



Zn–Ni Electrophosphating on galvanized steel using cathodic and anodic electrochemical methods



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ABSTRACT

Electrophosphating is the novel method for accelerating the low temperature phosphating bath. This method can be performed as cathodic and anodic treatments. Both of them influence the coating deposition mechanism and therefore coating properties. In this study Zn–Ni electrophosphate coating was applied on galvanized steel using cathodic and anodic electrochemical methods. Microstructure, composition and corrosion resistance of coating were characterized by using a scanning electron microscopy, X-ray diffraction method and potentiodynamic polarization test respectively. The results of this study indicated that, by using cathodic method, compact phosphate coating with high corrosion resistance can be obtained. The result of X-ray diffraction pattern indicated the presence of Zn and Ni along with zinc and nickel phosphate in the phosphate layer. It is indicated that the phosphate crystal shape of cathodically coating was flower and plate like and only flower like crystals are formed in anodically coating. Also results indicated that, the phosphate coating obtained by anodic electrochemical method has high porosity and consequently poor corrosion resistance. Also, based on the study results, applications proposed for coatings that obtained by cathodic and anodic electrochemical methods.

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1. Introduction

Hot-dip galvanizing is an effective protection measure for steel against atmospheric corrosion, however, the corrosion product of zinc coating formed in the atmosphere cannot provide sufficient protection for steel substrates [1–3]. For better protection of zinc-coated steel against corrosion, surface modification treatment is generally applied to galvanized steel. Phosphating is one of the most important chemical conversion processes for the purposes of corrosion protection, primer for painting, wear reduction, metal-forming lubricants, electrical insulation and even decoration, and has been widely applied in many industries [4–7]. Most conventional phosphating baths reported in the literature require very high operating temperatures ranging from 90 to 98 °C. The main concern with the use of high temperature operation bath is a high amount of energy consumption, which is a major crisis in present days. Moreover, application and maintenance of heating coils are difficult because of scale formation which leads to improper heating of the bath solution and consequently frequent replacement is required. Another problem that occurs in this condition is, overheating of bath solution, which causes an early conversion of the primary phosphate to tertiary phosphate before the metal is treated. These reasons lead to the increase in free acidity of the bath and consequently delay the

precipitation of the phosphate coating. Due to the high energy costs that used in the high temperature bath, the low-temperature phosphating processes have become more promising and popular. However, the low temperature phosphating baths are slow and need to be accelerated by some methods. Chemical, electrochemical and mechanical methods are used in order to accelerate the phosphating process. The chemical methods are most widely used in many industries. However the chemical accelerators such as nitrite are poisonous and have a detrimental effect on the environment and human health and it is desirable to be eliminated from the bath composition and replaced with some replacements such as electrochemical accelerator [8–12]. The electrochemical methods for accelerating phosphating process become recently popular for their low operating temperature, high coating speed and better properties formed coating. Electrochemical methods can be carried out using cathodic and anodic methods, both cathodic and anodic treatments can affect the deposition mechanism, corrosion resistance, porosity and other properties of the formed coating.

The presence of an additive such as Ni²⁺ ions apparently affects the properties of coating, for the phosphating of Zn-coated steel, the reduction of Ni²⁺ on the pores of the coating results in the formation of Zn–Ni alloy in the phosphate coating. The presence of cathodic sites associated with Ni deposition promotes both the etching of the substrate and the cathodic activity of the phosphating process [12–14]. Few studies have been carried out on the comparison between the cathodic and anodic electrochemical methods. Preference between cathodic and anodic electrochemical methods to phosphating of metals is ambiguous. Comparison between zinc phosphate coating formed by cathodic and anodic

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electrochemical method has been done by Jegannathan et al. [7]. But research on the comparison between the two cationic phosphate coating obtained by cathodic and anodic electrochemical method has not been done. The comparison between the two methods can be useful for industrial and scientific points of view. So the aim of this study is to compare between Zn–Ni electrophosphate coating properties obtained using cathodic and anodic treatments, also the limitation and advantage of each treatment will be discussed, and applications will be provided for each method.

2. Experimental

Hot-dip galvanized steel samples with dimension of 50 mm × 20 mm × 2 mm were used as substrate in this work, and the thickness of Zn coating was about 10 μm. The substrate was ultrasonically degreased in acetone for 12 min, then rinsed with de-ionized water and pickled in 4% H₂SO₄ for 20 s. The specimens then activated by dipping them into titanium phosphate solution (1 g/L) for 1 min [15]. Prepared specimens finally immersed into a phosphating solution contained in the cell. A galvanostat was used to apply constant direct current to electrophosphating cell. The deposition treatment was carried out at 5, 15, 25 and 35 mA/cm². The chemical composition and operating conditions of the bath used for cathodic and anodic processes are shown in the Table 1. Stainless steel plate was used as the anode and cathode in cathodic and anodic treatments respectively. Two sets of stainless steel were placed on both sides of the hot-dip galvanized steel substrate. Schematic of setup used for electrophosphating treatment is represented in Fig. 1. After the coating process, the coated samples were removed from the bath and then rinsed in de-ionized water to remove the acids and salt residues on the surface of coated substrate and then dried using an air stream. The corrosion resistance of phosphated coating obtained by cathodic and anodic treatments was evaluated using potentiodynamic polarization test. Electrochemical measurements were performed by a model 273 A potentiostat/galvanostat and, using a 3.5% sodium chloride solution, maintained at 27 °C as the electrolyte medium. The tested zone area was 1 cm² and the remaining areas were sealed. The corrosion evaluation cell consisted of three electrodes: the coated hot-dip galvanized steel as the working electrode; and a stainless steel plate and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. 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. The surface morphology and composition of the coating were characterized via scanning electron microscopy (Vega, Tescan) under back scattered electron scanning mode (BSE). In order for the surface of the samples to be a conductor, before characterization by SEM, the sample was subjected to coating with Au. The crystallinity and the phase of the coating were identified using X-ray diffractometer with Cu K α radiation and finally porosity of the coating was calculated by means of electrochemical method.

