Electrodeposition behavior of W- Ni-Fe alloys from their ionic electrolyte baths

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Abstract

The electrodeposition of W-Ni-Fe alloy is carried out from their ionic electrolytes using citrate and triethanol amine complexes in the deposition baths. The alloy electrodeposition is achieved in different pH and temperatures using current densities of 15 and 25 mAcm^{-2} for the galvanostatic electrodeposition. It is found that the maximum efficiency for the electrodeposition using citrate bath is ~ 90% with deposition current density 15 mAcm^{-2}, pH 6.8 at 80º C after 50 min. While, the efficiency of the deposition in TEA bath is ~120% for with the same conditions of deposition within 55 min for deposition time. The crystal structure of the obtained W-Ni-Fe alloy is face centered cubic with cauliflowers and dendritic morphology. Also, the cyclic voltammetric measurements are studied for the electrochemical behavior of this alloy.

Keywords: **Electrodeposition, W-Ni-Fe alloy, citrate and TEA baths.**

1. Introduction

Nickel-tungsten and iron-tungsten alloys are good materials due their good mechanical strength and great corrosion resistance. Electrodeposition of Ni–W alloys was studied by several researchers [1-7]. Also, the electrodeposition of Ni–Fe alloy is a phenomenon of anomalous co-deposition [8, 9]. The introducing of tungsten to these previous alloys to form ternary alloy W-Ni-Fe found an interest due to the excellent of magnetic, corrosion resistance, electrical, thermal mechanical strength properties [10-13].

Fe–Ni–W alloys with 18 wt% iron, 35 wt% nickel and 55 wt% tungsten were obtained by electrodeposition from an ammonium citrate bath. The deposits are smooth, of nice appearance, and adhere well to iron and steel. The alloys of 55 wt% tungsten, after heat treatment at 500°C, appeared good wear resistance and hardness. The alloys of 18 wt% tungsten were very corrosion-resistant [13].

Ni-Fe-W (66% Ni-24% Fe-11%W) powder of nano-structured was obtained and studied by electrodeposition using citrate electrolyte. The studies explained that the chemical composition of the powder depends upon current density and electrolyte temperature due to the diffusion control of the process of co-deposition of nickel, iron and tungsten [10].

A dark gray nanostructured coating of an alloy composed of 87.3 wt. % Ni, 11.3 wt. % Fe and 1.4 wt.% W was electrodeposited from an ammonia citrate bath on a titanium cathode at a current density of 500 mA cm^{-2}. Alloy deposition at current densities of up to 300 mA cm^{-2} was an activation-controlled process, which turned into a diffusion-controlled process at higher current densities [12].

The aim of the present work is a comparative study needed for the electrodeposition of W-Ni-Fe in citrate and triethanol amine baths with different current densities, pH, temperatures and deposition time.

2. Experimental

The electrolyte was prepared of 0.2 mol dm^{-3} Na$_2$WO$_4$·2H$_2$O, 0.05 mol dm^{-3} NiSO$_4$·6H$_2$O, and 0.05 mol dm^{-3} anhydrous FeSO$_4$. The dissolving of these salts was carried out separately. The concentration of the complexing agent: (1) tri sodium citrate (Na$_3$C$_6$H$_5$O$_7$·2H$_2$O) was 58.8 g/L and H$_3$BO$_3$ was 5g/L or (2) 35 ml tri-ethanol amine (TEA) and H$_3$BO$_3$ was 5g/L. After that the separate solutions were added together to form the electrolyte mixture. The mixture was stirred and heated near boiling and left to cool. The electrodeposition was conducted in a beaker cell (100 cm^3 volume). The pH of the solution was adjusted to 4, 6.8 and 8 using 10% ammonia or 10 % acetic acid solution. The anode is spiral Pt wire and the cathode (negative electrode) was a substrate from copper plate sheet with dimensions: 3 cm length, 1.8-2 cm width and 0.5 mm thickness. The tested solution volume was 80 ml. The solution was stirred with a magnetic stirrer. The used current densities in this stage of work were 15 and 25 mAcm^{-2}, respectively and the temperatures were 25 and 80°C. Cyclic voltammetry measurements were carried out using the same conditions of the electrolytes. The working electrode was Pt rotating disk electrode. The counter electrode was Pt wire and the reference electrode is Hg/ Hg$_2$SO$_4$/ H$_2$SO$_4$ (0.615 V vs. NHE). The scan rate was 10 mVs^{-1}. The weight of the

deposited alloy was recorded with time of deposition. Investigations of the samples were carried out by using XRD (Cu- target, 1.5406 Å) and SEM (Joel SEM-Model 5040).

