Electrodeposition of copper–zinc from an alkaline bath based on EDTA

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Abstract

The electrodeposition of copper–zinc on 1010 steel from a non-cyanide alkaline electrolyte based on EDTA (ethylenediaminetetraacetic acid, disodium salt) — alkaline with various proportions of copper and zinc ions, was investigated. The composition of copper and zinc by EDTA stabilized the solution. The deposition potential and the composition of the Cu–Zn bath were shown to influence the composition, morphology and phase composition of the Cu–Zn deposits. Scanning electron microscopy analysis showed that the best conditions to obtain smooth Cu–Zn deposits were at −1.45 V, with Cu70–Zn30 and Cu50–Zn50 baths, and at −1.50 V, with Cu30–Zn70. Besides being smoother than others, these deposits were golden in colour. Energy-dispersive X-ray spectroscopy analysis showed that a Zn content above 60 wt.% in the Cu–Zn deposits was achieved from the last bath, at −1.45 V. X-ray diffractograms of the Cu–Zn deposits produced at −1.45 V, from Cu70–Zn30, Cu50–Zn50 and Cu30–Zn70 baths, indicated the occurrence of phases Cu0.15Zn0.85, Cu, Cu2O, Cu2Zn, Cu2Zn5 and CuZn30, Cu3Zn, Cu5Zn, CuO, Cu0.63Zn0.37, respectively. For the Cu30–Zn70 bath at −1.60 V, Cu, CuZn, Cu2Zn5, and CuO phases were observed.

1. Introduction

Cu–Zn alloys are currently under study in this, as well as in other, laboratories [1–16], because they are interesting for their corrosion [15,16] and mechanical resistance, good conformability, decorative quality and greater hardness than pure copper [11].

Cu–Zn electrodeposits can be produced from electrolytes other than cyanide baths, namely, from electrolytic solutions based on sorbitol [1], nitritolriacetic acid (NTA) [3], pyrophosphate [4–7], citrate [8,9], tartrate [10], glycerol [2,11,17], sulphate [12] and mannitol [13]. In our previous work, an alkaline bath based on sorbitol [1] as a copper complexing agent was used successfully to deposit Cu–Zn alloy. Thus, motivated by these results, we decided to study these alloy deposits prepared from an alkaline EDTA bath developed in this laboratory with various Cu/Zn ratios, to explore how this chelating agent, which complexes both copper and zinc ions, would influence the deposition process and the morphology, composition and phase composition of the Cu–Zn electrodeposits. The process of Cu–Zn deposition on a 1010 steel electrode in an alkaline EDTA deposition bath was studied by voltammetry. The influence of the deposition potential (V) and composition of the deposition bath on the morphology, copper and zinc contents and phase composition of the Cu–Zn deposits were investigated by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) spectroscopy, respectively.

2. Experimental

All chemicals were of analytical grade. Double distilled water was used throughout the experiment. The electrochemical experiments were performed in a freshly-prepared non-cyanide bath, containing 3.0 M NaOH + CuSO4 and ZnSO4 and EDTA in various concentrations, respectively: 0.060 M/0.14 M/0.15 M; 0.10 M/0.10 M/0.25 M; 0.14 M/0.060 M/0.35 M. The proportion of cupric ion was 30 (0.060 M); 50 (0.10 M) and 70 (0.14 M) mol%. For convenience, the corresponding baths were labelled Cu30–Zn70; Cu50–Zn50 and Cu70–Zn30 plating baths. Experiments were also performed with single metal ion–EDTA solutions, at all the metal–ion concentrations used in the above three mixed metal baths, pH was measured and was −14 in all baths. It is well established [18–21] that Cu2+ and Zn2+ ions are complexed by EDTA. At pH−14 the copper(I) reduction occurred mainly from [Cu(OH)2EDTA]3− and the zinc(II) reduction from [Zn(OH)4]2− and [ZnEDTA]2− complexes.

