Journal of Applied Electrochemistry (2006) 36:727–732
DOI 10.1007/s10800-006-9133-z

The influence of sorbitol on zinc film deposition, zinc dissolution process and morphology of deposits obtained from alkaline bath

M.S. PEREIRA, L.L. BARBOSA, C.A.C. SOUZA, A.C.M. DE MORAES and I.A. CARLOS*
Departamento de Química, Universidade Federal de São Carlos, Via Washington Luiz, CP 676, 13565-905, São Carlos-SP, Brazil
*(*author for correspondence, e-mail: diac@power.ufscar.br)*

Received 25 April 2005; accepted in revised form 1 February 2006

Key words: alkaline bath, scanning electron microscopy, sorbitol, zinc deposition and dissolution

Abstract

A novel cyanide-free zinc deposition bath was developed in which sorbitol was added at various concentrations. Voltammetric studies indicated that the reduction process is influenced thermodynamically and kinetically by the sorbitol concentration. Also, two cathodic processes were observed, one (wave) associated with the hydrogen evolution reaction (HER) on 1010 steel, the other (peak) with zinc bulk reduction, simultaneous to the HER. Furthermore, the plating-process kinetics was controlled by mass transport. The presence of sorbitol in the bath led to formation of light-grey zinc films, even during the HER, without cracks and dendrites. Plating current efficiency decreased from ~62% to 43% on increasing the sorbitol concentration in the plating bath. In the presence of 0.1 M $[Zn(OH)_4]^{2-}$ and/or sorbitol concentrations higher than 0.2 M, Zn electrode dissolution was inhibited. However, a small dissolution of zinc electrode was observed with 0.05 M sorbitol in alkaline solution without zincate. SEM micrographs showed that the 1010 steel substrate was fully covered by Zn film and that the sorbitol affected the morphology of zinc films, acting as a grain refiner.

1. Introduction

In recent decades there has been considerable interest in the electrodeposition of zinc and zinc alloys [1, 2], since plating with zinc protects steel from corrosion. Apart from resisting corrosion, zinc improves the appearance of the articles and also serves as a good base on steel for painting [3]. Its properties facilitate its application on a number of components in the electrical, domestic and automobile industries. Much research effort has gone into finding suitable additives to aid the levelling of these zinc deposits.

An acid zinc bath is used where it is desirable to have a high plating rate with maximum current efficiency [4]. However, the critical pretreatment requirements and the poor throwing power of these solutions restrict their use to plating only regular-shaped articles [5]. The effectiveness and ease of operation of these baths are totally dependent on the brightener additive system used in the bath [6]. Bapu et al. [5] found that the best plating conditions and brightener concentration to obtain smooth and fine-grained bright zinc deposits in non-cyanide alkaline zinc containing gelatine were 2–4 A dm^{-2} at 303 K and pH = 10. The electrolyte had about 63% current efficiency and 25% throwing power. Inorganic and organic additives can play an important role in electroplating. Cachet et al. [7] reported the dissolution and deposition of zinc in 0.5 M ZnO electrolytes at various KOH concentrations in the presence of 5×10^{-4} M tetrabutylammonium bromide (NBu_4Br). It was observed that both deposition and dissolution of zinc were inhibited. The inhibition of zinc deposition and dissolution by an additive (NBu_4Br) depends on the KOH concentration and results from changes in the rates of interfacial processes. Diggle and Damjanovic [8] also studied the influence of an additive (NBu_4Br) on zinc electrodeposition in an alkaline bath. The authors showed that the additive inhibited the dendritic growth of zinc deposits.

Blinov et al. [9] showed that the tetraalkylammonium salt (TAS) is adsorbed on zinc in alkaline solutions at highly negative potentials and when added to a zincate bath alters the mechanism of the cathodic process, *viz.*, slow penetration of the electroactive zinc species through the adsorbate layer arises as a slow step preceding discharge. Then, TAS adsorption causes an additional inhibition of zinc electrodeposition and a change in the type of step that is rate-controlling.

Blinov et al. [10] communicated the special effect of the added TAS on zinc deposit structure. The adsorption of TAS causes zinc deposits to grow with a very pronounced texture and enhanced microdistortions. It is suggested that at potentials more negative than −1.8 V the zinc electrodeposited has a nonequilibrium microstructure, stimulating the formation of an intermetallic zinc-sodium compound which is responsible for a strong inhibition of hydrogen evolution. It is because of this effect of TAS that potentials more negative than −3.0 V can be reached. Litovaka et al. [11] has studied the electrolysis of zincate solutions with added polyethylenepolyamine and observed that slow discharge and diffusional limitations were the steps controlling zinc electrodeposition at more negative potentials. Moreover, the simultaneous process of hydrogen evolution was catalysed by the adsorbed amino groups. The authors concluded that special kinetic features of the cathodic process constitute an important limitation on the use of zincate electrolytes with added polyamines.

