

# EFFECT OF GLYCINE AND SODIUM ACETATE ON MORPHOLOGICAL AND STRUCTURAL CHARACTERIZATION OF ZnMn COATING ALLOY ELECTRODEPOSITED FROM ACIDIC CHLORIDE BATH

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**Abstract:** In this study, ZnMn alloy coatings were potentiostatically deposited on steel substrate from a chloride acidic bath. The effects of glycine, sodium acetate and applied potential on deposit kinetics, morphological and structural properties of ZnMn coatings were studied. The voltamperometric analysis indicated that the simultaneous codeposition of two elements Mn and Zn was possible under our experimental conditions. However, the deposition kinetics depends strongly of the additive type. The morphological and structural properties of ZnMn deposited with sodium glycine and acetate are completely different, indicating that electrodeposition process changes according to the additive type. The best microstructural and crystalline properties were obtained at low deposition potential in the presence of acetate.

**Keywords :** ZnMn coating, Electrodeposition, Acetate, Glycine, Cyclic voltammetry, SEM, XRD

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## 1. INTRODUCTION

Corrosion in all its forms is a major problem which affects many types of materials that can range from machining, to industrial and current use. Indeed, this phenomenon affects practically all the achievements of engineers, from the largest to the smallest such as energy production, construction, transport, the medical sector, electronics, etc.

In industrialized countries, the consequences of corrosion do not only concern the economic cost (waste of raw materials, energy and time) but also its impact on the environment, it is considered to be a highly polluting source for the environment.

To reduce this phenomenon, several methods of protection have been developed such as applying a coating on materials exposed to corrosion. In recent years, high performance sacrificial electroplated coatings have always been required in the metal finishing industry.

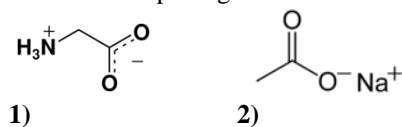
Zinc and its alloys are mainly used for the highly resistive protection of ferrous materials. Many studies have been reported and currently actived in order to produce new materials able to meet

Increasingly powerful requirements in terms of corrosion protection. In this context, various Zn-based coating alloys were exploited, such as ZnCo, ZnFe, ZnNi, ZnMn...etc and have been the subject of several works [1-7], these alloys exhibit a corrosion resistance better than the pure Zn.

ZnMn alloy is a potential candidate which exhibits a high corrosion resistance in several environments. In addition, it is also characterized by its strong reducer character, which means to be more active than zinc. The presence of Mn element characterized by a very negative corrosion potential offers simultaneous protection for zinc and iron as a sacrificial anode in the presence of pricks or roughness on the coating [8,9]. In the literature, a multitude of research works were devoted to the preparation and characterization of ZnMn system [10,11]. Generally, works cited in literature reported on ZnMn films prepared by electrodeposition. However, it is known that electrodeposition of alloys is frequently accompanied by a parasitic reaction that causes certain drawbacks, such as low current efficiency, poor adhesion and instability of electroplating bath.

In order to avoid these difficulties, it is important to introduce small quantities of organic or inorganic additives in the electrolytic bath. These additives are known to have a significant effect on physical properties such as structure, hardness, ductility, brilliance... etc. It is reported that the employed aromatic aldehydes additives has a positive effect on ZnMn alloy electrodeposition [12].

The aim of the present study was to investigate the influence of plating additives on the electrochemical deposition kinetics, physicochemical and structural properties of ZnMn system. The effect of two organic additives, namely sodium acetate and glycine (Fig.a) were studied in this work. Electrochemical measurements were used to study the role of the additives in the electrodeposition process. Scanning electron microscopy (SEM) and X-Ray diffraction (XRD) were employed to investigate both morphological and structural properties of ZnMn deposits obtained under different plating conditions.



**Fig.a** (1) The structure of glycine and (2) structure of sodium acetate

## 2. EXPERIMENTAL DETAILS

A vitreous carbon rotating disk electrode (RDE) ( $0.2 \text{ cm}^2$ ) with a rotation speed fixed at 250 rpm and either steel substrates were used as working electrodes in a classical three electrodes electrochemical cell. The counter electrode was a platinum wire immersed in a separate compartment containing solution without electroactive metallic cations. All potential values were measured with respect to a saturated calomel reference electrode (SCE).

