ORIGINAL PAPER

Effects of thiourea and urea on zinc–cobalt electrodeposition under continuous current

M. Mouanga · L. Ricq · P. Berçot

Abstract The effect of thiourea and urea on zinc-cobalt alloys obtained from chloride baths under continuous current deposition are described and discussed. The deposit morphology was analyzed using Scanning Electron Microscopy (SEM) and an X-Ray Diffraction (XRD) was used to determine the preferred crystallographic orientations of the deposits. The use of additives does not refine the grain size of the Zn–Co alloy and an especially porous alloy was produced in the presence of urea. The preferred crystallographic orientations of zinc–cobalt alloys do not change in the presence additives. Zinc–cobalt alloys were without texture in the presence and absence of additives. Also, in the absence of additive and in the presence of urea, the XRD lines of the Zn–Co alloys are slightly shifted with respect to the pure zinc XRD lines, whereas, in the presence of thiourea, the XRD lines are not shifted. The alloy composition was examined using Energy Dispersive X-ray Fluorescence Spectroscopy (EDXRF). The percentage of cobalt in the alloy decreases slightly from 1.04 to 0.91 wt.% in the presence of urea and in the presence of thiourea it increases from 1.04 to 7.70 wt.%. Voltammetric studies show that thiourea increases the reduction rate of cobalt. This explains the increase in cobalt percentage in the alloy in the presence of thiourea.

Keywords Zinc–cobalt · Electrodeposition · Additives · XRD · SEM

1 Introduction

The electrodeposition of zinc–cobalt alloys is of interest because these alloys exhibit significantly higher corrosion resistance than pure zinc [1, 2]. Furthermore, other properties such as ductility, weldability, hardness and paintability are also improved. Only about 1 wt.% of cobalt is needed when alloying zinc with cobalt to obtain similar corrosion resistance to Zn–Ni (10–14 wt.%) [2–5]. As characterized by Brenner et al., the electrodeposition of Zn–Co alloys from aqueous plating baths is codeposition of the anomalous type; that is, the less noble component, zinc, deposits preferably with respect to the more noble cobalt [6]. Because of this fact, the cobalt content in the zinc–cobalt alloys produced from aqueous plating baths is usually low. The electrodeposition of Zn–Co alloys with a controlled morphology and composition has been investigated as a consequence of their observed improved corrosion resistance [7–11]. It is well known that additives which are often organic compounds yield deposits with suitable properties. Organic compounds containing oxygen, sulphur and nitrogen are among the most widely used additives in modern electroplating [3, 12–15]. These compounds can adsorb on the growing deposits or on the substrate with an impact on deposit properties and the electroplating process. In our previous studies, we have investigated the influence of thiourea and urea on the zinc deposits under continuous current deposition and from a chloride bath [16]. The use of thiourea produced deposits with a finer grain size and the preferred crystallographic orientations were modified; whereas, a non-improvement in corrosion resistance was observed. Urea did not refine the grain size but the corrosion resistance was improved. These effects were attributed to the sulphur atom contained in thiourea and to the oxygen atom in urea. In this study,

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the influence of thiourea and urea on Zn–Co electrodeposition has been investigated. The composition, morphology and preferred crystallographic orientations of the deposits obtained in the presence and absence of additives has been analyzed and compared. The influence of each additive on the plating process is also discussed.

2 Experimental

Zn–Co samples were prepared by electrodeposition under a continuous current on the DC 01 steel panel from chloride baths at room temperature (Table 1). The electrolytes were prepared using milli-Q water. The thickness of the deposits was 12 ± 1 μm and the alloy area was (2×2 cm). Prior to each electrodeposition, the tested steels were degreased in sodium hydroxide solution (40 g L^{-1}; 64.5 °C) then mechanically cleaned with emery paper (1,000) and etched with a hydrochloric acid solution (pH = 0.5) for 2 min and rinsed with distilled water. The DC 01 steel panel was also used for the cathodic polarization measurements and chronopotentiometric experiments from various electrolytes with a platinum wire as counter electrode and a saturated calomel electrode (SCE) as reference electrode.

A scanning electron microscope (JSM-5600, SEM, JEOL) was used to analyze the morphology of the deposits obtained in the presence and absence of additives. The preferred orientations of the deposits were determined by X-Ray Diffraction (XRD) using a D8 advance Bruker (with Bragg-Bretano configuration) with Cu-Kα radiation (λ = 1.54 Å). The 2θ range of 30°–100° was recorded at a rate of 0.02° s^{-1}. The texture coefficients (Tc) of the zinc deposits were calculated from the X-ray data using a Bruker program.

The thickness of the deposits was determined by a High Performance Energy Dispersive X-Ray Fluorescence Measuring Instrument (EDXRF) using a Fischerscope X-Ray XDAL. The EDXRF was also used to determine the zinc–cobalt alloy composition.

