

A study on the electrochemical deposition of Ni–W- Co alloy in Citrate and Triethanol Amine Baths.

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Abstract

In this work, we study the effect of complexing agents like citrate and triethanol amine baths on the electrodeposition of W-Ni-Co layers from electrolytes based on Na_2WO_4 , NiSO_4 and CoSO_4 . Also, it is observed that the efficiency of the deposition increased at high temperature than the room temperature using the same other conditions of current density, quantity of electricity and bath concentration as detected from the weights of the deposited alloy. The maximum efficiency observed with W-Ni-Co alloy in triethanolamine (TEA) is 120%, while in citrate bath is 110% at 80°C , 15 mAcm^{-2} and 50 min. The deposition efficiency of the W-Ni-Co (TEA) alloy at 80°C , 25 mAcm^{-2} is better than 25°C , 25 mAcm^{-2} .

Keywords: Electrodeposition of W-Ni-Co alloy, citrate and TEA baths.

1. Introduction

The electrodeposition of pure Ni is not suitable for the uses of Ni in high temperature due to the losing in the hardness and the stability shape. Therefore, metal alloy with Ni such as W and Co is a promising alloy. Furthermore, a Ni–W alloy is an excellent material because it has high corrosion resistance and mechanical strength. Several authors have investigated electrodeposition of Ni–W alloys [1–13].

Alloys of tungsten exhibit good corrosion resistance towards highly corrosive media, which is one of the pre-requisites of electrode materials to perform better in fuel cell electrolytes [1]. A part of wide spectrum of work was carried out in the development of new electrode materials for H_2 – O_2 and methanol oxidative fuel cells [2–6]. It was reported on the electrochemical synthesis and characterization of Fe–W alloys to use as effective anode for methanol oxidation in H_2SO_4 medium. The electrode preparation was simple and cost effective. The prepared

electrode was stable and acted as electro-catalyst during anodic oxidation of methanol.

Unfortunately, the traditional bath for Ni–W plating, containing citrate and ammonia as complexing agents, is characterized by a low current efficiency and poor stability of the pH value [7]. Citrate is mainly responsible for the low current efficiency. Ammonia contributes to improving the current efficiency, but reduces the bath stability owing to its rapid evaporation. Therefore, in the use of other complexing agents with a high complex stability towards the nickel ion were investigated. Initially, tartaric acid, glycine, TEA and 5-sulfosalicylic acid were selected. It was found that tartaric acid and 5-sulfosalicylic acid gave rise to precipitation in the nickel sulfate and sodium tungstate based electrolyte.

NiCoW alloy electrodeposition was obtained on Al-substrates [14]. Two electrolytic baths, with and without sodium citrate were used having the same metal ion content. Temperature and current density operative conditions were varied. The electrodeposition carried out in the presence of sodium citrate exhibited better results in term of current efficiency and specific energy consumption rather than the bath without citrate ion.

The aim of the present work is a comparative study needed for the electrodeposition of Ni-W-Co 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} $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, 0.05 mol dm^{-3} $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 0.05 mol

$\text{dm}^{-3} \text{CoSO}_4 \cdot 7 \text{H}_2\text{O}$. The concentration of the complexing agent citric acid was 50 g/L and H_3BO_3 was 5g/L. On the hand, 35 ml TEA instead of citric acid was used in the second bath with the same previous chemicals. The dissolving of these salts was carried out separately. The mixture was stirred and heated near boiling. The electrodeposition was conducted in a beaker cell (100 cm^3 volume). The pH of the solution was adjusted at 4, 6.8 and 8 using 10 % acetic acid or 10% ammonia solution. The anode (positive electrode) was spiral Pt wire and the cathode (negative electrode) was a substrate from copper plate 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 selected current densities (j) in this stage of work were 15 and 25 mAcm^{-2} and the temperatures were 25 and 80°C . The weight of the deposited alloy was recorded with time of deposition. Cyclic voltammetry measurements were carried out using the same conditions of the baths electrolytes. The working electrode was Pt rotating disk electrode. The counter electrode was Pt wire and the reference electrode is $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{H}_2\text{SO}_4$ (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 \AA) and SEM (Joel SEM-Model 5040).

