

Obtaining and protective properties of passive films on Zn and Zn-Fe-P ternary alloys

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Abstract: Protective Zn and ternary alloy Zn-Fe-P coatings are electrochemically obtained and additionally treated in special elaborated solution for chemical passivating based on tri-valent chromium compound. The elemental composition and surface morphology of the newly obtained Zn-Fe-P coatings without or with additional passive (conversion) film is determined by using of EDS and SEM. The corrosion behavior and protective ability of the system coating / passive (chromite) film are investigated by means of potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) in model medium containing chloride ions as corrosion activators. As a result of the corrosion tests the influence of the passive film on the corrosion properties of the electrodeposited Zn and Zn-Fe-P alloy coating in that medium is analyzed and commented.

Key words: corrosion, passive films, zinc, Zn-Fe-P alloy

1. INTRODUCTION

Zinc coatings are widely used for metal prevention and protection against corrosion damages. The very strongly negative potential of the Zn (-0.76 V) defines its role of anodic (sacrificial) layer concerning the iron and steel substrate. The co-deposition of the zinc with other metals like Mn, Co, Ni, Fe leads to obtaining of coatings with improved physical and mechanical properties and increased corrosion resistance [1-11]. Contrary to the pure zinc most of these alloys have good adhesion concerning the finishing paints.

According to some investigations [12] the co-deposition of some of these alloys with P has a positive influence on their corrosion resistance. In addition, the incorporation of this element in the alloy in amounts less than 1 wt% usually decreases the residual stresses in the galvanic coatings.

Several patents for obtaining of thin alloy Zn-Fe-P coatings based on acidic or alkaline electrolytes are available in the literature [13-16]. The phosphorus content varies in the range 0 – 5 wt% while that of the iron is between 7 and 35 wt%. The authors report for good weldability, solderability and adhesion to finishing paints and coatings and increased corrosion resistance against local corrosion. The alloys with great zinc content have crystalline structure which changes to amorphous at higher P and Fe amounts.

Since the zinc coatings are not enough resistant in very aggressive environments additional surface treatment is applied in order to improve the

stability. The result is the appearing of a conversion (passive) film [17-22]. The so treated electrodeposits show lower susceptibility in aggressive corrosive solutions and can be an excellent basis for further treatment with organic paints or lacquers.

The tri-valent chromium-based (chromite) films have been developed due to the novel ecological requirements and are environmentally friendly compared to the Cr⁶⁺-based ones. Chromite layers on the metal surface play a very important role decreasing the zinc dissolution rate and lowering the rate of the oxygen reduction [23-26].

The present work is aimed to describe the experimental conditions for obtaining of passive films (PF) on zinc and Zn-Fe-P alloy coatings from environmentally friendly Cr³⁺-containing solution as well as to characterize their corrosion behavior in a model medium with chloride ions as corrosion activators.

2. EXPERIMENTAL

2.1. Sample preparation

All coatings are electrodeposited on a low carbon steel substrate with sizes 20x10x1 mm, whole surface area of 4 cm² and thickness of approximately 10 μm.

2.2. Electrochemical deposition

2.2.1. Zinc coatings are electrodeposited from electrolyte containing (in g/l): ZnSO₄·7H₂O - 150, NH₄Cl - 30, H₃BO₃ - 30, additives AZ-1 - 50 ml/l and AZ-2 - 10 ml/l at pH value between 4,5–5,0, ambient temperature of about 22 °C, zinc anodes and cathodic current density of 2 A/dm². No stirring or agitation is applied.

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2.2.2. Zn-Fe-P alloys are electrodeposited from electrolyte with a composition (in g/l): $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ - 200, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ - 70, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 5,5\text{H}_2\text{O}$ -50, $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ and H_3PO_2 - 11.4, NH_4Cl - 15 and additive ZC1 (20 ml/l) at pH 2.5, temperature of 40 °C, Ti-Pt anodes and cathodic current density in the range 5 - 20 A/dm², circulation of the electrolyte. In that case alloys with different Fe and P content are electrodeposited.