Table 1
Chemical composition and operating conditions of the bath used for cathodic and anodic processes.

Bath composition	Cathodic treatment	Anodic treatment
ZnO(g/L)	2.04	2.04
H ₃ PO ₄ (ml/L)	11	11
NaF(g/L)	0.3	0.3
Ni(NO ₃) ₂ (g/L)	1	1
NaNO ₂ (g/L)	0	0.5
Operating conditions		
pH	1.8	1.8
Temperature(C°)	45	45
Time(min)	20	20
Current density(mA/cm ²)	5, 15, 25, 35	5, 15, 25, 35

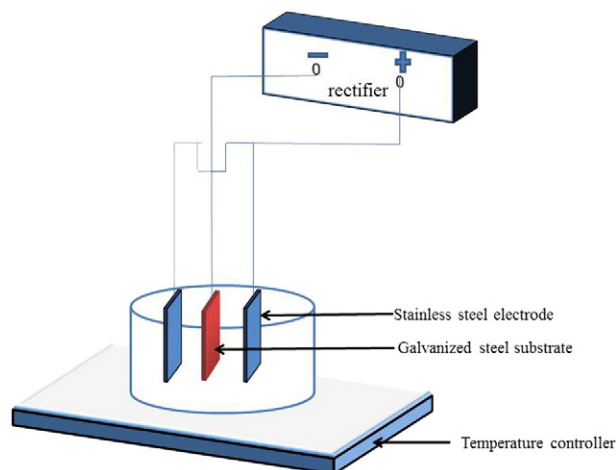


Fig. 1. Schematic of the setup used for electrophosphating treatment.

3. Result and discussion

3.1. Microstructure and composition of coating

3.1.1. Microstructure of coating obtained by cathodic electrochemical treatment

Fig. 2 shows the SEM micrograph of Zn–Ni electrophosphate coating obtained by the cathodic electrochemical method at different current densities. As can be seen the morphological features of phosphate crystals depend on the applied current density. In the coating obtained at 5 mA/cm², small needle like crystals are formed. These needle like crystals collide with each other and formed porosities, these porosity indicated by ellipses in Fig. 2(A). Flis et al. [16] have identified the formation of needle-like crystals on Zn and Zn–Ni coated steel immersed in dilute sodium phosphate solution and confirmed that they are indeed zinc containing phosphates. And also Kavitha et al. [17] have identified the formation of needle like crystals in Zn–Zn phosphate composite coating on aluminum. When the applied current density rises to 15 mA/cm² flower and plate like crystals are formed and a dense and uniform coating is formed on the surface. As can be seen, increasing applied current density to 25 mA/cm² does not change the morphology of the coating, but causes the growth of phosphate crystals. Formation of flower like crystals is a characteristic of the hopeite phase [17]. The EDAX spectrum and the corresponding chemical composition of the phosphate crystal in flower like and plate like areas are shown in Fig. 3. The presence of Zn, O and P in flower like region could be accounted for the formation of the zinc and zinc phosphate in the coating, also because the cathodic method was used for electrophosphating treatment, the presence of metallic zinc is possible. Oskuie et al. [18], Sankara Narayanan et al. [8–10] also have indicated the presence of zinc along with zinc phosphate during cathodic electrochemical treatment using zinc phosphating bath. Since the concentration of nickel in flower like crystals is lower than the plate like crystals, the flower like phosphate crystals can be zinc phosphate crystals. The presence of O, P, Zn and Ni in the plate like area in Fig. 3 could be accounted for the formation of Zn, Ni, zinc phosphate and nickel phosphate crystals in the coating, because in the electrophosphating treatment, the surface potential of the sample be polarized in cathodic direction, reduction of Zn²⁺ and Ni²⁺ can occur. Consequently the presence of elemental Zn and Ni will be possible in the coating. As can be seen in Fig. 2(D), when the applied current density raises to 35 mA/cm² the crystal size of the coating increases, and the porosity of the coating also will be increased. The formed porosity at higher applied current density is shown by rectangles in Fig. 2(D). The reason of crystal growth and, therefore, high porosity at high current density, is the high driving force for crystal growth at high applied current density. At high applied

