

ALLOY Zn-Fe ELECTRODEPOSITION FROM CHLORIDE ELECTROLYTE

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This study show that of the alloy zinc-iron electrodeposited on steel by electrodeposition from chloride acid electrolytes, the chloride electrolyte more advantages than the electrolyte sulphate. Furthermore the influence of various parameters (current densities, $[Zn(II)]/[Fe(II)]$ concentration ratio in electrolyte and the nature of additives: saccharin Na(S) and glycerol (J) ...) on the morphology and the structure of the deposits is discussed.

EDS Analysis making it possible to determine the composition of alloys obtained gives an increase in Fe content with the density of current. For high $[Zn(II)]/[Fe(II)] \sim 1/9$ concentration ratio in solution, Fe content remains constant independently of current densities. In the presence of brightener "J.S", the deposit contains a weaker content iron, which is in agreement with measurements of the cyclic voltammetry showing that the "J.S" inhibits the electroreduction of iron. X-ray diffractograms realized for Zn-Fe alloys, lead to the presence of the three phases of the alloy Zn-Fe: η , ζ and Γ .

Keywords: Electrodeposition, alloy, Zn-Fe, additive, chloride, electrolyte.

INTRODUCTION

Electrodeposited zinc coatings have found extensive use for the corrosion protection of steel. Over the last few years a great attention has been made to developing electrodeposition of alloys. It has been shown [1, 2] that zinc alloy improved corrosion resistance compared to zinc pure coating [3, 4]. Like all Zn alloys, Zn-Fe coatings are very attractive, since they combine high corrosion resistance with excellent mechanical performance [5]. However Zn-Fe alloys can be electrodeposited from various types of electrolytes.

In recent years chloride baths are preferred [6, 7] because of their higher conductivity. They contain also other species acting as a buffer, complexing agent and brightener for grain affiner etc...The deposit composition can be influenced by the addition to the solution of organic additives which have a favourable effect on the quality and on the bath stability. Forhermor, similar mechanically alloyed Zn, electrodeposited Zn-Fe alloys, show phase composition that different from the equilibrium diagram [8, 9].

In this work, the role of some additives such as saccharine and glycerol were investigated, to propose an electrolyte composition in order to obtain low iron content Zn-Fe alloy (15-25%) because of their excellent protective properties [10]. CV curves and X-ray diffraction analysis were performed on the obtained Zn-Fe alloys.

2. EXPERIMENTAL

Zn-Fe alloys were electrodeposited galvanostatically by 1.5-5.0 A/dm², at a room temperature (25°C), on a steel sheet (E24-steel low content carbon) of 2 cm² area, in a chloride electrolyte: 0.15 M ZnCl₂, 0.75 M FeCl₂, 180g/l KCl, 25g/l boric acid, 0.02 M L-ascorbic acid. pH =2.3. All chemicals were analytical grade. Before electrodeposition, each sam polished mechanically using silicon carbide of 4000 grade (sum of grain size), degreased ultrasonically in NaOH sat solution in ethyl alcohol, actived in HCl solution (1:1) for 30 s, rinsed with ultra pure water and cold dried.



quality and the Fe content in Zn-Fe coatings as a function of current densities, $[Zn(II)]/[Fe(II)]$ concentration ratio in electrolyte ($R = 1/3, 1/6$ and $1/9$) and the nature of additives: saccharin Na (S) and glycerol (J). The cyclic voltammograms (CV) were carried out in a conventional three-electrode cell, with a capacity of 0.5 dm^3 using an EG&G 273A controlled by a micro computer M352. Scanning process starts from the initial potential: -800 mV/ESC to -1800 mV/ESC , then returns to -500 mV/ESC with a scan rate of 20 mV/s . All potentials were given against Hg, $\text{Hg}_2\text{Cl}_2/\text{KCl}$ (SCE sat.) electrode. The morphology of deposits was observed using both optical microscopes X500 LEICA DMRM controlled by a logic iel Visilog and a scanning electron microscope (SEM) JEOL JSM-5410LV (20 kV , SS10, Wd20). Energy dispersive analysis of X-ray (EDS) was performed to determine the deposit composition value. X-ray diffraction (XRD) phase analysis was performed on Bruker AXS D8 Advance diffractometer. The $\text{Cu-K}\alpha$ radiation ($\lambda = 15.406 \text{ nm}$) was selected in symmetrical mode for 2θ in the range of 10° to 100° with a step of 0.02° .

