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CHROMIUM-RICH Zn–Cr ALLOYS: ELECTROCHEMICAL DEPOSITION, STRUCTURE AND CORROSION RESISTANCE

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In this work we have done an experimental study of Zinc-Chromium composite coatings. For this the influence of the Chromium concentration was the principal object in order to improve the resistance of the corrosion of the coatings, which has been made by electroplating on steel substrates previously treated, have been studied by several characterization methods, as the X-ray diffraction, micro-hardness measurement and scanning electron microscopy (SEM), protection against corrosion properties studied by potentiodynamic polarization measurements (Tafel) . the addition of Cr in the Zn alloys increases the micro-hardness, XRD and SEM results and identify any coatings Zn-Cr alloy composition reveals that zinc phase.

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1. Introduction

The use of coating as anticorrosive for metal substrates depends mainly on the sacrificial and the protection mechanisms barrier. In industry the main demand is coating substances with the highest resistance of corrosion and smallest thickness, which Zn coatings cannot provide, hence scientists replaced Zn coatings by Zn alloy coatings [1-2]. Electroplated binary Zn-Malloys, where metals are an Fe group such as Fe, Co, Sn, Ni, Mn and Cr [3] Electrodeposited zinc has been widely used in a variety of applications, including coatings for automotive and electronic parts [4]. The electrodeposition of zinc alloys is of great interest because these alloys exhibit significantly higher corrosion resistance than pure zinc [5]. It sensed that it will be important to accumulate the Zn alloys properties in one alloy through the electroplating of Zn-Cr alloy. The first aim of our study is to electrodeposite Zn-Cr alloy coatings on two steel substrates with useful form in sulphate bath. The second aim is to make a comparison between Zn and Zn-Cr alloys for structural phases, morphology of surface and the resistance of corrosion. The binary alloys are prepared under similar electrolysis conditions like the Zn alloy, 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 details

2.1. Coating preparation

The electroplating of Zn coatings was carried out on steel substrates, under conditions at operating current density of 30 A /cm2 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 Chromium sulfate concentration (CrSO4·7H2O) in the bath (0, 10, 15, 20 $g \cdot L^{-1}$).

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2.2. Coating characterization

The phase structure of the coatings is determined using X-ray diffractionwith a D8Advance-Brucker using a Cu Kα radiation (λ= 1.5406Å) and 2θ= 0.02° as a step.

Scherrer's formula is used for the determination of the coatings crystallite sizes from theX-ray peak broadening of the (101) diffraction peak at [6-9]:

$$D = 0.9\lambda/\beta\cos\theta \qquad (1)$$

where D is the grain size, λ is the X-ray wavelength, β is the corrected peak full width at halfmaximumintensity (FWHM), and θ is Bragg angle position of the considered peak.

The deposits surface morphology was studied by scanning electron microscopy (A JEOL model JSM6390LV).

Microhardness of coatings is 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-Cr composite coatings were studied by using electrochemical Tafel extrapolation (TE) in 3,5 % wt NaCl solution. The tests were performed using a potentiostatgalvanostat (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 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 30 mA cm^{-2} for 60s
H_3BO_3	9.3	
Na_2SO_4	56.8	
$Na_3C_6H_5O_7$	56.8	

3. Results and discussion

3.1. Phase structureand texture of zinc– Chromium deposits

XRD patterns for the "as deposited" Zn and Zn-Cr alloy coatings are presented in Fig.1. The Zn alloycoatings have the same structure as zinc deposits [8]. The metallic phases are well crystalline and can be ascribed to the zinc-rich (η-phase) hexagonal structure. Adding Chromium atoms in the zinc alloy shifted towards to more big reflection angles for all the η phases. A decrease of (101) peak was observed when Chromium level in the film was increased. The decrease of this peak may be attributed to the decrease of the zinc content in the coating. No Cr phase was observed. [11]

Crystallite sizes were determined using the Scherer formula. For all coatings, the profile of (101) peak exhibits Lorentzian line shape, The grain sizes significantly decrease from 52.3 nm to 39.66 nm with increasing Cr content (Table 2), indicates that the composite coatings have smaller grain size than alloy coatings. This shift may be due to the biggr radius fo zinc, compared to Cr one ($R_{Zn}{}^{2+}$=0.74 ,and $R_{Zn}{}^{2+}$=0.62) ,This finer structure may be at the origin of the decrease in the whole peaks intensity of the coated steel substrates and may be at the origin of the higher hardness of this deposit [12].

