JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. **14** No 6, 06022(5pp) (2022)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том **14** № 6, 06022(5cc) (2022)

Study of the Optimal Composition of the Bath on Nucleation and Growth of Ni-Fe Alloy Thin Films

F. Lekmine[1,2], I. Zidani[3], A. Chala[1,2], A. Gana[2]

[1] *University of Abbes Laghrour Khenchela*
[2] *Physic Laboratory of Thin Films and Applications, University of Biskra, Algeria*
[3] *University Hadj Lakhdar, Batna 1, Algeria*

(Received 28 October 2022; revised manuscript received 20 December 2022; published online 27 December 2022)

Ni-Fe alloy thin films are one of the oldest topics within the framework of electrochemistry because they exhibit a range of physical properties that lead to their widespread use in a variety of applications. In this study, the effects of bath composition and applied potential on Ni-Fe alloy thin films were investigated. Ni-Fe thin films were electrodeposited on copper substrates at a pH of approximately 3, and the experiments were performed at room temperature. The deposition time was equal to 10 min for all deposited samples and the applied potential (– 1.35 V, 1 V) and bath composition (0.0.05, 0.075 and 0.1 M). The experiments were performed using electrochemical techniques such as cyclic voltammetry (CV), and an electrochemical method called chronoamperometry was used to develop electrolytic alloys of the Ni-Fe type by considering the nucleation growth phenomenon. We demonstrated in fact, the concentration of the electrolyte had almost no effect on the type of nucleation, but its effect appeared in the linearity of the curve. The diffusion coefficient and nucleation density for instantaneous nucleation and the nucleation rate for progressive nucleation were also evaluated and the Ni-Fe thin film deposition reaction showed nucleation and growth (3D) under diffusion control. Germination of Ni-Fe is difficult on copper substrate surfaces for low overpotentials, and the maximum time decreases with increasing overpotentials.

Keywords: Bath composition, Potential, Cyclic voltammetry, Chronoamperometry, Ni-Fe alloy thin films, Nucleation, Growth, Germination.

DOI: 10.21272/jnep.14(6).06022

PACS numbers: 81.15.Pq , 68.55.at, 68.55.Ln, 68.55.Nq, 64.60.qj

1. INTRODUCTION

Ni-Fe alloy thin films have attracted the attention of many researchers because of their excellent properties, low thermal expansion coefficient, low coercively, high saturation magnetization, relatively high permeability, magnetic, corrosion, resistant properties and special optical properties. Ni-Fe is currently a key alloy for many applications due to its very low coefficient of thermal expansion [1-6]. Several techniques have been used to produce thin films such as molecular beam epitaxy, sputtering, evaporation, electrochemical deposition [6], vacuum deposition, rapid quenching, mechanical alloying, spray pyrolysis and electrodeposition [7-10]. Electrodeposition plays a crucial role in the formation of thin films on materials, through the electrochemical reduction of metal ions in electrolytic solutions [11]. Moreover, electrodeposition is related to several parameters (current density, adding agents, bath solution, voltage, temperature, and pH) that influence the structural properties [11, 12]. Thus, understanding the relationship between the microstructure of nanocrystalline Ni-Fe alloys and their electrodeposition parameters is a critical step in achieving progress in the alloy design and development of these materials for specific applications. In this study, we investigated the optimal experimental conditions to obtain these alloys. The effects of bath composition and potential on the nucleation and growth of Ni-Fe alloys were studied. Our studies were conducted using conventional electrochemical techniques, cyclic voltammetry, and chronoamperometry.

2. EXPERIMENTAL

The substrate used in this study was copper polished with 120-2000 grade SiC paper, rinsed with distilled water, degreased with acetone, rinsed with distilled water, pickled in a 10 % HCl solution to remove oxide traces, and finally washed with distilled water. The experimental setup for electrodeposition of the Ni-Fe coating was a Parstat 2253 Potentiostat/Galvanostat electrochemistry system equipped with Power Suite software and a cell with three electrodes, because the volume of the bath was 250 ml, without agitation; all the potentials were referred to the electrode at the saturated calomel (SCE) and other electrodes were constructed of industrial rectangular Ni and Cu, planes (1 cm × 1 cm). Copper foil substrates were used as the cathodes.