3. RESULTS

3.1. Zn-Fe alloys deposition

Initial Hull cell investigation was carried out to estimate the quality and the composition of Zn-Fe alloy deposits. Fig 4 to 6 present the dependence of the quality and the Fe content in Zn-Fe coatings, as function of current densities, $[Zn(II)]/[Fe(II)]$ concentration ratio in electrolyte and the nature of additives: saccharin Na(S) and glycerol (J) used to improve surface morphology of the deposits.

Addition of saccharin Na and glycerol have a beneficial effect (Fig.7-11) on deposit morphology; high-quality fine-grained deposits with Fe content of 5 to 66% could be obtained galvanostatically ($1.5\text{-}5.0 \text{ A/dm}^2$) under constant stirring conditions. The morphology was compact and homogenous. The addition of saccharin causes a slight decrease in Fe content (Fig 5, 9) and appreciably an increase in oxygen content from 9% to 17%. In fact local pH varies during the electrolysis and iron hydroxides can precipitate in the form of black nodules (Fig.11). This effect could be explained by the disappearance of oxidation peak recorded when scan was reserved (Fig.13).

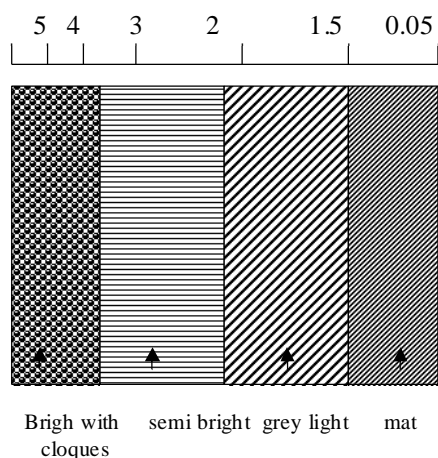


Fig1: Dependence of the quality of deposit as function of current densities for $R = 1/3$ without additive.

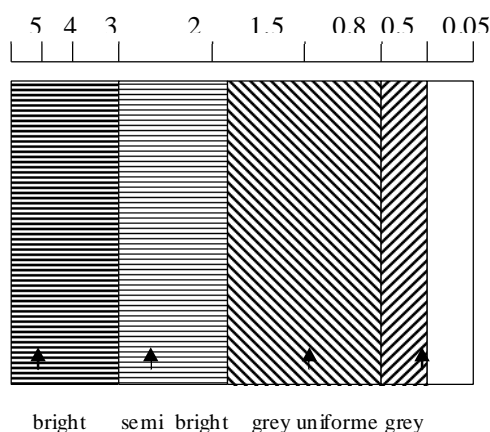


Fig2: Dependence of the quality of deposit as function of current densities for $R = 1/3$ with saccharin.

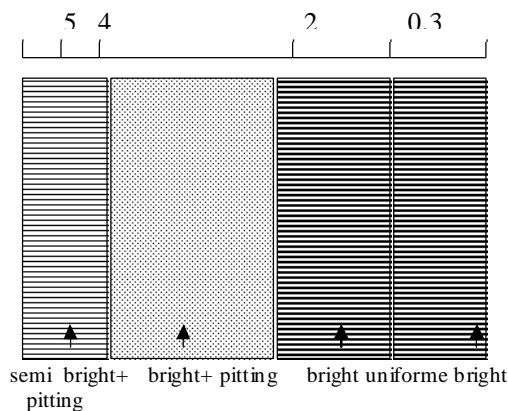


Fig3: Dependence of the quality of deposit as function of current densities for $R = 1/9$ without additive

