Effects of Al content on microstructure and corrosion behavior of Zn-Al alloy coatings

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Alloying Zn with other metals is an alternative method to create advanced alloys with better corrosion properties, in this work the electrodeposition of Zn-Al binary alloy in sulphate-based acidic bath and with different $Al_2O_{12}S_3$ content from 0.03 to 0.1M on a treated copper substrates was studied, the structure and microstructure of the coatings were analysed by X-ray diffraction (XRD) and scanning electron microscope (SEM) supported by (EDX) analysis, the microhardness was measured, the corrosion resistance was evaluated by potentiodynamic polarization (Tafel), the effect of Al ions was visible on the structure, (XRD) spectra showed zinc phase (η-phase), and Al phase (α-Al phase) with Al peak intensity increasing along with the increase of Al concentration, the microhardness also enhanced gradually to 252.33 HV, the corrosion current density decreased by almost 13 times and the corrosion resistance was drastically improved at 0.1M Al.

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1. Introduction

For many years, zinc has been the most widely used sacrificial coating for steel and other ferrous materials, due to it's effective, dependable corrosion resistance features at a low cost [1]. In recent years, zinc alloys with various metal elements have been studied such as Zn-Co, Zn-Ni, Zn-Mn, Zn-Pb, Zn-Sn resulting a superior characteristic compared with pure zinc [2-4]. Zn-Al binary is a promising alloy that possesses a good corrosion resistance with the lightweight aluminium that makes an advantage to this anomalous codeposition. Zn-Al alloys are frequently used to protect steel in the automotive and architectural, aeronautical industries [5]. In the attempt of further improve this binary and as believed there are several factors that influence the composition and microstructure of the coatings, such as composition and particle concentration of the plating bath, particle characteristics, solution temperature and pH, agitation, type of applied current and current density [6]. Zn-Al binary has been studied in this work under different Al^{+3} concentrations in sulphate-based acidic baths using copper substrates, DC applied current at room temperature, and with moderate agitation. The composite coatings have been characterized, morphological (SEM), structural (XRD), and electrochemical properties of the composite coatings have been studied by potentiodynamic polarization in a solution of 3.5% NaCl.

2. Experimental

2.1. Coating preparation

The chemical compositions of the electrolytes studied are given in Table 1. The solution pH was adjusted to 3.5 by the addition of Boric acid, the electroplating of Zn–Al coatings was carried out on copper substrates previously treated, at operating current density of 60 mA/cm^2 for

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1200s and a temperature of 30°C, after deposition, the coatings were washed in distilled water, and dried. Electrodeposits Zn were obtained by varying the aluminium sulphate concentration ($Al_2O_{12}S_3 \cdot 14H_2O$) in the bath (0.03, 0.05, 0.1mol/l).

Table 1. Solution composition and conditions for alloy electroplating [7-8].

Electrolyte I	Concentration ($g \cdot l^{-1}$)	Plating parameters
$ZnSO_4 \cdot 7H_2O$	57.5	30°C and pH=3,5 constant current densities at 60 mA/cm^2 for 20min
H_3BO_3	9.3	
Na_2SO_4	56.8	
$Na_3C_6H_5O_7$	56.8	

2.2. Coating characterization

The phase structure of the coatings is determined using X-ray diffraction with a D8Advance-Brucker using a Cu Kα radiation (λ= 1.5406Å) and 2θ= 0.02° as a step. The deposits surface morphology was studied by scanning electron microscopy (A JEOL model JSM6390LV).

Microhardness of coatings was measured using a load of 100 g with a holding time of 15s by using a Vickers hardness tester, and the average of ten hardness measurements was quoted as the hardness value [7].

The corrosion behaviour and the protection performance of Zn alloy and Zn-Al alloy coatings were studied by using electrochemical Tafel extrapolation (TE) in 3.5% wt NaCl solution. The tests were performed using a potentiostat galvanostat (a Volta Lab 40 model). A coated sample was served as a working electrode, the counter electrode was platinum with a surface of 1 cm^2 and the Hg/HgO/1 M KOH is used as a reference electrode. Potentiodynamic polarization with a scan rate of 50mV/s was applied in order to study the anodic dissolution of the coatings. The corrosion current density (I_{corr}) and corrosion potential (E_{corr}) were determined using TE.

