The influence of lead concentration on the properties of the electrodeposited zinc–lead alloy coatings

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The effects the concentration of lead on zinc-lead alloys obtained from sulphate baths under continuous current deposition are described. The deposit morphology was analyzed using Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) was used to determine the preferred crystallographic orientations of the deposits. Protection against corrosion properties studied in a solution of 3 % NaCl in the potentiodynamic polarization measurements (Tafel), It has been observed that the Zn–Pb alloy is characterized by enhanced the resistance of corrosion compared to the Zn alloys and the addition of Pb in the Zn-Pb increases the micro-hardness, XRD and SEM results an identify any coatings Zn-Pb alloy composition reveals that. Zinc - rich (η- phase).

1. Introduction

The electrodeposition technology is widely used due to its ease of use and low cost, and does not require difficult conditions or complicated equations [1-5]. The majority of these studies relate to the electrodeposition of inert metal alloys and metal oxide coatings [6]. Where many studies have been devoted to electrode-position of zinc because it offers corrosion resistance, decorative quality and conductivity [7]. Moreover, zinc acts as a self-sacrificial protective layer (anodized lid) [7]. Furthermore, metal coatings for zinc with other metals have been applied to improve zinc properties (Zn-Ni [8], Zn-Co [9], Zn-Cr [10], Zn-Cd [11]). At the same time, there are a large number of literatures concerning Zn-Pb binary alloy coatings. In comparison to the best Zn pure alloys, the presence of lead confers a prolonged resistance to corrosion of the coating [12-14,15]. In this context, the purpose of the ongoing work is to study the characterisation of Zn-Pb composite deposits on copper substrate by electrodeposition processing acid sulphate bath added to (PbSO4) at different concentrations. Modified Zn-Pb surface structures were studied and analyzed in detail. The corrosion resistance modified Zn-Pb coatings in 3% NaCl solution was investigated using Tafel polarization curve.

2. Experimental details
2.1. Coating preparation

The electroplating of Zn coatings was carried out on steel substrates, under the conditions at an operating current density of 30 A/cm^2 and a temperature of 30°C. The chemical composition of the used bath is given in Table 1 [6, 7]. Electrodeposits Zn were obtained by varying the lead sulphate concentration (PbSO4·7H2O) in the bath (0, 0.004, 0.03, 0.05mol/l).

2.2. Coating characterization

The phase structure of the coatings is determined using X-ray diffraction with aD8Advance-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 [10].

The corrosion behavior and the protection performance of Zn alloy and Zn-Pb alloy coatings were studied by using electrochemical Tafel extrapolation (TE) in 3% 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.

Table 1. Solution composition and conditions for alloy electroplating.

Electrolyte	Concentration ($g \cdot l^{-1}$)	Plating parameters
ZnSO4·7H2O	57.5	30°C and pH=3,5
H3BO3	9.3	constant current densities
Na2SO4	56.8	at30 mA $cm^{-2}$for 30min
Na3C6H5O7	56.8	

