DOR: 20.1001.1.2322388.2019.7.2.6.0

Research Paper

Effect of Bath pH on Microstructure and Corrosion Behavior of Manganese Phosphate Coating on SCM420H Steel

Hadi Ebrahimifar[1*], Farhad Mohsenifar[2]

1. Department of Materials Engineering, Faculty of Mechanical and Materials Engineering, Graduate University of Advanced Technology, 7631133131, Kerman, Iran.
2. Department of mechanical engineering, Higher Education Complex of Bam, P. O. Box: 76615-314, Bam, Kerman, Iran.

ARTICLE INFO

Article history:

Received 30 February 2019
Accepted 11 April 2019
Available online 1 May 2019

Keywords:
Coating
pH
Potentiodynamic polarization
Electrochemical impedance spectroscopy

ABSTRACT

In order to improve the surface quality and prevention of corrosion and reduction of wear in the components like gears and bearings, they can be covered with phosphate coatings. SCM420H alloy steel was coated with manganese phosphate deposition. The microstructure and corrosion resistance of the coating was studied by change of bath pH. In order to investigate the phase analysis and coating microstructure, X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used, respectively. XRD analysis from the coated surface revealed the phases of $MnFe_2(PO_4)_2(OH)_2H_2O$, $Mn(PO)_3$ ‹$Fe(PO)_3$ and $(Mn,Fe)_5H_2(PO_4)_4{\cdot}4H_2O$. Results showed the obtained coating at pH=2.1 was uniform and continuous and no crack or porosity was observed. The phosphate surface at pH=1.9 and pH=2.4 was non-uniform and included cracks. In order to investigate the corrosion resistance, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) tests were applied on coated and uncoated specimens in 3.5% NaCl solution. The results of potentiodynamic polarization and electrochemical impedance spectroscopy tests were in agreement with microscopic images. The results of electrochemical impedance spectroscopy demonstrated that the formed manganese phosphate deposition in the bath with pH=2.1 had the highest polarization resistance (28020 Ω) compared to the formed coating in the bath at pH=1.9 (1480 Ω) and the formed coating in a bath with pH=2.4 (3155 Ω).

---

[*] **Corresponding Author:**
E-mail Address: H.Ebrahimifar@kgut.ac.ir

1. Introduction

SCM 420H steel is an alloy containing chromium and molybdenum. Its symbol is SCM, and its specifications comply with Japanese Industrial Standards (JIS) that govern all industrial activities in Japan. SCM420H alloy structural steel hardenability is higher, no temper brittleness, weldability is quite good, form the cold cracking tendency is small, can cutting and cold strain plasticity is good, heat treatment deformation is smaller than 20CrMnTi steel. In conditioning or carburizing and quenching condition, used in the manufacture of the corrosive medium and low working temperature 250 °C, the medium containing hydrogen nitrogen mixture work of high-pressure pipe and all kinds of fasteners, the more senior carburized parts, such as gear, shaft, etc. [1]. Since this steel is used to produce sliding parts, it is required to have additional corrosion resistance, wear, or fatigue resistance. Therefore, the steel can be coated to improve the surface quality, prevent corrosion and reduce the wear of parts such as gears and bearings. Phosphate coatings are one of the most commonly used coatings [2,3]. Since in the forming process of phosphate coatings, a part of the base metal becomes a special compound and creates a protective film due to non-electrolytic chemical reactions with its surrounding solution, these coatings are considered as a conversion coating [4]. Phosphate coatings have different types, but manganese phosphate coatings, zinc, and iron have been used to protect steel against corrosive environments [5]. Phosphate coatings with higher compression and density, finer structure, and more adhesion to the substrate are more suitable for corrosion and abrasion resistance applications [6]. Andrew et al. investigated the effects of various phosphate coatings on steel and showed that manganese phosphate coatings provide better protective properties than zinc or iron phosphate coatings for steel surfaces [7].

In recent decades, extensive studies have been done on the corrosion behavior and the quality of phosphate coatings. Wang et al. showed that zinc phosphate and manganese phosphate coatings both increased the corrosion resistance of the 55SiMo8 tool steel, and in addition, the porosity of manganese phosphate coating was lower than that of zinc phosphate [8]. Pastorck et al. investigated the effect of sandblasting before applying manganese phosphate coating on the corrosion behavior of low-alloy steels [9]. Claasman et al. showed that the mechanism of phosphate reaction is controlled by the pH of the solution and depends on the dissolution of the substrate in local anodic locations and the insoluble phosphate sedimentation in local cathodic locations [10]. Zhang et al. studies showed that increasing the pH of the solution causes fine crystalline structure, increased mass, and thickness of zinc phosphate coating on stainless steel 304. They also showed that the increase in pH resulted in an improvement in corrosion resistance and, as pH rises, a critical amount of corrosion resistance was reduced [11]. Lee et al. also provided an optimal pH for the corrosion behavior of two-cationic Mn-Zn coatings on steel [12].

According to our survey of the literature, no research has

been done on the coating of manganese phosphate on SCM420Hsteel, by of the phosphating method for the application of corrosion resistant devices.

The present research aims to evaluate the microstructure and corrosion behavior of manganese phosphate-coated SCM420H steel that were coated using the phosphating method. To evaluate microstructure and phase identification scanning electron microscopy (SEM) and X-ray diffraction pattern was used. In order to investigate the corrosion behavior, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) tests were applied on manganese phosphate and uncoated specimens in 3.5% NaCl solution.