3. Results and Discussion

Galvanostatic electrodeposition was achieved in order to deposit the W-Ni-Fe with different current densities, temperatures and pH values and different deposition times. Fig. 1 shows the galvanostatic deposition efficiencies in citrate bath at current densities: 15 and 25 mAcm^{-2} using two bath temperatures, 25 and 80°C. The efficiency of the alloy deposition η is given by the following relations [10]:

$$\eta = \frac{\text{Experimental deposited weight (Wd)}}{\text{Theoretical weight (Wth)}}.100 \% \qquad (1)$$

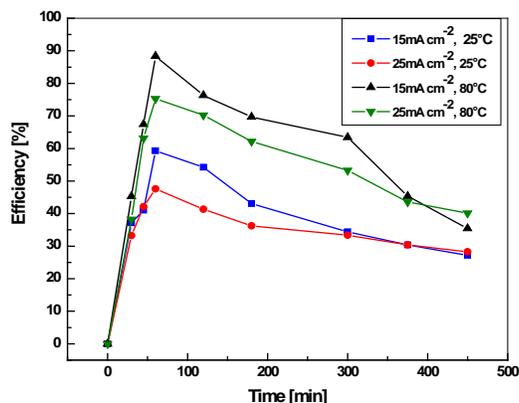$$\eta = \frac{Wd.nF}{A.I.t}.100 \% \qquad (2)$$

Fig. 1 Efficiency of W-Ni-Fe alloy deposition in citrate bath at different current densities and temperatures, pH = 6.8.

Where: W_d Experimental deposited weight, F: Faraday constant (96487 C Mol^{-1}), A: atomic weight of the deposited element, I: current intensity, and t: deposition time.

It is observed that the maximum deposition efficiencies are obtained at higher temperature, 80°C and lower current density, 15 mAcm^{-2}. Furthermore, the effect of pH on the deposition is studied using current density 15 mAcm^{-2} and temperature 80°C with different deposition times as recorded in Fig. 2. It is observed that pH of 6.8 gives maximum deposition efficiency at deposition time of 50 minutes.
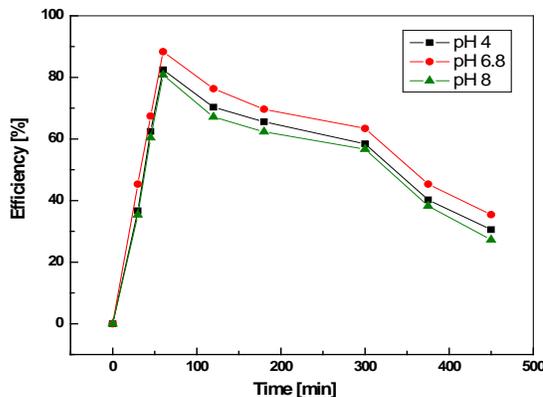

Fig. 2 pH effect on the Efficiency of the W-Ni-Fe alloy deposition in citrate bath at 80°C and 15 mAcm^{-2}.

On the other hand, the deposition efficiencies in TEA bath are studied and the results are recorded in Figs. 3 & 4 for different current densities, temperatures, pH values and deposition times. Similar results are obtained for TEA bath. Maximum deposition efficiencies, 90% are observed with 15 mAcm^{-2}, 80°C and pH value of 6.8 with 55 min. This behavior confirms that the deposition efficiency is enhanced by lower current density, higher temperature and neutral electrolyte medium.