2.3. Corrosion medium and reproducibility

A model corrosion medium of 5% NaCl solution with pH~6.7 at room temperature of 22 °C is used. The results from the investigations are an average of 3 samples per type i.e. for each measurement 3 replicates of a Zn or ternary alloy Zn-Fe-P. Prior to the beginning of the test all samples are temporized for a definite period in the model medium at conditions of open circuit potential (OCP).

2.4. Passive films

The additional surface treatment of the zinc and of the ternary alloys is carried out in a solution consisting of CrNO_3 , HNO_3 and NaH_2PO_2 with pH value of 1.2. The immersion time was 40 s for all investigated samples.

2.5. Sample characterization

The sample characterization is realized by using of electrochemical workstation PAR “VersaStat 4” and application of the following methods:

- Potentiodynamic (PD) polarization – the measurements are performed at a scan rate of 1 mV/s in the potential range between -1200 and – 200 mV.

- Electrochemical impedance spectroscopy – the measurements are carried out in the frequency range of 100 kHz to 10 mHz by superimposing an AC voltage of 10 mV.

Additionally, for observation of the sample surface morphology and its peculiarities Scanning electron microscopy (SEM) with coupled EDS device is applied by using of INCA Energy 350 unit.

The electrochemical measurements are performed in a common three-electrode experimental cell (volume of 250 ml) with a Luggin-capillary for minimizing the ohmic resistance of the medium. Platinum plate serves as a counter electrode while the potentials are measured with respect to the saturated calomel electrode (SCE).

2.RESULTS AND DISCUSSION

3.1. Potentiodynamic polarization (PDP)

The cathodic and anodic potentiodynamic polarization (PD) curves of pure Zn and Zn-Fe-P alloy coatings with different Fe and P content without and with additional passive film (PF) on the surface are demonstrated in Figure1(A,B). In addition, the PD curve of the low carbon steel at the same conditions is also demonstrated.

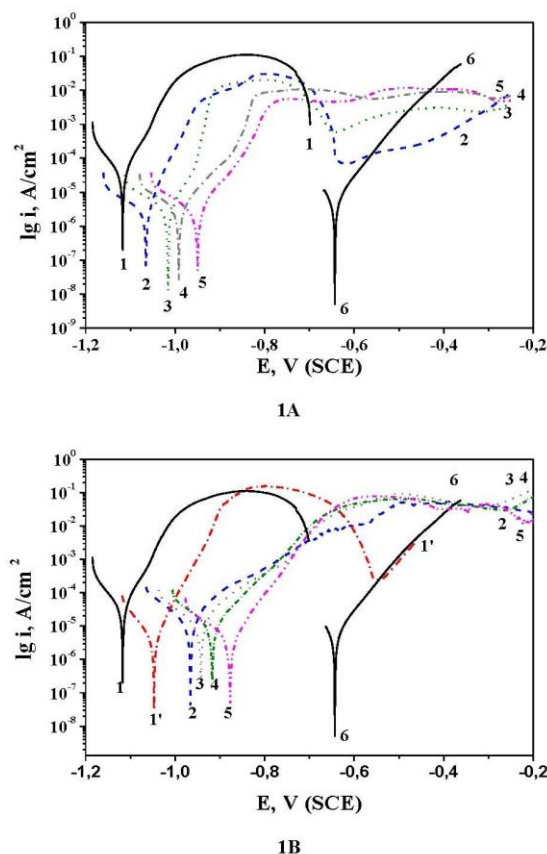


Figure 1. Potentiodynamic curves of Zn and Zn-Fe-P alloys: A – without passive film; B – with passive film. 1 – Zn (without PF); 1' – Zn (with PF); 2 – $\text{Zn}_{96}\text{Fe}_4\text{P}_0$; 3 – $\text{Zn}_{91.2}\text{Fe}_{8.5}\text{P}_{0.3}$; 4 – $\text{Zn}_{85.4}\text{Fe}_{14}\text{P}_{0.6}$; 5 – $\text{Zn}_{70.3}\text{Fe}_{28.5}\text{P}_{1.2}$; 6 – low carbon steel.