A 1010 steel disk (0.50 cm2), a Pt plate and an appropriate Luggin capillary containing Hg/HgO/NaOH (1.0 M NaOH, E0 = 0.097 V) were employed as working, auxiliary and reference electrodes, respectively. When indicated, the steel was replaced by Cu (0.280 cm2) or Zn (0.380 cm2) disk electrodes. Immediately prior to the electrochemical measurements, the steel working electrode, the Cu and Zn electrodes
were ground with 600 emery paper and rinsed with water. Potentiodynamic curves were recorded with a PARC electrochemical system consisting of a model 366A bipotentiostat, at a scanning rate of 10 mV s\(^{-1}\). All experiments were carried out at room temperature (25°C). Chronoamperometric Cu–Zn deposits were produced at a various deposition charge densities (\(q_{d}\)). Next, they were transferred to another electrochemical cell with 1.0 M NH\(_4\)NO\(_3\) solution and subjected to anodic linear stripping voltammetry (ALSV) at 10 mV s\(^{-1}\). The current efficiencies (CE) of Cu–Zn deposition process were calculated as the stripping/deposition charge ratio [1]. The error in the CE values was ±5%.

**Fig. 1** shows the anodic voltammetric curves of 1010 steel, copper and zinc electrodes in 1.0 M NH\(_4\)NO\(_3\) solution. It can be seen that dissolution/passivation of the 1010 steel electrode occurred in the potential range from \(-0.50\) V to \(+0.40\) V (Fig. 1(a)), while the zinc electrode (Fig. 1(b)) and copper electrode (Fig. 1(c)) dissolved at \(-0.70\) V and \(-0.20\) V, respectively. Therefore, when zinc dissolved nothing occurred with 1010 steel. However, when copper dissolved, 1010 steel was passivated. Thus, during dissolution of electrodeposits there was no active dissolution of 1010 steel, which would have contributed significantly to the CE. The 1010 steel was passivated (from \(-0.50\) V to \(+0.40\) V (Fig. 1(a))), its contribution to the CE was insignificant, relative to Cu–Zn deposit dissolution. Moreover, the passivation current density was \(-0.25\) mA cm\(^{-2}\) (Fig. 1(a)).

XRD patterns were produced with filtered Co K\(_\alpha\) radiation (1.78897 Å), using a Siemens D5000 automatic diffractometer set at 40 kV and 20 mA. The diffraction patterns were first collected in a \(\omega/2\theta\) scan and then repeated with a \(2\theta\) scan (fixing \(\omega = 3^\circ\)), to achieve a better resolution. SEM photographs were taken with a Leica Stereoscan 440 electron microscope. EDS readings were taken with an Oxford eLX device, EDS Si/Li, with ultrathin Be window. EDS analysis of the deposits was carried out over as much of the electrode as possible, perpendicular to the surface, without reaching the Teflon ring, that surrounded the 1010 steel disc electrode.

**Fig. 2.** Voltammetric curves on 1010 steel substrate in various electrolytic solutions: Cu\(_{70}\)–Zn\(_{30}\) (solid line), Cu\(_{50}\)–Zn\(_{50}\) (broken line) and Cu\(_{30}\)–Zn\(_{70}\) (dotted line), at 10.0 mV s\(^{-1}\). Inset: Voltammetric curves for 1010 Steel (solid line), Cu (broken line) and Zn (dotted line) substrates in 3.0 M NaOH+0.25 M EDTA, at 10 mV s\(^{-1}\).

**Table 1** Element contents of electrodeposits obtained by voltammetry in different baths, at \(E_{d} = -0.90\) V and \(-1.14\) V.

<table>
<thead>
<tr>
<th>Baths</th>
<th>(E_{d}) V</th>
<th>Element</th>
<th>EDS/wt.%</th>
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<tbody>
<tr>
<td>Cu(<em>{30})–Zn(</em>{70})</td>
<td>(-0.90)</td>
<td>Fe</td>
<td>96.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>3.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>(-1.14)</td>
<td>Fe</td>
<td>93.61</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>6.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn</td>
<td>0.23</td>
</tr>
<tr>
<td>Cu(<em>{50})–Zn(</em>{50})</td>
<td>(-0.90)</td>
<td>Fe</td>
<td>98.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>1.74</td>
</tr>
<tr>
<td></td>
<td>(-1.14)</td>
<td>Fe</td>
<td>88.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>12.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn</td>
<td>0.23</td>
</tr>
<tr>
<td>Cu(<em>{70})–Zn(</em>{30})</td>
<td>(-0.90)</td>
<td>Fe</td>
<td>95.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu</td>
<td>4.39</td>
</tr>
<tr>
<td></td>
<td>(-1.14)</td>
<td>Fe</td>
<td>84.90</td>
</tr>
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<td></td>
<td></td>
<td>Cu</td>
<td>15.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zn</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