3. Results and Discussion

Galvanostatic measurements were achieved in order to deposit the W-Ni-Co with different current densities, temperatures, 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 . It is observed that the maximum deposition efficiency is obtained at higher temperature, 80°C , lower current density, 15 mAcm^{-2} and 50 min. The efficiency of the alloy deposition, η is given by the following relations [15]:

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

$$\eta = \frac{W_d \cdot nF}{A \cdot I \cdot t} \cdot 100 \% \quad (2)$$

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

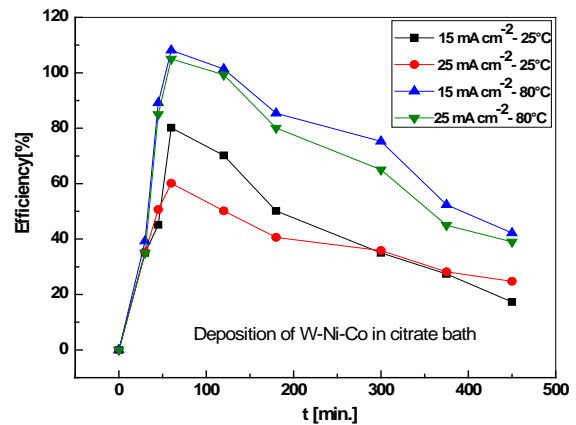


Fig. 1 Efficiency of W-Ni-Co alloy deposition in citrate bath at different current densities and temperatures, pH = 6.8.

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 given in Fig. 2. It is observed that pH of 6.8 gives maximum deposition efficiency with 50 min.

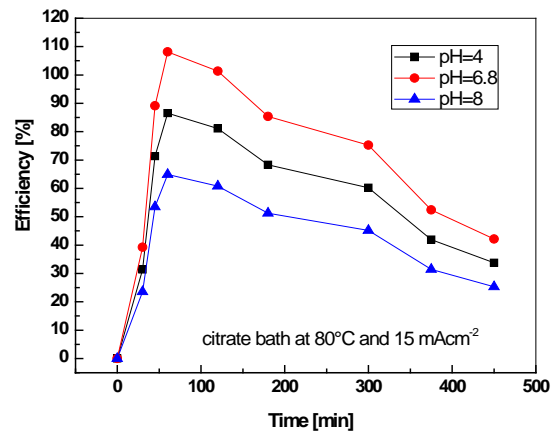


Fig. 2 pH effect on the Efficiency of the W-Ni-Co alloy deposition in citrate bath at 80°C and 15 mAcm^{-2} .

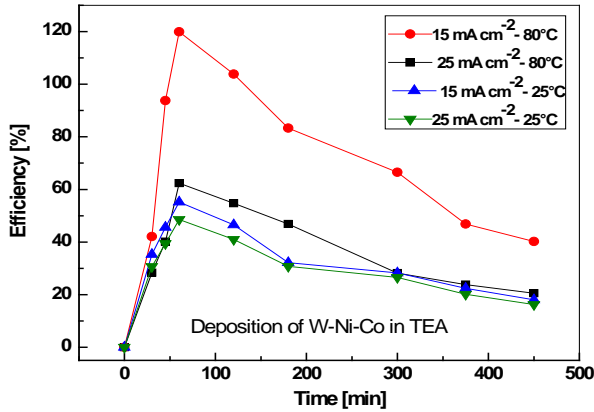


Fig. 3 Deposition efficiency of the W-Ni-Co alloy deposition in TEA bath at different current densities and temperatures, pH= 6.8 .

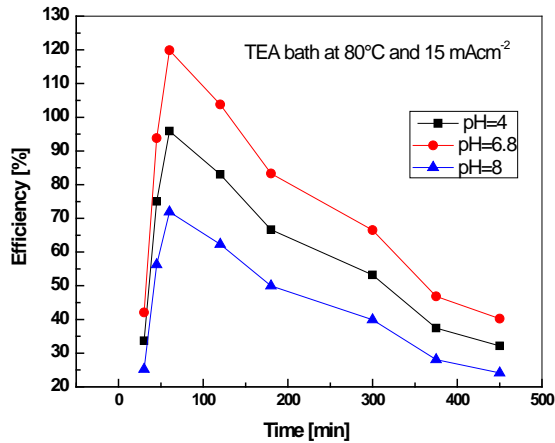


Fig. 4 Effect of pH on the efficiency of the W-Ni-Co alloy deposition in TEA bath at 80°C and 15 mA cm⁻².

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.

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-Co powders in citrate and TEA baths using

optimum conditions ($j= 15 \text{ mAcm}^{-2}$, $T= 80^\circ\text{C}$, $\text{pH} =6.8$, and $t = 50 \text{ min.}$) were heat treated at 500°C in $\text{Ar}+5\% \text{ H}_2$ gas for 6 h for XRD interpretation.

The alloys are investigated by XRD as shown in Fig.5. The crystal structure of the W-Ni-Co alloy is face centered cubic (fcc). The crystallite sizes are 34.6 and 29.43 nm for citrate and TEA baths, respectively using Scherer formula [16]:

$$L= 0.94 \lambda/\beta \cos \theta \tag{3}$$

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).

