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Electrodeposition of zinc–cobalt alloy from a complexing alkaline glycinate bath

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Abstract

The influence of cobalt on the electrodeposition of zinc onto AISI 1018 steel was studied in weakly alkaline glycine solutions. Thermodynamic calculations were performed to construct predominance-zone diagrams to identify the stability of the zinc and cobalt glycine complexes, and experimental studies of electrochemical behavior and deposit properties were conducted. When zinc is present, cobalt deposition shifts to more negative potentials, producing ZnCo alloys. Two main reduction steps were observed for electrodeposition from the ZnCo bath: the first at low potentials was due to ZnCo electrodeposition. In the second, at more negative potentials, cobalt content in the deposit increased forming a range of intermediate phases, and the hydrogen-evolution reaction became significant. The presence of Co(II) in the bath modified the morphology of the deposits as well as reducing the faradaic metal-deposition efficiency. ZnCo-deposit morphology was modified by the applied current density as well as the metal composition of the coating. X-ray diffraction studies revealed that cobalt oxide or hydroxide is formed during ZnCo electrodeposition, indicating that an elevation of the interfacial pH plays a role in the alloy deposition process. © 2007 Elsevier Ltd. All rights reserved.

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1. Introduction

Zinc coatings are used widely to protect iron and steel substrates against corrosion [1]. Metals like iron, cobalt and nickel have been incorporated in zinc plating baths to obtain coatings with higher corrosion resistance [1,2]. During zinc codeposition with metals of the iron group, the less noble metal, zinc, is electrodeposited preferentially; this phenomenon has been described as anomalous codeposition by Brenner [3].

According to Dahms and Croll [4], in the anomalous codeposition of Fe–Ni alloys a layer of iron hydroxide is formed, which adsorbs on the electrode and suppresses the nickel reduction. The metal hydroxide layer is formed as a consequence of elevated interfacial pH caused by the hydrogen-evolution reaction. Decroly and co-workers [5,6] proposed a similar mech-

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anism for Zn–Co codeposition, involving the formation of a zinc hydroxide layer on the electrode surface, which suppresses cobalt reduction. Higashi et al. [7] carried out a study of the electrodeposition of Zn in the presence of Co; the variation of the interfacial pH was determined, and the transition from normal to anomalous codeposition was associated with an increment of the interfacial pH. Stankeviciute et al. [8] applied electrochemical quartz-crystal microbalance measurements to analyze the deposition of Zn–Co alloys in terms of the mechanism of hydroxide suppression. On the other hand, other authors have argued that during the anomalous codeposition of Ni–Fe, Ni–Zn and Fe–Zn alloys, only soluble intermediate species are formed [9–14].

The concept of hydroxide oscillation [15] has also been used to explain anomalous deposition. According to this model, the thickness of the hydroxide layer changes periodically. When the zinc hydroxide layer is depleted, the reduction of both H^+ and cobalt occurs preferentially to that of Zn. Then, as the interfacial pH increases due to the hydrogen-evolution reaction, the hydroxide layer forms again favoring Zn reduction, and the codeposit becomes anomalous.

Inhibition of nickel reduction due to zinc underpotential deposition (upd) has been proposed by Nicol and Philip [16]. Ohtsuka and Komory found evidence for the formation of a zinc monolayer deposit that inhibits the nucleation and growth of nickel [17]. On this basis, Swathirajan has claimed that Ni–Zn anomalous deposition depends on the electrode potential and that the inhibition of Ni deposition is due to the underpotential deposition of Zn [18].

Differences in the values of exchange current densities have also been considered in the interpretation of anomalous codeposition [19,20]. The magnitude of the exchange current density is generally much greater for zinc compared to metals like iron, cobalt and nickel.

Tsuru et al. [21] showed that the nature of the solvent has an effect on Zn-Co codeposition. Normal codeposition occurs in pure methanol, whereas in the presence of water they obtained anomalous deposits. Similar results were obtained in ionic liquids for Zn-Fe deposition [22]. Recently, Fratesi and co-workers [23] studied the electrodeposition of ZnCo alloy from an acidic chloride bath. They investigated the effects of Zn^{2+}/Co^{2+} ratio and the applied potential on the formation of ZnCo-alloy phases and obtained a transition from the Zn-rich η -phase of ZnCo to a γ -phase and later to cobalt-rich deposits by increasing the cobalt amount in the bath or by increasing the applied potential. Clearly the composition of the coatings obtained during codeposition depends on several factors, such as the current density, the solution composition, pH, temperature, and agitation. Anomalous codeposition has been observed mostly at high current densities [24], whereas at low levels of current the codeposition may be normal. On the other hand, some authors have reported that cobalt-rich deposits are obtained at high current densities and zinc-rich coatings at lower values [25]. The presence of other metal ions and especially organic additives can also change the deposit type from anomalous to normal [26,27].