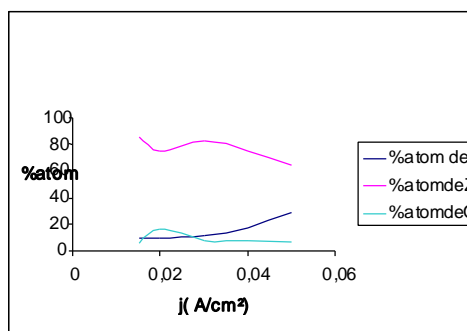


Fig4: dependence of Fe content as function of current densities for $R = 1/3$ without additive.

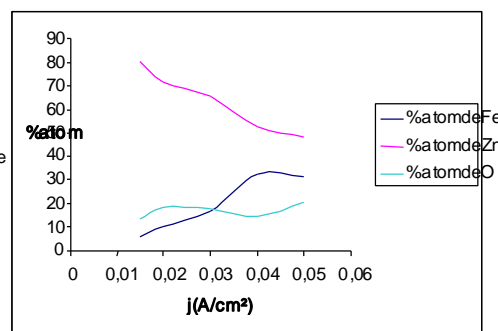


Fig5:dependence of Fe content as function of current densities for $R = 1/3$ with 1 g/l saccharin.

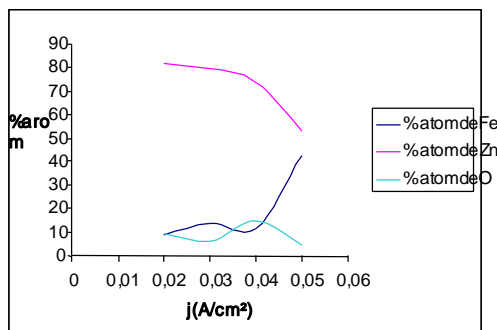


Fig6: dependence of Fe content as function of current densities for $R = 1/3$ with $10^{-3}M$ glycerol

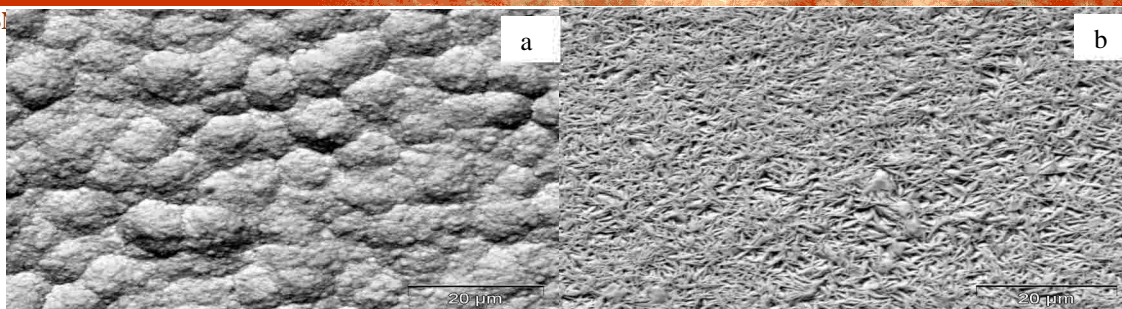


Fig.7 SEM micrograph of deposit obtained at 2A/dm^2 for $R=1/3$ without additive (a) and with 1g/l saccharin (b).

It should be noted that for $Zn=1/9$, Fe content remains constant, independently of current densities (Fig 8 -10). This fact requires a complementary investigation.

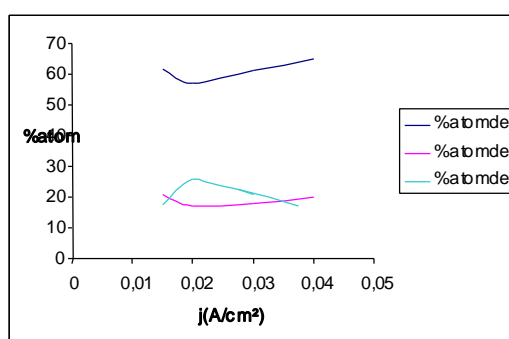


Fig8 : dependence of Fe content as function of current densities for $R=1/9$ without additive.