Table 2.Values of the crystallite size obtained from the strongest diffraction line of the metallic phases.

Electrolyte	**hkl**	**2θ(°)**	**Crystal size (nm)**
Zn (0 g /l Cr)	(101)	44.2	52,3
Zn-Cr (10 g /l Cr)	(101)	44.28	49,2
Zn-Cr (15g /l Cr)	(101)	44.38	45,13
Zn-Cr (20 g /l Cr)	(101)	44.59	39,66

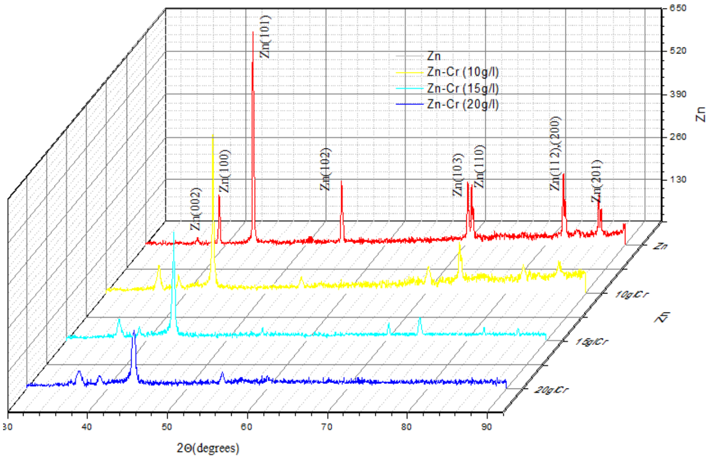


Fig. 1.XRD spectra of Zn-Cr alloy coatings electrodeposited at different concentrations of Cr (10, 15, 20 g /l).

The preferred orientations of zinc– Chromium alloys were determined using the Muresan method [9,13] calculating a texture coefficient (Tc) using the equation:

$$T_C(\mathrm{hkl}) = \frac{I(\mathrm{hkl})/I_\circ(\mathrm{hkl})}{N^{-1}\sum_n^N I(\mathrm{hkl})/I_\circ(\mathrm{hkl})} \quad (2)$$

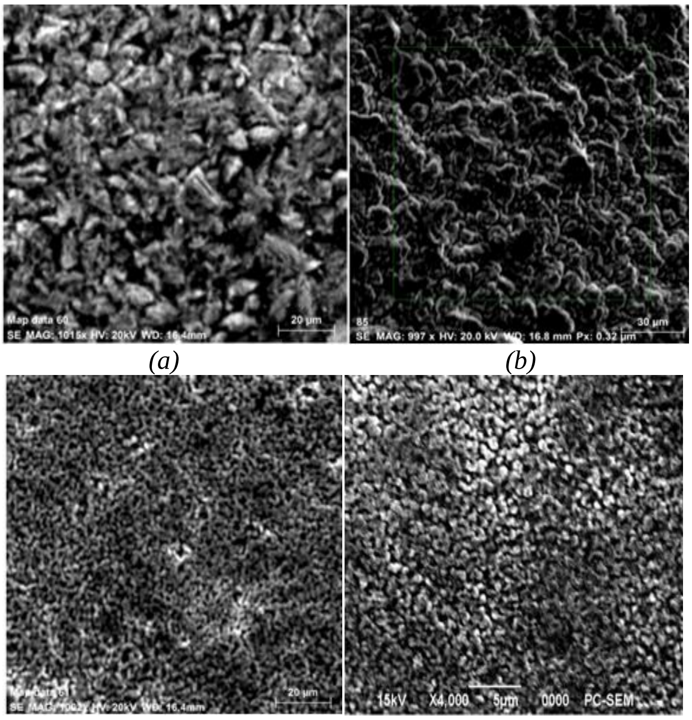
where I(hkl) is the peak intensity of the zinc– Chromium electrodeposits and ΣI(hkl) the sum of the intensities of the independent peaks. The index 0 refers to the intensities for the standard zinc powder sample. The preferred crystallographic orientation is indicated by a Tc value larger than unity. Tc are given in Table 3. From the data in Table 4, in the absence of Chromium , 39,32 of the zinc crystallites are oriented parallel to the (002) plane, 22.41 of the zinc crystallites are oriented parallel to the (100) plane, 48.34 of the crystallites are oriented parallel to the (101) , most intensity planes decrease in the presence of Cr .

