Original Article

The influence of anomalous codeposition on few coating alloys properties

Mariana Borges Porto*, Victor de Lima Bellia, Thayane Carpanedo de Morais Nepel, Fernando Leite Moreira, Ambrósio Florêncio de Almeida Neto

Laboratory of Electrochemical and Anticorrosion Process, Campinas State University, Campinas, Brazil

ARTICLE INFO

Article history:
Received 9 August 2018
Accepted 31 July 2019
Available online 24 August 2019

Keywords:
Tungsten
Iron
Electrodeposition
Anomalous codeposition
Corrosion.

ABSTRACT

Due to the presence of tungsten, Fe-W alloys can be applied as anticorrosive coatings. However, the conditions in which they are obtained influence their polarization resistance. This paper investigates how to electrodeposit them in order to increase their anticorrosive properties. The Fe-W alloys were produced by electrodeposition in different experimental conditions. The samples were characterized by X-ray diffraction (XRD) and scanning electronic microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX). The corrosion resistance was evaluated by Tafel extrapolation. This paper reports that alloys that have higher mass composition of tungsten have higher polarization resistance, up to 9924.05 ohm-cm². Fe-W alloys had 38.85–69.59% tungsten in mass basis, and the alloys with most tungsten were obtained with temperature of 60°C, continuous direct electric current density of 50 mA/cm², 0.01 mol/L iron sulfate concentration, 0.1 mol/L ammonium citrate and 0.1 sodium tungstate concentration. This study obtained alloys with higher tungsten composition, up to 69.59%, in comparison to papers with similar results of faradaic efficiency (10–15%). Using 0.1 mol/L iron sulfate concentration, the decrease of the temperature and the current density increases the tungsten composition, making the FeW alloys more anticorrosive.

© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Tungsten is a metal that has very desirable characteristics: high corrosion resistance and hardness even at high temperatures, the lowest thermal dilatation coefficient among all metals and high thermal conductivity [1]. However, it is not feasible to electrodeposit pure deposits of this metal from its aqueous solutions. According to Tsyntsaru et al. [2], this occurs because of the formation of an oxide layer on the cathode that cannot be reduced to metallic tungsten. However, it is possible to codeposit tungsten with metals from iron group, such as nickel and cobalt. Alloys that include tungsten have its same desirable properties and have considerable corrosion resistance [3].

According to Doughton et al. [4], iron-tungsten alloys are, in comparison to nickel-tungsten and cobalt-tungsten, harder and have better adherence to steel. Besides, these alloys show...
Table 1 – Fixed conditions for 2^3 planning.

<table>
<thead>
<tr>
<th>Component</th>
<th>Function</th>
<th>Concentration (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Tungstate</td>
<td>Tungsten source</td>
<td>0.3</td>
</tr>
<tr>
<td>Ammonium citrate</td>
<td>Complexing agent</td>
<td>0.3</td>
</tr>
<tr>
<td>Ammonium sulfate</td>
<td>Bath stabilizer</td>
<td>0.1287</td>
</tr>
<tr>
<td>Sodium Borate</td>
<td>Amorphizing agent</td>
<td>3.75 × 10^{-2}</td>
</tr>
<tr>
<td>Sodium dodecyl sulfate</td>
<td>Wetting agent</td>
<td>1.04 × 10^{-4}</td>
</tr>
</tbody>
</table>

desirable magnetic properties, like high magnetic moment, low coercivity and tunable magnetic anisotropy [5]. Iron-tungsten alloys are also cheaper in comparison to the nickel-tungsten and cobalt-tungsten alloys [6].

Because of these magnetic properties, amorphous iron-tungsten alloys can be used in sensors, transformers’ cores, inductive devices, recording media and magnetoresistive applications [7]. Due to its high hardness, the iron-tungsten alloys can also substitute hexavalent chromium alloys, which are toxic and present ecological risks [2].

