Evaluation of porosity and discontinuities in zinc phosphate coating by means of voltametric anodic dissolution (VAD)

E.P. Banczek [a,*], P.R.P. Rodrigues [b], I. Costa [a]

[a] Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN-SP, Centro de Ciência e Tecnologia de Materiais, São Paulo, Brazil
[b] Universidade Estadual do Centro-Oeste, Departamento de Química/Unicentro-Guarapuava, Brazil

A B S T R A C T

In this study, the porosity and the presence of discontinuities, such as cracks, in zinc phosphate coatings were evaluated by the voltametric anodic dissolution (VAD) method. Zinc phosphate (PZn), zinc phosphate with niobium (PZn+Nb), and zinc phosphate with ammonium niobium oxalate (Ox) and benzotriazole (PZn+Ox+BTAH) coatings deposited on SAE 1010 carbon steel were investigated. Coating porosity was evaluated by estimating the charge densities associated with the substrate passivation process for samples with a phosphate layer and comparing the results to the charge densities for passivation of the same substrate without a coating phosphate layer. Weight loss measurements, induced coupled plasma optical emission spectroscopy (ICP-OES), and scanning electron microscopy (SEM) were also used to investigate the solubility of the phosphate layers tested. The electrolytes used were four buffer solutions with pHs of 7.0, 8.0, 10, and 12. Scanning rates of 30, 50, 100, and 150 mV s^{-1} were used in the VAD tests. The porosities of the PZn, PZn+Nb, and PZn+Ox+BTAH layers were estimated by VAD to be 4.35, 1.96, and 1.37%, respectively. The lower porosities of the PZn+Nb and PZn+Ox+BTAH layers are related to their morphologies, which promote better surface coverage compared to the PZn layer.

1. Introduction

Phosphating is a surface treatment process used to prepare a surface prior to the deposition of a corrosion protection layer on metallic surfaces [1]. The phosphate layers are composed of numerous crystals of different sizes that nucleate and grow from small nuclei to cover the metallic substrate. Unfortunately, phosphate crystal growth produces cracks and pores that are inherent to the layer formation [2].

Low coating porosities are usually associated with low corrosion rates of the substrate. Consequently, the presence of pores or cracks in the coatings is detrimental to the substrate corrosion resistance [3]. Thus, techniques to evaluate the porosity and characterize the coating properties of these phosphate coatings are valuable for establishing proper conditions for the deposition of high quality coatings.

Porosity tests provide the number of pores per unit area of coating or the area of exposed substrate through pores [4]. The number of pores per area of phosphate coating is commonly determined by qualitative techniques. Many studies have investigated different kinds of porosity tests [2,5–7]. Many of these tests are based on the ability of the substrate to react with the environment under specific conditions. The surface can be attacked by certain reagents to forms identifiable colored compounds. In this particular case, the number of colored

points can be microscopically observed, counted, and the porosity estimated as the number of colored points per coated surface area.

Porosity evaluation methods can be divided in two types: (i) methods in which individual pores are determined by physical, chemical, or electrochemical evaluation and (ii) methods through which the total porosity is investigated by gas permeation or chemical and electrochemical analysis [7].

Electrochemical methods are adequate for evaluating the effective porosity, the area of exposed substrate underneath the pores, and defects in the coating. Several methods have been used to quantitatively evaluate phosphate coating porosity, such as:

1) polarization resistance measurements [3,8–11],
2) potentiodynamic polarization measurements [4,9,12–16],
3) electrochemical impedance spectroscopy (EIS) [16–18],
4) corrosion potential (E_{corr}) measurements [11,16,18],
5) corrosion current (i_{corr}) measurements [11,16,18], and
6) chronoamperometry [17].

Among the electrochemical methods used for porosity evaluation, special attention is given in this study to the voltametric anodic dissolution (VAD) technique. This technique is based on the dissolution and passivation of a coated or uncoated metallic surface [7,13]. In this method, coated and uncoated substrates are anodically polarized, and the charge densities associated with their passivation regions are compared.

* Corresponding author. IPEN/CNEN-SP (CCTM), Av. Prof. Lineu Prestes, 2242, CEP 05508-900, São Paulo, SP, Brazil. Tel.: +55 11 3816 9356; fax: +55 11 3816 9370.
E-mail address: edopradobanczek@yahoo.com.br (E.P. Banczek).

Table 1
Chemical composition of SAE 1010 carbon steel used as substrate for phosphating

Element	Composition (wt.%)
C	0.118
Si	0.023
Mn	0.310
P	0.020
S	0.016
Cr	0.024
Ni	0.028
Mo	0.002

Compared to other methods, VAD can quickly and quantitatively evaluate coating porosity, and is able to evaluate the discontinuities in metallic coatings associated with porosities or cracks in non-metallic coatings deposited on metal surfaces [12]. This porosity evaluation method has been used in the investigation of various types of coatings on metals in the literature, including phosphate coatings [13]. Among the coatings that had their porosities estimated by VAD the following might be mentioned: nickel on copper evaluated in Na_2SO_3 0.5 mol L^{-1} [2], Na_2SO_3, pH = 10 (50 g L^{-1}) [4], and Na_2SO_3 0.4 mol L^{-1} [12]; titanium and chromium carbide, titanium carbides (TiC–TCN–TiN, TiC, TiN, $Cr_7C_3 + Cr_{23}C_6TiC + Co + CO_3W_3C$) on W–Co, TiCN–Ni–Mo and W–Co tested in K_2SO_4 0.5 N [5], samples of AISI 4135 steel coated with Al, Ti, TiN and CrN tested in NaCl 3% solution [6]. Coatings on carbon steel have also been evaluated by VAD technique, for instance: tungsten/ nickel/cobalt carbide and chromium deposited on 1020 carbon steel tested in KOH 0.1 and 1 mol L^{-1} solutions [14,19]. The porosity of $(Ti_{0.83}Al_{0.17})N$, $(Ti_{0.67}Al_{0.33})N$, $(Ti_{0.85}nB_{0.15})N$ and $(Ti_{0.70}Nb_{0.30})N$ coatings deposited on carbon steel was also estimated by VAD in HCl 2×10^{-3} molL^{-1}.