Table 3. Texture coefficients (Tc) of Zn–Cr alloys.

Plane (hkl)	Tc (hkl) for alloy system			
	Zn (0 g /l Cr)	Zn-Cr (10 g /l Cr)	Zn-Cr (15g /l Cr)	Zn-Cr (20 g /l Cr)
002	39,32	35,21	31,01	25,04
100	22,41	21,44	19,03	13,22
101	48,34	44,57	41,84	39,80

3.2. Surfacemorphology

Scanning electron micrographs of the electrodeposits obtained from the sulphate Zn and Zn–Cr baths are shownin Fig. 3. Pure zinc deposit (Fig. 3a) presents the morphology commonly observed from the zinc deposit obtained from asulphate bath [9]. Also, zinc deposits have a clear grey colour appears well distributed, compact and continuous. Zn–Cr deposits (Fig. 3b, 3c, 3d) exhibit finer grain size and the grain size does decrease compared pure zinc deposits. The presence of Chromium modifies the growth of the zinc nuclei, leading to fine-grained deposits [14].



(a) (b)

(c) (d)

Fig. 2.Surface morphology of (a) Zn alloy coatings and (b) Zn-Cr(10 g /l Cr), (c) Zn-Cr(15 g / L Cr), (d) Zn-Cr(20 g /l Cr) Composite coatings.

3.3. Micro hardness measurements

The microhardness results are presented in Table 5, which shows the change in hardness as a function of the Cr content in the deposit. The microhardness test revealed that there was a linear increase in microhardness with increasing chromium content of the coating indicates that the microhardness of all Zn-Cr composite coatings is considerably high than the Zn alloy coatings [15], Hardness values enhance with Cr content, it can be correlated to the (i) formation of solid solution, (ii) formation of two phase structure, (iii) grain size effects [7, 16].

Table 5. Values of micro-hardness Vickers hardness (HV) registered different electro deposition.

Coating	hardness
Zn	149.1
Zn-Cr (10 g /l)	221,4
Zn-Cr (15 g /l)	365 ,3
Zn-Cr (20 g /l)	421,15

3.4. Potentiodynamic polarization studies

Tafel tests were performed on Zn alloy and Zn-Cr composite coatings in 3.5 % NaCl solution. Tafel polarization readings have been shown in Fig 3. The corresponding electrochemical parameters extracted from Tafel plots are summarized in Table 4. Results indicated that the corrosion potentials of Zn-Cr composite coatings shift to the positive direction and corrosion current density decreased significantly compared to Zn alloy coatings. The increase of chromium content in the deposits is caused a finer grain size and an increase in corrosion resistance of Zn-Cr alloys [17,18].

Table 4.Electrochemicalparameters of the coatings derived from Tafel plots.

Coating	E_{corr}	i_{corr}	Rp
Zn	-460	2,9868	12,04
Zn-Cr (10 g /l)	-432,5	1,3819	49,57
Zn- Cr (15 g /l)	-401,5	0,9141	57,01
Zn-Cr (20 g /l)	-389,5	0,6814	75,86

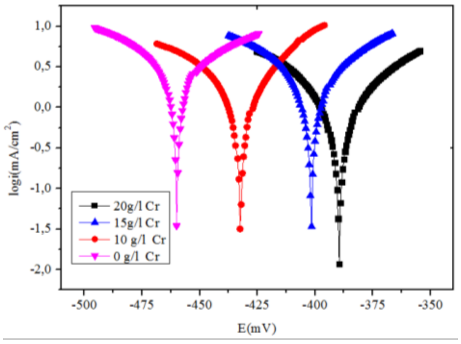


Fig. 3.Polarizing curves obtained for the alloy coatings in a 3.5 % NaCl solution at different concentrations ofCr.