Ravindran and Muralidharan [12] studied the role of furfuraldehyde on the electrodeposition of zinc on steel from an alkaline tartrate bath. It was found that additions of furfuraldehyde to the bath inhibited the rate of build-up and that the inhibition was due to adsorption of furfuraldehyde molecules at the growth sites of the nuclei, controlling their growth; this inhibition decreased with current density and the hydrogen evolution reaction was favoured by furfuraldehyde, so that the current efficiency decreased.

Nagarajan et al. [13] reported that a zincate bath solely consists of a small concentration of zinc in sodium hydroxide and depends entirely on organic additives and brighteners, the latter being the most critical for the success of the process. Moreover, comparing cathode efficiency, throwing power and plating rate of cyanide and non-cyanide alkaline baths, they observed that the latter was characteristically very similar to high cyanide plating bath. However, throwing power and covering power were found to be excellent with the non-cyanide process. Also, a non-cyanide alkaline bath produces a slightly yellowish white zinc deposit, whereas a cyanide bath produces bluish-white deposit.

Naik and Venkatesha [14] investigated the addition of a new brightener (salicylaldehyde) for zinc electrodeposition from non-cyanide alkaline solution. The results showed that the zinc films provide good protection of the base metal and the deposits showed fine-grained crystal growth.

Zuniga et al. [15] investigated the effects of a quaternary aliphatic polyamine (QAA) on zinc electrodeposition. They showed that the additive decreased the exchange current density (j_o), suggesting that QAA inhibits the zinc reduction process. Coatings grown in solutions containing QAA had a smaller grain size than crystals grown in QAA-free solutions and, as a result, coatings were compact and shiny. Zinc coatings grown in the presence of QAA displayed lower corrosion rates than those grown in its absence. Carlos et al. [16–20] have developed non-cyanide alkaline baths and studied the effects of organic additives on Zn [16, 17], Zn-Fe and Cu-Zn alloy deposition [18, 19], so as to improve the morphological characteristics and brightness of deposited films. Galvani and Carlos [17] investigated the effect of the additive glycerol on zinc chronopotentiometric electrodeposition on 1010 steel. The results showed that, in general, for density current values between 4 and 16 mA cm^{-2}, the lower the glycerol concentration the higher the electrochemical efficiency. Barbosa et al. [18] obtained light grey, grey and dark grey electrodeposits from an alkaline iron-zinc solution, in the presence of a polyalcohol. These films could only be obtained because of the beneficial effect of the polyalcohol, which brought the reduction potential of Fe(III) close to that of the zincate ion, allowing codeposition of iron and zinc to occur. Almeida and Carlos [19] developed and studied a copper-zinc alkaline bath with various proportions of the metal ions in the bath. They concluded that sorbitate anions prevent the deposits becoming dark and that the films were without stress and the substrate was totally covered.

The object of the present study was to develop an alkaline zinc plating bath containing sorbitol and to characterize the effects of this organic additive on the cathodic polarization, by means of cyclic voltammetry. The morphology of zinc films was evaluated by scanning electron microscopy (SEM).

2. Experimental details

All chemicals were analytical grade. Double-distilled water was used throughout. The electrochemical experiments were performed in freshly-prepared non-cyanide baths, containing 0.10 M $ZnSO_4$ + 2.0 M NaOH and sorbitol at various concentrations (0.05; 0.2; 0.4 and 1.0 M). An AISI 1010 steel disk (0.50 cm^2) and a zinc disc (0.38 cm^2) were employed as working electrodes and a Pt plate and an appropriate Lugging capillary containing Hg/HgO/NaOH (1.0 M NaOH, $E^0 = 0.0977$V) were employed as auxiliary and reference electrodes, respectively. The AISI 1010 steel, from CSN Co., (Brazil), contained 0.04% P, 0.08% C, 0.3% Mn and 0.05% S. Immediately prior to the electrochemical measurements, the working electrode was ground with 600 emery paper and rinsed with distilled water. Electrodeposition was carried out under potentiodynamic conditions. The curves were recorded using an EG & G electrochemical system consisting of a model 366A bipotentiostat. Deposition and dissolution charges were measured with an EG&G model 379 coulometer, using alkaline electrolytes. All experiments were carried out at room temperature (25 °C). The deposition current efficiency (ϕ_e) of the zinc electrodeposition process was obtained from the stripping/deposition charge ratio. Zinc films were produced chronoamperometrically from −0.8 V to −1.4 V, at a charge density (q_d) of 2.0 C cm^{-2} and anodic stripping was done in 1.0 M NH_4NO_3. Scanning Electron Microscopy (SEM) photographs were taken with an FEG X L 30.