Glycine has been used as a complexing agent in the electrodeposition of Zn-Ni [28], Cu-Co [29] and Zn-Co [30] alloys. It is an attractive medium due to its ability to form complexes with zinc and cobalt in weakly alkaline electrolytes. The characterization of glycine-based electrolytes in alkaline solution represents an interesting challenge because they offer a possible alternative to the use of toxic cyanide baths or zincate baths for zinc or zinc-alloy plating. No clear mechanistic model to describe the electrochemical behavior can yet be deduced from the previous studies devoted to Zn-Co alloy deposition in glycinate media [30]. The present work takes into account the solution chemistry as it seeks to elucidate the influence of cobalt on zinc electrodeposition in an alkaline glycine medium through electrochemical experimentation and microscopic deposit characterization. First, an understanding of ZnCo alloy electrodeposition with glycine requires a preliminary thermodynamic analysis to identify the different complexes that can be formed in solution depending on the experimental pH and, as a consequence, can affect the relative availability of the metals to form the alloy deposit. With that background information the study presents an electrochemical investigation of the system and reports on the effects of operating parameters on the electrodeposit properties, such as alloy composition, morphology, and current efficiency. The ultimate objective is to develop an efficient and environmentally benign zinc–cobalt plating bath.

2. Experimental

Electrodeposits were formed from aqueous 0.2 M ZnSO₄ (Merck) with CoSO₄ (Merck) at various concentrations from 0.005 to 0.1 M. All tests were performed in a complexing 2.2 M glycine (Aldrich) medium. The solution was made up first by zinc sulfate dissolution in a previously prepared glycine solution, cobalt sulfate being added later. The electrolyte pH was adjusted to 11 by adding sodium hydroxide. All the solutions were prepared with deionized water (18 M Ω cm). The Zn and Zn–Co coatings were electrodeposited on an AISI 1018 steel substrate. Stripping voltammograms were recorded using a slow sweep rate ($v = 1 \text{ mV s}^{-1}$) in 2.2 M glycine and pH 11 solution under a N₂ atmosphere.

The experiments were performed with a PAR 273A potentiostat. Cyclic and linear voltammetry were carried out in a typical three-electrode cell. AISI 1018 steel embedded in a PTFE rod was used as a disk working electrode with a geometrical area of 0.032 cm², a saturated calomel electrode was the reference electrode, and the counter electrode was a graphite bar. The trials were carried out under an ultrapure nitrogen atmosphere. Before each experiment, the steel electrode was polished with $0.05 \,\mu m$ alumina (Buehler) to a mirror surface appearance. The temperature was maintained at 25 °C. Deposit specimens for microscopic characterization were obtained on the steel electrodes by applying a constant current density without stirring. The morphology and composition measurements were done with a scanning electron microscope (JEOL DSM-5400 LV). The X-ray diffraction patterns were obtained with Cu Ka radiation in an Xray diffractometer (Brucker D8 Advance). The coating composition profile (GDS analysis) was determined by using a Glow Discharge Spectrometer (Leco 850A). The current efficiency was calculated by integrating the charge passed under the stripping curves and comparing that value with the total charge passed during the deposition process; these were performed in duplicate. The experimental error of the GDS experiments was estimated to be 1% for zinc, 4% for cobalt, and 11% for carbon; these magnitudes reflect the level of an element in the deposit. The primary goal of the elemental analysis and of the current-efficiency measurements was to show generally the qualitative effects of the plating parameters during ZnCo alloy electrodeposition.

3. Results and discussion

3.1. Thermodynamic analysis

Glycine is a complexing amino acid ($H_2NCH_2COOH = L'$) that provides two functional groups able to form coordination bonds with metal cations. Glycine also presents two acidities, the values of the acidity constants being 2.07 and 9.97 [31]. The pH used in this study (~11) thus falls sufficiently above the second acidity value for the divalent anion to be the predomi-

Table 1

	Metal-glycine			Metal-OH				
	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$	pKs
Zn	4.88	9.06	11.56	4.4	11.3	13.7	16.6	16.92
Co	4.69	8.46	10.81	4.3	8.4	9.7	10.2	14.8

Equilibrium constants for the overall formation of complexes in the zinc/glycine/OH⁻ and cobalt/glycine/OH⁻ systems and the hydroxide solubility products obtained from the literature [31], $\beta_n = [ML_n]/[M][L]^n$

nant form. Compared to other common complexing agents like EDTA, glycine forms less strong complexes; this makes it more amenable to effective effluent treatment.