Modifications in electrodeposition conditions, such as pH, temperature and bath composition are factors that can change characteristics of cobalt-tungsten alloys [8]. The electric current density and even the electrodeposition technique can modify coatings [9]. Different microstructures and properties are obtained depending on the electrodeposition conditions, showing the importance of studying them in order to improve electrical efficiency and specific characteristics.

Generally, iron-tungsten electrodeposited alloys have a peak of 30% in mass basis of tungsten [4,7]. According to Younes-Metzler et al. [10], the ammonia present in the bath is responsible for this effect in the case of the nickel-tungsten alloys. Nicolenco et al. [5] indicate that the presence of tungsten increases the corrosion and wear resistance of the other component of the alloy. Thus, the aim of this paper is to analyze Fe-W electrodeposition in a range of experimental conditions that favors the enrichment of tungsten in solid phase, and evaluate the impact of composition over the polarization resistance.

2. Materials and methods

The Fe-W coating alloys were electrodeposited over square copper foil of 4 cm² surface area. This substrate was mechanically polished with 400 then 1200 mesh sand paper, washed with 10 g/g sodium hydroxide for grease removal and then washed with 1% H2SO4 for oxides removal and surface activation [11].

Electrochemical bath composition and the electrodeposition parameters were defined based on two experimental planning. The first one was done to evaluate the influence of iron concentration, bath temperature and electrodeposition current on the coating alloy composition and the electrodeposition efficiency. A full factorial planning 2^3 experiments was made with 3 center point repetitions and the main fixed composition as described on Table 1. True values correspondent for each level of iron sulfate, current density and temperature from 2^3 planning are in Table 2.

After results analysis of the full factorial planning 2^3 experiments, intending to have in the composition high amounts of W, iron concentration was kept in the 2^2 planning lower level (0.01 mol/L) and a full factorial planning 2^2 was used to evaluate the influence of tungsten and complexing agent on the coating alloy composition and electrodeposition efficiency. Full factorial planning was made with 3 center points repetitions, varying ammonium citrate and sodium tungstate concentration, pH 7 and keeping the other parameters as described for the 2^3 planning. Temperature and current density were 60°C and 50 mA/cm² as these parameters were used to obtain the best efficiency with high amount of tungsten in the coating on 2^2 planning. True concentration values for the levels of full factorial planning 2^2 are indicated in Table 3.

For the electrodeposition tests, the previously treated copper substrate was plugged to a rotative system, model 616A, connected to a VersaSTAT 3 potentiostat/galvanostat, Princeton Applied Research. The rotative system was used to maintain a 30 rpm rotation on the copper electrodes and the VersaSTAT3 to apply the current set by the experimental planning using the galvanostatic function. A cylindrical platinum mesh was used as counter-electrode, the electrochemical bath temperature was kept constant with a thermostatic system and electrodepositions were done during 60 min.

Electrodeposition efficiency (ε) was calculated according to Eq. (1) and the results treatment was performed using Statistica 7 program:

$$\varepsilon = \frac{m \cdot F}{i \cdot t \sum \eta_j \cdot w_j \cdot M_j} \times 100$$  \hspace{1cm} (1)

In the Eq. 1, m is the mass coating alloy (g), t the electrodeposition time (s), i the total current applied in the electrodeposition (A), wj the metal mass fraction in the alloy determined by EDX, n_j the number of electrons transferred from each j metal atom considering the full reduction of Fe (II) and W(VI), Mj the molar mass of metal [g/mol] and F = 96,485 C/mol.

Scanning electronic microscopy (SEM) with energy dispersive X-ray detector (EDX) (LEO Electron Microscopy/Oxford 440i) was utilized for surface topography analysis and chem-
tical compositions determination. Coatings crystallinity was verified by X-Ray diffraction (Philips X’Pert) with Cu Kα radiation, wavelength 1.54 Å, 0.02 × 2θ step size and 1 s per step, 40 kV tension and electric current of 40 mA.

