

Niobium pentoxide coating replacing zinc phosphate coating

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ABSTRACT

A new coating made of niobium pentoxide, obtained through the sol-gel process, was developed for the carbon steel (SAE 1010). The corrosion protection provided by this coating was evaluated through electrochemical tests such as: open circuit potential, electrochemical impedance spectroscopy and anodic potentiodynamic polarization in NaCl 0,5 mol L⁻¹ solution. The morphology and composition of the coatings were analyzed using scanning electronic microscopy, energy dispersive spectroscopy and X-ray diffractions. A zinc phosphate coating was used as standard test for comparison of results. The electrochemical measurements revealed that: (1) The Nb₂O₅ coating dislocates the corrosion potential towards more positive values; (2) higher impedance values were found for the Nb₂O₅ coated samples; and (3) lower current density values were found for these samples. The electronic micrograph revealed that there was alteration in the morphology of the carbon steel surface due to the Nb₂O₅ deposition. The EDS spectra confirmed the niobium coating deposition, as a peak regarding this element was obtained in the spectra. The X-ray diffractograms confirmed the presence of the phases in the Nb₂O₅ coating. This new coating increases protection of the carbon steel against corrosion and presents an alternative to replace phosphating.

Keywords: Carbon steel, surface treatment, phosphating.

1. INTRODUCTION

Niobium oxides are new materials, with new applications based on their piezoelectric and ferroelectric properties with promising applications in electromechanics, non-linear optics, and other technological fields, presenting environmental compatibility [1-3]. These compounds can be used for water decomposition in hydrogen and oxygen [4,5]. Photocatalytic properties of niobates have been studied for degradation of dyes employed in textile industries [5].

There are reports on niobium oxides obtained on several materials surfaces [6, 10]. The main methods for deposition of niobium oxides on surfaces described in the literature are: (I) impregnation, in aqueous medium, of ammonium oxaloniobate or niobium acid (niobium oxalate) [11], (II) impregnation, in organic medium, of niobium ethoxide [12], (III) niobium ethoxide anchorage [13], the latter, provides better dispersion of niobia on the support surface, (IV) chemical composition in the steam phase [7], (V) anodic potentiostatic polarization [8], (VI) thermal aspersión [6], (VII) deposition in homogeneous solution [9], (VIII) Pechini method [10], sol-gel process [14]. The niobium pentachloride, in turn is an economically advantageous precursor in relation to the ethoxide and in the literature available there are no references regarding its use as an anchor.

The corrosion is an undesirable process which is present in all areas of human activity and, for this reason; there is great social and economical relevance in its study. It is a surface phenomenon and, due to the great variety of metallic materials used and their different properties of resistance to corrosion, a series of protection processes for metallic surfaces were and have been developed.

Amongst the most employed surface treatment processes, is phosphating [15, 19]. Phosphating is a conversion treatment which enables the surface coating with a phosphate insoluble salt layer, most of the times zinc phosphate [20, 21], aiming at protection against corrosion, preparation for painting, electrical separation, and decoration [20, 21].

In phosphating baths, chemical additives are used which cause problems due to the generation and discharge of residues that are inherent to phosphating process. Amongst the additives mentioned, the one that presents the biggest problems is nickel, as its use makes it difficult to control the residues generated, once this element is hazardous to the environment. Due to environmental problems created, the possibility of substituting phosphating processes by other surface treatments should be studied.

Niobium oxides have been reported in the protection against metallic materials corrosion. The use of conversion coatings containing cerium, zircon, and niobium is reported in the literature [22] for protection of magnesium alloys against corrosion.

Niobium coating obtained through ionic beam was used to protect stainless steel 316L against corrosion. From the conditions employed for the niobium coating deposition, the coated steel 316L presented corrosion behavior similar to the metallic niobium and did not present pitting corrosion (x3).

In this context, this study aims to develop a niobium coating, substituting phosphating, which can improve the corrosion resistance properties for the carbon steel alloy (SAE 1010).

2. MATERIAIS E MÉTODO

2.1 Carbon steel (sae 1010) preparation

Samples of 1,5 cm² carbon steel (SAE 1010) were submitted to sanding with #220, #320, #400, #600 e #1200 grit SiC jig paper, followed by degreasing in a sonicator for 5 min. (in ethanol and water) and drying.

