

## CORROSION STABILITY OF ELECTROCHEMICALLY DEPOSITED Zn-Mn ALLOY COATINGS

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**Abstract:** Zinc alloy coatings electrochemically deposited on steel from electrolytes with different components differ in their composition, homogeneity, porosity, structure and other characteristics that affect their corrosion resistance. Manganese is characterized by a very negative electrochemical potential and very high strength, prompting many researchers to study Zn-Mn alloys for the anti-corrosion purposes in the industry, especially automotive. In this work it was examined the influence of the type of the electrolyte deposition on the current efficiency during electrodeposition of Zn-Mn alloys. Zn-Mn alloys were deposited on steel from chloride, sulphate and pyrophosphate plating baths at different current densities. We have examined the influence of deposition current density on the current efficiency during electrodeposition, appearance of alloy coatings, as well as their corrosion stability. It was shown that Zn-Mn alloys with the best corrosion properties, among all examined ones, were obtained from chloride plating bath at 2 A dm<sup>-2</sup>.

**Keywords:** Electrodeposition of alloys, Zn-Mn alloys, morphology, corrosion properties.

### INTRODUCTION

Zinc and its alloys, particularly Zn-Fe, Zn-Co and Zn-Ni, are widely used for sacrificial protection of ferrous materials in the contemporary industry. Several authors have reported that, in some corrosion medium, Zn-Mn alloy has even better corrosion resistance [1, 2]. Zn-Mn layers can be electrodeposited from a simple sulphate bath [2], a sulphate bath containing citrates [3, 4], a chloride bath [5], a fluoroborate bath [6], an acidic bath containing EDTA [7]. Although Rama Char and co-workers showed in 1956 that zinc and its alloys can be electrodeposited from pyrophosphate-based bath [8], the first successful attempt to deposit Zn-Mn alloy from this bath was made only a few years ago [9, 10].

Zn-Mn alloys with 20-30 % Mn, though being less thermodynamically noble than Zn, show a passivating behavior in chloride environments and hence, the highest corrosion resistance known among Zn alloys [1, 11]. Coatings with lower Mn content (up to 10 %) have shown better mechanical properties needed for automotive applications. These alloys do not possess such corrosion stability like high-Mn

alloys, but their resistance still could be significantly improved as compared to pure zinc coatings. In this work, the galvanostatic deposition of Zn-Mn alloys from chloride, sulphate and pyrophosphate-based alkaline solution was investigated. An attempt was made to determine the influence of the applied current density on the current efficiency, morphology of deposits, as well as on their corrosion behavior in 3 % NaCl. The aim of the work is to find the electrodeposition parameters (plating bath and deposition current density) that would result with the low Mn alloy, providing improved corrosion stability.

### EXPERIMENTAL

The composition of the plating bath used is presented in the Table 1.

All solutions were made from analytical grade chemicals (Sigma Aldrich) and double distilled water.

Working electrodes were steel panels (ISO T 57). Prior to each experiment, the steel surfaces were polished successively with emery papers of the fol-

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lowing grades: 600, 1000, 1200 and then degreased in a saturated solution of NaOH in ethanol, pickled with a HCl 50% by volume for 30s and finally rinsed with distilled water.

Table 1. Plating baths

Solution	[mol dm <sup>-3</sup> ]	<i>j</i> / A dm <sup>-2</sup>	pH
ZnCl <sub>2</sub>	0,45		
MnCl <sub>2</sub> ·4H <sub>2</sub> O	0,22 – 1,80		
H <sub>3</sub> BO <sub>3</sub>	0,42	0,5 – 12,0	5,0
KCl	3		
ZnSO <sub>4</sub> ·7H <sub>2</sub> O	0,3		
MnSO <sub>4</sub> ·H <sub>2</sub> O	0,3		
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	0,2 – 0,8	0,5 – 12,0	5,0
K <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	1		
ZnCl <sub>2</sub>	0,05		
MnCl <sub>2</sub> · 4H <sub>2</sub> O	0,05	0,5 – 12,0	9,3
Ascorbic acid	0,01		

Electrodeposition of Zn-Mn alloys (10 μm thickness) was performed galvanostatically, at different current densities on steel panels (20 x 20 x 0,25 mm). Counter electrode used in corrosion testing was a Pt foil, placed parallel to the working electrode. In all other cases, cylindrical Zn foil (high purity zinc) placed close to the cell walls was used, providing a good current distribution in the cell, since working electrode was placed in the middle of the cell. The reference electrode was a saturated calomel electrode (SCE).