Corrosion tests were performed by Tafel curves extrapolation and electrochemical impedance spectroscopy (EIS) to obtain corrosion resistance for the coatings. These tests were done in the VersaSTAT 3 potentiostat, Princeton Applied Research, in a three-electrode cell and using 3.5% NaCl solution as the corrosion medium. The working electrodes were copper foils coated with the Fe-W alloys with a 1 cm² circle exposed area to the corrosion medium. Counter electrode was a square platinum mesh and a silver/silver chloride (Ag, AgCl/KCl 3.5 mol/L, 0.205 V) was used as reference electrode.

To perform both electrochemical tests, the corrosion cell was kept in open circuit during one hour, in order to reach equilibrium, and the experiments were realized at room temperature. For Tafel curves, after the OCP stabilization it was done a potential scanning from −0.25 V to +0.25 V around the open circuit potential with a sweep rate of 1.0 mV/s. From Tafel extrapolation results, the corrosion potential, corrosion current and polarization resistance for each alloy were obtained. The EIS tests were made applying alternating current, in a potential around the open circuit value, with a potential amplitude of 10 mV using a frequency range from 1000 to 0.01 Hz.

3. **Results and discussion**

3.1. **Chemical speciation**

Hydrogen potential and components concentration define the metallic species in the electrochemical bath, including metals complexes that will participate in the electrodeposition process [12–14]. In this context, chemical speciation diagrams for iron were obtained with HYDRA and MEDUSA software [15] as a pH function to evaluate the metallic species in the electrochemical baths under study. For tungsten, it is described in the literature the relation between pH, complexed metallic species and the tungsten alloys electrodeposition with iron group metals in citrate baths [16].

Tsyntsaru and coworkers [16] emphasized that the mechanism for electrodeposition occurred with the iron group metals and the tungsten complexed with citrate when the electrodeposition was conducted in citrate bath. The main metallic tungsten–citrate complexes are (WO₄)₂(H₃Cit)H⁺ and (WO₄)₂(H₃Cit)H₂⁻ between pH 4 and 9. Analyzing the iron chemical speciation diagrams (Fig. 1), in a similar pH range from 4 to 9.5, Fe²⁺ species are complexed by citrate independently of the iron sulfate concentration. Other authors also verified an increase of tungsten in alloys with the increase of pH up to 8 for CoW [14] and for FeW, but for the FeW coating alloys it was verified a decrease of efficiency after pH 6 [13]. It is also reported that above pH 7 the iron-citrate complexed species decrease and then tungstate and hydroxides compounds precipitate [2,5,14,17]. Thus, based on the literature, 2° planning was done in pH 6 to obtain an alloy with high amount of W and efficiency. The 2° planning was constructed with parameters used to obtain coatings with higher amount of tungsten conducted in pH 7 to increase tungsten composition in the coating alloy.

3.2. **Deposition efficiency and coating composition analysis**

Deposition efficiency and coating composition obtained in the full factorial planning 2² experiments, where the iron concentration, the current and temperature were changed, are presented in Table 4. The metal mass fractions presented were calculated as described in Equation 2.

\[
\%wt_W = \frac{\%wt_{Fe}}{(\%wt_{W} + \%wt_{Fe})} (2) \]

Results analysis indicates that increasing iron concentration in electrochemical bath there is an increase in the deposition efficiency and a decrease in the coating alloy tungsten concentration. Besides, when tungsten composition in the coating alloy is high, the deposition efficiency is low. In literature some authors [2,7,16,17] emphasize the importance of the iron-group metal concentration to increase the deposition efficiency. It is also reported for CoW, NiW and FeW that when tungstate concentration in bath is higher than the iron-group metal, the tungsten percentage is up to 35% and the efficiency was below 15%. In the present set of experiments, we confirmed the high efficiency related to high concentration of iron in the bath once the highest efficiency (50.05%) in experiment 2 (52.38% Fe; 47.62% W) was obtained with maximum iron concentration (0.1 mol/L). It was also confirmed that the low efficiency was related with the increase of tungsten, however the coating alloys produced in this study have tungsten up to 66.95 wt.% (38.15 at.%), which is higher than the values reported elsewhere [2,7,18].