The thermodynamic description of the complexes formed under our experimental conditions was obtained by constructing predominance-zone diagrams and Pourbaix diagrams for the systems of Zn–glycine and Co–glycine. The diagrams were computed using the method described in the literature by Rojas-Hernández et al. [32–34]. Table 1 gives the values of the overall formation constants β_n for the metal–glycine complexes, those for the metal hydroxides, and the solubility products for the hydroxides [31]. We assumed that there are no mixed complexes (i.e., hydroxy-glycine-metal species).

Fig. 1a and b shows the predominance-zone diagrams for the Zn(II)' and Co(II)' species. The generalized notation M(II)' for the dominant species (with M = Zn or Co) may represent either the free M^{2+} ions in the solution, the soluble metal–glycine complexes, or the metal hydroxide in either soluble or insoluble form;

L' is the glycine complexing agent whose form (acidity) depends on the pH. In our experimental range of pH and analytical concentrations of metals and glycine, the free glycine concentration will be about 1.6 M, corresponding to pL' = -0.204. Under these conditions the thermodynamic calculations show that ML'_3 is the predominant form for both the zinc and cobalt species. For the experimental zinc–cobalt mixed electrolytes, the glycine concentration was sufficiently elevated to keep these two species predominant.

The Pourbaix diagrams, Fig. 1c and d, show the variation of the equilibrium potentials for the redox couples M(II)/M(0) for zinc and for cobalt with 2.2 M glycine at pH 11. The complexing agent displaces the equilibrium potentials toward more negative values. It is seen that cobalt deposition still should occur at more positive potentials compared to zinc. It appears that a small pH interval is available for zinc-hydroxide precipitation between 12.6 and 13.2 before zincate forms. Insoluble cobalt-hydroxide formation may occur at pH higher than 12.7. We



Fig. 1. Predominance-zone diagrams for (a) Zn(II)'; (b) Co(II)'. Pourbaix diagrams for (c) Zn(II)'; (d) Co(II)'. The total metal cation concentrations considered in the computation of these diagrams were 0.20 M for zinc and for cobalt, 0.005 M (heavy line) and 0.1 M (thin line). Free L' was taken to be 1.6 M (pL' = -0.204), and hydroxide concentration was determined by the pH.

therefore assume that, from a purely thermodynamic point of view and with the parameters found in the literature, under our experimental conditions both zinc and cobalt reduction should involve primarily the single ML'_3 complexes, and the overall reactions will be the following:

$$\operatorname{ZnL}_{3}^{\prime} + 2e \to \operatorname{Zn}(0) + 3L^{\prime} \tag{1}$$

$$\operatorname{CoL}_3' + 2e \to \operatorname{Co}(0) + 3L' \tag{2}$$

Under our experimental conditions, the stability of insoluble zinc hydroxide, i.e. $Zn(OH)_2$, is restricted to a narrow pH interval above 12.6. In addition, the thermodynamic study predicts that the dominant cobalt species becomes insoluble $Co(OH)_2$ above pH 12.7.

4. Cyclic voltammetry

4.1. Zinc and cobalt electrodeposition from the glycinate electrolyte

Fig. 2 presents cyclic voltammograms for the alkaline glycine solutions of Zn(II)' and of Co(II)' individually and for the glycinate solution in the absence of metals. It is seen that Zn presents two reduction steps; a small peak A appears around -1.26 V, and peak Ic is located at -1.53 V versus SCE. The former could be associated with incipient hydrogen reduction, which is seen occurring with metal-free glycine solution in Fig. 2 (curve c) but then is presumably inhibited by underpotential deposition (UPD) of Zn. In the absence of metals, curve c indicates that the reduction of hydrogen begins at -1.2 V and shows its subsequent oxidation at peak B. On the other hand, the charge calculated by integration of peak A gives -364 mC cm^{-2} , which is greater than the theoretical amount required for the formation of a Zn monolayer. It is well known that the HER is very sensitive to the nature of the substrate; on Zn it proceeds very slowly, whereas on Co, Ni and Fe it exhibits a larger exchange current density [35]. Previous studies report the inhibition of HER in the presence of zinc ions in both alkaline [35] as well as acidic [36] baths



Fig. 2. Cyclic voltammograms for the electrodeposition on steel of zinc and of cobalt in 2.2 M glycine solution, pH 11, $v = 10 \text{ mV s}^{-1}$: (a) 0.20 M ZnSO₄; (b) 0.10 M CoSO₄; (c) no metal, 2.2 M glycine, pH 11.

due to the formation of even a sub-monolayer of Zn on ferrous substrates. Those authors propose that zinc upd competes with proton reduction [36]. On this basis, we suspect that a similar effect occurs in our system.

The second peak in curve a (Ic) is clearly associated with the massive reduction of Zn(II)' to Zn(0). When the sweep was reversed, an oxidation peak (Ia) was observed at -1.26 V versus SCE due to the oxidation of the deposit. As expected, peak Ic shifted to more positive potentials when the zinc concentration was increased. When the zinc concentration was 0.4 M, the oxidation peak became wider, and the peak current decreased. This could be attributed to changing structure of the deposit with increased thickness, but it is also possible that under these conditions the electro-oxidation process is limited by slow chemical reactions or diffusion.

