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The influence of substituted aromatic aldehydes on the electrodeposition of Zn–Mn alloy

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Abstract: Additives are necessary in the electrodeposition of Zn–Mn alloys at high current densities, in order to reduce the hydrogen evolution reaction and prevent dendrite formation. The influences of two aromatic aldehydes, 4-hydroxy-benzaldehyde and 3,4-dimethoxy-benzaldehyde, as additives in the Zn–Mn plating electrolyte, were examined in this study. The characterization of the coatings by scanning electron microscopy and X-ray energy dispersive spectroscopy, as well as an examination of the effect of the additives by electrochemical methods, indicated a complex involvement of additive molecules in hydrogen evolution, as well as in Zn²⁺ and Mn²⁺ reduction. Consequently, a levelling action could be achieved and the chemical composition of the Zn–Mn alloy tailored by the addition of the proper type and concentration of additive in the plating electrolyte.

Keywords: Zn–Mn alloy; plating additive; hydrogen inhibitor; leveller; surface morphology.

INTRODUCTION

Among the various zinc alloys, Zn–Mn alloy coatings have received wide attention in the automotive industry, due to their attractive features.¹ It has been reported that alloy coatings with a high Mn content (10–30 at. % Mn) show the highest corrosion resistance known among zinc alloys.^{2,3}

The large scale production of Zn–Mn coatings with varying Mn contents seems achievable by electrochemical deposition.⁴ However, the incorporation of higher percent of Mn in an alloy is a difficult issue, since the standard electrode potentials of the Zn²⁺/Zn and Mn²⁺/Mn couples are significantly different, *i.e.*, $-0.76 V_{SHE}$ for Zn vs. $-1.18 V_{SHE}$ for Mn.⁵ One way of overcoming this issue is

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to shift the deposition potential of Zn closer to that of Mn by using a complexing agent, as realized, for instance, with sodium citrate or EDTA² in an acidic sulphate bath, or pyrophosphate ion in an alkaline bath.⁶ The deposition process in these cases has important drawbacks, particularly with regards to process control and current efficiency.⁷

On the contrary, a simple bath without strong complexing agent shows several benefits, such as high current efficiency and good bath stability.⁵ A simple electrolyte consisting of boric acid, potassium, and zinc and manganese chlorides was proposed for Zn–Mn electrodeposition in the past decade,⁸ and this electrolyte was chosen for examination in the present study. However, in order to obtain a Mn-rich deposit from a simple chloride bath, significant cathodic polarization or high deposition current density (c.d.) is necessary. Under such conditions, the Zn reduction is under diffusion control, leading to the formation and growth of dendrites,^{9,10} and additionally, the accompanying intensive hydrogen evolution decreases the current efficiency and may lead to porous coatings.¹¹

Dendritic deposit formation and hydrogen co-deposition during Zn–Mn electrodeposition at high c.d.s, could be prevented by the use of plating additives. As a matter of fact, in the industrial production of pure Zn coatings, plating additives are mainly necessary,^{12,13} and the list of compounds investigated for this purpose is extremely long.^{12,14} Concerning pure Mn plating, sulphur and selenium compounds are normally used as additives, in order to increase the current efficiency, but at the cost of contamination of the Mn deposit with sulphur and selenium inclusions.¹⁵ The effect of various additives (*e.g.*, gelatine, agar-agar,¹⁶ ascorbic acid, alcohols, aromatic aldehydes and ketones,¹⁷ thiourea and thiocarbamide¹⁸) are well understood in Zn–Mn electrodeposition from a sulphate electrolyte. Contrarily, the list of additives studied in chloride electrolytes is appreciably shorter, including Fra 700 (a commercial additive for pure Zn),⁸ poly(ethylene glycol)⁵ and ammonium thiocyanate.¹⁹