\(^a\) <2 sigma.
3. Results and discussion

3.1. Voltammetric studies of Cu–Zn electrodeposition

Fig. 2 shows voltammograms for the stationary 1010 steel electrode in the Cu–Zn baths. The main features of these deposition voltammograms are a cathodic wave $c_1$ and a cathodic peak $c_2$ (Cu$_{30}$–Zn$_{70}$; Cu$_{50}$–Zn$_{50}$ and Cu$_{70}$–Zn$_{30}$ baths) and another cathodic wave $c_3$ (at $\sim -1.45$ V, Cu$_{30}$–Zn$_{70}$ bath). In addition, the increase in the current density at potentials more negative than $\sim -1.20$ V can be attributed to a significant hydrogen evolution reaction (HER) in parallel to Cu–Zn electrodeposition. The anodic process, in general, shows peaks $a_1$, $a_2$, $a_3$, $a_4$ and $a_4'$. Disc electrodes of 1010 steel, Cu and Zn were studied in the absence of the deposition salts and the cathodic voltammograms show that the current densities ($j$) increase steeply at approximately $-1.10$, $-1.40$ and $-1.70$ V, respectively (inset in Fig. 2). Moreover, a broad peak, two waves and a shoulder, before the commencement of hydrogen evolution, can be seen on the 1010 steel, Cu and Zn electrodes, which are due to the reduction of zinc, copper and iron oxides, respectively (produced at the beginning of the potential scan). The inset in Fig. 2, indicates that HER occurs in parallel to deposition which may be confirmed in the CE results.

Fig. 3 shows voltammograms recorded for the 1010 steel substrate, using only the Cu salt (broken line), Zn salt (dotted line) or both Cu and Zn salts (solid line) in the deposition solutions. It may be noted, in Fig. 3(a)–(c), that the deposition rate is affected in region I (solid line) by the concentration of [Cu(OH)EDTA]$^{3-}$, since the cathodic current density in this region decreased when the concentration of this complex in the bath decreased (6 mA cm$^{-2}$, Cu$_{70}$–Zn$_{30}$ bath; 4 mA cm$^{-2}$, Cu$_{50}$–Zn$_{50}$ bath; 2 mA cm$^{-2}$, Cu$_{30}$–Zn$_{70}$ bath). In this region a primary bulk nucleation and growth of copper occurred, as will be seen more clearly later. In region II (cathodic peak, solid line), it is difficult to analyze the influence of copper complex concentration on the deposition rate since, in this region, the deposition process control changed from charge transfer to mass transport. Moreover, in this region, a secondary bulk nucleation and growth of copper occurred. In previous work, it is reported that primary and secondary bulk nucleation and growth are observed for electrodeposition of other metal [22,23]. Beyond the cathodic peak, two copper complexes...
Fig. 6. (a) Voltammetric curves for 1010 steel substrates in 0.14 M CuSO₄ + 0.35 M EDTA + 3.0 M NaOH (solid line) and 0.14 M ZnSO₄ + 0.15 M EDTA + 3.0 M NaOH (broken line); effect of reverse potentials: −1.32 V (---), −1.42 V (----), −1.52 V (-----) for Zn (b) and −0.42 V (---), −0.52 V (----), −0.62 V (-----) for Cu (c), at 10 mV s⁻¹.

Fig. 7. Stripping voltammetric curves of Cu–Zn deposits obtained from Cu70–Zn30 bath at various E_d and different q_d: (a) 0.10, (b) 0.40, (c) 1.0 and (d) 2.0 C cm⁻² in 1.0 M NH₄NO₃ solution, at 10 mV s⁻¹.
[Cu(OH)EDTA]$^{3-}$ and [CuEDTA]$^{2-}$ and two zinc complexes [Zn(OH)$_4$]$^{2-}$ and [ZnEDTA]$^{2-}$ are reduced in parallel to HER. Also, it can be seen that the concentration of the copper complex, [Cu(OH)EDTA]$^{3-}$, does not affect significantly the deposition potential $(-0.50 \, \text{V}, \text{Fig. 3(a)-(c)}$. Moreover, Fig. 3(a)-(c) shows that Cu–Zn deposition (solid line) occurs close to Cu deposition (broken line). These results imply that the Cu–Zn deposits obtained from these baths, in different regions of the voltammetric curves, can be richer in copper, depending on the deposition bath, as shown in Section 3.2.