3. Results and discussion

3.1. Phase structure

XRD patterns of the “as deposited” Zn and Zn-Al alloy coatings are presented in Fig 1. The well- crystalline metallic phases that can be seen in the spectra are attributed to the Zn hexagonal structure in Fig 1(a). It can be observed that only the diffraction lines of zinc-rich (η-phase) (JCPDS: 65-5973 [8]). The presence of Aluminium in (Fig. 1(b c, d)) showed the existence of only pure zinc phase (η-phase), and Al phase (α-Al phase) the face-centered cubic (JCPDS 04-0787), in which the intensity of Al peaks increased with the increasing of Al concentration in the alloy. The electrodeposition creates mechanical bonds, and thus Zn and Al does not react with each other. Therefore, there is no sign of an intermetallic phase [9-14].

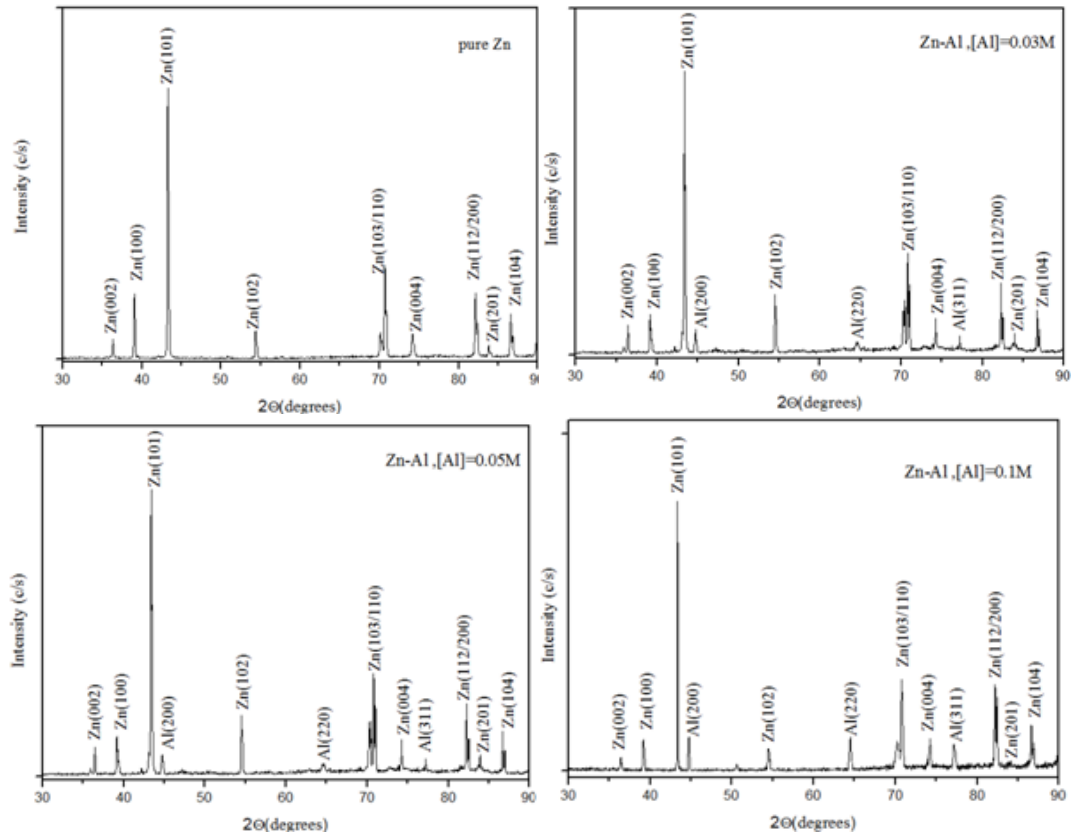

Fig. 1.XRD spectra of Zn-Al alloy coatings electrodeposited at different concentrations of aluminium (a, pure Zn; b, 0.03; c, 0.05; d, 0.1 M).