In order to study the electrochemical behavior of Ni-Fe and to determine the reduction potential of the electroactive species to be deposited in aqueous solutions, we carried out cyclic voltammetry of aqueous solutions of different concentrations (0.1, 0.075, and 0.05 M). We used the chronoamperometry electrochemical method to produce thin layers. For this technique, we have chosen six independent potential values, namely, – 1, – 1.10, – 1.15, – 1.20, – 1.25, – 1.30 and – 1.35 V/ECS. It should also be noted that all chronoamperometry experiments were carried out under the same operating conditions as those in cyclic voltammetry.

To identify the nucleation mechanism for different potentials applied to the electrode and for different concentrations, we used the Scharifker-Hills model and, compared the experimental and theoretical results. For instantaneous nucleation we have:

Table 1 – Bath compositions and deposition parameters of Ni-Fe alloy thin films

Bath composition	Concentration		
$[M^+] = [Ni^{2+}] + [Fe^{2+}]$ (M)	0.1	0.075	0.05
$NiSO_4$, $6H_2O$ (g/l)	9.46	7.09	4.73
$(NH_4)_2Fe(SO_4)_2,6H_2O$ g/l)	25.09	18.82	12.55
NaCl (g/l)	5	5	5
H_3BO_3 (g/l)	12.5	12.5	12.5
Saccharine (g/l)	0.5	0.5	0.5
Sodium Lauryl-Sulfate (g/l)	0.4	0.4	0.4
Time (min)	10	10	10
Temperature °C	25	25	25
pH	3	3	3

$$\frac{i^2}{i_{max}^2} = 1.9542\left(\frac{t_{max}}{t}\right)\left[1-\exp\left(-1.2564\frac{t}{t_{max}}\right)\right]^2,$$

for progressive nucleation:

$$\frac{i^2}{i_{max}^2} = 1.2254\left(\frac{t_{max}}{t}\right)\left[1-\exp\left(-1.3367\frac{t^2}{t_{max}^2}\right)\right]^2.$$

3. RSULTTS AND DISCUSSION

3.1 Analysis by Cyclic Voltammetry

The voltammograms (Fig. 1) obtained for different bath concentrations are characterized by the presence of a cathodic peak near – 0.8 V/ECS (indicated by the arrow) during the first cycle, corresponding to the reduction of Ni-Fe ions into metallic Ni-Fe deposited on the surface of the electrode according to the following electrolytic reactions:

$$Ni^{+2} + 2\,e^- \rightarrow Ni,$$

$$Fe^{+2} + 2e^- \rightarrow Fe.$$

It is also important to note here that the deposition of Ni-Fe is accompanied by the evolution of hydrogen according to the following chemical equation:

$$2H_3O^+ + 2e^- \rightarrow H_2 + 2H_2O.$$

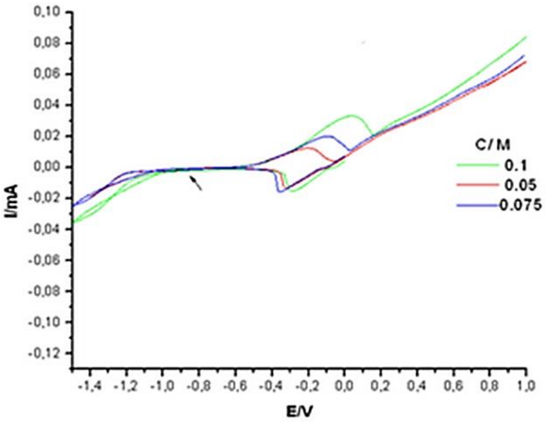
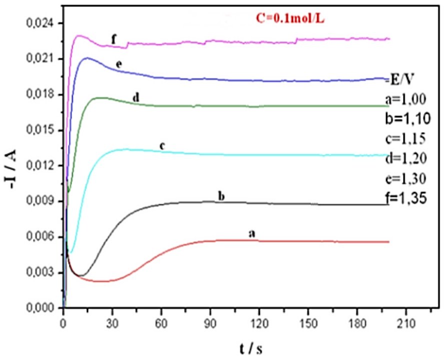