EDS analysis was performed on the Cu–Zn deposits obtained, at various Cu–Zn ratios in the bath, voltammetrically at reverse potentials in regions I and II, to verify whether copper and zinc codeposition occurred (Table 1). It is important to emphasize that in the voltammetric electrodeposition, the reversal potentials were at $-0.90 \, \text{V}$ and $-1.14 \, \text{V}$ and that the electrodeposition continued until current density returned to zero. It can be verify in Table 1 that only Cu deposition occurred in regions I and II. These results lead to infer that in region I a primary bulk nucleation and growth of copper on to 1010 steel occurred.

An experiment of zinc voltammetric deposition from 0.14 M ZnSO$_4$ + 0.15 M EDTA + 3.0 M NaOH onto a copper electrode was performed (Fig. 4). The results showed that the zinc deposition overpotential on this electrode was $-1.30 \, \text{V}$. In addition, this value was also observed in 0.10 M ZnSO$_4$ + 0.25 M EDTA + 3.0 M NaOH and 0.060 M ZnSO$_4$ + 0.35 M EDTA + 3.0 M NaOH baths. Also, as will be seen later, zinc deposition overpotential on 1010 steel ($-1.42 \, \text{V}$), in alkaline medium containing EDTA, is more negative than on the copper electrode. It can be concluded that beyond cathodic peak C$_2$ (Fig. 2) and region II (Fig. 3), copper and zinc codeposition occurred (see Fig. 5 and EDS results).

The various features of the Cu–Zn deposition and dissolution processes in the reverse sweep are shown in Fig. 5 for several final potentials ($E_d$). The electrodeposits were obtained from Cu30–Zn70 (Fig. 5) bath. When the sweep was reversed at $E_d = -0.90 \, \text{V}$, anodic peaks a$_2$, a$_3$, a$_4$ and a$_5$ were seen. These peaks correspond to cathodic wave C$_1$ (Fig. 2). For $E_d = -1.14 \, \text{V}$, the anodic peaks a$_2$, a$_3$, a$_4$ and a$_5$ were formed. The anodic peak a$_3$ is thus only observed in the region of cathodic peak C$_2$. When $E_d$ was more negative than $-1.14 \, \text{V}$, anodic peaks a$_1$, a$_2$, a$_3$, a$_4$ and a$_5$ were formed, hence peak a$_1$ is only formed beyond cathodic peak C$_2$. Similar results were obtained for other Cu/Zn ratios in the bath.

EDS analysis of deposits obtained voltammetrically at $E_d = -0.90 \, \text{V}$ and $E_d = -1.14 \, \text{V}$ (Table 1) showed that only copper deposition occurred. Thus, these results imply that anodic peaks a$_2$, a$_3$, a$_4$ and a$_5$ correspond to passivation of copper deposits, in this alkaline medium [19], obtained in the region of cathodic wave C$_1$ and peak C$_2$. Moreover, as can be seen in Fig. 6(a) (solid line), copper dissolution shows a plateau of current (from $-0.55 \, \text{V}$ to $-0.30 \, \text{V}$) before the anodic peak.