The aim of the present study is to quantitatively estimate the porosity of three different types of zinc phosphate coatings deposited on carbon steel (SAE 1010) by the VAD method.

2. Experimental

2.1. Sample preparation

Carbon steel SAE 1010, whose composition is described in Table 1, was used as a substrate for the phosphate coatings. The geometrical area of the samples was 1.5 cm^2.

The sample surfaces were prepared by grinding with SiC emery paper from #220 up to #600. After grinding, the samples were degreased in a commercial alkaline solution and then rinsed. Next, the sample surfaces were activated by immersion in an alkaline solution

Table 2
Chemical composition of the concentrated phosphating baths

Component (g/L)	PZn	PZn + Nb	PZn + Ox + BTAH
H_3PO_4 (85%)	521.4	521.4	521.4
HNO_3 (33%)	363.3	363.3	363.3
ZnO (99%)	160.0	160.0	160.0
$NiCO_3$ (47%)	5.0	–	–
H_2O_2 (30%)	0.032	0.032	0.032
H_2O	434.4	440.7	440.7
Nb	–	0.136	–

Table 3
Parameters used for phosphating of carbon steel in the diluted baths

Parameters	PZn	PZn + Nb	PZn + Ox + BTAH
Free acidity	1.6	1.6	1.6
Total acidity	28.0	28.0	28.0
Immersion time (min)	5	3	5
Temperature (°C)	25	25	25

Table 4
Chemical composition of the diluted baths after determination of total acidity and free acidity

Component (g/L)	PZn	PZn + Nb	PZn + Ox + BTAH
H_3PO_4 (85%)	19.7	19.7	19.7
HNO_3 (33%)	13.7	13.7	13.7
ZnO (99%)	6.04	6.04	6.04
$NiCO_3$ (47%)	0.18	–	–
H_2O_2 (30%)	0.0012	0.0012	0.0012
H_2O	16.4	16.6	16.6
Nb	–	0.008	–
Ox	–	–	0.024
BTAH	–	–	1.2

of titanium phosphate salt at a concentration of 3 g/L (pH = 7.5 to 9.0), for 90 s at (25 ± 2) °C. Subsequently, the samples were immersed in either zinc phosphate (PZn), zinc phosphate with the addition of niobium (PZn + Nb), or zinc phosphate with ammonium niobium oxalate (Ox) and benzotriazole (BTAH) (PZn + Ox + BTAH). The chemical composition of the various solutions and the immersion conditions are summarized in Tables 2, 3 and 4, respectively.

The weight of the phosphate layer was determined by solubilization of the deposited layer. After phosphating, the samples were dried and weighed, obtaining m_1. Subsequently, the deposited phosphate layer was dissolved in a 0.5 g L^{-1} chromium trioxide solution for 15 min at (75 ± 5) °C, and then the samples were weighed again, obtaining (m_2) according to procedure described in ASTM B767-88 [20]. The phosphate layer weight ($m_{phosphate}$) was estimated by Eq. (1):

$$m_{phosphate} = \frac{m_1 - m_2}{A} \tag{1}$$

where m_1 is the phosphated sample weight, m_2 is the sample weight after phosphate layer dissolution, and A is the surface area exposed to the phosphating bath.

The phosphating process was carried out according to the stages:

1) Alkaline degreasing at 70 °C, t = 5 min;
2) Rinsing at ambient temperature, t = 1 min;
3) Refining at 25 °C, t = 90 s;
4) Phosphating at 25 °C, t = 5 min;
5) Rinsing at ambient temperature, t = 1 min;
6) Weighing using analytical balance (m_1);
7) Immersion in CrO_3 0.5 g L^{-1} solution
8) Rinsing at ambient temperature, t = 1 min;
9) Weighing using analytical balance (m_2).

The baths used for phosphating were prepared by the dilution of more concentrated species (Table 2), followed by the addition of sodium hydroxide (NaOH 50%). The free and total acidities were determined by titration of the diluted bath using NaOH with a

Table 5
Chemical composition of buffer solutions used in phosphate porosity evaluation

pH	Composition		
	NaOH (0.1 mol L^{-1})	KH_2PO_4 (0.1 mol L^{-1})	Na_2HPO_4 (0.1 mol L^{-1})
7.0	296.3 mL	500.0 mL	–
8.0	468.0 mL	500.0 mL	–
10.0	150.0 mL	–	500.0 mL
12.0	500.0 mL	–	500.0 mL