Analyzing the deposition efficiency results, a transition of the system behavior from normal codeposition to anomalous codeposition depending of the experiment parameters is verified. The codeposition [19] in which the increase of the less noble metal in bath decreases the composition of the more noble metal in the coating alloy is called anomalous codeposition and in this kind of deposition, the increase of current enhances the deposition of the less noble metal. These authors highlighted that the temperature increase usually favors anomalous codeposition, but also that this mechanism depends on parameters process and bath ions concentration. Comparing with the data we verified that at low iron concentration (0.01 mol/L), low temperature (25°C) and low current (10 mA/cm²) the system behaves as anomalous codeposition but increasing the temperature and current the codeposition is normal. However, increasing the iron concentration (0.1 mol/L) the anomalous codeposition is independent of changes in temperature and current. This behavior also emphasizes the importance to study statistically the synergy of the parameters to understand the electrodeposition process.

Statistica 7 [7] software was used to understand better the influence and synergy of the variables about deposition efficiency and coating composition. This analysis pointed, with 90% confidence level (p > 0.1), that the temperature and the current do not affect individually the efficiency. The iron concentration affects significantly this parameter. There is also synergy between the iron concentration and the tem-
**Fig. 1** – Iron speciation diagrams for iron sulfate concentration of (A) 0.01 mol/L and (B) 0.1 mol/L.

**Table 4** – Efficiency and composition results from full factorial planning $2^3$.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>C$_{Fe}$(mol/L)</th>
<th>I (mA/cm$^2$)</th>
<th>T (°C)</th>
<th>Fe (%)</th>
<th>W(%)</th>
<th>$e$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.01 (−1)</td>
<td>10 (−1)</td>
<td>25 (−1)</td>
<td>52.38</td>
<td>47.62</td>
<td>9.65</td>
</tr>
<tr>
<td>2</td>
<td>0.1 (+1)</td>
<td>10 (−1)</td>
<td>25 (−1)</td>
<td>53.79</td>
<td>46.21</td>
<td>50.05</td>
</tr>
<tr>
<td>3</td>
<td>0.01 (−1)</td>
<td>50 (+1)</td>
<td>25 (−1)</td>
<td>33.05</td>
<td>66.95</td>
<td>7.99</td>
</tr>
<tr>
<td>4</td>
<td>0.1 (+1)</td>
<td>50 (+1)</td>
<td>25 (−1)</td>
<td>57.45</td>
<td>42.55</td>
<td>37.50</td>
</tr>
<tr>
<td>5</td>
<td>0.01 (−1)</td>
<td>10 (−1)</td>
<td>60 (+1)</td>
<td>38.10</td>
<td>61.90</td>
<td>11.91</td>
</tr>
<tr>
<td>6</td>
<td>0.1 (+1)</td>
<td>10 (−1)</td>
<td>60 (+1)</td>
<td>61.15</td>
<td>38.85</td>
<td>18.19</td>
</tr>
<tr>
<td>7</td>
<td>0.01 (−1)</td>
<td>50 (+1)</td>
<td>60 (+1)</td>
<td>33.62</td>
<td>66.38</td>
<td>10.68</td>
</tr>
<tr>
<td>8</td>
<td>0.1 (+1)</td>
<td>50 (+1)</td>
<td>60 (+1)</td>
<td>60.12</td>
<td>39.88</td>
<td>35.69</td>
</tr>
<tr>
<td>9</td>
<td>0.055 (0)</td>
<td>30 (0)</td>
<td>42.5 (0)</td>
<td>57.50</td>
<td>42.50</td>
<td>40.02</td>
</tr>
<tr>
<td>10</td>
<td>0.055 (0)</td>
<td>30 (0)</td>
<td>42.5 (0)</td>
<td>57.51</td>
<td>42.49</td>
<td>39.95</td>
</tr>
<tr>
<td>11</td>
<td>0.055 (0)</td>
<td>30 (0)</td>
<td>42.5 (0)</td>
<td>57.47</td>
<td>42.53</td>
<td>35.29</td>
</tr>
</tbody>
</table>