The scope of the present study was to investigate the influence of plating additives on the Zn–Mn alloy electrodeposits obtained from a chloride electrolyte, at a high c.d., where the onset of dendrite formation was observed, *i.e.*, at 90 mA cm⁻². The additives were expected to inhibit both dendritic growth and the hydrogen evolution reaction. According to the literature, substituted aromatic aldehydes are good candidates for both purposes.²⁰

The effects of two substituted aromatic aldehydes, namely 4-hydroxy-benzaldehyde (HBA) and 3,4-dimethoxy-benzaldehyde (DMBA), shown in Fig. 1, were studied in this work. Electrochemical techniques were used to investigate the role of the additives in the electrodeposition process, and scanning electron microscopy (SEM) coupled with X-ray energy dispersive spectroscopy (EDS) was used to characterize the deposits obtained under different plating conditions.

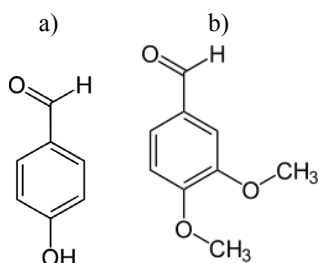


Fig. 1. a) The structure of 4-hydroxy-benzaldehyde and b) the structure of 3,4-dimethoxy-benzaldehyde.

EXPERIMENTAL

Electrolyte preparation

The electrodeposition of Zn–Mn alloys and the electrochemical experiments were performed using a chloride electrolyte containing 1.25 mol dm^{-3} KCl, 0.4 mol dm^{-3} H_3BO_3 , 0.3 mol dm^{-3} ZnCl_2 and 1 mol dm^{-3} MnCl_2 , pH 4.50. HBA and DMBA were added in concentrations of 0.25 or 0.5 g dm^{-3} . The electrolytes were prepared with analytical grade reagents and double distilled water.

Substrate preparation

The substrates for all experiments were steel (AISI 4340) panels with an active surface area of 3.68 cm^2 . Prior to each experiment, the steel surface was abraded successively with emery papers of the following grades: 600, 1000 and 1200, and then degreased in a saturated solution of NaOH in ethanol, pickled with 2 mol dm^{-3} HCl for 30 s and finally rinsed with distilled water.

Electrochemical studies and coating electrodeposition

A three-electrode cell arrangement was used for both the electrochemical (voltammetric and chronopotentiometric) studies and alloy electrodeposition, at the temperature of $25 \text{ }^\circ\text{C}$ without stirring. The reference electrode was a saturated calomel electrode (SCE) mounted in a Luggin capillary. All potentials in this paper are referred to this electrode. The counter electrode was a Zn plate (high purity Zn).

The Zn–Mn alloy coatings were electrodeposited galvanostatically at a c.d. of 90 mA cm^{-2} , using a PAR M173 galvanostat as the power supply. The deposition time was chosen to obtain layers of $10 \text{ }\mu\text{m}$ thickness, verified by a coating thickness measuring instrument Dualscope MPOR.

The voltammetric experiments (with IR correction) were performed at 5 mV s^{-1} between -800 and -1700 mV vs. SCE scanning to negative potentials, by using a ZRA Reference 600 potentiostat, Gamry Instruments.

Zn–Mn coating characterization

Surface morphology of the coatings was examined by scanning electron microscopy (SEM), using a Tescan, VEGA TS 5130 MM instrument. Chemical analysis of the deposits was performed by an attached energy dispersive X-ray spectrometer (EDS), INCAPenta-FETex3, Oxford Instruments.

The measurement of the surface roughness of the samples was performed using a TR200 surface roughness tester, over a length of 2.5 mm . The measured parameter was the average roughness, R_a , as denoted in Eq. (1), where “y” is the distance between the profile line and the average line:

$$R_a = \frac{1}{n} \sum_{i=1}^n |y_i| \quad (1)$$

RESULTS AND DISCUSSION

Effect of additives on the morphology of the Zn–Mn deposits

Zn–Mn coatings were preliminary electrodeposited from the chloride electrolyte free of organic additives, and it was observed that the samples obtained at c.d.s of up to 80 mA cm⁻² were smooth and homogeneous, *i.e.*, commercially acceptable deposits. However, the SEM photograph of a Zn–Mn coating plated at 90 mA cm⁻² (Fig. 2a) shows a deposit with cauliflower morphology and a very rough surface, on which precursors of dendrites are visible.⁹ Therefore, the effect of plating additives was further studied at 90 mA cm⁻², in order to clarify whether the additives could extend the operation window for the applied current density.

