

Characterization of Zn–Mn Phosphate Coating Deposited by Cathodic Electrochemical Method

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Abstract Electrophosphating is a novel method that is used for accelerating the low-temperature phosphating bath. In this study, Zn–Mn phosphate coating was fabricated on mild steel substrate using the cathodic electrochemical method. Afterward, the effect of electrolyte pH and applied current density was investigated on coating properties. Microstructure, phase analysis and corrosion resistance of coating were evaluated using SEM, X-ray diffraction, potentiodynamic, immersion test and electrochemical impedance spectroscopy tests, respectively. Results indicated that the metallic and nonmetallic phases are present in the coating fabricated by the cathodic electrochemical method. The results of the corrosion evaluation tests indicated that the best coating resistance is obtained at pH = 2.5 and 20 mA/cm² applied current density, due to compact phosphate layer of the coating. By further increase in pH and applied current density, the coating with poor corrosion resistance is formed due to high porosity of coating obtained at these conditions.

Keywords Electrophosphating · Zn–Mn · SEM · Corrosion resistance

1 Introduction

Phosphating process is the most applicable metal pre-treatment route for surface engineering and finishing of industrials metals. The main goals of this process are enhancing corrosion protection ability, assisting the cold forming of the metals, improving abrasion resistance, as well as insulation and decoration applications [1–4]. Most of the phosphating baths which are provided in the literature require high treatment temperature ranging from 80 to 90 °C. The main drawback of these baths is the high energy consumption, which is a major crisis in the world. Furthermore, using and maintaining heating coils of high-temperature baths are hard because of the scale formation, which leads to undesirable heating of the baths, and consequently, frequent replacements are required. The other problem that occurs during high-temperature phosphating treatment is the overheating of the bath which leads to fast conversion of primary phosphate to tertiary phosphate before treating the metal. These reasons lead to increase in the free acidity of the bath and consequently limit the formation of the phosphate coating. One solution for overcoming these problems is the use of low-temperature phosphating bath. However, the low-temperature phosphating baths are very slow and must be accelerated by some treatments. Chemical, electrochemical and mechanical procedures have been used for accelerating the phosphating treatments. In the most cases, the chemical accelerator has been used in many industries, but most of the chemical accelerators are classified as toxic materials. Hence, using chemical accelerator can have a harmful influence on the environment [5–9]. Recently, usage of electrochemical accelerator for phosphating bath has been developed [10–12]. These treatments are carried out to achieve coatings with high thickness in low temperature

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and a short duration of time by using electrical current as an accelerator. Therefore, by applying current, the chemical accelerator can be removed from the bath.

The presence of some additives such as Ni^{2+} and Mn^{2+} ions in the bath leads to the enhancement of the corrosion behavior of the coating due to the decrease in the grain size of the coating. The effect of Mn^{2+} on phosphate coating properties was studied by other researchers [13–16]. Su and Lin [17] found that the presence of Mn^{2+} in the solution facilitated the nucleation by increasing the impingement of reacting species and reduces the porosity of the coating. There are many factors which affect the properties of phosphate coatings such as the pH of the bath, the additive concentration in the bath, the duration time and the temperature of the bath. The effects of coating parameters and conditions on chemical phosphate coating were investigated by many researchers [18–20]. Optimization of coating parameters and conditions can be useful to industrial and scientific points of view. Thus, in this study, the effect of pH of electrolyte and applied current density on microstructure and the corrosion behavior of Zn–Mn electrophosphate coating obtained by the cathodic electrochemical method have been investigated.

2 Experimental

Mild steel samples with a dimension of 50 mm × 20 mm × 1 mm were used as the substrate in this study. The specimens were degreased ultrasonically in acetone for 12 min; afterward, specimens were rinsed with deionized water. Pickling treatment was done in 4% H_2SO_4 for 20 s. Activation of samples was done by dipping them into titanium phosphate solution (1 g/L) for 1 min [21]. Finally, prepared specimens were immersed in the phosphating bath for coating treatment under different conditions. A galvanostat was used in order to deposit the coating by constant direct current. The chemical composition and different operating conditions of the coating treatment are shown in Table 1. Stainless steel anodes were used in this study. In order to remove the residual acids and salts after the coating process, the coated samples were rinsed with deionized water and then dried using an air stream. The corrosion resistance of coated substrates was evaluated using the immersion test, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) test. Electrochemical tests were carried out by potentiostat/galvanostat and, using 3.5% sodium chloride as working solution, maintained at 27 °C as the electrolyte medium. The area of the tested zone was 1 cm², and the remaining areas were sealed. The cell used to study the corrosion resistance consisted of three electrodes in which the coated mild steel served as working electrode; stainless steel plate

Table 1 Bath composition and operation conditions of electrophosphating treatment

	Amount
Bath composition	
ZnO (g/L)	2.04
H_3PO_4 (ml/L) (85%)	11
NaF (g/L)	0.3
$\text{Mn}(\text{NO}_3)_2$ (g/L)	1
Operating conditions	
pH	2.3–2.5–2.8
Temperature (°C)	40
Time (min)	20
Current density (mA/cm ²)	10–20–30

was the counter electrode and saturated calomel electrode (SCE) used as reference electrodes. The polarization potentiodynamic tests were carried out in the range of – 300 mV (relative to OCP potential) to +300 mV at the scan rate of 1 mV/sec. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were evaluated using linear polarization method. For each coating treatment, three parallel tests were carried out and average of them was reported. Surface morphology and composition of the coatings were studied using scanning electron microscopy (Vega, Tescan-XMU). In order to make the surface of the sample a conductor, the sample was subjected to coating with Au. The crystal structure and phase of the coating were identified using X-ray diffraction method with Cu α radiation. The coating weight due to the formation of phosphate crystals on the substrate was evaluated using the following equation:

$$m = (m_2 - m_1) / A \quad (1)$$

where m_2 is the weight of the samples after coating treatment, m_1 is the weight before the phosphating treatment and A is the surface area of samples.

