

Electro chemical characterization of $V_XNb_YC_Z/Bi_XTi_YO_Z$ coatings produced through thermo-reactive diffusion and the sputtering technique

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We present an experimental study of the structural evolution of a bilayer $V_XNb_YC_Z/Bi_XTi_YO_Z$ coating produced via thermo-reactive diffusion (TRD) and the RF sputtering process on D2 steel substrate. The TRD treatments were carried out in a molten mixture consisting of borax, ferro-niobium, ferro-vanadium, and aluminum, at 1313 K for 3 hours, using a resistance-heating furnace. $Bi_XTi_YO_Z$ coatings were deposited using RF magnetron sputtering on TRD coatings, in order to carry out a study of the corrosion behavior of this compound. The crystallographic structure of the coatings was determined via X-ray diffraction (XRD), the corrosion resistance was analyzed through the potentiodynamic polarization test (Tafel Extrapolation) and electrochemical impedance spectroscopic analysis (EIS). XRD patterns showed that the ternary coating ($VNbC_2$) was preferentially oriented along the [200] direction with a cubic-centered face structure, and the $Bi_XTi_YO_Z$ coatings were amorphous. The electrochemical studies showed that the resistance corrosion of the coatings increased with respect to the bare substrate, and that polarization resistance in the bilayer coatings increased with respect to the ternary coatings, suggesting that the titanate has anticorrosive barrier effects.

Keywords: Thermo reactive diffusion; bismuth titanate coatings; corrosion resistance; RF sputtering.

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1. Introduction

The transition metal carbides have an unusual combination of physicochemical properties, among them high melting temperatures and hardness [1,2]. As one of the hardest transition metal carbides, vanadium carbide (VC) coating shows some other distinguishing properties, such as corrosion resistance [3]. In the same way, niobium carbide (NbC) studies have shown that it exhibits good resistance corrosion at high temperatures [4]. Nevertheless, there have been very few studies focused on the production and characterization of ternary carbides of these transition metals ($V_XNb_YC_Z$). These coatings have high hardness but their resistance corrosion is low, because have high percentage of porosity [5]. Furthermore, it has been found that bismuth titanate has very good protective behavior to chemical aggressive environment [6]. Nonetheless, the number of studies devoted to the corrosion resistance of these materials is still small. Coatings based on a multilayered structure produced through PVD techniques, such as magnetron sputtering, combine the effects of individual layers and can further improve the properties of the coating [7]. Thermo-reactive diffusion (TRD) coatings have applications similar to those of coatings produced by CVD or PVD [8]. The advantage of TRD is that dense and continuous carbide layers can be applied to steels containing carbon percentages higher than 0.3%. TRD is also used for coating surfaces with hard materials in fluidized beds, molten salt baths, or powder. In addition, TRD has been shown to be a simple and economical alternative for the pro-

duction of layers of binary carbides such as VC, NbC, TiC or Cr_7C_3 , which are formed by the reaction between the carbon atoms of the substrate and the atoms of the carbide-forming elements (CFE).

The main objective of this work is produce a bilayer on D2 steel substrates that combines the benefit of the individual components, the high wear and corrosion resistance of transition carbides produced via TRD and the passive and homogeneous surface properties, of the bismuth titanate coatings produced through sputtering. It is important to indicate that to our knowledge, this type of coating has not been studied previously; therefore this paper can potentially be useful for developing new coatings with high corrosion resistance.

2. Experimental Procedure

2.1. Materials and TRD treatment

Coatings of VC, NbC and $VNbC_2$ were deposited through TRD treatment on AISI D2 (1.55 wt.% C, 0.30 wt.% Si, 0.30 wt.% Mn, 11.00 wt.% Cr, 0.75 wt.% Mo, 0.75 wt.% V) tool steel and sized in samples of 12 mm diameter and 5 mm thickness with an upper hole of 2 mm in diameter for hanging purposes. All the samples were ground with 220 to 1200-grit silicon carbide sandpaper and then polished with alumina, and finally ultrasonically cleaned in isopropyl alcohol and acetone. The TRD treatments were carried out in a molten mixture consisting of borax ($Na_2B_4O_7$), ferro-vanadium (Fe-V), ferro-niobium (Fe-Nb), and aluminum (Al) at 1313 K for

TABLE I. Composition of salt bath used in TRD Treatment.

Coatings	wt.%Na ₂ B ₄ O ₇	wt.%Fe-V	wt.%Fe-Nb	wt.%Al
VC	81	16	0	3
NbC	81	0	16	3
VNbC ₂	81	8	8	3

3 hours using a resistance-heating furnace. The Borax salt was used to avoid the chemical reaction between Fe of the substrate and the Fe of the ferroalloy, this practice is common used in industrial process and is explained amply by Castillejo [9]. The composition of the salt bath for each coating is given in Table I. After the TRD process, the samples were cooled and cleaned in boiling water.