All experiments were carried out at ambient temperature in a chloride bath deoxygenated by nitrogen gas bubbling. This study was performed at different concentrations of acetate and glycine with various applied potentials. The electrochemical ZnMn bath consisted of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  ( $0.4 \text{ mol}\cdot\text{dm}^{-3}$ ),  $\text{ZnCl}_2$  ( $4 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ ),  $\text{NH}_4\text{Cl}$  ( $3 \text{ mol}\cdot\text{dm}^{-3}$ ) and  $\text{CH}_3\text{COONa}$ -glycine ( $0\text{-}0,6 \text{ mol}\cdot\text{dm}^{-3}$ ). The pH was adjusted to 4 by adding HCl or KOH solution. The solutions were prepared immediately prior to each experiment using deionised water and analytical grade reagents (Aldrich). The electrochemical measurements were performed using an EG&G 273A Potentiostat/Galvanostat controlled by a microcomputer via GPIB interface operated by M352 EG&G software.

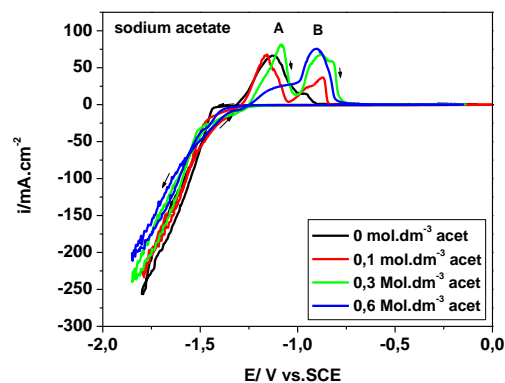
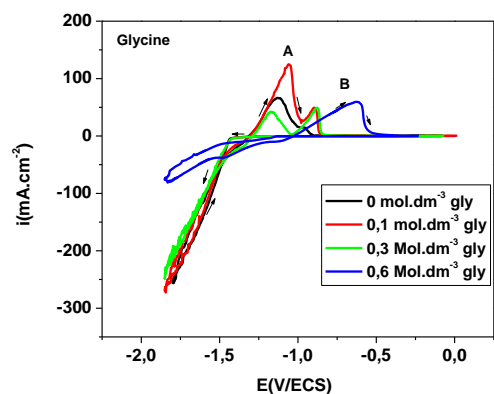
The morphology was examined by scanning electron microscopy (SEM). The crystalline structure was investigated by X-ray diffraction (XRD) with  $\text{CuK}\alpha$  radiation.

## 3. RESULTS AND DISCUSSIONS

### 3.1 Cyclic voltamperometric study : effet of sodium acetate and glycine

Cyclic voltammetry was used to determine the reduction and dissolution potential regions for the characterisation of ZnMn deposition process.

The voltperometric analysis of the deposition kinetics of ZnMn system was carried out in the presence of each additive are shown in Figure 1.a and b). The voltammograms thus recorded were obtained on a glassy carbon electrode at different additive concentrations. It is important to note that the different baths as used have the same ionic force and pH. The potential interval was scanned from 0 to  $-1,95 \text{ V}$ . The scan rate was fixed at  $50 \text{ mV/S}$



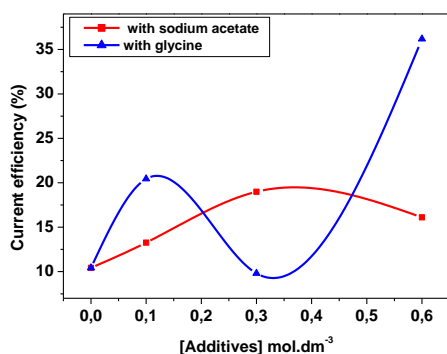
**Fig.1** Cyclic voltammetry on a vitreous carbon RDE electrode in  $0.4 \text{ mol}\cdot\text{dm}^{-3}$ ,  $\text{MnCl}_2$ ,  $4 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$   $\text{ZnCl}_2$  and  $3 \text{ mol}\cdot\text{dm}^{-3}$   $\text{NH}_4\text{Cl}$ , at different concentrations of glycine and sodium acetate,  $\text{pH} = 4$ ,  $\omega = 250 \text{ rpm}$