The morphologies of Zn–Mn deposits plated from the baths containing different concentrations of HBA or DMBA additive, are presented in Fig. 2b–e. It can be seen that the additive concentration had a higher impact on the coating morphology than the additive type. Namely, no dendrites are visible in Fig. 2b and c, but grain globules, ranging from 2–4 μm, are found for the Zn–Mn deposits plated from the baths containing 0.25 g dm⁻³ HBA or DMBA. Thus, both HBA and DMBA are powerful additives for depressing the formation of dendrites on Zn–Mn deposits formed at high c.d.s, *i.e.*, they act as levelling agents. The substituted aromatic aldehydes were reported as dendrite inhibitors due to their specific adsorption on the metallic surface and slow diffusion to the cathode.^{20,21} Namely, the rate of metal deposition is inhibited on the cathode locations where the additive molecules are adsorbed. Since the additive bulk concentration is very low, the adsorption of organic molecule is highly influenced by mass transport, *i.e.*, the molecules are preferentially adsorbed on those parts of the surface that are more accessible, *i.e.* on the precursors of dendrites. As a result, protrusions receive more additive molecules by diffusion and consequently become smaller as the deposit grows.²¹

When the concentration of HBA and DMBA additives was increased to 0.5 g dm⁻³, two strong effects could be observed, as shown in Fig. 2d and e. The Zn–Mn globules no longer exist, meaning that the growth of the crystallites perpendicular to the surface was inhibited, and they spread across the surface as smooth layers to produce deposits which are rather flat on the microscopic scale. It should be noticed that the deposits obtained appeared bright, as observed by the naked eyes. Thus, the levelling action of the additives examined in this study, strongly depended on their concentration. This is in agreement with data for some other additives. Thus, it was shown, for example, that coumarone in Ni plating produced levelled or bright deposits only as a function of its concentration.²² A similar result was found for thiourea and saccharin in Ni–P and Cu deposition.²³ In fact, aldehydes