3.2. Surface morphology

The surface morphology of the electrodeposited Zn–Al alloy was investigated by scanning electron microscope (SEM), the effect of Al concentration on the surface morphology of the electrodeposited samples can be seen in Fig. 2. Pure zinc deposit (Fig. 2a) shows the coatings are composed of hexagonal close-packed crystals which is a typical morphology of Zn deposit [7-8]. (Figure 2b –c) shows that Zn-Al coatings particles were distributed with a non-uniform coarse grain crystal size formation and as the increase of Al concentration the size of the Zn-Al particles increases. Additionally, the gaps between the Zn-Al particles decreases consistently with the growth of the particles, more nucleation disappeared gradually which results the Zn-Al deposit to become less porous, as in Fig. 2-d some particles grew (or joined together), also have a clear grey colour appears to be well distributed.

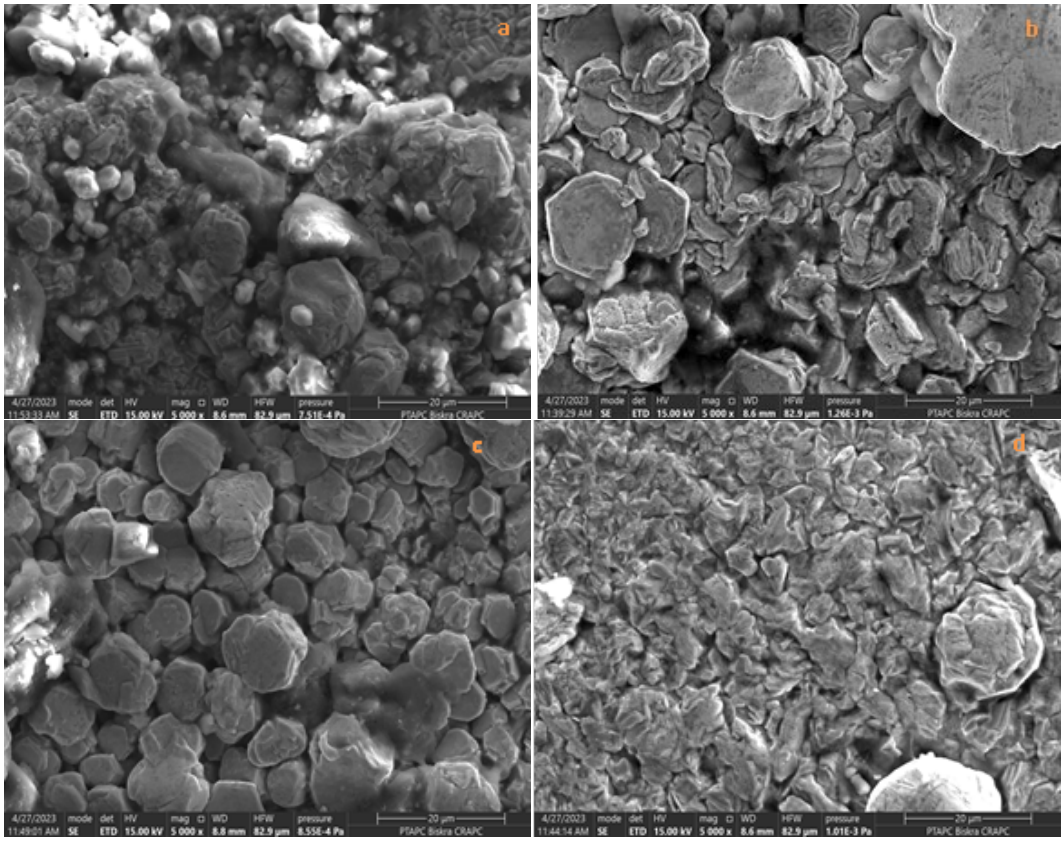

Fig. 2 Surface morphology of (a) Zn and (b) Zn-Al (0.03 Al), (c) Zn- Al (0.05 M Al), (d) Zn- Al (0.1 M Al) alloy coatings.