**Fig. 2** – Pareto Diagram from full factorial planning $2^3$. The statistics analysis was made with 90% confidence level and for variable efficiency.
temperature and between the current and temperature (Fig. 2). Analyzing the ratio Fe/W from composition data, with 95% confidence level \( p > 0.05 \), it is verified that iron bath concentration is the main factor to obtain higher amounts of iron in the coating (Fig. 3). It is also observed that synergy exists between iron bath concentration and the other factors. These results present more clearly how the studied factors influence the anomalous codeposition. Thus, increasing the iron concentration in bath (from 0.01 to 0.1 mo/L), even when the tungsten concentration is much higher (0.3 mo/L), leads to higher amount of Fe on the coating (anomalous codeposition) and increasing the temperature or the current density the anomalous codeposition is more pronounced.

Table 5 presents the results from full factorial planning \( 2^3 \) and confirms that for 0.01 mo/L, iron bath concentration the codeposition is normal and it is independent of citrate and tungsten bath concentration. Thus, all the range of ammonium citrate and sodium tungstate concentrations applied in this planning produce alloys containing more tungsten than iron. For this set of experiments, the electric efficiency had a smaller variation than the \( 2^3 \) planning, with values from 3 to 12.63%, which confirms the \( 2^3 \) planning highlights that electrodeposition of FeW containing more tungsten occurs with low deposition efficiency. It is also observed that using the lower concentration of both ammonium citrate and sodium tungstate the best results for tungsten fraction and deposition efficiency were obtained. This verification is beneficial in economic and environmental terms because it is possible to obtain alloys having a smaller reagent consumption, smaller cost and less dangerous wastes.

The results analysis using the Statistica 7 [7] software presents the importance of the complexing species during the electrodeposition. The Fig. 4 shows the Pareto Diagram from full factorial planning \( 2^3 \) for efficiency and a similar behavior was obtained to composition. This analysis pointed, with 95% confidence level \( p > 0.05 \), that the synergy between the tungsten and citrate concentration is the main factor to increase the efficiency and the tungsten on alloy coating. Other authors [14,16] pointed the importance of complexing species in the electrodeposition process proposing a mechanism in which these species are fundamental to promote the ion reduction. Thus, in this study we statistically prove the importance of the tungsten-citrate complexing species on FeW coating electrodeposition and highlight that having more complexing agent than tungsten bath concentration does not promote higher efficiency and tungsten concentration on FeW coatings.