Table 1 Plating bath composition for zinc–cobalt electrodeposition

Solution compositions
65 g L^{-1} ZnCl$_2$ + 20 g L^{-1} + CoCl$_2 \cdot$ 6H$_2$O + 200 g L^{-1} KCl + 20 g L^{-1} H$_3$BO$_3$ (basic solution)
Basic solution + 13×10^{-3} mol L^{-1} urea
Basic solution + 13×10^{-3} mol L^{-1} thiourea
With stirring
Room temperature
pH = 4.5

3 Results and discussion

3.1 Alloy characterization

3.1.1 Alloy composition and current efficiency

The alloy composition is given in Table 2. In the absence of additives, the percentage of cobalt in the zinc–cobalt alloy is 1.04 wt.%. In the presence of urea, the cobalt percentage decreases from 1.04 % to 0.91 wt.% and in the presence of thiourea, it increases from 1.04 to 7.70 wt.%. Ultimately, the presence of additives affects the alloy composition. Many authors have observed the effects of organic additives on the alloy composition. Lallemand et al. reported a decrease of iron content in iron–cobalt alloy (from 17.9 to 8.6 %wt. Fe in the presence of sodium saccharin and from 17.9 to 10.7 %wt. Fe in the presence of phthalimide) [13]. We have also observed that for the free bath and in the presence of urea, the percentage of cobalt in the alloy (1.04 and 0.91 wt.% for the free bath and in the presence of urea, respectively) is less than the percentage of cobalt in the electrolyte (7 wt.%). This indicates that the codeposition is of anomalous type [17]. In the presence of thiourea, the percentage of cobalt in the alloy (7.70 wt.%) is slightly more than the percentage of cobalt in the electrolyte (7 wt.%). In the presence of thiourea, the codeposition changes type. The codeposition becomes an equilibrium type in the presence of thiourea. The Zn–Co alloys with cobalt content of more than 6 or 7 wt.% have not been widely reported [5]. This may be due to the perceived limitations arising from anomalous codeposition according to Brenner's [6] definition of anomalous codeposition, since the preferential deposition of zinc was observed under a wide range of conditions, while the content of noble element cobalt in the deposits was much less than that in the bath. To obtain a higher percentage of cobalt in the Zn–Co alloy than the percentage of cobalt in the bath, some authors used pulse current deposition [5]. With our results, we have seen that it is possible to obtain more than 6 wt.% cobalt in the zinc–cobalt deposits using thiourea as an additive. From the comparison between thiourea and urea, it can be assumed that the sulphur atom contained in thiourea enhances the reduction rate of the cobalt ion while consequently increasing the percentage of

Table 2 Cobalt weight percentage in Zn–Co alloy in the presence and absence of additives

System	Current density (A dm^{-2})	Cobalt weight percentage (%)
Without additive	4	1.04
Urea	4	0.91
Thiourea	4	7.70

cobalt in the alloy as well. Voltammetric studies will be conducted in order to verify this hypothesis.

The current efficiency (CE) of the zinc deposits was estimated using the expression:

$$CE = \frac{m_1}{m_2} \times 100 \tag{1}$$

where m_1 is the zinc–cobalt electrodeposited mass and m_2 the mass calculated by applying Faraday's law with respect to the percentage of each metal in the deposit, m_2, given by:

$$m_2 = \frac{I \times t}{nF \left(\frac{X_{Zn}}{M_{Zn}} + \frac{X_{Co}}{M_{Co}} \right)} \tag{2}$$

where M_{Co} is the atomic molar mass of cobalt, M_{Zn} the atomic molar mass of zinc, X_{Co} the percentage of cobalt in the alloy, X_{Zn} the percentage of zinc in the alloy, I the current and t the time necessary to give 12 ± 1 μm deposit thickness. Table 3 shows the CE values obtained in the presence and absence of additives. The CE decreases from 68 ± 2 to $59 \pm 4\%$ in the presence of thiourea and urea. The influence of another additive on the CE of the alloy has been investigated in our laboratory. It has been assumed that additives affect the current efficient of single metal or alloy deposition [14, 18]. The presence of thiourea and urea in the plating bath decreases the current efficiency of zinc–cobalt alloys.

3.1.2 Morphology and texture of zinc–cobalt deposits

The Zn–Co alloy coatings have the same structure as zinc deposits [1]. The preferred orientations of zinc–cobalt alloys were determined using the Muresan method [19–21] calculating a texture coefficient (Tc) using the equation:

$$Tc(hkl) = \frac{I(hkl)}{\sum I(hkl)} \times \frac{\sum I_0(hkl)}{I_0(hkl)} \times 100 \tag{3}$$

where $I(hkl)$ is the peak intensity of the zinc–cobalt electrodeposits and $\sum I(hkl)$ the sum of the intensities of the independent peaks. The index 0 refers to the intensities for the standard zinc powder sample. The preferred crystallographic orientation is indicated by a Tc value larger than unity. The diffractograms are shown in Fig. 1 and Tc are

