MATERIALS AND ENERGY BALANCES DEVELOPMENT FOR THE NI–W ALLOY ELECTRODEPOSITION PROCESS AT DIFFERENT TECHNOLOGICAL PARAMETERS

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Abstract
The paper presents the results achieved on the correlation of between the separated quantities of substances at the two electrodes of a galvanic cell with the current efficiency, intensity and operational times, taking into account the initial composition of the electrodeposition bath of the Ni–W alloy at different technological parameters such as current density, temperature, pH. Energy dispersive spectrometry (EDS) was further used in order to determine the chemical composition of the Ni–W coatings for various plating current efficiencies calculation. As the current density increases, the current efficiency decreases and the wolfram content remains constant about 11% at current densities of 10 mA/cm² and 16 mA/cm² respectively. According to our findings, the tungsten and nickel contents and also the output current increase with temperature. When the pH value increases from 7 to 8, the wolfram content rises from 13.51 wt.% to 14.65 wt.%, the same behaviour could be observed for the current efficiency.

Another goal of our study was to investigate the material and the energy balances of the electrodeposition process of Ni-W alloy. The starting point is the theoretical materials balances. The real material balance is obtained after a series of experiments at different technological parameters values.

In all the cases, the material and the energy balances respectively are found to be affected by technological parameters, consequently having an influence on the material and, respectively, specific energy consumptions, indicating, in this way, the possibility of action in order to exploit energy in a useful purpose as much as possible.

Keywords: Ni-W alloys, electrodeposition, balance, materials, energy

1. INTRODUCTION
The nickel–tungsten (Ni–W) alloys exhibit excellent corrosion resistance [1], [2], [3], wear resistance, high hardness and magnetic properties [4], [5], so the interest in their electrodeposition has increased in recent years. It was reported that the hardness of Ni–W alloys is three times higher than that of pure electrodeposited Ni [6]. The present research focuses on the developing of the theoretical foundations of material and energy balances for the electrolytic deposition of Ni-W alloy and the influence of process parameters (current density, temperature and pH) on the real balance of materials and energy. The starting point is the theoretical materials balances. The real material balance is obtained after a series of experiments at different technological parameters values.

2. EXPERIMENTAL
Nickel–tungsten alloys were electroplated from aqueous solutions containing 26.286 [g·L⁻¹] NiSO₄·6H₂O (nickel sulphate hexahydrate, Sigma - Aldrich) and 131.944 [g·L⁻¹] Na₂WO₄·2H₂O (sodium tungstate dihydrate, Sigma - Aldrich) as the electro active species, and 147.00 [g·L⁻¹] C₃H₅Na₃O₇·2H₂O (tri-sodium citrate dihydrate, Sigma - Aldrich) as the complexing agent [7]. The classical electrochemical cell was equipped with a cathode (made of 99.98 % purity copper) and a carbon anode. The cathode dimensions are of 8.0 cm (height), 9.8 cm (length), and 0.1 cm (width) while the dimensions of anode were of 6.0 cm (height), 1.0 cm (length), 1.0 cm (width). The immersion surface of cathode was of 0.6 dm² and respectively the anodic immersion surface was of 0.045 dm². Before electrodeposition, the electrode surface was polished with emery paper (320 – 1000 grain size), then was had with distilled water, thoroughly degreased with acetone, activated with 20% H₂SO₄, washed once more with distilled water and immerse in the bath solution. The above described cell was connected to the GWINSTEK GPR-1810HD power supply, having a digital control of current and voltage. The tested conditions are given in Table 1. The cathode current efficiency (η) was calculated taking in consideration the weight of the deposit obtained experimental
The approximate composition of the alloy deposits was determined with a scanning electron microscope (SEM, VEGA II LMU - Tescan, Czech Republic) and the attached energy dispersive spectroscopy (EDS, Bruker AXS Microanalysis GmbH probe). Each sample was measured in three different locations to confirm uniformity.

Table 1.
Technological parameters used in the electrodeposition of Ni-W alloy

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Technological parameters</th>
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<tr>
<td></td>
<td>$i_i$ [mA/cm$^2$]</td>
</tr>
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<td>2</td>
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</table>

3. RESULTS AND DISCUSSION

3.1. Materials balances in cathodic compartment for the electrochemical Ni-W alloys

Eq. 2 reveals the stoichiometric equation of the process of electrodeposition process of Ni-W alloys for cathodic compartment at stable composition:

$$NiSO_4 + Na_2WO_4 + 4H_2O + 8e^- \rightarrow NiW + 8OH^- + Na_2SO_4$$  \hspace{1cm} (2.)