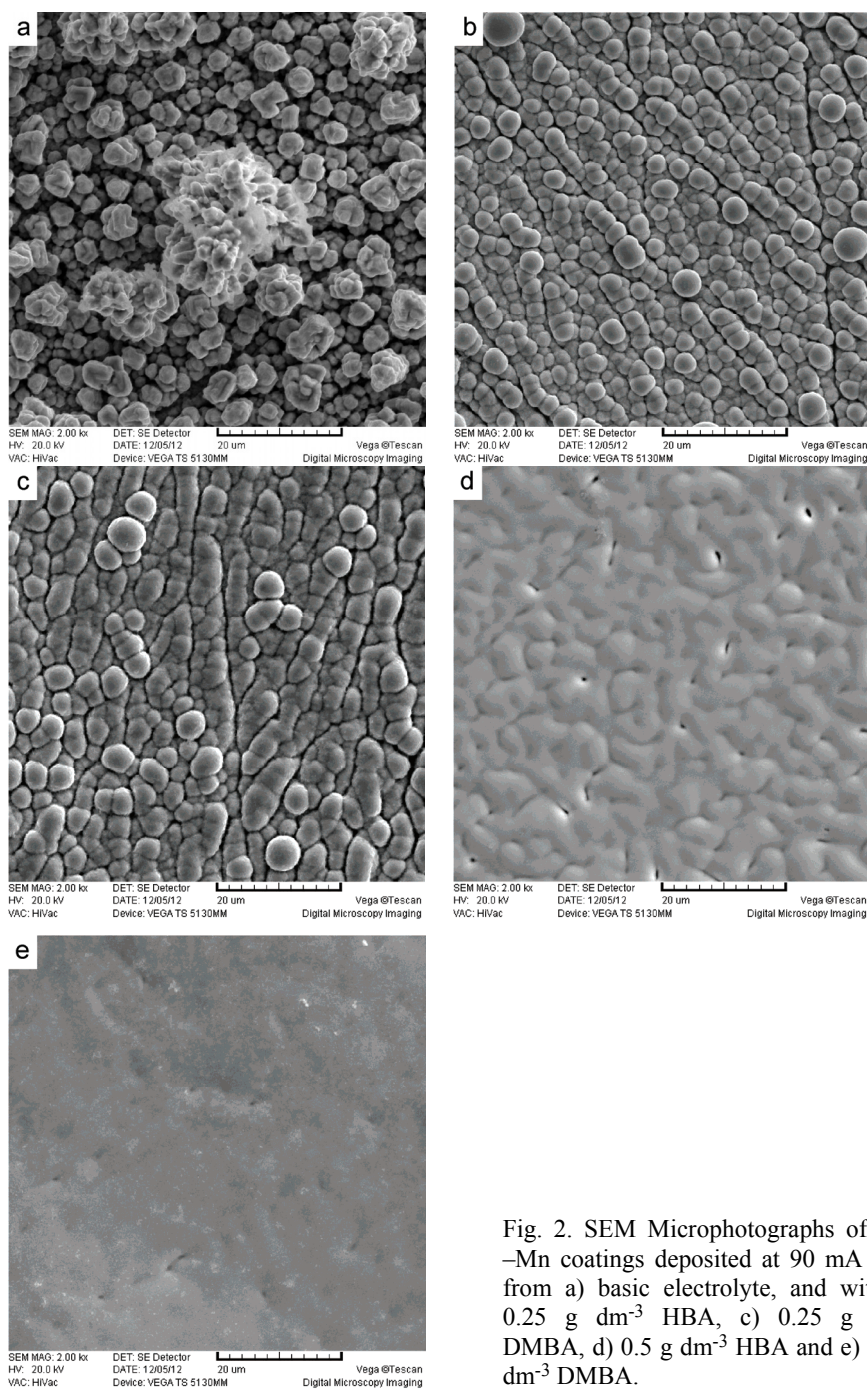


Fig. 2. SEM Microphotographs of Zn–Mn coatings deposited at 90 mA cm^{-2} from a) basic electrolyte, and with b) 0.25 g dm^{-3} HBA, c) 0.25 g dm^{-3} DMBA, d) 0.5 g dm^{-3} HBA and e) 0.5 g dm^{-3} DMBA.

are widely used as brightening agents in Zn electrodeposition, improving grain fineness.^{13,14,24} Additives that smooth the surface at the 1–500 μm lateral length are known as levellers and the ones responsible for surface brightening at 1–1000 nm lateral distance are known as brighteners.²⁵ Apart from visual examination, no additional experiment was conducted in order to evaluate further the brightening effect of the two additives in the present article.

However, as a second effect of the change in additive concentration from 0.25 to 0.5 g dm^{-3} was that an insufficient coalescence of the deposits could be noticed, with pitting-like morphology, particularly for the coating obtained with HBA (Fig. 2d), probably indicating that the additives and/or products of their decomposition act as organic contaminants in the electrolyte. As a matter of fact, many organic compounds, above some critical concentration in a plating bath, bond to specific parts of the substrate and consequently may be trapped in the deposit or cause a noticeable hydrogen gas bubbling, increasing thereby the chances for the formation of gas pits in that area. The pitting of the deposit due to organic impurities is a serious problem in Ni²² and Cr²⁶ electrodeposition, and probably is present in this work, for higher additive concentration (0.5 g dm^{-3}).