Some parts of the deposited alloys of W-Ni-Fe powders in citrate and TEA baths using optimum conditions (j= 15 mAcm^{-2}, T= 80°C, pH =6.8 and t= 50 min. fir cit. and 55 min for TEA) were heat treated at 500°C in Ar + 5% H$_2$ gas for 6 h for XRD interpretation.
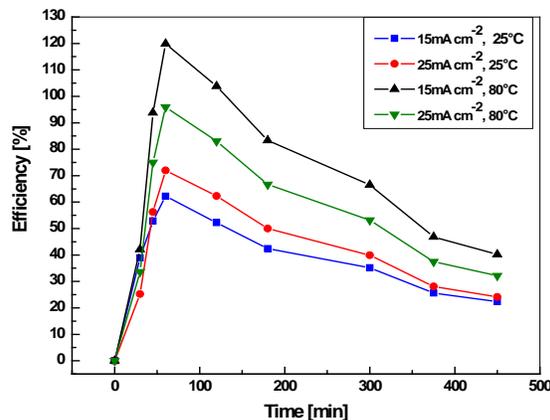

Fig. 3 Deposition efficiency of the W-Ni-Fe alloy deposition in TEA bath at different current densities and temperatures , pH= 6.8 .
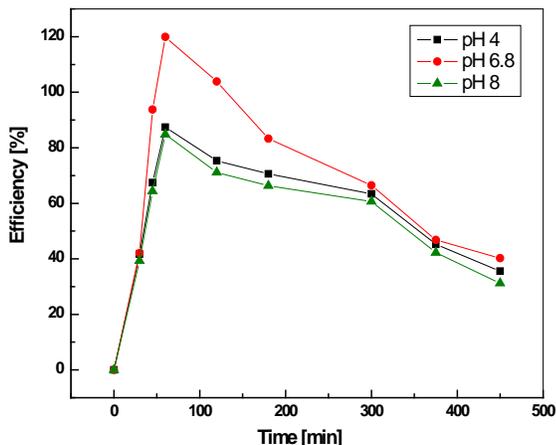
Fig. 4 Effect of pH on the efficiency of the W-Ni-Fe alloy deposition in TEA bath at 80°C and 15 mAcm^{-2}.

They are investigated by XRD as shown in Fig.5. The crystal structure of the W-Ni-Fe alloy is face centered cubic (fcc). The crystallite size is 12.95 and 11.8 nm for citrate and TEA baths, respectively using Scherer formula [10]:

$$L= 0.94\ \lambda/\beta \cos\theta \qquad (3)$$

Where; L is the crystallite size, λ is wavelength of the target (1.5406 Å for Cu) and θ is the chosen diffraction angle and β at full width half maximum (FWHM).
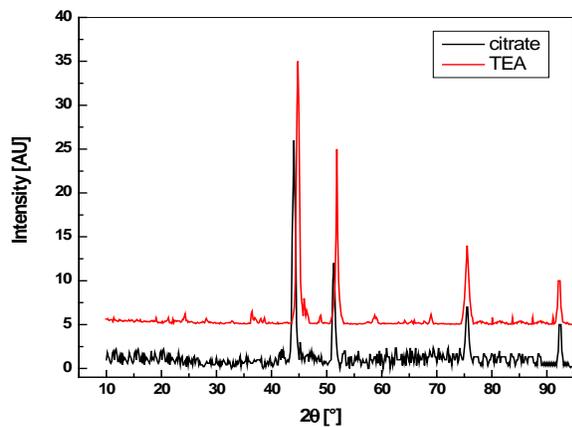

Fig. 5 XRD of W-Ni-Fe alloy deposited from citrate and

TEA baths, pH = 6.8, J =15mAcm^{-2}, T = 80°C for 50 min.

The morphologies of the deposited W-Ni-Fe alloy are investigated by SEM as shown in Fig.6. The deposition conditions are j= 15mAcm^{-2}, pH =6.8, t=50 min and T= 25
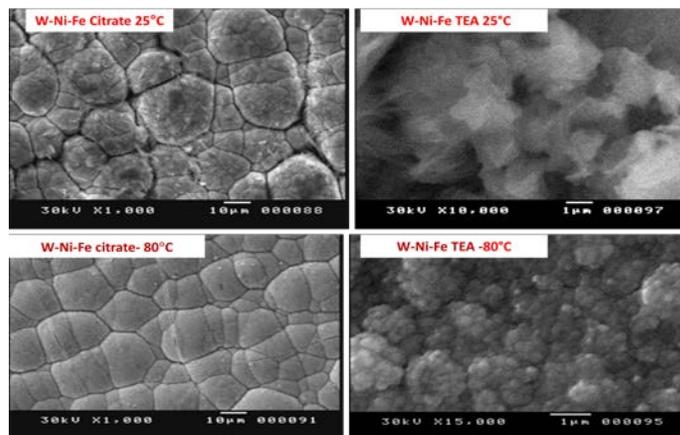
& 80°C. The structure of W-Ni-Fe alloy from citrate bath has cauliflower shape at both temperatures.