Table 6
Mean weight of phosphate layers obtained at various immersion times

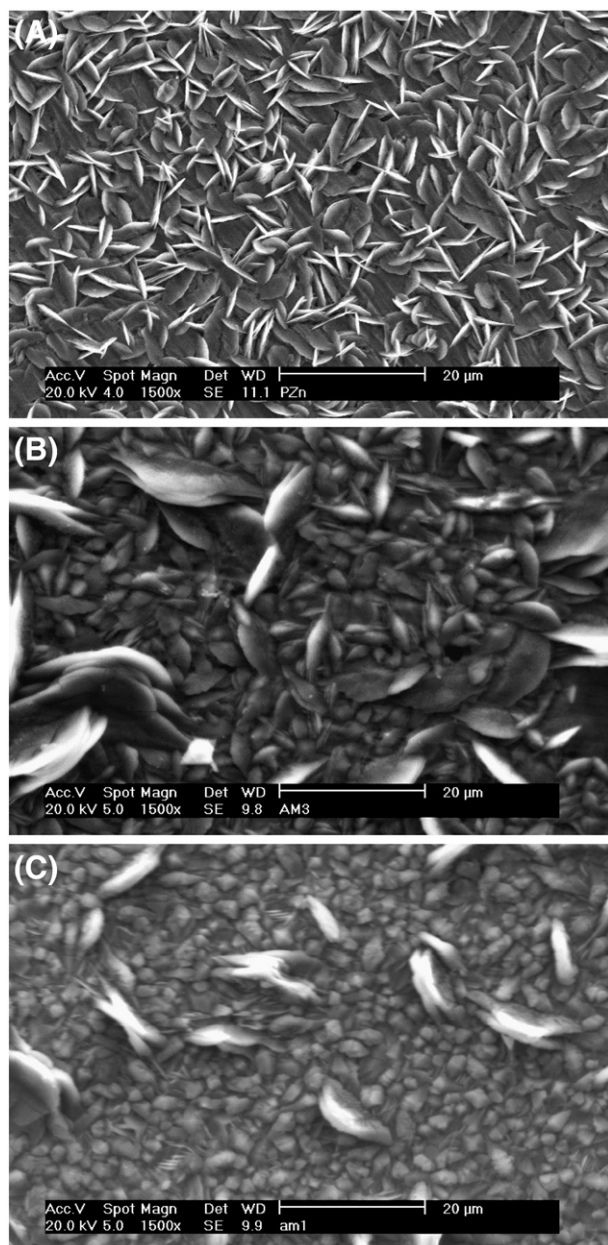| Parameters	PZn	PZn + Nb	PZn + Ox + BTAH
Immersion time (min)	5	3	5
Weight (g/m^2)	2.13	2.38	3.56

Fig. 1. SEM micrographs of SAE 1010 carbon steel phosphated in (A) PZn, (B) PZn+Nb, and (C) PZn+Ox+BTAH baths.

concentration of 0.1 mol L^{-1}. The time of immersion employed to obtain the phosphate layers was experimentally determined [21].

For the preparation of the PZn+Ox+BTAH bath, 0.024 gL^{-1} of niobium and ammonium oxalate and 10^{-2} mol L^{-1} of benzotriazole (BTAH) were added to the diluted PZn bath after total acidity and free acidity determination (Table 4).

The coating morphology and evaluation of the steel substrate coverage by the obtained phosphate layers were evaluated by SEM.

Table 7
Semi-quantitative composition of the obtained phosphate layers

Phosphate layer	Elements (wt.%)		
	Zn	Fe	P
PZn	23.4±2.6	67.7±3.5	8.9±1.2
PZn+Nb	25.1±1.0	64.2±2.3	10.0±0.6
PZn+Ox+BTAH	28.3±2.5	61.4±2.9	10.3±0.5

Table 8
Weight loss of the phosphate layers in the buffer solutions tested

Phosphate layer	pH	Weight loss (g/m^2)	Standard deviation
PZn	7.0	0.416	±0.094
	8.0	0.282	±0.092
	10.0	1.938	±0.177
	12.0	2.261	±0.624
PZn+Nb	7.0	0.553	±0.032
	8.0	0.243	±0.059
	10.0	0.632	±0.165
	12.0	0.894	±0.334
PZn+Ox+BTAH	7.0	0.449	±0.028
	8.0	0.328	±0.039
	10.0	0.932	±0.053
	12.0	1.336	±0.552

All the solutions used in this study were prepared with analytical grade chemical reagents and deionized water. The niobium added to the PZn+Nb bath was obtained by the alkaline fusion of 1 g of Nb$_2$O$_5$ and 5 g KOH [22]. The compound obtained by alkaline fusion is composed of niobates, specifically KNbO$_3$ and K$_4$Nb$_6$O$_{17}$ [22].

The test parameters for the evaluation of porosity of the various phosphate layers were obtained for the PZn coating using the VAD method.
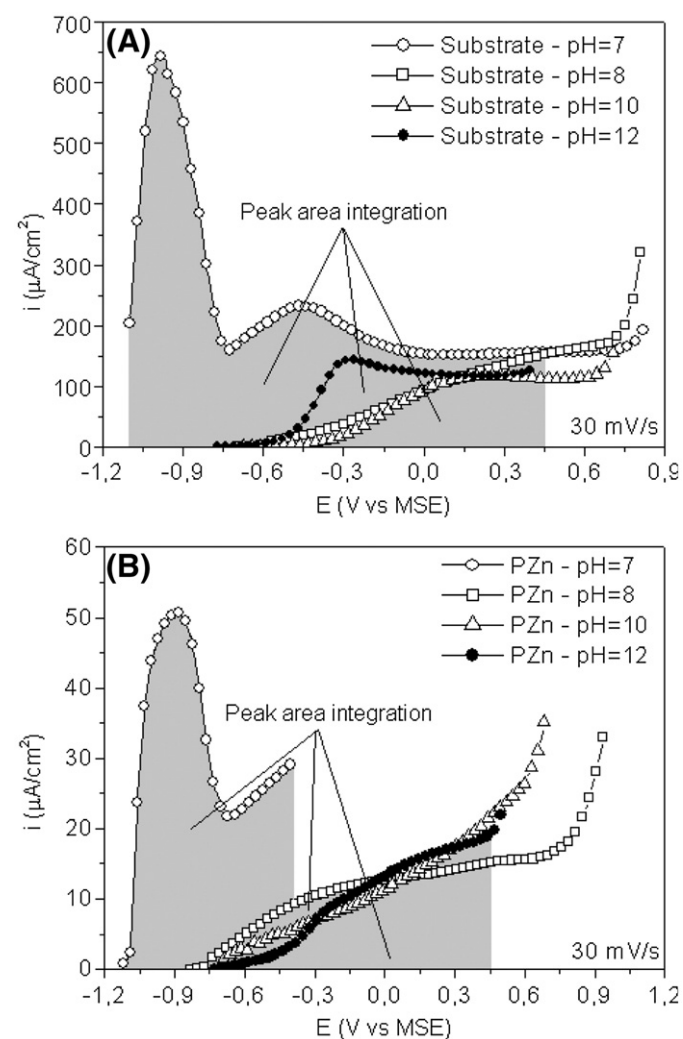