As it can be noted in Fig.1 the shape of the voltammograms changes with the additive type as well as with its concentration. In the presence of acetate, it can be noted that the current density recorded in the cathodic direction decreases slightly as the acetate concentration increases. This can be

attributed to the partial inhibition of hydrogen evolution. The appearance of two dissolution peaks in the anodic part of the voltammograms indicate the simultaneous co-deposition of zinc and manganese during cathodic scanning. The peak (A) observed at -1,42 V vs SCE is attributed to manganese dissolution whereas the peak (B) which appears at more anodic potential (-1,02 Vvs SCE), is attributed to zinc dissolution. However, the peaks intensity depends strongly on the additive concentration as used. Indeed, the peak of manganese increases at low acetate concentration (0.1M) while that of zinc shows a reverse evolution. In other words, the zinc peak increases as the concentration of the additive increases. Based on these results, it can be considered that the chemical composition of the ZnMn system will depend on the acetate concentration used. From these results, we can say that at low acetate concentrations, it is possible to obtain manganese-rich deposits, while at high concentrations, the deposits may be rich in zinc element.

The voltammograms obtained in the presence of glycine show a similar behavior compared to that observed in the presence of acetate. In the negative scan, it can be noticed that the current density decreases with increasing the glycine concentration. A significant decrease is observed at high glycine concentration. This may be explained by a partial inhibition of the deposition process induced by the adsorption of this additive on the electrode surface. In the anodic scan, the peak of manganese increases when the concentration of glycine is reduced, whereas the peak of zinc shows a very significant increase when the glycine is added to the plating bath at high concentration.

According to these results, we can say that zinc deposition is favored at high concentrations of the additives, while manganese deposition is favored at low concentrations. These results suggest a significant current efficiency when the glycine concentration increases (see Figure 2).

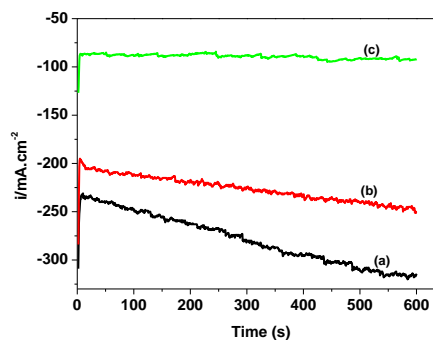


**Fig.2** Current efficiency for ZnMn alloys deposition with different concentrations of glycine and acetate additives, E = -1,8 Vvs.SCE

As shown in Fig.2, the current efficiency is strongly depends on the nature of additive. It is important to note that the highest current efficiency is observed when glycine is added in high concentration into the electrolysis bath. However, in all cases, the efficiency values are very less than 100%, due to the hydrogen evolution which occurs simultaneously with manganese reduction at high cathodic potential. This finding is very close to the results discussed through the previous voltammetric analysis.

### 3.2 Chronoamperometric study

In order to investigate the effect of additives on the morphological and structural properties of ZnMn deposits, a series of ZnMn samples were prepared in the presence of each additive at a fixed concentration of 0.1 mol.dm<sup>-3</sup>, and at different potentials. The chronoamperograms recorded on steel substrate in the complete ZnMn electrolyte are shown on Fig.3.



**Fig.3** Current-time transients for ZnMn alloy electrodeposition at -1,85V vs SCE from : (a) 0 mol.dm<sup>-3</sup>, (b) 0,1 mol.dm<sup>-3</sup> of acetate, (c) 0,1 mol.dm<sup>-3</sup> of glycine

In summary, the i(t) curves shown in Fig.3 reveal a high current density in the absence of additives (Fig 3-a). On the other hand, it should be noted that the current density depends strongly on the nature of the additive used. In this case, the evolution of the current density as a function of the additive corresponds the following order:

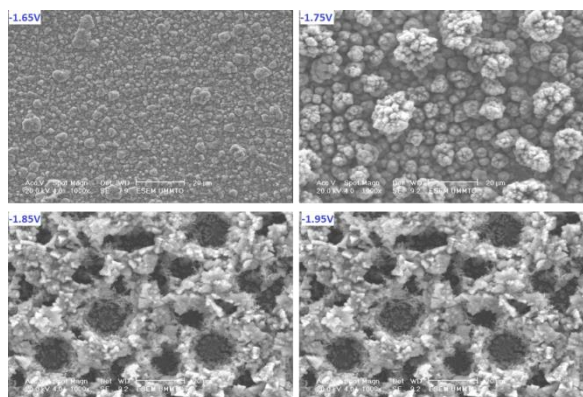
Glycine < Acétate < without additive.