2.2 Obtaining the Nb₂O₅ film

The Nb₂O₅ films were prepared through the Pechini method as presented in the flowchart in Figure 1. The resin preparation was carried out through the dissolution of citric acid (C₆H₈O₇) ethylene glycol (C₂H₄(OH)₂) at 60°C under magnetic agitation with the subsequent addition of niobium ammoniacal complex NH₄[(NbO)(C₂O₄)₂].nH₂O (CBMM). The resulting solution was kept under agitation for 30 minutes.

The Nb₂O₅ films were prepared via deposition through the immersion of samples in resin with a 15-minute immersion time. Later, the samples were treated at 500°C for densification for 30 minutes.

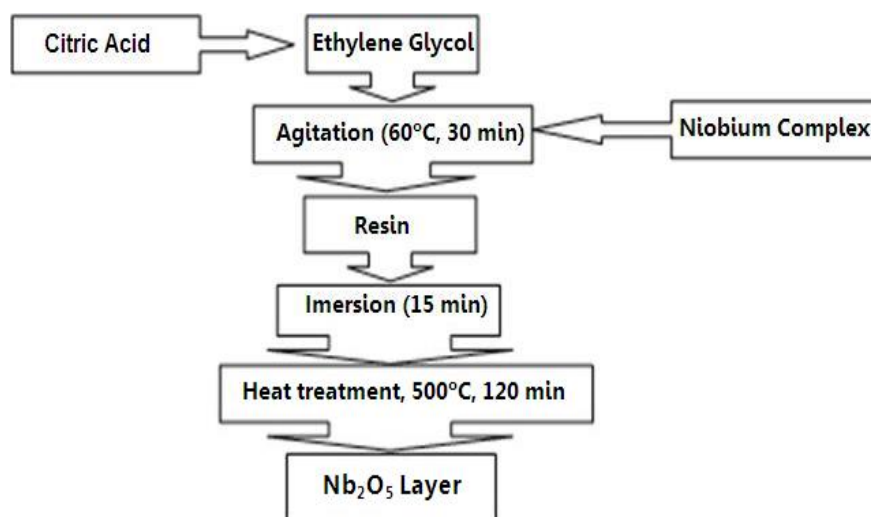


Figure 1. Fluxogram of the method to obtain the Nb₂O₅ film.

2.3 Obtaining zinc phosphate coating

The steel samples were degreased using an alkaline commercial solution. Then, they were immersed for 90 seconds in a solution of a 3 g L⁻¹ titanium phosphate commercial product, at (25 ± 2)°C. Next, the samples were immersed in a zinc phosphate (PZn) bath for 5 minutes at (25 ± 2)°C.

2.4 Surface Characterization

The surface characterization of the carbon steel (SAE 1010) alloy was carried out through scanning electronic microscopy (SEM). The semiquantitative composition was determined through the energy dispersive spectroscopy (EDS).

The niobium pentoxide characterization was carried out using the X-ray diffraction with a Rigaku 117 DEMAX 2000 diffractometer using $\text{CuK}\alpha$ (1.5418 Å) radiation.

2.5 Electrochemical characterization

The electrochemical characterization of the treated and non-treated samples was performed in a NaCl 0,5 mol L⁻¹ solution. The three electrode experimental arrangement was employed. The electrochemical measurements were performed in a frequency response analyzer (Gamry model EIS 300®) coupled to a Gamry PCI4/300® potentiostat and consisted of open circuit potential, electrochemical impedance spectroscopy (EIS) and anodic potentiodynamic polarization.

The impedance diagrams were obtained at the 10 kHz to 10 mHz band, with 10 mV (rms) disturbance amplitude and data acquisition rate of 10 points per decade. Anodic potentiodynamic polarization curves were obtained, after EIS tests, with 1 mVs⁻¹ scanning velocity.

3. RESULTS

3.1 Morphologic characterization

Figure 2 shows the micrographs and EDS spectra, from the carbon steel (SAE 1010) surface, phosphate free and coated with zinc phosphate and Nb₂O₅.

3.2 X-ray diffraction

Figures 3 (A), (B) and 3(C) show the X-ray diffractograms characteristic of the niobium pentoxide Nb₂O₅ and the carbon steel (SAE 1010) coated with Nb₂O₅.