3. Results and discussion

3.1. *Electrochemical study of zinc deposition*

Figure 1 shows cathodic linear sweep voltammograms recorded from the AISI 1010 steel substrate in electrolytic solutions containing 0.10 M $ZnSO_4$ + 2.0 M NaOH. While in region I the rate of deposition in the initial moments is slow, in region II, the current density increases steeply and then decreases sharply. In region II, bulk zinc electrodeposition occurs. This region is marked by one cathodic peak, attributed to diffusional control of the deposition process, which promotes a decrease in current density. In region III, the steep rise in the current density beyond the cathodic peak may be associated with the HER and zinc deposition.

With the purpose of studying the zinc electrodeposition process, voltammetric deposition experiments with sweep reversal were performed. Figure 2 shows the cathodic sweep reversed at various potentials. At −1.38 V, a cathodic wave was observed. This wave was attributed to the HER, which was observed in this region during the reduction process. Also, analyzing the anodic sweep, a zinc dissolution peak cannot be seen, corroborating the visual observation of HER during the cathodic sweep in region I. However, when the scan was extended to more cathodic potentials, *viz.* −1.39 V, −1.41 V and −1.45 V, the cathodic currents decreased on reversal [21]. This decrease can be attributed to the plating process kinetics being controlled by mass transport. Also, in the anodic sweep a zinc dissolution peak can be seen.

Figure 3 shows Zn voltammetric deposition and dissolution curves obtained from baths containing 0.1 M $ZnSO_4$ + 2.0 M NaOH and sorbitol at the concentrations 0.05 M, 0.2 M, 0.4 M and 1.0 M. The cathodic branch displays only one peak at ∼−1.4 V, which refers to bulk zinc deposition. In the anodic branch, one peak can also be seen, due to zinc dissolution. It can be observed in Figure 3 that the zinc plating rate is affected kinetically by the sorbitol, i.e., the presence of sorbitol at concentrations higher than 0.05 M decreases the cathodic current density (j_p). The reduction of j_p with rising sorbitol concentration is probably due to inhibition of deposition by adsorbed sorbitol. On the other hand, the displacement of E_p to more negative values with increasing sorbitol

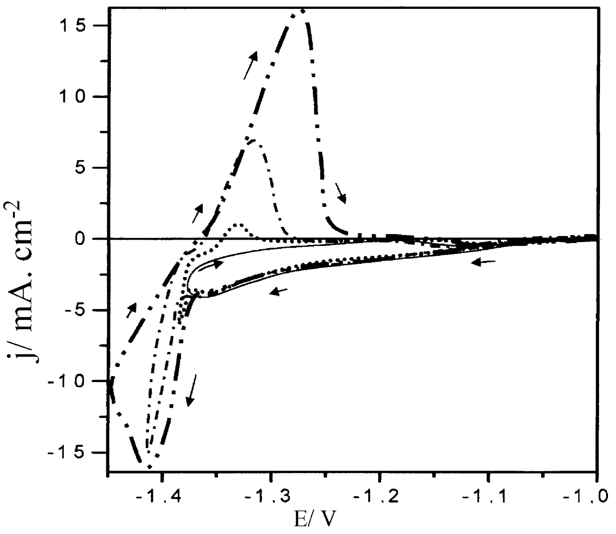

Fig. 2. Voltammetric curves for steel substrates in 20 M NaOH, 0.10 M $ZnSO_4$ and 0.2 M sorbitol, showing effects of the limit potentials: (_••_••_) −1.45 V, (_•_•_) −1.41 V, (••••••) −1.39 V and (—) −1.38 V. ν = 10 mV s^{-1}.