Fig. 6 SEM of W-Ni-Fe alloy deposited on copper substrate at sheet j=15 mAcm^{-2}, pH=6.8 and t =50 for cit & 55 min for TEA.

While, the morphology of the alloy in presence of TEA has dendritic shape for the deposition at temperature of 25°C. However, the increase of the bath temperature up to 80°C, the morphology becomes small spheres.

Cyclic voltammetry (CV) measurements were carried out in order study the electrochemical behavior for the mixture baths of citrate and TEA containing the three elements ions as shown in Figs.7&8. Fig.7 shows CV for the mixture bath containing citrate. The cathodic reduction occurs for the electro-co deposition in the potential range
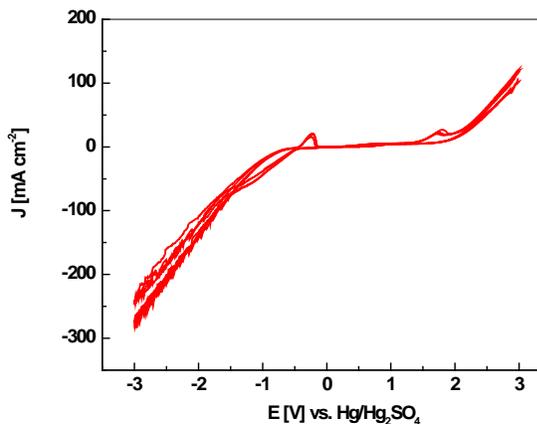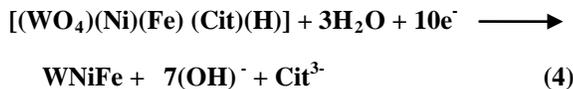

Fig. 7 CV of W-Ni-Fe in citrate, scan rate 10 mVs^{-1}, RDE=1000 rpm, pH = 6.8 at 80°C.

between -0.7 and -1.4 V vs. MSE. It was reported that the complexes of tungstates with citrates have the formula $[(WO_4)(Cit)(H)_x]^{x-5}$, as the citrate ion is trivalence [15]. Thus, the formula of the three ions complex is:

$$[(WO_4)(Ni)(Fe)\,(Cit)(H)] + 3H_2O + 10e^- \longrightarrow$$

$$WNiFe + 7(OH)^- + Cit^{3-} \qquad (4)$$

However, the electrocodeposition reduction of W-Ni-Fe alloy on the cathode is governed by the following equation [15, 16]:

$$E = 0.049 - 0.0788\,pH + 2.303\,RT/nF\,log\,[WO_4^{2-}] \quad (5)$$
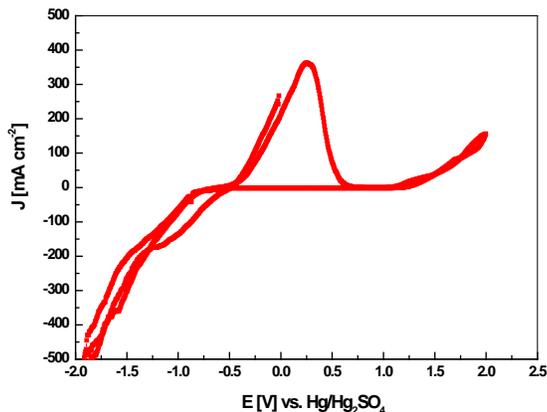
$E_{25°C} = -0.011V$ and $E_{80°C} = -0.012$ V

Fig. 8 CV of W-Ni-Fe in TEA, scan rate 10 mVs^{-1}, RDE=1000 rpm, pH = 6.8 at 80°C.