4. Conclusions

Conclusions must be comprehensive and not written like a report.

In this study, the effect of Cr contents, in the bath, on structural properties, microhardness and corrosion resistance of Zn-Cr alloy coating was investigated. The coatings were deposited on mild steel substrates by electrodeposition from a sulfate bath.

The Adherent alloy coatings light, compact and good were obtained with galvanostatic conditions. XRD and SEM results indicate all the Zn-Cr alloy coatings have similar composition phase zinc-rich (η-phase structure), Increasing the Cr concentration in the plating bath decrease in the pure Zn phase of the alloy.

The test of the micro-hardness on the various electro deposited coatings has a maximum value (20 g/l) Cr, because the increase of the Cr concentration in the plating bath increases of micro-hardness.

Also the surface morphology of the deposits was improved with increasing Cr concentration, gives a more uniform surface morphology and more compact deposits.

The study by the method from potentiodynamic polarization curves showed that the values of the corrosion current density (Icorr) decreases, the corrosion potential (Ecorr) and the polarization resistance (Rp) increases with increasing the concentration of Cr in the electrolyte bath.

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References

[1]. M. Diafi, A. Aidi, B. Benhaoua , Digest Journal of Nanomaterials and Biostructures**15**, 621 (2020).
[2]. M. Diafi, K. Degheche, H. B. Temam, Journal of Fundamental and Applied Sciences **9**, 89(2017).
[3]. M. Diafi, S. Benramache, E. G. Temam, A. M.Lakhdar, B. Gasmi, Acta Metallurgica Slovaca **22**, 171 (2016).
[4]. J.L. Ortiz-Aparicio, Y. Measa, G. Trejo, R. Ortega, T. W. Chapman, E. Chainet, P. Ozil, Electrochimica Acta **52**,4742 (2007).
[5]. S.M. Rashwan, A.E. Mohamed, S. M. Abdel-Wahaab, M.M. Kamel: Journal of Applied Electrochemistry **33**, 1035 (2003).
[6]. M. Diafi, N. Belhamra, B. T. Hachemi, B. Gasmi, S. Benramache:Acta Metallurgica Slovaca **21**, 226(2015).
[7]. M. Diafi, L. Tahraoui, K. Digheche, F. Khamouli, Acta Metallurgica Slovaca **24**,241 (2018).
[8]. M.S. Chandrasekar, S. Shanmugasigamani, M. Pushpavanam, Materials Chemistry and Physics **115**,603(2009).
[9]. M. Mouanga, L. Ricq, P. Berçot: Journal of Applied Electrochemistry **38**, 231 (2008).
[10].S. Ghaziof, W. Gao, Journal of Alloys and Compounds**622**, 918 (2015).
[11].I. H. Karahan, Optoelectron. Adv. Mat.**2**, 788 (2008).
[12].T. B.Scherzer, G. Avdeev, T. Vassilev, V. Chakarova, H. Kronberger, M. Monev, Surface Engineering, 1(2019).
[13].Y.Meftah, D.Bekker,B. Benhaoua,A.Rahal, Digest Journal of Nanomaterials and Biostructures **13**,465(2018).
[14].T. Yang, C. Peng, L. Xiang, H. Cao; Applied Mechanics and Materials **456**, 438 (2014).
[15].M. R. E. Sharif,Y. J. Su, C. U. Chisholm, A. Watson, Corrosion Science **35**,1259 (1993).
[16].A.M. Alfantazi, U. Erb,Materials Science and Engineering**212**, 123 (1996).
[17].V. Medeliene, E. Matulionis, Protection of Metals **38**, 275(2002).
[18].V. Chakarova, Tz. Boiadjieva-Scherzer, D. Kovacheva, H. Kronberger, M. Monev, Corrosion Science **140**, 73 (2018).