Fig. 2. Voltametric anodic dissolution (VAD) curves obtained for (A) uncoated and (B) PZn coated carbon steel.

2.2. Concerning the evaluation of the porosity

The porosity of the phosphate layer was quantitatively estimated using the VAD method. Charge density values, corresponding to the area of the peak in the I vs. E curve due to substrate passivation, were used in the coating porosity evaluation, which was estimated by integrating the area under the peak [7,13].

The following conditions must be fulfilled to validate the results of this technique: (i) the substrate must passivate in the solution used for porosity evaluation, (ii) the substrate must passivate during anodic polarization, and (iii) the coating must be inert or highly resistant to chemical attack in the potential range of substrate passivation used in the porosity evaluation to guarantee that the current related to the i vs. E peak is due to the substrate passivation exposed at the base of the coating porosities [7,12,13,19].

The charge densities due to the passivation of exposed substrate and uncoated carbon steel were compared and the coating porosity was determined using Eq. (2):

$$\theta = \frac{Q_P}{Q_P^o} \times 100 \tag{2}$$

where

Q_P is the charge due to the passivation of the coated substrate,
Q_P^o is the charge due to the passivation of the uncoated substrate, and
θ is the coating porosity.

Only the PZn coating was used for testing the conditions that must be obeyed to validate the VAD technique.

The chemical composition of the solutions used as electrolytes is shown in Table 5. The test solutions were buffered to pHs of 7.0, 8.0, 10.0, and 12.0, that is, in a pH range where the phosphate coatings have a low solubility [23]. The solutions were quiescent and the tests were carried out at (20 ± 2) °C.

The VAD tests were conducted in the potential range from E_{corr} up to 2 V vs. E_{corr}, with scan rates of 30, 50, 100, and 150 mV s^{-1}. The tests started after 60 min of immersion in the electrolyte.

In the electrochemical tests, a mercurous sulphate electrode (MSE) and a platinum wire were used as reference and auxiliary electrodes, respectively.

The electrochemical tests were carried out using a GAMRY PCI4/300 potentiostat. The software, *Echem Analyst*, was used for peak area integration at an overpotential of 1.4 V relative to E_{corr} once at this overpotential the samples were passive.

2.3. Coatings characterization

The morphology characterization of the phosphate layers was investigated by Scanning Electron Microscopy (SEM) using a Philips XL30 microscope and the method used for composition evaluation was Energy Dispersion Spectroscopy (EDS).

2.4. Evaluation of the phosphate coating solubility

The solubility of the phosphate coatings was evaluated by gravimetric tests in the aforementioned four buffer solutions. The samples used in this evaluation were prepared as described in Section 2.1. These were immersed in the test buffer solutions for 60 min.
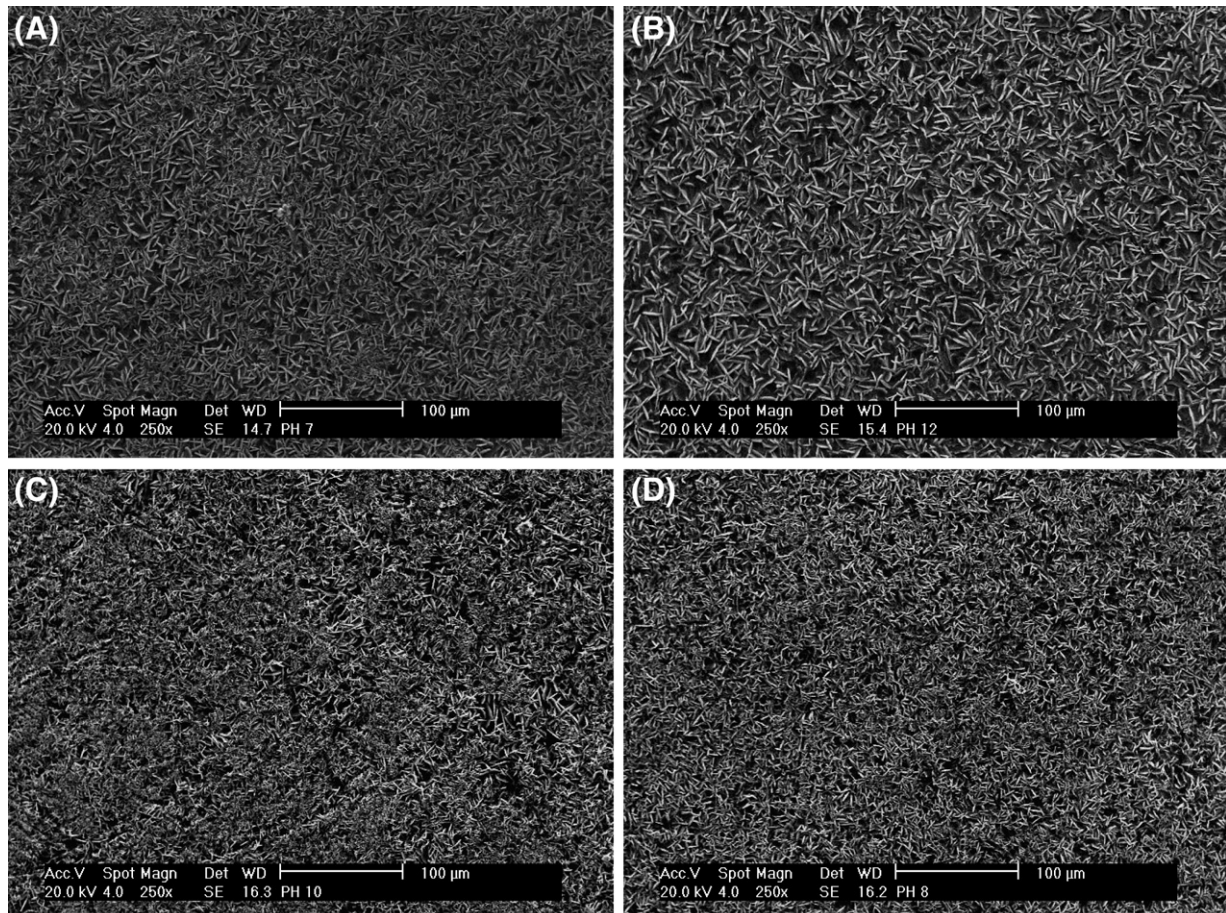