3 Results and Discussions

3.1 Phase Analysis and Deposition Mechanism

The XRD pattern of Zn–Mn phosphate coating obtained by the cathodic electrochemical method is represented in Fig. 1. As can be seen, hopeite, $\text{Mn}(\text{PO}_3)_3$, and elemental Zn and Mn are the major phases which exist in phosphate coating.

The phosphate coating is fabricated by the cathodic electrochemical method in which the cathodic current is applied on the mild steel substrate. With the onset of

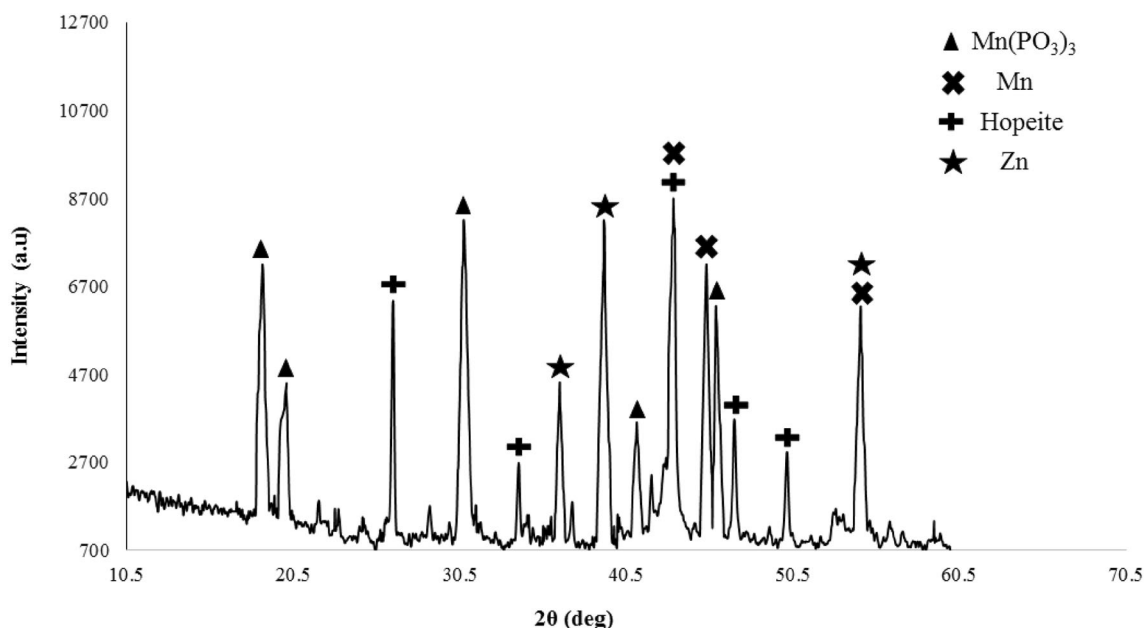


Fig. 1 XRD pattern of Zn–Mn phosphate coating obtained by cathodic electrochemical method deposited at pH = 2.5, time = 20 min and current density of 20 mA/cm²

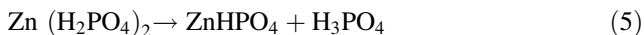
current, the hydrogen evolution reaction occurs on the substrate surface according to Eq. 2.



Also, due to the cathodic current, Mn^{2+} and Zn^{2+} ions which exist in the electrolyte will be deposited on the metal surface according to the following equations.



Further, Zn in the elemental form in the coating composition is reported by Jegannathan et al. [5], Narayanan et al. [8] and Oskuie et al. [22] in the Zn phosphating treatment using the cathodic electrochemical method. This is not observed in the chemical conventional phosphating treatments. Hydrogen evolution reaction at the substrate leads to an increase in interfacial pH that causes the conversion of soluble primary phosphate to insoluble tertiary phosphate based on the following equation [23].



where $\text{Zn}_3(\text{PO}_4)_2$ is known as ‘hopeite’ which is seen in the XRD pattern. In order to understand the deposition mechanism of Zn–Mn electrophosphate coating, the surface potential of substrate is monitored during phosphating treatment as a function of treatment time. The resulting curve is presented in Fig. 2. During the electrophosphate treatment, the variation of surface potential is indicative of

reactions which occur during coating treatment. As can be seen, based on potential-time curve, the electrophosphate treatment can be divided into three stages. In stage I, the surface potential moves toward anodic direction until reaching the maximum value. Afterward, in the second stage, the surface potential shifts toward cathodic direction from the maximum value until it reaches the constant value. Anodic shift in the initial stage is due to hydrogen evolution reaction and co-deposition of Mn^{2+} and Zn^{2+} ions on the metal surface [24]. Maximum value of potential suggests the start of conversion of primary phosphate to tertiary phosphate due to the increase in interfacial pH [5, 7]. Afterward, deposition of nonmetallic phosphate phases (hopeite and $\text{Mn}(\text{PO}_3)_3$) leads to cathodic shift in surface potential (stage II). At the constant potential value (stage III), co-deposition of nonmetallic phosphate phases and Zn and Mn occur. It should be mentioned that visual observation during electrophosphate treatment indicates that hydrogen evolution reaction occurs during all stages of the treatment. It is believed that deposition of Zn and Mn occurs in the form of a channel which is surrounded by nonmetallic phosphate phases [8]. Due to the existence of elemental Mn and Zn, along with nonmetallic phosphate crystals in the phosphate layer, the Zn–Mn phosphate coating, which is obtained using the cathodic electrochemical method can be categorized as Zn–Mn phosphate composite coating. Simultaneous presence of metallic and nonmetallic phases in the phosphate layer is a feature of Zn–Mn phosphate composite coatings obtained by cathodic electrochemical method.

