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Electrochemical study on the inhibitory effect of the underpotential deposition of zinc on Zn–Co alloy electrodeposition

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Abstract

Zn–Co alloy electrodeposition from chloride baths containing different Zn²⁺/Co²⁺ ratios was investigated by cyclic voltammetry and anodic linear sweep voltammetry using a Pt electrode. The peaks were attributed by means of EDX analysis, SEM and TEM observations performed on some alloys potentiostatically deposited. In the range of potential where zinc deposits underpotential, cyclic voltammetry showed a complex cathodic peak with one maximum and two shoulders, correlated with the deposition of different cobalt rich alloys. Up to four anodic peaks, two correlated with zinc oxidation from η and γ phases and two correlated with oxidation of solid solutions of zinc in cobalt, were observed. ALSV and TEM indicated that the remarkable increase in Zn content of the alloy, which occurs with a strong inhibition of the process at potentials more negative than that of the cathodic peak and more positive than the bulk deposition potential of zinc, is due to the deposition of γ phase. No inhibition of the alloy deposition process was observed with very low concentrations of zinc (<0.015 M) in the bath containing 0.19 M Co²⁺.

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1. Introduction

The electrodeposition of Zn–Co alloys is of interest because these alloys have a significantly higher corrosion resistance than pure zinc. The electrodeposition of zinc alloys with group eight metals (Ni, Co and Fe) is classified as anomalous co-deposition, according to the Brenner definition [1], because the less noble metal deposits preferably on the cathode with respect to the more noble one. However, in certain experimental conditions [2–4], the co-deposition of zinc alloys with group eight metals is not anomalous and deposits containing a percentage of the more noble metal higher than that of the bath can be obtained. On performing galvanostatic electrodepositions of zinc alloys, an abrupt change in potential, alloy composition and current efficiency can be observed at certain current density values,

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which depend on the experimental conditions [2–4]. Some authors [2] attributed this change to the transition from normal to anomalous co-deposition. Recently, both for Zn–Co and Zn–Ni alloy deposition, it was found that the abrupt change does not always correspond to the normal/anomalous transition, because this change was observed even at conditions where the transition does not occur [4–6].

Previously [4,6], by means of potentiostatic tests, the obtainment of Zn–Co and Zn–Ni alloys, rich in cobalt or nickel, respectively, at low polarization (from -0.700 to -1.000 V versus Ag/AgCl) was found to be due to zinc depositing at potentials more positive than its deposition potential (underpotential deposition), driven by reduction of the more noble metal, in agreement with the mechanism proposed by Fabri Miranda et al. for Zn–Ni alloys [7]. The underpotential deposition of Zn was observed also on a cobalt electrode from Co-free solution [8].

Previous work on Zn–Co electrodeposition [4] showed that in the normal co-deposition range the polarization curve exhibits a maximum, followed by a strong decrease in current

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density at potentials more negative than about -0.840 V. Analysis of the partial current density curves indicated that, under the experimental conditions used, the maximum cannot be attributed to hydrogen reduction only. This inhibition is probably the cause of the abrupt change in potential, alloy composition and current efficiency observed during galvanostatic electrodepositions when the current density applied drives the cathodic potential in this range. At potentials more negative than about -1.000 V, depending on the experimental conditions, the equilibrium potential of zinc is reached and very zinc-rich alloys are obtained, due to the large differences between the exchange current densities of zinc and nickel or cobalt [9–11].

Both for Zn–Co and Zn–Ni alloys, the deposition of alloys of different composition, morphology and structure depending on the cathodic potential was observed [4,6]. In particular, the maximum in the polarization curve, obtained by plotting as a function of the potential the stationary values of *j* measured during potentiostatic electrodepositions, coincides with a maximum in the internal stress of the deposits [4,6]. Previous results on Zn–Co alloy [4] showed that X-ray analysis is not always able to identify the deposited phases because this alloy is poorly crystallized in a wide range of composition, with a large amount of crystallites too small for resolution by this technique.

