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CHARACTERIZATION OF A NIOBIUM AND TITANIUM OXIDES COATINGs FOR THE PROTECTION OF CARBON STEEL SAE 1020

Rodrigo Helleis
Universidade Estadual do Centro-Oeste,
Departamento de Química
Guarapuava – PR
https://orcid.org/0000-0002-7666-4490

Ana Paula Camargo Matheus
Universidade Estadual do Centro-Oeste,
Departamento de Química
Guarapuava – PR
http://lattes.cnpq.br/9190332415879618

André Lazarin Gallina
Universidade Estadual do Centro-Oeste,
Departamento de Química
Guarapuava – PR
https://orcid.org/0000-0002-1535-7980

Bianca Vanjura Dias
Universidade Estadual do Centro-Oeste,
Departamento de Química
Guarapuava – PR
http://lattes.cnpq.br/6501821506452621

Guilherme Arielo Rodrigues Maia
Universidade Estadual do Centro-Oeste,
Departamento de Química
Guarapuava – PR
http://lattes.cnpq.br/9537655278043154

Paulo Rogério Pinto Rodrigues
Universidade Estadual do Centro-Oeste, Departamento de Química
Guarapuava – PR
https://orcid.org/0000-0001-8383-7225

Everson do Prado Banczek
Universidade Estadual do Centro-Oeste, Departamento de Química
Guarapuava – PR
https://orcid.org/0000-0002-6674-4710

Abstract: In this study, the protection against corrosion of carbon steel SAE 1020, promoted by a niobium and titanium oxides coating was investigated. The coating was produced by the Pechini method using different titanium proportions to prepare the resin and calcinating for 1 hour. The samples were characterized by open circuit potential, potentiodynamic anodic polarization, electrochemical impedance spectroscopy, scanning electron microscopy, energy dispersive spectroscopy and X-ray diffraction. The electrochemical analyses suggested protection against corrosion for the coated samples. The increase of the titanium proportion in the resin increased the protection of the substrate. Morphologic and structural analyses showed the deposition of low cristalinity non-homogenous layer of niobium and titanium oxides. The increase in the titanium proportion resulted in the decrease of defects on the surface.
Keyword: Electrochemistry, pretreatment, Pechini Method

INTRODUCTION

Corrosion in equipment and piping is a major problem for the industry, causing losses in the order of hundreds of billions of dollars annually (HOU et al., 2016). Carbon steel is widely used in tools, equipment and piping and although it has low cost and excellent mechanical properties, it is poorly resistant to corrosion, requiring the use of surface treatment to increase its useful life and reduce costs (DETLINGER et al, 2020).

The main forms of protection against corrosion are changing the environment, using corrosion inhibitors, cathodic protection, anodic protection and the use of coatings (GENTIL, 2003). Niobium and titanium are widely used in the field of implants due to their excellent biocompatibility, resulting from the formation of a thin film of oxides on the surface, ensuring mechanical properties and the ability to prevent the attack of corrosive body fluids. (BAI et al., 2016).

Based on this, the deposition of a coating of niobium and titanium oxides on the surface of carbon steel could potentially provide protection against corrosion. Oxides can be deposited on the surface of metallic materials by techniques such as chemical vapor deposition, physical vapor deposition and the sol-gel method. (PAN et al., 2016). The *Pechini* method is a modification of the sol-gel method that consists in the preparation of a resin by the reaction between a chelating agent and a metallic precursor, followed by a polyesterification reaction by the addition of a polyalcohol (TRACTZ, et al., 2021). The resin is then calcined to remove the organic fraction and form surface oxides. This method has the advantages of relatively low cost for large-scale production, easy operation and stoichiometric and morphological control of the oxides (TRINO et al., 2018).Given the above, the objective of this work was to develop and characterize a coating of niobium and titanium oxides prepared by the *Pechini* method with different proportions of reagents for the protection of carbon steel against corrosion.