Fig. 6(a) shows the voltammetric curves for the 1010 steel substrate, with only the Zn salt (broken line) and also the Cu salt (solid line) in the bath, both in the presence of EDTA and 3.0 M NaOH. To analyze zinc deposition onto 1010 steel substrate in more detail, voltammetric curves were recorded with various $E_d$ in the reversed sweep (Fig. 6(b)), and it was found that zinc deposition occurred at $-1.42 \, \text{V}$. It should be noted that the zinc overpotential on copper is $-1.30 \, \text{V}$ (Fig. 4). The cathodic wave on the voltammetric curve for zinc deposition (Fig. 6(a), broken line) is due to HER (seen by naked eye). The stability constants of [Zn(OH)$_4$]$^{2-}$ (10$^{15}$) and [ZnEDTA]$^{2-}$ (10$^{4.47}$) are close [21], so that the reduction potentials of these complexes are very close and their reductions occurred in the region of the cathodic peak (Fig. 6(a), broken line). The copper voltammetric curves with various $E_d$ in the reverse scan, were also investigated (Fig. 6(c)) and it was found that primary bulk nucleation and growth of copper occurred at $-0.52 \, \text{V}$, since an anodic peak for copper dissolution was observed. The fact that no nucleation loop is observed, when the sweep was reversed at $-0.52 \, \text{V}$, in Fig. 6(c), may be related to the similarity in roughness of the 1010 steel substrate and the copper electrodeposit.

These results indicate that copper deposition occurred in the regions of cathodic wave C$_1$ and peak C$_2$, and that zinc and copper codeposition occurred beyond cathodic peak C$_2$ (Fig. 2), see Table 1. It must be stressed that zinc and copper precipitation can occur at potentials more negative than $-1.20 \, \text{V}$ (Fig. 2), due to HER, which leads to a rise in pH at the metal/solution interface. Hence, the Cu–Zn electrodeposits can be contaminated with zinc and copper oxides, which prevent dissolution of electrodeposits (Fig. 2). Also, on completion of the anodic voltammetric curve, it was clearly visible that the electrodeposits had not dissolved completely. Moreover, some of the anodic peaks (Fig. 2), for example, peaks a$_2$, a$_3$, and a$_4$, can be due to passivation of copper in this alkaline medium [19], since as can be seen in Fig. 6(a) (solid line), copper dissolution shows a plateau of current (from $-0.55 \, \text{V}$ to $-0.30 \, \text{V}$) before the anodic peak.

Fig. 7 shows stripping voltammetric curves of Cu–Zn deposits produced in the Cu70–Zn30 bath at various $E_d$ and with various q$_d$. It can be seen that the dissolution charge density of Cu–Zn deposits depends on $E_d$ and q$_d$ as well as on, the range of stripping potentials, suggesting that the composition of deposits varied.

Fig. 8 illustrates the effect of $E_d$ and q$_d$ on the CE of the chronoamperometric Cu–Zn deposition process from the Cu70–Zn30 bath. The Cu–Zn deposits were obtained chronoamperometrically from $-0.30 \, \text{V}$ to various $E_d$ and q$_d$. Firstly, it can be seen that CE values decrease as $E_d$ becomes more negative, irrespective of q$_d$. This confirms the significance of the HER occurring parallel to deposition. Secondly, for $E_d = -0.90 \, \text{V}$ and for all q$_d$, the CE values were $90\%$, indicating that the contribution of HER to the deposition process was similar for all q$_d$. It must be stressed that at $-0.90 \, \text{V}$ only copper deposits, as shown in Section 3.2, and also that at this $E_d$ the HER

![Image](316x572 to 556x741)

**Fig. 8.** Values of current efficiency plotted against $E_d$ at q$_d$: 0.10 (▼), 0.40 (■), 1.0 (▲) and 2.0 (●) C cm$^{-2}$. Electrolytic solution: Cu70–Zn30.

| Table 2
| Contents of Cu and Zn electrodeposited from different baths at various deposition potentials ($E_d$), with q$_d = 2.0$ C cm$^{-2}$.
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Baths</td>
<td>$E_d$/V</td>
<td>EDS wt.% Cu.Zn</td>
<td>Deposit colour</td>
</tr>
<tr>
<td>Cu30–Zn70</td>
<td>-0.90</td>
<td>100.0</td>
<td>Light red</td>
</tr>
<tr>
<td></td>
<td>-1.45</td>
<td>34.66</td>
<td>Dark grey</td>
</tr>
<tr>
<td></td>
<td>-1.60</td>
<td>47.53</td>
<td>Golden</td>
</tr>
<tr>
<td>Cu50–Zn50</td>
<td>-0.90</td>
<td>100.0</td>
<td>Light red</td>
</tr>
<tr>
<td></td>
<td>-1.45</td>
<td>55.45</td>
<td>Golden</td>
</tr>
<tr>
<td>Cu70–Zn30</td>
<td>-0.90</td>
<td>100.0</td>
<td>Light red</td>
</tr>
<tr>
<td></td>
<td>-1.45</td>
<td>62.38</td>
<td>Golden</td>
</tr>
</tbody>
</table>
contribution to deposition is not significant (see inset in Fig. 2). For $q_d = 0.10 \text{ C cm}^{-2}$ and $E_d$ more negative than $-0.90 \text{ V}$, the CE values were higher than for other $q_d$ and the same $E_d$.