Polarization measurements were performed by a computer-controlled potentiostat (PAR M273A) by using the corrosion software (PAR M352/252 version 2,01) with the sweep rates of 1 mVs<sup>-1</sup>. The current interrupt technique was used with time of current interruption being 0.5 s for obtaining polarization curves corrected for IR drop. The same instrument was used for corrosion measurements.

Corrosion measurements were performed in an aerated 3% NaCl solution, which was appropriate for studying corrosion due to the presence of corrosion activators (chloride ions). The corrosion rates of the deposited Zn-Mn alloys were determined by using extrapolation of anodic polarization curves to the open circuit potential (OCP). Potential sweep rate of 0,2mVs<sup>-1</sup> was applied starting from - 250 mV vs OCP and ending at +250 mV vs OCP, after the constant OCP was established (up to 10 min). The corrosion behavior was determined also by following the open circuit potential during exposure of samples to aerated 3 % NaCl solution, until the OCP of steel substrate was reached.

The structural characterization was performed by optical microscope Olympys CX 41 with Olympys UC 30 camera.

## RESULTS AND DISCUSSION

### Deposition of Zn-Mn alloys

In order to determine the potential range where metal deposition takes place, polarization diagrams were recorded in different plating baths, by using linear sweep voltammetry at a sweep rate of 1mVs<sup>-1</sup> (Fig 1.). The significant difference could be observed for deposition of Zn-Mn alloy coatings from various plating baths. Namely, the deposition takes place with the smallest overvoltage from sulphate plating bath, in a wide range of deposition current densities. Deposition from pyrophosphate plating bath occurs at more cathodic potentials relative to the other two plating baths, indicating considerable overvoltage needed to initiate the deposition from this bath.

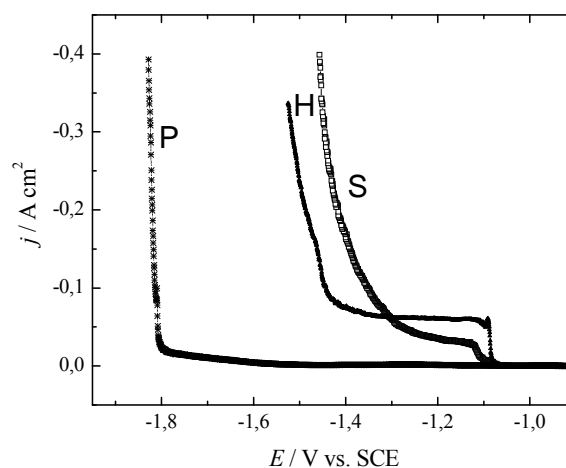


Figure 1. Polarization curves for deposition of Zn-Mn alloy coatings from:chloride (H), sulphate (S) and pyrophosphate (P) plating baths

Both Zn(II) and Mn(II) have deposition potentials more negative than the potential for hydrogen evolution reaction, so H<sub>2</sub> evolution is always a parallel reaction during the alloy deposition. The current efficiency, η<sub>i</sub>, (CE) for alloy deposition was calculated on the basis of the Faraday's law:

$$\eta_j(\%) = \frac{m \cdot z \cdot F}{q \cdot M} \cdot 100$$

where *m* is coating mass (determined by weighing samples prior to and after plating), *z* is the number of exchanged electrons during metal reduction, *F* is Faraday constant and *q* is charge passes during deposition.

The influence of the current efficiency on the deposition current density was determined for the range of current densities based on the rates of metal

deposition common in the industrial plating. The results obtained in the different plating baths are shown in the Table 2.