MATERIALS AND METHODS

The resins were prepared by *Pechini method*, according to the method described by Detlinger et al (2019), using citric acid (CA) as chelating agent, ethylene glycol (EG) as polyalcohol, niobium and ammonium oxalate ($NH_4[Nb(C_2O_4)_2(H_2O)].H_2O$) as precursor of niobium and potassium hexafluorotitanate (K_2TiF_6) as a precursor to titanium. The molar ratios used were EG:AC – 8:1, Nb:AC – 1:10 and varying the proportions of Ti:AC (0.4:10; 0.5:10 and 6:10). Citric acid was added to ethylene glycol at 60 °C under constant stirring until complete dissolution, then titanium and niobium precursors at 60 °C until complete dissolution and the system reacted for 1 hour.

2x2 cm sized SAE 1020 carbon steel plates were ground with #220, #320, #400, #600 and #1200 progressive *mesh* to remove surface impurities from the material. The polished plates were then immersed in the resin for 15 minutes and excess resin was removed by gravity for 5 minutes. Then calcination was carried out in a muffle furnace at 450 ºC for 1 hour.

For electrochemical characterization, a cell with three electrodes was used, with the working electrode being the coated plate, the metallic platinum counter electrode and an Ag/AgCl electrode as reference. The electrolyte used wasNaCl 0,5 $molL^{-1}$. Open circuit potential (PCA), anodic potentiodynamic polarization (PPA) analyzes were performed applying an overvoltage of +500 mV from the open circuit and electrochemical impedance spectroscopy (EIS), performed potentiostatically in the open circuit with disturbance of ± 10 mV, between 10 kHz and 10 mHz with acquisition of 10 points per decade. The morphological characterization was performed by Scanning Electron Microscopy (SEM), energy dispersive spectroscopy (EIS) and X-ray diffraction (XRD) with CuKα radiation (λ = 1.5418 Å) in the range of 10 to 80º with step0,02º.

The corrosion inhibition efficiency was determined by equation 1. In which θ is the corrosion inhibition efficiency, j_{corr} is the corrosion current density for the coated and j^{o}_{corr} is the corrosion current density for the substrate. Corrosion Potential Values (E_{corr}) and corrosion current density were obtained by linear extrapolation of the potentiodynamic polarization curves in the Tafel region.

$$\theta = \frac{j^{\circ}_{corr} - j_{corr}}{j^{\circ}_{corr}} \times 100 \quad (1)$$

RESULTS AND DISCUSSION

Substrate and plate micrographs coated at 500x magnification are shown in Figure 1.

It is noticed that there was the deposition of an inhomogeneous coating on the metal surface. With the increase in the proportion of titanium, it was found that the coating has a smaller amount of defects. The EDS analysis, as shown in Table 1, shows the presence of the elements Fe, O, Nb, Ti, K and F, indicating the formation of oxides on the surface, but also suggesting the formation of phases different from the expected niobium and titanium oxides.

The increase in the titanium concentration on the surface as the proportion in the resin increased was not observed by EDS. However, due to the semiquantitative characteristic of the technique and the small differences found between the samples, it is possible that these variations have been masked.

The diffractograms of the samples are visualized in Figure 2. It is noticed amorphous characteristic for the resin in all proportions of titanium. The peaks represent a mixture of phases containing Nb, Ti, K and F Due to the large number of phases that could be related to the peaks, in both diffractograms, no exact phase could be defined.

The open circuit potential curves are shown in Figure 3. According to Figure 3, it is observed that the potential stabilizes for the coated samples at values greater than that of the substrate, indicating greater nobility of the system (MENNUCCI et al., 2009; LI et al., 2017). Increasing the proportion of titanium in the coating resulted in a reduction in the equilibrium potential, indicating that the concentration of titanium in the system increases nobility.

