The influence of organic additives on the electrodeposition of iron-group metals and binary alloy from sulfate electrolyte


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Abstract

Thin films of the iron-group metals Fe and Co and binary CoFe alloy are galvanostatically electroplated from an acid sulfate electrolyte onto a copper rotating disk electrode. The use of organic additives in the electrolyte is widespread to produce thin films by electrodeposition. In the present work, the influence of organic additives containing a similar molecular structure on the anomalous codeposition behavior of the binary CoFe alloy is investigated. The partial current densities of the codepositing metals and of the side reaction in the presence of organic additives are determined from an analysis of the deposit and are compared with those measured for the pure metals and those electroplated without additive. Comparison of the electrodeposition results indicate that codeposition of cobalt and iron metals leads to a reduction of the reaction rate of the more noble component compared and an increase of the reaction rate of the less noble component to single-metal deposition. Organic additives do not affect the CoFe deposition mechanism. However, SAC and PHTA decrease the rate of iron deposition contrary to o-toluene sulfonamide (oTOL).

Keywords: Electrodeposition; Anomalous codeposition; Organic additives; CoFe alloy; Tafel slopes

1. Introduction

Iron-group metals and binary alloys have numerous important industrial applications in computer read/write heads and microelectromechanical systems (MEMS). The mutual codeposition of the iron-group pairs is characterized by the phenomenon known as anomalous codeposition [1–6]. The standard equilibrium potentials of the cobalt and the iron metals are equal to −0.23 and −0.44 V versus SHE, respectively. Thus, from thermodynamic considerations, it would be expected that the order of preferential deposition would be Co then Fe. The kinetics of the electrodeposition of the individual metals show that the rates follow the standard equilibrium potentials. However, for electrodeposition of the binary alloy, the opposite is true and the order of preferential deposition is reversed. The less noble metal is deposited preferentially to the more noble one. The different models published in the literature demonstrate that anomalous codeposition of iron-group metals involves both inhibiting and accelerating effects [1,7–9]. Even though there are many studies on anomalous codeposition behavior, there is a lack of systematic studies relating the effects of organic additives on this phenomenon.

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Indeed, practically, all commercial electroplating baths contain one or more addition agents, which improve coating characteristics. Several studies have investigated the influence of organic additives in the electrolysis bath on the alloy properties such as microstructure, stress, magnetic properties, as well as corrosion resistance [10–19]. Some additives are known to enhance the morphology and physical properties of metal electrodeposits [19–21]. Saccharin (SAC), thiourea and other compounds are commonly used as leveling and brightening agents in electroplating [16,22]. The difficulties introduced by the presence of organic additives have required empirically developed plating baths.

Many authors have studied the kinetics of single metal and alloy deposition of iron and cobalt and excellent reviews are available without additive in the plating bath [7,8,23,24]. This work is a continuation of previous works [20,22], which reported the effect of the organic additives saccharin (SAC), phthalimide (PHTA) and another additive containing the sulfur element (o-toluene sulfonamide (oTOL)) on the electrodeposition of iron-group metals and binary alloy from sulfate electrolytes. It is shown that the addition of additives containing the sulfonamide group (R-SO2-NHR) reduces considerably the stress [11]. Moreover, organic additives containing the sulfonamide group improve the anti-corrosion properties of CoFe deposits, contrary to the carbonyl group, which seems to interfere with material composition [20]. The ultimate purpose of this work is to investigate in detail the anomalous codeposition phenomenon in the presence of these organic additives having a similar molecular structure. For this purpose, single metals and binary alloys are deposited from acid aqueous sulfate electrolytes with and without organic additives using a copper rotating disk electrode.

2. Experimental section

2.1. Electrochemical cell

All galvanostatic electrodeposition experiments are performed with a three-electrode system using a platinum plate as the counter electrode and a mercury sulfate reference electrode (MSE), immersed in a separated compartment filled with a K2SO4 solution and fixed several millimeters away from the surface of the working electrode. The working electrode is a copper rotating disk (RDE) electrode having a diameter of 19 mm. The copper disk is polished with SiC-papers of grain sizes up to P4000 (Struers) then with 1 μm diamond powder. After an ultrasonic cleaning step, the preparation is completed by rinsing the copper disk with distilled water and drying it under a warm airflow. Just before the electrodeposition the copper electrode is immersed for 30 s in a sulfuric solution and rinsed. The distance between the different electrodes is fixed during all experiences. The anolyte is not separated from the catholyte. Consequently, a contamination of the electrolyte by anodically produced ferric ions could not be avoided.

