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## Electrodeposition of Mn-Zn Alloy Coatings with High Manganese Content from Sulfate-EDTA Solution in the Presence of Sodium Selenate Additive.

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### ABSTRACT

We obtained mirror-like coatings based on a nanocrystalline, globular-shaped Mn-Zn alloy with a high Mn content (98%) from a sulfate-ethylenediaminetetraacetic acid bath in the presence of sodium selenate ( $\text{Na}_2\text{SeO}_4$ ) as an additive. The nanocrystalline electrodeposited Mn-Zn alloy coating, featured broad and poorly defined X-ray diffraction patterns, which corresponded to a cubic  $\alpha$ -Mn crystal structure. The sodium selenate additive, concentrations and nature of components in solution affected the production of a mirror like coating of the Mn-Zn alloy. Using cyclic voltammetry and linear sweep voltammetry, we found that the sodium selenate additive hindered a hydrogen evolution side reaction, which proceeds in parallel with the manganese-zinc co-deposition process. In air, the coatings with a high content of manganese were covered with a black hydroxide. The corrosion of the alloy coating was studied in aerated 3.5% NaCl solution. The high content of manganese in the coating provides a high negative corrosion potential for the steel substrate therefore providing anodic protection of the steel.

**Keywords:** electrodeposition, Mn-Zn alloy, complexing ligands, chemical composition, current efficiency

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## INTRODUCTION

Galvanic coatings of manganese and its alloys as protective material have long attracted the attention of researchers owing to their high negative potential and ready availability. Manganese alloys with Cu, Zn, Fe, and Ni are characterized by high sacrificial protection characteristics and by their economic efficiency, which make these metals common components in protective coatings based on aluminum and magnesium [1].

A applications of pure manganese coatings have been hindered by their relatively high chemical activity and brittleness, which could be addressed by changing manganese of crystalline structure. Electrodeposition of Mn at room temperature from ultra-clean solutions by electrolysis yields plastic  $\gamma$ -Mn with a BCT (body central tetragonal) structure. In a short time, the deposited film transforms into a BCC (body centered cubic)  $\alpha$ -Mn form, which is stable but brittle [2]. The brittle,  $\alpha$ -Mn can be modified in the presence of additives, such as sulfite-ion ( $\text{SO}_3^{2-}$ ) or selenium compounds ( $\text{SeO}_3^{2-}$  or  $\text{SeO}_4^{2-}$ ) from manganese-ammonium sulfates or chloride solutions. These conditions support a stable cathodic process with a high current efficiency but also induce deterioration of the mechanical properties of coatings [3].

Many researchers have attempted to decrease the chemical activity and brittleness of manganese [4, 5]. It has been suggested that to alloying manganese with metals that have more positive standard potentials, e.g., Cu, Zn, and others, could stabilize the of  $\gamma$ -Mn form. For example, incorporation of 3% Cu into manganese contributes to stabilization of the  $\gamma$ -Mn form for a long period.

Special attention has been paid to coatings, that contain zinc and manganese. Such coatings with high and low manganese contents show good protective and mechanical properties [6, 7]. The application of Zn corrosion protection coatings for the of iron substrates is widespread. The protective properties of zinc coatings are based on their interactions with atmospheric  $\text{O}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{CO}_2$ , to form a dense and adherent film, which protects the iron from corrosion. Furthermore, in the case of galvanic corrosion, Zn is anodic to steel and as a result, it becomes the anode while the ferrous substrate becomes the cathode and does not corrode [8]. Corrosion resistance of zinc coatings depends on the composition of the atmosphere in which the steel is functioning. Its coatings are stable in dry atmospheres but unstable in humid sea environment (owing to the effects of Cl-ions). To increase the corrosion resistance of zinc coatings, Zn is alloyed with non-deficit metals such as manganese, which have a more negative potential than that of Zn. Manganese is anodic to Zn, thus, it protects Zn sacrificially. Furthermore, a synergistic effect is observed in the case of Mn-Zn alloys, resulting in better corrosion resistance compared with those of other Zn alloys. This is attributed to the formation of water insoluble basic salts of zinc and manganese on the surface of the coatings. These protective layers inhibit cathodic reduction of air oxygen therefore increasing the cathodic polarization of the corroded surface and decreasing overall corrosion [9]. Ukrainian researchers [10] have obtained Zn-Mn galvanic coatings with 55% current efficiency from manganese-zinc sulfate solutions containing sodium citrate as complexing agents. Testing of this coatings in aggressive environments showed that their corrosive resistance depends on the manganese content. Specifically, under high humidity conditions, traces of corrosion were observed on Zn-Mn coatings with 20% and 50% of Mn contents after 2402 and 2506 h., respectively. In the case of pure zinc coatings with the same thickness as the Zn-Mn coatings, protection was realized in the same environment for only 628 h. It should be noted that citrate-containing electrolytes used in the work mentioned above were unstable owing to the formation of precipitates in solution over the time.