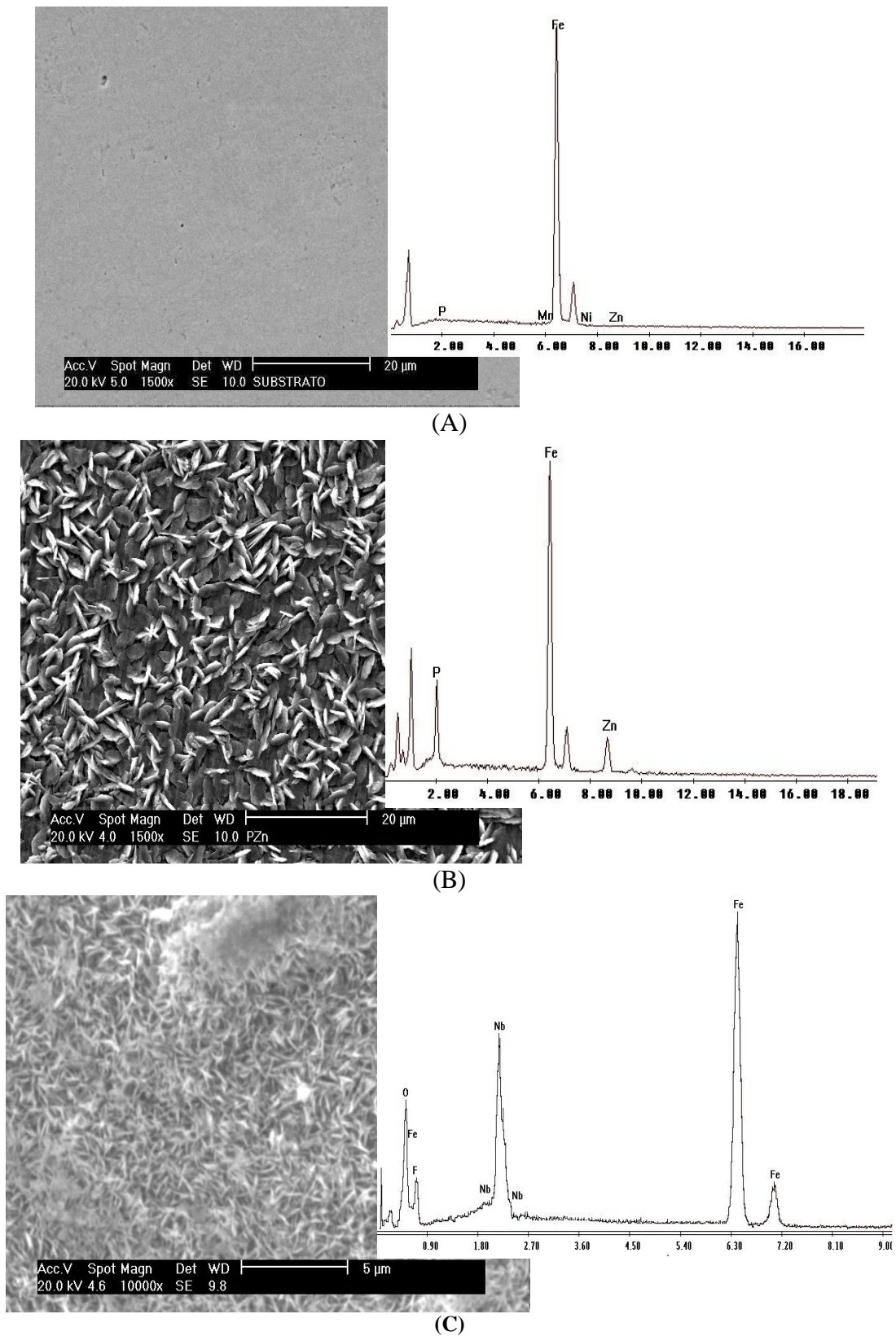


Figure 2. Micrographs obtained through SEM and EDS spectra for the (A) steel (1500x), (B) Steel + PZn (1500x) and (C) Steel + Nb₂O₅ (10000x).