### 3.3. Coatings crystallinity and morphology

The alloys crystalline arrangement was analyzed by X-ray diffraction and spectrum for experiments 8 (60.12% Fe; 39.88% W), 12 (30.41% Fe; 69.59% W), 15 (31.77% Fe; 68.23% W) and 17 (30.61% Fe; 69.39% W) (central point for full factorial planning \( 2^3 \)) are presented on Fig. 5. All the coating alloys have similar behavior with low crystallinity independently if it was normal or anomalous codeposition and of the coating composition. In each spectrum, it is verified a broad peak around \( 2\theta = 42^\circ \) exists, characteristic of the Fe-W amorphous coating [2,18,20]. In Exp.12, 15, 17 spectra, diffraction peaks in \( 2\theta = 74^\circ \)
Table 5 – Efficiency and composition results from full factorial planning $2^3$.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>$C_{\text{Cu}}$ (mol/L)</th>
<th>$C_{\text{W}}$ (mol/L)</th>
<th>Fe (%)</th>
<th>W (%)</th>
<th>$\epsilon$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>0.1 (−1)</td>
<td>0.1 (−1)</td>
<td>30.41</td>
<td>69.59</td>
<td>12.63</td>
</tr>
<tr>
<td>13</td>
<td>0.3 (+1)</td>
<td>0.1 (−1)</td>
<td>35.60</td>
<td>64.40</td>
<td>7.51</td>
</tr>
<tr>
<td>14</td>
<td>0.1 (−1)</td>
<td>0.3 (+1)</td>
<td>44.15</td>
<td>55.85</td>
<td>3.00</td>
</tr>
<tr>
<td>15</td>
<td>0.3 (+1)</td>
<td>0.3 (+1)</td>
<td>31.77</td>
<td>68.23</td>
<td>9.81</td>
</tr>
<tr>
<td>16</td>
<td>0.2 (0)</td>
<td>0.2 (0)</td>
<td>31.37</td>
<td>68.63</td>
<td>11.27</td>
</tr>
<tr>
<td>17</td>
<td>0.2 (0)</td>
<td>0.2 (0)</td>
<td>30.61</td>
<td>69.39</td>
<td>11.55</td>
</tr>
<tr>
<td>18</td>
<td>0.2 (0)</td>
<td>0.2 (0)</td>
<td>30.04</td>
<td>69.96</td>
<td>11.48</td>
</tr>
</tbody>
</table>

Fig. 5 – X-Ray diffraction from Fe-W alloys of Exp. 8, Exp. 12, Exp. 15 and Exp. 18.

and $2\theta = 50^\circ$ from the copper substrate is observed due to the low quantity of coating [21].

Micrographs from experiments 8 (60.12% Fe; 39.88% W), that presents higher amount of iron and anomalous codeposition, and from experiments 12 (30.41% Fe; 69.59% W), 15 (31.77% Fe; 68.23% W) and 17 (30.61% Fe; 69.39% W), which had higher amount of tungsten and normal codeposition, are presented in Fig. 6. In all samples it is verified a preferential growth direction, homogeneous and uniform topography, with presence of nodules. The nodules presence in FeW, NiW and NiCoW are reported by other authors [11,20,22]. The nodular formation is related with the different atomic ratio between iron and tungsten. This information is confirmed since the nodules are more pronounced in experiment 8, which has a higher iron fraction. Analyzing the micrographs, it is also possible to verify the presence of few microcracks in the coating of experiments 8 (60.12% Fe; 39.88% W) and 12 (30.41% Fe; 69.59% W). The microcracks appearance is described in the literature that can be produced by many processes, like hydrogen evolution and the atomic ratio difference [22,23]. In this study the microcracks are probably established due to reticulum distortions. The cracks may compromise the corrosive protection because a corrosive medium can penetrate through the crack until it reaches the substrate, working as an electrolyte in corrosive process.

3.4. Corrosion resistance electrochemical studies

Electrochemical Studies of Corrosion Resistance were performed for the most relevant Fe-W alloys, which presented higher adhesion at the substrate, from $2^3$ and $2^2$ design, using Tafel extrapolation. Fig. 7 illustrates the results obtained from the Tafel polarization experiment. The values of corrosion current ($j_{\text{corr}}$) and polarization resistance ($R_p$) were calculated using Stern-Geary equation as described in the literature [24–27] and are presented on Table 6. The lower values of corrosion current obtained in this work from $2^2$ design have magnitude similar with amorphous FeW described in the literature obtained by heat treatment (1.5–4.48 $\mu$A in NaCl 0.1 mol/L) [20] and these corrosion currents are considerably less than reported for NiFeW (27–82 $\mu$A in 3.5% NaCl) [28].