2.2. Sputtering Deposition

$Bi_xTi_yO_z$ thin films was deposited on carbide coatings through RF sputtering, using Alcatel HS 2000 equipment, described in a previous paper [10]. These coatings were obtained from a $Bi_4Ti_3O_{12}$ target (99.9%) located at a distance of 5.0 cm from the substrate in an atmosphere of Ar (99.999%) with a constant flow of 20 sccm. The base pressure was 5.4×10^{-3} Pa, and the total working pressure was maintained constant at 7.4×10^{-1} Pa. The deposition conditions for $Bi_xTi_yO_z$ coatings were: Discharge was 150 W, substrate temperature was 293 K, and deposition time was 30 min.

2.3. Characterization of the coatings

The crystallographic structure of the bilayer coatings was analyzed through X-ray powder diffraction (XRD) in the Bragg-Brentano configuration, using Cu-K α radiation in the interval between 20° and 100° in steps of 0.02°. The thicknesses of the NbVC coatings were measurement with electronic scanning microscope and the BiTiO films were measurement with a Veeco Dektak 150 surface profilometer. The corrosion resistance was analyzed using the potentiodynamic polarization test (Tafel Extrapolation), and the electrochemical impedance spectroscopic (EIS) using a GAMRY 600 Potentiostat/Galvanostat. The samples were placed in a galvanic cell with an exposure of 0.159 cm² that came into contact with the test solution (3.5% NaCl). The electrochemical tests were done with three electrode cells, consisting of a Saturated Calomel Electrode (SCE), a coated steel surface as a working electrode, and a platinum auxiliary electrode, placed inside a Faraday cage in order to minimize the effects of the electrical fields in the environment. The samples were immersed in the test solution for 1 hour before starting the potentiodynamic polarization test, at room temperature. The measurements were carried out in a range between -0.3 and 0.3 V with respect to open-circuit potential (OCP) at a scan rate of 0.5 mV/s. In order to investigate the corrosion performance and polarization resistance of the different coatings, electro

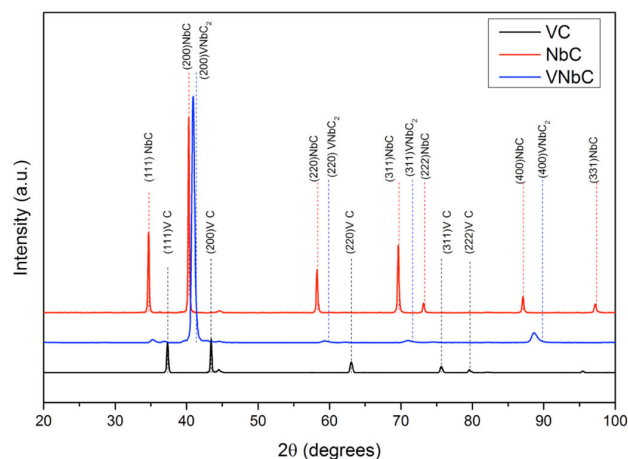
FIGURE 1. X-ray diffraction patterns of VC, NbC and VNbC₂ coatings, produced via the TRD process.

TABLE II. Thickness (d), lattice parameters (a), crystallite sizes (L), the carbide coatings.

Coatings	d (μm)	a (nm)	L (nm)
VC	5.1±0.2	0.4164 ±0.0003	47.32218
NbC	7.3±0.3	0.4473±0.0003	42.27256
VNbC ₂	2.7 ±0.2	0.4370±0.0021	10.98685

chemical impedance spectroscopy (EIS) data were obtained for 1 h, 24 h, 48 h, 72 h and 168 h immersion times in the test solution and in the frequency range from 100 kHz down to 10 mHz. Analysis of the potentiodynamic polarization curves and the equivalent circuits was done with Gamry Echem Analyst software.

3. Results and discussion

3.1. Phase identification

Figure 1 shows the XRD patterns of the carbides produced through TRD. These allow establishing that the coatings were formed by polycrystalline binaries NbC, VC and ternary VNbC₂ preferentially oriented along [200] direction with a cubic-centered face structure (FCC). The planes that belong to vanadium carbide are consistent with PDF 01-073-0476, the niobium carbide planes are in agreement with PDF 00-038-1364, and the ternary compound matches that reported by Castillejo *et al.* [11,12]. Probably VC did not grow because its activation energy (199.3 kJ/mol) [1,13] is higher than that of NbC (91.2 kJ/mol) [13,14]. Additionally, the high temperatures used in the test cause the system grow in the [200] direction, that is of lower surface energy in the FCC structure [15].