The voltammetric behavior of the 0.1 M CoSO₄ solution (curve b) presents an electroreduction peak current (IIc) located at -1.426 V versus SCE. A subsequent increase in current is observed at more negative potentials due to the hydrogen evolution reaction, which is not inhibited as in the case of the zinc solutions, zinc having a higher overpotential for hydrogen evolution. When the direction of the potential sweep is reversed, a crossover potential associated with nucleation is observed at -1.23 V versus SCE. When the potential scan is reversed in the rising portion of peak IIc, the crossover potential varies, indicating additional processes during cobalt nucleation. An oxidation peak for pure Co is observed at -0.756 V versus SCE (peak IIa). According to the equilibrium potential of cobalt shown in Fig. 1d $(E_{eq Co(II)'/Co(0)} = -0.912 \text{ V} \text{ versus SCE})$ and the gap between the oxidation and reduction peaks, the Co(II)' reduction exhibits greater overpotential on the AISI 1018 steel substrate than does Zn ($E_{eq Zn(II)'/Zn(0)} = -1.384$ V versus SCE for 0.2 M ZnSO₄).

4.2. Influence of cobalt on zinc electrodeposition

When both metal ions are present in the glycinate solution, new stripping peaks (IIIa, IVa and Va) appear in Fig. 3 between the pure zinc and pure cobalt oxidation peaks, thus indicating



Fig. 3. Influence of the cobalt concentration on the cyclic voltammograms for the electrodeposition from zinc solution (0.2 M ZnSO₄) in 2.2 M glycine, pH 11, $v = 10 \text{ mV s}^{-1}$.

the formation of several ZnCo alloys or, at least, intermediate phases. As with pure zinc ZnCo electrodeposition in the presence of 0.005 M cobalt presents two reduction peaks. Upon reversal of the potential-sweep direction, an electrooxidation peak was observed at -1.17 V versus SCE (IIIa), associated with the formation of a Zn-rich ZnCo alloy phase. When the cobalt concentration was increased to 0.025 M, the electroreduction peak (Ic) was practically unaffected, but the electrooxidation of the deposit showed a decrease of peak IIIa and the appearance of a shoulder at -1.09 V versus SCE (IVa), a peak at -0.92 V versus SCE (Va), and another shoulder at -0.86 V versus SCE (VIa). For this higher cobalt concentration, the broadening of peak IIIa suggests that the deposit is composed of a mixture of diverse ZnCo phases. When the cobalt concentration was increased to 0.1 M, the reduction peak Ic shifted slightly toward more positive potentials, and the peak reduction current density decreased slightly. Increases were also observed in the currents produced at peak Va and shoulder VIa. Both cathodic and anodic peak positions correspond to formation of nobler Zn-Co phases, i.e. with richer Co content. Moreover, a second cathodic peak (IIIc) appeared, and hysteresis was observed when the scan was inverted, both effects attributed to the enhancement of the hydrogen-evolution reaction due to the increase of cobalt content in the deposit and to the formation of a new phase.

According to Swathirajan [37] and to Gómez and Vallés [38,39], the multiple oxidation peaks for the electrodeposits of Zn–Co alloys are associated with the formation of several phases with different cobalt contents. In our electrolyte conditions, Peaks IIIa, IVa and Va may be associated with different intermediate ZnCo alloy phases, while the peak VIa is attributed to pure cobalt (see Fig. 2). It is interesting to note that the presence of cobalt does not affect sharply the potential position of cathodic peak IC, although the current density diminished slightly as higher cobalt concentrations were introduced.

It is also observed that the presence of zinc increases the hydrogen-evolution overpotential relative to that of pure Co as reported previously [35,36]. In alkaline conditions [35], this inhibition is attributed to the formation of a Zn upd layer, which also inhibits the cobalt deposition. The latter exhibits a considerable increase in its electrodeposition overpotential leading to an anomalous Zn-Co codeposit. Such an effect may be involved also in this alkaline electrolyte. Furthermore, the hydroxidesuppression mechanism [4–8] suggests that a zinc hydroxide layer may also adsorb on the electrode, further inhibiting cobalt reduction. According to Fig. 1a and b, at pL' = -0.204, zinc hydroxide precipitation can occur when the pH reaches 12.6, and cobalt precipitation takes place at pH above 12.7. Thus, insoluble hydroxides could form on the electrode surface and impede cobalt reduction. Given that the theoretical pH values for the precipitation of the two metals are so close, both cobalt and zinc precipitates may be involved in the codeposition process.