Table 3 Current efficiency of Zn–Co alloys in the presence and absence of additives

System	Current density (A dm^{-2})	Current efficiency (%)
Without additive	4	68 ± 2
Urea	4	59 ± 4
Thiourea	4	59 ± 4

given in Table 4. From the data in Table 4, in the absence of additives, no significant value of Tc was obtained. Nevertheless, 21.7% of the zinc crystallites are oriented parallel to the (102) plane, 20.4% of the zinc crystallites are oriented parallel to the (110) plane, 20.6% of the crystallites are oriented parallel to the (101) and 20.4% of the crystallites are oriented parallel to (110). Zinc–cobalt alloy is without texture in the absence of additives. In the presence of thiourea and urea we have recognized the same observation. Zinc–cobalt is without texture except for an increase in the intensity of the (002) and (201) planes. Nevertheless, most intensity planes decrease in the
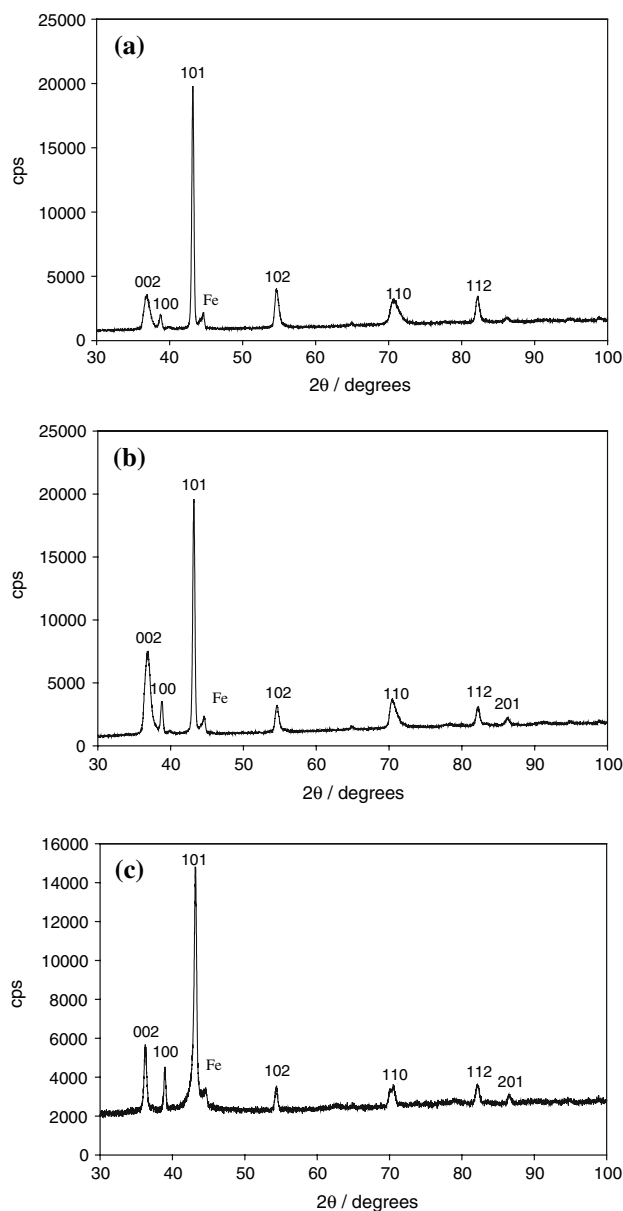

Fig. 1 X-ray diffractograms of Zn–Co alloys electrodeposited from chloride bath: (**a**) in the absence of additives, (**b**) in the presence of urea, (**c**) in the presence of thiourea

Table 4 Texture coefficients (Tc) of Zn–Co alloys

Plane (hkl)	Tc (hkl) (%) for alloy system		
	Basic solution	Urea	Thiourea
002	7.2	15.6	13.5
100	4.9	10.4	14.91
101	20.6	17.8	19.3
102	21.7	14.2	13.1
103	0	0	0
110	20.4	19.5	14.9
004	0	0	0
112	20.4	13.3	14.2
200	0	0	0
201	4.7	9.3	10.1
104	0	0	0