Fig. 1 – Cyclic voltammograms of Ni-Fe for different bath concentrations

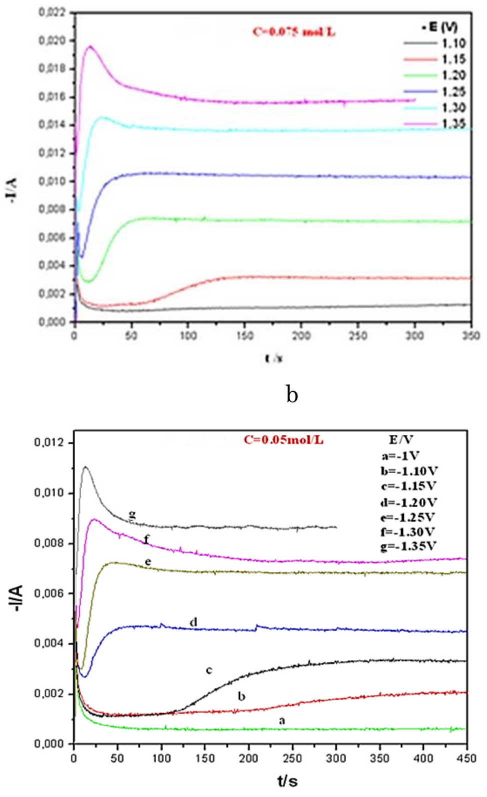
3.2 Analysis by Chronoamperometry

We observe in all the chronoamperograms (Fig. 2) that the current starts with a very intense cathodic value (a capacitive current peak), which corresponds to the charge of the double layer, then it increases and reaches a maximum. This results in an increase in the number of germ cells and the individual growth of each germ (the germination and growth of Ni-Fe grains on the surface of the copper substrate). From there, we notice a decrease in the current density for a few seconds, which stabilizes after approximately 20 s, which is explained by the existence of a diffusion regime governing the growth of the film formed. This behavior is described by Cottrell law. It should be noted that the current jump towards the maximum value indicates the formation of a new phase. After the germination phase, the transient currents converge towards diffusion limit currents, which appear in the curves as plateaus and only appear when the diffusion step is decisive in the deposition process. In other words, the attenuation of the transition current after a certain time is explained by the birth of diffusion zones that coalesce. By comparing the responses in the transient currents, it can be said that the chronoamperograms are generally similar. The appearance of these curves is a typical response of the transient current of a nucleation phenomenon and growth under diffusional control. The results obtained show that the elaboration of Ni-Fe alloys depends essentially on the experimental conditions, the substrate used and that for low overpotentials; the germination of Ni-Fe on the surfaces of the copper substrate is difficult. In other words, the maximum current related to nucleation and growth increased with increasing overpotential. The maximum time decreases with an increase in the overpotential. It can be seen that the applied potential is mainly sensitive to the concentration of the electrolyte, according to the chronopapmometric curves, the values indicate precisely that the maximum times associated with the electrolyte with a concentration of 0.05 mol/l are greater than those associated with the electrolyte of 0.075 and 0.1 mol/l, on the other hand the values of the currents are important for the most concentrated electrolyte.