2.2. Instrumentation

All electrochemical measurements are carried out using a potentiostat (PGP 301 (Tacussel, France)) connected to a computer. The Voltamaster 4 software compensated the Ohmic drop between working and reference electrodes. All potentials reported here are corrected for Ohmic drop. Galvanostatic deposition experiments are performed at a total applied current of −6 to −120 mA cm−2 during 6000–150 s, respectively. This corresponds to a consumption of an electrical charge of 17 C cm−2. When the potential varied slightly with time, the average of the measured potential is recorded as the deposition potential. A Pine Instrument rotator controlled the rotation rate. All experiments are performed at a rotation rate of 800 rpm.

2.3. Electrolytes

An acid sulfate solution is chosen for this study. The electrolytes are prepared from reagent analytical grade chemicals using ultrapure water (Millipore MilliQ system) and consisted of boric acid, sodium sulfate, metal sulfates (CoSO4·7H2O and/or FeSO4·7H2O) and organic additives (Table 1). When preparing metal salt solutions with various concentrations of metallic species the amount of sulfate ions is kept constant by the addition of sodium sulfate. Organic additives have been added in the electrolyte with a 2.5×10−3 mol l−1 concentration. Saccharin (SAC), phthalimide (PHTA) and o-toluene sulfonamide are from Aldrich.
The structure of organic compounds used as additives and their abbreviations are shown in Fig. 1. The electrolyte used for studies is deaerated with N₂ bubbling for 60 min prior to use and maintaining over the solutions during all the experiments in order to inhibit the absorption of oxygen. The temperature is constant to \(30 \pm 0.5 \, ^\circ C\). The pH is adjusted by the addition of an aqueous H₂SO₄ solution until a value of \(3.00 \pm 0.05\) is reached. The bulk pH is measured before and after every deposition. In the event of a pH change, the value is corrected by adding sulfuric acid.

2.4. Deposit analysis

After each electrodeposition at a fixed potential, the binary alloy is stripped in a known volume of HCl and HNO₃ (2:1 of concentrated solutions) in preparation for atomic absorption spectrophotometry (AAS) with a Perkin-Elmer spectrometer. Nitric acid, hydrochloric acid and copper ions were found not to cause interference with AAS measurements of cobalt and iron species. The results of metal concentrations from AAS allowed for the calculation of the weight fractions for binary alloys. Calibration standards for atomic absorption indicated an accuracy of \(\pm 3\%\) for analysis of the solution concentration. Like for voltammetry curves and CoFe mass determination by AAS, each experimental value given in this paper is the average of five results. The partial current densities of the alloy components are calculated from the AAS data using Faraday’s law. The current density of the side reaction is obtained by subtracting the sum of the metal deposition partial current densities from the total current density at the same potential.

3. Experimental results

As stated earlier, the experimental conditions of deposition used simple plating solutions without and with organic additives. Thus, the thin films deposited for both elemental and alloy electrodeposition are found to yield nonlustrous, granular surfaces. Surface irregularities from hydrogen evolution are evident on many of the thin films. The morphology of the CoFe films has been studied previously [20,22] and it has been determined that radial variations in alloy composition are not significant [3]. AAS analysis is used to determine the concentrations of the metals in the acid solutions used to dissolve the thin films from the copper RDE. This, in conjunction with the assumption that hydrogen evolution accounted for all charge transfer not directed toward metal deposition, allowed for the calculation of all the relevant partial current densities.

3.1. Partial current densities for elemental electrodepositions

The cathodic linear sweep polarization curves for cobalt electrodeposition in the presence of additives are shown in Fig. 2. The cobalt reduction potential for the single-metal deposition is about \(-1.2 \, V$/MSE$ for all experimental conditions, but the cathodic polarization depends on the nature of the additive. The highest polarization is observed for SAC while oTOL, PHTA have no effect.

The cathodic linear sweep polarization curves for iron electrodeposition in the presence of additives are shown in Fig. 3. Contrary to the single cobalt deposition, a slower electrolytic deposition kinetic of iron is observed in the presence of PHTA and SAC.

The kinetic parameters for single-metal deposition are determined from the cathodic linear sweep polarization curves using the same method. The results are given in Table 2. The additives do not affect significantly the Tafel slopes which remain in the vicinity of

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>H₃BO₃</th>
<th>CoSO₄</th>
<th>FeSO₄</th>
<th>Na₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.4</td>
<td>0.2</td>
<td>0.525</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.4</td>
<td>0.2</td>
<td>0.525</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.4</td>
<td>0.2</td>
<td>0.2</td>
<td>0.325</td>
</tr>
</tbody>
</table>

Table 1 Electrodeposition electrolyte composition (mol l⁻¹)