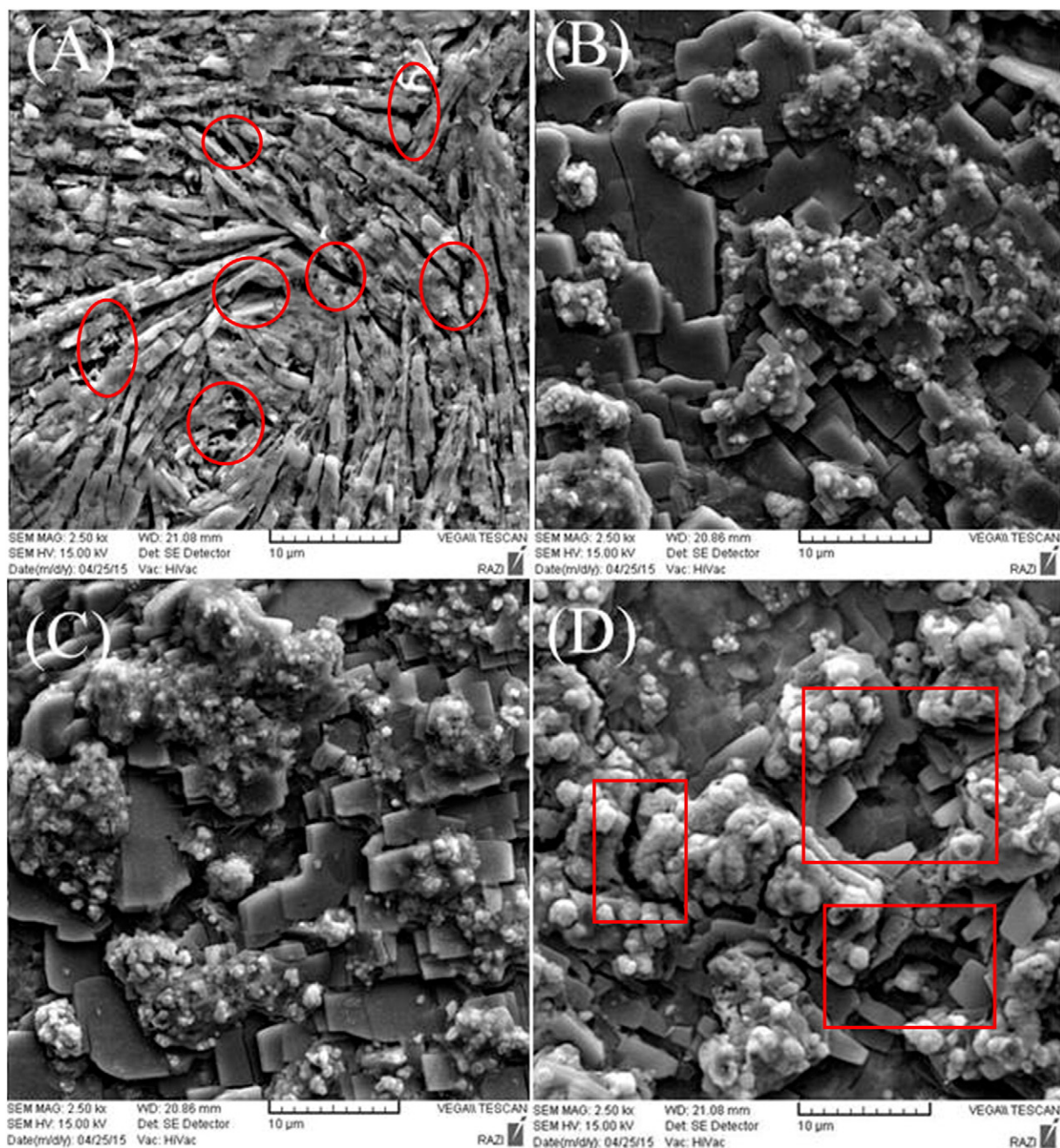


Fig. 2. SEM micrograph of Zn-Ni electrophosphate coating obtained by the cathodic electrochemical method at different current densities A) 5, B) 15, C) 25, D) 35 mA/cm².

current density, where the zinc content of the coating is high, the morphology of the coating resembles that of electrodeposited zinc [7]. So generally, the morphological features of the Zn-Ni phosphate crystals obtained by the cathodic electrochemical method are flower, plate and needle like crystals. Also the presence of elemental zinc and nickel is possible in the coating. The elemental mapping of zinc and nickel in the coating shown in Fig. 4 reveals that the distribution of these elements is uniform throughout the coating.

3.1.2. Characterization of phases in the phosphate layer obtained by cathodic electrochemical treatment

The phases in the phosphate layer obtained by the cathodic electrochemical method were analyzed by X-ray diffraction analysis and the result is shown in Fig. 5. As it is seen, the XRD pattern shows the presence of hopeite ($Zn_3(PO_4)_2 \cdot 4H_2O$), nickel phosphate ($Ni_2P_2O_7$), nickel

and zinc and $NiZn_3$ phases. Since the polarization in cathodic direction is the driving force for the reduction of ions in the bath and because during cathodic electrochemical operation, the surface potential of substrate polarized in cathodic direction, therefore, the presence of zinc and nickel in the XRD pattern is due to the reduction of Zn^{2+} and Ni^{2+} ions on the substrate. In the cathodic electrochemical method, hydrogen evolution leads to the increase in interfacial pH between electrode and electrolyte. Increase in interfacial pH results in conversion of soluble primary phosphate to insoluble tertiary phosphate [9,10]. So the formation of hopeite and nickel phosphate phases are due to the conversion of soluble primary phosphate to insoluble tertiary phosphate. The presence of $NiZn_3$ phase in the phosphate layer can be performed according to the following reaction. 1 [12].



