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Pulsed electrodeposition of Zn in the presence of surfactants

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Abstract

The preparation of Zn deposits has been performed by galvanostatic pulsed electrolysis, from acidic zinc sulphate solutions, on a stainless steel substrate. The influence of the surfactants (cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl sulphate (SDS) and octylphenolpoly(ethyleneglycolether)_n, n = 10, Triton X-100) on the voltammetric behaviour, structural and morphological characteristics of the deposits have been investigated. The characterization of the samples was made by X-ray diffraction (XRD) and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDS). The experimental data shows that the presence of surfactants affects the zinc deposition process. The electrodeposits are mainly composed by Zn with different texture, crystal shape and size (grain size ranging from 40 to 20 nm). The obtained results led us to conclude that the Zn deposits prepared in the absence of surfactants and in the presence of SDS are more crystalline and with a higher grain size than the ones obtained in the presence of CTAB and Triton X-100. These facts may be justified by the increase on the overpotential deposition as the electrochemical studies confirm.

The XRD results show that the deposits prepared, in the absence of surfactant and in the presence of SDS, contain $ZnSO_4$ and $Zn_4SO_4(OH)_6$ as oxidation products. ZnO is also detected on the deposits obtained in the presence of CTAB and Triton X-100. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Zn deposition; Pulsed electrodeposition; Surfactants; Steel substrate; Crystal structure

1. Introduction

The electrodeposits of zinc on different metals, namely steel, have special relevance due to their anticorrosive properties by the formation of passive layers in contact with air, and in aqueous solution.

In practice, it is well known that the introduction of small amounts of adequate organic additives in the electrodeposition bath results in beneficial quality changes on the deposits, namely the homogeneity. Organic additives, such as surfactants are commonly used in zinc electrodeposition to control the metallic crystal shape and size, in order to produce smooth and bright deposits [1–4]. Other additives such as polyacrylamine [5], thiourea [5] and benzylideneacetone [6] have been also used for zinc deposition. Common effects of the organic additives are changes in the preferred deposit orientation, morphology and an increase in the deposition overpotential.

The specific activity of the surfactants are generally understood in terms of adsorption at the cathode surface during deposition and depends on the concentration of the surfactant molecules. When the concentration approaches the critical micelle concentration (cmc) the formation of bilayers or multilayers at the electrode interface occurs [7].

The adsorption of surfactants aggregates onto electrodes can have large effects on the kinetics of the electron transfer and consequently on the electrodeposition process. The effect on the electron transfer rates includes blocking of the active sites by the surfactants, and electrostatic interactions between electroactive species and adsorbed surfactants [8]. Due to those effects it is possible to modify the growth mode of the crystals and tailor the morphology and structure of the electrodeposits.

On the other hand the electrolysis conditions also have a profound effect on the properties of zinc deposits, such as

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 Table 1

 Physico-chemical properties of the used surfactants

Surfactant	Chemical formula	Туре	cmc (mM)	Aggregation number	References
СТАВ	C ₁₉ H ₄₂ BrN	Cationic	0.85	78	[10]
SDS	C ₁₂ H ₂₅ NaO ₄ S	Anionic	8.10	87	[10]
Triton X-100	$C_{34}H_{62}O_{11}$	Non-ionic	0.24	100	[11]

grain size, surface morphology and preferred orientation. It is known that pulse plating improves the morphology and properties of the deposits due to its positive effects on mass transport, electrode kinetics and the nucleation of growth centres [9–11]. Youssef et al. [5] report modifications on the grain size and crystal orientation by changing the pulse electrodeposition parameters, for zinc deposition from chloride electrolytes in the presence of additives.

In a previous work we have studied the influence of the cationic surfactant, CTAB, on the characteristics of $Zn-TiO_2$ composite prepared by pulsed electrodeposition. It was conclude that the use of the surfactant leads to a decrease in the grain size of the zinc matrix, but little effect is observed on the dispersion of the semiconductor particles [12].

