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Short communication

Evolution of morphology in electrodeposited nanocrystalline Co–Ni films by in-situ high magnetic field application

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ABSTRACT

The effect of high magnetic fields up to 12 T, applied during electrodeposition process, on the morphology of nanocrystalline CoNi films has been investigated. The magneto-induced dramatic modifications in the morphology were observed by using field-emission scanning electronic microscopy and atomic force microscopy. Along with the increase of magnetic flux density (B), the grain size and the surface roughness of the films increased to reach a maximum value at a field of 9 T. Meanwhile, higher magnetic flux density could improve cobalt atomic percentage in the film due to the impacts of magnetohydrodynamic effect. However, at a high field of 12 T, the paramagnetic force played a predominant role in a decrease of mass transport, resulting in minimum grain size and roughness, even smaller than that of the ordinarily (B = 0 T) sample.

1. Introduction

It is well known that the magnetic properties of deposits (such as GMR effect, coercivity fields, moment per atom, etc.) are strongly related to the morphology, i.e., grain shape, grain size, and layer roughness. For instance, the lower the roughness of Co–Cu multilayers, the higher the GMR effect is visible. On the opposite, an increase in roughness of the magnetic layer leads to an increase of its coercivity fields H_c [1]. The morphology of electrodeposits is especially sensitive to mass transport and chemical reactions, which can be controlled by a magnetic field due to the Lorentz force induced by the interaction of magnetic field and current (magnetohydrodynamic effect, MHD). Therefore, superimposing a magnetic field during electrodeposition is an interesting interdisciplinary zone, with promising opportunities for producing or tailoring novel nanocrystalline materials with better magnetic properties. For instance, as a non-contact method, magnetic field can be used for optimization of electrodeposited CoNi alloys that can be used in wireless micro-robots for biomedical applications [2].

Recently weak magnetic field (lower than 1 T) effects on the electrodeposition process and the morphology of ferromagnetic deposits have been reported by different groups [3–6]. Krause et al. [7] reported that Co deposit shape changed into double sized hexagonal crystallites, if a 1 T magnetic field was applied parallel to the surface of substrate. Ispas et al. [8] found that smaller grains and lower roughness for NiFe electrodeposits have been obtained with superimposition of a magnetic field up to 0.7 T. A similar observation of reducing the grain size and roughness in NiCu alloy with an application of a parallel-to-electrode magnetic field has been made by Tabakovic et al. [9]. On the contrary, atomic force microscopy in Ref. [10] showed that a magnetic field induced an increase in the surface roughness of the Ni-layer electrodeposits. Many other experimental results highlight that the influence of magnetic field on morphology of electrodeposits is varied between different reports, and not fully understood. Thanks to the development of superconducting technology, similar studies for electrochemical reaction with an in-situ high magnetic field (HMF) application [11,12] can be conducted to undertake other experimental investigations in order to understand the magnetically induced effects and obtain new materials due to better control of ion transport in bath and crystallization process, and in turn better control of the magnetic properties of deposits by the application of magnetic fields. In this work, we focus on the effects of HMF on the morphology of the nanocrystalline CoNi film. A clear dependence of grain shape, grain size, and layer roughness on magnetic flux density was characterized by field-emission scanning electronic microscopy (FE–SEM) and atomic force microscopy (AFM).

2. Experimental

All electrodeposition experiments were performed in a three-electrode cell without agitation. ITO (1000 Å) glass of 1 cm diameter was used as the working electrode, the counter

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electrode was a quadrate Pt plate of 1 cm × 2 cm, and $Hg/Hg_2SO_4/K_2SO_4$(sat.) was used as reference electrode. The aqueous electrolyte contained 0.3 M $CoSO_4 \cdot 7H_2O$ + 0.7 M $NiSO_4 \cdot 6H_2O$ + 0.4 M H_3BO_3 + 0.015 M saccharin. The pH was adjusted to 4.7 by adding 1 M NaOH solution. Galvanostatical deposition, using a current density of 10 mA/cm^2 was performed at 50 °C for 1 min. A water-cooled superconducting magnet (CNRS, Grenoble, France) supplied a magnetic flux density up to 12 T, which was superimposed to the electrochemical cell during the electrodeposition process in the parallel direction to the vertical electrode surface. Surface morphology and chemical composition of the deposited films were investigated by FE–SEM appended with an energy-dispersive X-ray spectroscope (EDX, SUPRA 35, Japan) at three points of the CoNi films. The topography and the roughness were investigated with AFM (NTEGRA AURA, NT-MDT, Russia). Each sample was measured in areas of 5 μm × 5 μm at three different positions on the film.