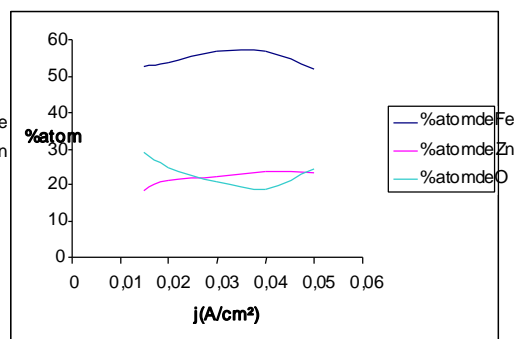


Fig9: dependence of Fe content as function of current densities for $R=1/9$ with 1 g/l saccharin.

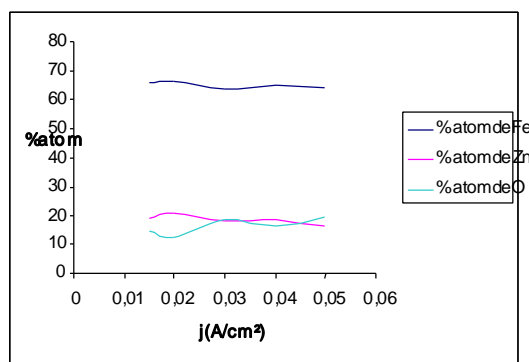


Fig10: dependence of Fe content as function of current densities for $R=1/9$ with 10^{-3}M glycerol.

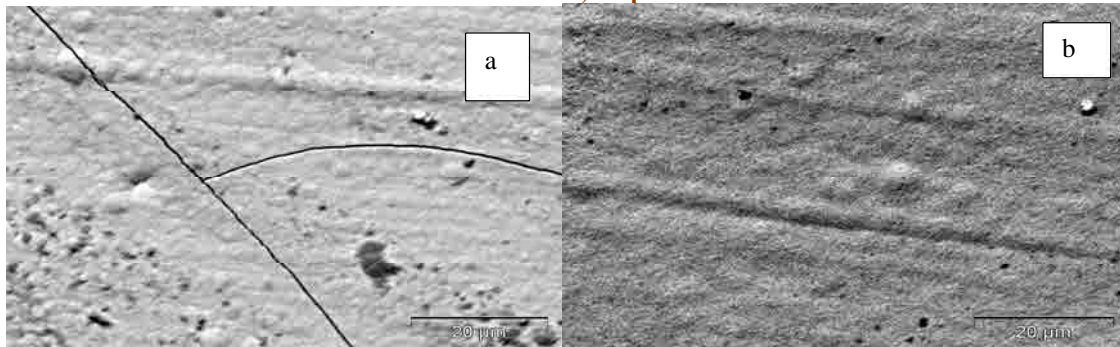


Fig.11.SEM micrograph of deposit obtained at 1.5A/dm² for R=1/9 in the presence of 1 g/l saccharin (a) and 10⁻³M glycerol (b).

Small concentration additive 1- 2 g/l of saccharin Na is sufficient to obtain bright deposits with fine grains. Furthermore, the role of sodium saccharin as a brightener [10] is confirmed. But, it is not excluded that saccharin as a polyfunctional ligand, can be engaged in N, O_{co} or O_{oso} coordination [9-12]. Thus, saccharin may be an interesting complexing agent. However in contrast to that, glycerol has practically, no notable effect neither on Fe content nor on oxygen content. The Hull test shows a slight beneficial effect on the quality of deposits, when the glycerol was added to the electrolyte containing saccharin.

Since the aim of this work was to propose an electrolyte composition to deposit Zn-Fe alloy with Fe content of 15 to 25%, our investigation was limited to the ratios 1/3 at 1/6 of the solution.