In order to additionally examine the levelling effect of substituted aromatic aldehydes, the macroscopic roughness was measured for the Zn–Mn coatings deposited at different concentrations of the two additives, and the values of average roughness are presented in Table I. Similarly to the SEM observations, it is clear from Table I that the roughness of the samples depended strongly on the concentration of the additives, regardless of their structure, in terms of a decrease in the average roughness on addition of more additive to the plating solution. The lower R_a values for the samples deposited in the presence of additives, compared to the sample from blank electrolyte, clearly denote the smoothening effect. This is particularly visible for 0.5 g dm^{-3} of additives, where the R_a values of $\approx 0.5 \mu\text{m}$ indicate very flat deposits.

TABLE I. The values of average roughness, R_a , for Zn–Mn coatings deposited from different plating electrolytes

Additive type	Additive concentration / g dm^{-3}	R_a / μm
No additive	0	1.65
HBA	0.25	1.03
	0.5	0.47
DMBA	0.25	0.98
	0.5	0.62

EDS Analysis

The chemical composition analysis revealed that in addition to Zn and Mn, various amounts of oxygen were present in the Zn–Mn coatings obtained at 90 mA cm^{-2} . The atomic contents of Mn and O in the samples deposited from

electrolytes with different additive concentrations are shown in Fig. 3. The oxygen content was between 5 and 7 at. % for the samples obtained in the presence of additives, which could be related to alloy oxidation during air-exposure.¹ On the contrary, the coating obtained in the blank electrolyte contained 18 at. % oxygen, indicating either rapid corrosion of the dendritic sample or, more probably, the inclusion of metallic hydroxides, due to the increased pH in the near-cathodic layer, as a result of fast hydrogen evolution.²⁷ The issue of hydroxide inclusions was reported for Mn alloy coatings obtained at high c.d.s, where the oxygen content reached even 60 at. %, ^{11,27} and also for pure Zn coatings, where 18 mass % of oxygen was reported.²⁸

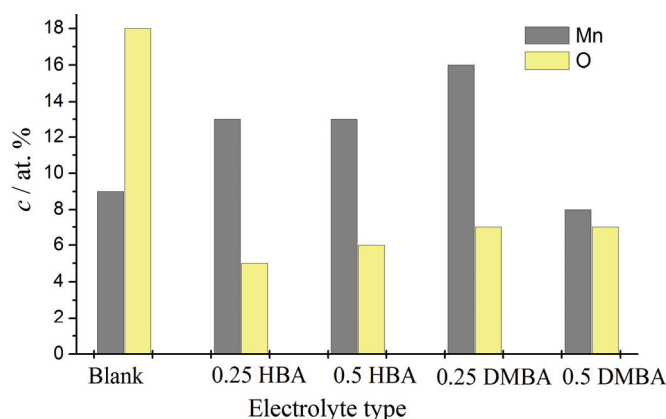


Fig. 3. The dependence of the Mn and O content in the Zn–Mn coatings obtained at 90 mA cm⁻² on the type and concentration of the plating additive.

Hence, the low oxygen percent in the coatings obtained with additives, probably means that the deposits were hydroxide-free, *i.e.*, the hydrogen evolution process during alloy deposition is not fast enough to create alkaline media in the near-cathodic layer.²⁹ It could be concluded that the EDS analysis gives circumstantial, but strong evidence that the additives are hydrogen inhibitors in Zn–Mn electrodeposition.

When it is assumed that the total applied deposition c.d. is related to Zn and Mn reduction and hydrogen formation, then the zinc and manganese atomic percentage determined by EDS, allows an evaluation of the partial current densities for each reaction.³⁰ While the surface morphology was quite similar for both additives, the elemental composition of the Zn–Mn deposits depended greatly on the additive type. The Mn content was 9 % in the coating obtained at 90 mA cm⁻² without additives in the electrolyte (Fig. 3) and it increased to 13 % when HBA was added, independent of the additive concentration. This indicates that the adsorbed HBA molecules do not affect the reduction of both metals equally, *i.e.*, either Zn reduction is more inhibited or Mn reduction is favoured in the presence

of HBA. On the other hand, in the case of DMBA, the role of its concentration is quite ambiguous, because at the lower DMBA concentration, the Mn content in the deposit reached 16 %, whereas it was only 8 % when 0.5 g dm^{-3} DMBA was present in the electrolyte.