According to the chronoamperograms obtained for different concentrations, we can say that for the two potentials $E = -1.35$ V and -1.30 V/ECS, the three zones indicated in Fig. 2 are clearer compared to the other applied potentials.



a



b

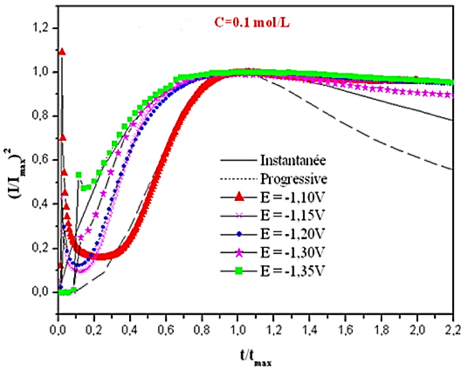
c

Fig. 2 – Chronometric curves of Ni-Fe alloy thin films that were electrodeposited in different solutions and with different potentials: (a) 0.1 (mol/l), (b) 0.075 (g/l), (c) 0.05 (mol/l)

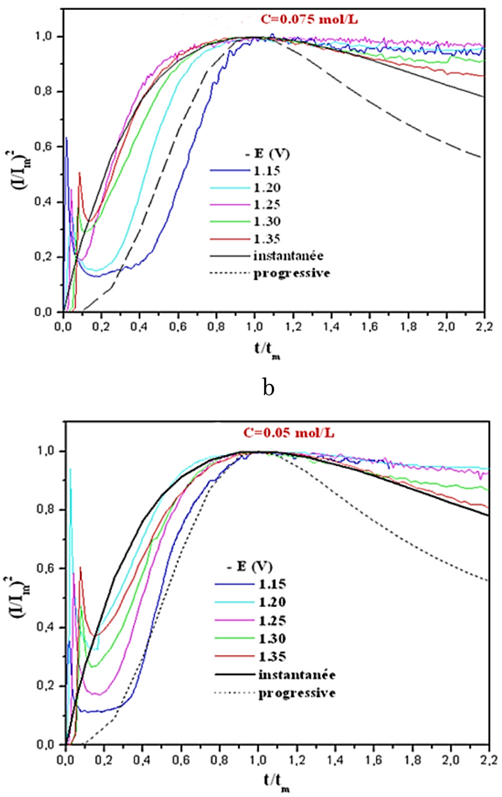
3.3 Numerical Analysis of the Results

The following Fig. 3 shows typical examples of normalized transients of the experimental curves for different concentrations and theoretical curves corresponding to progressive and instantaneous nucleation.

The confrontation of the curves plotted in the overpotential regime of ($-1.1 \leq E \leq -1.35$ V (ECS)) for different concentrations and the Scharifker-Hills model shows that the nucleation of Ni-Fe on the copper substrate is performed by 3D germs, following an instantaneous nucleation mechanism at the first stage of nucleation for all applied potentials, except for $E \leq -1.15$ V/ECS it is a progressive nucleation. The curves converge for values $t/t_{\max}$ greater than unity at instantaneous nucleation, which is strongly linked to the existence of the concurrent reaction of hydrogen on the electrode surface [14]. According to the experimental results, it can be said that the transition from a progressive-type nucleation to an instantaneous-type nucleation occurs when the cathodic overvoltage increases. In other words, the model adapts well for high overpotentials, which means that the higher the imposed potentials, the more ion reduction predominates and hence the slower the hydrogen reaction. In all cases, it appears that the concentration of the electrolyte used has a significant influence on the nucleation of Ni-Fe alloys deposited on the copper substrate, as shown in the following Fig. 4.



a



b

c

Fig. 3 – Normalized current transients $(i/i_{\max})^2$ as a function of $(t/t_{\max})$ on a Cu substrate during Ni-Fe deposition for: (a) 0.1 mol/l, (b) 0.075 mol/l, (c) 0.05 mol/l

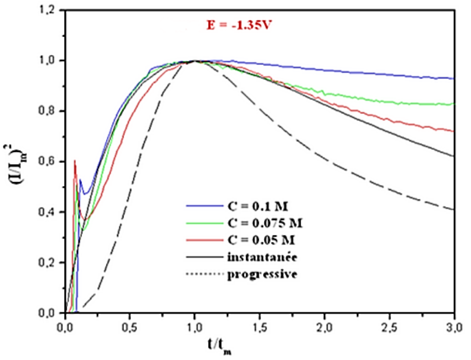


Fig. 4 – Normalized current transients $(i/i_{\max})^2$ as a function of $t/t_{\max}$ on a Cu substrate during the deposition of Ni-Fe at different concentrations for $E = -1.35$ V