2. Experimental Procedure:

2.1 Material:

In this research, SCM420H steel was used as substrate (Fe-balance,% 0.17-0.23C,% 0.15-0.35Si,% 0.55-0.9Mn,% 0.85-1.25Cr,% 0.15-0.3Mo, Ni <% 0.25, S%, 0.03, P <% 0.03, Cu <% 0.3). Four samples with a size of 10 mm × 10 mm × 5 mm were made from this steel. The sequence and steps of the phosphating process are shown in Figure 1. In order to investigate the effect of pH on microstructure and corrosion behavior, three pHs of 1.9, 2.1, and 2.4 were selected. The selection of this range of pH was based on previous researches [5,13,14]. The initial phosphate solution contained 14.7 g/l phosphoric acid, 25.2 g/l nitric acids, and 11.5 g/l manganese carbonate, and its pH was 1.9. To reach pH=2.1 and pH=2.4, a solution of sodium hydroxide was added to the initial solution. The phosphate bath was kept at a constant temperature of 90 °C.

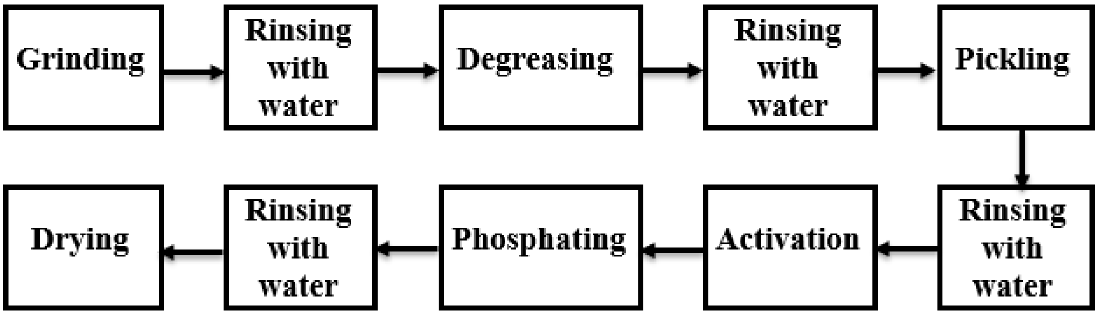

Fig. 1. Phosphating process steps

2.2 Methodology:

2.2.1 Microstructural characterization:

Surface morphology study of the coated specimens was performed by Scanning Electron Microscopy (SEM) (Camscan MV 2300). To identify the formed phases of phosphate coating, an X-ray diffraction pattern of PHilips type with Cu Kα radiation (λ = 1.5405 Å) was used.

2.2.2 Electrochemical tests:

Polarization resistance experiments and electrochemical impedance spectrometry experiments were performed to determine the electrochemical behavior of the coating in 3.5% NaCl solution by EG&G Princeton Applied Research PARSTAT 2273 potentiostat/galvanostat Model 273A. A commonly used three-electrode consisting of an electrode (coated and uncoated sample), a Saturated ***calomel*** Electrode (SCE) electrode as a reference electrode, and a platinum rod was used as an auxiliary electrode. All experiments were performed in distilled water containing (Merck) NaCl 3.5% at ambient temperature. Before each test, each sample was connected to a copper wire and then mounted with an epoxy resin. Before starting the experiment, the samples were prepared with a surface equal to 1 cm^2, and the rest of the parts were completely covered with epoxy. The samples were immersed in a solution of 3.5% NaCl for 60 min in order to achieve a stable state. Changes of less than 5 mV in 5 minutes were considered as stable state. The electrochemical impedance spectroscopy was performed at the frequency range of 10^{-2}-10^{5}. The polarization experiments were carried out at the desired voltage level at a sweeping rate of 1 m/s and a constant temperature of 25 °C. The equivalent circuit was used to analyze the impedance results from the Z-View software.

Princeton Applied Research PowerSuite2.58 software and Zview 3.1 software from Scribner were used to check corrosion behavior. PowerSuite software converts information obtained by the device into numerical data. In order to analyze the results obtained from PowerSuite, the information obtained from this software was transferred to another software, and the Zview software was used to analyze the obtained graphs. Impedance spectra were analyzed by Zview software, and finally, the equivalent circuit was proposed for corrosion.

3. Results and discussion

3.1 Effect of pH on the microstructure of the coating:

To evaluate the effect of pH on microstructure and the quality of manganese phosphate coating; baths with different pH values (1.9, 2.1, and 2.4) were used. The effect of bath pH on the morphology of manganese phosphate coating is shown in Figure 2. As shown in Figure 2, the coating obtained at pH = 1.9 (Figure 2a) is non-uniform, with a number of cracks in it, while the coating obtained at pH=2.1 is uniform and continuous (Figure 2b). Also, some of the areas on the phosphate surface at pH=2.4 is uncovered, and in some places, the surface is cracked (Figure 2c). At low pHs, Mn^{2+} is predominantly manganese hydrate, and at higher pHs, it is a complex of hydrated manganese [15]. Therefore, at low pHs, the formation of suitable complexes for the manganese phosphate precipitation can improve the quality of the coating [16]. Additionally, sodium hydroxide concentration is affected by the pH of the bath. At higher pH than 2.1, in the presence of manganese hydroxide, the color of the bath was dark, and this is due to the formation of sludge, which leads to a decrease in the efficiency of the bath. Another reason for increasing the quality of the coating by increasing the pH and, consequently, reducing the quality of the coating by increasing the pH is related to the concentration of H$^+$ ions in the bath. With increasing pH, the release of hydrogen decreases, and therefore, the bath efficiency and deposition rate increase. At higher pHs, the formation of manganese hydroxide and its products leads to a reduction in the amount of free metal cations and phosphate compounds. The formation of such compounds leads to a decrease in the bath efficiency and deposition rates that are consistent with microscopic images (Figure 2).

