# INFLUENCE OF A MAGNETIC FIELD ON THE ELECTRODEPOSITION OF NICKEL AND NICKEL-IRON ALLOYS

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**Introduction.** Nickel and nickel alloys find various applications, like decorative electroplating, corrosion protection, electroforming, or new magnetic materials [1]. In most electroplating applications the deposition rate is limited by mass transport. A superimposed magnetic field can be used to increase the mass transport in electrochemical reactions or to change the properties of the electrodeposited layers [2]. In order to tailor the magnetic fields for electrochemical reactions (such as nickel plating), it is important to understand the effects of a magnetic field in electrochemical processes. It is generally accepted that the main influence produced by an external magnetic field in electrochemical systems is due to the Lorentz force that acts on the moving ions. Therefore, if a magnetic field is applied perpendicular to the electric field lines, the effects should be maximal. If **B** is parallel to **E**, the effects due to the Lorentz force should be negligible. The works of Iwakura [3], Aogaki [4, 5], Shannon [6], Arumugam [7] show the role of the direction of **B** with regard to the **E**. In this work, we investigated how the magnetic field influences the hydrogen evolution reaction, the roughness and the morphology of Ni and Ni-Fe layers, as well as the composition of the Ni-Fe alloys.

**1. Experimental.** Nickel was deposited from a sulphamate bath (pH 4). The deposition of nickel-iron alloy was made from a sulphate bath (pH 2–3). The electrolytes were made with p.a. grade chemicals and bidestilled water.

10 MHz optically polished quartzes were used for the Electrochemical Quartz Crystal Microbalance (EQCM) measurements. The electrodeposition was done in a three electrode arrangement cell, made from Teflon. One gold electrode of the quartz was used as the working electrode, and a double junction electrode (Ag|AgCl|3M KCl) was the reference electrode. The counter electrode was a nickel disc. A water-cooled electromagnet could furnish a homogeneous magnetic field of maximum 740mT (for 46 mm gap), that was superimposed to the electrochemical cell. An Advantest R3758BH network analyzer was used to record the resonance spectrum of the quartz, to obtain besides the frequency shift, also the damping of the quartz [8]–[10]. A potentiostat model 263A from EG&G Instruments, was used for the electrochemical experiments.

The morphology of the deposited layers and the roughness was investigated with a contact mode AFM (atomic force microscopy), using silicon nitride pyramidal tips. Energy Dispersive X-ray analysis (EDX) yielded information about the alloy composition. Besides AFM, Scanning Electron Microscopy (SEM) was used to investigate the morphology of the alloys.

**2. Nickel deposition in a superimposed magnetic field.** The sulphamate bath was chosen for the deposition of nickel, because it provides very high plating rates and low internal stress in the deposit. The deposition of nickel from aqueous solution is always accompanied by the evolution of hydrogen bubbles (HER). EQCM is a technique that allows to calculate the current efficiency of nickel deposition ($\eta$), from the ratio of the mass deposited on the quartz, (which is calculated from the shift of the resonance frequency of the quartz crystal) and the theoretical mass (given by Faraday's law). The partial current of hydrogen evolution reaction, ($j_{\mathrm{HER}}$) was calculated by multiplying the total current density with $(1-\eta)$.

Prior to the depositions, we checked if the superimposed magnetic field represents a source of perturbation for the quartz crystal. During the operating of the electromagnet, the resonance behaviour of the quartz was not influenced.

In a previous paper [10] we discussed the effects produced by a magnetic field, applied perpendicular to the electric field lines (in the following called "perpendicular **B**"). We observed that for small polarizations ($-0.1$ mA $\cdot$ cm$^{-2}$), the partial current of the HER increases with the magnetic field, whereas it remains constant for relatively large polarizations ($-50$ mA $\cdot$ cm$^{-2}$). To understand this result, one has to take in account that for small cathodic polarizations, the hydrogen evolution is usually mass transport limited, while nickel reduction is activation (or mixed) controlled.

In the presence of a magnetic field, the limiting current densities for nickel and hydrogen increase due to the magnetohydrodynamic stirring. This increase depends on the concentration and magnetic flux density. When the potential is close to the equilibrium potential of nickel, the magnetic field will increase mainly $j_{\mathrm{HER}}$. At higher polarization, both partial currents ($j_{\mathrm{Ni}}$ and $j_{\mathrm{HER}}$) will be increased. The relative increase will be the same for both species. The final effect is that the $j_{\mathrm{HER}}$ will not change significantly with **B**.