According to these results, it can be noted that the deposition rate decreases in the presence of glycine whereas in the presence of acetate, the cathodic reduction process seems to be accelerated. Under such conditions, it is likely that the hydrogen evolution will become more significant. Moreover, in the presence of glycine in the electrolytic bath, the current density related to the reduction process decreases. This effect of glycine can be attributed to

the partial inhibition of both processes ZnMn electrodeposition and hydrogen evolution. This behaviour can be related to the adsorption of glycine on the electrode surface which blocks the active reduction sites. This result has been reported in the literature [13].

### 3.3 Morphological analysis

To illustrate the effect of potential, acetate and glycine on ZnMn surface morphology, SEM analysis of samples deposited in the presence of each additive at various potentials were carried out. Figure 4 shows surface morphologies of ZnMn coatings deposited in the presence of sodium acetate ( $0,1\text{mol.dm}^{-3}$ ) at different deposition potentials.

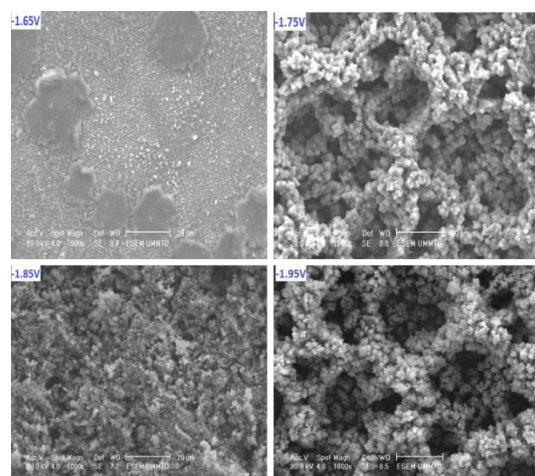


**Fig.4** Surface morphologies of ZnMn coatings deposited in the presence of sodium acetate ( $0,1\text{mol.dm}^{-3}$ ) at different deposition potentials, pH = 4

The coating deposited at  $-1,65\text{ Vvs SCE}$  shows that the steel substrate is completely covered by the deposit without cracks. This surface morphology looks very compact and uniform. The later exhibits a homogeneous deposit with a granular structure. The same behavior was also observed at  $-1,75\text{ Vvs SCE}$ . However, it is noted that the grains grow and form more pronounced agglomerates with a cauliflower shape. Such morphology is specific to the  $\epsilon\text{-ZnMn}$  phase [14].

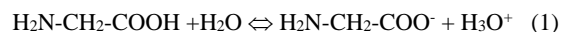
When the cathodic potential is increased to  $-1,85$  and  $-1,95\text{V}$ , the cauliflower shape is completely perforated where a pores are clearly observed and uniformly distributed over the entire steel surface. From these results, it is noted that The ZnMn deposits is clearly more porous. This means that hydrogen evolution becomes more significant in this range of potential. These results are perfectly consistent with those obtained from chronoamperometric and voltammetric analysis, where a high current density was observed in the presence of sodium acetate.

The images shown in Figure 5 correspond to the microstructures of ZnMn coating prepared in the presence of glycine with a concentration of  $0,1\text{mol.dm}^{-3}$  and at several applied potentials.



**Fig.5** Surface morphologies of ZnMn coatings deposited in the presence of glycine ( $0,1\text{mol.dm}^{-3}$ ) at different deposition potentials, pH = 4

In the presence of glycine, the morphological aspect of the deposits has completely changed, which indicates a significant effect of this additive. For a potential  $-1,65\text{ Vvs SCE}$ , the grain size has decreased considerably and the deposit seems to cover the complete substrate surface. Another microstructure with different sizes and a sludge shape has been also formed on the surface of the deposit. The appearance of microcracks on this last type of morphology means that the deposition is highly affected by hydrogen evolution. This reaction seems to be important in the presence of glycine. This is evident since glycine provides additional protons to the starting solution according to the following reaction (1):



Therefore, an additional reaction related to the  $\text{H}^+$  reduction will be added to the one that exists already in the electrolysis bath.