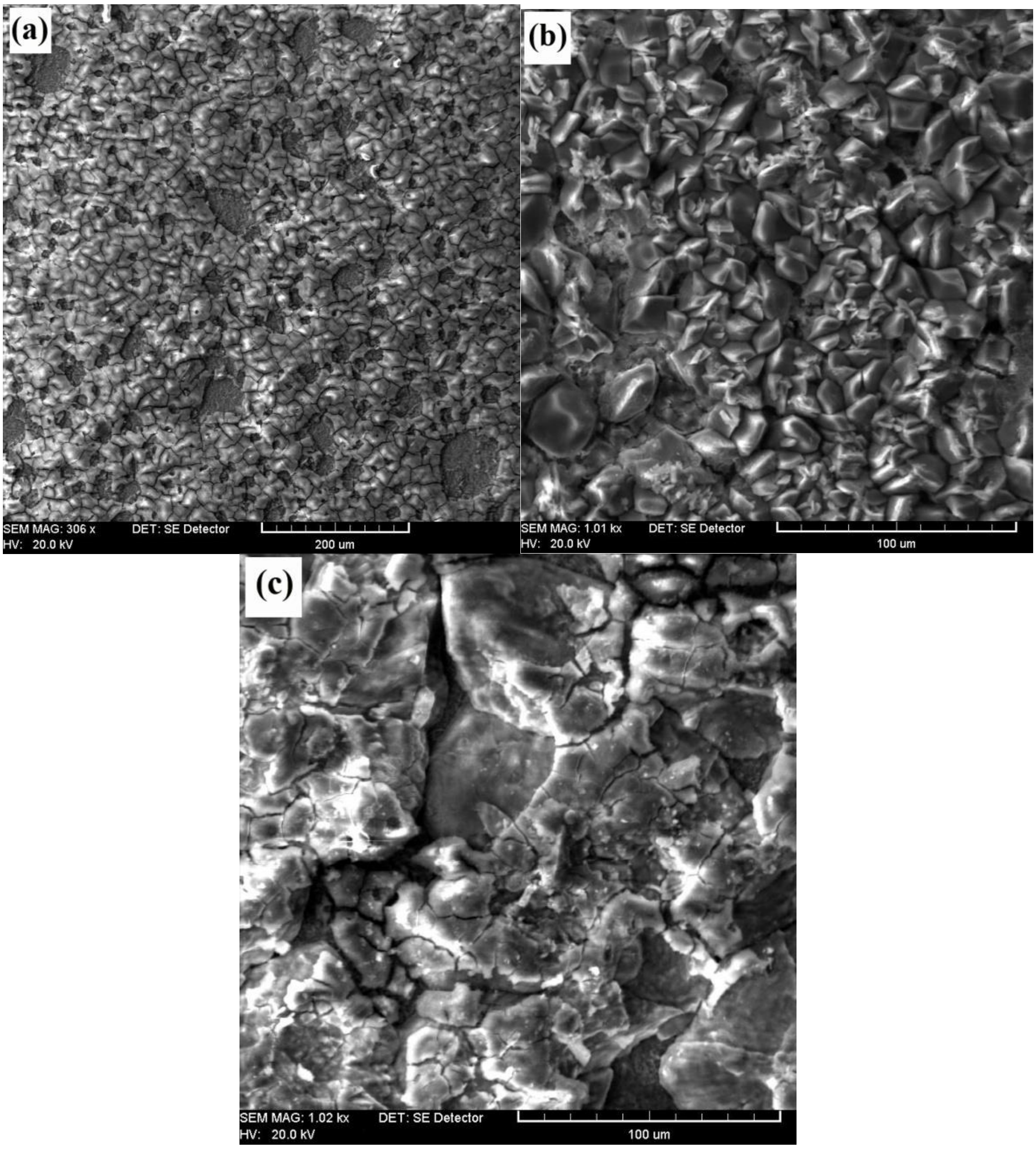

Fig. 2. SEM image of surface morphology of phosphate samples with (a) pH = 1.9, (b) pH = 2.1 and (c) pH = 2.4

Bath pH is one of the most important and controlling factors in phosphate baths. The excessive dilution of the bath will result in an excessive concentration of OH^-, resulting in a decrease in phosphate deposition. On the other hand, in over-saturated baths (low pH baths), deposition of insoluble crystalline phosphate monoxide occurs after a long time. So the excess concentration of the bath leads to a decrease in deposition rate [17]. At low pHs (pH=1.9 and less), due to the low speed of the reactions and the undesirable reactions, some parts of the sample remain uncovered. As the pH rises from 1.9 to 2.1, the speed of the reactions increases, and the uniform coating is deposited on the surface. Also, in low pHs, due to high concentrations of H^+ ions and H_2 reduction in cathodic locations, it causes a rise in pH in the bath/substrate interface, which leads to the deposition of insoluble manganese phosphate crystals in longer time periods. Some parts of the surface coated at pH=1.9 is uncoated (Figure 2a). In baths with low pHs (in baths with low free acid ratio), dissociation of the phosphates takes place in solution (as well as at the substrate interface) and leads to precipitation of insoluble phosphates as a sludge [17,18]. Low concentrations of insoluble manganese phosphate crystals and unwanted reactions result in the non-uniformity of the coating at low pHs. Therefore, the deposition time should be increased to create a uniform coating. Also, the release of hydrogen and the formation of brittle hydroxide compounds cause cracks in the coating produced at pH=1.9 [19].