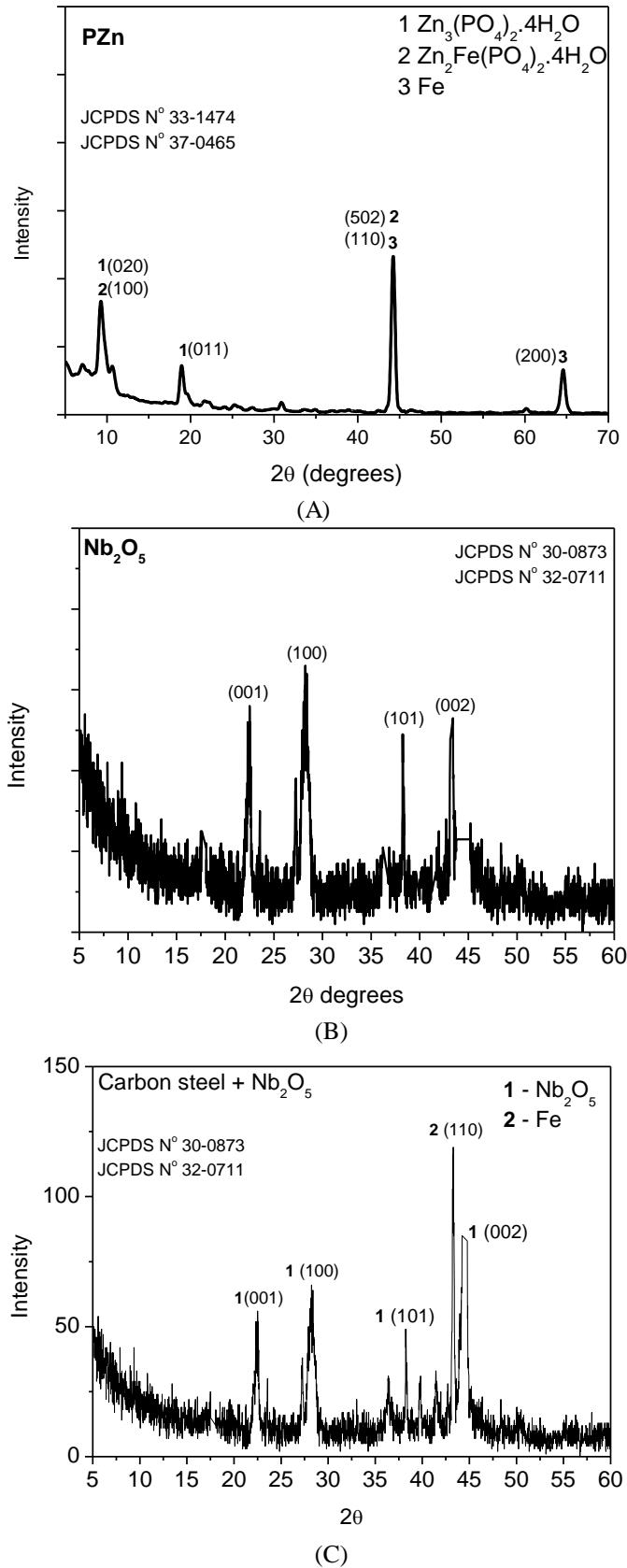


Figure 3. X-ray diffractograms of Nb_2O_5 (A) and the carbon steel (SAE 1010) surface coated with layers of (B) zinc phosphate and (C) Nb_2O_5 .

3.3 Open Circuit Potential

The open circuit potential variation curves of the carbon steel (SAE 1010) in NaCl 0,5 mol L⁻¹ solution, uncoated and covered with the layers, are presented in Figure 4.