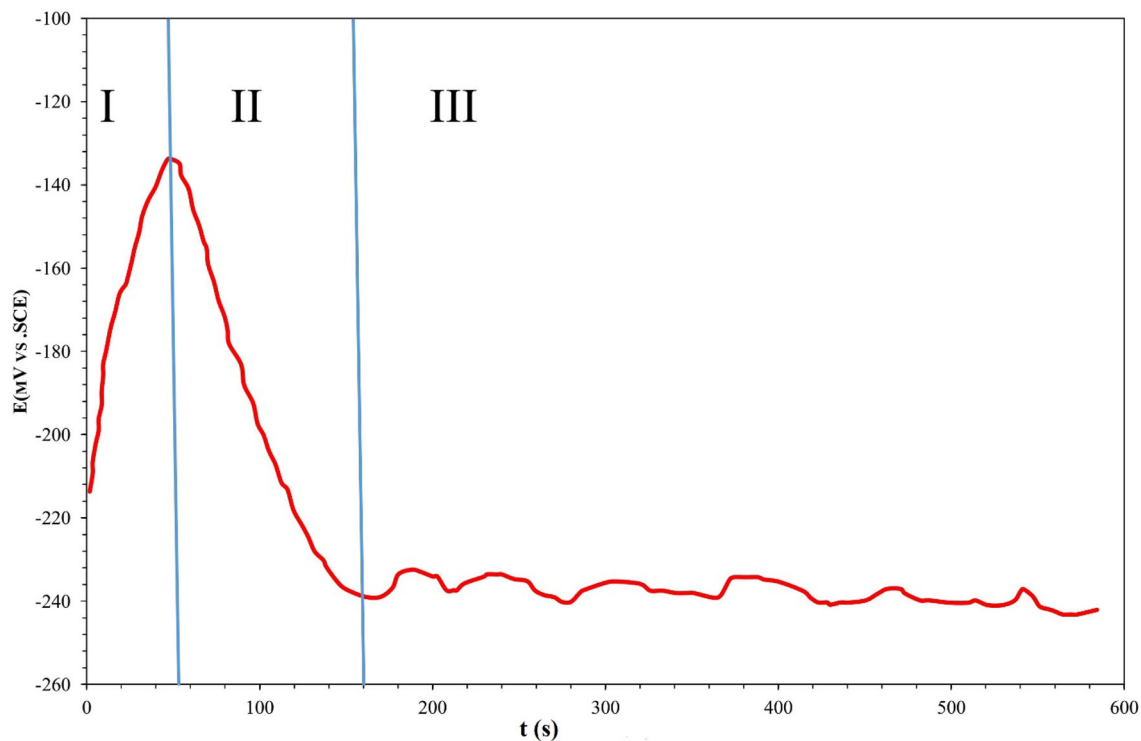


Fig. 2 Variation of OCP potential as a function of treatment time during electrophosphate treatment

3.2 Microstructure of Coating

3.2.1 Effect of pH on Microstructure of Coating

The SEM images of the coating which is fabricated at different pH values are presented in Fig. 3. As it is observed, the morphological characteristic of Zn–Mn phosphate coating that is formed by cathodic electrochemical method is comprised of platelike and needlelike crystals. As can be seen, the morphology of the coatings is highly dependent on pH. In Fig. 3a, when the coating is formed at pH = 2.2, appreciable phosphate crystals cannot be formed on the surface and the substrate cannot be fully covered by phosphate crystals. This is because at this pH value, the acidity of the metal electrolyte is very high which leads to delay in the formation of phosphate crystals. When the pH of electrolyte increases to 2.5, compact phosphate crystals is formed that covers the entire metal surface. This is attributed to the pH of metal electrolyte which increases well into the basic range in which good precipitation of phosphate crystals occur. In Fig. 3c, when phosphating treatment is done at pH = 2.8, the rapid conversion of soluble primary phosphate to insoluble tertiary phosphate leads to very high crystal growth and formation of coarse phosphate crystals. Li et al. [25] reported that the pH range in which the best microstructure can be obtained is between 2.15 and 2.5. Also, Abdalla et al. [26] reported that the coating with the best properties can be obtained in

a narrow range between 2.25 and 2.75. It can be concluded that the formation of phosphate coating depends on the pH and the best coating is formed in a narrow pH range.

3.2.2 Effect of Applied Current Density on Microstructure of Coating

The SEM images of the Zn–Mn phosphate coating deposited in three different current densities are shown in Fig. 4. SEM images reveal that similar to phosphate crystals deposited with indifferent pH values, the morphological feature of the phosphate crystals deposited at different current densities are also comprised of platelike and needlelike crystals. As it is seen, the applied current density affects the phosphate crystals formations. In Fig. 4a, when the phosphate coating formation is done in low applied current density, the platelike crystals are formed which do not cover the entire surface. Generally, the formation of phosphate crystals can be divided into nucleation and growth stages. In 10 mA/cm² applied current density, the phosphate crystals are nucleated, but due to low driving force (attributed to low applied current density) the growth stage is not completed, and consequently, the phosphate crystals cannot cover the entire surface. By increasing the applied current density to 20 mA/cm², compact phosphate crystals are formed which cover the entire surface of substrate, due to sufficient driving force for nucleation and growth. When the phosphating treatment is carried out at