The current efficiency sharply increases with the increase of the deposition current density and then decreases again for Zn-Mn alloys electrodeposited from sulphate and chloride plating baths. The CEs during electrodeposition from those two baths are quite high, above 80 % for all examined deposition current densities. This correlation of CE with deposition current density is quite typical for a regular codeposition system [12,13]. For Zn-Mn alloys, electrodeposited from pyrophosphate plating bath, the CE continuously decreases with the increase of deposition current density within a broad range of current densities. However, the current efficiency for alloy plating in this plating bath is quite low, below 25 %, for all examined deposition current densities. The lower current efficiency for Zn-Mn deposition from this bath indicates that hydrogen evolution, which is a parallel reaction taking place on a cathode, is higher in the case of deposition from this plating bath.

Table 2. The current efficiency,  $\eta_i$ , for deposition of Zn-Mn alloy coatings from different plating baths and at different current densities,  $j_{dep}$

Plating bath	$j_{dep} / A\ dm^{-2}$	$\eta_i / \%$
Sulphate	2	90
	4	94
	6	87
	8	84
	12	79
Chloride	2	83
	4	88
	6	95
	8	83
	12	81
Pyrophosphate	2	25
	4	23
	6	23
	8	21
	12	20

#### Corrosion behavior

In order to determine corrosion stability, the plated specimens (10  $\mu m$  thickness) were immersed in a 3% aqueous NaCl solution and the open circuit potential ( $E_{ocp}$ ) was measured daily. The 10  $\mu m$  thick zinc coating was tested for comparison. Fig. 2 shows the time dependence of  $E_{ocp}$  for steel plated by Zn-Mn alloys deposited at the same current density, 2  $A\ dm^{-2}$ , from different plating baths. The open circuit potential of bare steel surface in 3% NaCl

was  $-640\ mV$  vs. SCE and it is marked with a line in Fig. 2. The potentials of the Zn-Mn alloys are more negative than  $E_{ocp}$  of steel base, so Zn-Mn deposits offer sacrificial cathodic protection. The  $E_{ocp}$  values of steel modified by Zn-Mn alloys increase positively with time of immersion and reach the steel  $E_{ocp}$ , which represents the deposit loss and start of the corrosion process. The open circuit potentials of alloys deposited at the same current densities from different plating baths slightly differ initially and eventually reach almost the same values. The small initial  $E_{ocp}$  difference is due to the alloy phase difference and the difference in the chemical composition. The results of the visually observed alloy destruction in 3% NaCl solution, or the appearance of red rust on the steel base, are presented in Table 3. It can also be seen from the Table that a better corrosion stability of Zn-Mn coatings is obtained by deposition from chloride plating bath. The longest time to rest rust appearance, indicating the best corrosion stability, was observed for Zn-Mn alloy deposited from chloride plating bath at 2  $Adm^{-2}$ .

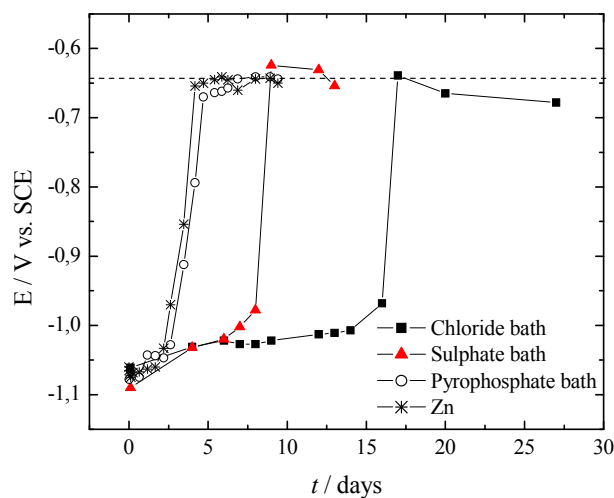


Figure 2. The dependence of  $E_{ocp}$  for Zn and Zn-Mn alloys deposited on steel from different plating baths at 2  $A\ dm^{-2}$  (10  $\mu m$  thickness).