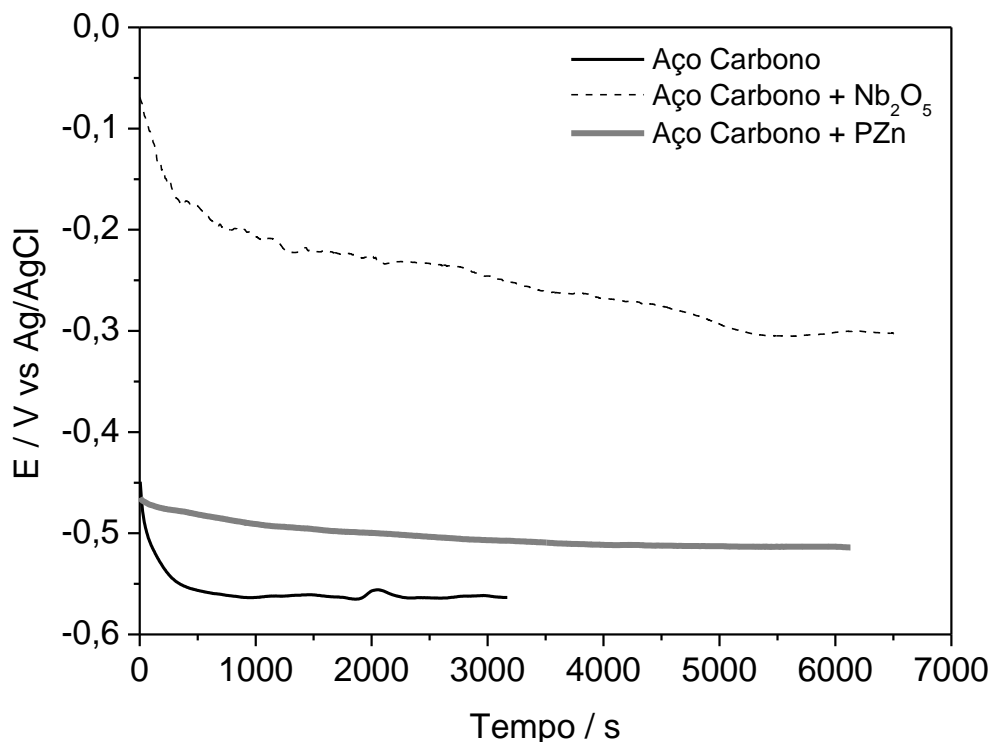


Figure 4. Open circuit potential for the steel samples in NaCl 0,5 mol L⁻¹.

3.4 Electrochemical impedance spectroscopy (EIS)

EIS tests were carried out after the open circuit potential stabilization. Results obtained are shown in Figure 5, as a Nyquist diagram and the Bode phase angle diagram.

3.5 Anodic potentiodynamic polarization curves (APP)

Tests of anodic potentiodynamic polarization, in 0,5 mol L⁻¹ NaCl medium were carried out to evaluate the corrosion resistance of carbon steel (SAE 1010) samples, phosphate free and phosphatized with PZn and Nb₂O₅. Results obtained are shown in Figure 6.