4.3. Influence of the switching potential, E_{λ}

The anodic voltammetric profile observed with Zn–Co alloy deposition depends strongly on the switching potential E_{λ} , the potential at which sweep direction is inverted. The switching

potential evidently influences the elemental composition of the deposit. Gómez and Vallés [38,39] observed on vitreous carbon in an acidic chloride ZnCo solution that oxidation peaks associated only with the formation of high-zinc-content phases appeared when E_{λ} was only moderately negative, but when the applied potential was taken to more negative values, there appeared several oxidation peaks associated with phases richer in cobalt content. Similar results were obtained in the ZnCo electrodeposition on AISI 1018 steel electrode [27]; Zn-rich deposits were obtained when the cathodic potential was inverted at low values, whereas at more negative values higher cobalt content was obtained in the deposit. On the other hand, Fratesi and co-workers [23] observed three reduction processes on Pt in the Zn upd potential region, where cobalt-rich deposits were obtained. The Zn content increased at more negative potentials. Although they report similar behavior on steel, these reduction peaks were not observed by Gómez and Vallés [38,39] nor by Trejo et al. [27], who found that cobalt reduction was strongly inhibited. The electrochemical behavior of ZnCo electrodeposition observed in our conditions, i.e. in alkaline electrolyte, shows an increase of the cobalt deposition overpotential with Zn presence similar to that observed in acidic conditions [27,36,37].

Fig. 4 shows the influence of E_{λ} on the CV for the Zn–Co glycinate system with 0.025 M CoSO₄. When the E_{λ} value was low, $E_{\lambda 1} = -1.45$ V, peak Ia was the major anodic signal and represented Zn oxidation. With $E_{\lambda 4} = -1.70$ V, two reduction processes (peak Ic and signal IIc) were observed: the first one (Ic) was due to the electroreduction of Zn, and the second (IIc) appeared at a more negative potential and was associated with the hydrogen evolution reaction combined with cobalt deposition. When the scan direction was reversed, several oxidation peaks appeared. In agreement with the observations of Gomez and Vallés in acidic conditions [38,39], signal Ia appeared predominantly with low values of the inverting potential. When the E_{λ} value was increased to more negative potentials, several other oxidation processes were observed (peaks IIIa, IVa, Va and VIa). The three first oxidation peaks represent phases with increasing



Fig. 4. Influence of the switching potential on the anodic behavior of the deposits from 0.20 M ZnSO₄ + 0.025 M CoSO₄ in 2.2 M glycine, pH 11, $v = 10 \text{ mV s}^{-1}$: $E_{\lambda 1} = -1.50 \text{ V}$ vs. SCE (curve 1); $E_{\lambda 2} = -1.55 \text{ V}$ vs. SCE (curve 2); $E_{\lambda 3} = -1.60 \text{ V}$ vs. SCE (curve 3); $E_{\lambda 4} = -1.70 \text{ V}$ vs. SCE (curve 4).

cobalt content, while signal VIa may be associated with a pure cobalt phase.

The mechanism of anomalous electrodeposition of the ZnCo alloy is still not clear; the hydroxide suppression model [4–8] predicts the formation of anomalous ZnCo alloys when hydrogen evolution occurs. Accordingly, as the applied potential is made more cathodic, the hydrogen reaction is favored, and the appearance of the oxidation peaks associated with ZnCo alloy phases are observed. However, at low switching potentials, the anodic peak Ia appears, indicating that the deposit is more anomalous when less hydrogen evolution occurs. It is possible that a combination of Zn upd with Zn and Co hydroxide precipitation inhibits Co reduction during the ZnCo electrodeposition. It is noted that the faint reduction peak (A) presents itself again around -1.2 V in Fig. 4. This small current is characteristic of cyclic voltammetry on ferrous substrates [36,40] and is attributed to the underpotential deposition of Zn and its subsequent inhibition of hydrogen reduction.

5. Characterization of the deposits

5.1. Composition of the coating

Thin deposits were formed on the steel disks under nonstirring conditions from a solution containing 0.2 M ZnSO₄ and various levels of Co by applying a constant current for 300 s. Fig. 5 presents the stripping voltammograms of the ZnCo deposits obtained under galvanostatic conditions at different current densities. The profile observed is similar to that observed in Fig. 3, i.e. several oxidation peaks appear corresponding to different phases of the ZnCo alloy. Curve f corresponds to the stripping of a pure cobalt deposit.