Anodic polarization curves in a small range of potential near to OCP were obtained in a 3% NaCl solution. Some of the  $E-\log j$  dependences obtained are shown in Figs. 3 and 4 for Zn-Mn alloy coatings deposited from pyrophosphate and chloride plating baths, respectively. The corrosion current densities,  $j_{corr}$ , were estimated from the intersections of the anodic Tafel plots with the OCP. The corrosion potentials,  $E_{corr}$ , and corresponding corrosion currents for the alloy samples are given in the Table 4. Data in the Table 4 are mean values of three to five measurements. The polarization curve for pure Zn coating is shown in the Fig. 3, for the purpose of comparison.

Table 3. The time of red rust appearance, corrosion potentials for Zn-Mn alloys deposited from different plating baths at different current densities

Plating bath	$j_{\text{dep}} / \text{A dm}^{-2}$	Time / days
Sulphate	1	12
	2	9
	3	8
	4	2
	12	3
Chloride	1	9
	2	17
	3	13
	5	11
	8	9
Pyrophosphate	2	7
	3	6
	8	6
	12	5
Zn		4

The influence of deposition current density on the corrosion stability for Zn-Mn alloy coatings, deposited from pyrophosphate plating bath, is clearly seen from the Fig. 3. The Zn-Mn alloy coating deposited at  $12 \text{ A dm}^{-2}$  showed the highest  $j_{\text{corr}}$  value among Zn-Mn deposits investigated, but all of them had greater corrosion stability than a pure Zn coating. The  $E_{\text{corr}}$  values of Zn-Mn coatings altered between  $-1162$  and  $-1061 \text{ mV}_{\text{SCE}}$ , but no correlation could be found in the deposition current density.

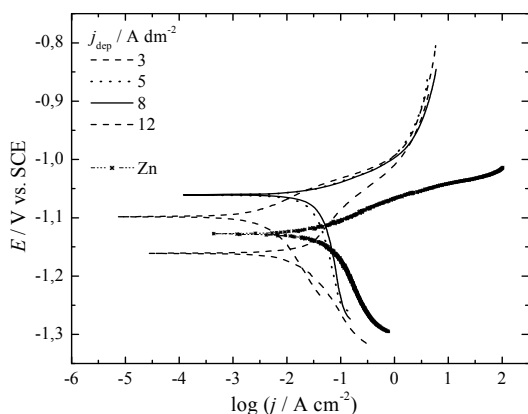


Figure 3. Anodic polarization curves in 3 % NaCl for pure Zn and Zn-Mn alloy coatings deposited from pyrophosphate bath at different current densities.

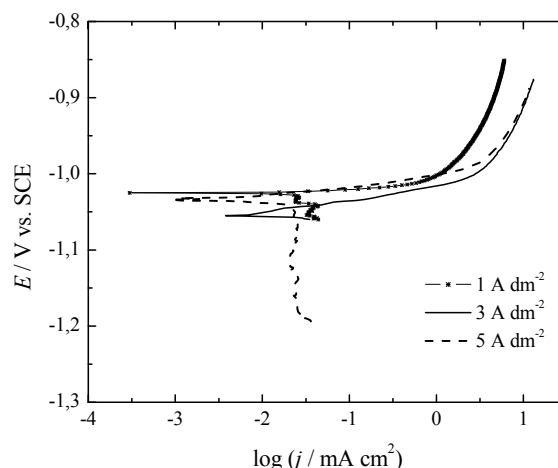


Figure 4. Anodic polarization curves in 3 % NaCl for Zn-Mn alloy coatings deposited from chloride bath at different current densities.

In the course of the past ten years, the literature has explained in detail that the corrosion resistivity of Zn alloys containing up to 10 at.% Mn (all examined Zn-Mn coatings had up to 10 at.% Mn), in NaCl solution, is the consequence of a passive layer formed on the attacked surface [2,14,15]. In the present research, the Tafel polarization curves (Fig. 3 and 4) did not show a typical passive behavior of coatings, neither for pure Zn nor for alloys. However, slower dissolution rate of alloys at potential of  $-1000 \text{ mV}_{\text{SCE}}$ , as compared to dissolution of pure Zn (Fig. 3), could be assigned to the formation of adherent corrosion products with low solubility.