In the case that the magnetic field was applied parallel to the electric field lines (in the following called "parallel **B**"), the partial current due to HER was not significantly influenced by the magnetic field. This proves the statement that the Lorentz force is the main force that influences the deposition process. However, in [4] it is claimed that microturbulences will appear, which will locally suppress the nucleation. Therefore, a specific morphology will be generated [4, 11]. One can see in Fig. 1*b* that a perpendicular **B** generates more specific geometrical forms (more "round" grains, due to the MHD), while a parallel **B** (Fig. 1*c*) seems to keep the growth pattern that is obtained without the magnetic field (Fig. 1*a*).

The roughness of the deposited layers can be monitored in-situ by evaluating the damping of the quartz. Rough layers increase the damping of the quartz, whereas smooth layers cause no damping effects. The EQCM data were in accordance with the ex-situ AFM data.

The roughness of the deposited layer depends on the direction and the intensity of the magnetic field (Fig. 2). In the case of a perpendicular **B**, the roughness of nickel layers increases with the magnetic field. This can be explained from the

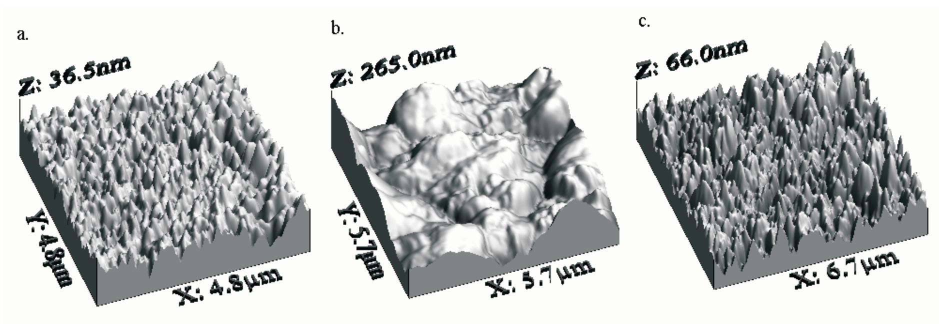


*Fig. 1.* The morphology of a nickel layer deposited galvanostatically at $j = -50\,\mathrm{mA}\cdot\mathrm{cm}^{-2}$, in a $B = 0$ mT (*a*), in a perpendicular **B**, 740 mT (*b*), and in a parallel **B**, 406mT (*c*).

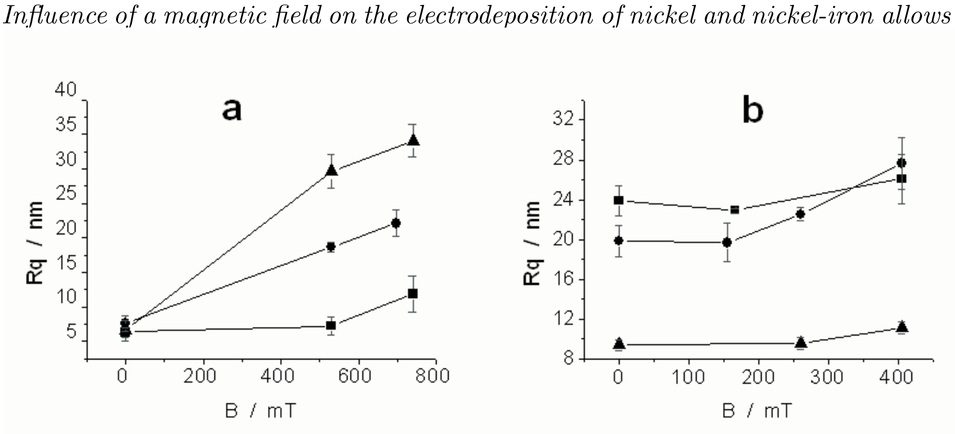


*Fig. 2.* Dependence of the standard deviation of the height values from the AFM images, Rq, on the magnetic field, in the case of nickel deposition. (*a*) **B**⊥**E** ■ $j_{\text{total}} = -0.5$ mA · cm$^{-2}$; ● $j_{\text{total}} = -10$ mA · cm$^{-2}$; ▲ $j_{\text{total}} = -50$ mA · cm$^{-2}$; (*b*), **B** ∥ **E** ■ $j_{\text{total}} = -1$ mA · cm$^{-2}$; ● $j_{\text{total}} = -15$ mA · cm$^{-2}$; ▲ $j_{\text{total}} = -50$ mA · cm$^{-2}$.

interplay of the MHD effect and the generation of the hydrogen bubbles. The hydrogen bubbles can be obstacles for the flow profile induced by the magnetic field. As higher current densities induce higher Lorentz forces and thus stronger convection, the effect will be more important for the higher current densities.