The obtained results clearly show that all coatings have corrosion potentials strongly negative compared to the steel which means that they will play a role of sacrificial coating i.e. they will be firstly dissolved in the case of corrosion attack protecting in such a way the underlying steel substrate – Fig. 1A.

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It can be also concluded that at external anodic polarization the pure Zn coating lasts up to about -720 mV while all ternary alloy sample curves are much longer. The corrosion current density values of the alloys (in the order of magnitude 10^{-6} A/cm²) are much lower compared to that of the zinc. The anodic parts of the PD curves of the alloys are generally with lower slope indicating slowing in the anodic rate and in addition a passive zone (although at relatively high current density value) seems to appear for the sample Zn₉₆Fe₄P₀. The latter has no P content registered by EDS analysis but is obtained from electrolyte containing this element. Generally, these PD curves could be divided in two groups according to their position and electrochemical parameters. Curves 4 and 5 which are the samples with greater P content have close anodic behavior and steep slopes indicating inhibiting of the anodic dissolution. Both other samples with lower P content (curves 2 and 3) show steeper anodic slopes and are placed at more negative potential values—Fig. 1A. The PD curves of the same sample types but with PF are shown in Figure 1B. Also here, the curve of the pure zinc is added for more clarity. The presence of PF on Zn changes its corrosion behavior leading to shifting of the corrosion potential in positive direction and to lower corrosion current density value. The passivated alloy samples show closer corrosion potentials compared to the non-passivated ones most probably due to the better surface homogeneity as a result of the treatment in the Cr³⁺-containing solution. The anodic slopes of the curves are much lower compared to these from Fig. 1A which means that the anodic process is to a certain degree inhibited.

3.2. Electrochemical impedance spectroscopy (EIS)

The results from the EIS measurements for the zinc and ternary alloys without PF are demonstrated in Figure 2(A,B). It can be concluded that most of the obtained EIS spectra responses are more or less depressed capacitive loops and in general two groups of samples could be divided – Zn₉₆Fe₄P₀ and Zn_{91.2}Fe_{8.5}P_{0.3} (and also pure Zn) from one side and Zn_{85.4}Fe₁₄P_{0.6} and Zn_{70.3}Fe_{28.5}P_{1.2} - from another. Both latter show polarization resistance values between 350 and 470 ohms, while the other three coatings have lower Rp - in the range between 150-200 ohms – Fig. 2A.

The results from the EIS investigations of Zn and ternary Zn-Fe-P alloys with PF are presented in Figure 2B. It can be registered that the sample with the highest Fe and P contents (No. 5) has the greatest Rp value – about 2200 ohms - followed by

sample No. 4 – 900 ohms. The other investigated samples have Rp values about 400-500 ohms.