At high pHs (pH=2.4 and above), unwanted reactions result in the formation of hydroxide and oxide compounds. The dark color of the bath solution is a reason for unwanted reactions (formation of manganese hydroxide and their products)that can lead to unwanted and brittle compounds [12, 19]. Also, in high pHs, due to the formation of soluble and unstable phosphates on the surface, some parts remain uncovered. In the coating formed at pH=2.4, a number of cracks are seen. Creating brittle hydroxide and oxide compounds leads to cracking the coating. Also, the formation of unwanted compounds in the deposited layer or the formation of these compounds at the interface of the deposit-substrate can reduce the adhesion of the coating to the substrate [20].

As indicated by SEM images, with increasing pH, the grain size decreases (Figure 2). Bath pH is one of the most important controlling factors in surface morphology. At low pHs, due to high concentrations of H^+ ions, the amount of hydrogen reduction increases. By increasing the hydrogen reduction, the number of micro-cathodic sites and micro-anodic sites increase. Thus, with the increase of the micro-cathodic sites and micro-anodic sites, the deposition rate increases. On the other hand, with the increased release of hydrogen, there is the possibility of the formation of brittle hydride compounds. At low pHs, due to high concentrations of H^+ ion, the amount of H_2 reduction on the surface increases, and as a result, nucleation locations (micro-cathodic sites) increase for coating growth. Therefore, the nucleation rate is higher than the growth rate, and therefore fine grains are formed (Figure 2a). With increasing pH, the concentration of H^+ ion decreases, and the amount of hydrogen reduction on the surface decreases. Therefore, active cathodic sites for nucleation are reduced. As a result, the speed of nucleation will be less than the rate of growth. For this reason, the coating produced in the higher pH is coarser (Figure 2c). Therefore, based on microscopic SEM images, the best coating of manganese phosphate was formed on the substrate SCM420H at pH=2.1. Figure 3 illustrates the XRD analysis of the coated sample. XRD analysis from the coating surface indicates that the coating layer consists of $MnFe_2(PO_4)_2(OH)_2H_2O$ (JCPDS, Card No. 005-0110), $Mn(PO_3)_3$ (JCPDS, Card No. 044-0078), $Fe(PO_3)_2$ (JCPDS, Card No. 030-0661) and $(Mn,Fe)_5H_2(PO_4)_4{\cdot}4H_2O$ (JCPDS, Card No. 016-0383) phases.