In one theory about the mechanism of nucleation in the absence of a magnetic field are proposed two types of fluctuation responsible for the electrodeposition [12]. A parallel **B** will induce two types of vortices from these fluctuations, and the interaction between them will generate a velocity of the fluctuations [4]. The final effect will be local Lorentz forces around the growing nuclei. As these forces are acting locally, the roughness of the layer on macroscopic scale will be slightly influenced by the variation in the magnetic field. An increase of current densities produces smoother layers. This can be due to stronger vortices that appear from the nucleation fluctuations, which will suppress the growing of the nuclei. As a result the layer becomes smoother with increasing current density for parallel **B**.

**3. Ni-Fe alloy deposition in a superimposed magnetic field.** The deposition of alloys from the iron group (Ni, Fe, Co) is facilitated by the fact that their standard potentials are close to each other. Their special magnetic properties, which make them very interesting in microelectronics, depend on the composition of the deposit, crystal size and internal stress in the deposit.

Due to anomalous codeposition [13, 14], the iron is deposited preferentially compared to the nickel, even if it is less noble. It is generally found that the iron content in the alloy decreases with the absolute value of the current density. At a given current density, a perpendicular **B** field induced a slight decrease in the iron content of the layer, while a parallel **B** induced a slight increase, relative to the situation without a **B** field. This may be due to the MHD effect. The limiting current depends normally on the diffusivity of the species, on the agitation of the bath and on the concentration of the electroactive species. A perpendicular **B** induces additional convections. In a galvanostatic experiment the deposition potential becomes less negative. Thus, in function of this additional stirring, the alloy composition will be modified. At the moment, the mechanism of influence of the parallel **B** on the composition of the layer is not clear.

A perpendicular **B** makes the layers more compact and more homogeneous (Fig. 3).

The roughness of the layers increases with the parallel **B**, but in function of the total current density had the same behaviour as mentioned before for nickel.

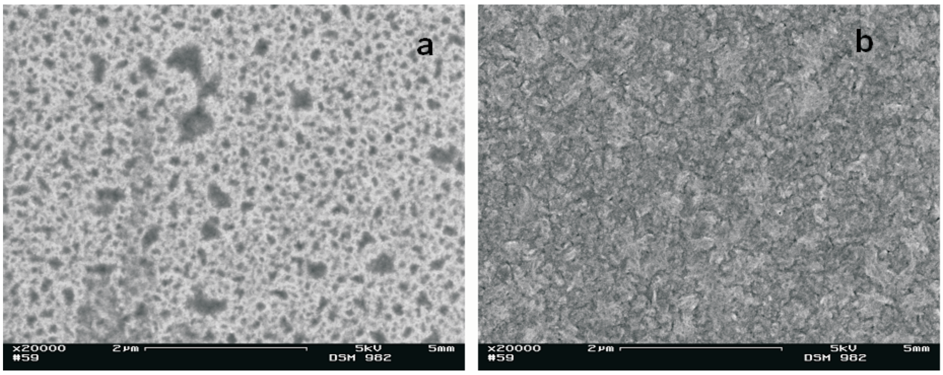


*Fig. 3.* SEM images of the Ni-Fe layer deposited at $j = -25$ mA $\cdot$ cm$^{-2}$. (*a*) In absence of a magnetic field; (*b*) in a $B = 740$ mT, perpendicular to the **E** field.

**4. Conclusions.** We demonstrated in the present work that the direction and the magnitude of a superimposed magnetic field significantly influence the electrodeposition of ferromagnetic layers. A perpendicular **B** increases the roughness of nickel layers, and makes the Ni-Fe layers more compact. In the same time, it affects the hydrogen evolution. In the case of nickel, an increase of the perpendicular **B** induces an increase of the partial current due to the hydrogen evolution at current densities around $-1$ mA $\cdot$ cm$^{-2}$, but it does not influence the hydrogen evolution reaction at current densities of $-50$ mA $\cdot$ cm$^{-2}$.

A parallel **B** does not change significantly the efficiency of the nickel deposition, but induces specific morphologies. The roughness of the layers is slightly modified with the increasing of **B**, and its evolution in function of the current density has an opposite behaviour compared to the case of a perpendicular **B**. The direction of the magnetic field influences also the composition and roughness of Ni-Fe alloys. Future work will aim at detailed investigations regarding the influence of a magnetic field on the magnetic properties of the layers.

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