3. Results and discussion

Typical FE–SEM morphologies of CoNi films electrodeposited with different magnetic intensities up to 12 T are shown in Fig. 1. The figure demonstrates drastic morphological variations with the magnetic flux density (B). The short-clavated shape of the grains is similar in two cases: electrodeposition without magnetic field and with weak magnetic field of 1 T (Fig. 1a and b). When the applied magnetic field was increasing from 3 T to 12 T, nanosheets-like structures in a three-dimensional network without obvious grain boundary are clearly observed in CoNi deposits. The morphologies of these deposits are very similar to those reported in Bai. et al.'s work [13], although these authors found this kind of nanowires structure in Fe–Co deposits. The dependence of the mean diameter of these nanosheets on the magnetic flux density shows a tendency to firstly increase and then decrease. In the case of electrodeposition under superimposition of 12 T magnetic field (Fig. 1f), the mean size of the silk-like nanosheets in the film reaches a minimum with some agglomerate distributing in it, which can also be observed in Fig. 1(a). In addition, there is an evolution of

Table 1
Compositions of the deposited CoNi films as a function of the magnetic flux density.

Applied magnetic field (T)	Co (at%) in the film	Co/Ni composition ratio
0	70.4 ± 0.6	2.38
1	76.6 ± 0.4	3.27
3	76.5 ± 0.6	3.26
6	77.4 ± 0.3	3.43
9	78.8 ± 0.5	3.72
12	76.3 ± 0.4	3.22