It can be inferred from these results that the appreciable decrease in the value of CE, as deposition potentials become more negative than $-1.10 \text{ V}$, is due to the HER, which becomes more significant than zinc and copper electrodeposition.

These results imply that the control of $E_d$ and $q_d$ is very important for achieving a high CE in the Cu–Zn deposition process.

Similar stripping voltammograms for Cu–Zn deposits and similar CE were obtained in the two other baths.

The colour of the Cu–Zn deposits (Table 2) produced from Cu–Zn baths was, in general, golden. However, the deposit obtained from the Cu30–Zn70 bath at $E_d = -1.45 \text{ V}$ was dark grey. The dark grey colour of this deposit is due to non-uniformity of its morphology and the high content of Zn, as will be shown in Sections 3.2 and 3.3.

The Cu–Zn deposits obtained from sorbitol–alkaline [1] or EDTA–alkaline plating baths do not, in general, vary in colour as much as those obtained from glycerol–alkaline [2,17] or NTA alkaline [3] Cu–Zn plating baths. Thus, as for sorbitol–alkaline baths, rigorous control of the EDTA–alkaline bath and of the deposition conditions is unnecessary.

3.2 Energy-dispersive X-ray spectroscopy

EDS analysis was performed on the Cu–Zn deposits obtained at various Cu/Zn ratios in the bath, at different $E_d$ and with $q_d = 2.0 \text{ C cm}^{-2}$, to determine the Cu and Zn content. Table 2 shows that both $E_d$ and the Cu/Zn ratio in the bath influence the content of Cu and Zn in the electrodeposits. Also, it can be seen that the higher the Cu/Zn ratio in the bath, the higher is the Cu/Zn ratio in the deposit. Brenner [17] reports that when the noble metal content in the deposit is higher than the less noble metal, normal codeposition is observed, and that when the noble metal content in the deposit is lower than the less noble metal, anomalous codeposition occurs. Thus, it may be suggested from the results in Table 2 that the Cu–Zn codeposition type was normal for deposits obtained from the Cu30–Zn70 and Cu50–Zn50 baths at $E_d = -1.45 \text{ V}$ and at $-1.60 \text{ V}$ from Cu30–Zn70 bath. However, at $E = -1.45 \text{ V}$, from Cu70–Zn30 bath, the codeposition type was anomalous. These results are consistent with the golden or greyish colour of the resulting deposits. Moreover, Table 2 shows that, for all baths and at $-0.90 \text{ V}$, there was no variation in deposit colour.

Carlos and Almeida [1] report that Cu–Zn voltammetric deposition curves recorded from sorbitol–alkaline baths lie between the Cu and Zn deposition curves, regardless of the Cu/Zn ratios in the baths. Also, for Cu–Zn deposits obtained from sorbitol–alkaline baths containing Cu70–Zn30, at $-1.45 \text{ V}$, the codeposition type was normal, while for the Cu50–Zn50 and Cu30–Zn70 baths, at the same deposition potential, it was anomalous. However, for the alkaline EDTA bath, the Cu–Zn electrodeposition is closer to copper deposition in the Cu50–Zn50 and Cu30–Zn70 baths, while in the Cu70–Zn30 bath, the Cu–Zn electrodeposition lies between Cu and Zn. Thus, these results indicate that the deposition bath composition seems to determine the Cu–Zn deposit composition.

Finally, analysis of the potentiodynamic curves for the 1010 steel electrode in the Cu, Zn and Cu–Zn baths suggested that, in general,
Cu–Zn deposits are rich in copper. The EDS analysis of the Cu–Zn deposits corroborates these results since, except those obtained from the Cu30–Zn70 bath at $E_d = -1.45 \text{ V}$ or at $-1.60 \text{ V}$, all Cu–Zn deposits are rich in copper.