presence of additives. Even though the use of additives affects the electrocrystallization process with a consequence of altered deposit texture, the use of thiourea and urea did not cause this result. Also, for the free bath and in the presence of urea, the XRD lines of the Zn–Co alloys are slightly shifted with respect to the pure zinc XRD lines (Fig. 2). Under these conditions of low cobalt content (1.04 and 0.91 wt.% for the free Zn–Co and in the presence of urea respectively), metallic zinc can incorporate the cobalt atoms in its lattice. The inclusion of cobalt causes a significant distortion in the hexagonal structure of zinc. Gomez et al. also reported distortion of the structure of zinc with a low cobalt content [4]. The distortion of the structure of zinc can be inferred by a shift of the XRD lines of Zn–Co alloy with respect to those of pure zinc. In the presence of thiourea, the shift of the XRD lines is not observed whereas; the alloy contains 7.70 wt.% cobalt
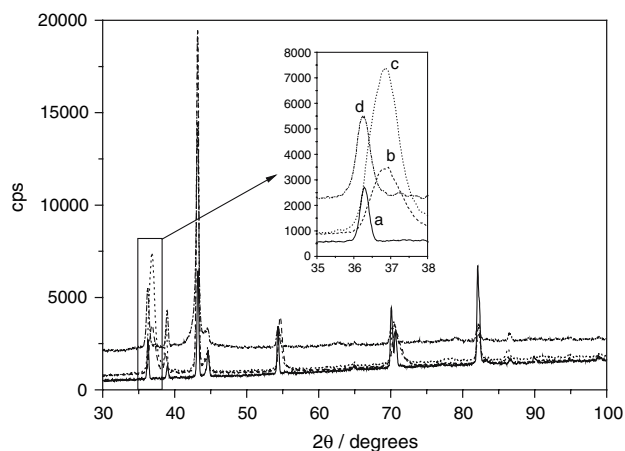

Fig. 2 X-ray diffractograms of Zn–Co alloys and Zn electrodeposited: (**a**) zinc electrodeposited from chloride bath, (**b**) zinc–cobalt in the absence of additives, (**c**) zinc–cobalt in the presence of urea, (**d**) zinc–cobalt in the presence of thiourea

(Fig. 2). The XRD studies show that in the presence of thiourea, the alloy behaves as pure zinc. With about 1 wt.% of cobalt, metallic zinc incorporates the cobalt atoms in its lattice with distortion of the hexagonal structure of zinc as consequence [4]. With an increase in the cobalt percentage in the alloy, the metallic zinc does not incorporate all the cobalt in its lattice. Gomes et al. [4] have noticed that at about 4–10 wt.% of cobalt content, the alloy is formed by the η-phase of zinc and the γ-phase of the zinc–cobalt alloy, whereas, Yan et al. [22] found that deposits obtained from an acidic sulphate bath with cobalt content about 6.6 wt.% were heterogeneous and contained Zn, ZnO and α-Co. In our conditions, in the presence of thiourea, the absence of a shift of the XRD lines of the alloys suggests that the alloy obtained is also heterogeneous but possess two crystal lattices; one crystal lattice of Zn and the second of Co. Our results are similar to those of Yan et al.; however in our conditions, it seems that the ZnO does not form. Nevertheless, supplementary investigations are needed to better understand the crystal lattice of zinc–cobalt alloy containing a high percentage of cobalt.

Scanning electron micrographs of the electrodeposits obtained from the chloride Zn and Zn–Co baths are shown in Fig. 3. Pure zinc deposit (Fig. 3d) presents the morphology commonly observed from the zinc deposit obtained from an acidic chloride bath [16, 18]. Also, zinc deposits have a clear grey colour (Fig. 3a). The Zn–Co alloy appears well distributed, compact and continuous, having a clear brown colour. Zinc–cobalt deposits exhibit finer grain size compared to pure zinc deposits. The Zn–Co alloys obtained in the absence of additives also appear well distributed, compact and continuous. The presence of cobalt modifies the growth of the zinc nuclei, leading to fine-grained deposits. In the presence of urea, zinc–cobalt alloy appears porous (Fig. 3b) and the grain size does not decrease; however, the morphology is the same with the free zinc–cobalt deposits. In the presence of thiourea (Fig. 3c), well-distributed and compact deposits were obtained. It seems that the deposit grain size does not decrease. Thiourea and urea do not act as levelling agents for zinc–cobalt deposition.

3.2 Voltammetric studies

Voltammetric experiments were conducted in order to study the influence of each additive. Chronopotentiometric experiments were carried out on DC 01 panel steel at a current density of 4 A dm^{-2} (current density used to prepare the deposits). The composition of each electrolyte is given in Table 5. The voltammetric experiments have been conducted by a number of authors to study the anomalous codeposition of various metals [15, 23, 24]. Abou-krisha