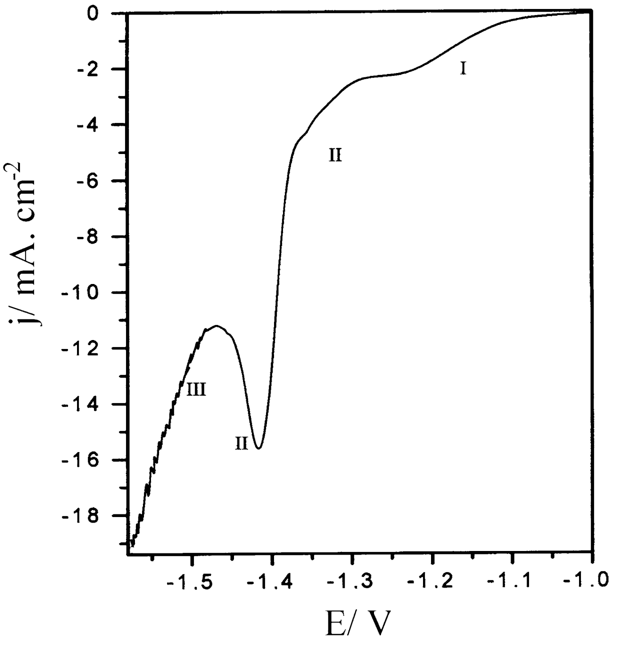

Fig. 1. Cathodic voltammetric curves for electrodeposition of zinc onto AISI 1010 steel substrate in solution containing 2.0 mol l^{-1} NaOH and 0.1 mol l^{-1} $ZnSO_4$, ν = 10 mV s^{-1}.

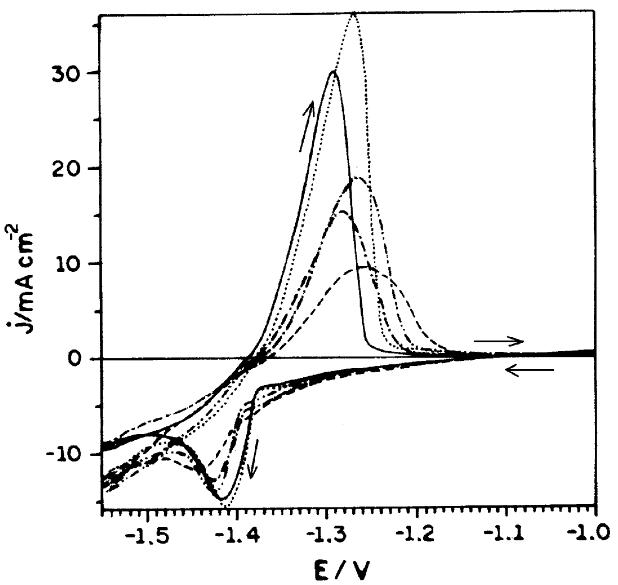

Fig. 3. Dissolution and deposition voltammograms of zinc film on AISI 1010 steel substrate in 2.0 M NaOH + 0.10 M $ZnSO_4$ + sorbitol in concentrations 0.0M (—), 0.05 M (·········); 0.2 M (—··—··—); 0.4 M(– · – · –) and 1.0 M (- - - -). ν = 10 mV s^{-1}.

concentration suggests that sorbitol is probably adsorbed on to the 1010 steel substrate, affecting the thermodynamics of the cathodic process.

Figure 4 shows the effect of varying the sorbitol concentration on the current efficiency (ϕ_e) of the zinc electrodeposition process. The zinc films were deposited potentiostatically from − 0.8 V to −1.4 V, with a charge density of 2.0 C cm^{-2}. The deposits were then dissolved voltammetrically in a solution of 1.0 M NH_4NO_3. It can be observed in Figure 4 that the presence of sorbitol in the plating bath reduced ϕ_e from ~62% to 43%, due to the inhibition of electrodeposition by adsorbed sorbitol.

Zn voltammetric deposition was studied at various sweep rates (ν). Figure 5 shows that the increase in the peak current density (j_p) is proportional to $\nu^{1/2}$. Also, this graph indicates that the area of the electrodeposited zinc film does not alter significantly during the voltammetric deposition, as observed for silver [22] and tin films [23], for which, however, the graphs of j_p against $\nu^{1/2}$ pass far from the origin. These results corroborate those obtained for copper electrodeposition [20].