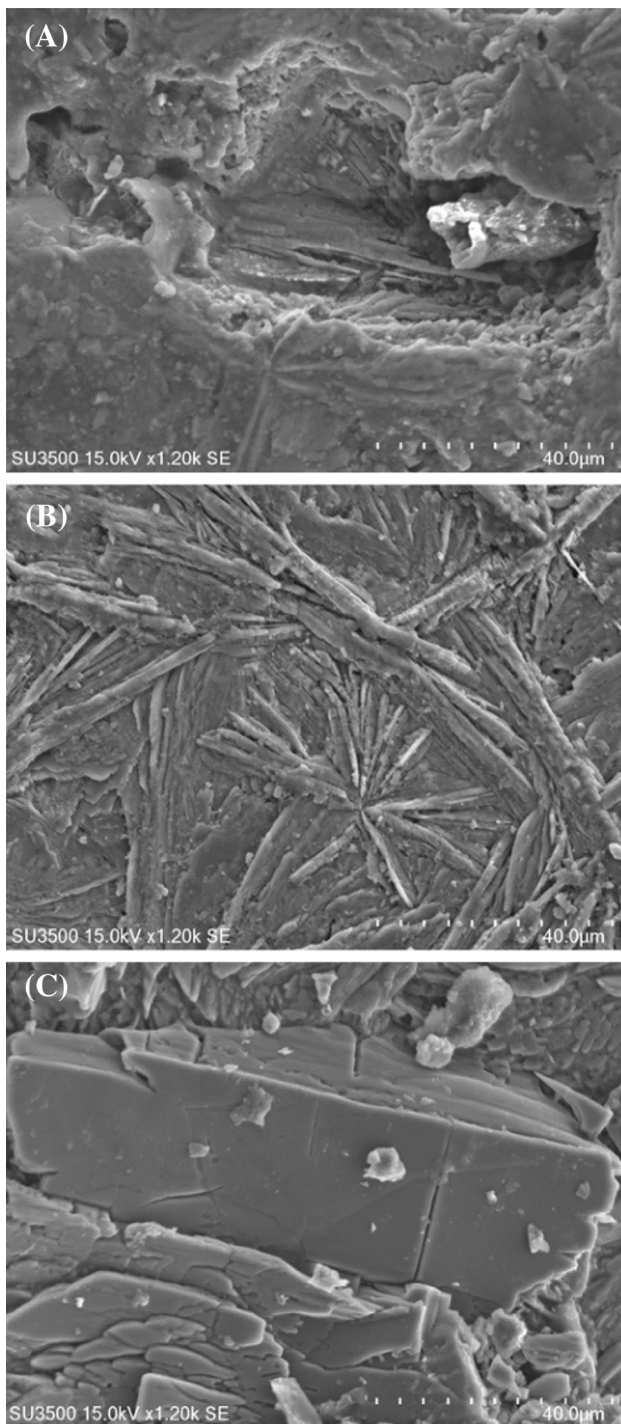


Fig. 3 SEM images of the coating that is fabricated at different pH values **a** 2.3, **b** 2.5, **c** 2.8

30 mA/cm^2 , a very high driving force leads to a high growth rate of phosphate crystals. In this situation, the porosity between crystals also grows and coating with high porosity is obtained (Fig. 4c). This porosity can affect the corrosion resistance of coating, which will be discussed in the following sections.

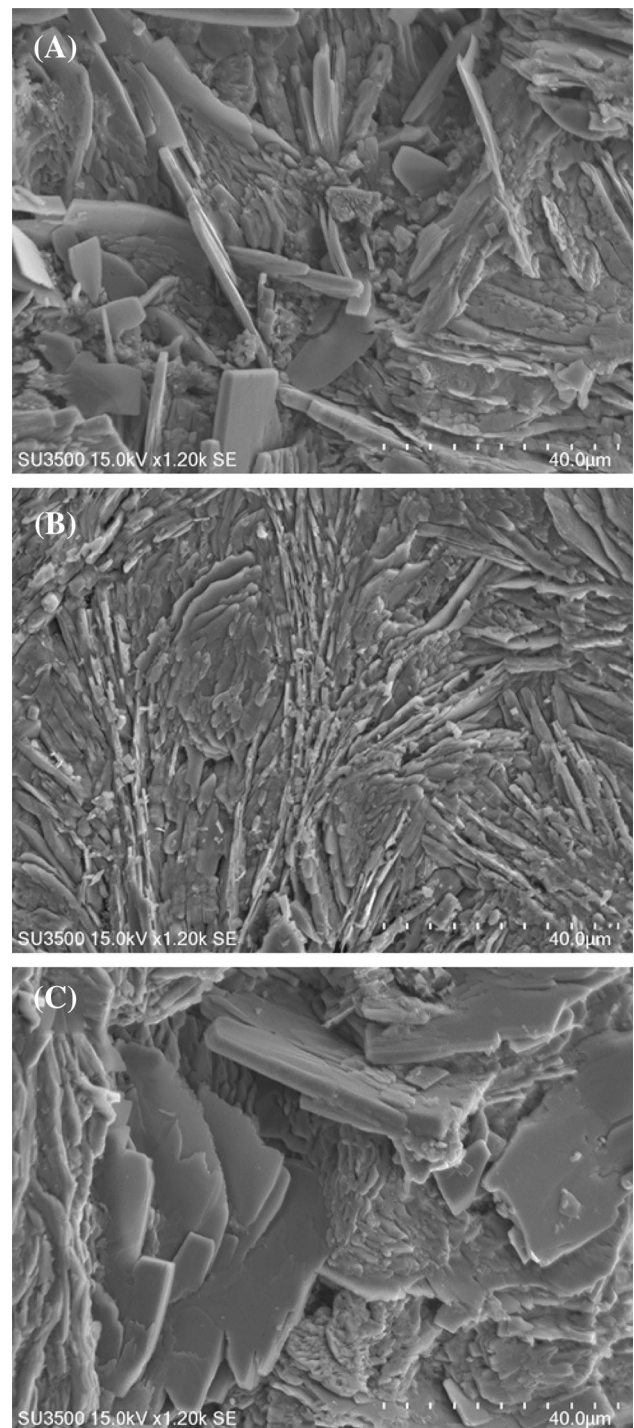


Fig. 4 SEM images of the coating that is fabricated at different applied current densities **a** 10, **b** 20, **c** 30 mA/cm^2