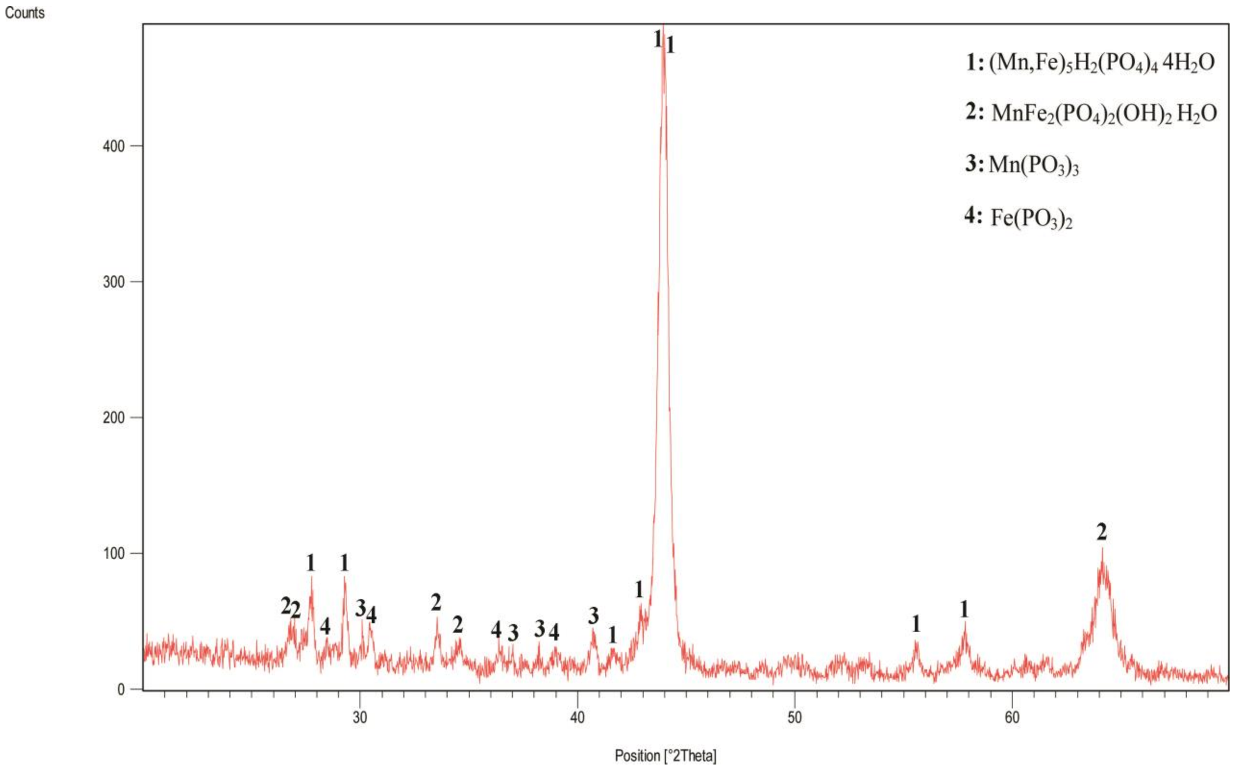

Fig. 3. XRD analysis from the sample surface phosphated at pH = 2.1

3.2 Electrochemical tests:

3.2.1 Potentiodynamic Polarization:

Potentiodynamic polarization curves in sodium chloride solution 3.5% for a uncoated steel sample and steel samples coated in phosphate baths with different pH values are shown in Figure 4. The data analysis of these curves was performed using Powersuite software, and the results are presented in Table 1. Stern-Geary (Equation 1) was used to calculate polarization resistance:

$$R_p = \frac{\beta_a \beta_c}{2.3 i_{corr} (\beta_a + \beta_c)} \quad (1)$$

In this equation, Rp is the polarization resistance, and βa and βcare the slopes of the cathodic and anodic regions of the Tafel curve, respectively, and icorr is the corrosion current.

The results showed that at pH=2.1, the polarization resistance has the highest amount and the corrosion current has its lowest value, and therefore the coating formed at this pH exhibits higher corrosion resistance. At pH=1.9, the corrosion rate has increased significantly due to the lack of uniform coating on the substrate or the coarse structure of the coating. Low levels of polarization resistance are also due to the severe corrosion effect of acidic phosphate solution. In addition, at pH=1.9, due to the higher rate of hydrogen reduction and as a result of high levels of hydrogen on the surface, phosphate coating deposits are prevented, and the formation of a uniform coating layer is not possible [21]. As the pH increased from 2.1 to 2.4, the polarization resistance decreased sharply, indicating an increase in the corrosion rate in this case. This can be due to an increase in the amount of sludge present in the test solution at pH=1.9 due to the higher consumption of H+ and the formation of insoluble phosphates.

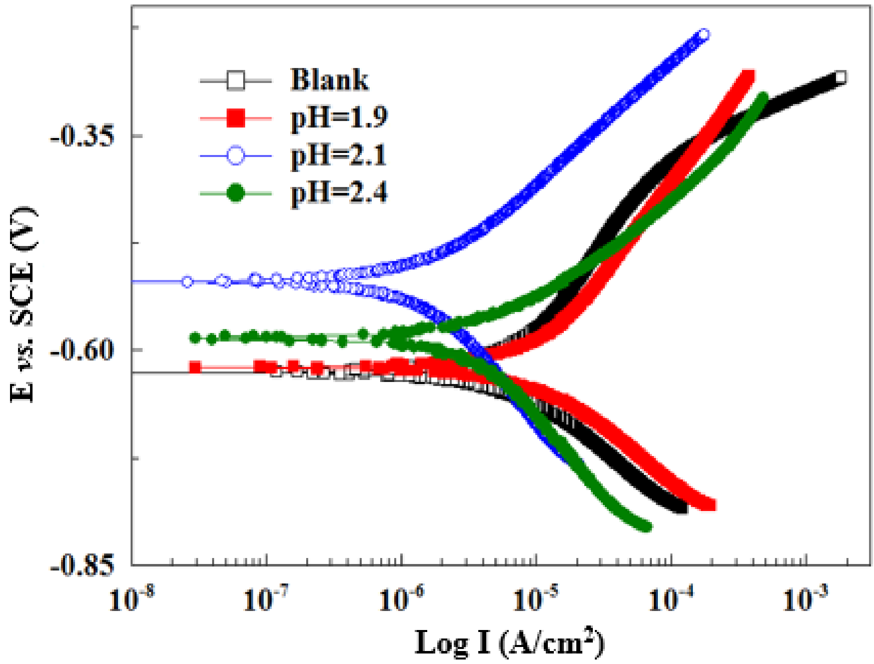

Fig. 4. Potentiodynamics polarization curves of uncoated and coated SCM420H steel in phosphate solution with different pH in NaCl 3.5%.