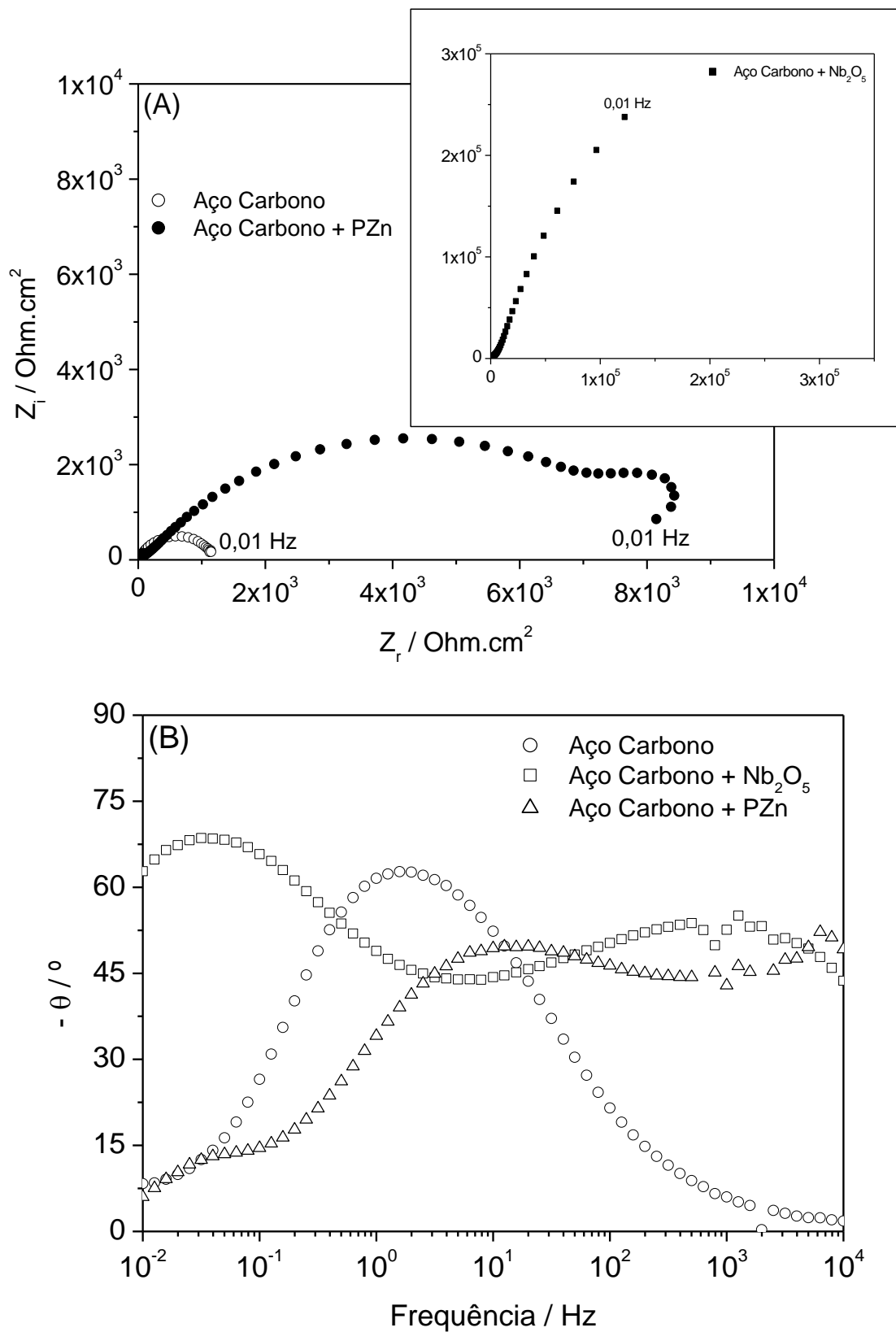


Figure 5. Nyquist diagrams (A) and Bode phase angle (B) in NaCl 0,5 mol L⁻¹.

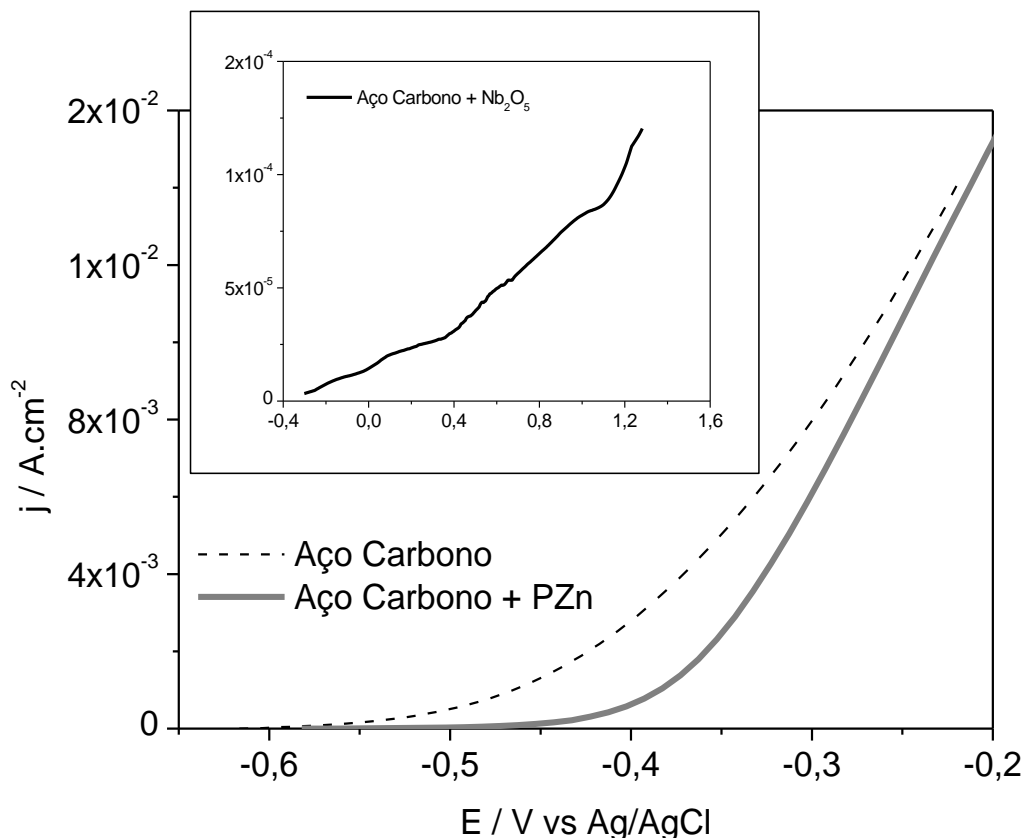


Figure 6. Anodic potentiodynamic polarization curves obtained in NaCl 0,5 mol L⁻¹ solution.

4. DISCUSSIONS

4.1 Morphologic characterization

Figure 2 it was observed that the phosphate deposition alters the morphologic characteristics and the roughness of the substrate surface, making it even rougher. The phosphate layer formation, from PZn baths, occurred through the precipitation of hexagonal strip shaped crystals, as shown in Figure 2 (B).