3.2. *Dissolution of zinc electrode*

Figure 6 shows voltammograms for a zinc electrode in an alkaline zinc-plating bath and a similar bath without zinc ions. These voltammograms indicate the occurrence of three different processes: active dissolution, passivation and transpassivation. Zn is actively dissolved in region I of Figure 6. Here, the current density increases with potential in the anodic direction, up to peak a_1. Region II, between the peaks a_1 and a_2, is denominated pre-passive and region III, which is characterized by a low current density relative to regions I and II, is the passive region. Beyond 1.5 V vs. Hg/HgO/1.0 M NaOH (region IV), dissolution of metal continues. Figure 7 shows the voltammetric curves for a Zn electrode in a bath containing NaOH with several concentrations of $ZnSO_4$. In baths containing $ZnSO_4$ in 2.0 M NaOH, Zn^{2+} reacts with NaOH to form zincate ion ($[Zn(OH)_4]^{2-}$). In solution, the zincate ions cover the anode area, preventing the diffusion of oxidizing agent and consequently inhibiting the anodic process. Figure 7 show that addition of 0.1 M $ZnSO_4$, the concentration usually present in the Zn deposition bath, decreases

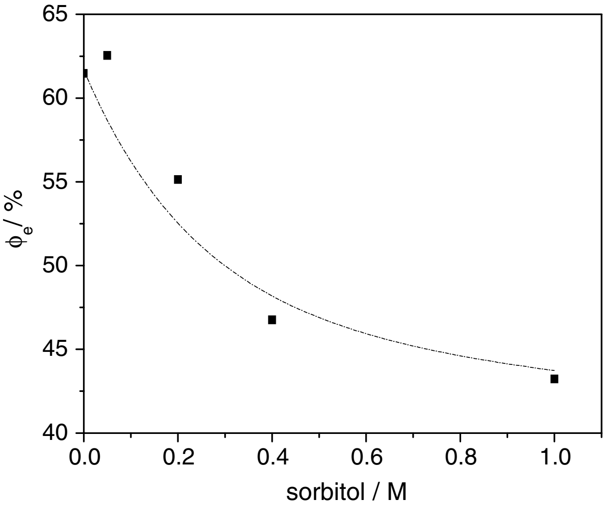

Fig. 4. Zinc deposition current efficiency (ϕ_e) calculated from voltammetric measurements, versus sorbitol concentration. (data Figure 4).

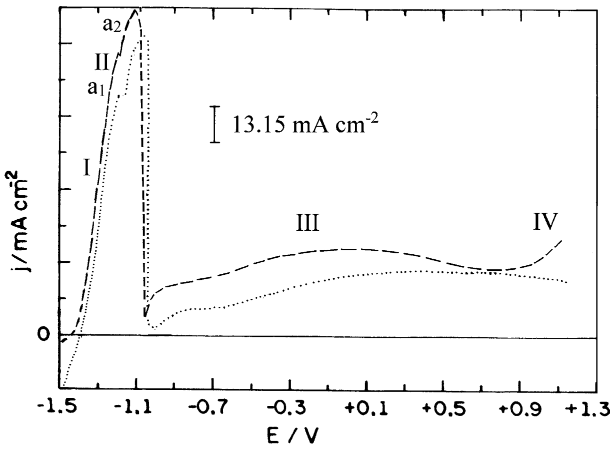

Fig. 6. Voltammetric curves for a zinc electrode in solutions containing NaOH 2.0 M (- - - -) and 2.0 M NaOH + 0.1 M $ZnSO_4$ (··· ·····), at 10 mV s^{-1}.

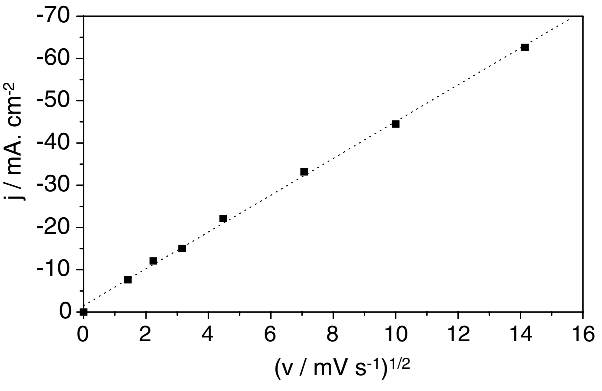

Fig. 5. Variation of j_p with $\nu^{1/2}$, for zinc electrodeposition on steel substrate.