3.2. Electrochemical results.

The effects of organic compounds such as saccharin Na, glycerol and saccharin+ glycerol on Zn-Fe alloy electrodeposition from chloride electrolytes, were characterized by cyclic voltammetry (Fig. 12-13).

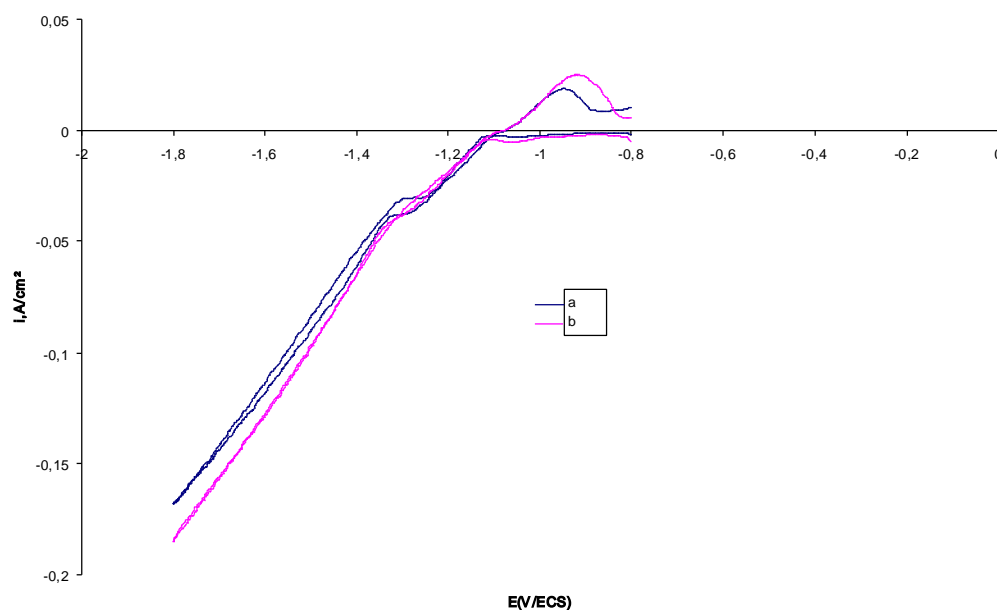


Fig.12. Cyclic voltammograms at 50mV/s of (a)-0.15 M ZnCl₂, 0.75 M FeCl₂, 180g/l KCl, 25g/l boric acid, 0.02 ascorbic acid, (b)- a+ 1g/L saccharin +10⁻³M glycerol for R=1/3.

Voltammetric results indicated that the presence of saccharin in the chloride bath inhibited (Fig. 12) the Zn-Fe alloy deposition, since the potential necessary to begin the alloy deposition shifted to more negative values (Fig. 12 curve b). Two clear reduction stages may be distinguished. On the reverse scan, an oxidation peak appeared around -0.9V .

***[Zn (II)]/[Fe (II)] = 1/6**

Fig.13 (curves a- b) represent CV curves for the electrodeposition of Zn-Fe alloy without (a) and with saccharin Na and saccharin (b). The same effect was observed for $[\text{Zn (II)}]/[\text{Fe (II)}] = 1/3$: saccharin inhibits Zn-Fe alloy electrodeposition, contrary to glycerol.

It should be noted that the oxidation peak corresponding to oxidation of Zn disappeared for $[\text{Zn (II)}]/[\text{Fe (II)}] = 1/6$. It is, probably, due to higher Fe content in the Zn-Fe alloy, for which oxidation potential occurs at more positive values.