Zn-Mn coatings are usually electrodeposited from chloride, sulfate or pyrophosphate baths containing complexing agents, such as-citrate-ions or ethylenediaminetetraacetic acid (EDTA) [11-17], to bring deposition potentials close to each other, because the standard electrode potential of  $\text{Zn}^{2+}/\text{Zn}$  and  $\text{Mn}^{2+}/\text{Mn}$  couples are considerably different, (- 0.76 V/SHE for Zn and -1.18 V/SHE for Mn). The potentials of zinc and manganese are much more negative than the potential for hydrogen evolution; hence, the reaction of hydrogen evolution occurs during the Zn-Mn coating deposition. This effect results in low current efficiency, inhomogeneous coverage of surface and poor adhesion on the coating to the substrate.

The main problems of the Zn-Mn deposition process are poor bath solution stability and very low current efficiency, especially for the case of high Mn contents. The Mn content in coatings has been increased to more than 50% by electrodeposition under a pulse regime with a very low current efficiency.

Bozzini et al. [20] found that the addition of thiocarbamide to a sulfate-citrate bath increased current efficiency and achieved a Mn content of 70-80% in the alloy with the favored phase being a nanocrystalline globular  $\epsilon$ -phase.

The goal of the present research was to obtain high quality Mn –Zn coatings with a high content of Mn at acceptable current efficiencies, from sulfate-citrate, sulfate-EDTA solutions, containing sodium selenate (NS) additives. NS was selected because the addition of selenite or selenate inhibits hydrogen evolution, increases the over potential of manganese deposition, facilitates crystallization of  $\alpha$ -Mn, improves the leveling effect of the electrolyte, and ultimately improves the manganese current efficiency [21].

Mn-Zn alloys obtained galvanostatically were characterized by analyzing their chemical composition, morphology, structure and the corrosion behavior of coating. Electrochemical reactions of interest were examined by cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry.

## EXPERIMENTAL SECTION

Electrolytes were prepared from analytical grade reagents. Electrolyte preparation, conditions of electrolysis and calculation of alloys cathodic current efficiency have been previously reported in detail [22]. Mn-Zn deposits were obtained from base sulfate electrolytes which contained:  $2\text{-}5\text{g}\cdot\text{l}^{-1}$   $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ ,  $6\text{-}10\text{g}\cdot\text{l}^{-1}$  EDTA ( $\text{Na}_2\text{H}_2\text{C}_2\text{O}_8\cdot 2\text{H}_2\text{O}$ ) or trisodium citrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7\cdot 5.5\text{H}_2\text{O}$ ),  $29\text{-}58\text{ g}\cdot\text{l}^{-1}$   $\text{MnSO}_4$ ,  $34\text{-}68\text{g}\cdot\text{l}^{-1}$   $(\text{NH}_4)_2\text{SO}_4$ . Furthermore, NS ( $\text{Na}_2\text{SeO}_4$ ) in the range of  $0.33\text{-}1.25\text{ g}\cdot\text{l}^{-1}$  was added to the basic bath.

The electrochemical characterization was performed in a conventional three-electrode cell with a water jacket. In this study, the working electrode was a carbon steel (C 0.22%, Mn 0.52%, Si 0.18%, P<0.04%, S<0.05%, As<0.08%) electrode, composed of the same material as the substrate for the deposition of the Mn-Zn coatings, with a surface area of  $0.2\text{ cm}^2$ . The reference electrode was a saturated Ag/AgCl electrode contacted with the cell through a Luggin capillary. All potentials in this paper are referenced to this electrode. The counter electrode was a Pt plate. No stirring was applied during the measurements. Prior to each experiment, the working electrode was polished with emery papers of 600 and 1200 grades, cleaned with a soda wet swab, pickled with  $1\text{M H}_2\text{SO}_4$  for 20 s, and finally were rinsed with distilled water. The morphology and structure of deposits were estimated from the current efficiency of the electrodeposition and densities of the alloys, and also confirmed by scanning electron microscope (SEM) cross-section measurements.