These results (shown in the Fig. 3 and 4, as well as in the Tables 3 and 4) clearly indicate that the highest corrosion resistance is accomplished for Zn-Mn coatings deposited from chloride plating bath, with the highest corrosion stability obtained for Zn-Mn alloy deposited from chloride plating bath at  $2 \text{ A dm}^{-2}$ .

### Surface morphology

The surface morphology of electrodeposited Zn-Mn alloys was examined by using optical microscopy. Typical surface morphologies of some of the deposits obtained from different plating baths are shown in the Fig. 5 -7.

Table 4. The corrosion potentials,  $E_{\text{corr}}$ , and corrosion current densities,  $j_{\text{corr}}$ , for Zn-Mn alloys deposited from different plating baths at different current densities

Plating bath	$j_{\text{dep}} / \text{A dm}^{-2}$	$E_{\text{corr}} / \text{V}$	$j_{\text{corr}} / \mu\text{A cm}^{-2}$
Sulphate	2	-1,022	11
	3	-1,060	14
	5	-1,030	22
	9	-1,077	36
	12	-1,084	41
Chloride	1	-1,024	7
	2	-1,055	4
	5	-1,033	5
	9	-1,051	8
Pyrophosphate	2	-1,082	13
	3	-1,099	8
	5	-1,061	18
	8	-1,062	20
	12	-1,162	22
Zn		-1,128	27

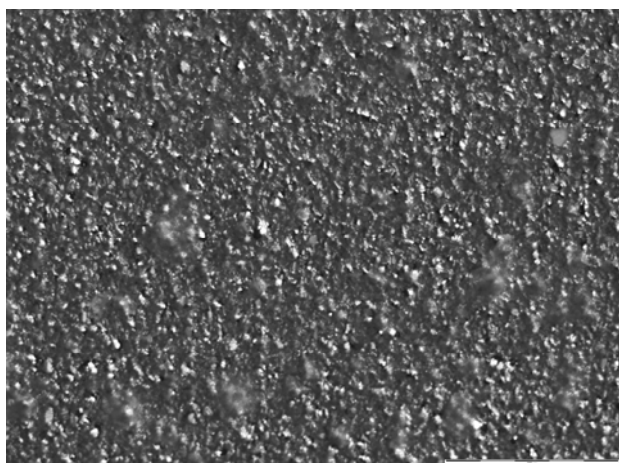


Figure 5. The microphotographs of Zn-Mn alloy coating deposited from sulphate bath at  $5 \text{ A dm}^{-2}$  (magnification 10 x).

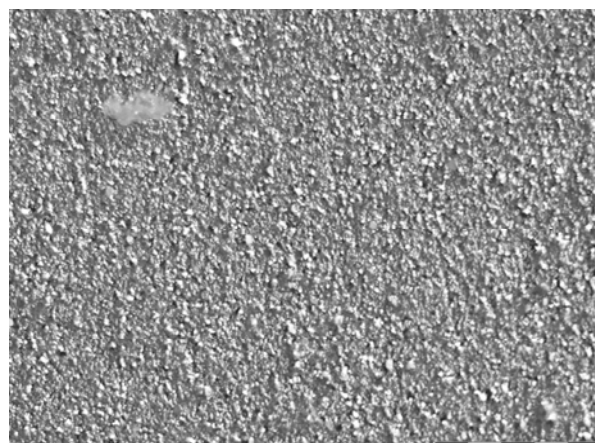


Figure 6. The microphotographs of Zn-Mn alloy coating deposited from chloride bath at  $5 \text{ A dm}^{-2}$  (magnification 10 x).

Adherent Zn-Mn deposits of good quality are generally obtained at current densities from 3 to  $12 \text{ A dm}^{-2}$ . Deposits obtained at current densities lower than  $1 \text{ A dm}^{-2}$  do not cover the entire steel surface, even for a long deposition times, so that the protective behavior of Zn-Mn alloy cannot be accomplished. On the other hand, deposits at current densities higher than  $12 \text{ A dm}^{-2}$  have non-homogenous appearance and, furthermore, after achieving thickness of a few micrometers, they do not adhere well to the substrate.