$$E = -0.4 + 2.303\,RT/nF\,log\,[Ni^{2+}] \qquad (6)$$

$E_{25°C} = -0.438V$ and $E_{80°C} = -0.445$ V

$$E = -0.6 + 2.303\,RT/nF\,log\,[Fe^{2+}] \qquad (7)$$

$E_{25°C} = -0.638V$ and $E_{80°C} = -0.645$ V

So, for pH 6.8, $[WO_4^{2-}] = 0.2M$, $[Ni^{2+}] = 0.05$ M, and $[Fe^{2+}] = 0.05$ and T = 298 or 353K. The cyclic voltammogram of Fig. 7 shows the start of the electrocodeposition reduction at potential of -0.5V vs. MSE at T = 353K at zero current crossing potential (ZCCP) and continued until H_2 evolution with the increase of the cathodic negative potential.

With respect to the anodic oxidation, it has a plateau in the region between -0.98 and -0.43V. This region expresses about the oxidation of W to WO_4^{2-} (-0.55V vs. NHE), Ni to Ni^{2+} (-0.4V vs. NHE) and Fe to Fe^{2+} (-0.5V vs. NHE) as confirmed by the Pourbaix diagrams [15-18]. After that, there are two peaks observed at -0.23 and 1.77V vs. MSE. The first peak is attributed to the oxidation of Fe^{2+} into Fe_3O_4 (0.385V vs. NHE). The second one is for the oxidation of Ni^{2+} into NiO_2 (H_2O) (2.38V vs. NHE)

On the other hand, the CV in TEA bath has a cathodic reduction of WNiFe starts at -0.625 V vs. MSE as shown in Fig. 8. The formula of the three ions complex is given by:

$$[(WO_4)(Ni)(Fe)\,(TEA)(OH)_2] + 3H_2O + H^+ + 10e^-$$

$$\longrightarrow WNiFe + 9(OH)^- + TEA \qquad (8)$$
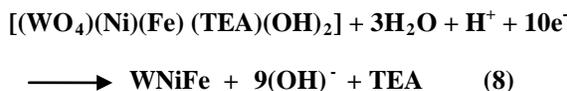
Also, this CV shows the start of the electrocodeposition reduction at potential of -0.503V vs. MSE at T = 353K at zero current crossing potential (ZCCP) and continued until H_2 evolution with the increase of the cathodic negative potential.

The cyclic voltammogram of Fig.8 shows a great anodic oxidation peak of the deposited alloy at ~ 0.25 V. This peak is attributed to the oxidation of Fe^{2+} into Fe^{3+} (0.8V vs.NHE) [18].

Conclusion

The electrochemical deposition of ternary W-Ni-Fe alloy was studied in citrate and TEA. The maximum efficiency for the electrodeposition using citrate bath is ~ 90% with deposition current density 15 mAcm^{-2}, pH 6.8 at 80° C after 50 min. While, the efficiency of the deposition in TEA bath is ~120% for with the same conditions of deposition with 55 min. The crystal structure of the obtained W-Ni-Fe alloy is face centered cubic with cauliflowers and dendritic morphology.

Acknowledgement

References

[1] O. Younes, and E. Gileadi, "Electroplating of Ni /W Alloys", J. Electrochem. Soc., Vol.149, No.2, 2002, pp. C100-C111.

[2] Y. Wu, D.-Y. Chang, S.-C. Kwon, and D. Kim, "Ni-W Alloy Electrodeposition From a Bath Containing an Organic Amine Substitute for Organic Ammonia", Plat. Surf. Finish. Vol. 2, 2003, pp. 46-49.

[3] M.P. Quiroga Argãnaraz, S.B. Ribotta, M.E. Folquer, E. Zelaya, C. Llorente, J.M. Ramallo-López, G. Benítez, A. Rubert, L.M. Gassad, M.E. Vela, and R.C. Salvarezza, "The chemistry and structure of nickel–tungsten coatings obtained by pulse galvanostatic electrodeposition", Electrochim. Acta, Vol.72, 2012, pp. 87-93.

[4] M. Benaicha, M. Allam, A. Dakhouche, M. Hamla, "Electrodeposition and Characterization of W-rich NiW Alloys from Citrate Electrolyte", Int. J. Electrochem. Sci., Vol. 11, 2016, pp. 7605 – 7620.