The aim of this work was to study the Zn–Co alloy electrodeposition from chloride baths without complexing agents by cyclic voltammetry (CV) and anodic linear sweep voltammetry (ALSV), to identify the deposited phases at the various potentials and to investigate the cause of the inhibition observed at low polarizations. Scanning electronic microscopy (SEM) and transmission electronic microscopy (TEM) observations together with energy dispersive X-ray (EDX) analysis were carried out on some deposits obtained potentiostatically. The attention was particularly focused on the range of potential where zinc deposits underpotential.

2. Experimental details

Zn–Co alloy potentiostatic electrodepositions were carried out at 55 °C for 200 s, using a bath of the following composition: 54.57 g dm^{-3} (0.40 M) ZnCl₂; 45.30 g dm^{-3} (0.19 M) CoCl₂·6H₂O; 26 g dm^{-3} (0.42 M) H₃BO₃; 220 g dm^{-3} (2.95 M) KCl (pH 4.2). This bath was chosen in order to correlate of the present results with those obtained previously [4]. Cyclic voltammetry was carried out from similar baths, changing the concentrations of Zn²⁺ (0, 0.0015, 0.015, 0.1 and 0.4 M) or Co²⁺ (0, 0.002, 0.02, 0.1 and 0.19 M), while maintaining constant Co²⁺ (0.19 M) or Zn²⁺ (0.4 M) concentrations, respectively. All the solutions were prepared with doubly distilled water and analytical grade reagents.

Potentiostatic electrodepositions were carried out on mild steel and platinum disks. Cyclic voltammetry and anodic linear sweep voltammetry were performed on a platinum disk; a platinum substrate was used because the corrosion potential of iron in the deposition bath (-0.600 V versus Ag/AgCl)is lower than that of cobalt and cobalt-rich alloy dissolution potential. Stripping analysis was performed immediately after potentiostatic depositions at different potentials without removing the electrode from the solution and selecting, in each case, an initial potential for which deposition did not occur. The deposition and stripping charges were calculated by integrating the current/time curves. All the potentiodynamic polarizations were carried out using a scanning rate of 5 mV s^{-1} , chosen after preliminary tests. A conventional three-electrode cell was used. The working electrode was mounted in a flat specimen holder with an exposed area of 0.71 cm^2 ; the counter-electrode was a platinum spiral and the reference electrode was a Ag/AgCl electrode, mounted inside a Luggin capillary, whose tip was placed next to the working electrode surface. Before each experiment, solutions were deaerated with N2 inside the cell. Electrochemical measurements were performed using an EG & G Princeton Applied Research potentiostat/galvanostat Mod. 273 controlled by a personal computer. In order to determine the percentage composition of the electrodeposited alloys, some deposits were stripped in a minimum volume of 1:3 HCl solution and analysed for cobalt and zinc by means of an inductively coupled plasma spectrometer (Perkin-Elmer Optima 3200 XL).

The deposits obtained potentiostatically were characterized by means of a Philips XL 20 scanning electron microscope and an energy-dispersive X-ray spectrometer (Edax PV9800). The phases of the deposit obtained potentiostatically at -0.96 V were identified by means of a Philips CM 200 transmission electron microscope.

3. Results and discussion

Potentiostatic electrodepositions in the potential range from -0.760 to -1.100 V were performed on iron and platinum cathodes from the bath containing 0.19 M Co²⁺ and 0.40 M Zn²⁺ (Co²⁺ percentage in the bath (Co_b): 30 wt.%), in order to study the effect of the change in substrate. The results indicated that the change in substrate does not significantly affect the polarization curves and the composition of the deposits (Fig. 1). On the contrary, some tests performed on glassy carbon electrode showed a strong decrease in the deposition current density, which starts to increase only when the electrode surface was totally covered by the alloy. These results agree with those of other authors [8,12] that found a strong inhibition of the process on glassy carbon cathode.