Fig. 1. Chemical structure of (A) saccharin (SAC), (B) phthalimide (PHTA) and (C) o-toluene sulfonamide (oTOL).
16.0 ± 1.0 V⁻¹ for single cobalt deposition and of 24.0 ± 1.0 V⁻¹ for single iron deposition. The study of cobalt deposition revealed a reaction order of one with respect to the metal ion and a Tafel slope of about 19.5 V⁻¹ in sulfate electrolytes at a low pH [25], while at a high pH the reaction order is two and the Tafel slope close to 78 V⁻¹ [26]. Iron deposition shows different features depending on the acidity of the solution. For the iron reduction in sulfate solutions Bockris et al. [24] found a Tafel slope of about 19.5 V⁻¹ and a reaction order of one with respect to the concentration of Fe²⁺ as well as of OH⁻. In our case, we cannot compare iron deposition results with the bibliography values because the anolyte is not separated from the catholyte. A contamination of the electrolyte by anodically formed ferric ions could not be avoided.

For iron and cobalt dissolution, several authors proposed a mechanism consisting in two consecutive one-electron steps with an adsorbed intermediate [7,8,24,27]:

\[
\begin{align*}
\text{Co}^{2+} + \text{OH}^- + e^- & \rightarrow \text{CoOH}_{\text{ads}} & (1) \\
\text{CoOH}_{\text{ads}} + \text{H}^+ + e^- & \rightarrow \text{Co}^2 + \text{H}_2\text{O} & (2) \\
\text{Fe}^{2+} + \text{OH}^- + e^- & \rightarrow \text{FeOH}_{\text{ads}} & (3) \\
\text{FeOH}_{\text{ads}} + \text{H}^+ + e^- & \rightarrow \text{Fe}^2 + \text{H}_2\text{O} & (4)
\end{align*}
\]

From the point of view of our results, we conclude that the organic additives do not affect the cobalt and iron deposition mechanism proposed for an electrolyte without additive. The organic additives influence only the exchange current density \(J_0\). A decrease in \(J_0\) in the presence of SAC may be attributed to the adsorption of the additives on the cathode surface thereby lowering the rate of electron transfer reaction. The decrease in \(J_0\) for iron deposition is found to be in the order SAC > PHTA. The possible explanation is based on the electrostatic cation adsorption effect, in which the presence of an adsorbate alters the double layer structure and decreases the rate of the iron electrochemical reaction. We can also conclude that the extent of the cathodic polarization depends on the degree of adsorption of the additive at the electrode surface.

### 3.2. Partial current densities for CoFe alloy codeposition

The cobalt and iron weight percentage determination allows the calculation of the cobalt and the iron...
partial current densities. After every experiment, the partial current densities are determined for each species. The total current density is equal to the sum of each partial current densities:

\[ J_{\text{tot}} = J_{\text{Co}} + J_{\text{Fe}} + J_{\text{side}} \]  

It is assumed that the current density \( J_{\text{side}} \) is mainly due to hydrogen formation. The polarization curves for iron and cobalt codeposition are not represented because they are similar to the polarization curves for single-metal deposition. As with the elemental electrodepositions, there is an influence of the organic additives on the kinetic parameters (Table 3). A slower deposition kinetics of cobalt is observed only in the presence of SAC. The deposition kinetics of iron is decreased in the presence of SAC and in the presence of PHTA and SAC.

The mechanism of anomalous codeposition of iron-group metals has been studied by many authors and several hypotheses have been presented in the literature [7,8,28–32]. However, these studies have been carried out in a plating bath without additive. The results, shown in Figs. 4–9 obtained with various electrolyte compositions, demonstrate the effect of inhibition and enhancement observed during codeposition iron-group metals in presence of additives. In these experiments the iron and cobalt concentrations in the electrolyte are kept constant to 0.2 mol l\(^{-1}\). The results show that the presence of iron reduces the cobalt partial current densities in the potential range up to \(-1.2\) V/MSE. From these results, we conclude that the organic additives do not affect the anomalous CoFe deposition mechanism. Even if organic additives such as SAC or PHTA are adsorbed on the electrode surface and affect the polarization curves, we observe the inhibition of the more noble metal by the less noble one. Moreover, deposition of the less noble metal is enhanced by the codepositing more noble iron-group metal. To allow an enhancing effect of codepositing species, the following catalytic reaction is proposed which is assumed to take place in addition to reactions (1)–(4) [8]:

\[ \text{Fe}^{2+} + \text{Co}^{2+} + \text{OH}^- + e^- \rightarrow (\text{FeCoOH})_{\text{ads}}^{2+} \]  

\[ (\text{FeCoOH})_{\text{ads}}^{2+} + \text{H}^+ + e^- \rightarrow \text{Fe}_x + \text{Co}^{2+} + \text{H}_2\text{O} \]  

The exact stoichiometry of the reaction intermediate \((\text{FeCoOH})_{\text{ads}}^{2+}\) is not known.