Linear sweep voltammetry

In order to further examine the influence of additives on the coating morphology and chemical composition, electrochemical techniques were applied. For characterization of the substituted benzaldehydes as hydrogen evolution inhibitors, linear voltammetry was performed at 5 mV s^{-1} . The polarization curves, shown in Fig. 4, were recorded in plating solutions free of Zn and Mn ions; thus the increase in the cathodic current could be attributed to only one process, *i.e.*, hydrogen evolution. The polarization curves in Fig. 4 reveal that hydrogen evolution started at the same potential, around -1200 mV , in all electrolytes. However, at more negative potentials, the suppression of hydrogen evolution by the additives was seen as a decrease in the j - E slope.³¹ According to the literature, substituted aromatic aldehydes are strong hydrogen evolution inhibitors, due to the interaction of the negative charge centre in the organic molecule ($-\text{CHO}$) with the positive charge carriers at the cathode/electrolyte interface, *i.e.*, with the adsorbed hydrogen ions from acidic plating baths.³² It is also clear from Fig. 4 that HBA provides stronger inhibition as compared to DMBA.

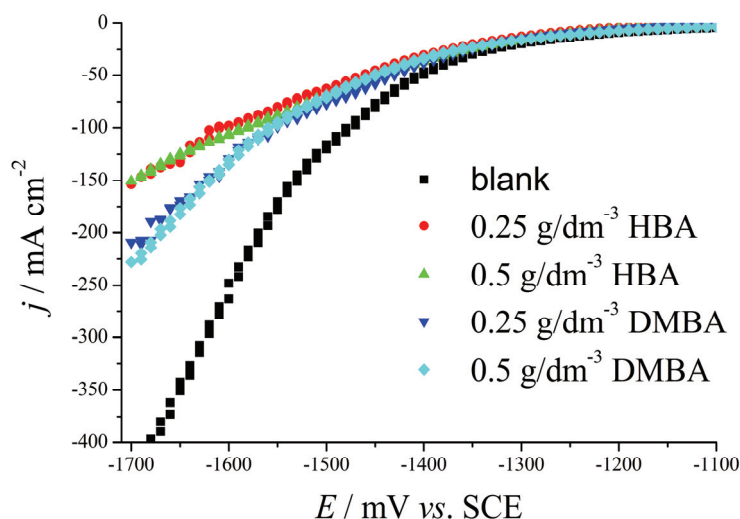


Fig. 4. Linear voltammograms of a steel electrode in $1.25 \text{ mol dm}^{-3} \text{ KCl} + 0.4 \text{ mol dm}^{-3} \text{ H}_3\text{BO}_3$, with different concentrations of HBA and DMBA additives.

It should be additionally stressed that the increase in the additives concentration from 0.25 to 0.5 g dm^{-3} did not bring any improvement in the suppression

of hydrogen evolution. In fact, it is quite common with many additives that the slopes of the cathode potential vs. additive concentration curves decrease with increasing additive concentration, and that a polarization plateau is reached at a certain amount of additive.³³

To conclude, it is clear that both additives are beneficial for Zn–Mn electrodeposition because they inhibit the hydrogen evolution reaction, thus increasing the current efficiency and preventing coating porosity. Moreover, as the most important fact, they enable the formation of hydroxide-free Zn–Mn deposits even at 90 mA cm^{-2} .