Fig. 2 shows the cyclic voltammogram obtained from the same bath used for the potentiostatic tests. The scan was started from the rest potential of Pt (-0.100 mV) and reversed at -1.100 V. The curve shows that the alloy deposition starts at about -0.750 V, according to the potentiostatic tests results (Fig. 1); the cathodic current peak, observed in the polarization curve obtained by means of the potentiostatic tests (Fig. 1), is a complex peak with one maximum (C₂) and



Fig. 1. Polarization curves and effect of the deposition potential on zinc percentage (Zn_d) in the Zn–Co alloy electrodeposition on iron (**I**) and on platinum (**A**) substrate. 0.40 M Zn²⁺; 0.19 M Co²⁺. CRL: composition reference line.

two shoulders (C_1 and C_3). In the reverse scan, C_2 slightly increases and the deposition continues until about -0.670 V, at potential values where the deposition does not occur in the direct scan; this fact indicates that the presence of the alloy on the cathode surface enhances the process. Three peaks (A_1 - A_3) appear in the anodic scan.

To attribute the peaks observed by CV, a wide range of Zn^{2+} and Co^{2+} concentrations in the bath were used. Fig. 3 shows cyclic voltammograms obtained by adding different concentrations of Co^{2+} to the bath containing 0.40 M Zn^{2+} . Pure zinc deposition (Fig. 3a) starts at about -1.070 V; in fact, on performing CV with less cathodic reverse potentials, no anodic peaks were observed. The pure zinc oxidation peak (A₄) was found at about -0.980 V, in agreement with the results obtained in chloride media by other authors [13]. This peak has been attributed to the dissolution of zinc from η phase (hexagonal structure). By adding up to 0.002 M Co^{2+} to the bath (curve not shown in the figure), only a slight shift towards more positive potentials of the zinc dissolution peak was found, due to the presence in the alloy of a small amount



Fig. 2. Cyclic voltammogram. 0.40 M Zn^{2+} ; 0.19 M Co^{2+} ; 5 mV s^{-1} .



Fig. 3. Cyclic voltammograms obtained with various Co^{2+} concentrations in the bath containing 0.4 M Zn²⁺. (a) 0 M Co²⁺, (b) 0.02 M Co²⁺ and (c) 0.10 M Co²⁺; 5 mV s⁻¹.

of Co, which increases its oxidation potential. No anodic peaks at more noble potentials appear, indicating that a solid solution of cobalt in zinc n phase is deposited [14]. The curve obtained from the bath with 0.02 M Co^{2+} (Fig. 3b) shows in addition to A₄ an anodic peak at -0.450 mV; on magnifying the curve (inset in Fig. 3b) a small reduction wave around -0.800 V in the direct scan and a reduction peak in the reverse scan can be observed. The charge related to the anodic peak at $-0.450 \,\mathrm{mV}$ is almost equal to the sum of that related to the reduction wave and that of the reduction peak; this suggests that the second anodic peak is mainly related to the oxidation of the alloy obtained at potentials more anodic than that of the bulk deposition of zinc. On cutting off the reverse scan at -0.800 V, EDX analysis performed on the cathode revealed that the deposit contains Zn 40%. On increasing Co^{2+} content in the bath to 0.10 M (Fig. 3c), the cathodic curve becomes similar to that obtained from the bath with 0.19 M Co^{2+} (Fig. 2). The anodic curve does not show the peak of the Zn dissolution from η phase (the current density