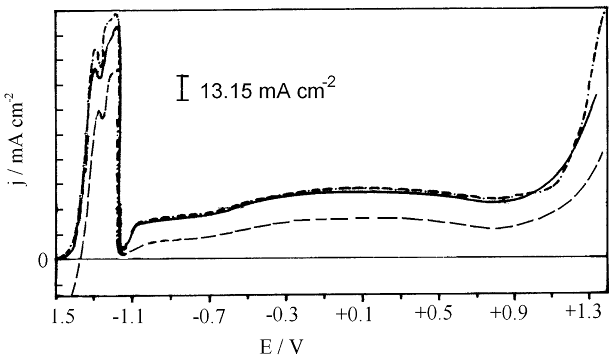

Fig. 7. Dissolution of zinc electrode in solutions containing 2.0 M NaOH and several concentrations of $ZnSO_4$: 0.0 M (—) 0.001 M (– –•– –) and 0.100 M (– –), $\nu = 10$ mV s^{-1}

significantly the transition current density, $j_{A/P}$, and the passive current density, j_p.

To analyse the effect of sorbitol on the corrosion resistance of Zn electrodes, Zn voltammetric dissolution was studied in its presence. Figure 8 illustrates voltammetric curves for the zinc electrode in alkaline solutions containing 2.0 M NaOH and several sorbitol concentrations. As can be seen in this Figure, the presence of additive changes the behavior of the Zn electrode. Thus, at a low concentration of the additive (0.05 M), there is an increase in the transition current density $j_{A/P}$, but an insignificant increase in the current density, j_p, in the passive region. However, both $j_{A/P}$ and j_p decrease as the amount of additive rises. This behavior shows that the presence of additive decreases the amount of corrosion of the product enough for a passive film to be formed, which then inhibits significantly the Zn electrode dissolution, indicating that the presence of additive favours the formation of a passive film. Also, the voltammetric curves in Figure 8 show that at sorbitol concentrations higher than 0.20 M the charge densities in the passive region decrease significantly, as a consequence of lower Zn dissolution. It is possible that the sorbitol, which is an organic substance ($C_6H_{14}O_6$), acts as an inhibitor by being adsorbed on the Zn anode surface, leading to the formation of a film, similarly to quaternary aliphatic polyamine (QAA) [6]. The formation of such a film would affect the electrochemical process, inhibiting Zn corrosion. The results in Figure 8 indicate that the sorbitol contents above 0.20 M may allow the formation of enough adsorbed film to inhibit Zn dissolution, while 0.05 M additive is not sufficient to form the protective film. It is possible that, at 0.05 M, the adsorbed film does not completely cover the electrode surface. Thus, galvanic cell formation would occur, with the covered region acting as cathode and uncovered region as anode, resulting in a higher rate of dissolution of Zn than in the absence of additive. Figure 9 shows voltammetric curves for the zinc electrode in the solution containing NaOH + $ZnSO_4$ and several concentrations of sorbitol. It can be seen in Figure 9 that the addition of sorbitol in this electrolytic solution also decreases both $j_{A/P}$ and j_p, indicating the inhibition of zinc electrode dissolution. However, the addition of 0.05 M sorbitol does not result in any increase of zinc electrode dissolution, in contrast to the zinc-free solution. This behavior may be attributed to the presence of zincate, inhibiting the anodic process.

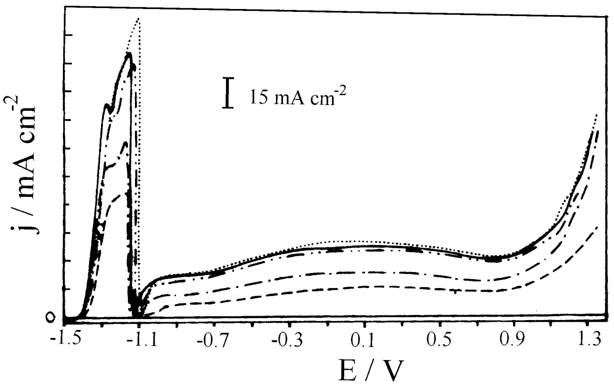

Fig. 8. Voltammetric curves for zinc electrode in solutions containing 2.0 M NaOH and several concentrations of sorbitol: 0.0 M (—), 0.05 M (·········); 0.2 M (– – ●● – –); 0.4 M (–·–·–) and 1.0 M (- - - -), at 10 mV s^{-1}.