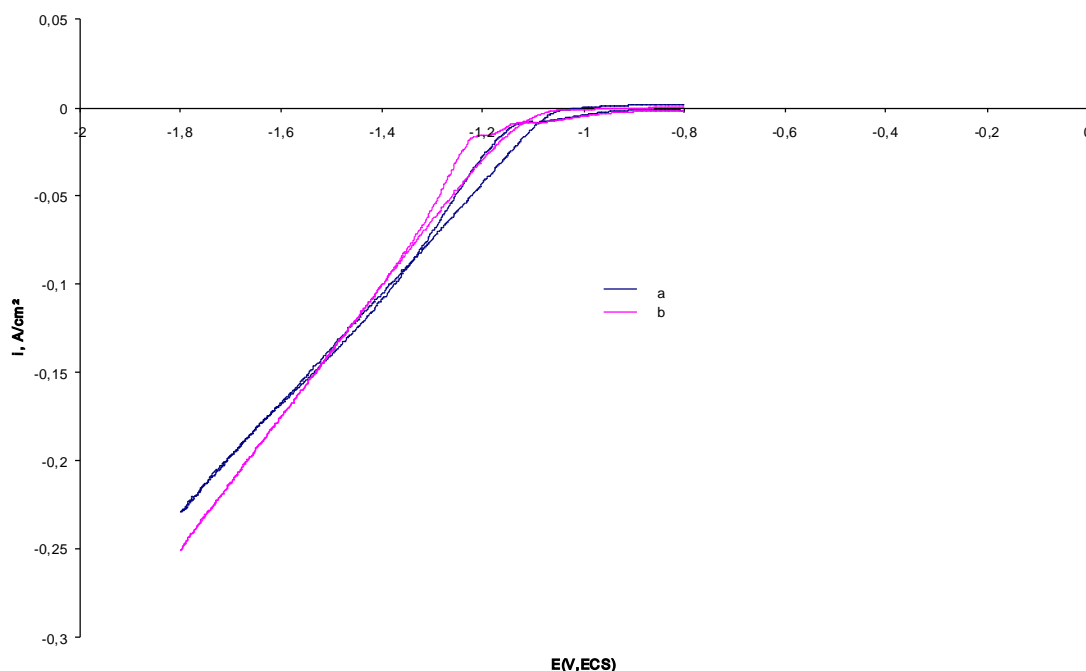
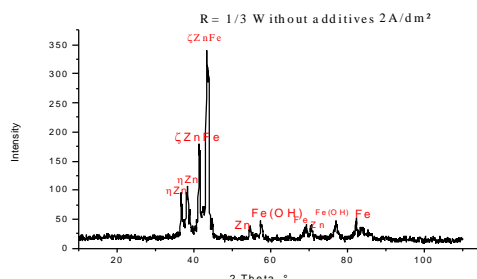


Fig.13. Cyclic voltammograms at 50mV/s of (a) - 0.15 M ZnCl_2 , 1.50 M FeCl_2 , 180g/l KCl, 25g/l boric acid, 0.02M L-ascorbic acid, (b)- a+ 1g/L saccharin + 10^{-3}M glycerol for $R=1/6$.

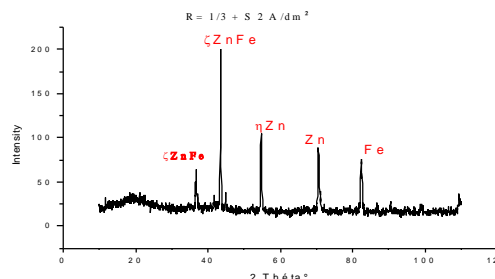
3. 3 Morphology and structural analysis

XRD patterns showed in Fig.14-19 exhibit several peaks. The relative intensity of the ligne 2 $\Theta = 43.5$ indicated the dominant phase- ζ when $R = 1/3$ (Fig. 14-16). A second η -phase corresponding to an hexagonal structure of Zn takes place. Contrary to that when $R = 1/6$ the Γ -phase becomes the more important and some peaks appear to correspond to α -Fe structure (solid solution). For high iron content samples the shape is strongly irregular (Fig.19), which is, probably, due to imperfections in the crystalline structure of the obtained alloys. Finally the diffractograms indicated a clear mixture of η , ζ and Γ -phases.