By comparing the different curves, it can be seen that the mode of nucleation remains of the same "instantaneous type", where the growth rate is very high and there is little formation of active sites. However, it is clear that the red curve for $C = 0.05$ mol/l is similar to the theoretical curve and shows perfect linearity compared to the other curves, which explains why the concentration of the electrolyte has practically no effect on the nucleation type, but its effect appears on the linearity of the curve. To verify that the nucleation mode is instantaneous and has a 3D type under diffusional control, we show Fig. 4. The curves correspond to the relation that connects the current density to $t^{1/2}$ (for instantaneous nucleation):

$$i(t) = \frac{8nFM^2c^3D^{3/2}}{\rho^2\pi^{1/2}} N_\circ t^{1/2} .$$

The relationship linking the current density to $t^{3/2}$ (for progressive nucleation) is as follows:

$$i(t) = \frac{16nFM^2c^3D^{3/2}}{3\rho^2\pi^{1/2}} AN_\circ t^{3/2} .$$

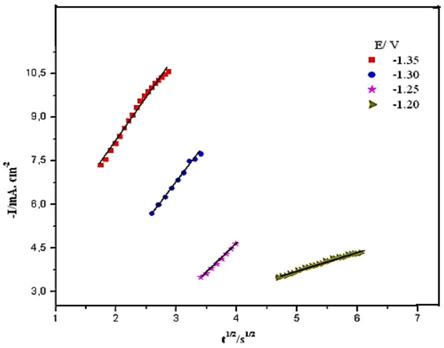


Fig. 5 – Transient curves of $i(t) = f(t^{1/2})$ during the electrodeposition of $Ni_{36}Fe_{64}$ on a Cu substrate for $C = 0.05$ M

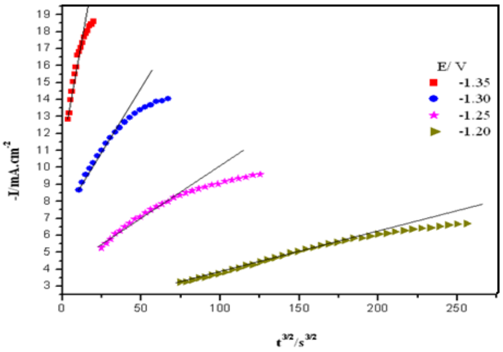


Fig. 6 – Transient curves of $i(t) = f\ (t^{3/2})$ during the electrodeposition of $Ni_{36}Fe_{64}$ on a Cu substrate for $C = 0.05$ M

Curves a, b and c in Fig. 3 drawn for the overpotential regimes studied ($-1.10 < E \leq -1.35$ V (ECS)) and for different concentrations, in particular for the first stages of nucleation, show perfect linearity when $-1.15 \leq E \leq -1.35$ V (ECS) for $i(t) = f(t^{1/2})$ compared to $i(t) = f(t^{3/2})$ during the electrodeposition of Ni-Fe. On the other hand, when $-1.1 \leq E \leq -1.15$ V (ECS), the curve is linear for $i(t) = f(t^{3/2})$ with respect to $i(t) = f(t^{1/2})$. This behavior further constitutes support for saying that the nucleation mode is instantaneous for high $-1.15 \leq E \leq -1.35$ V and progressive $E \leq -1.15$ V/ECS overpotentials.

3.4 Determination of Kinetic Parameters

We used the results obtained from the Scharifker-Hills model to determine the diffusion coefficient of the electroactive species and the nucleation density on the surface of the substrate when the nucleation mode is instantaneous and the nucleation rate when the mode is progressive.

The product $i^2_{\max} \cdot t_{\max}$ associated with nucleation allows us to estimate the diffusion coefficient D, density N_0, and nucleation rate AN_0 using the Charifker-Hills model.