Fig. 3. SEM micrographs of the phosphated (PZn) carbon steel surface after polarization test. (A) pH=7.0, (B) pH=8.0, (C) pH=10.0, and (D) pH=12.0.

3. Results and discussion

3.1. Weight of deposited phosphate layers

The weight of the deposited phosphate layers and the time necessary for each layer *stabilization* were determined [21] and the results obtained are presented in Table 6.

The weight of the phosphate layers increased in the following order: PZn, PZn+Nb and PZn+Ox+BTAH, suggesting that the niobium compounds lead to the increase in the mass deposited. This result might be explained by the greater acceleration necessary for phosphating in these baths [21].

3.2. Morphology and composition

SEM micrographs of the various phosphate layers studied (PZn, PZn+Nb and PZn+Ox+BTAH) are shown in Fig. 1.

The phosphate coating deposited from the PZn bath shows a predominance of needle like crystals [24,25], as depicted in Fig. 1(A), whereas the coating deposited from the PZn+Nb solution exhibits platelet-like grains, as depicted in (Fig. 1(B)). The latter morphology promotes better substrate coverage than that of the former. The morphology of the coating deposited from the PZn+Ox+BTAH bath, as depicted in Fig. 1(C), exhibited a prevalence of smaller rounded grains, with few platelets, which improved the quality of the surface coverage in comparison to the surface morphologies of the other two coatings. Based on the morphological analysis, it is expected that the phosphate coating porosity should decrease in the order of PZn, PZn+Nb, and PZn+Ox+BTAH. It has been reported [3] that the PZn coatings are highly porous and the porosity is due to the morphology of their phosphate crystals.

The composition of the phosphate layers is shown in Table 7. It shows that the phosphate is mainly composed of Fe, Zn and P. The increased amounts of Zn in the PZn+Nb and PZn+Ox+BTAH layers, comparatively to the PZn one, might be associated to their different morphologies, as it has already been proposed in literature [26].

Another possible reason for the morphology of the phosphate layers obtained in Nb containing baths, is their larger amounts of $Zn_2Fe(PO_4)_2 \cdot 4H_2O$ (*phosphophyllite*). This last phase which was detected by X-ray diffraction, might change the crystals morphology from hexagonal needles to grain shape types [21].

3.3. Evaluation of the layer dissolution

The mean and standard deviation of the weight loss measurements obtained from gravimetric testing of the phosphated samples immersed for 60 min in each of the solutions with pHs of 7.0, 8.0, 10.0, and 12.0, are shown in Table 8. Each measurement was conducted in quadruplicate.

The results of Table 8 indicate that the zinc phosphate coatings exhibited the lowest solubility in solutions with pHs of 7.0 and 8.0 and lowest weight loss in the solution with a pH of 8.0. Other studies in the literature [23] have reported that phosphate is stable in a pH range of 4.0 to 10.0.