The faradaic current efficiency for metal deposition was determined by doing anodic stripping of the deposit and integrating the anodic current in order to calculate the ratio of the anodic to cathodic charges. The results are shown in Fig. 6 as a function of the relative level of cobalt in the bath. The elemental composition of the alloy deposits was also determined using an



Fig. 5. Stripping voltammograms for ZnCo alloy deposits formed from 0.20 M ZnSO₄ + 0.025 M CoSO₄ in 2.2 M glycine under constant current conditions: (a) -1 mA cm^{-2} ; (b) -5 mA cm^{-2} ; (c) -10 mA cm^{-2} ; (d) -20 mA cm^{-2} ; (e) -30 mA cm^{-2} ; (f) pure Co from 0.1 M CoSO₄ + 2.2 M glycine, pH 11 at -20 mA cm^{-2} ; $v = 1 \text{ mV s}^{-1}$, deposition for 300 s.



Fig. 6. Faradaic efficiency and variation of the cobalt content in constantcurrent deposits on steel as functions of the relative level of cobalt in the bath. $0.2 \text{ M} \text{ ZnSO}_4$, 2.2 M glycine, pH 11. Deposits produced at $j = -10 \text{ mA cm}^{-2}$ for t = 300 s, no stirring.

energy dispersion spectrometer coupled to the scanning electron microscope and presented in Fig. 6. The results demonstrate that all the deposits were anomalous in the sense that the Co content in the deposit was always less than the relative proportion present in the bath. It is seen that the current efficiency at this current density decreased with increasing cobalt concentration, falling from 90% with pure zinc to about 67% when the cobalt concentration was 0.025 M. This result confirms the interpretation of the CV results, namely, that higher Co levels in the bath and in the deposit promote the hydrogen-evolution reaction.

Fig. 7a shows the alloy composition profile with depth within the deposit formed under unstirred conditions from the 0.4 M ZnSO₄–0.05 M CoSO₄–glycine solution at -10 mA cm^{-2} . It is seen that the alloy composition was not constant across the film. Close to the steel substrate, the cobalt content was almost 4%. Further out in the film, in the portion formed as electrodeposition continued, the cobalt content decreased and maintained a value of about 2.7% until dropping off further near the outer surface. This graph shows again that under these conditions the codeposition was anomalous as the relative cobalt concentration in the solution was 11%. No significant level of oxygen was detected in the film except on the outer surface. In this case zinc or cobalt oxide or hydroxide may have formed on the surface, but none was incorporated in the deposit. It is possible that the electrochemical reduction reaction is faster than the rate of crystal growth, thus releasing the hydroxide anions to the bulk solution. This profile for cobalt level in the deposit suggests that several steps take place during ZnCo electrodeposition, and indeed different mechanisms may apply as the interface changes and the film grows.

When the deposits were obtained from a $0.2 \text{ M ZnSO}_4-0.1 \text{ M}$ CoSO₄-glycine solution, a change in the composition profile was observed. Fig. 7b shows that at -10 mA cm^{-2} the cobaltcontent profile across the deposit seems to be similar to that observed in Fig. 7a, but the oxygen content in the deposit increased. Both the oxygen and the cobalt content in the deposit increased with an increase in the applied current density to -30 mA cm^{-2} as seen in Fig. 7c, indicating occlusion of a



Fig. 7. Composition profiles with depth by GDS analysis for ZnCo deposits obtained from (a) $0.4 \text{ M} \text{ ZnSO}_4 + 0.05 \text{ M} \text{ CoSO}_4 + 2.2 \text{ M}$ glycine, pH $11, j = -10 \text{ mA cm}^{-2}$; (b) $0.2 \text{ M} \text{ ZnSO}_4 + 0.1 \text{ M} \text{ CoSO}_4 + 2.2 \text{ M}$ glycine, pH $11, j = -10 \text{ mA cm}^{-2}$; (c) same electrolyte as in (b) with $j = -30 \text{ mA cm}^{-2}$. Cobalt scale is amplified by 10 times in (a) and (b). Carbon scale is amplified by 100 times.

metal-hydroxide precipitate related to the occurrence of hydrogen reduction. Furthermore, the cobalt content is higher and more homogeneous than that observed in Fig. 7a and b, indicating the formation of a new phase. According to the ratio of Zn to Co, the new alloy was a γ -phase. This result can be correlated with the additional anodic peaks appearing in Figs. 3 and 4. At the same time, the carbon distribution also changed with Co(II) level. In Fig. 7a and b, it is observed that the C profile is similar to that of cobalt, rising near the steel interface, whereas at the higher current density it falls off from the outer surface of the deposit. This change may be related to the morphological changes observed in the SEM images that are presented in Fig. 9. In an acid electrolyte, the transition from a η -phase to a γ -phase was found to occur with an increase of the cobalt level in the bath [23].

The effect of current density on current efficiency was also determined for the alloy bath with 0.025 M Co. Fig. 8 shows the metal-deposition current efficiency as a function of current density. Also plotted is the cathode potential. It is seen that the current efficiency is low at low current densities but increases rapidly to about 80%. At higher current densities, the efficiency falls off as the hydrogen reaction becomes significant. Alcalá et al. [25] found that anomalous codeposition is favored at low applied overpotentials and at high Zn(II)/Co(II) ratios. Accordingly, loss of current efficiency was related to increased cobalt concentration in the deposit at higher current densities because of activation of the hydrogen-evolution reaction by increased cobalt content.