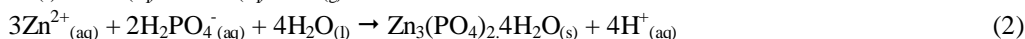
The deposition of Nb₂O₅ promoted the surface conditioning, enabling to obtain a coating with smaller hexagonal crystals than those formed by the zinc phosphate. The smaller Nb₂O₅ crystals cover the surface better and can increase the resistance to corrosion, as this layer is less porous, as it can be seen in Figure 2 (C).

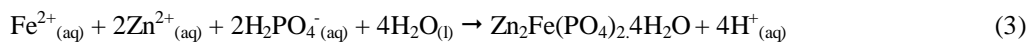
The EDS spectra obtained for the samples under study indicate the presence of peaks regarding the elements phosphorus, zinc and iron, for the PZn layer, as it can be observed in Figure 2 (B) spectrum. The peaks mentioned indicate that there was deposition of the zinc phosphate coating and that the phosphate coating is mainly composed by P, Zn and Fe.

The EDS spectra obtained for the Nb₂O₅ coating, presented in Figure 2 (C), shows the presence of peaks related to the niobium, oxygen and iron elements, and suggests that the Nb₂O₅ layer was suitably formed on the carbon steel surface.

4.2 X-ray diffraction

The diffractogram in Figure 3 (A) is characteristic of zinc phosphate coatings with the following main phases: Zn₃(PO₄)₂·4H₂O (*hopeite*) and Zn₂Fe(PO₄)₂·4H₂O (*phosphophyllite*). From the results obtained by the diffractograms, the following phosphating mechanism could be proposed:





Other reactions could have occurred before the phosphate deposit formed, however, previous chemical equations describe the reactions that effectively promoted the formation of phosphate coatings, even if other intermediate reactions may have occurred.

The reaction described by Equation (1) corresponds to the iron attack, which composed the metallic substrate, by the phosphating acid solution; and other reactions (2 and 3) were responsible for the formation of phosphate crystals and their deposition on the metallic surface.

The highest intensity peak in the diffractograms corresponds to the *phosphophyllite* phase. This result is in accordance with the literature [23], according to which, in non-agitated phosphating baths, as it is the case of the baths used in this study, the proportion of *phosphophyllite* in the phosphate layer obtained is higher than the *hopeite*. The results of phase characterizations in the phosphate coating in this study, obtained through X-ray diffraction, agree with those published in the literature [24, 25].

Figures 3 (B) and 3(C) show the X-ray diffractograms characteristic of the niobium pentoxide Nb_2O_5 and the carbon steel (SAE 1010) coated with Nb_2O_5 . All peaks correspond to the phase TT Nb_2O_5 (JCPDS, 28-317), the main peaks can be indexed as (001), (100) and (002), respectively. These characteristic peaks are in accordance with the literature [26, 27].

X-ray diffraction results are in accordance with results obtained through the scanning electronic microscopy and confirm the formation of a Nb_2O_5 coating on the metal surface.

4.3 Open Circuit Potential

The electrochemical behavior of the uncoated samples as well as the ones with Nb_2O_5 and PZn treatment were evaluated through the open circuit potential measurements up to the stabilization of the potential. A potential band with values below ± 5 mV for 30 minutes was considered. Results are shown in Figure 4.

These curves show a tendency of the samples potential to dislocate towards more negative values, mainly, for times longer than 500 seconds. However, more positive potential values were obtained for the coated samples. Such result suggests an increase in the superficial quality, promoted by the covering of the base metal with the coaters. Additionally, it could be seen that in the niobium layers, the potential remained in more positive values throughout the whole test, suggesting higher quality and, possibly better protection of the carbon steel (SAE 1010) against corrosion.

4.4 Electrochemical impedance spectroscopy (EIS)

Figure 5 (A) represents the Nyquist diagrams for uncoated steel and with the surface treatments. The diagram for carbon steel presents only one capacitive arch. In the same diagram, the PZn treatment, presented two capacitive arches which might suggest the presence of two time constants. Comparing with the substrate, it can be seen that higher impedance values were found, indicating increase in the corrosion resistance. In the carbon steel treatment with Nb_2O_5 , only one capacitive arch was verified and higher impedance values were measured, when compared to the values for the uncoated substrate and that coated with zinc phosphate. It was observed that the capacitive arch for the Nb_2O_5 does not close in a semicircle, due to its high resistance to corrosion. This behavior suggests that this treatment promoted higher resistance to corrosion than the PZn layer.