3.3. EDX analysis

Fig.3 showed the variation (EDX) results of various developed deposits, the spectrum of EDX mainly consists of Zn, Al, O and C. The basic compositions of the coating are Al and Zn, the O is introduced from atmosphere or partial oxidation of metals during the deposition of coating [13,15]. The presence of Al in the Zn alloy indicate that Al particles were successfully incorporated into the Zinc matrix, the rate of Al co-deposition reaches the maximum value (0.71 wt% at 0,1M) (Fig.3. d)

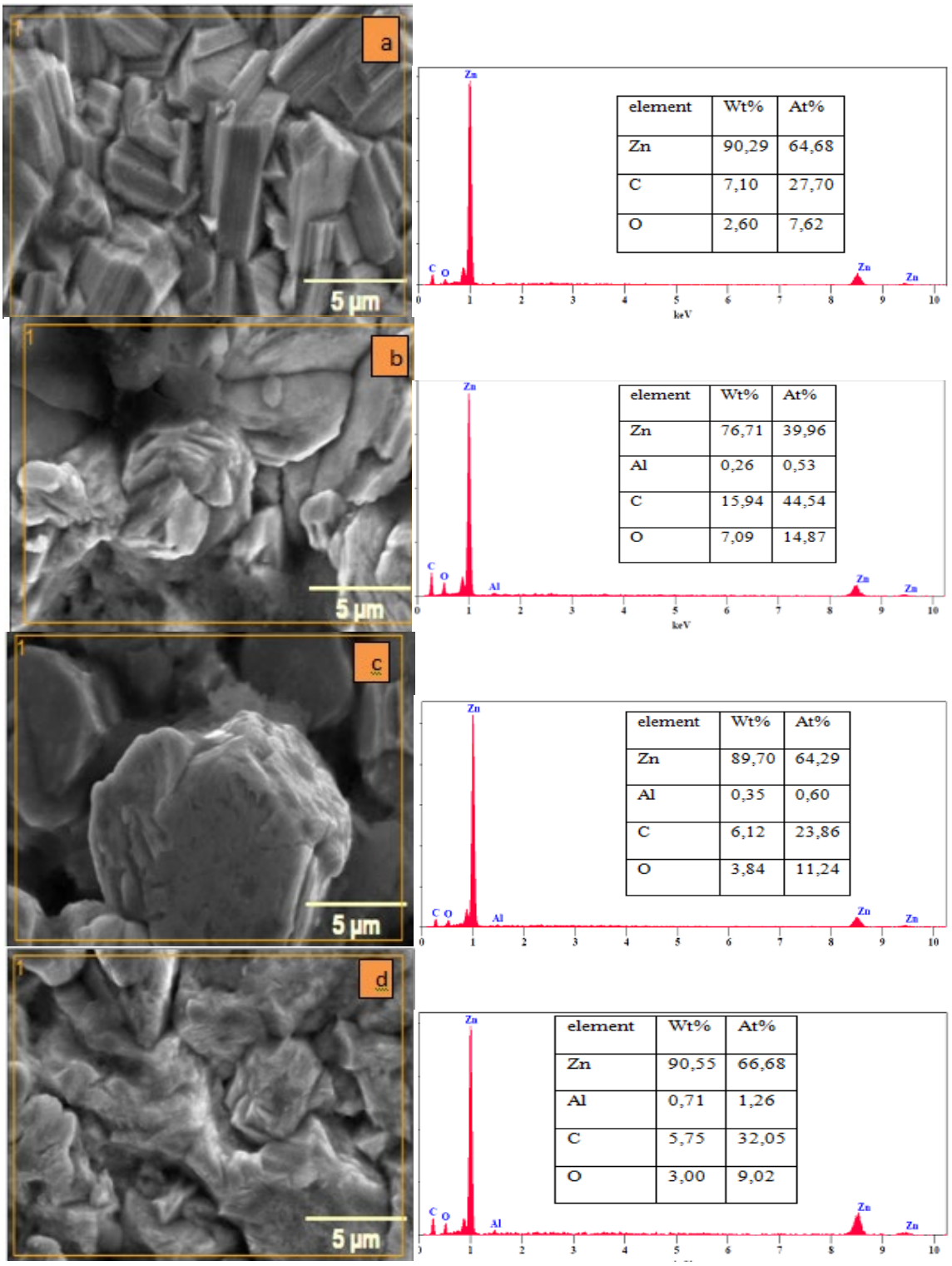

Fig. 3.EDX of (a) Zn and Zn-Al coatings obtained from baths containing different contents of Al (b, 0.03M; c, 0.05 M; d, 0.1 M).