The weight loss results presented in Table 8 show that all three phosphate layers obtained have high resistance to corrosive attack in the buffer solution of pH 8.0. The three phosphate layers studied showed similar and low weight losses indicating their low solubility in
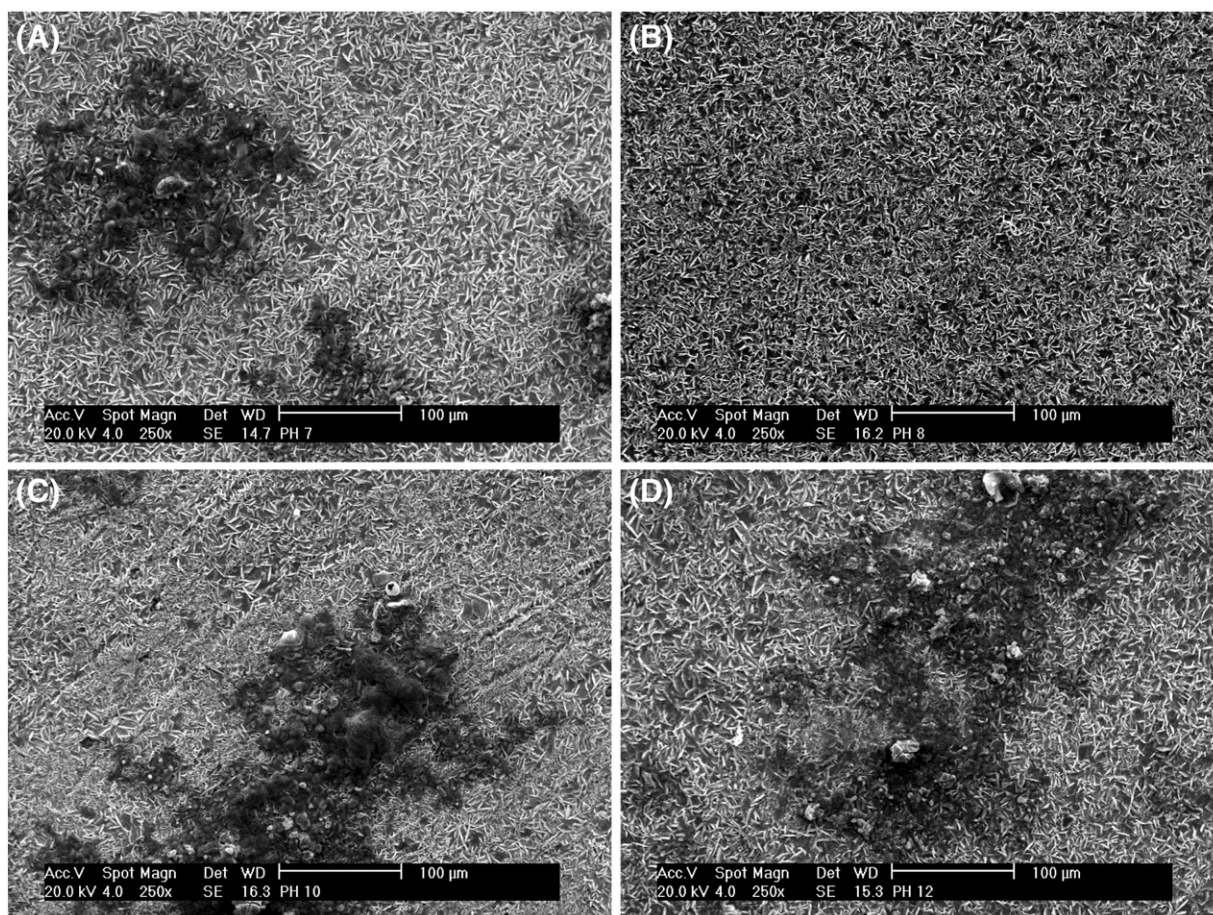

Fig. 4. SEM micrographs of the phosphate layers (PZn) showing areas attacked during polarization in the buffer solutions of (A) pH = 7.0, (B) pH = 8.0, (C) pH = 10.0, and (D) pH = 12.0.
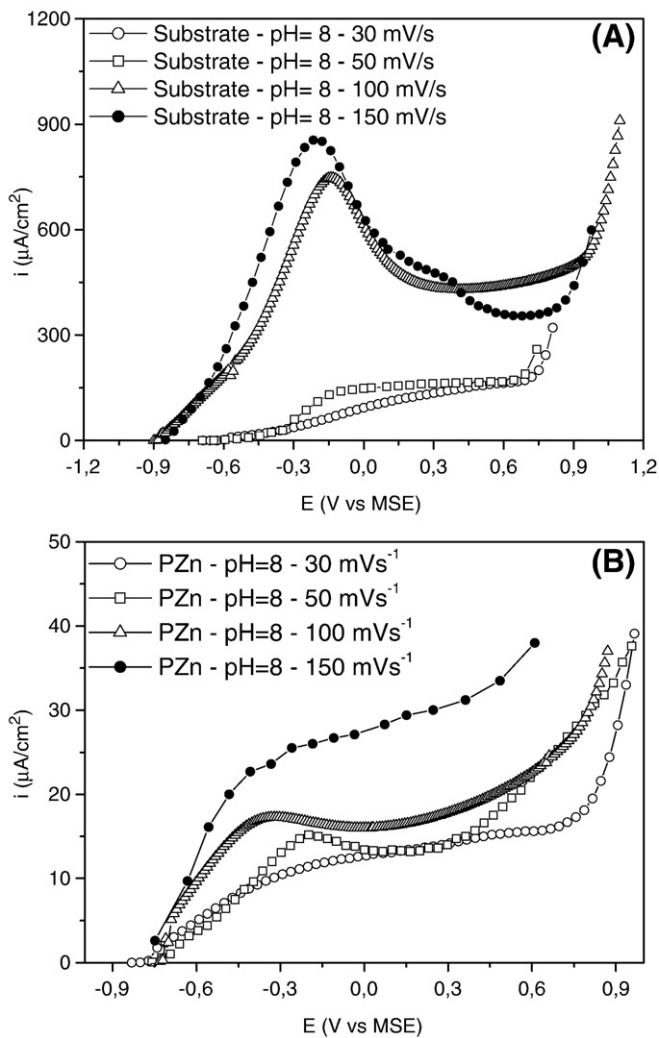
Fig. 5. Voltametric anodic dissolution (VAD) curves obtained for (A) uncoated and (B) PZn coated carbon steel.

this solution. The PZn layer was used in the tests for selection of the experimental conditions to evaluate the porosity of phosphate layers.

3.4. Selection of test solution

Anodic polarization curves were obtained for coated substrate and uncoated steel in order to select a proper buffer solution for porosity evaluation from the ones tested. A scan rate of 30 mV s^{-1} was used in this test. The anodic polarization curves obtained are depicted in Fig. 2(A) and (B) for a bare steel substrate and PZn coated steel, respectively.