of the reverse scan is almost the same as the direct one in the range of potential where η phase dissolution occurs), but shows peak A₁, shifted by $\sim 80 \text{ mV}$ towards more cathodic potentials with respect to that obtained from the bath with 0.19 M Co^{2+} (Fig. 2). An anodic peak at about -0.600 Vhas also been found by other authors [11,14] and has been attributed to the oxidation of zinc from γ phase (Co₅Zn₂₁, bcc structure, equilibrium zinc percentage 82%). The presence of A₁ and the absence of A₄ indicate that the phase prevalently deposited at the more cathodic potentials changes from η to γ . The shift of the peak potential with respect to that obtained from the bath with $0.19 \,\mathrm{M}\,\mathrm{Co}^{2+}$ is due to the higher zinc percentage in the deposit. On cutting off the reverse scan after A1 peak (-0.580 V), EDX analysis performed on the remaining deposit indicates that it contains about 9% Zn; so A₂ and A₃ are related both to the dissolution of Co remaining after Zn oxidation from γ phase and to the oxidation of cobalt rich Zn-Co alloy deposited in correspondence of the reduction peak.

Fig. 4 shows the effect of different concentrations of Zn^{2+} in the bath containing 0.19 M Co²⁺. The curve related to the pure cobalt bath (Fig. 4a) shows that the cathodic current density reaches a limit value because the process is under mass transfer control [15,16]. The corresponding anodic peak was observed at -0.140 V, a potential value similar to that found by other authors for the dissolution of electrodeposited pure cobalt [12,15]. Previous results [4] showed that pure cobalt deposited in these experimental conditions is poorly crystallized and X-ray diffrattograms showed only low peaks related to the presence of α phase (hexagonal structure). A structure prevalently hexagonal-close-packed (from 96 to 100%) has also been found by other authors for pure cobalt deposited from chloride media [17,18]. It is noteworthy that this peak is very large: the presence of a large shoulder may imply that the cobalt deposits with different energy states. Two oxidation waves for pure cobalt deposited from low melting point molten salts have been found by other authors [8]. The curve obtained by adding 0.0015 M Zn²⁺ shows the appearance of C_1 in the cathodic scan, which leads to a slight increase in the whole cathodic curve (Fig. 4b). The anodic curve does not change appreciably: only a slight increase in A3 can be observed as a consequence of the higher cathodic current. This result indicates that a low amount of zinc is incorporated in the cobalt lattice without perceptive changes in the electrochemical characteristics of the alloy. With 0.015 M Zn²⁺ in the bath, a slight decrease in the deposition current at potentials more cathodic than -0.950 V (Fig. 4c) was observed, indicating an inhibition of the cathodic process; the anodic curve shows the appearance of A_2 at -0.250 V and a decrease of A₃. Peak A₂ potential corresponds to that of the shoulder in the curve of pure cobalt oxidation (Fig. 4a), so it can be related to the dissolution of a solid solution of zinc in cobalt at a higher energy than that oxidized in peak A₃. The alloys potentiostatically electrodeposited in the potential zone of peak C₁ (-0.780 V) from pure Co bath and from the baths containing 0.0015 and 0.015 M Zn²⁺ were black and dull, almost similar



Fig. 4. Cyclic voltammograms obtained with various Zn^{2+} concentrations in the bath containing 0.19 M Co_b. (a) 0 M Zn^{2+} , (b) 0.0015 M Zn^{2+} , (c) 0.015 M Zn^{2+} and (d) 0.10 M Zn^{2+} ; 5 mV s⁻¹.

to the pure cobalt deposit. SEM images of these alloys show that the increase in zinc content leads to a strong decrease in grain size (Fig. 5a and b, related to the deposits obtained from a zinc-free bath and from the bath containing 0.015 M Zn^{2+} , respectively). Their Zn percentage ($\leq 2.6\%$) is in the range of the equilibrium solubility of Zn in electrodeposited cobalt α phase (<3% [19]). Alloys obtained potentiostatically from the bath containing 0.015 M Zn^{2+} at -0.945 V and at more negative potentials, where a slight inhibition of the codeposition was found, were grey bright and strongly cracked. The deposit obtained at -0.945 V (in the potential zone of peak C₂) contains 9.5% Zn; on depositing at potentials more cathodic than -0.945 V, the alloy zinc content (9.6%) does not increase appreciably, but the deposit morphology has a fluffy aspect (Fig. 5c). On performing cyclic voltammetry with reverse potential -0.800 V, only A₃ was observed in the anodic scan. Therefore, peak A2 can be attributed to the dissolution of the alloy deposited in the potential zone of peak