3. Results and discussion

3.1. Structural properties

XRD patterns for the "as deposited" Zn and Zn-Cr alloy coatings are presented in Fig.1.The metallic phases are well crystalline and can be ascribed to the Zn hexagonal structure in Fig 1(a). Only the diffraction lines of zinc-rich (η-phase) (JCPDS: 65-5973 [8,9,10]).
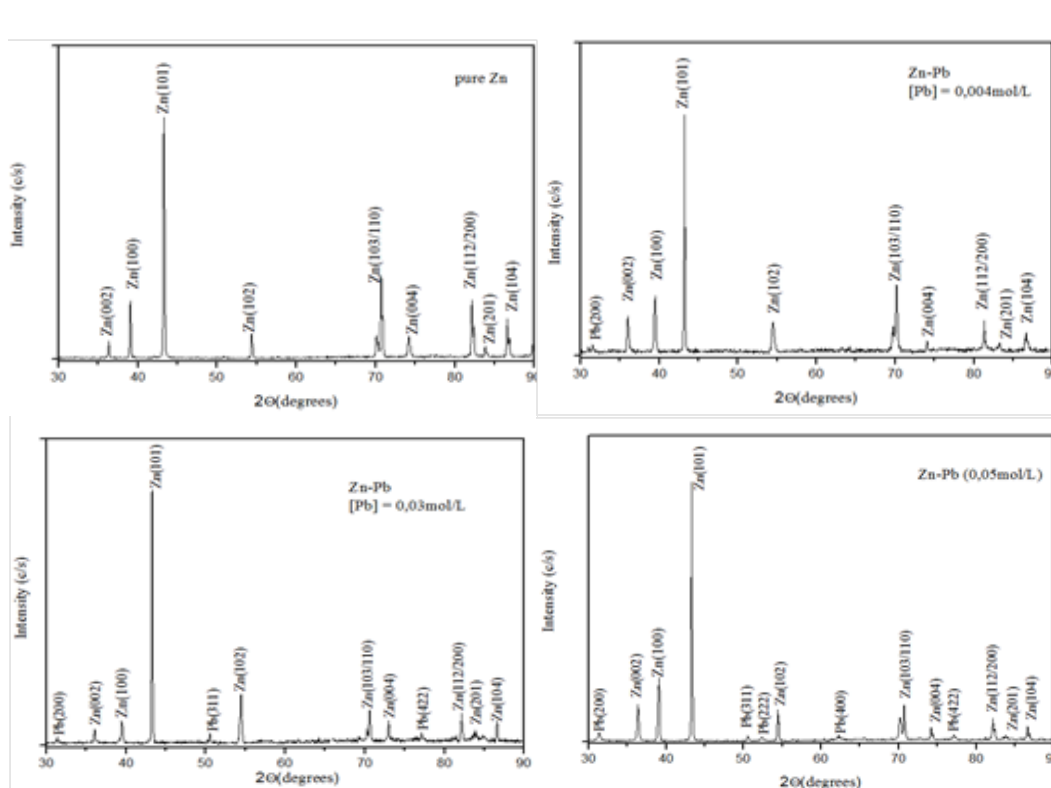

Fig. 1.XRD spectra of Zn-Pb alloy coatings electrodeposited at different concentrations of lead (a, pure Zn; b,0.004; c, 0.03; d,0.05 mol/l).

The presence of lead (Fig. 1(b c, d)) showed that there exist only pure zinc phase (η-phase) and lead phase (JCPDS: 87-663 [15-17]) on the coating surface, which accords to the Zn–Pb phase diagram the intensity of the (101) peak increases and the peak width is broader, which indicates the decrease in the grain size, the intensity of the peaks for planes (101) increases further. The increase of intensity is also observed in other peaks related to phase of zinc-rich.
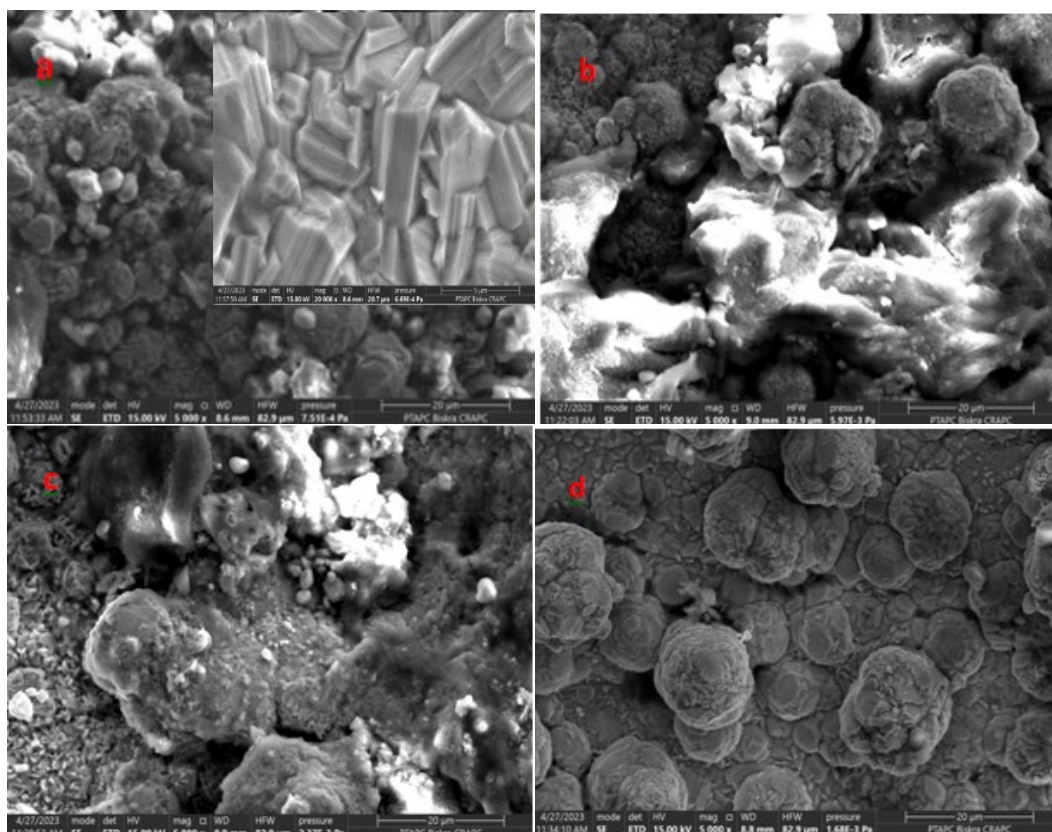