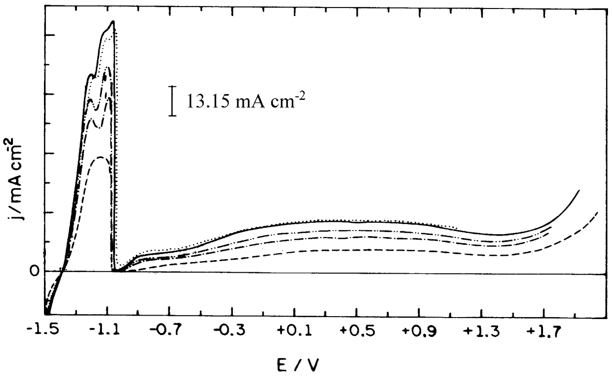

Fig. 9. Voltammetric curve for zinc electrodes in solutions containing 2.0 M NaOH + 0.1 M $ZnSO_4$ and several concentrations of sorbitol: 0.0 M (—), 0.05 (·········); 0.2 M (– – ●● – –); 0.4 M(–·–·–) and 1.0 M (- - - -)., at 10 mV s^{-1}.

3.3. *Morphological study of electrodeposits*

Figure 10 (a)–(f) show SEM photographs of electrodeposited zinc films. Deposits were obtained chronoamperometrically from $ZnSO_4$ + NaOH, in the absence and presence of sorbitol at several concentrations. The micrographs indicate that the sorbitate anion gives rise to smaller crystallites of zinc as the sorbitol concentration in the plating baths increases. Thus, it may be inferred that sorbitate anions favour deposition of finer zinc grains.

4. Conclusions

Zn alkaline plating baths containing sorbitol were found to yield light grey zinc films. Cyclic voltammograms displayed a cathodic wave and peak, which refer to HER and Zn bulk deposition simultaneously to HER, respectively, and in the anodic branch a peak of zinc film dissolution. In the presence of sorbitol at concentrations higher than 0.05 M, the cathodic peak current decreased and the peak potential was displaced to more negative values. Zinc deposition was controlled by mass transport, since j_d increased with rising sweep-rate (v). Plating current efficiency decreased from ~62.0% to 43% as sorbitol content rose from 0.05 M to 1.0 M in the plating bath. Zn voltammetric dissolution was significantly inhibited in the presence of sorbitol concentrations ≥0.2 M, in the presence or absence of zincate in the electrolytic solution. However, a small dissolution of zinc electrode was observed for 0.05 M sorbitol in alkaline solution without zincate. SEM results showed that the 1010 steel substrate was fully covered by zinc film and that sorbitol led to a refining of the zinc grains.