Table 1. Electrochemical data derived from potentiodynamic polarization curves of uncoated and coated SCM420H steel in phosphate solution with different pH in NaCl 3.5%

Sample	E_{corr} $(\pm 10^{-3})$*vs.* SCE mV	I_{corr} $(\pm 10^{-7})$ µA	$_a$ $(\pm 10^{-3})\beta$ mV/dec	$_c$ $(\pm 10^{-3})\beta$ mV/dec	R_p $\Omega.cm^2$
Uncoated	-638	6.1	229	102.6	5.1
Coated at pH=2.4	-596	3.5	112	178	8.6
Coated at pH=2.1	-520	1.4	132.3	191	24.6
Coated at pH=1.9	-613	8.25	168	125.6	3.8

The porosity of the phosphate coating is calculated according to the linear polarization results by equation (2) [22]:

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

In this equation, P is the coating porosity, Rps and Rp are the polarization resistance of the uncoated sample and the coated specimens, respectively, ΔEcorr is the potential corrosion difference between the coated and uncoated specimen and$\beta_a$is the slope of the anodic curve in the uncoated sample. The porosity for the sample coated in a solution with pH=1.9, pH=2.1, and pH=2.4 was 1.717, 0.673, and 0.906%, respectively. These results indicate that the coating formed at pH=2.1 is uniform with less porosity, and the coating formed at pH=1.9 has more discontinuity. In addition, the corrosion protection efficiency can also be calculated from equation (3) [23]:

$$P_e(\%) = (1 - \frac{i_{corr}}{i^0_{corr}}) \times 100 \quad (3)$$

In this equation, P_e is the corrosion protection efficiency, i^0_{corr} and i_{corr} are the corrosion current density of the sample without coating and coating(uncoated sample), respectively. The corrosion efficiency of the sample coated in a solution with pH=2.4, pH=2.1, and pH=1.9 was 42.55%, 76.9% and -35.84%, respectively. The negative value of corrosion protection efficiency indicates the coating formed at pH=1.9 does not protect the substrate against corrosion [24].

3.2.2 Electrochemical Impedance

Nyquist curves derived from electrochemical impedance in a 3.5% sodium chloride solution refer to the uncoated steel specimen and the steel samples coated in phosphate baths with different pH values are shown in Figure 5. Data on these curves were extracted by PowerSuite software and sent to Zview software for analysis. The equivalent circuits proposed by the software for the uncoated sample and the phosphate samples are shown in Figures 6a and 6b, respectively.

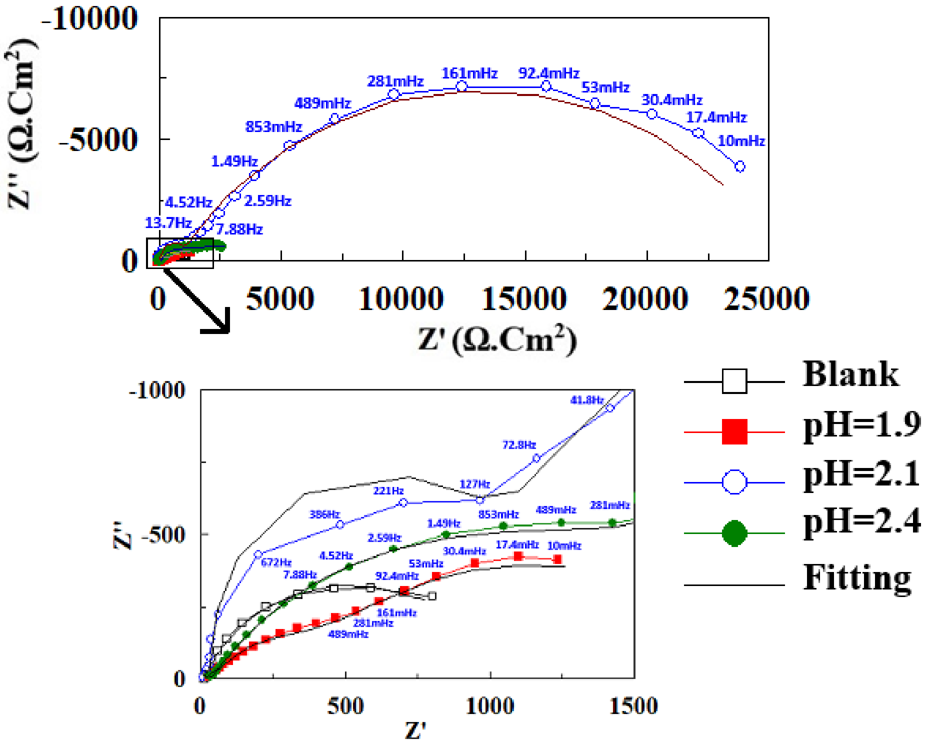

Fig. 5. Impedance curves of uncoated and coated SCM420H steel in phosphate solution with different pH in NaCl 3.5%.

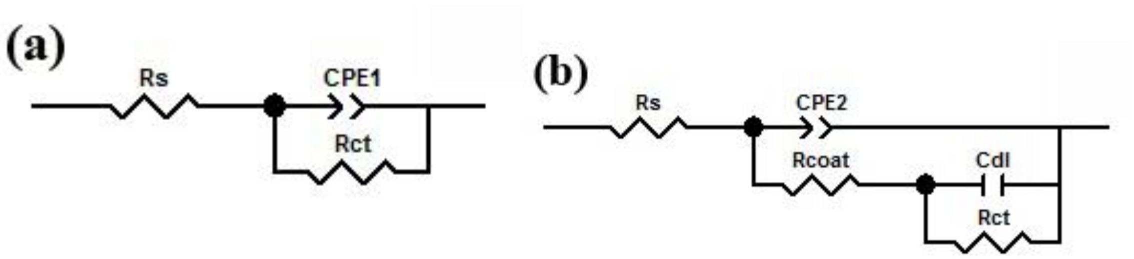

Fig. 6. Equivalent electrical circuit used forthe uncoated sample (a) and coated samples (b).