3.2.3 Coating Weight

The coating weight is the main factor which is used to evaluate the coating quality, and it is recommended by many standards. The variations of coating weights as a function of time in different pH values of electrolyte and

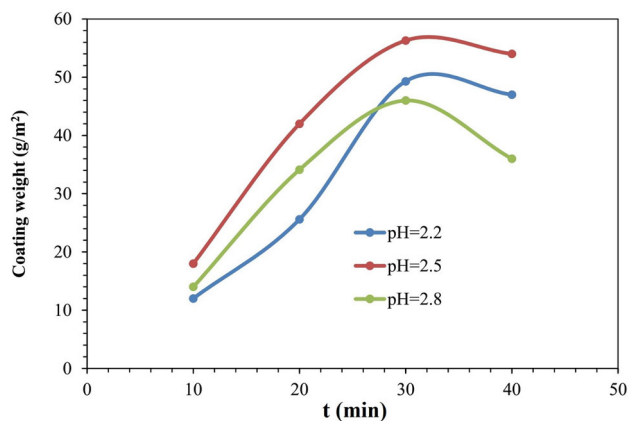


Fig. 5 Variation of coating weight as a function of phosphating time at different pHs

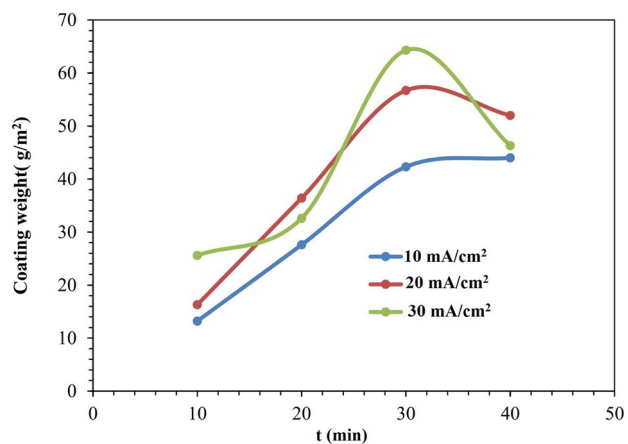


Fig. 6 Variation of coating weight as a function of phosphating time at different applied current densities

applied current densities are presented in Figs. 5 and 6, respectively. As shown in Fig. 5, at the pH = 2.2, by increasing the treatment time, coating weight is increased linearly until 30 min, at the rate of 1.864 g/m² min. After that, the coating weight reaches the constant value. By increasing the pH to 2.5, the coating weight increases in comparison with pH = 2.2, due to more conversion of primary phosphate to tertiary phosphate at pH = 2.5. At pH = 2.8, the coating weight is decreased due to the rapid conversion of primary phosphate to tertiary phosphate crystals. The decrease in coating weight is observed at pH = 2.8 and higher treatment times due to the spallation of coating in these situations. It is clear in Fig. 6 that the kinetic of coating growth in different applied current densities is also linear for 30 min, and after that, the coating weight approximately reaches the constant value. At 30 mA/cm², the spallation of coating occurs due to high input energy.

3.3 Porosity and Uniformity of the Coating

The fabricated coating on mild steel substrate using the cathodic electrochemical method is very uniform. In this study, the chemical method is used. The coated samples are dipped into the solution containing ferricyanide. As a result of the interaction between ferrous ions in the bare areas and ferricyanide in the working solution, Prussian blue color is formed. Dipping of samples into the solution do not cause any blue spots to appear on the whole area of the coated substrate. As stated earlier, in the first stage of coating formation, thin layers of Mn and Zn are formed on the substrate. It can be said that this thin layer inhibits the interaction of ferrous ions and ferricyanide and therefore prevents the formation of blue spots on the surface. Jegannathan et al. [7] also reported that no blue spots are formed, due to the dipping of Zn electrophosphated samples into solutions containing ferricyanide.

3.4 Corrosion Behavior of Coating

Corrosion behavior of Zn–Mn phosphate coating fabricated by cathodic electrochemical method was evaluated by the immersion test in 3.5% NaCl, the potentiodynamic polarization test and the electrochemical impedance spectroscopy tests.

3.4.1 Immersion in 3.5% NaCl

Immersion in 3.5% NaCl solution is simple test which provides an insight into the corrosion behavior of the coating. In this test, the amount of corrosion is assessed by visual observation after 12 h of immersion, and by measuring the loss in mass due to corrosion after 24 h of immersion. Observation after 12 h indicates that the cathodically formed phosphate coating remains in good condition. One of the observations after immersion test is the formation of white rust on the surface of coating, because of the existence of elemental zinc in the coating, which reacts with the electrolyte that diffuses in the pores of coating, and as a result, corrosion products are formed. Jegannathan et al. [5] also detected the formation of white rust corrosion products in the zinc phosphate coating obtained by cathodic electrochemical method. Deposition of zinc oxide and hydroxide in the cathodically formed phosphate coating improves the protective ability of the fabricated coating due to filling the porosity of coating, and consequently inhibiting the penetration of aggressive ions to the substrate [5]. It is reported that the zinc hydroxychloride is the main corrosion product which is formed in the chloride environment. Kavitha et al. [9] reported the possibility of formation of ZnCO₃, Zn(OH)₂ in the NaCl environment, due to the absorption of CO₂ from the

Table 2 Results of immersion and polarization test of samples formed under different conditions