The same behavior was observed in the anodic potentiodynamic polarization curves, as shown in Figure 4. The coated plates presented a displacement of the curve to regions of lower current density when compared to the substrate, indicating greater protection of the system (ZHAO et al., 2017; DETLINGER et al., 2020). Similar curves were observed for the proportions Ti:AC – 0.4:10 and Ti:AC – 0.5:10, indicating similar corrosion protection behavior. The Ti:AC – 0.6:10 ratio presented a greater displacement, being the best result obtained for the analysis.

From the polarization curves, it was possible to obtain the corrosion potential and the corrosion inhibition efficiency, according to Table 1. The results obtained show a corrosion inhibition efficiency of 49.44% for the Ti:AC ratio – 0.6:10, being the best result obtained for the resins in question, being considerably higher than resins prepared with Ti:AC – 0.5:10 and Ti:AC – 0.4:10 ratio with inhibition efficiency of 41.29% and 37.72% respectively. It was also verified that the corrosion potential is reduced as the proportion of titanium increases, suggesting the increase in the nobility of the system observed in the open circuit potential curves in Figure 2.

The impedance measurements in the form of the Bode diagram for the phase angle and the Nyquist diagram can be seen in Figure 5 and Figure 6 respectively.

In the Bode diagram, for coated boards, the time constant is shifted to regions of lower frequency compared to the substrate, indicating a delay in the kinetics of corrosion reactions (MENNUCCI et al., 2009; DETLINGER et al., 2019). The similar behavior for coatings prepared with Ti:AC – 0.4:10 and Ti:AC – 0.5:10 ratio, already observed in the anodic potentiodynamic polarization curves in Figure 4, indicates similar protection for the coatings. As for the Ti:AC - 0.6:10 ratio, a smaller displacement was found for low frequency regions, but the time constant with the largest base and the highest value for the phase angle indicate greater protection against corrosion for the coating.