[5] E. Beltowska-Lehman, P. Indyka, A. Bigos, M. Kot and L. Tarkowski, "Electrodeposition of nanocrystalline Ni–W coatings strengthened by ultrafine alumina particles", Surf. Coat. Technol., Vol. 211, 2012, pp. 62-66.

[6] Io Mizushima , Peter T. Tang, Hans N. Hansen, Marcel A.J. Somers, "Development of a new electroplating process for Ni–W alloy deposits", Electrochimica Acta, Vol.51, 2005, pp. 888-896.

[7] K. H. Hou, Y.F. Chang, S.M. Chang, C.H. Chang, "The heat treatment effect on the structure and mechanical properties of electrodeposited nano grain size Ni–W alloy coatings", Thin Solid Films, Vol. 518, 2010, pp. 7535-7540.

[8] T. Ruei Lee, L. Chang, and C. H. Chen, "Effect of electrolyte temperature on composition and phase structure of nanocrystalline Fe–Ni alloys prepared by direct current electrodeposition", Surf. Coat. Technol., Vol. 207, 2012, pp. 523 -528.

[9] R.A.C. Santana, S. Prasad, E.S. Moura, A.R.N. Campos, G.P. Silva, and P. de Lima-Neto, "Studies on electrodeposition of corrosion resistant Ni–Fe–Mo alloy ", J. Mater. Sci., Vol.42, 2007, pp. 2290-2296.

[10] A.L.M. Oliveira, J. D. Costa, M.B. de Sousa, J. N. Alves a, A. R. N. Campos b, R. Alexandre c. Santana, Shiva Prasad., "Studies on electrodeposition and characterization of the Ni–W–Fe alloys coatings." J. Alloys & Compds.,Vol. 619, 2015, pp. 697–703.

[11] L. Ribi-Zelenovi, N. Cirovi, M. Spasojevi, N. Mitrovi, A. Marici, and V. Pavlovi, "Micro structural properties of electrochemically prepared Ni-Fe-W powders", Mater. Chem. & Physics, Vol.135, 2012, pp. 212-219.

[12] M. Spasojević a, L. Ribić-Zelenović, A. Maričić, and P. Spasojević, "Structure and magnetic properties of electrodeposited $Ni_{87.3}Fe_{11.3}W_{1.4}$ alloy", Powder Technology, Vol. 254, 2014, pp. 439–447.

[13] F. He, J. Yang, Tongxin Lei, and Chunyan Gu, "Structure and properties of electrodeposited Fe–Ni–W alloys with different levels of tungsten content: A comparative study", Applied Surface Science, Vol. 253, 2007, pp.7591–7598.

[14] A. Y. Shenouda, and N. Munichandraih, "Synthesis and electrochemical performance of $Li_2V_xMn_{1-x}O_3$ positive electrode for lithium batteries", J. Materials Science: Materials in Electronics,Vol. 29, 2018, pp. 8167–8175.

[15] L. Ma, X. Xi, Zuoren Nie, Tingting Dong, and Yuhui Mao, "Electrodeposition and Characterization of Co-W Alloy from Regenerated Tungsten Salt", Int. J. Electrochem. Sci.,Vol. 12, 2017, pp. 1034 – 1051.

[16] M. Pourboix, "Atlas of electrochemical equilibria in aqueous solutions.", NewYork, USA: Pergamon Press, 1966

[17] F. Basharat, U. A. Rana, M. Shahid, and M. Serwar, "Heat treatment of electrodeposited NiO films for improved catalytic water oxidation."RSC Adv.,Vol. 5,2015, pp.86713–86722.

[18] "Atlas of Eh-pH diagrams Intercomparison of thermodynamic databases." National Institute of Advanced Industrial Science and Technology, Research Center for Deep Geological Environments, Naoto TAKENO, May 2005.

[19] E. Go´mez, E. Pellicer, and E. Valle´s, "An approach to the first stages of cobalt–nickel–molybdenum electrodeposition in sulphate–citrate medium." J. Electroanalytical Chem.,Vol. 580, 2005, pp. 222–230.