Fig. 3 SEM micrographs of Zn–Co electrodeposited from chloride bath at J = 4 A dm^{-2}: (**a**) in the absence of additives, (**b**) in the presence of urea, (**c**) in the presence of thiourea, (**d**) zinc electrodeposited from chloride bath at J = 4 A dm^{-2} in the absence of additives
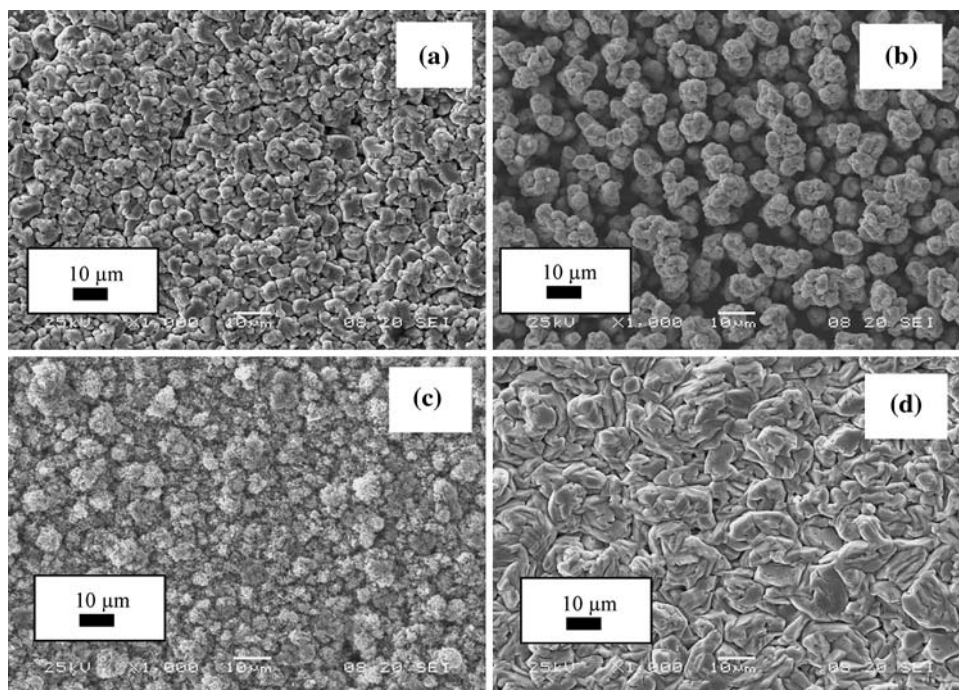
used cathodic polarization experiments to study zinc–nickel codeposition [23]. Results obtained from the cathodic polarization experiments were confirmed by the chronopotentiometric experiments.

The mechanism of zinc–cobalt codeposition from an acidic chloride bath is not well investigated. Nevertheless, for cobalt deposition, several authors [25–27] have proposed a mechanism consisting of two consecutive one-electron steps.

$$Co^{2+} + OH^- + e^- \rightarrow CoOH_{(ads)} \tag{4}$$

$$CoOH_{(ads)} + H^+ + e^- \rightarrow Co + H_2O \tag{5}$$
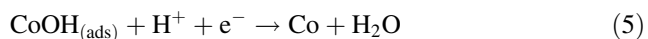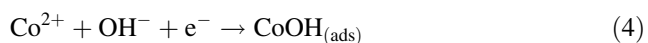
The combination of these two equations gives the simplified equation:

$$Co^{2+} + 2e^- \rightarrow Co \tag{6}$$

Zinc deposition from a chloride bath as proposed by a number of authors [28–31] proceeds via the reduction of the complex ion $[ZnCl_4]^{2-}$ according the reaction:
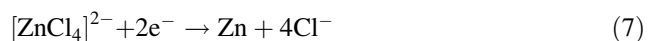
$$[ZnCl_4]^{2-} + 2e^- \rightarrow Zn + 4Cl^- \tag{7}$$

Table 5 Electrolyte composition (g L^{-1}) for voltammetric studies; (a) electrolyte containing $[ZnCl_4]^{2-}$ only, (b) electrolyte containing Co^{2+} only, (c) electrolyte containing the two ions

Electrolytes	H$_3$BO$_3$	KCl	ZnCl$_2$	CoCl$_2 \cdot$ 6H$_2$O
Zn	20	200	65	0
Co	20	200	0	120
Zn–Co	20	200	65	20

Figures 4–6 show that in the presence and absence of additives, the cathodic polarization curves satisfy the conditions to prepare the Zn–Co alloys [32]. The potentials of the chronopotentiometric curve obtained with the electrolyte containing both ions (Co^{2+} and $[ZnCl_4]^{2-}$) are more negative than that from the less noble metal ion ($[ZnCl_4]^{2-}$).

To observe the influence of each additive on the codeposition process, we have traced the chronopotentiometric curves obtained with only the Co^{2+} ion, with only the $[ZnCl_4]^{2-}$ ion and with both ions in the presence and absence of additives.