Fig. 5. SEM images of some Zn–Co alloys obtained potentiostatically with various Zn^{2+} concentrations in the bath containing 0.19 M Co_b: (a) 0 M Zn²⁺, -0.780 V; (b) 0.015 M Zn²⁺, -0.780 V; (b) 0.015 M Zn²⁺, -0.780 V; (c) 0.015 M Zn²⁺, -1.070 V, 9.6% Zn_d; (d) 0.10 M Zn²⁺, -0.920 V, 19.5% Zn_d.

 C_2 . With 0.10 M Zn²⁺ in the bath (Fig. 4d), the direct cathodic scan shows an abrupt decrease in current density at potentials more negative than -0.900 V; the curve becomes similar to that observed with 0.4 M Zn^{2+} and C_3 appears, which remarkably increases in the reverse scan. Both A2 and A3 decrease and shift towards more negative potentials, according to the higher zinc content; the absence of A₁ indicates that no appreciable amount of γ phase is deposited. The zinc percentage of the deposit obtained potentiostatically at -0.920 V (in the potential zone of peak C_3) from the bath containing 0.10 M Zn^{2+} reaches 19.5%; the deposit shows a nodular morphology with very low grain size (Fig. 5d). Similar structures are attributed to a renucleation process, due to the incorporation of impurities to the grain boundaries, which stops the grain growth and leads to a globular deposits [20]. Probably, in this case zinc acts as an impurity. Other authors attributed the nodular structures in Zn–Co alloys to the coexistence of γ and α phases [19]. However, in this case peak A₁, correlated to the dissolution of γ phase, was not observed in the anodic curve (Fig. 4d). On increasing Zn^{2+} content in the bath to 0.40 M, the alloy obtained potentiostatically in the potential zone of peak C_3 (-0.880 V) contains 20.5% Zn (Fig. 1); it is noteworthy that this small increase in zinc content causes a further strong inhibition of the process, in fact the deposition

current density decreases from 14.9 to 7.0 mA cm^{-2} (Figs. 4d and 2, respectively).

Cyclic voltammograms show the deposition of several different phases during the potential sweep. The deposition of cobalt rich alloys during the reverse scan can lead to phase transitions of the zinc rich alloys deposited at the lower potentials; this could explain why A1 does not appear in the curve of Fig. 4d. To investigate if γ phase Co₅Zn₂₁ deposits in the range of potential where the co-deposition is strongly inhibited, stripping analyses after potentiostatic depositions from the bath containing 0.4 M Zn^{2+} were also performed. Only A₃ peak was observed on the curves related to the deposits obtained at -0.800 V (Fig. 6a, curve 1). The stripping curves of the alloys deposited at -0.840 and -0.880 V (in the potential zone of peaks C_2 and C_3 , respectively) show the presence of A₂ and a progressive decrease of A₃ (Fig. 6a, curves 2 and 3, respectively). During the stripping tests of the alloys obtained in the range from -0.880 to -1.000 V it was very difficult to find an initial potential value where the current was zero. In fact, even upon changing the initial stripping potential of 1 mV, a low anodic or cathodic current was always observed. In some cases, the current was initially anodic and then became rapidly cathodic. This fact could indicate the occurrence of two opposite reactions (dissolution and