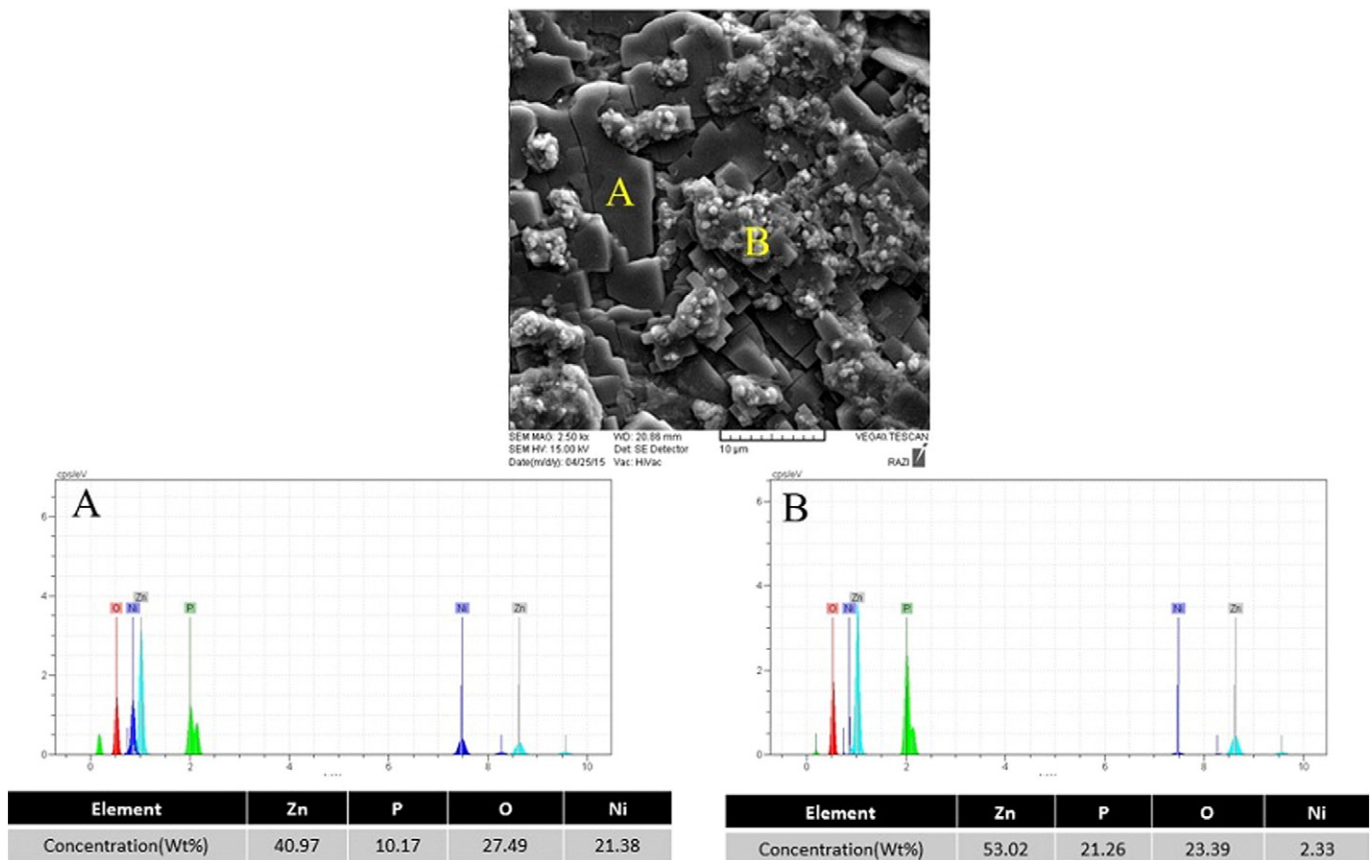


Fig. 3. EDAX spectrum and the corresponding chemical composition of the phosphate crystal in flower and plate like region.

Based on the phase constituents, the Zn–Ni phosphate coating obtained by the cathodic electrochemical method can be classified as Zn–Ni phosphate composite coating. Jegannathan et al. [9] created a zinc phosphate coating on steel surface using cathodic electrochemical method and they classified their coating as Zn–Zn phosphate composite coating. It is suggested that, to use several anodes or several species in the bath to obtain several phosphate composite coating.

3.1.3. Microstructure of coating obtained by anodic electrochemical treatment

Fig. 6 shows the SEM micrograph of Zn–Ni electrophosphate coating obtained by anodic electrochemical method at different current densities. As can be seen at 5 mA/cm² no noticeable coating is formed. At this applied current density only a few crystals are emerged after 20 min, indicating that although the reactions occur at low applied current density but their kinetics are so slow. When the applied current density rises to 15 mA/cm², more crystals appear on the surface. Increase applied current density to 25 mA/cm² does not change the morphology of the coating, but causes the growth of phosphate crystals.

When the applied current density raises to 35 mA/cm² the crystal size of the coating increases. As can be seen, in all applied current densities the morphological features of phosphate crystals are flower like crystals, and plate like crystals not be seen. The EDAX spectrum and the corresponding chemical composition of the phosphate crystal obtained using anodic electrochemical method are shown in Fig. 7. The presence of Zn, O and P, could be accounted for the formation of hopeite crystals in the coating layer. Also flower like crystals formed on anodically phosphate substrate is the characteristic of the hopeite phase. The refinement of crystals observed in the morphology of the coating is due to the continuous dissolution and re-precipitation of the phosphate coating by the regenerated phosphoric acid under the influence of anodic current during the anodic electrochemical process [7,8].

3.1.4. Characterization of phases in the phosphate layer obtained by anodic electrochemical treatment

The phases in the phosphate layer obtained by the anodic electrochemical method were analyzed by X-ray diffraction analysis and the result is shown in Fig. 8. X-ray diffraction pattern of the sample

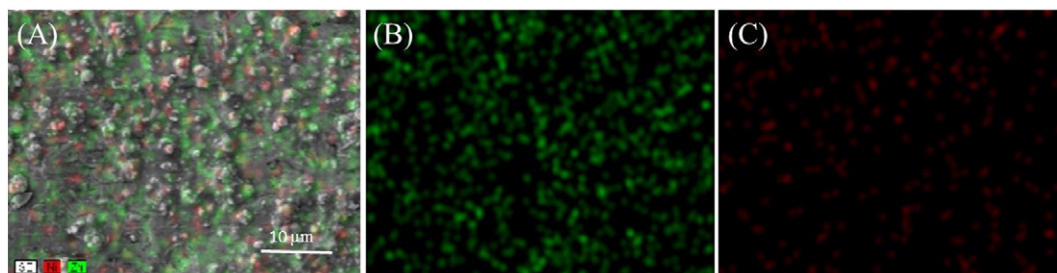


Fig. 4. Elemental mapping of Zn and Ni in the coating. A) Coating B) elemental mapping of Zn C) elemental mapping of Ni.

