

MAGNETIC AND ELECTROCHEMICAL STUDIES ON ELECTRODEPOSITED Ni-Fe ALLOYS

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Introduction. Metallic alloys obtained by electrochemical or metallurgical procedures are important due to their various applications. Among them, Ni-Fe alloy electrodeposition has received much attention because of the anomalous deposition rates [1] and numerous investigations have concerned the effects of polarization and plating bath constituents on the metal ratio [2] and/or on the deposit aspect [3].

In a recent paper [4], results have demonstrated that, during codeposition, the Ni-Fe film composition and morphology can change due to an increase of the surface concentration of inhibiting species (iron) by the MHD effect. In this study, a mathematical model of the anomalous codeposition of Ni-Fe alloys, based on steady state and dynamic (EIS = electrochemical impedance spectroscopy) techniques, is proposed. The model involves two parallel reaction paths, each one proceeding in two consecutive steps and involving an adsorbed intermediate [5]. The results show good agreement between theory (simulation result) and EIS data. They confirm the MHD mass transport effect that acts on the covering of the electrode by adsorbed Fe (II) species.

Other authors [6, 7] have studied the structure and the magnetic properties in the region of invar[®] composition (Fe₆₄Ni₃₆). Around the invar[®] composition, the crystal structure is modified and is progressively transformed from α phase (*bcc* structure) to γ phase (*fcc* structure) as the Ni amount increases. When both phases ($\alpha + \gamma$) are present, the Ni-Fe alloy exhibits a drop of its average magnetic moment. In this study, we have compared the evolution of the magnetic moment *vs* the nickel atomic percentage of the alloy realized in the absence or presence of magnetic induction.

1. Experimental. The electrolyte used in this study was an acid bath solution containing Fe (II) and Ni (II) species. According to the experiments, we have used different concentration Fe (II)/Ni (II) ratios: either 0.1/0.5 (solution A) or 0.1/0.1 (solution B).

Classical electrochemical experiments were conducted with a Tacussel potentiostat-galvanostat PGZ 301 with a 0,2 cm² working electrode area.

For EIS studies, the electrodes were connected to an electrochemical interface (Solartron 1258) connected with a frequency response analyser (Solartron 1250). EIS studies of the electrodeposition process were conducted in the potentiostatic mode.

For the experiments under moderate magnetic fields, the cell was put into the gap of an electromagnet (Drusch EAM 20G) that imposed a uniform magnetic field, \mathbf{B} . The latter was kept parallel to the horizontal electrode surface.

The chemical compositions of the electrodeposits were determined by ICP-AES technique with a Varian spectrometer.

The magnetic moment measures were realized using a home-made Gouy style balance.

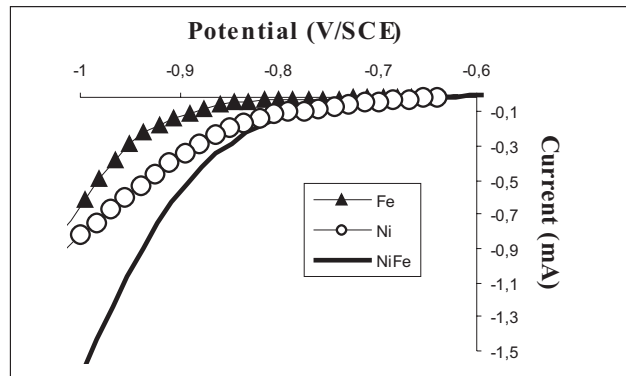


Fig. 1. Intensity-potential curves for Fe, Ni and NiFe systems. Solution B.

2. Results and discussion. Fig. 1 exhibits the intensity-potential curves obtained with iron, nickel and nickel-iron solutions for weak overpotentials in the absence of magnetic field.

Fig. 2 shows the comparison between intensity-potential curves realized in the presence and in the absence of magnetic induction for polarisations that lead to a similar to invar[®] composition.

We can note that the cathodic current amplitude is slightly smaller with magnetic field. In many experiments the MHD convection increases the diffusion currents [8] but here, this current decrease is due to the MHD convective effect on Fe(II) species that is mass-transport controlled and responsible for the Ni reaction inhibition [4].

To analyze the MHD effect on the electrodeposition mechanism, we have undertaken some dynamic experiments by means of EIS measurements. In this case to have a more significant effect of the magnetic field, the experiments were performed at higher cathodic overpotentials.

Typical results in Nyquist diagrams are reported in Fig. 3.

According to the Matloz model [5], Fe(II) and Ni(II), are involved in competitive adsorption reactions that occur in two steps:



Note that Fe(II) species is under mass transport control. Assumed this mechanism, we can express the electrochemical impedance [9] and therefore determine the different parameters of the model and compare them with experimental data. The

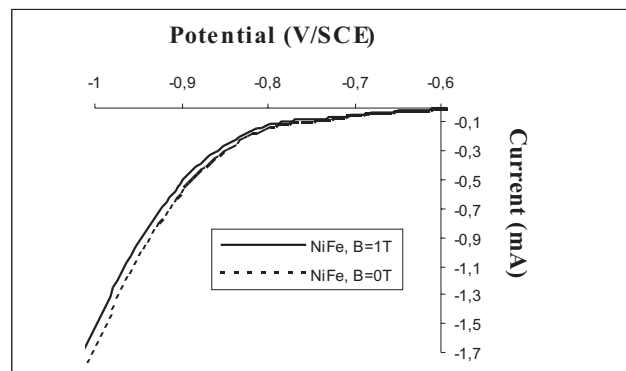


Fig. 2. Intensity-potential curves with and without magnetic field. Solution B.