To express the quantitative stage of the electroplating bath at a given time one may use the transformation degrees of the component of interest ($\eta_{NiSO_4}$) or of any other component ($\eta_{Na_2WO_4}$) \cite{8} \cite{9}. In the present study the transformation degree of the component of interest ($\eta_{NiSO_4}$) was calculated according to Eq 3., where: $m_i^0$ - initial mass of $i$ reactant ($i = NiSO_4, \ Na_2WO_4, \ H_2O, \ NiW, \ OH^-, \ Na_2SO_4$), [g]; $m_i$ - mass of reactant $i$ at a given time, [g]; $M_i$ - atomic mass of $i$ reactant; $v_i$ - stoichiometric ratio of reactants.

$$\frac{m_{NiSO_4}^0 - m_{NiSO_4}}{M_{NiSO_4} \cdot v_{NiSO_4}} = \frac{m_{Na_2WO_4}^0 - m_{Na_2WO_4}}{M_{Na_2WO_4} \cdot v_{Na_2WO_4}} = \frac{m_{H_2O}^0 - m_{H_2O}}{M_{H_2O} \cdot v_{H_2O}} = \frac{m_{OH^-} - m_{OH^-}}{M_{OH^-} \cdot v_{OH^-}} = \frac{m_{Na_2SO_4}^0 - m_{Na_2SO_4}}{M_{Na_2SO_4} \cdot v_{Na_2SO_4}}$$  \hspace{1cm} (3.)

The amount of each component at a given time may be calculated with the following balance equations \cite{8}:
\[ m_{\text{NiSO}} = m_{\text{NiSO}}^0 - m_{\text{NiSO}}^0 \cdot \eta_{\text{NiSO}} \]  \hspace{1cm} (4)

\[ m_{\text{NaWO}_4} = m_{\text{NaWO}_4}^0 - \frac{M_{\text{NaWO}_4} \cdot V_{\text{NaWO}_4} \cdot m_{\text{NiSO}}^0}{M_{\text{NiSO}}} \cdot \eta_{\text{NiSO}} = m_{\text{NaWO}_4}^0 - \frac{M_{\text{NaWO}_4} \cdot m_{\text{NiSO}}^0}{M_{\text{NiSO}}} \cdot \eta_{\text{NiSO}} \]  \hspace{1cm} (5)

\[ m_{H_2O} = m_{H_2O}^0 - \frac{M_{H_2O} \cdot V_{H_2O} \cdot m_{\text{NiSO}}^0}{M_{\text{NiSO}}} \cdot \eta_{\text{NiSO}} = m_{H_2O}^0 - 4 \cdot \frac{M_{H_2O} \cdot m_{\text{NiSO}}^0}{M_{\text{NiSO}}} \cdot \eta_{\text{NiSO}} \]  \hspace{1cm} (6)

\[ m_{\text{NiW}} = \frac{M_{\text{NiW}}}{M_{\text{NiSO}}} \cdot \frac{V_{\text{NiW}}}{V_{\text{NiSO}}} \cdot m_{\text{NiSO}}^0 \cdot \eta_{\text{NiSO}} = \frac{M_{\text{NiW}}}{M_{\text{NiSO}}} \cdot m_{\text{NiSO}}^0 \cdot \eta_{\text{NiSO}} \]  \hspace{1cm} (7)

\[ m_{\text{OH}^-} = \frac{M_{\text{OH}^-}}{M_{\text{NiSO}}} \cdot \frac{V_{\text{OH}^-}}{V_{\text{NiSO}}} \cdot m_{\text{NiSO}}^0 \cdot \eta_{\text{NiSO}} = \frac{M_{\text{OH}^-}}{M_{\text{NiSO}}} \cdot m_{\text{NiSO}}^0 \cdot \eta_{\text{NiSO}} \]  \hspace{1cm} (8)

\[ m_{\text{NaSO}_4} = \frac{M_{\text{NaSO}_4}}{M_{\text{NiSO}}} \cdot \frac{V_{\text{NaSO}_4}}{V_{\text{NiSO}}} \cdot m_{\text{NiSO}}^0 \cdot \eta_{\text{NiSO}} = \frac{M_{\text{NaSO}_4}}{M_{\text{NiSO}}} \cdot m_{\text{NiSO}}^0 \cdot \eta_{\text{NiSO}} \]  \hspace{1cm} (9)