Electrochemical experiments were performed with an Electrochemical Analyzer (CH Instruments, Austin, TX, USA) operated with CHI600E software.

Galvanostatic electrodeposition of Mn-Zn alloys was performed on steel plates with a geometrical area of  $4\text{ cm}^2$ . The thickness was verified by a coating thickness measurement instrument DCFN 3000EZ. The thickness of the deposited alloy also was examined with a (SEM), (JSM-6510 series JEOL Ltd. Japan) and by X-ray diffraction (Russian production, copper anode  $K\alpha$ -emission,  $\lambda=1.54184\text{ \AA}$ ). The chemical composition of the coating was determined by the X-ray-fluorescence analysis method (Delta-Analyzer, < Innov-X Systems >USA) and with an X-ray energy dispersion micro-spectral analyzer (JSM 6510 LM, Japan).

## RESULTS AND DISCUSSION

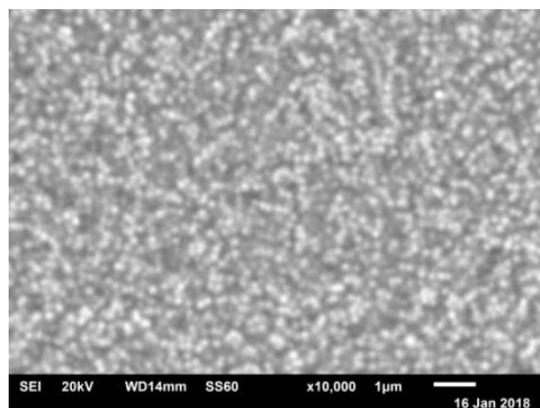
The presence of the additive NS in solution  $5\text{ g}\cdot\text{l}^{-1}$   $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ ,  $10\text{ g}\cdot\text{l}^{-1}$  EDTA,  $58\text{ g}\cdot\text{l}^{-1}$   $\text{MnSO}_4$ , and  $68\text{ g}\cdot\text{l}^{-1}$   $(\text{NH}_4)_2\text{SO}_4$  was effective in obtaining a mirror-like surface based on Mn-Zn alloy electrodeposition with a Mn high content. The influences of the current density on the chemical composition of the alloy coating and current efficiency are shown in Table 1.

Table 1 shows that a small increase of the current density resulted in a marked increase of the manganese content and a decrease of current efficiency. Further increases of the current density made the coating dendrite-like and of poor quality. Note that after removing the coating from the bath and washing in water, it became black after several min owing to oxidation in air. This is a characteristic of freshly deposited pure metallic manganese coating surfaces. To avoid oxidation of the deposited alloy, after removing the electrodes from the bath they were immersed in 10%  $\text{K}_2\text{Cr}_2\text{O}_7$  solution for 10 s. The electrodes were washed

with distilled water and dried in air. SEM images (Fig. 1) of the mirror-bright coatings show that coatings featured a nanocrystalline and globular texture.

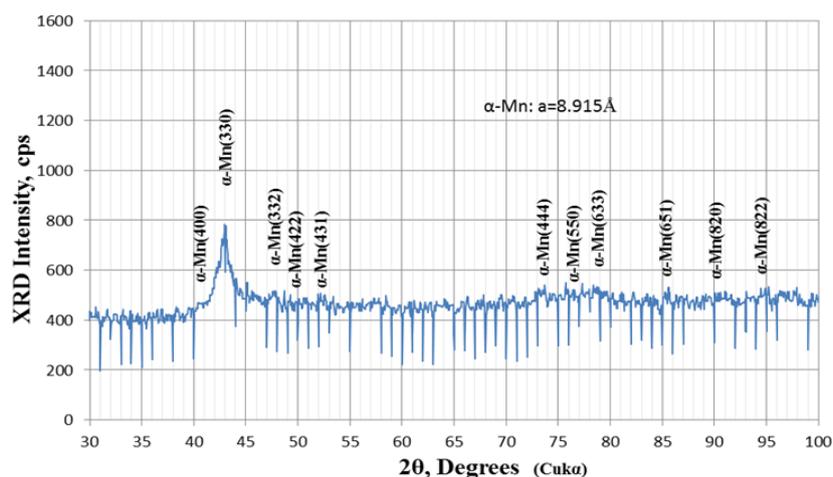
**Table 1. The influence of current density on chemical composition and current efficiency of coating.**  
 Solution: 5 g·l<sup>-1</sup> ZnSO<sub>4</sub>·7H<sub>2</sub>O, 10 g l<sup>-1</sup> EDTA, 58 g·l<sup>-1</sup> MnSO<sub>4</sub>, 68 g·l<sup>-1</sup> (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and 0.33g·l<sup>-1</sup> NS; pH 3.5-5.0;  
 t=30°C; plating time 15 min