Fig. 3. EIS data in the Nyquist plane for various magnetic fields. Solution A.

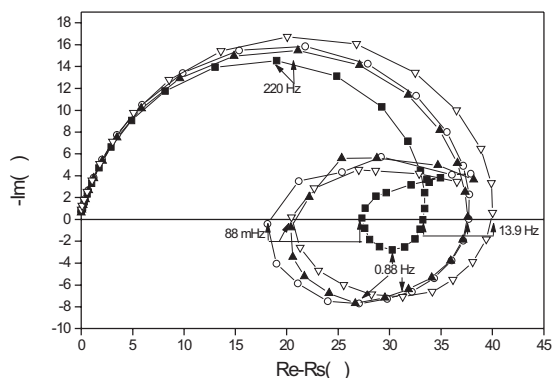


Table 1. Experimental (exp) and calculated (cal) values from EIS data. $E = -1.4$ V/SCE. Solution A. Electrode surface 0.6 cm².

B/T	0	0.3	0.6	0.9
I (cal)/mA	2.00	1.76	1.70	1.80
I (exp): mA	1.96	1.74	1.72	1.79
R_{ct} (cal)/ Ω	36	48	52	57
R_{ct} (exp)/ Ω	34	35	35	39
% Fe (cal)	26	57	59	62
% Fe (exp)	31	58	60	62
$\delta/\mu\text{m}$	101	28	26	18
Θ_{Ni}	0.38	0.16	0.15	0.12
Θ_{Fe}	0.24	0.68	0.71	0.75

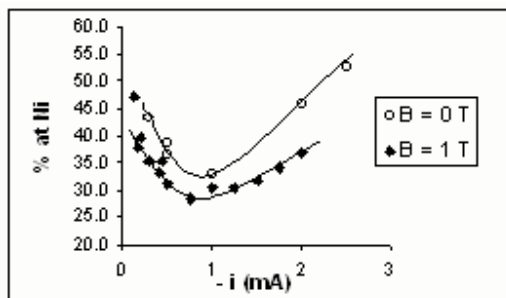
Table 1 gives these parameters for solution A and an applied potential value equal to -1.4 V/SCE.

I is the reduction current intensity, R_{ct} is the charge transfer resistance, % Fe is the iron atomic amount in the deposit (experimental values have been obtained by ICP method), δ is the thickness of the iron diffusion layer, Θ_{Ni} and Θ_{Fe} are the adsorbed surface proportion of nickel and iron intermediates, respectively.

The good agreement between the experimental and calculated values validates the proposed mechanism. The evolutions with **B** of the diffusion layer thickness and the proportion of the adsorbed surface by Fe(I) demonstrate the convective effect of the magnetic field upon the Fe(II) species and explain the decrease of the electrodeposition current under the magnetic field superimposition.

Fig. 4 shows (again in the invar[®] area) the atomic nickel percentage in the deposit versus the current deposition without or with magnetic field.

Fig. 4. Nickel atomic percentage vs cathodic current. Solution B.



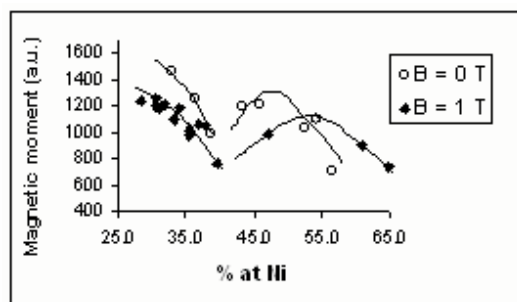


Fig. 5. Magnetic moment vs nickel atomic percentage.

The nickel percentage is relatively low compared to the ratio of individual nickel and iron intensity-potential curves (Fig. 1). This is due to the inhibition of nickel by iron species. In the same way, the decrease of the nickel percentage with the decrease of the magnetic field confirms the enhancement of inhibition in presence of the magnetic induction.

The general aspect of the curves (decrease and then increase of nickel percentage versus reduction current) reveals the presence of a competition between the reduction kinetics of nickel and iron and the inhibitor effect of iron species. This type of curve is relatively important to select the electrodeposition parameters and shows that two different currents may give the same composition of the alloy in the invar area. Note that in this study, we have not found any fundamental difference on the magnetic moment value whatever the applied current for one composition of the alloy.

In Fig. 5 the evolution of magnetic moment (arbitrary unity) versus atomic percentage of nickel is reported.

In this work (Fig. 5), we have obtained (on a tin substrate) the magnetic moment drop between 35 and 40 %, i. e. near the invar[®] composition. This drop point was weakly affected by the magnetic induction during electrodeposition. Nevertheless, with others plating conditions (change of substrate and/or support electrolyte), we have obtained the drop for another percentage (30 %). According to literature results, the above decrease seems to depend on the alloy preparation. For example, by melting preparation, Crangle [7] gets the drop for a nickel fraction of 30 % and Ueda [6] obtains it for 45 % by electroplating. Consequently, these differences could be imputed to a phase shift change according to the alloy elaboration conditions. At last, we observe some differences for the magnetic moment value for a same composition (and curve appearance), according to the presence of magnetic field. These variations could be due to morphology, roughness or grain size differences. Some complementary studies by X ray diffraction and SEM are actually in progress to verify these hypotheses.

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