Fig. 2. Surface morphology of Zn(a)and Zn-Pb coatings obtained from baths containing different contents of lead (b, 0.004mol /l; c,0.03mol /l; d,0.05 mol/l).

3.2. Surface morphology and EDX analysis

Scanning electron micrographs of the electrodeposits obtained from the sulphate Zn alloy and Zn–Pb alloy coatings baths are shown in Fig. 2. Pure zinc deposit (Fig. 2a) presents the coatings are made up of hexagonal close-packed crystals. This is a typical morphology of Zn deposit [17-19]. Fig. (2-b, 2-c), shows coarse-grained deposit with non-uniform crystal size. This Zn-Pb deposit is clearly more porous, also have a clear grey colour appears well distributed. In Fig. 2-d some particles grew (or joined together) to form big cauliflowers 'to a more coarse-grained cauliflower'[17-18].

Fig. 3 shows the EDS analysis of the Zn alloy and Zn–Pb alloy coatings. A small peak of Pb has been identified on Zn–Pb alloy coating, the increase of the Pb concentration leads to an increase in zinc content. The rate of Pb co-deposition reaches the maximum value (5,96wt% at 0.03mol /l (Fig.3 .C).
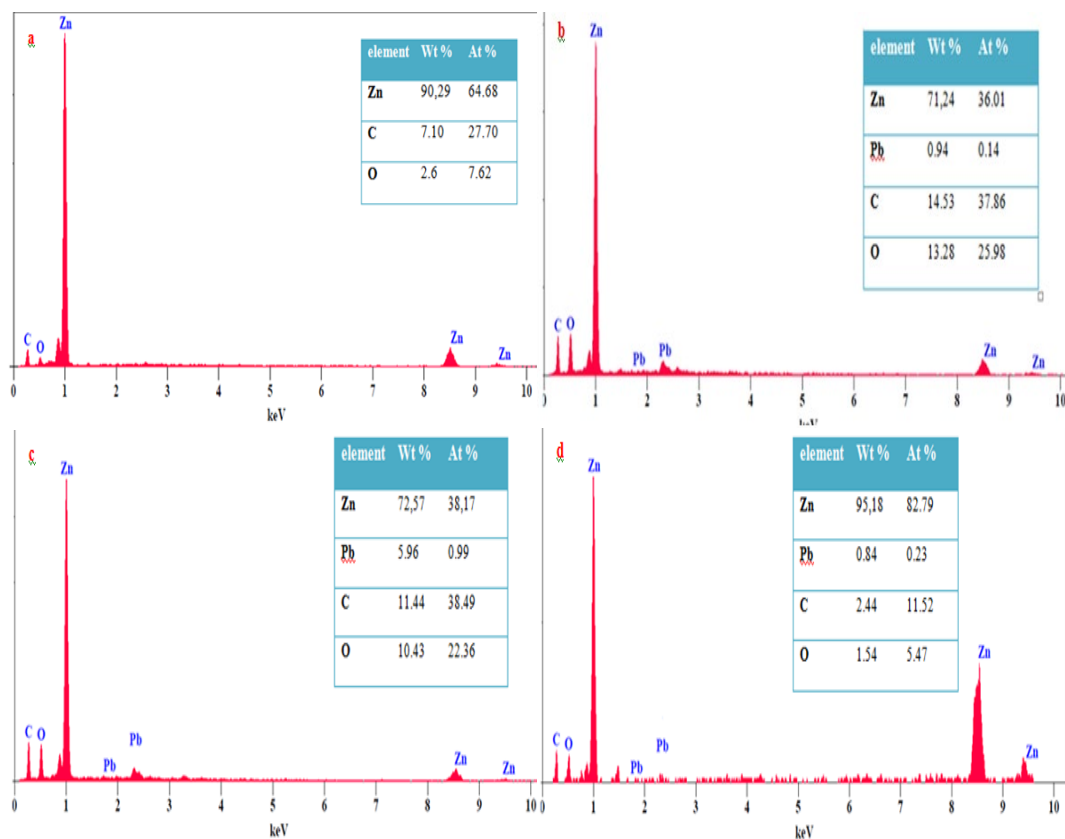
Fig. 3.EDX of(a) Zn and Zn-Pb coatings obtained from baths containing different contents of lead (b, 0.004mol /l; c,0.03mol /l; d,0.05 mol /l).