Type of studied system	Loss in weight (g/m ²)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	E_{corr} (mV vs. SCE)	β_a (mV/decade)	β_c (mV/decade)	R_p ($\Omega \text{ cm}^2$)
Cathodically phosphated mild steel at pH = 2.2	8.12	13.8	− 361	36	33	921
Cathodically phosphated mild steel at pH = 2.5	2.2	1.2	− 276	32	57	7425
Cathodically phosphated mild steel at pH = 2.8	6.14	11.4	− 450	46	33	1331
Cathodically phosphated mild steel at 10 mA/cm ²	9.13	17.4	− 367	23	39	361
Cathodically phosphated mild steel at 20 mA/cm ²	1.8	1.3	− 452	18	32	4698
Cathodically phosphated mild steel at 30 mA/cm ²	8.14	14.6	− 447	25	56	923

atmosphere. The loss in weight of the coating due to corrosion is measured after 24-h immersion in 3.5% NaCl solution, and the results are demonstrated in Table 2. As it is seen, the lowest loss in weight which corresponds to best corrosion resistance is obtained in pH = 2.5 and 20 mA/cm² applied current density.

3.4.2 Potentiodynamic Polarization Studies

The corrosion behavior of Zn–Mn phosphate coating obtained by cathodic electrochemical method at different pHs and in applied current densities has been characterized using potentiodynamic polarization test. The potentiodynamic polarization curves of coating obtained at different pHs and in applied current densities are represented in Figs. 7 and 8, respectively. Corrosion potentials (E_{corr}), corrosion current densities (i_{corr}) and anodic/cathodic Tafel constant (β_a and β_c) have been calculated from the potentiodynamic curves. The polarization resistance (R_p) can be determined from Stern–Geary equation, according to the following equation [27]:

$$R_p = \frac{\beta_a \times \beta_c}{2.033(\beta_a + \beta_c)i_{\text{corr}}} \quad (7)$$

The electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), and cathodic and anodic slopes which have been estimated using the linear polarization method for coatings obtained under different conditions are reported in Table 2. As it is seen, by increasing the pH of electrolyte from 2.2 to 2.5, the corrosion current density is decreased from 13.8 to 1.2 $\mu\text{A}/\text{cm}^2$, and then by increasing the pH of electrolyte to 2.8, an increase to 11.4 $\mu\text{A}/\text{cm}^2$ is observed. It is indicated that the coating with best corrosion resistance can be obtained at pH = 2.5, and it can be understood that the

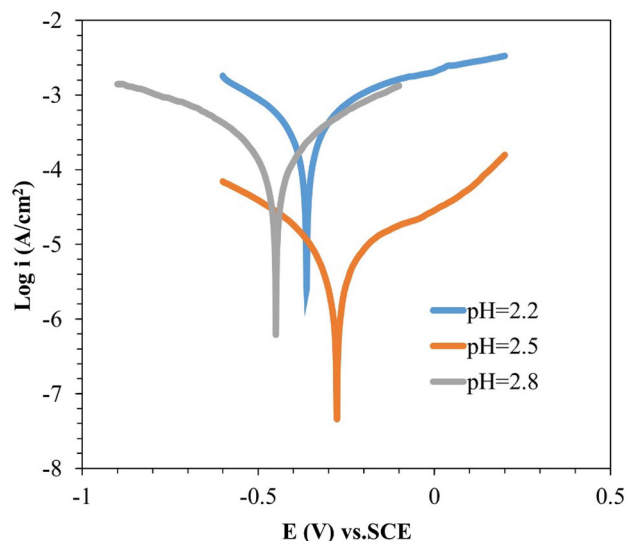


Fig. 7 Polarization curves of the samples that were fabricated at different pH values and time = 20 min and applied current density = 20 mA/cm²

electrophosphate coating depends on the pH of electrolyte, and the best properties of coating can be achieved within a very narrow pH range. One of the main factors which affect the corrosion resistance of coating is the microstructure and morphology of coating. If the coating has compact phosphate crystals, then aggressive ions cannot penetrate into substrate, and consequently, the corrosion increases in this situation. As it is observed in Fig. 3a, in the coating which is fabricated at pH = 2.2, significant phosphate crystals are not formed at the substrate; therefore, aggressive ions can simply penetrate the substrate surface, leading to poor corrosion resistance. Very compact and uniform coating which is formed at pH = 2.5 results in good corrosion resistance. Finally,

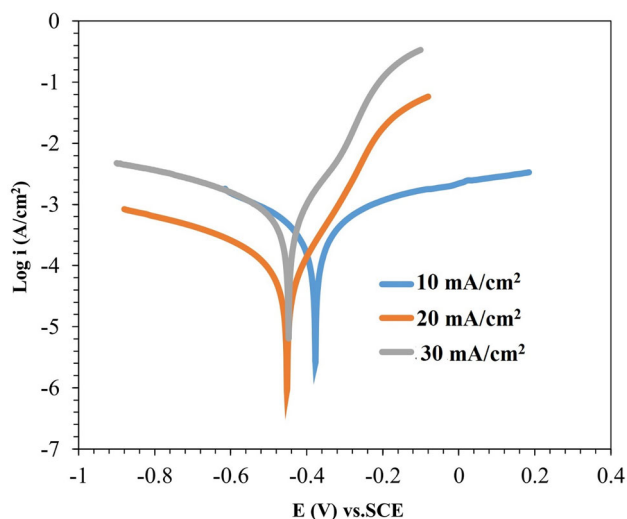
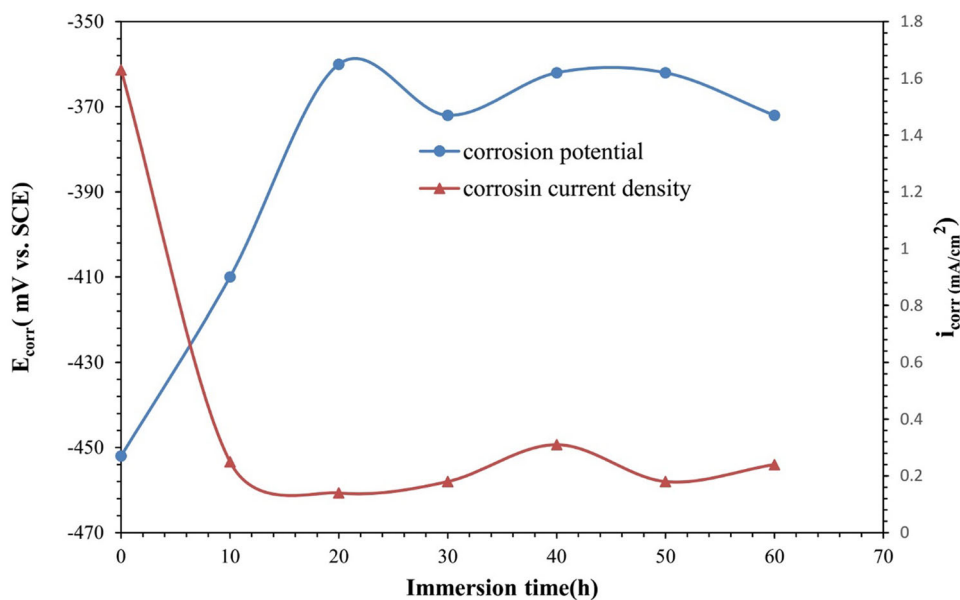