Current density, (A cm <sup>-2</sup> )	Mn content, (Wt%)	Current efficiency of alloy, (%)
0.1	97.5	51.7
0.125	98.0	49.4
0.15	98.3	47.7
0.175	98.5	45.2



**Fig.1. SEM micrograph of a Mn-Zn (Mn 98%) alloy electrodeposited at 0.1A·cm<sup>-2</sup>**

Results of X-ray analysis of electrodeposited Mn-Zn alloy are shown on Fig.2. Owing to the nanocrystalline size of the electrodeposited coating, the peaks of the diffractograms were broad and poorly defined. The diffractograms corresponded to a cubic  $\alpha$ -Mn crystal structure. A small amount of zinc was dissolved in the  $\alpha$ -Mn and the most intense diffraction peak of Zn(101) was overlapped by the  $\alpha$ -Mn (330) peak.

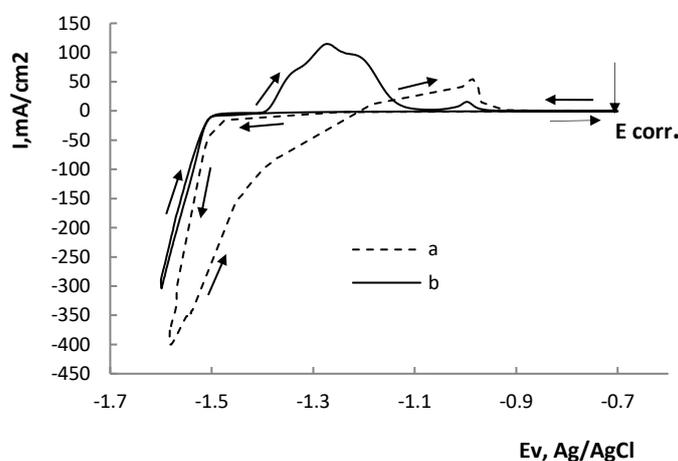


**Fig.2. X-Ray diffractogram of an electrodeposited Mn-Zn (Mn 97.8%)**

Grains in the coating had an average size of less than 10 nm as evaluated by the Scherrer method based on the half width of the diffraction maximum.

Any change of concentration of the solution components, either an increase or decrease, notably decreased the mirror like appearance of the coating; the surface changed to a cloudy grey-black color, with a spongy, non-adherent, and powdery texture. Such layers were inappropriate for applications as protective coatings. Our efforts to achieve the desired results by maintaining a constant ratio of the solution components, and substituting EDTA with other complexing agents (such as gluconate, tartaric acid, and seignette salt), were unsuccessful. Only when citrate-ions were used (at the same concentration as EDTA) and at high current densities ( $\geq 0.4 \text{ A}\cdot\text{cm}^{-2}$ ), were high quality, white, dense coatings with a high content of manganese obtained. The effects of the solution composition on the appearance of the coatings could be explained by the specific adsorption of EDTA and NS on the surface of electrode. Their concentrations on the surface effected the content of the electrochemically active zinc and particles manganese containing complexes. Solution pH also effected the production of high quality Mn-Zn alloy coatings. Specifically, the Mn-Zn alloy mirror-like coatings were obtained only in the range of pH 3.0-5.5. We selected  $30^\circ \text{C}$  as the temperature for electrodeposition. The thickness measured by a DCFN 3000EZ instrument for coatings deposited for 15 min varied in the range of 15-20  $\mu\text{m}$ .