In this work we present a study on the effect of different type of surfactants on the electrochemical deposition of zinc, and the resulting changes on the morphology and structural characteristics of the electrodeposits. Cationic, anionic and non-ionic surfactants have been used to investigate the effect of the charge of headgroups on the electrodeposition process. X-ray diffraction, scanning electron microscopy and X-ray dispersive analysis were used to characterize the structure, morphology and composition of the electrodeposits, respectively. Correlation between electrochemical data and structure and morphology were attempted.

2. Experimental

The electrodeposition was carried out in a twocompartment glass cell using a stainless steel disc (AISI 316, diameter of 10 mm) as substrate, a platinum spiral as the counter electrode and a commercial saturated calomel electrode (SCE) as the reference electrode. Before the experiments, the stainless steel discs were mechanically polished to a mirror finish using silica powder and ultrasonically cleaned during 2 min with Millipore Milli-Q ultra pure water (18 M Ω). The electrochemical cell was connected to an EG & G Princeton Applied Research potentiostat/galvanostat model 263.

The electrolyte was prepared dissolving $ZnSO_4 \cdot 7H_2O$ (Merck) and $(NH_4)_2SO_4$ (M & B) in Millipore Milli-Q ultra pure water. Separately, cetyl trimethyl ammonium bromide (CTAB, Aldrich), sodium dodecyl sulphate (SDS, Sigma) and octylphenolpoly(ethyleneglycolether)_n, n = 10 (Triton X-100, Fluka) were added to this base solution. All chemicals were analytical grade. The surfactants were used without further purification and Table 1 presents their physico-chemical properties [13,14]. For all the solutions the pH value was 4. Table 2 shows the chemical composition of solutions studied. It is noteworthy that the surfactants concentrations were above their critical micelle concentration values.

All the experiments were carried out at room temperature and the deposition was performed under magnetic stirring. N_2 was bubbled through the solution for 15 min before each experiment and during the deposition, a weak flux of N_2 was maintained.

Zinc electrodeposits were prepared applying a galvanostatic square wave during 60 min with a pulse peak current of 100 mA and a current-on time and a current-off time of 4 and 40 ms, respectively. This corresponds to an average current density of -11.5 mA cm⁻². This value was chosen on the basis of the voltammetric curves. After the deposition the samples were washed with Millipore Milli-Q ultra pure water and dried under an N₂ flux. The deposits prepared with Triton X-100 were also washed with ethanol. The weight of the zinc deposits, was calculated by weighing the samples before and after deposition and was used to calculate the average film thicknesses. Assuming that the deposits were composed only by zinc, a value of 18.3 ± 0.9 µm was obtained.

Linear voltammetry experiments were carried in a threeelectrode glass cell with a stainless steel disc as the working electrode, a platinum mesh as the counter electrode and a commercial saturated calomel electrode (SCE) as the reference electrode. These electrochemical measurements were carried out using a Voltalab 32 Radiometer apparatus connected to an IMT 102 interface, controlled by a personal computer through the VoltaMaster 2 software.

A JEOL scanning electron microscope (model JSM-6301F) coupled with an energy-dispersive spectroscopic (Noran/Voyager) were used to characterize the surface morphology and to analyse the elemental composition of the zinc electrodeposits. The energy of the primary electrons beam was 15 keV.

X-ray diffraction analysis was carried out using a Philips X-ray diffractometer (model PW 1710) with Cu K α radiation

 Table 2

 Chemical composition of the used solutions

Solution	Composition
1	$0.6 \text{ mol } dm^{-3} \text{ ZnSO}_4 + 0.1 \text{ mol } dm^{-3} \text{ (NH}_4)_2 \text{SO}_4$
2	$0.6 \mathrm{mol}\mathrm{dm}^{-3}\mathrm{ZnSO_4} + 0.1 \mathrm{mol}\mathrm{dm}^{-3}$
	$(NH_4)_2SO_4 + 1 \text{ mM CTAB}$
3	$0.6 \mathrm{mol}\mathrm{dm}^{-3}\mathrm{ZnSO}_4 + 0.1 \mathrm{mol}\mathrm{dm}^{-3}$
	$(NH_4)_2SO_4 + 10 \text{ mM SDS}$
4	$0.6 mol dm^{-3} ZnSO_4 + 0.1 mol dm^{-3}$
	(NH ₄) ₂ SO ₄ + 0.3 mM Triton X-100



Fig. 1. Linear voltammetric curves obtained for a stainless steel electrode from solutions containing $0.6 \text{ mol } \text{dm}^{-3} \text{ ZnSO}_4 + 0.1 \text{ mol } \text{dm}^{-3} (\text{NH}_4)_2 \text{SO}_4$ (a) and adding SDS (b), CTAB (c) and Triton X-100 (d). Sweep rate of 1 mV/s.