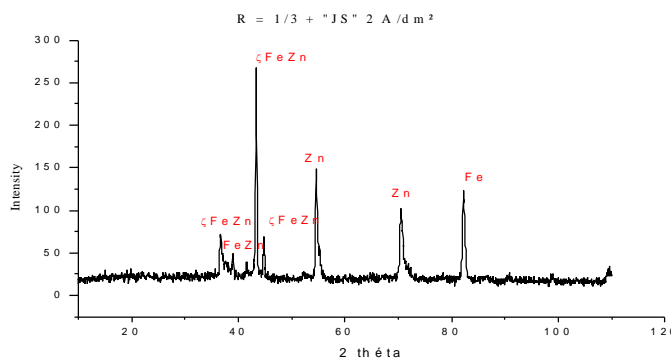
(% Fe 10.75)

Fig. 14. X-ray diffractograms of Zn-Fe alloy deposit obtained at 2 A/dm² for $R=1/3$ without additive



(% Fe 09.87)

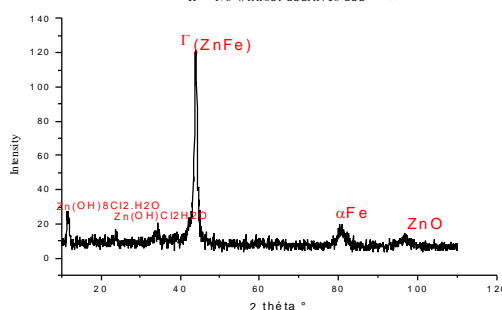
Fig. 15. X-ray diffractograms of Zn-Fe alloy obtained at 2 A/dm² for $R=1/3$ in the presence of 1 g/l saccharin.



(% Fe 08.96)

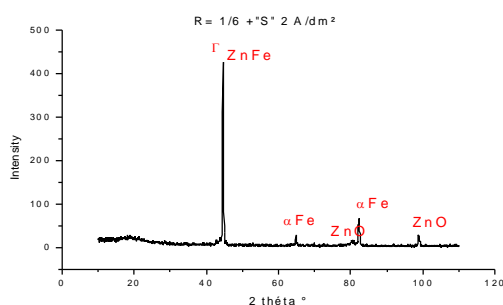
Fig. 16. X-ray diffractograms of Zn-Fe alloy deposit obtained at 2 A/dm² for $R=1/3$ in the presence of 1 g/l saccharin + 10³M glycerol.





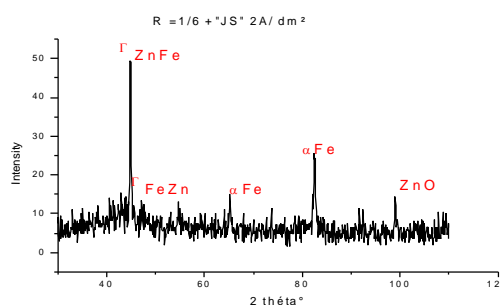
(% Fe 39.85)

Fig.17.X-ray diffractograms of Zn-Fe alloy deposit obtained at 2 A/dm² for R=1/6 without additives..



(% Fe 36.00)

Fig. 18.X-ray diffractograms of Zn-Fe alloy deposit obtained at 2 A/dm² for R=1/6 in the presence of 1 g/l saccharin.



(% Fe 37.62)

Fig.19.X-ray diffractograms of Zn-Fe alloy obtained at 2 A/dm² for R=1/6 in the presence of 1 g/l saccharin +10³ M glycerol.

CONCLUSION

The different EDS analysis, SEM and X-rays diffraction of Zn-Fe alloy obtained galvanostatically provided the following:

1. The Zn-Fe alloy composition is strongly affected by the [Zn (II)]/ [Fe (II)] concentration ratio in solution.
2. Saccharin Na behaved one's self as a grain affiner (brightener). Despite the fact that its role was established to be a complexant agent [10, 14].
3. Glycerol and saccharin Na have a beneficial effect on Zn-Fe deposit morphology.
4. For R= 1/9 the Fe content remains constant, independently of current densities his fact requires a complementary investigation.
5. The electrodeposition of Zn-Fe alloys leads to the presence of three phases: η, ζ and Γ [14].

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