ratio (Mᵣ/Mₛ) with Mᵣ the remanent magnetization and Mₛ the magnetization at saturation. The squareness is found to be correlated to the magnetic anisotropy. The squareness decreases in Co₁₋ₓNiₓ as Ni content increases while the crystalline anisotropy, which favours out-of-plane anisotropy, is improved (Figure 5). The evolution of coercive field is more difficult to explain as many parameters (and their distribution) play significant role in the irreversible magnetization reversal process (e.g. magnetization, exchange interaction, grain structure, magneto-crystalline anisotropy, domain wall
motion and pinning). Increasing the Cr amount in Co$_{1-x}$Cr$_x$ (for films annealed at 200 and 300°C) leads first to an increase and then a decrease of coercive fields with a maximum at around 16 at. %. This may originate from a competition between $M_s$ and $K_v$ (large $M_s$ induces an increase of coercive field, and low $K_v$ tends to decrease the coercive field). We also observe that the coercive field keeps increasing continuously with the Cr content even after 16% for 400°C annealed samples. As no structural modification was observed (see Figure 3), we expect this behavior to be induced by the segregation of Cr to the Co-rich grain boundary, which proceeds around this Cr content (~20 at. %) for high temperature [38]. The magnetic behavior of Co$_{1-x}$Ni$_x$ films is different. There is mostly two regimes most probably related to the degree of magnetocrystalline anisotropy. For low Ni content, a lower coercive field and a larger coercive field is observed for Ni content larger than 20 at. %. Similar variations were reported by S. Armyanov for electrodeposited CoNi coatings [39].

4. Conclusions

The influence of Cr and Ni on the structural and magnetic properties of sputtered CoNi and CoCr alloy 1 µm thick films, grown by magnetron physical vapor deposition was studied. For Ni and Cr concentration ranging from 0 to 35 at. %, all films crystallize in an hcp lattice. The structural study showed that the ratio of hcp phase with [0001] axis orientated perpendicular to the film as compared with in-plane orientation increases (resp. decreases), when Ni (resp. Cr) concentration increases independently of the post-annealing temperature. The crystalline magnetic anisotropy is found to align preferentially the magnetization along the [0001] axis and mostly opposes the demagnetization field which favors in-plane anisotropy. Co$_{1-x}$Ni$_x$ alloys crystalline anisotropy constants can be up to twice larger than the best Co$_{1-x}$Cr$_x$ anisotropy, while maintaining a magnetization at saturation above 1200 kA/m. Post-annealing until 300°C does not alter the magnetic features of both type of alloys, as requested for their integration in manufacturing processes for magnetic printing media.

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References


**Figures caption**

**FIG. 1** Evolution of target voltages ($V_{Cr}$, $V_{Ni}$, $V_{Co,Cr}$ and $V_{Co,Ni}$ (Co voltages as a function of the alloying element), chemical compositions ($C_{Cr}$ and $C_{Ni}$), and deposition rates ($V_{d, Cr}$ and $V_{d, Ni}$) of cosputtered Co$_{1-x}$Cr$_x$ and Co$_{1-x}$Ni$_x$ films as a function the current intensity dissipated in Cr or Ni target.

**FIG. 2** X-ray diffractograms of cosputtered Co$_{1-x}$Cr$_x$ and Co$_{1-x}$Ni$_x$ films after annealing at different temperatures.

**FIG. 3** Lotgering factor of (0002) plane as a function of the Cr or Ni content in Co-base alloy film after annealing at different temperatures.

**FIG. 4** Magnetization as a function of the applied magnetic field parallel to the film plane ($H//\parallel$) or perpendicular ($H\perp\perp$) for Co$_{92}$Cr$_8$, Co$_{74}$Cr$_{26}$, Co$_{93}$Ni$_7$ and Co$_{75}$Ni$_{25}$ films.

**FIG. 5** Dependence of magnetic properties on the alloying element content for different annealing temperatures. For anisotropy $K_v$ values all the annealing temperature lead to similar values so that only one point per concentration was plotted with an error bar (mostly due to the measurement error of saturation field).
Figure 1.
Figure 2.
Figure 3.
Figure 4
Figure 5