 $(\lambda = 0.15604 \text{ nm})$, working at 30 mA and 40 kV. The diffractograms were obtained in the 2 θ range of 20–90° using a 0.02° step and acquisition time of 2 s/step.

3. Results and discussion

3.1. Voltammetric study

Fig. 1 shows the *i* versus *E* curves obtained for the Zn^{2+} solution in the presence and absence of the surfactant molecules, at a sweep rate of 1 mV/s. For comparison linear voltammograms obtained in the same conditions without Zn(II) in solution are presented in Fig. 2.



Fig. 2. Linear voltammetric curves obtained for a stainless steel electrode from solutions containing $0.1 \text{ mol dm}^{-3} (\text{NH}_4)_2 \text{SO}_4$, in the presence and absence of surfactant molecules. Sweep rate of 1 mV/s.

For the Zn(II) containing solutions, in the absence of surfactant, and on the potential range between -870 and -1080 mV versus SCE a cathodic peak appears followed by a sharp increase of current. Our results are in accordance with those obtained by Casanova et al. [15] that found a peak in the same potential region and assigned it to the hydrogen evolution, and formation of an adsorbed zinc layer that occurs before zinc crystallization.

According to the model proposed by Wiart et al. [16] for the electrodeposition of zinc in acidic sulphate electrolytes, the formation of ZnH, ZnO, ZnOH and hydrogen can occur in the peak region. As a consequence zinc hydroxide may also be formed, by hydrolysis, due to a local pH increase. This assumption is in accordance with a model proposed by Yan et al. for zinc electrodeposition via a zinc hydroxide layer formation [17].

At more negative potential region, the reduction of the Zn^{2+} ions to Zn can occur, as the calculated equilibrium potential (-1040 mV versus SCE) indicates.

For this potential region the mechanism proposed by Wiart et al. involves various reduction steps, including the formation of active sites for the Zn deposition.

In the presence of the surfactant molecules the shape of the curves is similar to the ones obtained, in the absence of the surfactants, in the peak region. As it was expected the presence of the surfactant affects the peak size and causes a negative shift on the peak potential value. The increase on the current density should be attributed to an enhancement of the zinc reduction in comparison with the hydrogen evolution. This conclusion is supported by the experimental results obtained in the absence of Zn(II) in solution (Fig. 2). It is clear that the current density under these conditions is very low and no cathodic peak is observed.

For the potential region between -1080 and -1300 mV, the shape of the curves are similar but a shift to more negative potential and a decrease on the current density are observed, depending on the presence and nature of the surfactant. This behaviour is more evident in the presence of Triton X-100. The comparison between the polarisation curves, shows that the negative shift on the potential, increases in the following order: SDS, CTAB and TritonX-100. Increases on the zinc deposition overpotential have been observed in the presence of commercial additives [18], polyethoxylated additives [4] and gelatine [19]. This result is usually interpreted by a partial coverage of the electrode surface by the additive which blocks the active sites, decreasing the nucleation rate and affecting the nucleation mechanism [17]. In addition, adsorption of the surfactanct molecules on the growing zinc deposit can also occur, blocking the electrocrystallization process. This inhibition depends on the size of the organic molecules and the specific interactions between the surfactant and the substrate and the surfactant and the deposit.

Considering the polarity of the CTAB and SDS surfactants it is expected that they present mostly surface active properties. The surface coverage of the referred surfactants has be estimated by the equation $\theta = 1 - (i_S/i)$ where *i* and i_S are the current density without and with surfactants at a constant potential value, respectively [20]. The coverage values obtained for E = -1275 mV versus SCE were 0.19 and 0.36 for the SDS and CTAB, respectively.