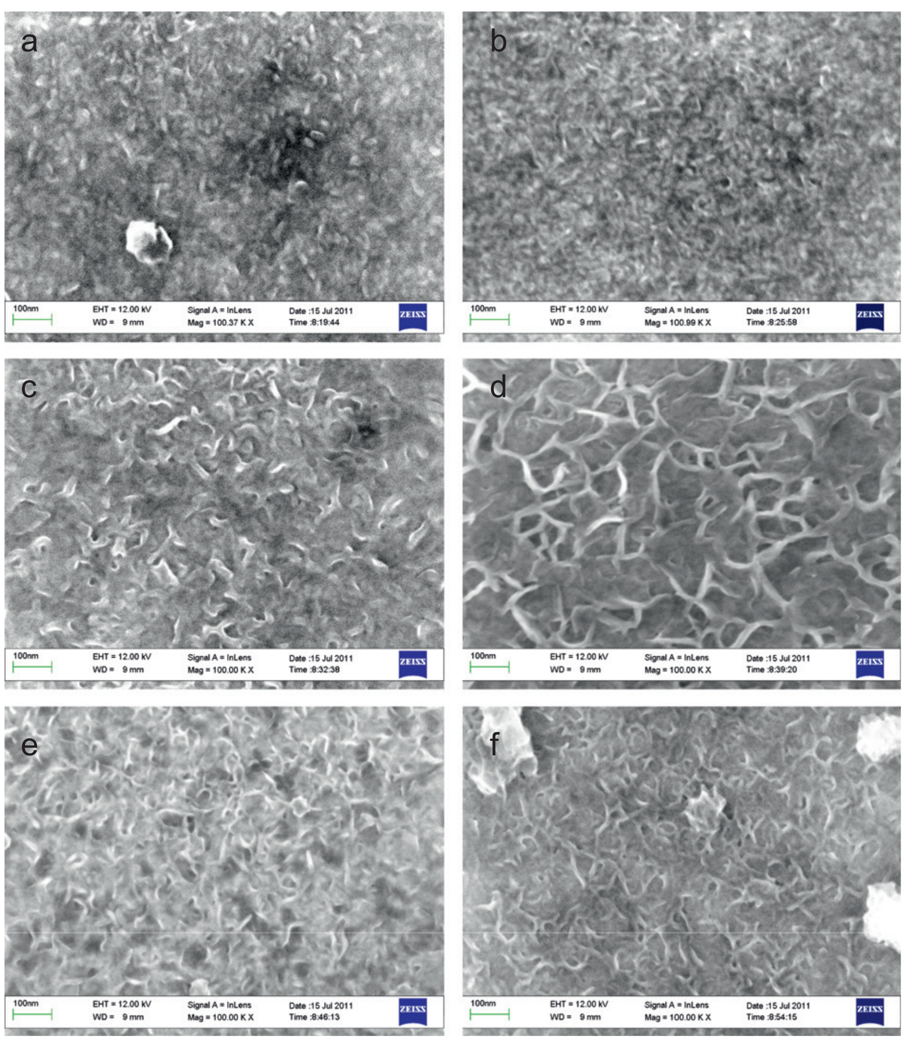

Fig. 1. FE–SEM images showing the morphology of CoNi films electrodeposited with high magnetic fields of (a) 0 T, (b) 1 T, (c) 3 T, (d) 6 T, (e) 9 T, (f) 12 T.