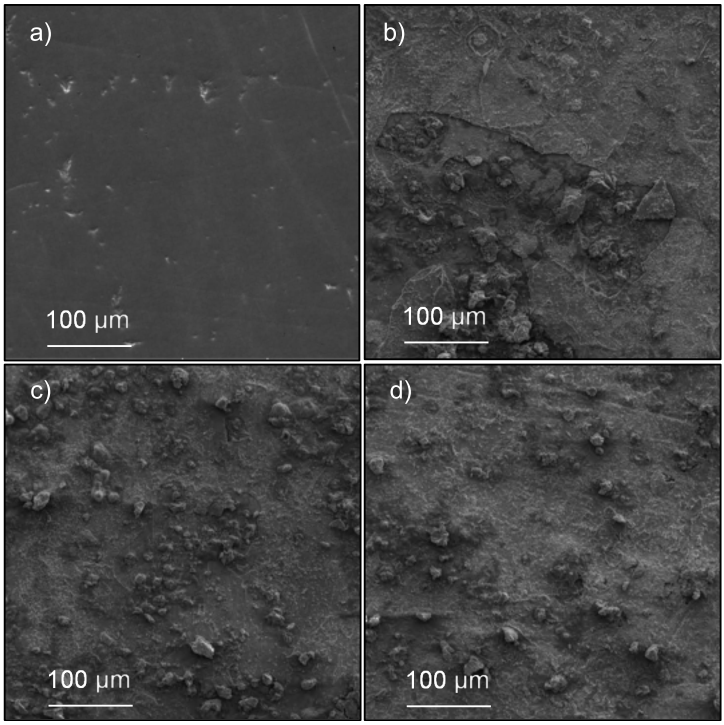


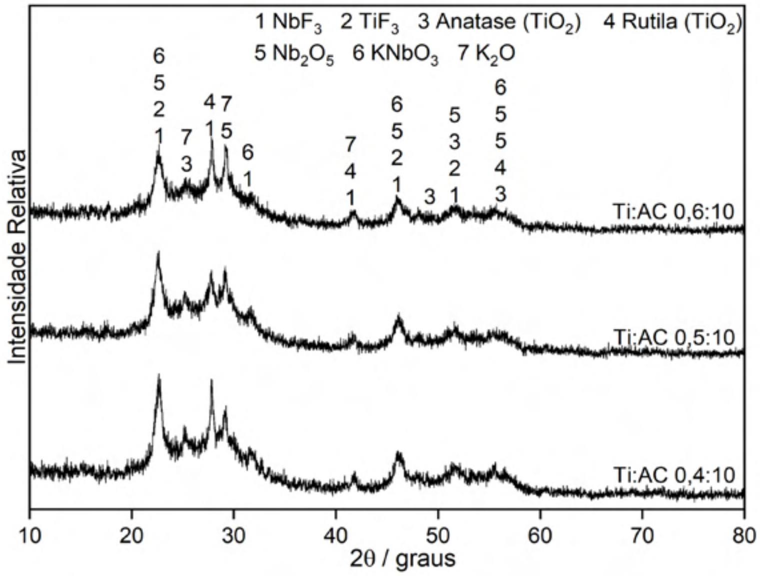
Figure 1 – Micrographs for substrate and coated plates: a) Substrate ; b) Ti:AC – 0,4:10; c) Ti:AC – 0,5:10; d) Ti:AC – 0,6:10

Source: The author, 2018.

Element	Mass concentration		
	Ti:AC – 0,4:10	Ti:AC – 0,5:10	Ti:AC – 0,6:10
Fe	69,5 %	70,8 %	71,8 %
O	23,1 %	23,2 %	22,8 %
Nb	5,33 %	4,21 %	3,50 %
Ti	1,11 %	0,75 %	0,85 %
K	0,66 %	0,62 %	0,69 %
F	0,30 %	0,32 %	0,27 %

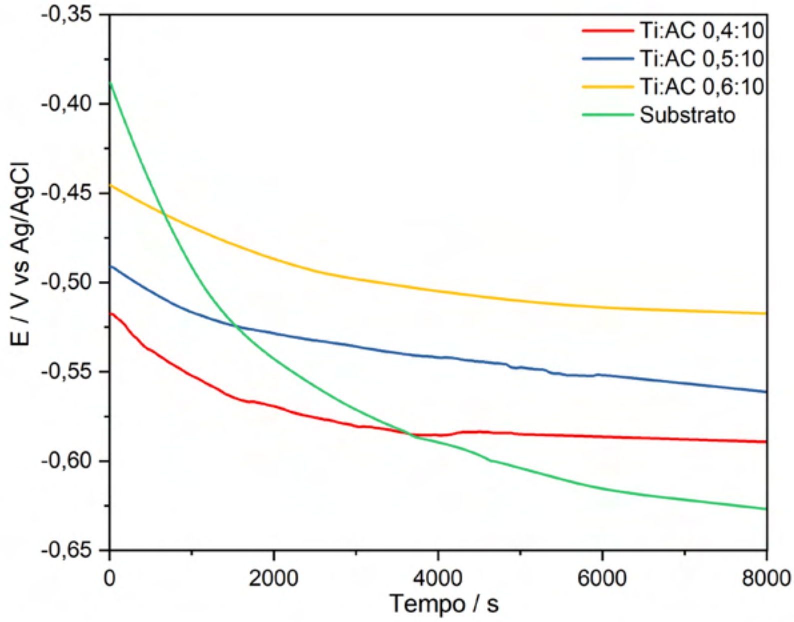
Table 1 – Mass concentration of elements on the coating surface obtained by EDS analysis

Source: The author, 2018.