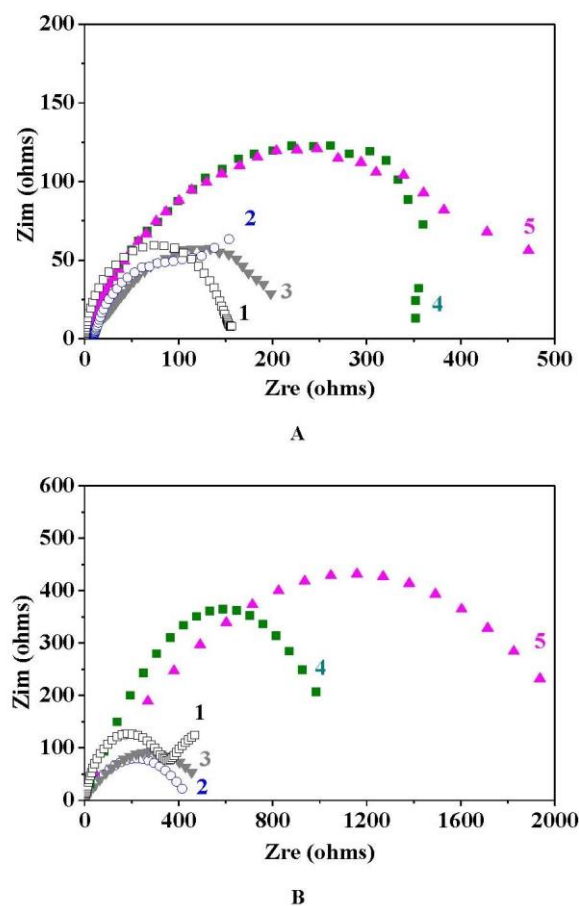


Figure 2. Overlay EIS spectra response of Zn and Zn-Fe-P alloys: A – without passive film; B – with passive film; 1 – Zn; 2 - Zn₉₆Fe₄P₀; 3 - Zn_{91.2}Fe_{8.5}P_{0.3}; 4 - Zn_{85.4}Fe₁₄P_{0.6}; 5 - Zn_{70.3}Fe_{28.5}P_{1.2}.

Compared to the non-passivated samples the passivated ones have greater Rp values – between two and four and a half times - which clearly demonstrate the positive influence of the additional treatment in Cr³⁺-containing solutions on the protective characteristics of the Zn and the ternary alloys. For most of the hereby discussed cases, the initial EIS response is modeled by an equivalent circuit presented in Figure 3A. The time constant Rp.CPE1 is attributed to the electrochemical reaction while Rs.CPE2 – to the surface properties. In one case (pure zinc with passive film shown in Fig. 2B) also Warburg impedance W is added – Fig. 3B. The replacement of pure capacitance with constant phase element (CPE) in the equivalent circuits is generally accepted, being denoted to inhomogeneities at different levels i.e. steel surface roughness, product layer heterogeneity [27], etc.

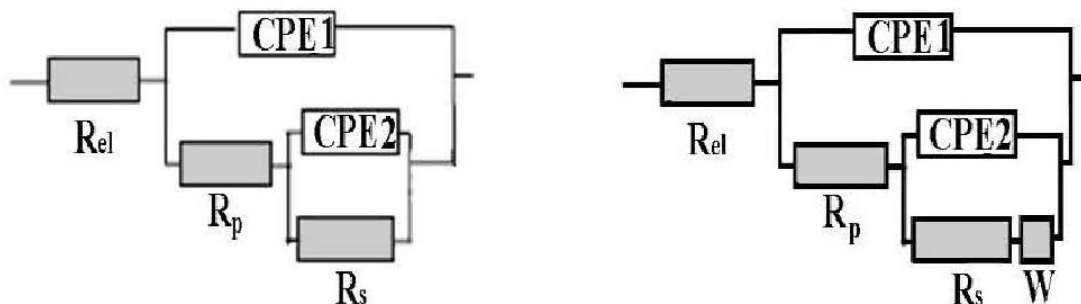


Figure 3. Equivalent circuits used in the EIS investigations.

At first look some of the obtained results seem to be to a certain degree controversial compared to the data registered from the PD curves. This phenomenon could be explained to some extent with the nature of the applied methods – the anodic polarization is a destructive method and during the dissolution of the coating the appearance of newly formed corrosion products is expected. The latter (depending on the value of their solubility) could inhibit for a definite period the dissolution process due to the so called “barrier effect”.

The type of the newly formed corrosion products strongly depend on the composition of the alloys so it can be expected that alloys with different composition will lead to different amounts or ratios of corrosion products. In the case of EIS the appearance of these products is less likely due to the non-destructive principle of this method.

3.3. EDS analysis and SEM

The results from the EDS analysis concerning the composition of the investigated ternary alloys before and after treatment in the solution for chemical passivating are demonstrated in Table 1.

It can be registered that as a result of the chemical passivating the zinc content in all alloy coatings become lower while the amounts of all other elements increase. These changes in the chemical composition of the passivated coatings can to a certain degree explain the differences registered by using of PD polarization and EIS methods.

As well known, during the chemical passivating the coating surface is partially dissolved as a result of the low pH - value predominantly the Zn which is the more negative metal. Also other elements like Fe and P will be included in the structure of the passive film together with Cr forming oxides and phosphates and leading in such a way to change in its potential. This newly formed film has a “barrier effect” and ensures the protection of the passivated zinc toward the steel substrate. In addition, it can be expected that if the surface is enriched with elements with more positive potential the sample will be more resistant against the corrosion attack.