3.4. Hardness of Zn-Al coatings

The Vickers microhardness HV of the electroplated samples are presented in table 2, the results exhibit the increase of the microhardness of the alloy as the Aluminium content in the bath increases, the HV of the Zn-Al alloy reaches it's maximum value at 0.1M Al content, this is because of the Al hardness is greater than Zn, it was observed that the hardness of Zn-Al was

208.4 HV at 0.03M, then enhanced gradually to 252.33 HV for 0.1M, and as believed the higher number of Al atoms in the deposits lead to a higher microhardness [10, 12].

Table 2. Values of micro-hardness Vickers hardness (HV) registered on different electrodeposition.

Alloy composition	Microhardness (HV)
Zn- 0 Al	205
Zn- 0.03 Al	208.4
Zn- 0.05 Al	221.76
Zn- 0.10 Al	252.33

3.4.1 Potentiodynamic polarization studies

Figure 4 presents the corrosion curves of Zn, Zn-Al alloy coatings deposited with different Al content. Additionally, Table 4 presents corrosion potentials (E_{corr}), corresponding values for corrosion current densities (I_{corr}), anodic Tafel slopes (β_a), cathodic Tafel slopes (β_b), polarization resistances (R_p) that were obtained from the potentiodynamic polarization tests in 3.5% NaCl solution, Zn exhibits the highest corrosion current density (0.250 mA/cm2), the effect of Al is visible on the value of I_{corr} that had decreased by almost 13 times to (0.02 mA/cm2) compared to pure zinc, the results obtained show an obvious corrosion resistance improvement when adding Al to the alloy up to 0.1M as observed [12,16,17].

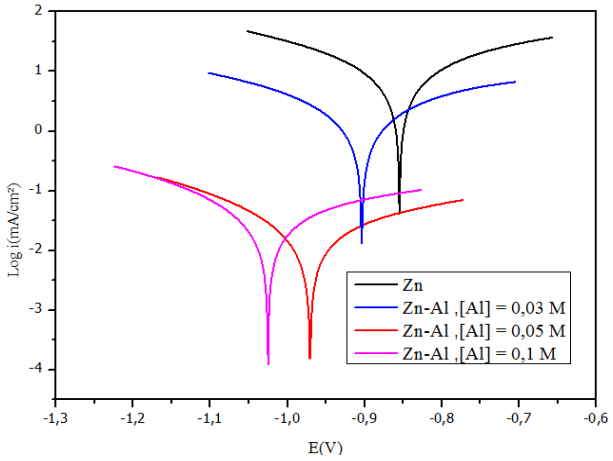

Fig. 4. Polarizing curves obtained for the alloy coatings in a 3.5 % NaCl solution at different concentrations of Al.

Table 4. The electrochemical parameters (E_{corr}, I_{corr}) of the samples in a 3.5 % NaCl solution.

coatings	E_{corr}(V)	I_{corr} (mA/cm^2)	β_a	β_c	Rp (Ω cm^2)
Zn	-0,855	0,250	0,377	-0,319	1,97
Zn-Al,[Al] = 0,03M	-0,904	0,152	0,449	-0,343	2,39
Zn-Al,[Al] = 0,05 M	-0,971	0,021	0,425	-0,290	2,56
Zn-Al,[Al] = 0,1 M	-1,025	0,020	0,277	-0,365	4,91

4. Conclusion

The following conclusions can be drawn from this experimental investigation of the electrodeposited binary Zn-Al from sulphate based acidic bath:

The XRD analysis showed a structure improvement with 0.1M Al content which significantly refines the microstructure of the deposit, the presence of only pure zinc phase (η-phase), and Al phase (α-Al phase) were observed, with the increase of peak intensity as the Al content increase.

The SEM images exhibit the surface morphology with less gaps between the nodules, more nucleation disappeared gradually as the Al concentration increased

The microhardness results indicate a better hardness 252.33 HV of the deposit 0.1M Al.

The potentiodynamic polarization tests showed 0.1M Al has the highest corrosion resistance among the deposits studied with increased value of the corrosion current density (I_{corr}), polarization resistance (Rp).

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