These various results show that codeposition of the two elements does not occur according to the pure-metal deposition kinetics. Cobalt deposition is inhibited by zinc at low current densities or low applied potential. At the same time zinc deposition is retarded by the presence of cobalt. Cobalt deposition becomes favored at more negative applied potentials and leads to the formation of several Zn–Co alloy phases and even a pure



Fig. 8. The current efficiency for ZnCo electrodeposition (t = 300 s) from 0.2 M ZnSO₄ + 0.025 M CoSO₄ + 2.2 M glycine, pH 11, plotted as a function of the applied current density (curve a). Curve b shows the cathode potential recorded during the galvanostatic deposition experiments, no stirring.

Fig. 9. Influence of the cobalt concentration and current density on the morphology of the deposits obtained from glycinic 0.2 M ZnSO₄ at pH 11, j = -10 mA cm⁻², t = 300 s. Cobalt concentrations: (a) 0.0 M; (b) 0.01 M; (c) 0.02 M; (d) 0.03 M; (e) 0.05 M; (f) 0.05 M with j = -30 mA cm⁻².

cobalt phase. Hydrogen evolution is promoted by the presence of cobalt in the deposit, and combination of the information in Figs. 5–8 shows that the cobalt level in the deposit affects current efficiency. The enhancement of the hydrogen reaction with the concomitant rise in interfacial pH probably plays a role in moderating the rate of zinc reduction as well as in the overall alloy-formation process.

5.2. Morphology of the deposits

The presence of other metals in Zn plating baths modifies the morphology of the deposits because of their influence on the growth of the initial crystal nuclei [25,41,42]. Fig. 9 shows the SEM images for electrodeposits obtained from the alkaline Zn and Zn-Co glycine solutions. Pure zinc deposits (Fig. 9a) present characteristic hexagonal crystals, which are normally obtained in zinc deposition [43,44]. The zinc crystals exhibited a range of sizes, and the larger grains were of approximately 5 µm in diameter on which smaller crystals grew. In the presence of 0.01 M cobalt in the bath, an appreciable change was observed in the deposit morphology with the grain size decreasing to around 1 µm diameter, the deposits being compact and presenting a clear gray color. The presence of cobalt apparently modified the growth of zinc nuclei, leading to the fine-grained deposits obtained under anomalous composition. This observation is in accord with the results reported by Alcalá et al. [25]

and Karwas and Hepel [43] for acidic-chloride electrolytes. They obtained fine-grained deposits in the presence of high zinc/cobalt electrolyte ratios but dendritic deposits when the relative cobalt concentration was increased.

With a cobalt concentration of 0.02 M, a deposit with even smaller grain size was observed (Fig. 9c), presenting an amorphous structure, and this was also observed at higher cobalt concentrations (up to 0.05 M).

Fig. 9f shows the influence of the current density on the morphology of the deposits of the ZnCo alloy. It is seen that the deposit obtained with 0.05 M Co at -30 mA cm^{-2} presented a compact polyhedral morphology, in contrast to the deposits with fine grains obtained at -10 mA cm^{-2} . Therefore, Co plays the role of a grain-size refiner at low current densities even at high Co concentrations. At higher current density and high Co content in the deposit, Co imposes its own structure with a more columnar growth. In order to verify this last assumption, we performed crystallographic analysis of all the deposits.

5.3. Crystallographic structure

The preferential crystal orientation of zinc electrodeposits depends on the experimental conditions [44,45], such as current density, pH and temperature. Plane (002) has been associated with the growth of hexagonal zinc crystals parallel to the substrate [44]. Fig. 10 shows the X-ray diffraction patterns obtained



Fig. 10. X-ray diffraction patterns for Zn and alloy electrodeposits obtained on AISI 1018 steel, $j = -10 \text{ mA cm}^{-2}$, t = 300 s. Bath cobalt concentrations: (a) 0.0 M; (b) 0.01 M; (c) 0.05 M; (d) 0.10 M; (e) 0.05 M with $j = -30 \text{ mA cm}^{-2}$.

for several Zn and ZnCo alloy deposits. In the absence of cobalt, the peaks associated with the characteristic crystallographic planes for zinc were observed, the peak associated with plane (002) having the highest intensity.