Here R_s is the solution resistance between the reference electrode and the specimens, R_{ct} is the charge transfer resistance of steel, Rcoat is the corrosion resistance of coating versus diffusion of corrosive environment, C_{dl} is the dual-layer capacity, and CPE is the constant phase element used instead of the simple capacitor for the metal.CPE for the substrate and coating are shown with CPE1 and CPE2, respectively. The results obtained from the analysis of Nyquist curves using Zview software are presented in Table 2. The reason for using the constant phase element instead of the ideal capacitor is related to the roughness of the electrode surface, the non-homogeneous reactions on the electrode surface, and the non-uniform current distribution during the corrosion process [25]. The constant phase element consists of two components of admittance (CPE-T) and power index number (CPE-P). The power index number (CPE-P) is between 0.5 and 1, and the more deviation from 1, the heterogeneous and roughness of the surface is more [26, 27].

The power index number of the coated samples is close to 0.5, which indicates the non-homogeneity of the coating and hence the non-uniform distribution of the current on the surface. Jabat et al. [28, 29] also showed that conversion coatings increase surface roughness. The higher admittance values indicate greater porosity in the coating. Admittance is minimum in pH of 2.1, which indicates that the protective properties of the coating are better in this case. With a pH drop of up to 1.9, the amount of admittance increases, resulting in reduced corrosion resistance. The solution resistance for coated samples was always higher than the uncoated specimen due to the interaction between the substrate and the ions in the bath coating. The higher value of the solution resistance at pH = 2.1 can be attributed to the better performing of reaction of forming the coatings and thus to provide a better coating on this pH. In addition, the double layer capacity for the coating formed at this pH is lower than other conditions, which indicates the lower penetration of the corrosive solution into the metal/coating interface. These results are fully consistent with the results of the Tafel polarization.

Table 2 Electrochemical data derived from impedance curves of uncoated and coated SCM420H steel in phosphate solution with different pH in NaCl 3.5%.

Sample	R_s (±10) Ω.cm^2	R_{coat} (±10) Ω.cm^2	CPE-T (±10^{-3}) Ω^{-1}cm^{-2}S^n	CPE-P (±10^{-2})	R_{ct} (±10) Ω.cm^2	C_{dl} (±10^{-3}) F.cm^{-2}
Uncoated	11.6	-	0.0007	0.74	992	-
Coated at pH=2.4	18	2400	0.0001	0.538	755	0.0015
Coated at pH=2.1	35	9995	0.00003	0.53	18115	0.00001
Coated at pH=1.9	15	850	0.0014	0.54	630	0.03

4. Conclusion

Alloy steel SCM420H was coated with a manganese phosphate coating. The effect of three pHs (pH=1.9, pH=2.1, and pH=2.4) on morphology, microstructure of coatings, and corrosion resistance were investigated. The results showed that the manganese phosphate deposited in the bath at pH=2.1 was uniform, and there was no cracking or porosity in it. The results of the potentiodynamic polarization test in sodium chloride solution (3.5%) showed that the coated sample in the bath with pH=2.1 had the lowest corrosion current (1.402μA) compared to the bath coated sample at pH=1.9 (8.246 μA) and the sample coated in a bath with pH=2.4 (3.487 μA). The results of electrochemical impedance spectroscopy (EIS) in aqueous NaCl 3.5% showed that the sample coated in the bath with pH=2.1 had the highest polarization resistance (28020 Ω) compared to the bath coated sample at pH=1.9 (1480 Ω) and the sample coated in a bath with pH=2.4 (3155 Ω).

References

[1] C. Fang, J. Shi, L. Zhu, Research and Development of High Grade Gear Steel SCM420H for Automobile. Adv. Mater. Research. Vol. 859, 2014, pp. 11-14.

[2] M. T. Devlin, T. L. Turner, K. Thompson, K. Kolakowski, K. Garelick, J. M. Guevremont, T. Jao, Effect of Phosphate Coatings on Fatigue and Wear, Presented at the NLGI 74th Annual Meeting, Scottsdale, Arizona, (2007).

[3] J.R. Davis, Surface Engineering for Corrosion and Wear Resistance, ASM International, USA. 2001, pp. 95-124.

[4] M.A. Kuehner, Phosphate Conversion Coating.Metal Finishing. Vol. 83, 1985, pp. 8-15.

[5] Ch-M. Wang, H-Ch. Liau, W-Ta. Tsai, Effects of temperature and applied potential on the microstructure and electrochemical behavior of manganese phosphate coating. Surf. Coat. Technol., Vol. 201, 2006, pp. 2994-3001.

[6] B-l. Lin, J-t. Lu, G. Kong, Synergistic corrosion protection for galvanized steel by phosphating and sodium silicate post-sealing. Surf. Coat. Technol., Vol. 202, 2008, pp. 1831-1838.

[7] J.F.Andrew, S.G. Clarke, E.E. Longhurst, The Protective Properties of Various Phosphate Coatings on Steel. J. Chem. Technol. Biot.Vol. 4, 1954, pp.581-595.

[8] D.Weng, P.Jokiel, A. Uebleis, H. Boehni, Corrosion and protection characteristics of zinc and manganese phosphate coatings. Surf. Coat. Technol., Vol. 88, 1997, pp.147-156.