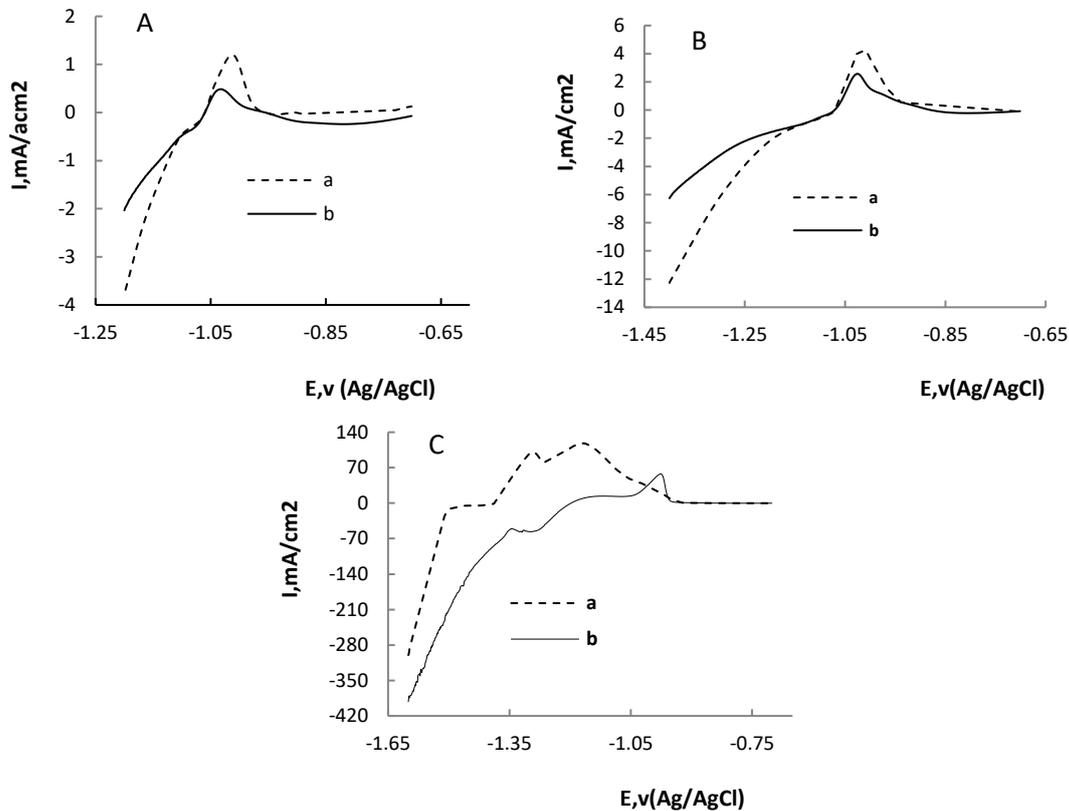
The electrochemical reactions occurring at the steel electrode in basic solutions were studied by cyclic voltammetry (Fig. 3) without NS (curve a) and with NS (curve b).



**Fig.3. Typical cyclic voltammogram obtained on carbon steel from aerated basic solution:  $5 \text{ g l}^{-1} \text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $10 \text{ g l}^{-1} \text{EDTA}$ ,  $58 \text{ g l}^{-1} \text{MnSO}_4$ , and  $68 \text{ g l}^{-1} (\text{NH}_4)_2\text{SO}_4$ ; pH 3.5;  $t=30^\circ\text{C}$ ; without NS additive (a) and with  $0.33 \text{ g l}^{-1}$  NS additive (b); scan rate  $10 \text{ mV}\cdot\text{s}^{-1}$ .**