The corrosion results indicate that, as reported in the literature, the composition is really important for corrosion resistance. The tungsten percentage increase the iron group-tungsten alloys corrosion resistance [18,22]. Comparing the experiment 4 (57.45% Fe; 42.55% W) and 8 (60.12% Fe; 39.88% W) with the set of $2^2$ design experiment (12 to 17), the increase of tungsten composition increases the corrosion resistance significantly. Thus, the coating alloys obtained with normal codeposition have more tungsten in their composition and they have a better resistance behavior. Besides the composition, morphology is really important for corrosion resistance behavior. Analyzing the data, it is verified that for experiments 8 (60.12% Fe; 39.88% W) and 12 (30.41% Fe; 69.59% W), that have higher efficiency but few microcracks (Fig. 6), corrosion resistance is lower. Although experiment 12 (30.41% Fe; 69.59% W) has higher tungsten concentration, the corrosion resistance is lower than the other experiments from the set of $2^2$ design which do not have microcracks [29]. Likewise, the XRD informs that all coatings are amorphous, which contributes to increase the corrosion resistance [22].

EIS results are presented by Nyquist diagram (Fig. 8). The results for the $2^3$ factorial design indicate a small electrolyte electric resistance in the high frequency region and the capacitive arc from electric double layer. Higher values of real impedance were obtained for experiment 10, which also presented higher polarization resistances in Tafel results, confirming them. In $2^2$ planning it is possible to verify a diffusive control in low frequency region, characterizing the Warburg impedance [27].
**Fig. 6** – SEM micrographs of FeW alloy, with 1500 x amplification, from experiments 8, 15, 12 and 17.

**Fig. 7** – Tafel Slopes for the Fe-W alloys obtained with 3.5% NaCl corrosive environment after OCP stabilization. (a) $2^3$ factorial design (b) $2^4$ factorial design.

**Table 6** – Corrosion current and resistance results obtained with Tafel extrapolation in 3.5% NaCl corrosive environment for Fe-W coating alloys.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>$%$ (%)</th>
<th>Fe (%)</th>
<th>W (%)</th>
<th>$i_{corr}$ (μA/cm$^2$)</th>
<th>Rp (ohm cm$^2$)</th>
<th>Anodic beta (mV)</th>
<th>Cathodic beta (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>37.50</td>
<td>57.45</td>
<td>42.55</td>
<td>34.39</td>
<td>1211.72</td>
<td>160.12</td>
<td>205.12</td>
</tr>
<tr>
<td>8</td>
<td>35.69</td>
<td>60.12</td>
<td>39.88</td>
<td>38.80</td>
<td>890.15</td>
<td>232.38</td>
<td>127.91</td>
</tr>
<tr>
<td>9</td>
<td>40.02</td>
<td>57.50</td>
<td>42.50</td>
<td>4.58</td>
<td>6025.01</td>
<td>182.55</td>
<td>103.67</td>
</tr>
<tr>
<td>10</td>
<td>39.95</td>
<td>57.51</td>
<td>42.49</td>
<td>4.79</td>
<td>5649.65</td>
<td>172.12</td>
<td>89.34</td>
</tr>
<tr>
<td>12</td>
<td>12.63</td>
<td>30.41</td>
<td>69.59</td>
<td>4.43</td>
<td>6926.79</td>
<td>171.23</td>
<td>120.52</td>
</tr>
<tr>
<td>13</td>
<td>7.51</td>
<td>35.60</td>
<td>64.40</td>
<td>2.63</td>
<td>8434.92</td>
<td>95.01</td>
<td>110.51</td>
</tr>
<tr>
<td>15</td>
<td>9.81</td>
<td>31.77</td>
<td>68.23</td>
<td>2.01</td>
<td>9924.04</td>
<td>86.12</td>
<td>98.25</td>
</tr>
<tr>
<td>17</td>
<td>11.27</td>
<td>31.37</td>
<td>68.63</td>
<td>2.00</td>
<td>8581.16</td>
<td>88.41</td>
<td>76.37</td>
</tr>
<tr>
<td>18</td>
<td>11.48</td>
<td>30.04</td>
<td>69.96</td>
<td>1.97</td>
<td>8260.38</td>
<td>86.64</td>
<td>66.12</td>
</tr>
</tbody>
</table>
Fig. 8 – Nyquist diagrams for FeW alloys, obtained with 3.5% NaCl corrosive environment (a) $2^3$ factorial design (b) $2^2$ factorial design.