For the galvanic processes, the use of current efficiency (\( \eta_{\text{current}} \)) instead of the degree of transformation [8] [9] is more useful. In this case, it is desired to achieve higher current efficiency for the reaction product of interest (Ni-W alloy):

\[
\eta_{\text{current},\text{NiW}} = \frac{m_{\text{NiW,real}}}{m_{\text{NiW, theoretical}}} = \frac{1}{F} \left( \frac{M_{\text{Ni}} \cdot \%\text{Ni}}{z_{\text{Ni}}} + \frac{M_{\text{W}} \cdot \%\text{W}}{z_{\text{W}}} \right) \cdot I \cdot \tau
\]

\[ m_{\text{NiW, theoretical}} = \frac{1}{F} \left( \frac{M_{\text{Ni}} \cdot \%\text{Ni}}{z_{\text{Ni}}} + \frac{M_{\text{W}} \cdot \%\text{W}}{z_{\text{W}}} \right) \cdot I \cdot \tau \cdot \eta_{\text{current},\text{NiW}} \]  \hspace{1cm} (10), where:  \( M_{\text{Ni}} \) - atomic mass of Ni component, \([g]\);  \( M_{\text{W}} \) - atomic mass of W component, \([g]\);  \( \tau \) - times of deposition, \([s]\);  \( \eta_{\text{current},\text{NiW}} \) - current efficiency of Ni-W alloy;  \( I \) - current intensity, \([A]\);  \( F \) - Faraday’s number (\( F = 96500 \, C \));  \( z_{\text{Ni}} \) - Ni valence;  \( z_{\text{W}} \) - W (VI) valence;  \%\text{Ni}, \%\text{W} - percentages of nickel and tungsten respective in the deposit. From equations (7.) and (10.) the transformation degree (\( \eta_{\text{NiSO}} \)) may be calculated. The stoichiometric equation of the electrodipositive process for the Ni-W alloys, in the cathodic compartment is:

\[
\frac{1}{F} \left( \frac{M_{\text{Ni}} \cdot \%\text{Ni}}{z_{\text{Ni}}} + \frac{M_{\text{W}} \cdot \%\text{W}}{z_{\text{W}}} \right) \cdot I \cdot \tau \cdot \eta_{\text{current},\text{NiW}} = \frac{M_{\text{NiW}}}{M_{\text{NiSO}}} \cdot m_{\text{NiSO}}^0 \cdot \eta_{\text{NiSO}} \]

\[
\frac{1}{F} \left( \frac{M_{\text{Ni}} \cdot \%\text{Ni}}{z_{\text{Ni}}} + \frac{M_{\text{W}} \cdot \%\text{W}}{z_{\text{W}}} \right) \cdot \frac{2}{6} \cdot I \cdot \tau \cdot \eta_{\text{current},\text{NiW}} = \frac{M_{\text{NiW}}}{M_{\text{NiSO}}} \cdot m_{\text{NiSO}}^0 \cdot \eta_{\text{NiSO}} \]  \hspace{1cm} (11)

\[ \eta_{\text{NiSO}} = \frac{m_{\text{NiSO}} \cdot I \cdot \tau}{F \cdot m_{\text{NiSO}}^0} \cdot \eta_{\text{current},\text{NiW}} \]

Substituting the degree of transformation \( \eta_{\text{NiSO}} \) in each cathode compartment balance equation with eq. (11.), we obtain the following theoretical balance equations:

\[ m_{\text{NiSO}} = m_{\text{NiSO}}^0 - \frac{M_{\text{NiSO}} \cdot I \cdot \tau}{F} \cdot \eta_{\text{current},\text{NiW}} \]  \hspace{1cm} (12)

\[ m_{\text{NaWO}_4} = m_{\text{NaWO}_4}^0 - \frac{M_{\text{NaWO}_4} \cdot I \cdot \tau}{F} \cdot \eta_{\text{current},\text{NiW}} \]  \hspace{1cm} (13)

\[ m_{H_2O} = m_{H_2O}^0 - 4 \cdot \frac{M_{H_2O} \cdot I \cdot \tau}{F} \cdot \eta_{\text{current},\text{NiW}} \]  \hspace{1cm} (14)

\[ m_{\text{NiW}} = \frac{M_{\text{NiW}} \cdot I \cdot \tau}{F} \cdot \eta_{\text{current},\text{NiW}} \]  \hspace{1cm} (15)
Based on relations (12), (13), (15) and (17) the numerical values of the theoretic and real material balances for the cathodic compartment during the W-Ni alloys electrodeposition processes were achieved and are shown in Figure 1. Instead of transformation degree, the current efficiency was used in our calculations, being considered 100% for the theoretical material balance and the experimental values for the real one.

![Figure 1. Theoretic and real balances for the cathodic compartment during the electrodeposition of Ni-W alloys at the studied operational parameters (Table 1)](image)

### 3.2. Influence of technological parameters on current efficiency and tungsten content

It was noted from the results obtained and used to calculate the material and energy balances that the current efficiency decreased with the current density increase and the tungsten content remained constant at around 11 wt.% W for the current densities of 10 mA/cm² and of 16 mA/cm² respectively. Krishnan and his collaborators also presented in their work [10] a decrease in the current efficiency with the increasing of the current density. The same results showed that the tungsten and, respectively, nickel content as well as the current efficiency increases with the increasing of temperature, while the pH of the bath has a significant effect on current efficiency as well as on the tungsten content in the deposit. For example, pH increased from 6.78 to 8 increases the tungsten content from 13.51% to 14.65% and, at the same time, the current efficiency increases. A further increase in pH from 8 to 9.23 causes a decrease in both the current efficiency, and the content of tungsten and nickel, respectively. Krishnan and his collaborators [10] also showed an increase in the current efficiency with the increasing of temperature, while Yamasaki and collaborators [11] described the effects of temperature on both the tungsten content and the ductility of the deposit. Atanassova and collaborators [12] have observed an increase of the tungsten content with the increasing of temperature in both the baths without agitation and those with agitation and put this behavior on the conditions that encourage the transport of tungsten towards the cathode surface.