[9] F.Pastorek, K.Borko, S.Fintová, D. Kajánek, B.Hadzima, Effect of Surface Pretreatment on Quality and Electrochemical Corrosion Properties of Manganese Phosphate on S355J2 HSLA Steel.Coatings. Vol. 6, 2016, pp. 46-54.

[10] E. Klusmann, J.W. Schultze, pH-Microscopy: technical application in phosphating solutions. Electrochim. Acta.,Vol. 48, 2003, pp. 3325-3332.

[11] X.Zhang, G-y. Xiao, C-c.Jiang, Bing.Liu, N-b.Li, R-f. Zhu, Y-p.Lu, Influence of process parameters on microstructure and corrosion properties of hopeite coating on stainless steel. Corros. Sci.,Vol. 94, 2015, pp. 428-437.

[12] F. Li, G.Wang,A Black Phosphate Conversion Coating on Steel Surface Using Antimony(III)-Tartrate as an Additive. J. Mater. Eng. Perform. Vol. 25, 2016, pp.1864-1869.

[13] X. Ding, L. Xue, X-Ch. Wang, K-H. Ding, S-L. Cui, Y-C. Sun, M-S. Li,Influence of bath PH value on microstructure and corrosion resistance of phosphate chemical conversion coating on sintered Nd–Fe–B permanent magnets. J. Magnet. Magnetic. Mater.Vol. 416, 2016, pp.247-255.

[14] K. Abdalla, A. Rahmat, A. Azizan, The Effect of pH on Zinc Phosphate Coating Morphology and its Corrosion Resistance on Mild Steel. Adv. Mater. Research. Vol. 626, 2013, pp. 569-574.

[15] L.J.Boucher,L.Gmelin, K. Koeber, D. Tille, Gmelin handbook of inorganic chemistry, in: Mn-Manganese, D4toD8:Coordination Compounds, 8th ed", Springer, Heidelberg, Germany. 1988.

[16] F. Mangolini, L. Magagnin, P. L. Cavalloti, Pulse plating of Mn–Cu alloys on steel. J. Electrochem. Soc.,Vol. 153, 2006, pp.623-628.

[17] S. R. Taylor, Encyclopedia of Materials: Science and Technology, Coatings for Corrosion Protection: Inorganic,Elsevier, Virginia, Usa. 2001, 1263-1269.

[18]T.S. N. Sankara Narayanan, Surface pretreatment by phosphate conversion coatings. Rev. Adv. Mater. Sci., Vol. 9, 2005, pp. 130–177.

[19] L. Fang, L.Xie,Study on the growth and corrosion resistance of manganese phosphate coatings on 30CrMnMoTi alloy steel. Physics Procedia. Vol. 18, 2011, pp. 227–233.

[20] F. Fang, J. Jiang, Characteristics of a fast low-temperature zinc phosphating coating accelerated by an ECO-friendly hydroxylamine sulfate. Surf. Coat. Technol., Vol. 204, 2010, pp.2381–2385.

[21] Y.Su,Y.Guo,Z.Huang,Z.Zhang,G. Li, J. Lian, L.Ren,Preparation and corrosion behaviors of calcium phosphate conversion coating on magnesium alloy. Surf. Coat. Technol., Vol. 307, 2016, pp. 99-108.

[22] H.Y. Su, C-S. Lin, Effect of additives on the properties of phosphate conversion coating on electrogalvanized steel sheet, Corros. Sci.,Vol. 83, 2014, pp. 137-146.

[23] B-L. Lin, J-T. Lu, G. Kong, Effect of molybdate post-sealing on the corrosion resistance of zinc phosphate coatings on hot-dip galvanized steel. Corros. Sci.,Vol. 50, 2008, pp. 962-967.

[24] L. A. Oliveira, O. V. Correa,A. A. Z. Páez, M. C. L. Oliveira, R. A. Antunes, Effect of silicate-based films on the corrosion behavior of the API 5L X80 pipeline steel. Corros. Sci.,Vol. 139, 2018, pp. 21-34.

[25] D. Huang, J. Hu, G-L. Song, X. Guo, Inhibition effect of inorganic and organic inhibitors on the corrosion of Mg–10Gd–3Y–0.5Zr alloy in an

ethylene glycol solution at ambient and elevated temperatures. Electrochim. Acta.,Vol. 56, 2011, pp. 10166-10178.

[26] I.D.Raistrick, D.R. Franceschetti, J.R.Macdonald, Impedance Spectroscopy Theory, Experiment, and Application. John Wiley & Sons, New Jersey. 2005.

[27] M.A. Amin, K.F.Khaled, Q. Mohsen, H.A. Arida, A study of the inhibition of iron corrosion in HCl solutions by some amino acids. Corros. Sci.,Vol. 52, 2010, pp. 1684–1695.

[28] J. Bajat, V. B. MiškovicStankovic, N. Bibic, D. M. Drazic, The influence of zinc surface pretreatment on the adhesion of epoxy coating electrodeposited on hot-dip galvanized steel. Prog. Org. Coat.,Vol. 58, 2007, pp. 323-330.

[29] J. Bajat, V. B. MiškovicStankovic, J. P. Popic, D. Drazic, Adhesion characteristics and corrosion stability of epoxy coatings electrodeposited on phosphated hot-dip galvanized steel. Prog. Org. Coat.,Vol. 63, 2008, 201-208.