Figure 7 shows the chronopotentiometric curves obtained with the electrolyte containing only $[ZnCl_4]^{2-}$ in the presence and absence of thiourea. In the presence of thiourea, the cathodic polarization curves are near to those obtained for the free $[ZnCl_4]^{2-}$. This indicates that, in our conditions the presence of thiourea does not affect the reduction process of the $[ZnCl_4]^{2-}$ ion. Figure 8 shows the chronopotentiometric curves obtained in the presence and absence of thiourea with the electrolyte containing only the Co^{2+} ion. The presence of thiourea shifts the cathodic potentials negatively. This shows that thiourea affects the deposition of cobalt. The shift to more negative potential has been observed in the presence of additives [33–36]. Adsorption of the additive molecules on the growing deposits has an impact on the nucleation rate and nucleation mechanism. In addition, adsorption of thiourea molecules on the growing cobalt occurs and affects the nucleation rate of cobalt. Also, in this case, we think that
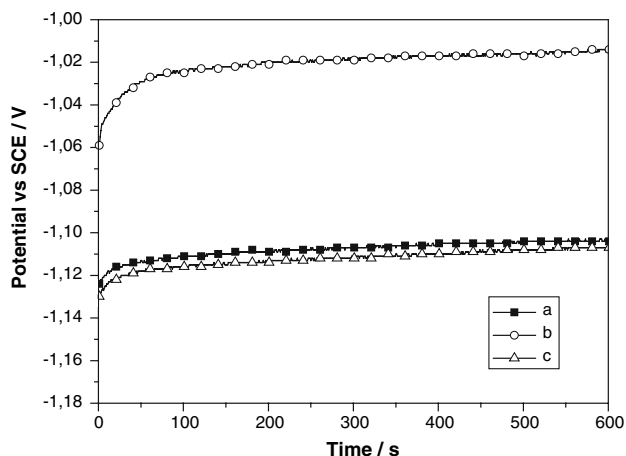
Fig. 4 Chronopotentiometric curves obtained at $J = 4$ A dm^{-2} from chloride bath in the absence of additives: (a) the electrolyte containing only $[ZnCl_4]^{2-}$, (b) the electrolyte containing only Co^{2+}, (c) the electrolyte containing the two ions
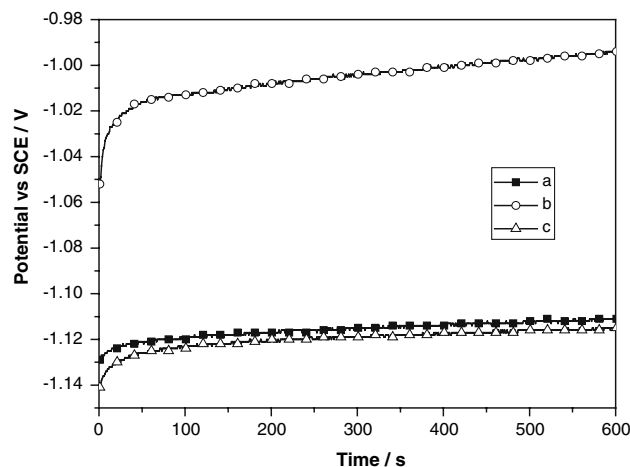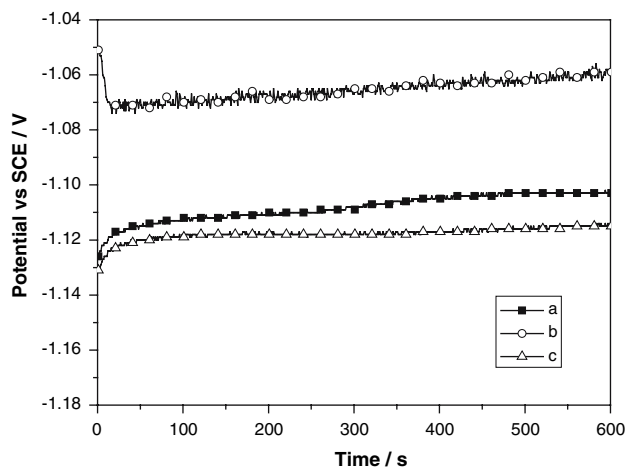

Fig. 6 Chonopotentiometric curves from chloride bath in the presence of urea: (a) the electrolyte containing only $[ZnCl_4]^{2-}$, (b) the electrolyte containing only Co^{2+}, (c) the electrolyte containing the two ions

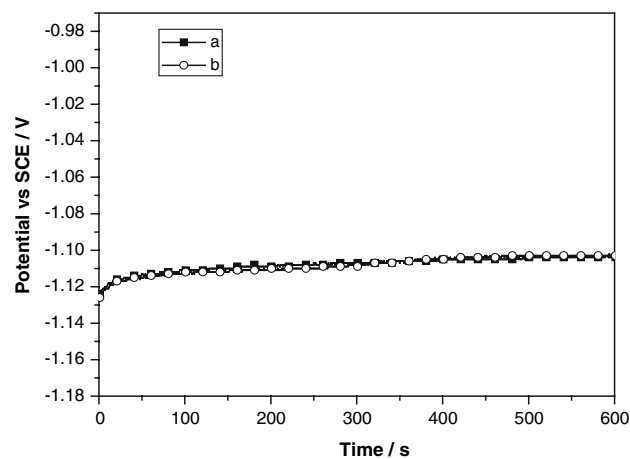**Fig. 5** Chronopotentiometric curves obtained at $J = 4$ A dm^{-2} from chloride bath in the presence of thiourea: (a) the electrolyte containing only $[ZnCl_4]^{2-}$, (b) the electrolyte containing only Co^{2+}, (c) the electrolyte containing the two ions