Fig. 8 Polarization curves of the samples that were fabricated at different applied current densities and time = 20 min and pH = 2.5

again the porous coating that is formed at pH = 2.8 allows the penetration of aggressive ions, and therefore to poor corrosion resistance.

As can be seen in Table 2, by increasing the applied current density from 10 to 20 mA/cm², the corrosion current density decreases from 17.4 to 1.3 μA/cm² and then increases to 14.6 μA/cm² by further increase in applied current density to 30 mA/cm². The corrosion behavior of these coatings can also be attributed to the microstructure of coatings. Compact and uniform coating at 20 mA/cm² applied current density leads to good corrosion resistance. High input energy corresponding to high applied current density of 30 mA/cm², leads to the formation of porous coating and therefore low corrosion resistance at the

Fig. 9 Variation of corrosion current density and corrosion potential of coating as a function of immersion time in 3.5% NaCl solution



coating. In order to investigate the effect of immersion time in 3.5% NaCl on corrosion behavior, the potentiodynamic test for the sample formed at 20 mA/cm² and pH = 2.5 is performed as a function of immersion time, and the results of variation of corrosion current density and corrosion potential as a function of immersion time are represented in Fig. 9. As it is seen in the initial stage of immersion time, the corrosion potential shifts towards anodic direction, and the corrosion current density also decreases in the initial stage. Anodic shift of corrosion potential means that in the initial stage, the tendency of the coating to corrode decreases. The formation of Zn corrosion products as a result of immersion in NaCl fills the porosity of phosphate layer, prevents the penetration of aggressive ions and, consequently, leads to higher corrosion resistance. The small variation of corrosion potential and corrosion current density after 20 h of immersion time is due to repetitive formation and spallation of the corrosion product.

3.4.3 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy method has also been used to obtain more information about corrosion resistance, and corrosion mechanism of the Zn–Mn electrophosphate coating obtained by the cathodic electrochemical method. Nyquist plots of the coatings which are fabricated at different pHs and in different applied current densities are represented in Figs. 10 and 11, respectively. The equivalent circuit depicted in Fig. 12 has been used to analyze the impedance plots. In Fig. 12, R_s is solution resistance, R_{ct} refers the charge transfer resistance, R_{coat} is the coating resistance, CPE_c is the coating constant phase element and CPE_{dl} is the charge transfer constant phase

Fig. 10 Nyquist plots for the coating which were fabricated in the electrolytes with different pH values, time = 20 min and applied current density = 20 mA/cm²