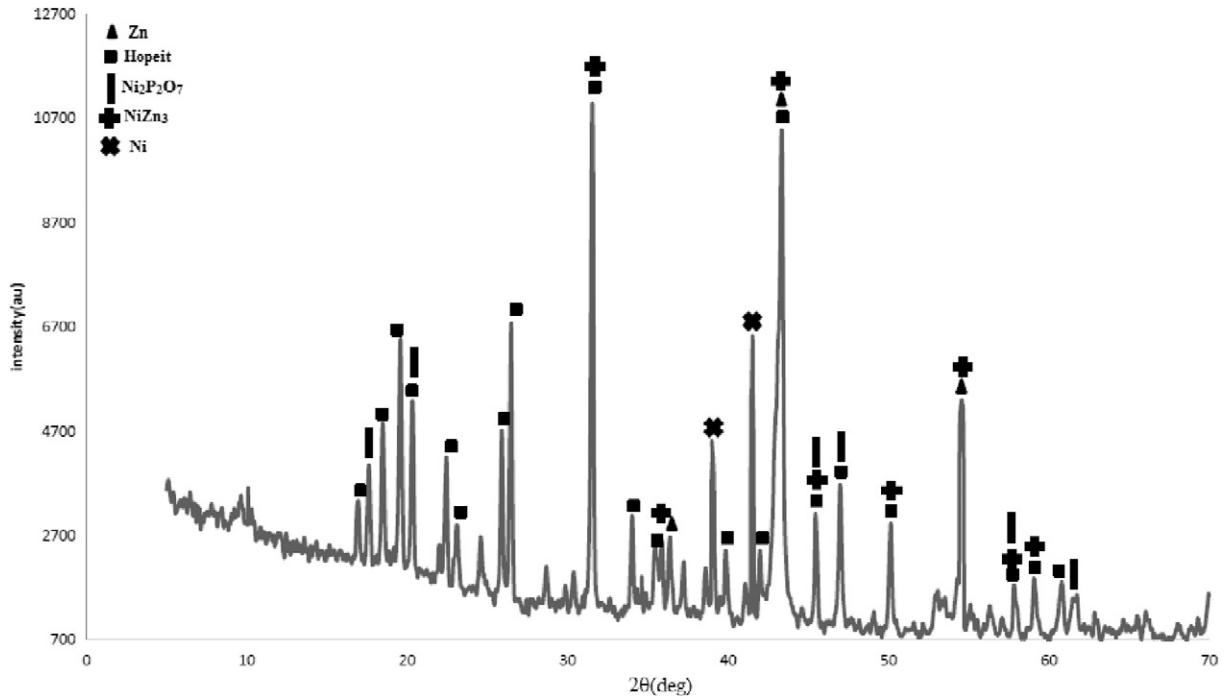


Fig. 5. XRD pattern of coating obtained by the cathodic electrochemical method.

illustrates that the anodically phosphate coating formed on the substrate rich in hopeite phase with the chemical formula of $Zn_3(PO_4)_2 \cdot 4H_2O$. In XRD pattern, all of the peak related to hopeite except the three at $2\theta = 36.37, 43.36$ and 54.33 which related to zinc and originate from galvanized steel substrate. The existence of these 3 peaks is because of the penetration of X-ray into the substrate. In the anodic electrochemical method, the surface potential of substrate polarized to anodic direction and this situation results in dissolution of substrate. As soon as the anodic current is applied, dissolution of zinc occurs. The presence of many dissolved zinc ions in the electrode–electrolyte interface, lead to the displacement of protons away from the interface and increase in interfacial pH between electrode and electrolyte. Increase in interfacial pH leads to the conversion of soluble primary phosphate to insoluble tertiary phosphate. Hence the formation of flower like crystals which is the characteristic of hopeite phase is due to the conversion of soluble primary phosphate to insoluble tertiary phosphate.

3.2. Porosity of coating

Phosphate coating porosity can be detected by various methods. Those methods can be divided into three main categories [19].

- Physical porosity test using microscopy
- Chemical methods using different test reagent
- Electrochemical methods

In this study electrochemical method was used for the evaluation of coating porosity. In this method the phosphate coating porosity can be evaluated using Eq. (2)

$$p = \frac{R_{ps}}{R_p} \times 10^{-(\Delta E_{corr}/\beta_a)} \quad (2)$$

Where p is the coating porosity, R_{ps} is the polarization resistance of substrate, R_p is the polarization resistance of the phosphated substrate, ΔE_{corr} is the corrosion potential difference between the substrate and the phosphated substrate and β_a is the anodic Tafel coefficient of the

substrate [20] the calculated porosities for the coating obtained by cathodic and anodic electrochemical methods at different operation current densities are presented in Table 2. As it can be seen the porosity for coating formed using cathodic electrochemical method in all operation current density is much lower than the coating formed by anodic electrochemical method. During cathodic electrochemical method reduction of ions and deposition of phosphate crystals on metal substrate leading to decrease the porosity of the coating. S. Jegannathan et al. [9] evaluated the coating porosity of zinc phosphate coating on steel substrate obtained by cathodic electrochemical method using chemical method based on prussian blue color formation as a result of the interaction between the ferrous ions in the uncoated areas and the ferricyanide present in the test solution and they did not observe any blue spot over the entire area of the coated substrate. This could be attributed to the very low porosity of the coating obtained by the cathodic electrochemical method. The cause of the increase of porosity in coating obtained using anodic electrochemical method can be understood from the mechanism of coating deposition. As mentioned, in the anodic electrochemical method the surface potential of substrate polarized into anodic direction, this situation significantly increases the extent of metal dissolution during phosphating treatment and increases the porosity of the obtained coatings. Research shows that, the porosity of the anodically phosphated mild steel substrate is relatively higher than that of conventionally phosphated ones [8]. Generally it can be concluded that, the porosity of the coating obtained using cathodic electrochemical method is lower than the coating obtained by conventionally phosphate treatment, and the porosity of the conventionally phosphated coating is lower than the anodically phosphate coating.

3.3. Corrosion behavior

3.3.1. Immersion in 3.5% NaCl

Immersion in 3.5% NaCl solution provides an insight into the corrosion behavior of phosphated galvanized steel substrates. The extent 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 [8]. Observation after 12 h indicated that, the cathodically formed coating remains in good condition and shows no rust formation in