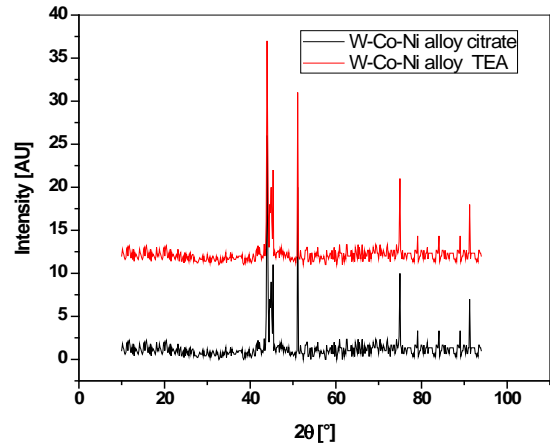


Fig. 5 XRD of W-Ni-Co alloy deposited from citrate and TEA baths, pH = 6.8, J=15mAcm⁻², T = 80°C for 50 min.

The morphologies of the deposited W-Ni-Co alloy are investigated by SEM as shown in Fig.6. The deposition conditions are $j= 15\text{mAcm}^{-2}$, $\text{pH} =6.8$, $t=50 \text{ min}$ and $T= 25 \text{ \& } 80^\circ\text{C}$. The structure of W-Ni-Co alloy from citrate bath has cauliflower-like of various sizes and shapes. While, the morphologies of the alloy in presence of TEA are flaky and dendritic at 25 & 80°C, respectively.

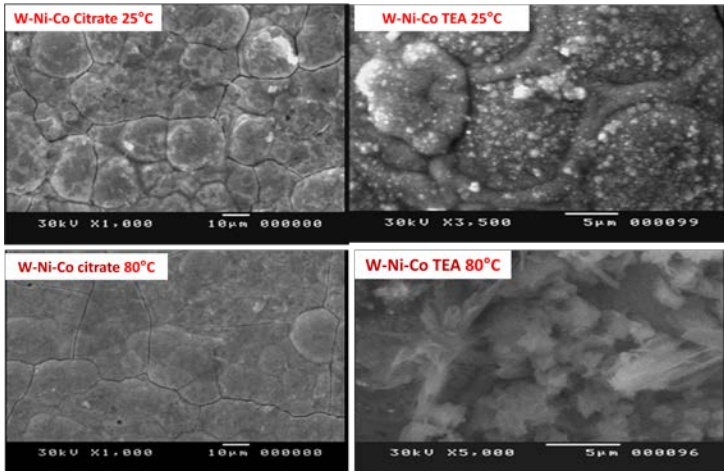
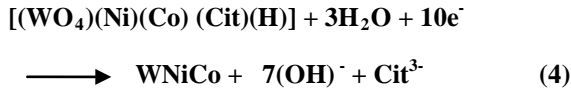


Fig. 6 SEM of W-Ni-Fe alloy deposited on copper substrate at sheet $j = 15 \text{ mA cm}^{-2}$, $\text{pH}=6.8$ and $t = 50 \text{ min}$.

Cyclic voltammetry (CV) measurements are 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 electrocodeposition in the potential range between -0.73 and -1.44 V vs. MSE. It was reported that the complexes of tungstates with citrates have the formula $[(\text{WO}_4)(\text{Cit})(\text{H})_x]^{x-5}$, as the citrate ion is trivalence [17]. Thus, the formula of the three ions complex is:



However, the electrocodeposition reduction of W-Ni-Co alloy on the cathode is governed by the following equation [17, 18]:

$$\mathbf{E} = \mathbf{0.049 - 0.0788 \text{ pH} + 2.303 \text{ RT/nF} \log [\text{WO}_4^{2-}] \quad (5)$$

$$E_{25^\circ\text{C}} = -0.011\text{V} \text{ and } E_{80^\circ\text{C}} = -0.012 \text{ V}$$

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

$$E_{25^\circ\text{C}} = -0.438\text{V} \text{ and } E_{80^\circ\text{C}} = -0.445 \text{ V}$$

$$\mathbf{E} = \mathbf{-0.6 + 2.303 \text{ RT/nF} \log [\text{Co}^{2+}] \quad (7)$$

$$E_{25^\circ\text{C}} = -0.388\text{V} \text{ and } E_{80^\circ\text{C}} = -0.395 \text{ V}$$