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**Table 3**

CoFe alloy deposition inverse Tafel slopes \( (V^{-1}) \) and exchange current density \( J_0 \) \( (\mu\text{A cm}^{-2}) \)

<table>
<thead>
<tr>
<th>Species</th>
<th>Electrolyte</th>
<th>Inverse Tafel slopes</th>
<th>( J_0 ) ( (\mu\text{A cm}^{-2}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>C</td>
<td>15.8</td>
<td>2.1</td>
</tr>
<tr>
<td>Co</td>
<td>C + SAC</td>
<td>16.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Co</td>
<td>C + PHTA</td>
<td>16.1</td>
<td>1.7</td>
</tr>
<tr>
<td>Co</td>
<td>C + oTOL</td>
<td>16.7</td>
<td>1.4</td>
</tr>
<tr>
<td>Fe</td>
<td>C</td>
<td>20.6</td>
<td>21.0</td>
</tr>
<tr>
<td>Fe</td>
<td>C + SAC</td>
<td>19.0</td>
<td>4.1</td>
</tr>
<tr>
<td>Fe</td>
<td>C + PHTA</td>
<td>20.6</td>
<td>8.7</td>
</tr>
<tr>
<td>Fe</td>
<td>C + oTOL</td>
<td>20.4</td>
<td>23.6</td>
</tr>
</tbody>
</table>

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**Fig. 4.** Enhancing effect due to codeposition of the more noble element. Partial current density of Fe during deposition from electrolytes C without or with oTOL (●) and from electrolyte B without or with oTOL (○).

**Fig. 5.** Inhibiting effect due to codeposition of the less noble element. Partial current density of Co during deposition from electrolytes C without or with oTOL (●) and from electrolyte A without or with oTOL (○).
3.3. Partial current densities for hydrogen evolution

The current density of hydrogen evolution during the cobalt and iron codeposition is shown in Fig. 10 as a function of the measured disk potential. The partial current densities for hydrogen evolution observed for alloy electrodeposition are relatively independent of cathodic disk potential whatever the electrolyte composition used. The current densities are found to reach a plateau for each metal sulfate bath. This is indicative of a diffusion-limited process.

3.4. Current efficiency for alloy codepositions

The influence of organic additives on the cobalt–iron codeposition can be estimated by measuring...
changes in the efficiency which is given by: $m_{\text{exp}}/m_{\text{theo}}$
where $m_{\text{exp}}$ is the experimental mass and $m_{\text{theo}}$ the mass calculated with Faraday’s law. The efficiencies for CoFe electrodeposition varied from 0 to 95%, as shown in Fig. 11. The efficiency increased as the applied cathodic potential increased. We can observe that for all electrolytes except in the case of SAC, for potential more negative than $-1.8 \text{ V/MSE}$, the value stays constant at about $0.90 \pm 0.05$. The calculated efficiency under the same experimental conditions for various additives is slightly higher in the presence of PHTA, oTOL and without additives, compared to the results with SAC.

3.5. Alloy compositions

According to Fig. 12 which represents the iron weight percentage as the function of applied potential, we can observe that the iron percentage increases from 30 to 55% for CoFe produced with SAC and PHTA when the applied potential varies from $-1.25$ to $-1.5 \text{ V/MSE}$. The explanation for the increase of the iron weight percentage is put forth by Sasaki and Talbot [3] who proposed that at least the initial monolayer of the deposited thin film is exclusively composed of the more noble metal. Thus at lower cathodic potentials, since the thickness of the thin film deposited is not as great as that found at higher cathodic potentials, this initial, preferential deposition of the more noble metal will produce a correspondingly lower content of the less noble metal in the alloy than that expected from a steady-state deposition. For potential more negative than $-1.5 \text{ V}$, the iron percentage stays constant at $55 \pm 5 \text{ wt.\%}$. In the presence of SAC, we can observe that the iron weight percentage is smaller for potentials in the range of $-1.5$ and $-2.0 \text{ V/MSE}$. This effect of inhibition of the iron element has been observed previously [11,20,22].

4. Conclusion

In this paper, the kinetic of single metal and alloy deposition of iron and cobalt is studied from acid electrolyte using a copper rotating disk electrode. The experimental results demonstrate that the cobalt and iron deposition mechanism consisting of two consecutive one-electron steps with an adsorbed intermediate is not changed by the presence of the organic additives SAC, PHTA and oTOL. Moreover, these
organic compounds do not affect the anomalous CoFe deposition mechanism. Codeposition of cobalt and iron leads to a reduction of the reaction rate of the more noble component and an increase of the reaction rate of the less noble component even if organic additives adsorb on the electrode surface and affect the polarization curves of single metals.

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References