Fig. 2(A) depicts two anodic peaks from the anodic polarization scan of the uncoated carbon steel in the solution with a pH of 7.0, which are related to its dissolution and subsequent passivation. The first peak, observed at approximately −1.0 V, corresponds to the Fe→Fe (II) reaction, and the second peak, observed at a potential of −0.45 V, corresponds to the Fe (II)→Fe (III) reaction.

Fig. 2(B) depicts the anodic polarization curves for the PZn coated steel. No anodic peak was evident in electrolytes with pHs of 8.0, 10.0, and 12.0, while a unique anodic peak was observed at a potential of approximately −0.9 V in the solution with a pH 7.0. The corrosion potential increased with an increase in pH, owing to the passivating effect of the oxide layer which was favored by the increase in pH. Ponte et al. [13] associated this effect in coated samples to the ohmic drop of the phosphate layer.

The solution with a pH of 8.0 was selected for the porosity evaluation, primarily because the phosphate layer associated with it was the most inert among all the phospate coatings investigated. The resistance of this particular phosphate layer to attack from this solution was confirmed by SEM observation. In contrast, the coatings immersed in solutions with a pH of 7.0, 10.0, and 12.0 exhibited signs of corrosive attack, as depicted in Figs. 3 and 4.

SEM micrographs of the phosphated and polarized samples in the four aforementioned electrolytes (Fig. 4) clearly show signs of corrosive attack with phosphate coating dissolution on the samples tested in the solutions with pHs of 7.0, 10.0, and 12.0. The only sample that did not exhibit attack was the sample tested in the solution with a pH of 8.0.

The phosphate layer is firstly attacked, once the pH range adopted for the test solutions corresponds to the limit range of phosphate stability. It is proposed that corrosive attack occurs at some weak points of the phosphate layer and, subsequently, the substrate is attacked.

Using weight loss measurements, Shoeib et al. [23] also observed that phosphate coatings exhibit a low solubility in solutions with a pH of 8.0, further supporting the results obtained in this report.

Based on the results of the present study, a buffered solution with a pH of 8.0 was selected for the porosity evaluation of the aforementioned types of phosphate coatings.

3.5. Selection of the scan rate for porosity evaluation

The selected scan rate for the evaluation of coating porosity impacts the test results by influencing the active–passive transition peak resolution, that is, a higher scan rate usually provides a better peak resolution. In this study, the impact of the VAD test scan rate on the porosity testing was investigated using a buffer solution with a pH of 8.0. Scan rates of 30, 50, 100, and 150 mV s^{-1}, were tested. The subsequently obtained VAD polarization curves are depicted in Fig. 5.

Fig. 5 confirms that the resolution of the *i* vs. *E* anodic peak is strongly impacted by the scan rate, and therein, the peak resolution increases with the scan rate. The *i* vs. *E* peak is poorly defined for the uncoated steel sample at scan rates less than 100 mV s^{-1} (Fig. 5(A)), suggesting that scan rates less to 100 mV s^{-1} are inappropriate. For the phosphated samples, an anodic peak is defined only for the samples polarized at 50 and 100 mV s^{-1}. For coated and uncoated samples, the anodic peak was observed to occur at potentials around −0.20 V vs. the mercurous sulphate electrode. Based on these results, a scan rate of 100 mV s^{-1} was selected for the polarization evaluation test (Fig. 5(B)).

The low current density values, on the order of 10^{-5}–10^{-6} A cm^{-2}, obtained in the entire polarization range of the phosphated steel are
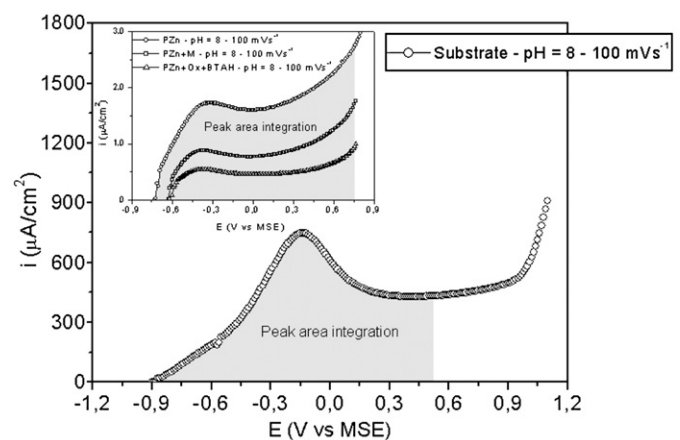

Fig. 6. Voltametric anodic dissolution (VAD) curves obtained for (A) uncoated and (B) coated carbon steel.

Table 9
Charge density and porosity values of the various phosphate layers obtained

Sample	Charge density	Porosity
	$(\mu C/cm^2)$	θ (%)
Steel substrate	6750±385	–
PZn	294.0±34.9	4.35
PZn+Nb	132.5±28.4	1.96
PZn+Ox+BTAH	92.5±22.5	1.37

The experimental data were estimated from the polarization curves obtained in the buffer solution of pH 8.0 with a scan rate of 100 mV s^{-1}.

typical for passive materials, which validates the use of high scan rates in this investigation.

3.6. Porosity evaluation

Fig. 6 shows the polarization curves of uncoated and carbon steel phosphated in the PZn, PZn+Nb, and PZn+Ox+BTAH solutions.

The charge density values, estimated by integration of the active–passive peak in the polarization curves of Fig. 6, are shown in Table 9.