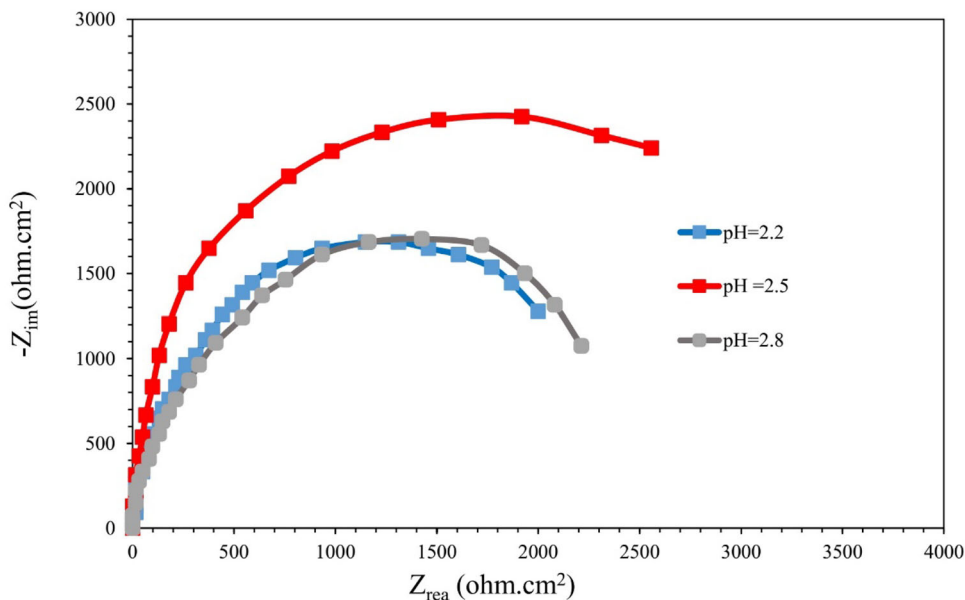
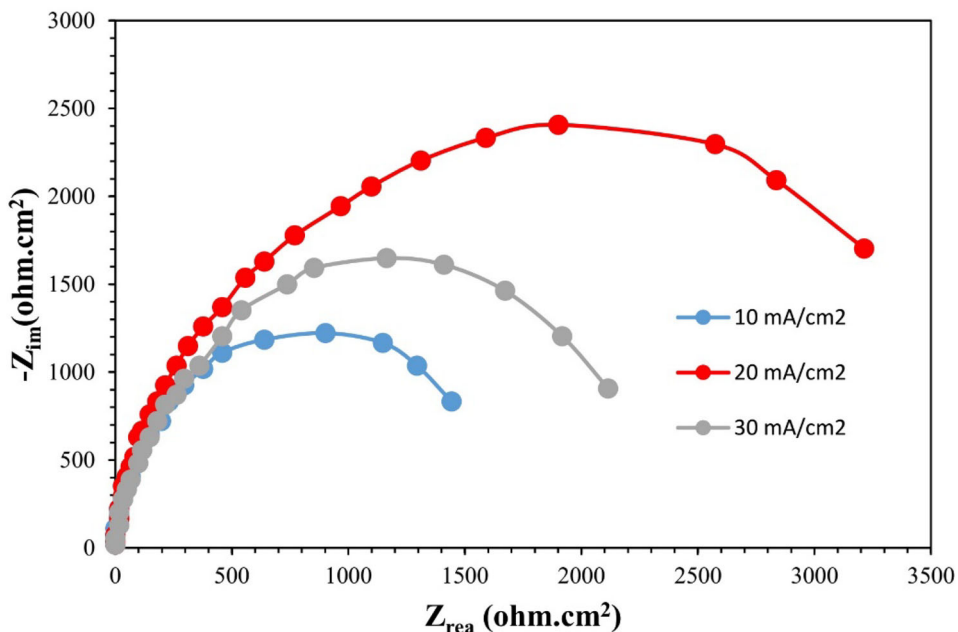


Fig. 11 Nyquist plots for the coating which were fabricated in different applied current density values, time = 20 min and pH = 2.5

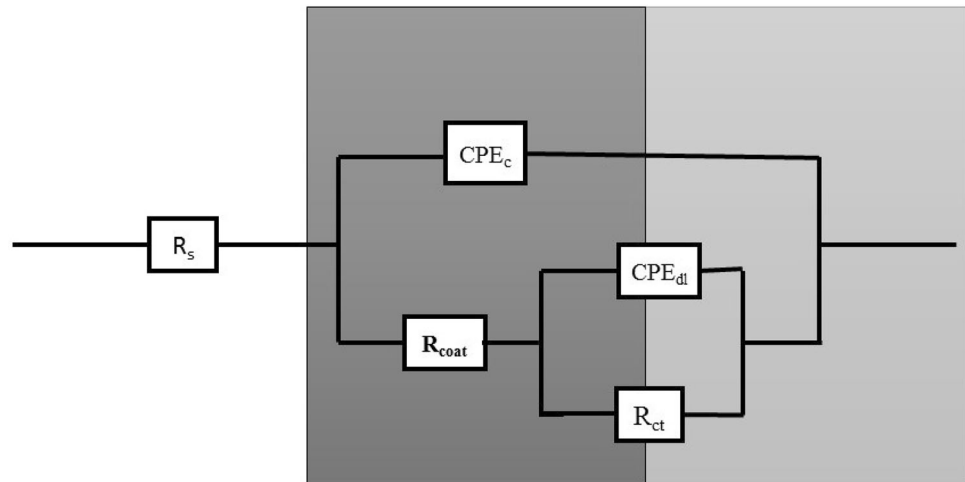


element. Here, a more general term of constant phase element is used instead of the capacitor. The use of constant phase element (CPE) in the equivalent circuit of the impedance minimizes the systematical error and also provides more detailed information about the interface of coating and solution. The impedance function of CPE element is defined according to the following equation:

$$Z = \frac{(j\omega)^{-n}}{Y_0} \tag{8}$$

where Y_0 and n are the admittance and empirical exponent of the CPE, respectively, j is an imaginary number and ω is the angle frequency. For $n = 1$, an ideal capacitor is defined. For $n = 0$, the CPE represents an ideal resistor. For $n = -1$, the CPE is equivalent with an inductance [28]. As it is seen in Fig. 10, the highest impedance is observed in

Fig. 12 Equivalent electronic circuit of the coating



the coating which is fabricated at $\text{pH} = 2.5$, which relates to higher compactness and lower porosity of obtained coating at this pH . As it is observed in Fig. 11, the highest impedance is observed in the coating when it is fabricated in 20 mA/cm^2 applied current density. Higher impedance indicates higher corrosion resistance of coating. By comparison between the results of the Nyquist plots and those of the polarization curves, it can be found that both the methods have detected a similar corrosion behavior.

4 Conclusion

Zn–Mn phosphate composite coatings were successfully deposited on mild steel, using the cathodic electrochemical method. The main conclusions of this study can be summarized as follows:

1. Due to the presence of metallic and nonmetallic phases in the phosphate coating layer, the Zn–Mn phosphate coating obtained by cathodic electrochemical method can be categorized as Zn–Mn phosphate composite coating.
2. The best corrosion resistance can be obtained at $\text{pH} = 2.5$, due to the compact phosphate layer and inhibition of aggressive ions penetration.
3. The best applied current density to achieve the optimum coating properties is 20 mA/cm^2 ; also, the high energy input in higher current density results in porous coating and therefore poor corrosion resistance.
4. The kinetic of coating growth is linear for 30 min, and after that, the coating weight reaches a constant value.

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