Chronopotentiometric study

From the previous analysis, it could be concluded that two general effects were noticed concerning the influence of the additives: an increase in the smoothness of the samples with increasing additive concentration and the Mn content change in the alloys. A number of theories concerning the influence of additives on metal deposition start from the principle of electrosorption of additives at the metal/electrolyte interface;²⁹ hence this approach may also be used to relate the structure and concentration of the additives analysed in this work with their effect on Zn–Mn deposits. A strong influence of additives on the cathodic overpotential is often used as a selection criterion for efficient plating agents. It is thought that the main cause of the changes in the cathode potential is the coverage of the electrode interface by additive molecules, which increases the effective c.d. and, consequently, the overvoltage.³³

The effect of HBA and DMBA additives on the cathodic potential related to the Zn–Mn electrodeposition at a c.d. of 90 mA cm^{-2} is shown in Fig. 5. It can be seen that the curves recorded in the presence of the additives are 55–70 mV more negative as compared to the curve of the blank electrolyte. The SEM photographs showed that such an overpotential difference is sufficient for the production of smooth, non-dendritic deposits with a fine-grained structure.

When the influence of additive concentration is analyzed, it is seen that the overpotential only slightly increases when the additives concentration increases from 0.25 to 0.5 g dm^{-3} , *i.e.*, the change is approximately 5–20 mV. Nevertheless, it seems possible that such a small increase in the cathodic overpotential is related to the change in surface morphology from spherical agglomerates to a completely flat surface, as SEM analysis showed. This is consistent with the literature, because it was reported, for example, that the brightening of a nickel deposit was accompanied by a cathode polarization of only 20 mV.³⁴ Based on the overpotential change seen in Fig. 5, it could be assumed that a more uniform distribution of the adsorbed additive molecules could occur on the surface when a higher additive concentration is applied, leading to significant reduction in the Zn–Mn aggregate size, which resulted in a smoother appearance.²⁵

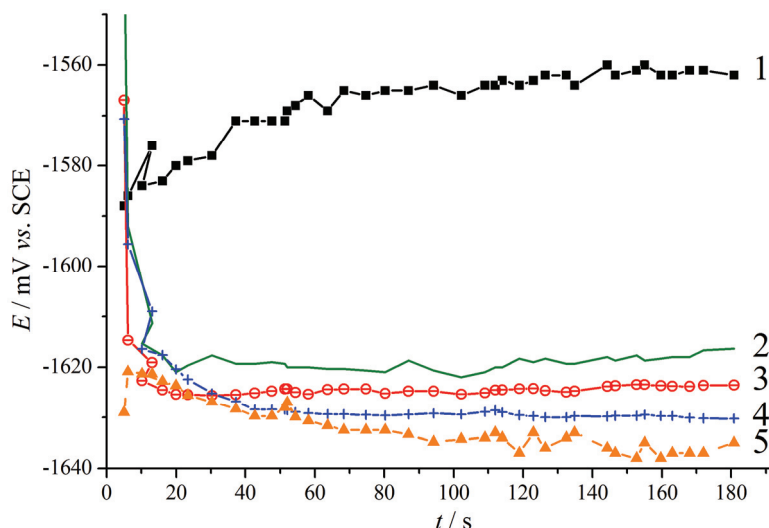


Fig. 5. Potential – time transients for Zn–Mn alloy electrodeposition at 90 mA cm^{-2} from: 1) basic electrolyte, with 2) 0.25 and 3) 0.5 g dm^{-3} HBA; with 4) 0.25 and 5) 0.5 g dm^{-3} DMBA.

Concerning the additive structure, an analysis of the voltammograms shown in Fig. 4, which refer to hydrogen evolution, and of the $E-t$ curves in Fig. 5, where the main reactions are Zn and Mn reduction, indicates that the DMBA additive is a weaker inhibitor for hydrogen evolution, as compared to HBA additive, but it has a stronger inhibiting influence on the reduction of metal ions. Furthermore, the EDS analysis showed that the Mn at. % in the Zn–Mn deposits was principally higher for the depositions in the presence of additives and, additionally, that DMBA had a more pronounced effect on the Mn content in alloy deposit. Based on all these results, it could be inferred that the molecular structure of the investigated additives plays an important role in their interaction with Zn^{2+} , Mn^{2+} or H^+ reduction.