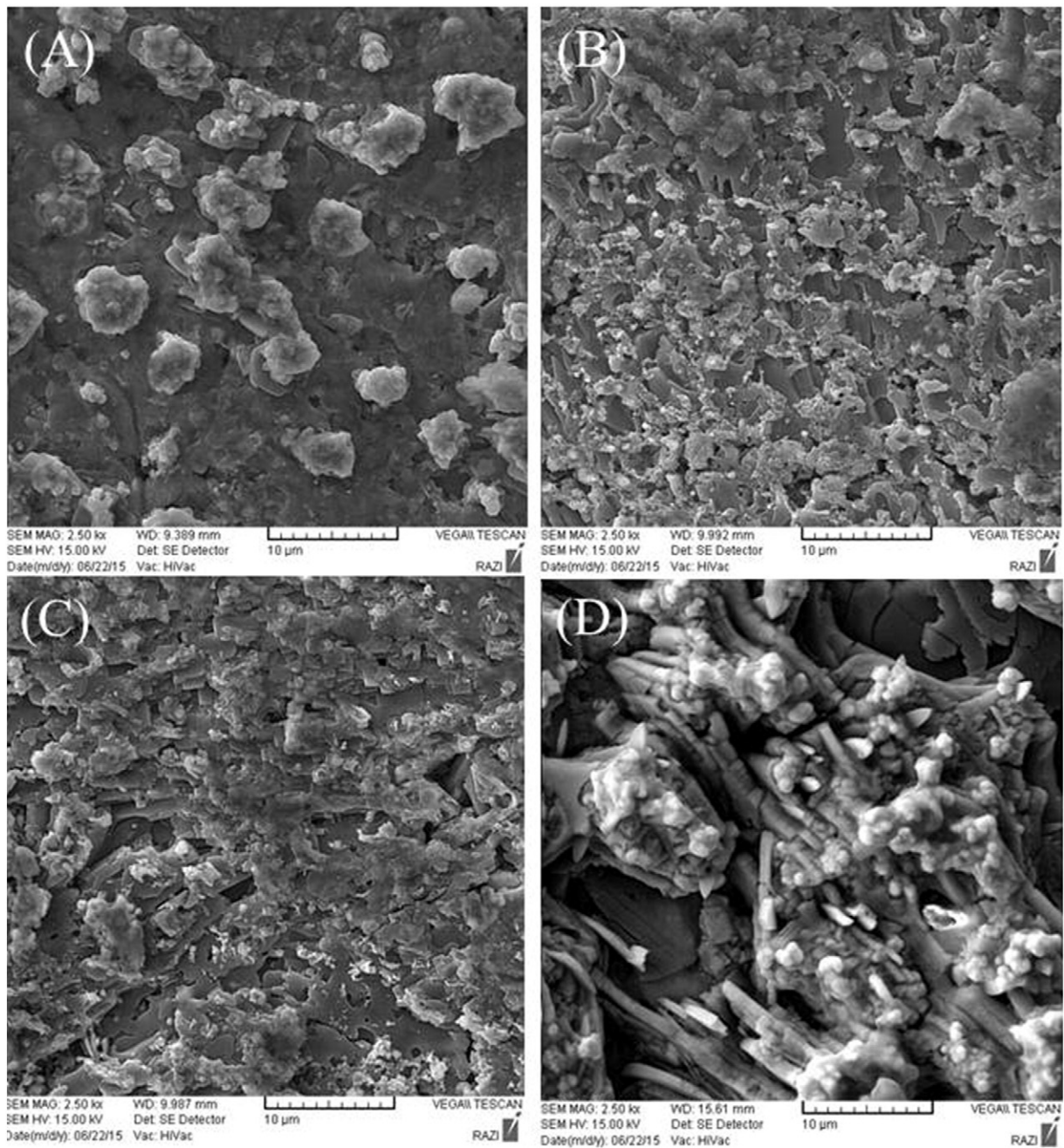


Fig. 6. SEM micrograph of Zn-Ni electrophosphate coating obtained by the anodic electrochemical method at different current densities A) 5, B) 15, C) 25, D) 35 mA/cm².

comparison with the anodically and chemically formed coating. One of the observations on the cathodically phosphate galvanized steel substrate is the formation of white rust on the surface of coating, the reason for this observation is the presence of Zn in the phosphate composition which is formed as a result of dissolution of zinc, dissolved zinc re-deposited on the surface and causes the white rust formation. Consequently the presence of phosphate and elemental zinc in the composition of phosphate layer obtain by cathodic electrochemical method provides both sacrificial and barrier protection for substrate and thereby improves the corrosion resistance of the coating. The loss in weight due to corrosion of coatings after 24 h immersion is present in Table 2. As can be seen, the loss in weight of cathodically substrate is less than the chemically phosphated galvanized steel and chemically phosphated galvanized is less than the anodically phosphated galvanized steel. These results are in agreement with the results of visual observations.

3.3.2. Potentiodynamic polarization studies

Corrosion behavior of the coating obtained using anodic and cathodic electrochemical methods was characterized by potentiodynamic polarization test. Fig. 9 shows the potentiodynamic polarization curves of the coating obtained by cathodic electrochemical method and Fig. 10 shows the potentiodynamic polarization curves of the coating obtained by anodic electrochemical method. Corrosion potentials (E_{corr}), corrosion current densities (i_{corr}) and anodic/cathodic Tafel constant (β_a and β_c) are derived from the potentiodynamic curves. The polarization resistance (R_p) can be determined from Stern-Geary equation based on the approximately linear polarization behavior near open-circuit potential (OCP) according to the following equation.

$$R_p = \frac{\beta_a \times \beta_c}{2.033(\beta_a + \beta_c)i_{corr}} \quad (3)$$