The EDS analysis show that the greatest Fe and P amounts can be observed in alloys No. 3 and 4 from Table 1. The EIS data demonstrate that these coatings have the greatest R_p values to the dissolution reaction. EIS is an express and non-destructive investigating method and its conditions are close to the open-circuit conditions (OCP). Comparing the EIS data with the PD curves from Figure 1B it can be also registered that the same alloys with the highest Fe and P amounts distinguish with the most positive corrosion potentials. The surface morphology of the pure zinc and of the ternary Zn-Fe-P alloys is demonstrated in Figure 4. Marked differences can be observed between the presented samples. The zinc coating shows smooth and even surface with several “nodular” zones the latter most probably being a result from included contaminations during the electrodeposition.

Table 1. Chemical composition of ternary Zn-Fe-P alloys before and after passivating.

No	ELEMENTS						
	Alloy before passivating			Alloy after passivating			
	Zn	Fe	P	Zn	Fe	P	Cr
1	96.0	4.0	0.0	93.7	4.0	0.6	1.7
2	91.2	8.5	0.3	88.3	9.3	0.8	1.6
3	85.4	14.0	0.6	74.3	22.4	1.7	1.6
4	70.3	28.5	1.2	45.7	49.3	3.3	1.7

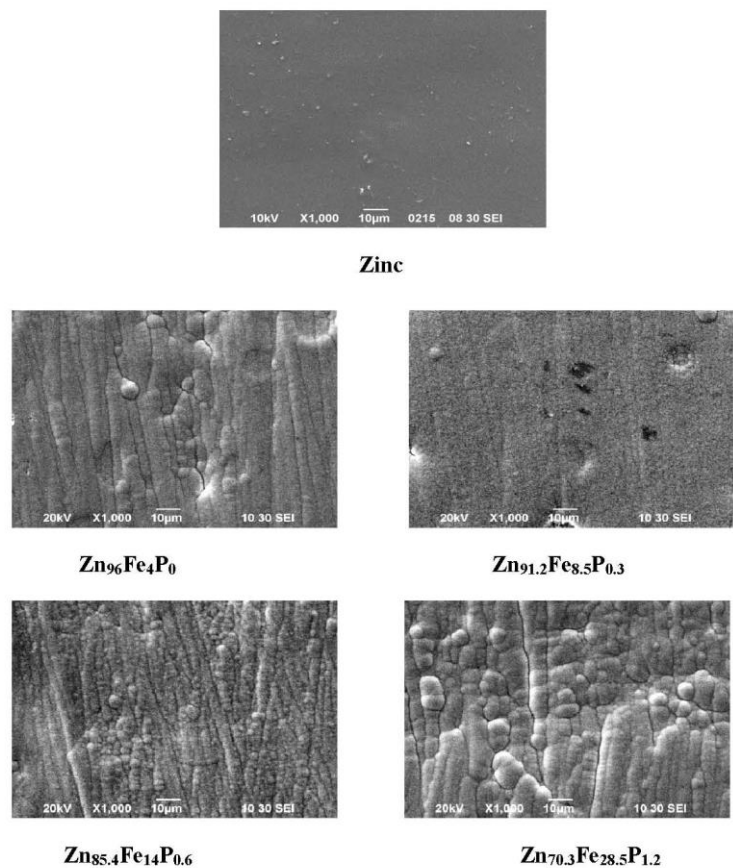


Figure 4. Surface morphology (SEI) of non-passivated Zn and ternary Zn-Fe-P alloys.