Intensidade relativa = relative intensity

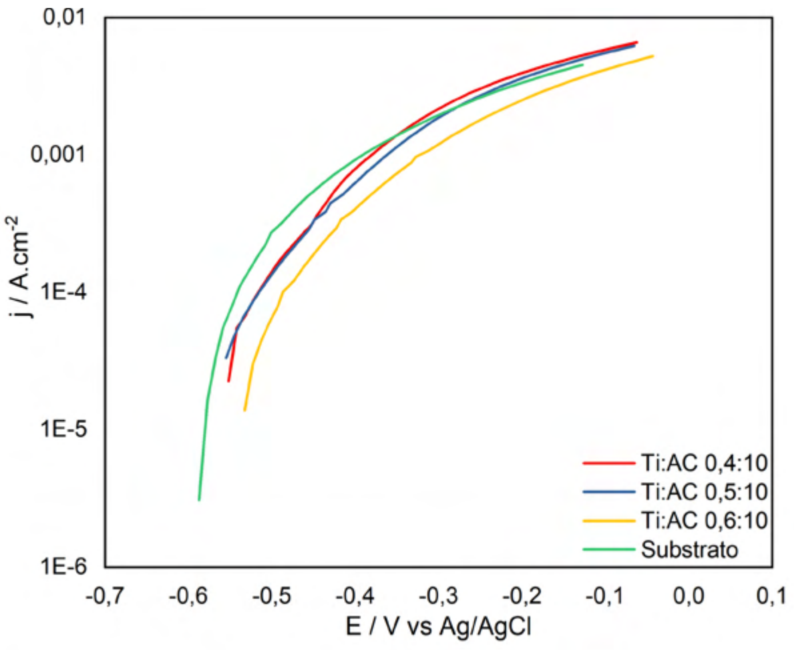
Figure 2 – Diffractograms for the powder of calcined resins .



Tempo = Time

Substrato = Substrate

Figure 3 – Open circuit potential curves for substrate and coated samples .

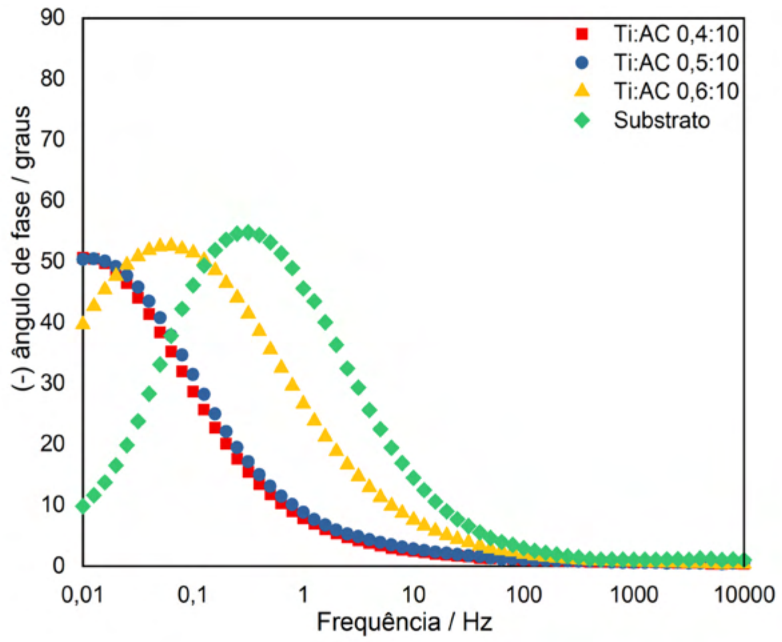


Substrato = Substrate

Figure 4 – Anodic potentiodynamic polarization curves for substrate and coated samples .

Sample	E_{corr} (mV)	j_{corr} (A cm^{-2})	j^{o}_{corr} (A cm^{-2})	θ
Ti:AC - 0,6:10	-531	4,53E-05	8,96E-05	49,44%
Ti:AC - 0,5:10	-548	5,26E-05	8,96E-05	41,29%
Ti:AC - 0,4:10	-558	5,58E-05	8,96E-05	37,72%

Table 2 –Corrosion Potential and Corrosion Inhibition Efficiency Values for Prepared Coatings .



Frequencia = Frequency

(-) ângulo de fase/graus = (-) phase angle/degrees

Substrato = Substrate

Figure 5 – Phase Angle Bode Diagram for Substrate and Coated Boards .