![Nyquist diagrams](image)

Fig. 9 – Equivalent circuit of a corrosive process involving mass transport under the Warburg conditions of semi-infinite linear diffusion. [27].

![Equivalent circuit](image)

The equivalent circuit analysis of Nyquist diagrams from $2^3$ factorial design pointed out a resistor related with the electrolyte resistance and a depressed capacitive loops explained in the literature due the low homogeneity of the metallic coating showing a more porous layer at high frequency and a more resistant layer at low frequency. However, the high noise at low frequencies did not allow the correct electric circuit fit.

The Nyquist plots from the $2^2$ factorial design is associated with a circuit configuration including the double layer capacitor ($C_{dc}$), the electrolyte resistance ($R_e$), the coating resistance ($R_f$) and also the Warburg impedance element ($Z_w$), as shown in Fig. 8b. The Warburg impedance is related with the semi-infinite linear diffusion of corrosive processes, characterized by the presence of a rectilinear section, forming an angle of 45° with the real axis [27]. Accordingly, the corresponding Randles equivalent circuits were applied in this work for data fitting. The equivalent circuit model is illustrated in Fig. 9. The simulation parameters obtained using EIS Spectrum Analyzer software are listed in Table 7.

Table 7 – Simulated impedance parameters.

<table>
<thead>
<tr>
<th>Exp</th>
<th>C (cm$^{-2}$)</th>
<th>$R_e$ (ohm.cm$^2$)</th>
<th>$R_i$ (ohm.cm$^2$)</th>
<th>$E^*$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>7</td>
<td>14.55</td>
<td>391.8</td>
<td>9.88</td>
</tr>
<tr>
<td>13</td>
<td>17</td>
<td>14.266</td>
<td>500.98</td>
<td>7.98</td>
</tr>
<tr>
<td>15</td>
<td>10.8</td>
<td>14.23</td>
<td>351.65</td>
<td>13.72</td>
</tr>
<tr>
<td>17</td>
<td>13.1</td>
<td>13.73</td>
<td>528.57</td>
<td>3.49</td>
</tr>
<tr>
<td>18</td>
<td>8.5</td>
<td>20.008</td>
<td>564.4</td>
<td>7.04</td>
</tr>
</tbody>
</table>

*error of $R_i$

(Fe, W). Low $R_e$ values also emphasize the high electrolyte conductivity.

4. Conclusion

This study produced coating alloys with high tungsten concentration up to 69.59%, higher than the reported values in the literature with similar faradaic efficiency (10-15%). It was also confirmed that the low efficiency is related with the increase of tungsten in the deposit and the increase of iron elevates the electrodeposition efficiency.

This scientific production brings more information regarding the anomalous codeposition and indicates that increasing the iron concentration in bath (from 0.01 to 0.1 mol/L) even when the tungsten concentration is much higher (0.3 mol/L) it is obtained higher amount of Fe on the coating (anomalous codeposition). Decreasing the temperature or the current the anomalous codeposition is more pronounced. Therefore, FeW coating alloys with higher amount of tungsten were obtained on low concentration of iron (0.01 mol/L) or high concentration of iron (0.1) and low current (10 mA/cm$^2$) and temperature (25 °C).

All coating alloys obtained are amorphous independently from composition, with homogeneity morphology and presence of nodules. The electrochemical corrosion resistance studies indicate that tungsten concentration increases extensively the corrosion resistance and so the coating obtained with normal induced codeposition was more resistant than the ones obtained with anomalous codeposition. This study also highlights that microcracks decrease the corrosion resistance.
Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

This research was financed by FAPESP (project number 2013/25357-9). The authors also acknowledge CNPq and CAPES for the research grant.

REFERENCES