Fig. 7 Chronopotentiometric curves obtained at $J = 4$ A dm^{-2} from the electrolyte containing only $[ZnCl_4]^{2-}$: (a) in the absence of thiourea, (b) in the presence of thiourea

the presence of thiourea in the electrolyte facilitates the deposition of cobalt. On the other hand, its presence increases the reduction rate of cobalt. We have already observed that with the use of coumarin during zinc deposition, an increase in CE was observed [18]. Figure 9 shows the chronopotentiometric curves obtained from the electrolyte containing both ions. A shift to more negative potential value is observed. Ricq et al. also observed this shift to more negative potentials in the presence of sodium saccharin during iron-cobalt deposition process [15]. Considering the effects of thiourea on $[ZnCl_4]^{2-}$ and Co^{2+} deposition (Figs. 7 and 8), the shift of potentials observed with the electrolyte containing both ions is due to the effects of thiourea on the deposition of Co^{2+}. Thiourea

affects the deposition rate of Co^{2+-}. Therefore, thiourea facilitates the reduction of Co^{2+}, by increasing the reduction rate of Co^{2+-} and has no effects on the reduction of $[ZnCl_4]^{2-}$. Consequently, the percentage of cobalt in zinc–cobalt alloy increases. Thiourea considerably affects the zinc–cobalt deposition by increasing the reduction rate of Co^{2+}. This result is in accordance with the literature. Trejo et al. reported an increase in cobalt content in the presence of benzylideneacetone [24]. They noticed, by investigating the cathodic polarization curves, that the current density of cobalt reduction was greater than that of zinc reduction, promoting the deposition of cobalt in the presence of benzylideneacetone.

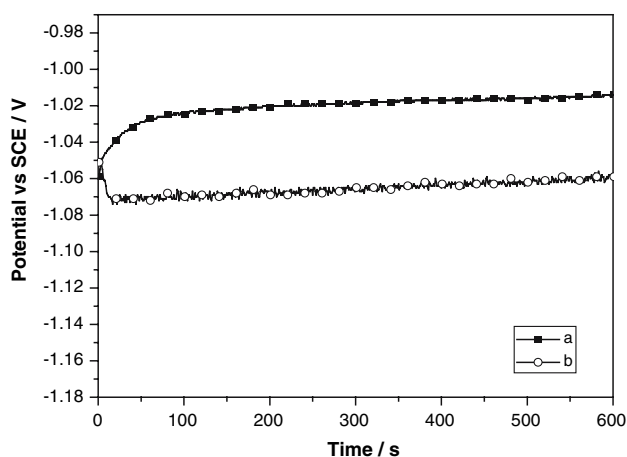The chronopotentiometric curves obtained in the presence and absence of urea are shown in Figs. 10–12. In the

Fig. 8 Chronopotentiometric curves obtained at $J = 4$ A dm^{-2} from the electrolyte containing only Co^{2+}: (a) in the absence of thiourea, (b) in the presence of thiourea

Fig. 10 Chronopotentiometric curves from the electrolyte containing only $[ZnCl_4]^{2-}$: (a) in the absence of urea, (b) in the presence of urea

presence of urea, from the electrolyte containing only $[ZnCl_4]^{2-}$, the shift of potential to a more negative value is observed at $J = 4$ A dm^{-2} (Fig. 10). This shift in potential is not significant; therefore, urea only slightly affects the deposition rate of $[ZnCl_4]^2$. From the electrolyte containing only Co^{2+}, a negative shift in potential is not observed (Fig. 11). It seems that urea does not increase the reduction rate of Co^{2+}. The negative shift observed in the presence of urea from the electrolyte containing both ions is due to the effects of urea on $[ZnCl_4]^{2-}$ reduction (Fig. 12). Urea slightly affects the zinc-cobalt deposition process. Its presence slightly increases the reduction rate of $[ZnCl_4]^{2-}$; consequently, the percentage of cobalt in the alloy decreases. All these results obtained by the chronopotentiometric experiments have been confirmed by the cathodic polarization experiments.
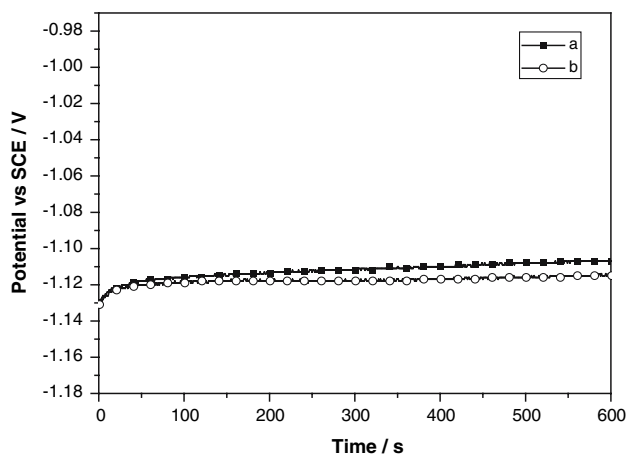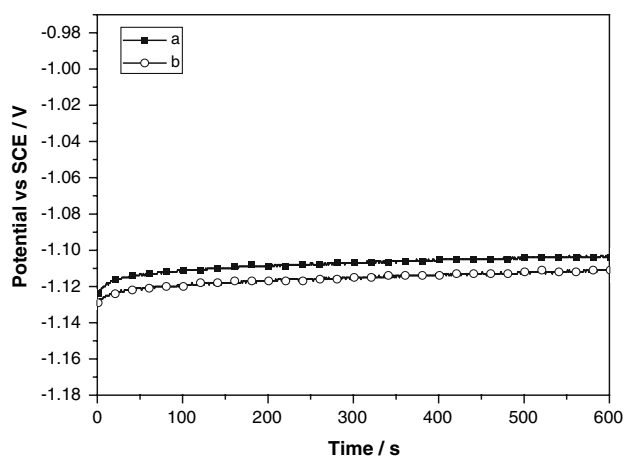
By comparing the effects of thiourea and urea, the voltammetric experiments suggest that thiourea, through the sulphur atom, affects Zn–Co deposition considerably. Urea, in which the sulphur atom is replaced by the oxygen atom, also affects Zn–Co deposition, but its effects are weak. The difference observed in the use of thiourea and urea is attributable to the sulphur atom in thiourea and to the oxygen atom in urea.