### 3.3. The energy balance for cathode compartment in the electrodeposition of Ni-W alloys

For the determination of the specific energy consumption per mass unit of Ni-W alloy cathode the expressions of electricity in an electrical circuit with resistive consumer and the material balance for any component (in this case Ni-W alloy deposit) are considered [8] [9]:

\[ m_{\text{Ni-W}} = \left( \frac{M_{\text{Ni}} \cdot \% \text{Ni}}{z_{\text{Ni}}} + \frac{M_{\text{W}} \cdot \% \text{W}}{z_{\text{W}}} \right) \frac{I \cdot \tau}{F} \cdot \eta_{\text{current,Ni-W}} \]  \hspace{1cm} (18.)
Considering that the specific energy is expressed as: \[ W = \frac{m_{NiW}}{m_{NiW}} = U \cdot I \cdot \tau \]

The specific energy \( W_{sp} \) for any component may be calculated as:

\[
W_{sp} = \left( \frac{F \cdot U_{cell}}{M_{NiWO} \cdot \%Ni + M_{W} \cdot \%W} z_{Ni} + z_{W} \right) \cdot \eta_{current,NiW} \tag{20}
\]

where: \( W_{sp} \) - specific energy, [J/kg]; \( U_{cell} \) - voltage applied, [V]. Based on material balance and the previous equations the energy balance for the electrodeposition of Ni-W alloys is:

\[
W_{NiSO_{4},sp} = \frac{U_{cell} \cdot I \cdot \tau \cdot F}{M_{NiSO_{4}} \cdot M_{NiWO} \cdot \%Ni \cdot I \cdot \tau \cdot \eta_{current,NiW}} \tag{21}
\]

\[
W_{Na_{2}WO_{4},sp} = \frac{U_{cell} \cdot I \cdot \tau \cdot F}{M_{Na_{2}WO_{4}} \cdot I \cdot \tau \cdot \eta_{current,NiW}} \tag{22}
\]

\[
W_{H_{2}O,sp} = \frac{U_{cell} \cdot I \cdot \tau \cdot F}{M_{H_{2}O} \cdot I \cdot \tau \cdot \eta_{current,NiW}} \tag{23}
\]

\[
W_{NiSO_{4},sp} = \left( \frac{M_{NiSO_{4}} \cdot \%Ni + M_{W} \cdot \%W}{z_{Ni} + z_{W}} \right) \cdot \eta_{current,NiW} \tag{24}
\]

\[
W_{OH^{-},sp} = \frac{8 \cdot M_{OH^{-}} \cdot I \cdot \tau \cdot \eta_{current,NiW}}{U_{cell} \cdot I \cdot \tau \cdot \eta_{current,NiW}} \tag{25}
\]

\[
W_{Na_{2}SO_{4},sp} = \frac{M_{Na_{2}SO_{4}} \cdot I \cdot \tau \cdot \eta_{current,NiW}}{U_{cell} \cdot I \cdot \tau \cdot \eta_{current,NiW}} \tag{26}
\]

Based on the actual material balances for the electrodeposition processes of Ni-W alloys at various technological parameters (Table 1) and on the relations (18.) + (26.) real energy balances were developed for the components of the cathodic compartment (Figure 2).

**Fig. 2.** The real energy balance for cathode compartment at the electrodeposition of Ni-W alloys (Table 1).
4. CONCLUSIONS

The development of material and energy balances for the active species present during the Ni-W alloy cathodic electrodeposition improves the efficiency of galvanic processes at different operational parameters. As the current density increases, the current efficiency decreases and the wolfram content remains constant about 11% at current densities of 10 mA/cm² and 16 mA/cm² respectively. According to our findings, the tungsten and nickel contents and also the output current increase with temperature. When the pH value increases from 7 to 8, the wolfram content rises from 13.51 wt.% to 14.65 wt.%, and the same behaviour could be observed for the current efficiency increment. In all the cases, the material and the energy balances respectively are found to be affected by technological parameters, consequently having an influence on the material and, respectively, specific energy consumptions, indicating, in this way, the possibility of action in order to exploit energy in a useful purpose as much as possible.

Research will continue to optimize the process of electrodeposition of Ni-W alloy in relation to technical and economic criteria.

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