Fig. 6. Potentiodynamic stripping curves obtained after potentiostatic deposition at different potentials from the bath containing $0.40\,M\,Zn^{2+}$ and $0.19\,M\,Co^{2+}$: (a) curve 1: $-0.800\,V$, 15.6% Zn_d; curve 2: $-0.840\,V$, 20.5% Zn_d; curve 3: $-0.880\,V$, 19.2% Zn_d; (b) curve 4: $-0.960\,V$, 39.5% Zn_d; curve 5: $-1.050\,mV$, 76.2% Zn_d; 5 mV s^{-1}.

deposition) at these potentials. The stripping curve related to deposits obtained at a potential corresponding to the minimum in deposition current density (around -0.960 V) shows a small peak at -0.600 V (Fig. 6b, curve 4). The peak potential corresponds to the dissolution of zinc from γ phase, but the charge related to the peak is less than 2% of the total one, very low compared to the strong increase in zinc content with respect to the deposit obtained at -0.880 V (from 22 to 46%, Fig. 1). The comparison of the oxidation and the deposition charge showed that the former (0.85 C) is remarkably lower than the latter (1.35 C); this difference is higher than that expected on the basis of the current efficiency data $(\eta_{\text{alloy}} = 81\%)$ and may indicate a reduction process during the anodic stripping. The small peak at -0.600 V is probably the result of two simultaneous reactions: the dissolution of the zinc-rich γ phase and the reduction of a cobalt rich phase or hydrogen discharge. The curve related to the oxidation of the alloy obtained at -1050 mV (Fig. 6b, curve 5) clearly shows peak A₁. It is noteworthy that when the peak at -0.600 V is present, A₂ disappears; this suggests that the deposition of γ phase suppresses the incorporation of zinc in the cobalt lattice.

TEM observations (Fig. 7a) on the deposit obtained potentiostatically at -0.960 V show that the alloy is made of crystallites, with dimensions ranging from 15 to about 30 nm, uniformly distributed in an amorphous matrix. The electron diffraction pattern of the crystalline phase corresponds to the γ phase (Co₅Zn₂₁) (Fig. 7b). The identification was carried





Fig. 7. (a) TEM image (dark field) of the alloy obtained potentiostatically at -0.960 V from the bath containing 0.40 M Zn²⁺ and 0.19 M Co²⁺. (b) Corresponding electron diffraction pattern.

out on the basis of JPDF 22–521 and of the results of other authors [8,14].

4. Conclusions

In the range of potential where underpotential zinc deposition occurs, cyclic voltammograms performed in chloride baths containing various Zn^{2+}/Co^{2+} ratios showed a complex cathodic peak with one maximum (C₂) and two shoulders (C₁ and C₃). Four anodic peaks (A₁–A₄), which indicate the formation of different phases during the potential sweep, were observed:

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- At potentials more positive than C_1 solid solutions of Zn in α Co correlated to the anodic peak A₃, are deposited. Zn percentage in the deposit appreciably increases with the decrease in potential.
- At potentials around C_2 the deposit appears structureless, with very small grain size; in the anodic curve, A_2 and A_3 peaks appear, both correlated to the oxidation of solid solutions of zinc in the cobalt lattice. In this range of potential, the deposition current density decreases on increasing Zn concentration in the bath.
- At potentials around C₃ nodular deposits were obtained. On passing from C₂ to C₃, Zn content in the alloy increases very slightly.
- At potentials more negative than that of C₃ a remarkable increase in Zn content of the alloy occurs, followed by a strong inhibition of the alloy deposition process. The deposition of γ phase in this range of potential, not shown by CV, was observed using ALSV, which showed the anodic peak A₁, correlated to the dissolution of Zn from γ phase. TEM analysis confirmed the deposition of γ phase together with an amorphous one.
- At potentials lower than about -1.000 V the equilibrium deposition of zinc-rich phases (γ, correlated to anodic peak A₁ or η, correlated to A₄, depending on the bath composition) leads to the increase in deposition current density.

No inhibition of the alloy deposition process was observed with very low concentrations of zinc (<0.015 M) in the bath containing 0.19 M cobalt.

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