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3.3. Effect of lead content of the bath on coatings microhardness

The variation of microhardness vs lead content in the deposited Zn-Pb alloy coatings is shown in Table 2. These results show that the coatings prepared from the bath have shown good hardness, and the addition of Pb in the zinc matrix increases micro-hardness, this is because that the hardness of Pb is greater than Zn, a higher Pb content in the coating provides higher hardness, and we note the maximum hardness is obtained for 0,05M Pb. The presence of smaller grains impedes dislocation motion and results in an increase in microhardness [20].

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

coatings	microhardness (HV)
Zn	205
Zn-Pb ,[Pb] = 0,004 mol/L	216
Zn-Pb ,[Pb]= 0,03 mol/L	251
Zn-Pb ,[Pb]= 0,05 mol/L	296

3.4. Potentiodynamic polarization studies

Fig.4, shows the recorded potentiodynamic polarization curves of Zn–Pb alloy coatings by variation of lead content during corrosion tests in the 3.5% NaCl corrosive medium at room temperature. The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) calculated from the intersection of the cathodic and anodic Tafel slopes in the range of ±50 mV of the open-circuit potential (Eocp). Values were determined from this figure and cited in Table 3.
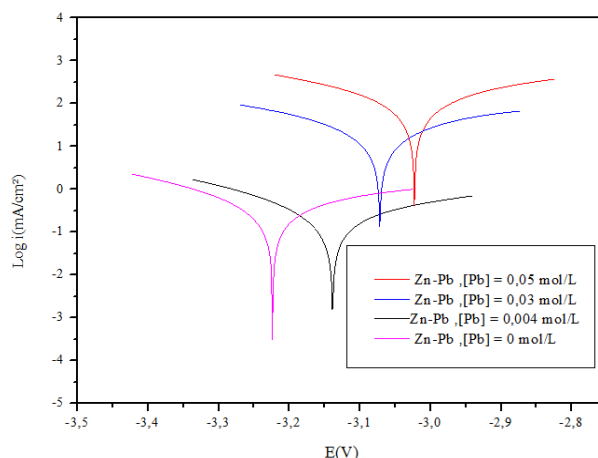
Fig. 4. Polarizing curves obtained for the alloy coatings in a 3.5% NaCl solution at different concentrations of Pb.

Deposited alloys from sulphate bath with lower lead concentration (0.004mol/l) have slightly higher i_{corr} values as compared with deposited alloys from sulphate bath with higher lead concentration (0.004mol/l) (Table 3), which is probably can be the consequence of smaller Pb content in the deposit, since higher lead content in the plating bath results the higher lead amount in the deposit [17]. Increasing the lead concentration in the plating bath increases the corrosion resistance of the deposit. The derived polarization resistance (Rp) values indicated that the Zn–Pb alloy exhibits much higher corrosion resistance than pure zinc Rp (Zn) = 12,04Ω cm^{2}vs Rp (Zn–0.05M Pb) = 133,45Ω cm^2) [13].

Table 3. Electrochemical parameters of the coatings derived from Tafel plots.

coatings	E_{corr}(V)	I_{Corr}(mA/cm^2)	Rp(Ω cm^2)
Zn	-3,22	0,0302	12,04
Zn-Pb ,[Pb] = 0,004 mol/L	-3,13	0,0486	43,12
Zn-Pb ,[Pb]= 0,03 mol/L	-3,07	0,4151	73,82
Zn-Pb ,[Pb]= 0,05 mol/L	-3,02	0,6847	133,45

4. Conclusions

The influence of Pb content on the application properties of electrodeposited zinc-Pb alloy layers has been studied in detail, and the main conclusions are the following:

XRD and SEM results indicate all the Zn-Pb alloy coatings have similar composition phase zinc-rich (η-phase structure), Increasing the Pb concentration in the plating bath increase in the pure Zn phase of the alloy.

The deposited coating with 0,05 mol/l Pb showed the maximum value of hardness 296 HV, because of the increase of Pb concentration in the plating bath.

Polarization resistances of Zn-Pb composite coating increased with increasing the Pb content.

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