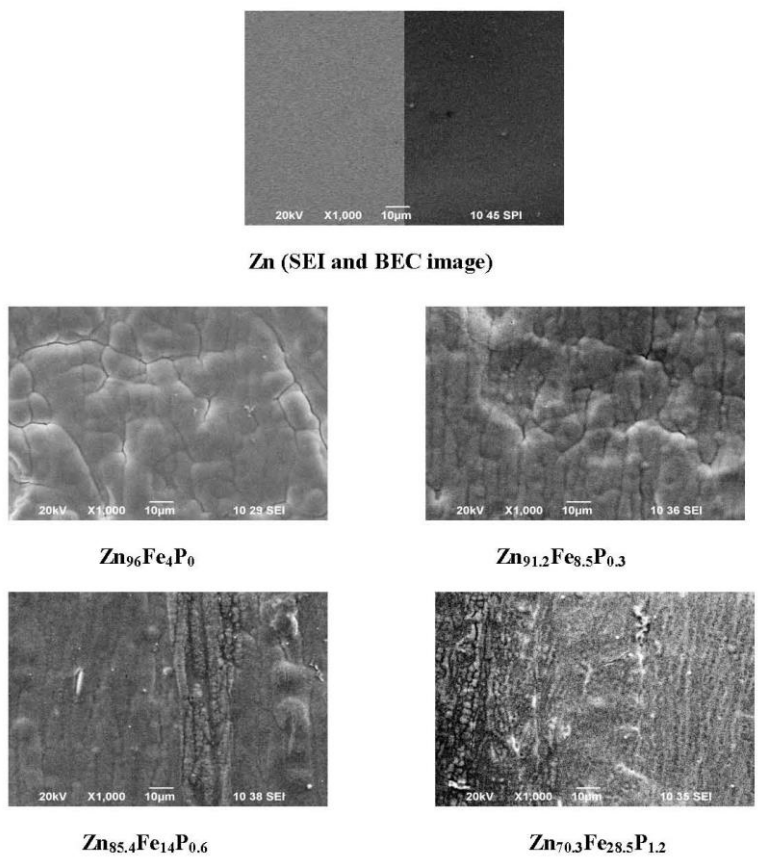


Figure 5. Surface morphology of Zn (SEI and BEC) and ternary Zn-Fe-P alloys (SEI) with passive films.

Contrary to this, the ternary alloys demonstrate practically uneven surface with some hackly areas as well as protruded and concaved zones depending on the electrodeposition conditions but mainly from the applied current density value.

The Zn and ternary alloys change their surface morphology after the chemical treatment in passivation solution – the surface looks more smooth and even which seems to be one of the reasons for their improved protective action compared to the samples without conversion passivation film (Figure 5).

4.CONCLUSIONS

The present work shows the possibility for obtaining of a solution for chemical passivating of Zn and ternary Zn-Fe-P alloys. This solution is based on Cr^{3+} - compounds and lead to appearance of additional protective layer on the coating surface aimed to improve the corrosion resistance.

The obtained passive films are investigated concerning their chemical composition and surface morphology as well as their corrosion behavior in model medium containing Cl^- ions as corrosion activators.

The PD curves demonstrate that the pure zinc has greater corrosion current density and dissolves with higher anodic current densities compared to the non-passivated Zn-Fe-P alloys. The treatment with the chemical conversion solution leads to delay of the anodic dissolution both for the Zn and for the ternary alloys.

The obtained results from the EIS measurements qualitatively confirm the improved protective characteristics of the passivated zinc and passivated ternary alloys compared to these without additional surface layer.

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ПОЛУЧАВАНЕ И ЗАЩИТНИ СВОЙСТВА НА ПАСИВНИ ФИЛМИ ВЪРХУ ЦИНК И ТРОЙНИ ЦИНКОВИ СПЛАВИ Zn-Fe-P

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(Резюме)

Представени и дискутирани са резултати, свързани с електрохимичното получаване на композитни електрохимично са получени защитни покрития от цинк и тройни сплави Zn-Fe-P с различен състав. Всички те допълнително са третирани в специално разработен състав за химично пасивиране на базата на тривалентни хромни съединения. С помощта на сканираща електронна микроскопия е изследвана повърхностната морфология на цинка и тройните сплави. С EDS анализ е определен елементния състав на сплавите с и без наличие на пасивен филм. Изследвани са корозионното поведение и защитната способност на системата покритие / пасивен (хромитен) филм в моделна среда, съдържаща хлорни йони като корозионни активатори, с помощта на потенциодинамични поляризационни криви и електро-химична импедансна спектроскопия. Анализирани и коментирани са получените от корозионните тестове резултати относно влиянието на пасивния филм върху защитните свойства на електроотложените покрития от цинк и сплавта Zn-Fe-P.