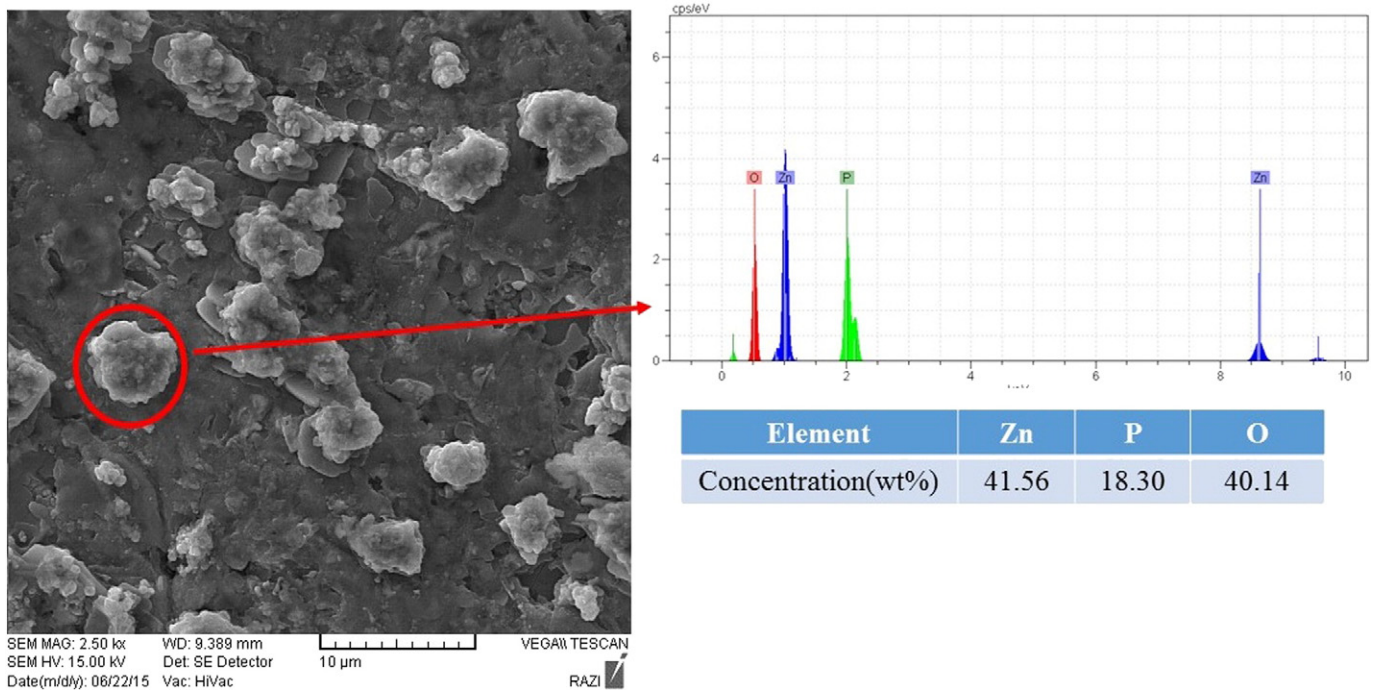


Fig. 7. EDAX spectrum and the corresponding chemical composition of the phosphate coating obtained by anodic electrochemical method.

The electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}) and cathodic and anodic slopes calculated from linear polarization method for cathodic and anodic electrochemical methods are reported in Table 2. It can be seen that, the corrosion resistance of the coating obtained by the cathodic electrochemical method is much better than the coating obtained by anodic electrochemical method. The cause of higher corrosion resistance of cathodic coating can be understood from the coating porosity, generally a low value of coating porosity results in a better corrosion resistance of the coating. As stated, the porosity of cathodically phosphate crystals is very low, therefore, it is expected that, the corrosion resistance of this coating to be high. The higher porosity of coating formed by anodic treatment leads to poor corrosion resistance of the coating. The corrosion potential and corrosion current density of phosphate coatings obtained by anodic treatment are quite similar to those obtained by chemical treatment [7].

3.4. Advantage, limitation and proposed application for coatings

Both cathodic and anodic electrochemical methods can be used for deposition of Zn–Ni electrophosphate coating on galvanized steel. The use of these methods has limitations and advantages. As it was seen, the anodic treatment significantly increases the extent of metal dissolution during phosphating treatment and increases the porosity of the obtained coatings and, therefore leads to produce coating with poor corrosion resistance. Hence, in the situation where the coating with high corrosion resistance is required, the use of coating obtained by anodic electrochemical method is not recommended. But in application where high porosity is required, such as tube and wire drawing operations, the use of anodically phosphate coating is recommended. In this application, oil absorbed in the porosity of the coating and stress needs for wire drawing are reduced. It is recommended that, use of

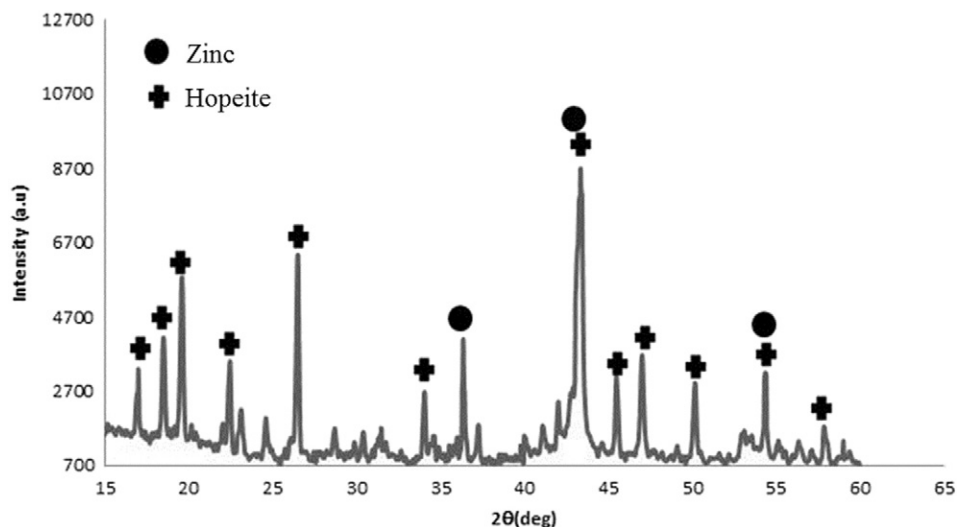


Fig. 8. XRD pattern of coating obtained by the anodic electrochemical method.

Table 2
Corrosion resistance and porosity of the obtained coating calculated by immersion test and potentiodynamic polarization method.