For instant nucleation:

$$D = \frac{i^2_{\max} t_{\max}}{0.1629\left(nFC\right)^2} ,$$

$$N_0 = 0.065\left(\frac{8\pi CM}{\rho}\right)^{-1/2}\left(\frac{nFC}{i_{\max} t_{\max}}\right)^2 .$$

For progressive nucleation:

$$D = \frac{i^2_{\max} t_{\max}}{0.2598\left(nFC\right)^2} ,$$

$$AN_0 = 0.2898\left(\frac{8\pi cM}{\rho}\right)^{-1/2} \frac{\left(zFc\right)^2}{i^2{}_{\max} t^3{}_{\max}} ,$$

where $M_{Ni} = 58.69$ g/mol, $M_{Fe} = 55.84$ g/mol, $\rho_{Ni} = 8.9$ g/l, $\rho_{Fe} = 7.86$ g/l, $z = n = 2$, $F = 964853$ [C mol^{-1}].

The results obtained are grouped in Table 2 and Table 3. From these results, it is evident that with an increase in the applied potential, the maximum current ($i_{\max}$) increases, and the maximum time ($t_{\max}$) decreases. This behavior is typical of 3D electrochemical nucleation and growth. The diffusion coefficient value is around 10^{-5} cm^2·s^{-1}, which indicates that the nucleation and growth mechanism of Ni-Fe depend on the diffusion of other electroactive species (Cl^-, H^+, etc.), nucleation sites (electrode surface) [14]. For instantaneous nucleation, the number of nucleons increases with the overpotential applied and it is important for the most concentrated electrolyte. For gradual nucleation, the rate of nucleation increases with the overpotential applied and it is important for the most concentrated electrolyte.

Table 2 – The influence of potential and bath concentrations on the diffusion coefficient and the number of nucleation sites

Instant nucleation					
C (mol/l)	$-E$ (V)	$i_{\max}$ (mA/cm)	$t_{\max}$ (s)	$D10^{-5}$ (cm^2/s)	$N_0 10^{-4}$ (cm^{-2})
0.05	1.35	11	13.43	10.72	0.94
	1.30	8.9	21.99	11.49	0.54
	1.25	7.2	39.33	13.45	0.26
	1.20	4.6	101.88	14.22	0.1

Table 3 – The influence of potential and concentration on the diffusion coefficient and the nucleation rate

Gradual nucleation					
C (mol/l)	– *E* (V)	i_{max} (mA/cm)	t_{max} (s)	$D10^{-5}$ (cm^2/s)	$AN_0 10^{-7}$ (cm^{-2})
0.05	1.15	3.1	264.86	10.53	0.515
	1.10	2	372.85	6.17	0.444
0.1	1.10	5.7	100	3.36	1.40

4. CONCLUSIONS

The nucleation-growth mechanisms of Ni-Fe alloys on copper electrodes have been studied using electrochemical techniques such as cyclic voltammetry and chronoamperometry.

- We demonstrate that the deposition reaction of the Ni-Fe alloy obeys the phenomenon of nucleation and 3D growth under diffusional control. Germination of Ni-Fe on copper substrate surfaces is difficult for low overpotentials, and the maximum time decreases with increasing overpotentials.
- The maximum times associated with the electrolyte with a concentration of 0.05 mol/l are greater than those associated with electrolytes with concentrations of 0.075 and 0.1 mol/L, the values of the currents are high for the most concentrated electrolyte.
- The Scharifker-Hills model shows that the nucleation of Ni-Fe on the copper substrate is done by 3D seeds, following an instantaneous nucleation mechanism at the first stage of nucleation for all applied potentials, except for $E \leq -1.15$ V/ECS with progressive nucleation. The curves converged for values t/t_{max} are greater than unity during instantaneous nucleation.
- In fact, the concentration of the electrolyte had almost no effect on the type of nucleation, but its effect appeared in the linearity of the curve. The diffusion coefficient and nucleation density for instantaneous nucleation and the nucleation rate for progressive nucleation were also evaluated.