So, for $\text{pH} 6.8$, $[\text{WO}_4^{2-}] = 0.2\text{M}$, $[\text{Ni}^{2+}] = 0.05 \text{ M}$, and $[\text{Co}^{2+}] = 0.05$ and $T = 298$ or 353K . The cyclic voltammogram of Fig. 7 shows the start of the electrocodeposition reduction at potential of -0.414V vs. MSE at $T = 353\text{K}$ 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 -0.85 and -0.4V. This region expresses about the oxidation of W to WO_4^{2-} (-0.55V vs. NHE), Ni

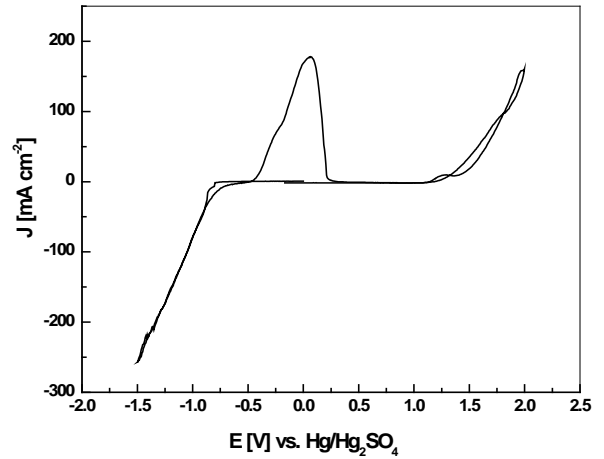
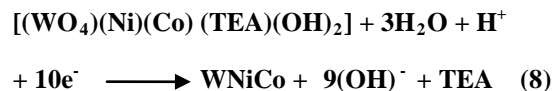


Fig. 7 CV of W-Ni-Fe in citrate, scan rate 10 mVs^{-1} , RDE=1000 rpm, $\text{pH} = 6.8$ at 80°C .

to Ni^{2+} (-0.4V vs. NHE) and Co to Co^{2+} (-0.3V vs. NHE) as confirmed by the Pourbaix diagrams [17-21]. There is a peak for the oxidation of W-Ni-Co alloy observed at -0.057 vs. MSE (0.558V vs. NHE). This peak is attributed to the oxidation of Co^{2+} to H_3CoO_3 in the W-Ni-Co alloy [20, 21].

On the other hand, the CV in TEA bath has a cathodic reduction of WNiCo starts at -0.625 V vs. MSE as shown in Fig. 8. The cathodic reduction region for the electrocodeposition occurs in the potential range between -0.75 and -1.75 V vs. MSE. The formula of the three ions complex is given by:



Also, this CV shows the start of the electrocodeposition reduction at potential of -0.61V vs. MSE at $T = 353\text{K}$ at zero current crossing potential (ZCCP) and continued until H_2 evolution with the increase of the cathodic negative potential.

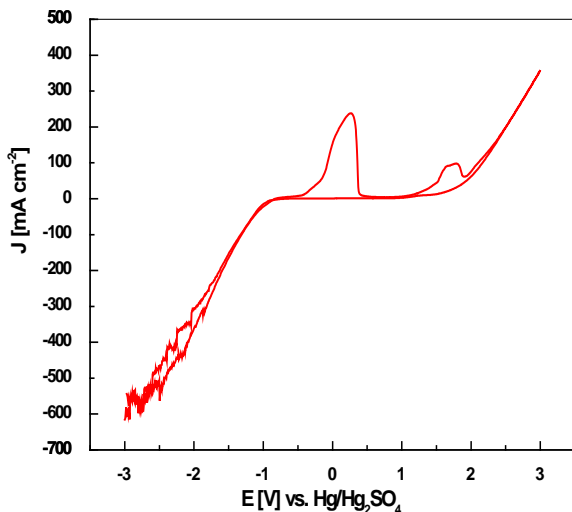


Fig. 8 CV of W-Ni-Fe in TEA, scan rate 10 mVs^{-1} , RDE=1000 rpm, pH = 6.8 at 80°C .

Furthermore, a great anodic oxidation peak of the deposited alloy is observed at $\sim 0.248\text{ V}$. This peak is attributed to the oxidation of Co^{2+} to H_3CoO_3 in the W-Ni-Co alloy [20, 21]. Also, there is another oxidation peak at 1.71V . This peak is due to the oxidation of Ni^{2+} to Ni^{3+} [19, 20].

Conclusion

The electrochemical deposition of ternary W-Ni-Co alloy was studied in citrate and TEA baths. The maximum efficiency for the electrodeposition using citrate bath is $\sim 110\%$ 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 $\sim 120\%$ with the same conditions of electrodeposition. The crystal structure of the obtained W-Ni-Co alloy is face centered cubic with cauliflower and dendritic morphology.

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