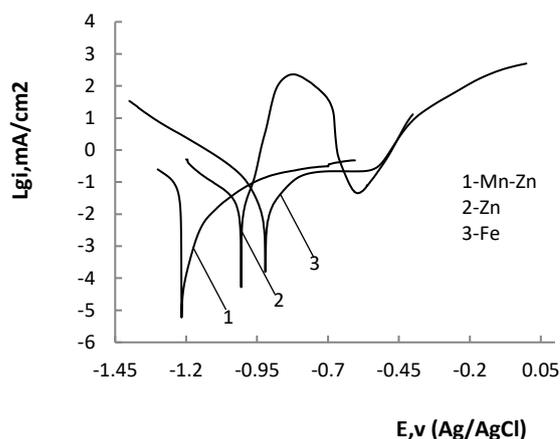
Scanning of the potential ( $10 \text{ mV}\cdot\text{s}^{-1}$ ) was performed from the stationary potential of steel  $-690 \text{ mV}$  (Ag/AgCl) towards more negative potentials until a cathodic potential of  $-1.6 \text{ V}$  (Ag/AgCl) was reached. The direction of the potential scan was then reversed in the positive direction until the initial stationary potential was reached. For cyclic voltammograms, when the potential was scanned in a negative direction a visible increase of the current was observed from  $-1.42 \text{ V}$  (Ag/AgCl) in solution without NS additive (Fig. 3, curve a). At  $-1.6 \text{ V}$  (Ag/AgCl) after reversal of the scanning in a positive direction, the cathodic current increased, which indicated the formation of a new phase before reverse scanning. An anodic peak was observed at  $-0.975 \text{ V}$  (Ag/AgCl). In the case of the NS additive (curve b) the cathodic parts of the voltammograms measured in negative and positive directions essentially overlapped. However, the voltammograms differed considerably in their anodic area when obtained without the NS additive (curve a); specifically, a change in the anodic area was observed at  $-1.41 \text{ V}$  (Ag/AgCl) and anodic current were detected at  $-1.34 \text{ V}$  (Ag/AgCl) and  $-1.20 \text{ V}$  (Ag/AgCl) with a peak current at  $-1.26 \text{ V}$  (Ag/AgCl). For further scanning of the potential in a positive direction a current peak appeared at  $-0.98 \text{ V}$  (Ag/AgCl) similar to that of the voltammograms obtained without an NS additive; however, smaller in size. For the steel electrode, in a solution of manganese-ammonium sulfate, without zinc ions, EDTA, and NS additives, the potential scanning in a negative direction showed a considerable increase of the current resulting from the reduction of hydrogen or water molecules at  $-0.8 \text{ V}$  (Ag/AgCl). The formation of hydrogen gas at the electrode was detected. Reduction of  $\text{Mn}^{2+}$  occurred from  $-1.40 \text{ V}$  (Ag/AgCl), determined by conducting electrolysis at a controlled potential and analysis of the solution after dissolution of the deposited coating. In a solution of manganese-ammonium sulfate with  $\text{Zn}^{2+}$  ions, when the potential was scanned in a negative direction, an increase of the cathodic current was observed at  $-1.0 \text{ V}$  (Ag/AgCl), which was associated with

reduction of  $Zn^{2+}$  (result not presented). Owing to dissolution of the deposited Zn, the anodic current peaks appeared at  $-0.98$  V (Ag/AgCl) in the curves when the potential was scanned in the positive direction. This result is in agreement with voltammetric investigations of Zn reduction by other researchers [23]. To understand the nature of the current peaks in cyclic voltammograms measured in basic solutions with and without NS additive, we performed cathodic polarization of a steel electrode for 10 s at potentials of  $-1.2$  V (Ag/AgCl),  $-1.4$  V (Ag/AgCl),  $-1.6$  V (Ag/AgCl). We recorded voltammograms by scanning the potential in a positive direction up to the stationary potential of the steel electrode (Fig. 4-A, B, C).



**Fig.4.** Linear voltammograms obtained for steel electrode at scanning rate  $10\text{mVs}^{-1}$  in aerated solution  $5\text{ g l}^{-1}$   $ZnSO_4 \cdot 7H_2O$ ,  $10\text{ g}\cdot\text{l}^{-1}$  EDTA,  $58\text{ g}\cdot\text{l}^{-1}$   $MnSO_4$ ,  $68\text{ g}\cdot\text{l}^{-1}$   $(NH_4)_2SO_4$ ; pH 3.5;  $t=30^\circ\text{C}$ . A- cathodic polarization at  $-1.2$  V (Ag/AgCl) for 10 s without additive NS (a) and with  $0.33\text{g}\cdot\text{l}^{-1}$  NS additive (b); B- cathodic polarization at  $-1.4$  V (Ag/AgCl) for 10 s without additive NS (a) and with  $0.33\text{g}\cdot\text{l}^{-1}$  NS additive (b); C- cathodic polarization at  $-1.6$  V (Ag/AgCl) for 10 s without additive NS (a) and with  $0.33\text{g}\cdot\text{l}^{-1}$  NS additive (b).

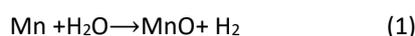
Fig. 4-A,B,C shows that the NS additive in solution hindered the hydrogen evolution process and together with EDTA facilitated the manganese and zinc co-deposition processes. Oxidation peaks in the curves scanned in a positive direction, were located between  $-1.34$  and  $-1.2$  V (Ag/AgCl), which represented characteristics of the alloy phase composition. Notably, similar anodic voltammograms were obtained by Sylla and coworkers [24] in basic pyrophosphate solutions for Zn-Mn alloy coatings, but with manganese contents of 25%.