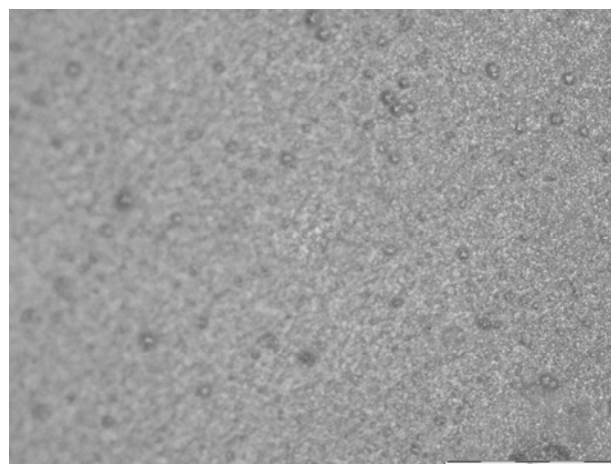


Figure 7. The microphotographs of Zn-Mn alloy coating deposited from pyrophosphate bath at  $5 \text{ A dm}^{-2}$  (magnification 10 x).

The Zn-Mn electrodeposits obtained from chloride plating bath, for all examined deposition current densities, are homogenous. The influence of deposition current density on the Zn-Mn alloy appearance was more prominent for the deposits obtained from sulphate plating bath, and nonhomogenous deposits, with poor surface coverage, were obtained at higher current densities. The Zn-Mn alloy coatings deposited from pyrophosphate plating bath were not homogenous for all examined deposition current densities.

In addition, it could be seen from the Fig. 5-7, that the deposit obtained at 5 A dm<sup>-2</sup> from sulphate bath has a much coarser morphology than the one obtained from chloride bath. Finer grained structure of Zn-Mn alloy obtained from chloride bath, as compared to the microstructure of deposit obtained from sulphate bath, resulted in a better corrosion stability, probably due to the fact that small grain size create more grain boundaries that act as a corrosion barrier [44]. In addition, the non-homogenous morphology of Zn-Mn deposits obtained from pyrophosphate bath resulted with the increased corrosion rate.

## CONCLUSIONS

On the basis of the presented results, it could be concluded that the type of the plating bath and deposition current density have a significant influence on the current efficiency, morphology, as well as on the corrosion stability of Zn-Mn electrodeposited alloys.

The overall greater corrosion stability of Zn-Mn deposits was obtained from the chloride plating bath. Coatings deposited at 2 A dm<sup>-2</sup> from chloride bath proved to be compact, smooth and with the best corrosion behavior in chloride medium, whereas deposits obtained from pyrophosphate bath were non-homogenous and yielded the highest corrosion rate.

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## КОРОЗИОНА СТАБИЛНОСТ ПРЕВЛАКА Zn-Mn ЛЕГУРА ДОБИЈЕНИХ ЕЛЕКТРОХЕМИЈСКИМ ПУТЕМ

**Сажетак:** Преваке легура цинка електрохемијски добијене из електролита са различитим компонентама имају разлике у свом саставу, хомогености, порозности, структури и другим карактеристикама које утичу на њихову корозиону отпорност.

Манган се одликује јако негативним електрохемијским потенцијалом и јако великом чврстоћом, што је навело многе истраживаче на испитивања легуре Zn-Mn у антикорозионе сврхе, за потребе у индустрији, нарочито аутомобилској. У овом раду испитиван је утицај врсте електролита на таложење Zn-Mn легура, као и на искоришћење струје приликом електрохемијског таложења. Легуре су таложене на челику из хлоридног, сулфатног и пиродифосфатног електролита различитим густинама струје. При задатим условима таложења испитиван је хемијски састав, хрупавост, изглед превлака легура, и њихова корозиона стабилност. Показано је да највећу корозиону стабилност имају легуре добијене таложењем из хлоридног електролита густином струје од  $2 \text{ A dm}^{-2}$ .

**Кључне речи:** Електрохемијско таложење легура, Zn-Mn легуре, морфологија, корозиона својства.