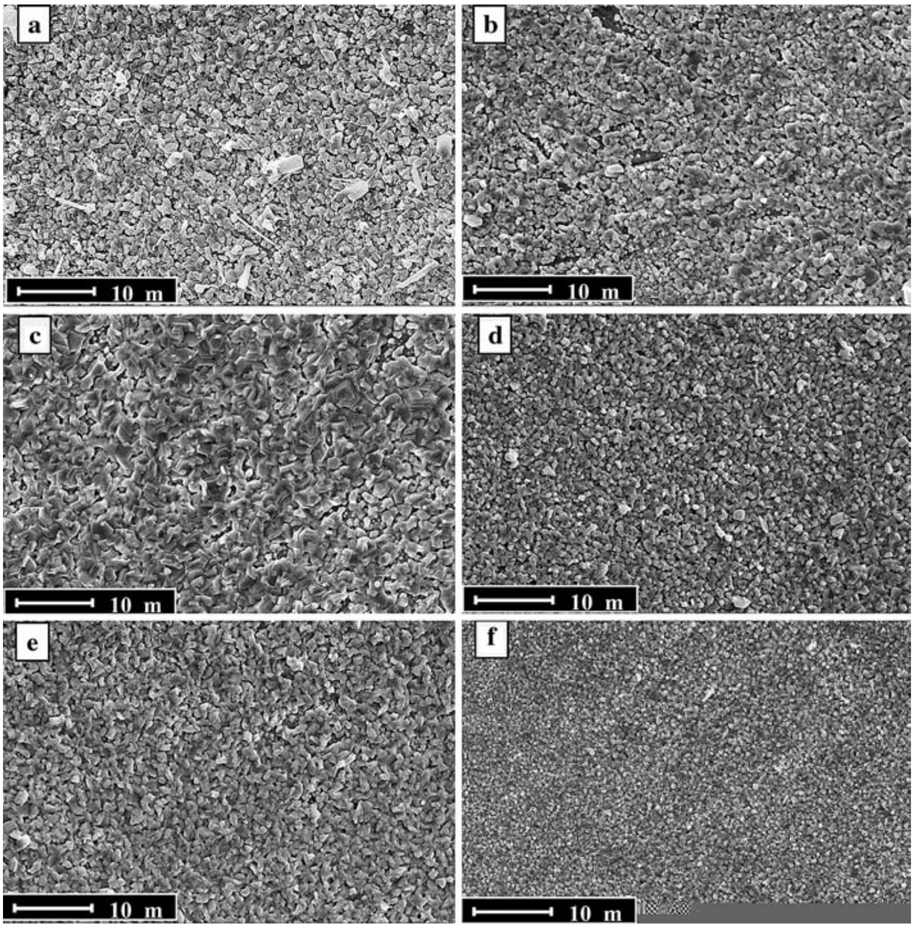

Fig. 10. SEM micrographs of Zn films of 2.0 C cm^{-2} obtained chronoamperometrically at potential −1.4 V. Electrolytic solution: 0.10 M $ZnSO_4 + 2.0$ M NaOH, without sorbitol (a) and with sorbitol 0.05 M (b), 0.2 M (c), 0.4 M (d), 0.6 M (e) and 1.0 M (f) at 10 mV s^{-1}.

Acknowledgements

Financial support from the Brazilian research foundations: Capes and FAPESP (Proc. no 01/13740-5) are gratefully acknowledged.

References

1. F.A. Lowenheim, *Modern Electroplating* (John Wiley & Sons, New York, 1974), pp. 436.
2. M. Pushpavanam, *Bull. Electrochem.* **16** (2000) 559–566.
3. N.V. Partasaradhy, *Practical Electroplating* (Prentice Hall, New Jersey, 1989), pp. 193.
4. H.S., *Schneider Plating Surf. Finish.* **64** (1977) 52.
5. G.N.K.R. Bapu, G. Devaraj and J. Ayyapparaj, *J. Solid State Electrochem.* **3** (1998) 48.
6. A. Ramachandran and S.M. Mayanna, *Met Finish.* **90** (1992) 61.
7. C. Cachet, U. Stroder and R. Wiart, *Electrochim. Acta.* **27** (1982) 903.
8. J.W. Diggle and A. Damjanovic, *J. Electrochem. Soc.* **119** (1972) 1649.
9. V.M. Blinov, A.V. Kuprit, L.Yu. Gnedenkov, Yu.M. Loshkarev and V.V. Trofimenko, *Élektrokhimiya* **24** (1988) 461.
10. V.M. Blinov, L.M. Burov, V.V. Trofimenko, L.Yu. Gnedenkov and Yu.M. Loshkarev, *Élektrokhimiya* **25** (1989) 930.
11. G.P. Litovka, Yu.M. Loshkarev, V.V. Trofimenko, V.E. Kazarinov and N.B. Grigorev, *Élektrokhimiya* **15** (1979) 1229.
12. V. Ravindran and V.S. Muralidharan, *Bull. Electrochem.* **16** (2000) 60.
13. K.S. Nagarajan, S. Rajendran, K. Vembu and S. Rengarajan, *Bull. Electrochem.* **15** (1999) 199.
14. Y.A. Naik and T.V. Venkatesha, *Indian Journal of Engineering and Materials Sciences* **10** (2003) 318.
15. V. Zuniga, R. Ortega, Y. Meas and G. Trejo, *Plat Surf. Finish.* **91** (2004) 46.
16. M. S. Pereira, Estudo da influência do sorbitol no processo de deposição de zinco: caracterização eletroanalítica e espectrofotométrica do banho de deposição e morfologia dos de zinco, Dissertation (Universidade Federal de São Carlos, São Carlos, 2003).
17. F. Galvani and I.A. Carlos, *Metal Finish.* **2** (1997) 70.
18. L.L. Barbosa, G.M. Oliveira and I.A. Carlos, submitted to *Surf. Coat. Technol.* 2005.
19. I.A. Carlos and M.R.H. de Almeida, *J. Electroanal. Chem.* **562** (2004) 153.
20. L.L. Barbosa, M.R.H. de Almeida, R.M. Carlos, M. Ionashiro, G.M. Oliveira and I.A. Carlos, *Surf . Coat. Technol.* **192** (2005) 145.
21. S. Fletcher, C.S. Halliday, D. Gates, M. Wescott, T. Lwin and G. Nelson, *J. Electroanal. Chem.* **159** (1983) 267.
22. P. C. Túlio, Estudo dos mecanismos de eletrodeposição de prata sobre platina a partir de soluções de nitrato de prata, Dissertation (Universidade Federal de São Carlos, São Carlos 1996).
23. T.M.C. Nogueira, PhD Thesis, (Universidade Federal de São Carlos, São Carlos 1996).