4 Conclusion

The influence of thiourea and urea on zinc–cobalt alloys obtained from acidic chloride electrolyte has been investigated. In the presence of urea, the codeposition is anomalous, whereas, in the presence of thiourea, the codeposition is of equilibrium type. Also in the presence of urea, the cobalt atoms are incorporated into the zinc crystal
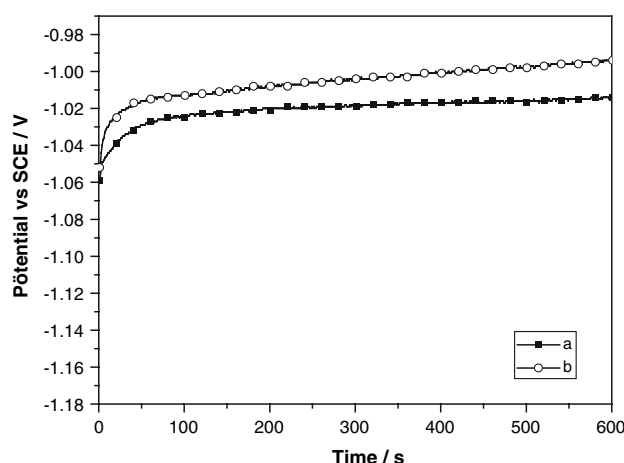

Fig. 9 Chronopotentiometric curves obtained at $J = 4$ A dm^{-2} from the electrolyte containing $[ZnCl_4]^{2-}$ and Co^{2+}: (a) in the absence of thiourea, (b) in the presence of thiourea

Fig. 11 Chronopotentiometric curves from the electrolyte containing only Co^{2+}: (a) in the absence of urea, (b) in the presence of urea
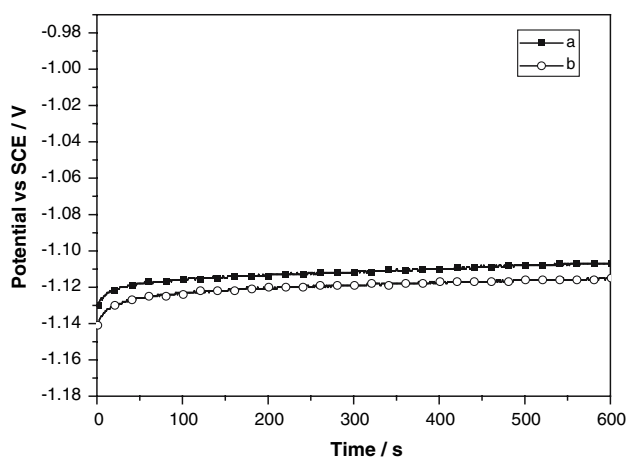
Fig. 12 Chronopotentiometric curves from the electrolyte containing $[ZnCl_4]^{2-}$ and Co^{2+}: (a) in the absence of urea, (b) in the presence of urea

lattice. However, in the presence of thiourea, due to the high percentage of cobalt in the alloy, Zn–Co alloy is formed by two distinct crystal lattices; the crystal lattice of zinc and the crystal lattice of cobalt. The presence of thiourea increases the percentage of cobalt in the alloy whereas the presence of urea decreases it.

The different effects observed on Zn–Co deposition using thiourea and urea is attributable to the sulphur atom in thiourea and to the oxygen atom in urea.

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