In the case of Triton X-100, a non-ionic surfactant with oxyethylene groups, it is possible that both adsorption and complex formation occur. Taking into account that the surfactant concentration is above the cmc, complex formation with the adsorbed molecules could be promoted what would explain the strong increase on the zinc deposition overpotential. Stoychev et al. proposed a similar interpretation for the electrodeposition of copper in the presence of polyethyleneglicol [21].

3.2. SEM/EDS characterization

The electrochemical studies have shown that the addition of small amounts of surfactant modifies the electrodeposition process. In order to determine whether these changes were reflected in the deposit morphology and composition, an SEM/EDS study was performed.

The data show that the surface morphology and the crystal shape and size are markedly affected by the presence and nature of the surfactants. The EDS spectra obtained in different local points of the electrodeposits surface showed that they were mainly composed by zinc. Sulphur and oxygen were also detected and their presence may be associated with the corrosion of the deposits or with occluded solution. Finally the detected carbon can be due to either some surfactant incorporation on the deposit or atmospheric contamination. A complementary analysis must be performed in order to clarify this situation.

In the absence of organic molecules in the electrodeposition bath (Fig. 3a), the deposit display the hexagonal zinc plates aligned parallel to the substrate as usual for zinc electrodeposits [11].

The deposits, prepared from solutions with SDS (Fig. 3b), are very uniform with plate form crystals, perpendicularly oriented to the substrate. When compared with the zinc deposits from additive-free solution, the grains are relatively smaller. Kelly et al. observed similar effects [22] for copper deposition in the presence of sulphur containing compounds. EDS analysis reveals the presence of Zn, O and S. Sulphur could be due to the incorporation of the surfactant in the coating.

In the presence of CTAB (Fig. 3c), the zinc grain size is smaller, indicating a modification on the competition between nucleation and crystal growth. It is also noteworthy to mention the porous nature of the coating due to the needle shape grains. The morphology change can be associated to a strong blocking effect of the cationic surfactant, which causes an enlargement of the nuclei renewal rates, leading to an increase of nuclei number and needle growth. On the coating surface, the presence of black points was observed associated with an S line in the corresponding EDS spectrum. The deposits obtained in the presence of Triton X-100 (Fig. 3d), are more irregular, with a distinct morphology, constituted by cauliflower type agglomerates. Comparing with the previous micrographs it can be concluded that this nonionic surfactant have a strong influence on the Zn deposition process. Trejo et al. have reported a similar morphology [4] for zinc electrodeposits obtained from acidic solution in the presence of organic polyethoxylate (PEG) additives. Sulphur is also detected on the coating surface.

For the deposits obtained with the surfactant-free solution, some protuberances were observed, due to the presence of hydrogen bubbles adsorbed on the substrate surface and/or on the zinc deposits (Fig. 4), during the deposition process. The morphology found in this region is very peculiar. Flake forms constituted by Zn, S and O, were identified using EDS. Similar features were observed by Cachet et al. [23] for the corrosion of zinc coatings in sulphate medium. This fact was explained by the formation of a zinc-hydroxi-sulphate, due to local pH changes. For the deposits obtained in the presence of the organic molecules, this morphology due to the adsorption of hydrogen bubbles was not detected. It seems that the surfactant molecules on the electrode interface inhibit this phenomenon.

3.3. Structural characterization

Figs. 5–8 display the diffractograms for the hexagonal Zn deposits obtained in different conditions. It is clear that the presence of the surfactant, on the electrodeposition bath, affects the crystallographic orientation and crystallinity of the deposits.

In the absence of organic molecules in the deposition bath (Fig. 5), the relative intensity of the lines indicates a strong $(0\,0\,2)$ orientation for the zinc electrodeposits [24]. This texture is in accordance with the hexagonal surface morphology usually detected for these deposits. According to Li et al. [25], the development of different textures is possible during the growth of metal coatings. This is a consequence of surface energy differences, which are responsible for the selective growth of the grains that have the lowest surface free energy. For the zinc crystal the lowest surface free energy is the basal $(0\,0\,2)$ plane, owing to its compactness [26]. Therefore, this texture develops during the zinc growth in the absence of surfactants, assuming that the adsorbed hydrogen does not modify the metal surface energy.