REFERENCE

1. G. Maizza, H. Eom, M. Lee, T.H. Yim, E. Nakagawa, R. Pero, T. Ohmura, *J. Mater. Sci.* **54**, 13378 (2019).
2. E.I. Manimaran, K. Antonyraj, E.R. Navaneetha, V.S. Kumar, P. Rajesh, *J. Mater. Sci. Mater. Electron.* **29**, 3715 (2018).
3. S. Arabi, G. Avramovic-Cingara, G. Palumbo, U. Erb, M. Niewczas, *Mater. Sci. For.* **706-709**, 1642 (2012).
4. T.-R. Lee, L. Chang, C.-H. Chen, *Surf. Coat. Technol.* **207**, 523 (2012).
5. L.X. Phuaa, N.N. Phuoc, C.K. Ong, *J. Alloy. Compd.* **520**, 132 (2012).
6. V. Torabinejad, M. Aliofkhazraei, S. Assareh, M.H. Allahyarzadeh, A.S. Rouhaghdam, *J. Alloy. Compd.* **691**, 841 (2017).
7. J.Y. Ping, D.G. Rancourt, R.A. Dunlap, *J. Magn. Magn. Mater.* **103**, 285 (1992).
8. G. Le Caër, P. Matteazzi, *Hyperfine Interact.* **90**, 229 (1994).
9. C. Kuhrt, L. Schultz, *J. Appl. Phys.* **73**, 1975 (1993).
10. S. Eroglu, S.C. Zhang, G.L. Missing, *J. Mater. Res.* **44**, 2131 (1996).
11. F. Lekmine, K. Digheche, M. Naoun, H. Bentemam, A. Gana, *Metallofiz. Nov. Tekhnol.* **43** No 10, 1351 (2021).
12. F. Lekmine, H. Ben Temam, M. Naoun, M. Hadjadj, *J. Nano- Electron. Phys.* **12** No 1, 01001 (2020).
13. I. Giouroudi, A. Ktena, E. Hristoforou, *J. Opt. Adv. Mat.* **6**, 661 (2004).
14. R. Fàbio Bento, H. Lucia, Mascaro, *Surf. Coat. Technol.* **201**, 1752 (2006).

Дослідження оптимального складу ванни на зародження та ріст тонких плівок сплаву Ni-Fe

F. Lekmine[1,2], I. Zidani[3], A. Chala[1,2], A. Gana[2]

[1] *University of Abbes Laghrour Khenchela*
[2] *Physic Laboratory of Thin Films and Applications, University of Biskra, Algeria*
[3] *University Hadj Lakhdar, Batna 1, Algeria*

Тонкі плівки сплаву Ni-Fe є однією з найстаріших тем в області електрохімії, оскільки вони демонструють низку фізичних властивостей, що призводить до їх широкого використання в різних додатках. У статті було вивчено вплив складу ванни та прикладного потенціалу на тонкі плівки сплаву Ni-Fe. Тонкі плівки Ni-Fe електроосаджували на мідні підкладки при pH приблизно 3, і експерименти проводили при кімнатній температурі. Час осадження дорівнював 10 хв для всіх нанесених зразків, прикладеного потенціалу (– 1,35 В; 1 В) і складу ванни (0,005; 0,075 і 0,1 М). Експерименти проводилися з використанням електрохімічних методів, таких як циклічна вольтамперометрія (CV), а хроноамперометрію використовували для розробки електролітичних сплавів типу Ni-Fe з урахуванням явища росту зародків. Ми продемонстрували, що фактично концентрація електроліту майже не впливає на тип нуклеації, але її вплив виявляється в лінійності кривої. Коефіцієнт дифузії та густина нуклеації для миттєвої нуклеації та швидкість нуклеації для прогресивної нуклеації також були оцінені, а реакція осадження тонкої плівки Ni-Fe показала нуклеацію та ріст (3D) під контролем дифузії. Проростання Ni-Fe є важким на поверхнях мідної підкладки за низьких перенапруг, і максимальний час зменшується зі збільшенням перенапруг.

Ключові слова: Потенціал, Циклічна вольтамперометрія, Хроноамперометрія, Тонкі плівки сплаву Ni-Fe, Нуклеація, Ріст, Проростання.