When the deposit was formed in the presence of 0.01 M Co(II), a considerable decrease of the (002) peak was observed, as well as of the peaks associated with planes (102), (103) and (110), due to the change in orientation of the Zn crystallographic planes by the incorporation of cobalt. The persistence of those peaks, although with lesser intensity, suggests the appearance of a zinc-rich (η -phase) ZnCo alloy [46], since the diffraction pattern of the Zn–Co solid solution η -phase is very similar to pure Zn diffraction pattern [44]. When the cobalt content in solution was increased to 0.05 M, the peak associated with plane (002) diminished further. A peak then appeared at a value of $2\theta = 42.5^{\circ}$ (peak i), which is associated with the formation of cobalt oxide (PDF 43-1004).

An increase of peak (i) was observed when the cobalt level in the solution was increased to 0.1 M. At the same time, the intensity of the peaks for planes (0 0 2) and (1 0 1) of the η -phase decreased further. The decrease of those peaks may be attributed to the decrease of the thickness of the coatings obtained when the cobalt concentration in the bath increased because of the loss of current efficiency with increasing cobalt levels.

The deposit obtained at higher current density and 0.05 M Co(II) (Fig. 9e) presents a change in the X-ray diffraction pattern. Three peaks appear at $2\theta = 37.64^{\circ}$ (peak ii), 68.04° (peak iii), and 69.56° (peak iv), which are associated with the presence of cobalt hydroxide (PDF 45-0031). These results agree with the presence of oxygen observed in Fig. 7c, its level increasing as the distance from the substrate increases. The peak associated with the plane (1 0 1) shifted from 43.25° to 43.02°, indicating that the ZnCo alloy crystal lattice was deformed. At the same time, the peak associated with plane (0 0 2) disappeared completely, showing a preferential orientation of the crystals. There

is evidence of the formation of $Zn_{13}Co$ due to the presence of small peaks at 40.3° and 41.2° as well as the peak at $2\theta = 43.02^{\circ}$ (PDF 29 0523). The wide peak located at $2\theta = 44.56^{\circ}$ (peak v) may be associated with the presence of a pure cobalt phase (PDF 01-1255). These changes in the X-ray patterns for higher current density correspond to the changes in the electrochemical behavior seen in Fig. 3 and to the morphology observed in Fig. 9f, and they reflect the modifications of the composition profiles of the ZnCo alloy shown in Fig. 7c. All of the observations with the crystallographic structures, the morphology, and the composition of the coatings may be associated with changes in the electrochemical conditions under which the deposits are formed.

Rashwan et al. [30] also studied ZnCo electrodeposition in glycine solution; they obtained anomalous deposits and observed that the crystallographic structure depended on applied current density. They reported the appearance of Co_5Zn_{21} and $CoZn_{13}$ phases at low and higher current densities, respectively.

The GDS analysis showed the presence of oxygen within the deposit, and this may be attributed to an increase in the interfacial pH during deposition. The formation of cobalt hydroxide at increased current density or higher Co(II) concentration is confirmed by the appearance of the X-ray peaks associated with cobalt hydroxide.

6. Conclusions

This work has explored the influence of cobalt on zinc electrodeposition from alkaline glycine solutions. Thermodynamic stability calculations identified the potential stability of the various complexes that can form in this complexing medium. These thermodynamic calculations showed that the experimental conditions favor the formation of Zn–glycine and Co–glycine complexes, the dominant species being ZnL'_3 and CoL'_3 . The effects on the electrochemical behavior of the system of the zinc and cobalt concentrations were studied experimentally.

The cobalt-deposition overpotential increased in the presence of zinc ions, while the presence of Co(II)' ions favored the hydrogen-evolution reaction. Based on the predominance zone diagrams and according to the electrochemical studies performed, it is suggested that the alloy deposition process can be explained in terms of the metal hydroxide suppression mechanism, in which the initial formation and adsorption on the electrode surface of an insoluble $Zn(OH)_2$ and, later on, of insoluble $Co(OH)_2$, moderate the reduction of both zinc and cobalt, especially when the hydrogen-evolution reaction becomes more intense. A switching-potential study showed that Zn-rich ZnCo deposits are obtained at the early stages of electrodeposition, i.e. at moderately negative potentials.

The presence of cobalt in the deposit was evidenced by the appearance of several stripping peaks associated with different phases of Zn–Co that depend on the cobalt bath concentration and on the applied potential or current density. The cobalt content modified the growth habit of the deposits, favoring the formation of smaller grains and increasing the number of crystals formed. When the cobalt concentration was increased, finer-grained deposits were obtained. When current density increased,

the deposit morphology was modified, exhibiting polyhedral crystals.

The study of X-ray diffraction patterns showed that cobalt affects the dominant zinc plane (002). The presence of cobalt oxide and hydroxide in the alloy was also indicated, possibly formed by the occlusion of $Co(OH)_2(s)$ from a surface precipitate. Cobalt content was not homogeneous across the deposited film, indicating that several processes are probably involved during electrodeposition and film growth.

Further studies of the system, leading to quantitative electrode-kinetics models, are required to predict the alloy composition of coatings produced under various operating conditions.

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