One of the reasons for these results is related to the phosphate and Nb_2O_5 crystal morphology. The PZn coating is composed by crystals of a hexagonal shape [28] which did not cover the surface entirely and, coincidentally, this layer was associated to lower protection to the substrate corrosion. This phosphate coating is also too porous [28], promoting a less efficient barrier against corrosion. On the other hand, the Nb_2O_5 coatings presented hexagonal shaped crystals, but smaller than those in the PZn, as it will be seen in a later section, which apparently provide better coverage to the metallic surface and also were revealed as a more efficient barrier to corrosion.

In the Bode phase angle diagrams, presented in Figure 5 (B), it was observed that there is a single time constant at the medium (MF) to the low frequency (LF), between 10 and 1 Hz, for the uncoated carbon steel, associated with the charge transfer processes.

Additionally, for the phosphatized sample, there is a constant phase angle region from the high frequency (HF) region to the medium frequency (MF) 10000 – 10 Hz suggesting the overlapping of time constants in this region. The first is detected in high frequency (HF) (10^4 Hz) related to the phosphate

coating. The second is verified in MF (10 Hz) and ascribed to the pores response (product in the pores) of the phosphate layer. The third constant can be determined in LF regions (between 0,1 and 0,01 Hz) which might be attributed to the charge transfer processes related to the corrosion in the base metal interface. This result agrees with studies presented in the literature [29, 31], in which porous materials presented similar response.

Comparatively, the Bode diagram of the Nb₂O₅ coated sample shows impedance behavior different from the other samples, as two well defined time constants are observed. The first is observed at HF (10⁴ Hz) related to the Nb₂O₅ coating. The second constant can be determined in LF regions (between 0,1 and 0,01 Hz) which might be ascribed to the charge transfer processes related to the corrosion in the base metal interface. Additionally, the Bode phase angles of the second constant were dislocated towards higher values in relation to the PZn, indicating that there was increase in the resistance to the charge transfer process. No displacement of time constants in relation to the frequency was observed, indicating that there was no kinetic alteration of processes and that the coatings acted as a barrier.

4.5 Anodic potentiodynamic polarization curves (APP)

The polarization curves presented in Figure 6 show dislocation of the corrosion potential towards more positive values in relation to the substrate due to the presence of PZn and Nb₂O₅. However, the treatment with niobium promoted bigger dislocation, indicating increase in the superficial quality.

For low potential, the coatings presented current densities of typically passive materials, suggesting considerable increase in the base metal resistance to corrosion, with advantages to the Nb₂O₅ coating which presented the best rates.

Additionally, over the whole voltage region studied, the coatings yielded lower current densities than those found for the substrate, indicating that they increased the polarization resistance. However, the Nb₂O₅ treatment presented much lower current densities than the PZn.

The polarization curves revealed that the anodic reaction is more polarized to the Nb₂O₅ coating, as the current density elevation occurs in potentials around 0,4V, which is much more positive than -0,4 and -0,5 V for PZn and carbon steel, respectively. These results are in accordance with the literature [20], on the PZn coatings, in which lower current densities were obtained through NaCl.

5. CONCLUSIONS

A new coating for carbon steel based on niobium pentoxide was developed in this study and the following conclusions were obtained from the characterization of such coating.

The protection against corrosion provided by this coating was studied through electrochemical measurements. The open circuit potential curves demonstrated that the Nb₂O₅ coating dislocated the corrosion potential of the carbon steel towards more positive values and this result suggests that this layer provides more resistance to corrosion. The potentiodynamic polarization results and electrochemical impedance spectroscopy complemented the open circuit potential results, as lower anodic current densities and higher impedance values were obtained with the Nb₂O₅ coating indicating that this coating was more resistant to corrosion.

The scanning electronic microscopy indicated that the layer studied alters the metallic substrate morphology. The PZn and Nb₂O₅ crystals show the shape of hexagonal strips which do not cover the surface entirely. However, the Nb₂O₅ crystals are smaller which indicates that these crystals cover the base metal surface more efficiently. The results of the energy dispersive microscopy revealed the presence of niobium on the surface of the Nb₂O₅ coated metal and suggest that the niobium pentoxide was suitably formed on the carbon steel. The X-ray diffraction results confirm the SEM results, from which the TT Nb₂O₅ phase was determined and the main peaks were indexed.

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