3.3. Scanning Electronic Microscopy

Fig. 9 shows SEM micrographs of deposits formed from the Cu30–Zn70 (Fig. 9(a) and (d) and (g)); Cu50–Zn50 (Fig. 9(b) and (e)) and
Cu70–Zn30 (Fig. 9(c) and (f)) baths at various $E_d$ and with $q_{d} = 2.0 \ \text{cm}^{-2}$. Fig. 9(a)–(c) shows that the morphologies of the deposits obtained at $-0.90 \ \text{V}$, irrespective of the bath, are similar, i.e., formed by small globular crystallites. However, the Cu–Zn deposits obtained from three baths at $-1.45 \ \text{V}$ were formed by crystallites: irregular (Fig. 9(d)), globular (Fig. 9(e)) and non-coalesced globular (Fig. 9(f)).

The morphology of the Cu–Zn deposits obtained from the Cu30–Zn70 bath (Fig. 9(d)) is consistent with its colouration, i.e., dark grey (Table 2). Comparing Cu–Zn deposits obtained from sorbitol–alkaline [1] and EDTA–alkaline baths at $-1.45 \ \text{V}$, it can be seen that the former was smoother than the latter. This is possibly due to the differences in the complexing agents of the Cu and Zn ions, i.e., sorbitol and EDTA. In the bath containing sorbitol, the species reduced are Cu(II)–sorbitate and [Zn(OH)$_4$]$^{2-}$ complexes [1], while in that containing EDTA, the species are [Cu(OH)EDTA]$^{3-}$, [Zn(OH)$_4$]$^{2-}$ and [ZnEDTA]$^{2-}$. Thus, the discharge mechanism of these complexes at the metal/solution interface is possibly different, leading to different morphologies of Cu–Zn deposits and also different copper and zinc contents in these deposits (Table 2). Fig. 9(g) shows SEM micrographs of the deposit formed from the Cu30–Zn70 bath at $-1.60 \ \text{V}$ and $q_{d} = 2.0 \ \text{cm}^{-2}$. It can be seen that the Cu–Zn deposit was smooth. The content of Zn, 53 wt.% (Table 2), in this deposit was lower than the deposits obtained from glycerol–alkaline or pyrophosphate alkaline EDTA did not indicate elemental zinc and or zinc oxide or hydroxide.

4. Conclusions

The electrodeposition of Cu–Zn alloys can be achieved from alkaline baths containing EDTA, which are compatible with environmental requirements. The Cu–Zn deposition voltammetric curves obtained for various Cu/Zn ratios indicated that the Cu30–Zn70 bath gave the lowest deposition rate. SEM results showed that the best conditions to obtain smooth Cu–Zn deposits were at $-1.45 \ \text{V}$, with Cu70–Zn30 and Cu50–Zn50 baths, and at $-1.60 \ \text{V}$, with Cu30–Zn70. Besides being smoother than others, these deposits were golden in colour. EDS analysis showed that deposits obtained at $-1.45 \ \text{V}$ from Cu30–Zn30 bath has 62 wt.% Cu content and Cu–Zn codeposition type was anomalous, while for Cu30–Zn70 and Cu50–Zn50 baths at $E_d = -1.45 \ \text{V}$ and at $-1.60 \ \text{V}$ from Cu30–Zn30 bath, the Cu–Zn codeposition was normal.

X-ray diffraction analysis of the deposits obtained at $-0.90 \ \text{V}$ indicated the occurrence of Cu and CuO (Cu70–Zn30 bath) and only Cu for other Cu/Zn ratios in the bath; at $-1.45 \ \text{V}$, Cu$_{61}$Zn$_{39}$ (Cu70–Zn30 bath), Cu, Cu$_{Zn}$, Cu$_{5Zn8}$ (Cu50–Zn50 bath) and Cu, Cu$_{Zn}$, Cu$_{5Zn8}$, CuO, Cu$_{61}$Zn$_{39}$ (Cu30–Zn70 bath) and at $-1.60 \ \text{V}$, Cu, Cu$_{Zn}$, Cu$_{5Zn8}$, CuO (Cu30–Zn70 bath).

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References