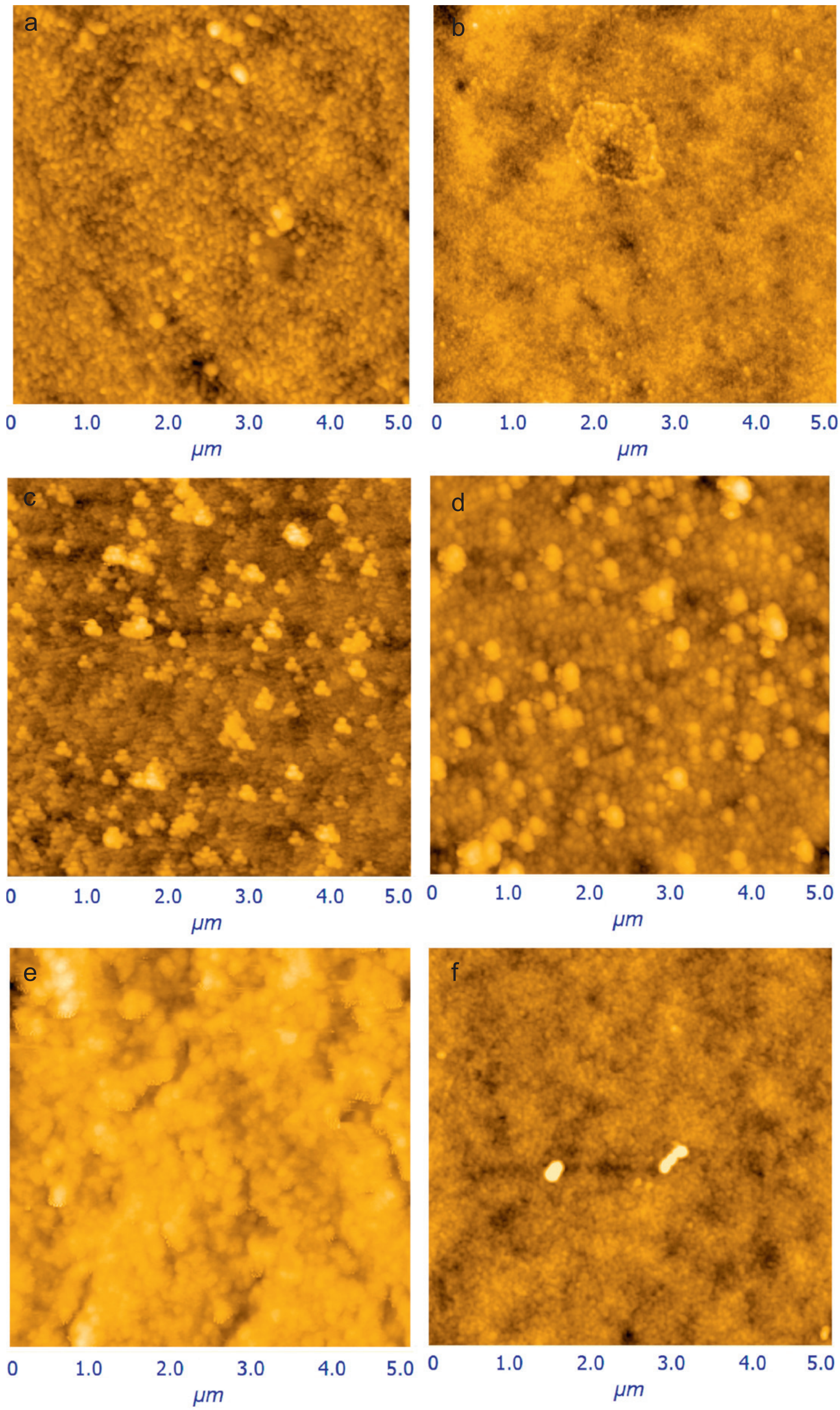

Fig. 2. AFM images of top-view of CoNi films electrodeposited under high magnetic fields of (a) 0 T, (b) 1 T, (c) 3 T, (d) 6 T, (e) 9 T, (f) 12 T.

grain shape from short-clavate in case of 0–1 T to nanosheets at 3–12 T.

Table 1 displays the magnetic field effect on CoNi film composition during the electrodeposition. It can be seen that cobalt contents in the film augmented from 70% to around 79% with the increase of B from 0 T to 9 T, but decreased when the magnetic fields increased from 9 T to 12 T. The dependence of Co/Ni ratio on B exhibits a similar trend as the evolution of morphology. To discuss the field-dependent behavior of the composition and morphology, it has to be considered that the magneto-electrochemical process is both Co (Ni) deposition and hydrogen-ion reduction at the meantime. As generally known, magnetohydrodynamic effect in a magnetic field oriented parallel to the electrode surface yields significant convection, which diminishes the diffusion layer thickness in the vicinity of electrode, and therefore increases the current efficiency. However, at high magnetic flux densities the Co deposition is diminished, since the hydrogen-ion reduction dominates the total reduction process resulting in the decrease of the current efficiencies of Co. This retarded effect is in agreement with the results obtained in the experiments of Uhlemann et al. [11] under similar conditions.

In order to quantitatively analyze the effects of HMF on grain size and roughness of the electrodeposited film, AFM top view ($5\ \mu m^2 \times 5\ \mu m^2$) image of the surface topography of nanocrystalline films are shown in Fig. 2. The shape and size of the grains are different in these typical samples deposited with imposed magnetic fields, being small and uniform in the case of (0–1 T); larger and irregular with accumulative cluster in the case of (3–9 T); smallest shape and more uniform in the case of 12 T. This difference indicates that the application of HMF modified the film nucleation and growth processes on the surface of cathode. It should be mentioned that the disappearance of "nanosheets" in the AFM image comparing with its existence in the SEM image is probably related to the difference in surface analysis between AFM (3D overview with the tip scanning in perpendicular to the surface) and SEM (2D morphological structure in the direction parallel to the surface).

The average values of surface roughness and lateral feature size, which can be used to characterize the grain size, were calculated using standard Nova software of AFM as shown in Fig. 3. AFM investigations show that the curves of the feature size and roughness exhibit non-monotonic increase up to 9 T. In contrast, feature size and roughness decreased dramatically

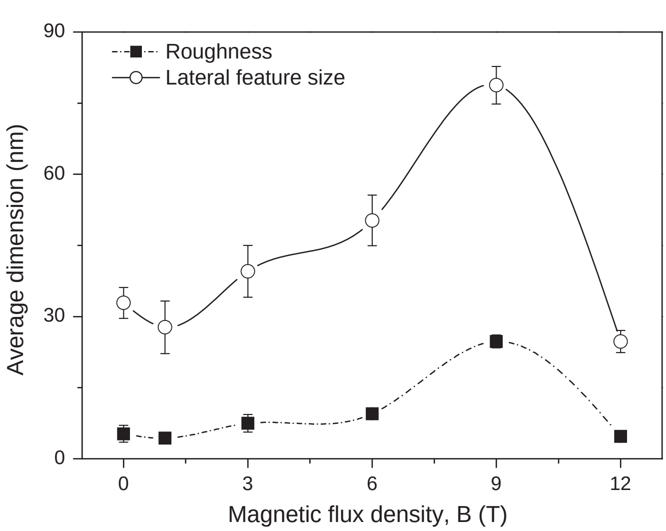

Fig. 3. The dependence of roughness and grain size of CoNi films on the magnetic flux density.