**Fig5. shows Tafel polarization curves, obtained for Mn (98%Wt)-Zn alloy (a), for pure Zn coated on steel (b) and carbon steel (c) in 0.5 M NaCl as a corrosive aggressive media (Cl<sup>-</sup> ions).**

The potential scanning ( $10\text{mV}\cdot\text{s}^{-1}$ ) was performed, without stirring the solution, from a potential 200 mV more negative than the corrosion potential in the anodic direction until an anodic current of 15 mA was obtained. The thickness of the coating in the case of Mn-Zn and Zn was 20  $\mu\text{m}$ , which as measured by a DCFN 3000EZ instrument and confirmed by SEM observations.

Fig. 5 shows that the high content of manganese in the alloy determined its more negative corrosion potential compare with that of the zinc and steel electrode. The linear parts of the curves were extrapolated to the corrosion potential to determine the corrosion current. The corrosion current densities were 0.56, 4.78, and 8.078  $\mu\text{A}\cdot\text{cm}^{-2}$  for the Mn-Zn alloy, pure Zn coating and carbon steel, respectively. The corrosion potential of the mirror-bright surface of electrodeposited Mn (98%Wt)-Zn alloy in aerated 3.5 % NaCl solution (pH 6.6), at 30<sup>o</sup> C was -1.269 V (Ag/AgCl). After 25 days, the corrosion potential increased to -1.260 V (Ag/AgCl); gas formation on the surface was not observed; however, the surface became black owing to the formation of hydroxides of manganese. The observed corrosion potential of the coating was considerably more negative than that of carbon steel corrosion (-690mV, Ag/AgCl), which indicates that the coating was a good protector of steel against corrosion. Anodic polarization of the Mn-Zn alloy coating in 0.5 M NaCl solution showed intensive evolution of hydrogen and loss of the coating from the active area of the surface. This effect was attributed to the removal of the passivation layer of dichromate on the coating owing anodic dissolution and interaction of the nanocrystalline sized active manganese with water (1):



On the basis of these results we can conclude that, although the Mn-Zn alloy nanocrystalline mirror-like coating with a high manganese content featured a high negative value of the corrosion potential, for corrosion stability it was necessary to treat the coating with a solution of 10%  $\text{K}_2\text{Cr}_2\text{O}_7$  -to create a stable passive layer on the surface.

### CONCLUSIONS

We obtained mirror-bright nanocrystalline, globular shaped Mn-Zn alloy coatings with a high manganese content from the solution. The conditions included:

5  $\text{g}\cdot\text{l}^{-1}$   $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ , 10  $\text{g}\cdot\text{l}^{-1}$  EDTA, 58  $\text{g}\cdot\text{l}^{-1}$   $\text{MnSO}_4$ , 68  $\text{g}\cdot\text{l}^{-1}$   $(\text{NH}_4)_2\text{SO}_4$ , 0.33  $\text{g}\cdot\text{l}^{-1}$  NS, pH 3-5.5;  $t=30^\circ\text{C}$ ; current density 0.1 - 0.175  $\text{mA}/\text{cm}^2$ ; plating time  $\tau=15\text{min}$ ; coating composition: 97.5 - 98.5% Mn, 2.5-1.5 % Zn; and current efficiency 45.2 - 51.7%.

Owing to the nanocrystalline size of the electrodeposited Mn-Zn alloy coating, peaks in diffractograms obtained by X-ray analysis were broad and poorly defined. The diffractograms corresponded to cubic  $\alpha$ -Mn diffraction peaks.

The concentration of additives, such as sodium selenate (NS), and the nature of the solution components effected the production of mirror-bright Mn-Zn alloy coatings. We found that without additive, low quality, cloudy, grey-blackish, non-uniform coating were obtained.

Using cyclic voltammetry and linear sweep voltammetry we determined that the additive NS hindered a hydrogen evolution side reaction, which occurred in parallel with the manganese-zinc co-deposition process. Electrodeposited Mn (98%Wt)-Zn alloy coatings maintained a more negative corrosion potential in the aggressive environment compared with that of bare carbon steel. This layer protected the steel against corrosion.

Treatment of the coating in a solution of 10%  $K_2Cr_2O_7$  helped to preserve mirror-bright nanocrystalline Mn-Zn coating and enhanced corrosion stability owing to the formation of a passivation layer.

#### ACKNOWLEDGMENTS

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