For the deposits obtained from solutions containing SDS (Fig. 6), CTAB (Fig. 7) and Triton X-100 (Fig. 8), the most intense diffraction lines are (101), (110), and (101) respectively. In addition, a marked decrease on the basal (002) plane intensity is found. The crystallographic orientation changes because the metal's surface energy is modified by the adsorption of the organic molecules [27]. The variation on the crystallographic orientation by the presence of the surfactants should be due to their different specific interactions with the different crystal planes, that induces different growth mechanisms. The hindrance of the



Fig. 3. Scanning electron micrographs and respective EDS spectra of the surface of the electrodeposits obtained in the absence of the surfactant (a) and in the presence of SDS (b), CTAB (c) and Triton X-100 (d).



Fig. 4. Scanning electron micrographs of the surface of the electrodeposits obtained in the absence of the surfactant. EDS spectrum of the surface region where the flakes forms are observed.

development of the basal (002) plane can be attributed to an increase of the surface energy of this plane in these conditions.

For the deposits prepared in presence of SDS, similar results were obtained by Tripathy et al. [3] for the electrode-position of zinc in sulphate solution.

Tripathy et al. [2] also investigated the zinc electrowinning from acidic sulphate solutions in the presence of CTAB and have found by XRD, that the strongest reflexion was the (101). The different results are possible due either to the concentration of the surfactant employed or to the electrodeposition technique used. To explain the preferential growth in the (110) plane, Baik et al. [28] assumed that this is associated to a low rate for the zinc ion discharge, originated by the organic molecules presented in the solution, which have an inhibiting effect on the electrocrystalization process.

Least-square refinements of the cell parameters (*a* and *c*) of the hexagonal structure were performed, from the position of the peaks indexed as Zn in the different diffractograms [24]. The cell parameters and the cell volume were found to depend weakly on the presence of the surfactant at the deposition bath (Table 3). The data show a small decrease on the cell volume of the Zn structure for the samples prepared with the presence of surfactants molecules. This fact is more evident for the sample prepared with Triton X-100. This contraction of the zinc structure may be associated to the other phases present in the deposit.



Fig. 5. X-ray diffraction pattern of the electrodeposited film obtained in the absence of surfactant in the solution. The inset shows the expanded diffractogram (\star : reflexions due to the steel substrate).



Fig. 6. X-ray diffraction pattern of the electrodeposited film obtained in the presence of SDS in the solution. The inset shows the expanded diffractogram (*: reflexions due to the steel substrate).



Fig. 7. X-ray diffraction pattern of the electrodeposited film obtained in the presence of CTAB in the solution. The inset shows the expanded diffractogram (*: reflexions due to the steel substrate).

Table 3 Average grain size, cell parameters and unit cell volume for the zinc structure of the different samples

Surfactant	Cell paran	neters	Unit cell volume	Grain size (nm)	
	<i>a</i> (nm)	<i>c</i> (nm)	$(\times 10^{-3} \text{ nm}^3)$		
None	0.26616	0.49308	30.25	50.4	
SDS	0.26602	0.49308	30.22	40.3	
CTAB	0.26611	0.49199	30.17	20.4	
Triton X-100	0.26608	0.49182	30.16	29.0	

In Table 3, it is also presented the average grain size calculated from the line broadening of the most intense X-ray peak according to Scherrer's formula. The average grain size of zinc deposits decreases with the presence and type of surfactant that confirms the results obtained by SEM. The smallest value was obtained for the sample prepared with CTAB in the solution. This result indicates once again that this cationic surfactant inhibits drastically the growth process of zinc, at the experimental conditions used.