Type of studied system	Corrosion current density ($\mu\text{A}/\text{cm}^2$)	Corrosion potential (mV vs. SCE)	Porosity (%)	Loss in weight (g/m^2)
Cathodically phosphated galvanized steel at 5 mA/cm ²	3.28	−1028	1.23	5.3
Cathodically phosphated galvanized steel at 15 mA/cm ²	1	−1006	0.3	1.23
Cathodically phosphated galvanized steel at 25 mA/cm ²	2.28	−1043	0.63	0.98
Cathodically phosphated galvanized steel at 35 mA/cm ²	22.43	−1120	8.4	6.2
Anodically phosphated galvanized steel at 5 mA/cm ²	78	−1040	48	12.04
Anodically phosphated galvanized steel at 15 mA/cm ²	9.6	−1011	15.3	8.06
Anodically phosphated galvanized steel at 25 mA/cm ²	4.11	−972	8.42	7.3
Anodically phosphated galvanized steel at 35 mA/cm ²	35.14	−1004	27.4	11.25
Chemically phosphated galvanized steel	–	–	–	8.23

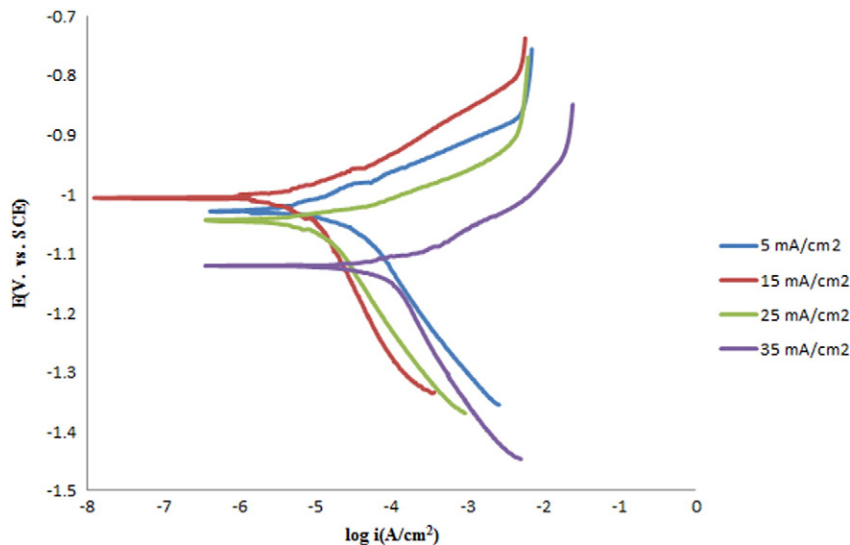


Fig. 9. Polarization curves of the coating obtained by cathodic electrochemical methods.

anodic electrochemical method will be beneficial in depositing manganese phosphate coatings on steel [7]. According to the results of experiments, by using cathodic electrochemical accelerator, compact phosphate coating with high corrosion resistance can be obtained, thus in the situation where the coating with high corrosion resistance is required, the use of coating obtained by cathodic electrochemical is

recommended. Base on X-ray diffraction studies the coating that obtained by cathodic method contain elemental Zn, Ni and hopeite and nickel phosphate. Where the presence of elemental zinc and nickel and zinc and nickel phosphate increased corrosion resistance through both sacrificial and barrier layer protection. The coating obtained through cathodic treatment can be classified in phosphate composite coating.

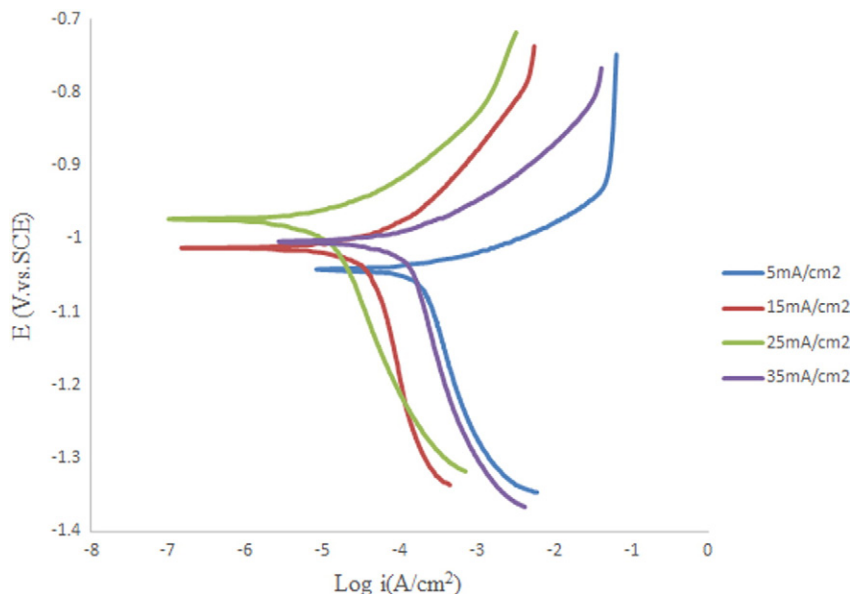


Fig. 10. Polarization curves of the coating obtained by anodic electrochemical methods.

Therefore, by using different cations in the phosphating bath or by using different anodes, different phosphate composite coatings can be obtained. One of the main limitation of the cathodic electrochemical method is the possibility of occurrence of hydrogen embrittlement during electrophosphating [7]. Because in this treatment, the substrate serves as the cathode, hydrogen evolution occurs on the cathode substrate during phosphating treatment, crated atomic hydrogen is able to penetrate into metals and causes hydrogen embrittlement which can weaken the mechanical properties of substrate.

4. Conclusion

In this study Zn–Ni electrophosphate coating was applied on galvanized steel using anodic and cathodic electrochemical methods and properties of coatings obtained by these methods were compared. The results of the investigation indicated that, through using the cathodic electrochemical method, coating with low porosity and good corrosion resistance can be obtained. Also, due to the presence of elemental zinc and nickel along with phosphate crystals, the coating obtained by the cathodic electrochemical method can be classified as Zn–Ni phosphate composite coating. Results showed that, the anodic treatment significantly increases the extent of metal dissolution during phosphating treatment and increases the porosity of the obtained coatings and, therefore leads to produce the coating with poor corrosion resistance. Based on the properties of obtained coating, applications provided for each of the coatings. In application where high porosity is required, the use of anodically phosphate coating is recommended but in the situation where the coating with high corrosion resistance is required, the use of coating obtained by cathodic electrochemical is recommended. And also it is suggested to use several anodes or several species in the cathodic electrochemical method, to obtain several phosphate composite coatings.

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