The experimental results of Table 9 demonstrate that the porosity of the phosphate layer decreases in the following order PZn, PZn+Nb, and PZn+Ox+BTAH, as previously suggested by morphology observations of the various phosphate coatings.

The results obtained in this study confirm previous findings [3,13,16,18], which report porosity values for phosphate coatings in the range of 2 to 10%.

4. Conclusions

The voltametric anodic dissolution (VAD) technique is an efficient method for evaluating phosphate layer porosity quantitatively in significantly less compared to other methods.

Various VAD solutions and scan rates were tested for optimal porosity assessment, and the results indicated that a buffer solution with a pH of 8.0 (NaOH (0.1 mol L^{-1}) and KH$_2$PO$_4$ (0.1 mol L^{-1}) and a scan rate of 100 mV s^{-1} provided an assessment with the highest resolution.

The phosphate coatings deposited on carbon steel substrates by immersion in different phosphating baths exhibited different morphologies and also had significantly different porosities. The lowest coating porosity was associated to the coating produced from the solution composed of zinc phosphate with ammonium niobium oxalate and benzotriazole (PZn+Ox+BTAH), whereas the highest porosity was observed in the zinc phosphate (PZn) coating. The addition of Nb to phosphating baths decreased the porosity of the obtained coatings.

References

[1] S. Rebeyrat, J.L. Grosseau-Poussard, J.F. Silvain, B. Panicaud, J.F. Dinhut, Appl. Surf. Sci. 199 (2002) 11.
[2] G. Lorin, Phosphating of Metals, Finishing Publications, Middlesex, 1974.
[3] D. Weng, P. Jokiel, A. Uebleis, H. Boehni, Surf. Coat. Technol. 88 (1996) 147.
[4] A.M. Maul, Porosity analysis of coatings on metallic surfaces by electrochemical techniques, MSc dissertation, Universidade Federal do Parana, Curitiba, 2001, 224 pp. *In Portuguese*.
[5] I.Y. Konyashin, T.V. Chukalovskaya, Surf. Coat. Technol. 88 (1996) 5.
[6] J. Creus, H. Mazille, H. Idrissi, Surf. Coat. Technol., 130 (2000) 224.
[7] H.A. Ponte, A.M. Maul, J. Appl. Electrochem., 32 (2002) 641–646.
[8] M.S. Frant, J. Electrochem. Soc. 8 (1961) 774.
[9] V.F. Cunha, M.M.R. Castro, G.F.A. Reis, C.R. Araujo, T. Matencio, The use of electrochemical impedance spectroscopy in the evaluation of porosity of phosphate conversion coatings on galvanized steels, Proceedings of EUCORR 2005, 2005, Portugal.
[10] E.B. Mathes, J. Aromaa, H. Ronkainen, S.P. Hannula, A. Leyland, A. Matthews, Surf. Coat. Technol., 49 (1991) 489.
[11] I.M. Notter, D.R. Gabe, Corros. Sci. 5 (1993) 851.
[12] A.M. Maul, H.A. Ponte, Analysis for electrochemical technique of the coatings porosity on metallic surfaces, Proceedings of the Brazilian Congress of Mechanical Engineering and Proceedings of XV Brazilian Congress of of Mechanical Engineering, Águas de Lindóia, Brazil, November 1999, (In Portuguese).
[13] H.A. Ponte, A.M. Maul, E.A. Alvarenga, Mater. Res. 4 (2002) 439.
[14] H.A. Ponte, L.F. Kaefer, A.C.T. Gomes, Discontinuities analysis in carbides coatings on steel, Proceedings of 6th COTEQ Conference of Technology of Equipments and 22nd CONBRASCORR — Brazilian Corrosion Congress, August 2002. Salvador, Bahia, Brazil, 2002, (In Portuguese).
[15] J.P. Celis, D. Drees, E. Maesen, J.R. Roos, Thin Solid Films 224 (1993) 58.
[16] C.A.L. Santos, E. Leite, A.F. Filho, Z. Panossian, Corros. Prot. Mater. 4 (2006) 114.
[17] F. Vacandio, Y. Massiani, P. Gergaud, O. Thomas, Thin Solid Films 359 (2000) 221.
[18] V.F.C. Lins, G.F.A. Reis, C.R. Araújo, T. Matencio, Appl. Surf. Sci. 253 (2006) 2875.
[19] H.A. Ponte, A.M. Maul, D. Abramchuk, Discontinuities analysis in chrome coatings on steel, Proceedings of 6th COTEQ Conference of Technology of Equipments and 22nd CONBRASCORR — Brazilian Corrosion Congress. August 2002. Salvador, Bahia, Brazil, 2002, (In Portuguese).
[20] American Society for Testing Materials, Standard Guide for Determining Mass Per Unit Area of Electrodeposited and Related Coatings by Gravimetric and Other Chemical Analysis Procedures, , 1988 (ASTM B767-88).
[21] E.P. Banczek, P.R.P. Rodrigues, I. Costa, Surf. Coat. Technol. 202 (2008) 2008.
[22] BR n. PI 0602009-7, 18 jul. 2006, Manufacture of niobium soluble compounds for metallic surface treatments, Universidade Estadual do Centro-Oeste. (In Portuguese).
[23] M. Shoeib, M. Farouk, F. Hanna, Met. Finish. (Sept. 1997) 62.
[24] D. Zimmermann, A.G. Munoz, J.W. Schultze, Electrochim. Acta, 48 (2003) 3267.
[25] P.K. Sinha, R. Feser, Surf. Coat. Technol. 161 (2002) 158.
[26] J.S. ian, G.Y. Li, L.Y. Niu, C.D. Gu, Z.H. Jiang, Q. Jiang, Surf. Coat. Technol., 200 (2006) 5956.