In order to make possible the identification of the other phases present on the deposits and whose existence was



Fig. 8. X-ray diffraction pattern of the electrodeposited film obtained in the presence of Triton X-100 in the solution. The inset shows the expanded diffractogram (\star : reflexions due to the steel substrate).

pointed out by the EDS measurements, the X-ray patterns were analysed in more detail (inset diffractograms), and the obtained data is shown in Table 4. In what concerns the electrodeposits prepared in absence of surfactant molecules, it can be seen that ZnSO₄ and Zn₄SO₄(OH)₆ are present in small amounts [29]. These products are normally obtained as a result of the zinc oxidation in sulphate solutions, associated to local pH changes, due to the hydrogen evolution at the substrate [23,30]. Similar products were obtained for the samples prepared in the presence of SDS. This result indicates that the zinc dissolution during the electrodeposition process is not totally inhibited by the presence of this anionic surfactant at the interface.

For the samples prepared in the presence of CTAB and Triton X-100, ZnO was identified [31]. This result could be justified by the modification on the zinc deposition mechanism as a consequence of the blocking effect due to the surfactants molecules adsorbed on the metal surface. In the reaction model proposed by Wiart [16] for the zinc deposition in acidic electrolytes, it was assumed that the species ZnOH_{ad} and ZnO_{ad} are involved in the deposition process when a low cathodic polarisation is applied. Our voltammetric results for the zinc electrodeposition in the presence of Triton X-100 show that the deposition potential is the most negatively shifted. This result could be explained by the formation and incomplete reduction of ZnO.

Table 4

Identification of the others phases presented in the Zn electrode	eposits
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Surfactant presence											
None		SDS		СТАВ			Triton X-100				
2θ (°)	$I_{\rm rel}$ (%)	Identified phases	2θ (°)	$I_{\rm rel}$ (%)	Identified phases	2θ (°)	$I_{\rm rel}$ (%)	Identified phases	2θ (°)	$I_{\rm rel}$ (%)	Identified phases
21.385	0.1	ZnSO ₄	21.465	0.1	ZnSO ₄	35.270	0.1	ZnSO ₄ or Zn ₄ SO ₄ (OH) ₆	32.125	5.3	ZnO
32.900	0.4	Zn ₄ SO ₄ (OH) ₆	33.090	0.1	Zn ₄ SO ₄ (OH) ₆	48.025	0.1	ZnO	34.775	4.5	ZnO
34.940	0.5	$ZnSO_4 + Zn_4SO_4(OH)_6$	35.315	0.2	$ZnSO_4 + Zn_4SO_4(OH)_6$	56.860	0.1	ZnO	41.695	0.8	$ZnSO_4 + Zn_4SO_4(OH)_6$
41.515	0.1	ZnSO ₄ + Zn ₄ SO ₄ (OH) ₆	41.550	0.4	ZnSO ₄ + Zn ₄ SO ₄ (OH) ₆	63.150	0.3	ZnO	47.830	1.5	ZnO
						67.450	0.2	ZnO	56.935	2.9	$ZnO + Zn_4SO_4(OH)_6$
									63.160	2.1	ZnO
									66.685	0.4	ZnO
									68.265	2.0	ZnO
									69.340	1.1	ZnO

4. Final remarks

The galvanostatic electrodeposition of Zn using a square wave and in the presence of surfactants makes possible the preparation of metallic deposits with different preferential orientation, crystal shape and size.

When the electrodeposition process occurs in the absence of organic molecules, the morphological and structural analysis show that the Zn deposition is accompanied by the evolution and adsorption of hydrogen bubbles and in consequence the surface is not uniform.

The electrodeposits prepared from solutions containing SDS, exhibit a regular and uniform morphology where the Zn presents a pyramidal orientation. The adsorption of the anionic surfactant should occur at the metallic surface during the on-time pulse and consequently a modification of the Zn crystal shape takes place.

In the presence of CTAB, very porous Zn deposits with needle shape and small size crystals were obtained. This could be due to the formation of an adsorbed superficial film of CTAB, on the metallic surface and consequently, Zn^{2+} ions approach the surface with increasing difficulty, resulting in an inhibition of the crystal growth.

For the electrodeposits prepared in the presence of Triton X-100, cauliflower clusters were obtained. In addition, ZnO was identified in the deposits, what can be explained by the overpotential increase for the Zn deposition, that makes impossible the total reduction of ZnO to Zn.

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