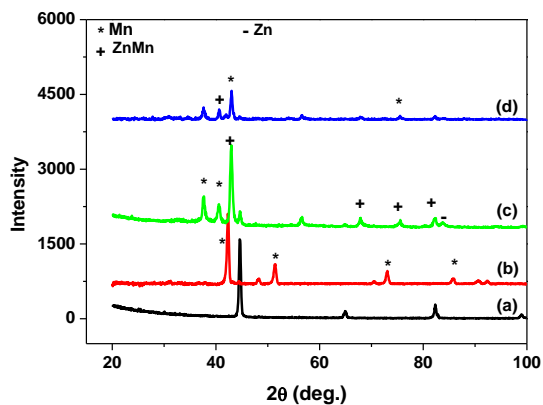
When the potential becomes more cathodic ( $-1,75 - 1,85\text{ Vvs SCE}$ ), a very refined cauliflower microstructure with deep type has been observed. The coatings deposited in this range of potentials are distributed homogeneously on the surface of the substrate. These results are very similar to those reported in the literature [15-17].

From the morphological analysis which carried out in the presence of each additive, it is clear that the ZnMn deposits obtained with low cathodic potentials in the presence of acetate have a better morphological aspect compared to those prepared in the presence of glycine but at higher cathodic potential, the ZnMn deposits are strongly affected

by the hydrogen evolution in the presence of both additives (acetate and glycine).

### 3.4 X-rays analysis

To illustrate the effect of acetate and glycine on the structural properties of the ZnMn system, we have plotted on the same graph (Fig. 6) the spectrum of the ZnMn coating elaborated without additives and those obtained under the same conditions, in the presence of each additive.



**Fig.6** X-rays diffraction patterns of ZnMn coatings obtained in the absence and in the presence of each additive, pH = 4, E = -1,85 Vvs SCE, (a) substrate, (b) without additives, (c) 0,1mol.dm<sup>-3</sup> sodium acetate, (d) 0,1mol.dm<sup>-3</sup> glycine

As we can see on the Figure 6, the crystal properties change considerably according to the type of additive.

The spectrum related to ZnMn coating obtained in the absence of additives shows only the peaks characteristic of manganese phases  $\alpha$ -Mn(111) (body centred cubic system) and  $\gamma$ -Mn, (411) (body centred tetragonal system). It is clear from Fig.6.b that there are no significant peaks related to the crystalline structure of ZnMn alloy. This indicates that the amount of zinc in the deposit is insufficient to make a phase between manganese and zinc. We can also attributed this behaviour to the presence of oxy/hydroxides inclusions which are strongly incorporated into ZnMn deposits.

In the case of acetate (spectrum b), several peaks are observed, which are mainly attributed to the alpha-manganese phase and to the different phases characteristic of ZnMn system in its monoclinic structure [18].

The ZnMn coating obtained in the presence of glycine (spectrum c) is characterized by a significant appearance of peaks related to the alpha manganese phase. The peaks attributed to ZnMn phases are less present.

From these results, we can be concluded that at low cathodic potentials, sodium acetate has improved the morphological and structural properties of the ZnMn system.

## 4. CONCLUSIONS

The effects of the addition of glycine and sodium acetate to the plating electrolyte on the properties of ZnMn coating electrodeposits were investigated. Based on the results obtained, several conclusions are presented.

The electrochemical study of the deposition kinetics of ZnMn system was carried out in a chloride bath with and without additives. In both cases, it has been shown that the simultaneous co-deposition of zinc and manganese is possible in our experimental conditions. However, the deposition kinetics revealed a strong dependence on the nature of the additive and its concentration. The results obtained revealed that zinc deposition is favored at high additive concentrations, while manganese deposition is favored at low concentrations.

The type of additive and deposition potential significantly affects the morphology and crystal structure of the ZnMn alloy coatings.

It appears that the coatings morphology is very sensitive to the type of additive and the applied potentials. Indeed, at lower cathodic potentials, the deposits obtained in the presence of acetate shows a better morphological aspect compared to those obtained in the presence of glycine. At higher cathodic electrodeposition potentials, the deposits formed in the presence of both acetate and glycine are less covering and becomes porous. Under such conditions, the morphological aspects of the coatings are considerably affected by the hydrogen evolution.

In the absence of additives, the XRD spectrum attributed to ZnMn coating revealed only the peaks related to manganese phases. The XRD analysis carried out in the presence of additives indicated that the structural properties of the coating are highly dependent on the type of additive. In the presence of acetate, the results show the appearance of several peaks, attributed principally to the alpha-manganese and ZnMn phases. However, in the presence of glycine, manganese peaks are more pronounced than ZnMn phases.

## 5. REFERENCES

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