with further magnetic field increase up to 12T, eventually becoming smaller than in the case without magnetic field. It must be pointed out that the mean grain size obtained here based on the AFM images agrees well with the calculated result by using Scherrer's formula according to the X-ray diffraction.

The main focus of this short communication is high magnetic field effects on the electrodeposition of CoNi alloy. As regards deposition rate, the effect is observed in the mass transport limited regime [14], where the magnetic field influences the diffusion of the ions towards the cathode, but not the redox reaction. The results can be discussed by the overlapping effects of two types of force under a HMF in the direction parallel to the surface of cathode [3]. One is the Lorentz force given by $F_L = q(E + v \times B)$ (where, q is the electrical charge of an ion, E is the electrical field vector, v is the velocity of ions in electrolyte), which is responsible for a macro-MHD to decrease the thickness of the diffusion layer near the electrode, and in turn to improve the current efficiency of deposition. Whereas, at high fields the other paramagnetic force has to be taken into account, given by $F_m = \chi_m B^2 \vec{\nabla} c / 2\mu_0$ (where χ_m is the molar susceptibility of the ions, c is the molar concentration, μ_0 is the permeability of free space), which causes paramagnetic ions to move in the direction of concentration gradient. In other words, the mass transport from electrolyte to the surface of cathode is modified by the paramagnetic force, which is in a perpendicular direction to the magnetic field. First, the force acts near the edge of the electrode due to the concentration gradient in the applied magnetic field. Second, it acts on the whole electrode surface most likely combining with the gravitational effect and the secondary effect of the Lorentz force on the concentration profile. According to the estimation of Coey et al. [15], the value of paramagnetic force acting in aqueous electrolytes is of order $10^4\ (N/m^3)$ with a field of 1 T. Therefore, a dramatic increase of F_m in a 12 T magnetic field up to about $10^6\ (N/m^3)$, which has a magnitude comparable to that of the Lorentz force, changes the mass transport regime, and then the deposit morphology.

Obviously, the combined effects of these forces, depending on the magnetic field amplitude, cannot be discriminated in a simple way. Adsorption phenomena of ionic species and hydrogen evolution have to be regarded as very important reactions that govern the deposition process. The magnetic convection can dramatically modify these two reactions, changing the local pH and therefore texture and morphology of the deposits [16].

The present work paves the way for optimized electroplated alloys, which have been far found the most utility in micro/nano electro mechanical systems (MEMS/NEMS). These MEMS devices such as microactuators, mocrorobots, sensors, require excellent magnetic properties for actuated wirelessly by application of external magnetic fields. From the morphological viewpoint, the magnetic properties depend not only on the chemical position, but also strongly on the grain size and roughness [2,17]. Therefore, the in-situ application of high magnetic field during the electrodeposition is exceptionally well suited for tailoring the magnetic properties of Co-based magnetic alloy for MEMS applications, by non-contact controlling compositions, grain shape, grain size and roughness.

4. Conclusions

The influence of a parallel (with respect to the surface of the working electrode) high magnetic field on the morphology of electrodeposited CoNi film has been investigated. The FE-SEM figures demonstrated that magnetic field induced drastic morphological variations from short-clavated grain shape to silk-like nanowires. Applied magnetic fields led to an increase of the Co/Ni atomic ratio in the deposits. AFM characterization showed that the grain size and the surface roughness firstly increased with increasing magnetic flux density (0–9 T) and then decreased (9–12 T). The non-monotonic dependence of morphology on magnetic flux density could be explained by the overlapping of cumulative effects of Lorentz force on the current efficiency and of paramagnetic force on the mass transport during the electrodeposition process that induce no obvious modifications on ionic adsorption, hydrogen evolution and local pH.

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