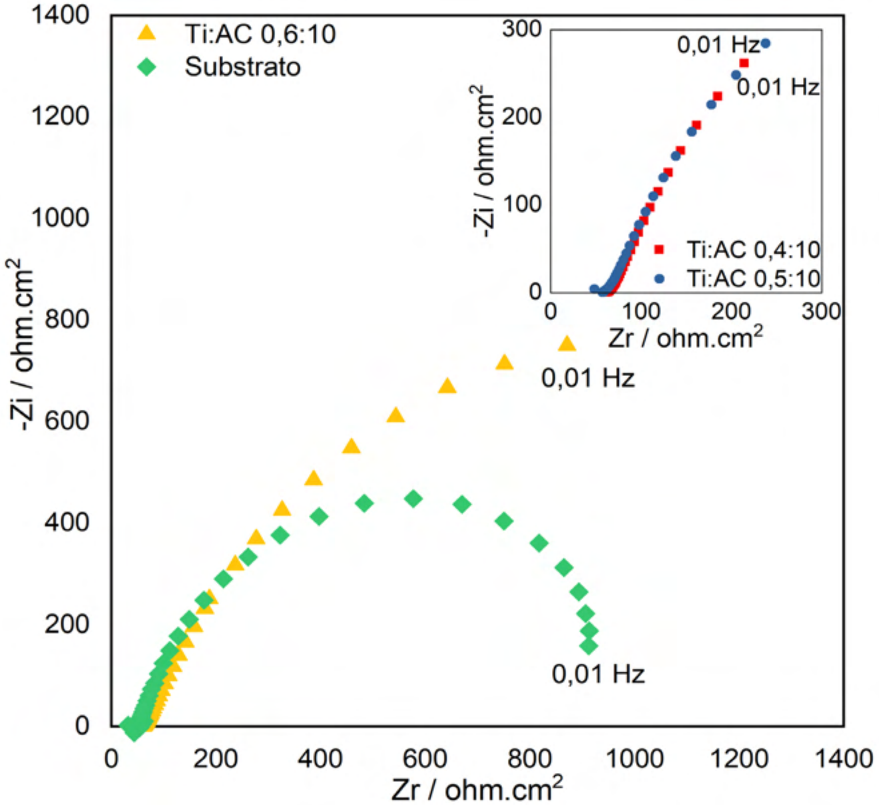


Figure 6 – Nyquist diagram of phase angle for substrate and coated boards.

In the Nyquist diagram, it is possible to verify incomplete arcs that present higher impedance values for the coated plates, when extrapolated to regions of lower frequency, in relation to the substrate. This behavior indicates greater resistance to surface corrosion (PILLIS et al., 2016; DETLINGER et al., 2019). As in Bode's diagram, the Ti:AC – 0.4:10 and Ti:AC – 0.5:10 ratios show similar results, indicating similar protection of the coatings and greater protection for the coating with Ti:AC – ratio – 0.6:10.

The presence of only one time constant in the Bode diagram in regions of lower frequency and incomplete arcs in the Bode diagram indicate a dielectric behavior of the system, due to the presence of niobium in different oxidation states. This characteristic allows the passage of current in regions of higher frequency and with resistance to irregularities of the coating in regions of lower frequency

CONCLUSION

Electrochemical analyzes showed a reduction in equilibrium potentials and an increase in impedance values for the coated plates. This behavior indicates that the deposition of a layer of niobium and titanium oxides, produced by the Pechini method, increases the nobility of the system and protects the surface of carbon steel SAE 1020 against corrosion. The titanium concentration in the coating influences the system's corrosion protection. Micrographs of the coated surfaces suggest that increasing the amount of titanium resulted in coatings with fewer defects. The electrochemical analysis indicated that the increase in the proportion of titanium in the coating increases its protection against corrosion, with the best result obtained for the proportion Ti:AC – 0.6:10.

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