The adsorption of aromatic aldehydes, such as vanillin and its derivatives, is well documented and examined,^{32,35} and it was shown that the adsorption on a steel surface would occur through carbonyl, methoxy and hydroxyl functional groups arranged on the benzene ring.³⁵ In addition, it was assumed that the organic molecules preferably interact with the positive cathodic sites, and the strength of the negative charge centre in the molecule (carbonyl group) is influenced by side groups of the benzene ring ($-\text{OH}$, $-\text{OCH}_3$).³² It should be emphasized that besides adsorbed hydrogen ions, the metallic species participating in Zn–Mn deposition may also be positive charge carriers adsorbed on the cathode (for instance, Zn_{ad}^+ , ZnH_{ad}^+ , etc.).³⁶ As Fig. 1 shows, the HBA molecule has a hydroxyl, while the DMBA molecule has two methoxy groups as functional side

groups. It can be summarized that due to different side groups, the molecules have different affinities to various adsorbed species, which results in the slight overpotential deviations observed in Fig. 5, but leads to significant changes in Mn at. % in the coatings.

CONCLUSIONS

The effects of the addition of two aromatic aldehydes to the plating electrolyte on the properties of Zn–Mn alloy electrodeposits were studied. The SEM micrographs showed that the Zn–Mn coatings obtained at 90 mA cm^{-2} in the presence of additives were smooth and homogeneous. A levelling action was observed with 0.25 g dm^{-3} additive and that it increased when the additive concentration was increased to 0.5 g dm^{-3} , regardless of the additive type.

The EDS results showed that the sample deposited from the electrolyte free of additive possesses high amount of oxygen, indicating rapid corrosion or metallic hydroxide inclusions in the sample. The very low oxygen percent in the samples deposited with additives, as well as a voltammetric examination, gave evidence for strong inhibiting actions of the additives on hydrogen evolution. Furthermore, the observed changes in Zn and Mn atomic content in the coatings revealed that the additive molecules interact with all reactions in the process, *i.e.*, the Zn^{2+} , Mn^{2+} and hydrogen ion reduction. It is assumed that the molecule structure of the additives (*i.e.*, the presence of methoxy or hydroxyl groups) affects their adsorption ability and, consequently, modifies the kinetic parameters of all reactions participating in the electrodeposition of Zn–Mn alloys.

It could be concluded that the employed aromatic aldehydes are beneficial additives for Zn–Mn alloy electrodeposition, because they extend the operative window of the current density, thereby increasing the Mn content and enabling the formation of smooth deposits.

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ИЗВОД

УЛОГА СУПСТИТУИСАНИХ АРОМАТИЧНИХ АЛДЕХИДА У ЕЛЕКТРОХЕМИЈСКОМ ТАЛОЖЕЊУ Zn–Mn ЛЕГУРА

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У циљу успоравања реакције издвајања водоника и спречавања настајања дендрита приликом електрохемијског таложења Zn–Mn легура високим густинама струје, неопходна је примена специфичних додатака. У овом раду је испитиван утицај два ароматична алдехида, 4-хидрокси-бензалдехида и 3,4-диметокси-бензалдехида, као специфичних додатака у таложењу Zn–Mn легура. Карактеризација превлака скенирајућом електронском микроскопијом и енергетском дисперзионом спектроскопијом X-зрака, као и испитивање утицаја специфичних додатака на процес таложења електрохемијским

методама, указују на сложене интеракције молекула ароматичних алдехида у процесима издвајања водоника и редукције јона цинка и мангана. У раду је показано да се само применом одређене концентрације и врсте специфичног додатка може мењати хемијски састав Zn–Mn легуре и могу се добијати превлаке мање храпавости.

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