Table II shows the lattice parameters calculated using Bragg's law and the Nelson-Riley method [16,17] using the picks (111), (200) and (220) mainly. The values of these parameters indicate that the lattice parameter of NbC is greater than that of the ternary, this is evidence by the shift of the

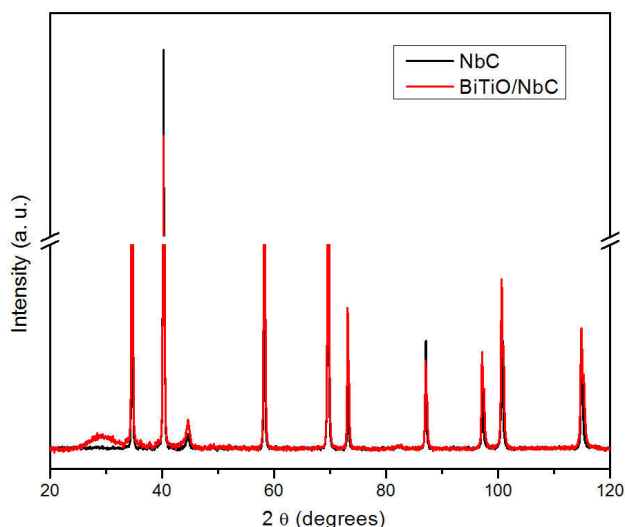


FIGURE 2. X-ray diffraction patterns of $\text{Bi}_x\text{Ti}_y\text{O}_z$ deposited on NbC via sputtering.

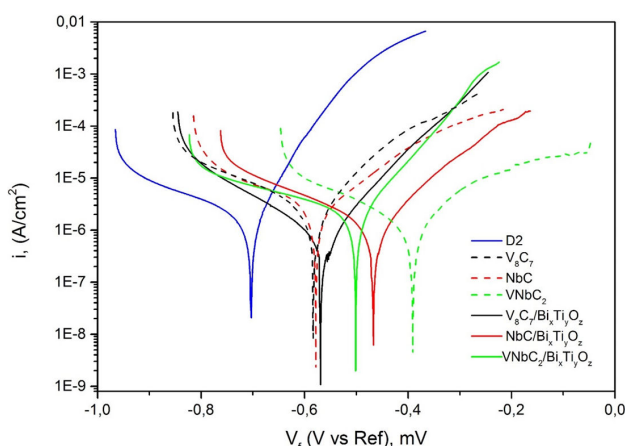


FIGURE 3. Potentiodynamic polarization curves for D2 steel, carbides and carbide-titanate coatings measured in a 3.5% NaCl test solution.

planes towards the right, probably caused because Nb ions have replaced in the crystalline lattice to V ions.

Using the Scherrer equation [16], average crystallite sizes “L” were calculated. L and thickness of the carbides are shown in Table II. In previous work, XRD patterns of $\text{Bi}_x\text{Ti}_y\text{O}_z$ allowed establishing that the coatings have an amorphous phase (see Fig. 2) with regular thickness of approximately 250 nm [6]. The amorphous phase is due to that the temperature of the substrate is very low to reach the crystalline phase.

3.2. Corrosion behavior

3.2.1. Potentiodynamic polarization tests

The potentiodynamic polarization curves of the AISI D2 substrate, carbides coatings, and carbide-titanate bilayer measured in a 3.5% NaCl test solution are shown in Fig. 3. The electrochemical parameters, corrosion current density (i_{corr}),

TABLE III. Electrochemical parameters for the D2 substrate, carbides and carbide-titanate coatings: corrosion current density (i_{corr}), corrosion potential (E_{corr}) and polarization resistance (R_p).

Sample	i_{corr} (A/cm^2)	E_{corr} (mV)	R_p (Ω)
D2	4.18×10^{-6}	-703	5.10×10^4
VC	1.48×10^{-6}	-583	8.34×10^4
$\text{VC}/\text{Bi}_x\text{Ti}_y\text{O}_z$	6.43×10^{-7}	-567	2.36×10^5
NbC	3.06×10^{-6}	-578	8.48×10^4
$\text{NbC}/\text{Bi}_x\text{Ti}_y\text{O}_z$	1.37×10^{-6}	-466	1.61×10^5
VNbC_2	2.60×10^{-6}	-393	1.49×10^5
$\text{VNbC}_2/\text{Bi}_x\text{Ti}_y\text{O}_z$	1.58×10^{-6}	-499	1.17×10^5

corrosion potential (E_{corr}), and polarization resistance (R_p), are shown in Table III. Polarization resistance was calculated using the Tafel slopes [18]. All carbide and carbide-titanate coatings exhibited lower corrosion current density and greater polarization resistance than D2 steel, as well as better resistance to corrosion. A higher value of R_p suggests an improvement in the corrosion resistance of the bilayer-substrate set. Compared with steel, R_p measurements were higher in all coatings. In addition, the corrosion potentials were nearer to the reference electrode potential than those of the bare steel, signifying the beneficial barrier effect of the coatings. Among carbide coatings, the ternary carbide exhibited better corrosion behavior than the niobium and vanadium carbides; it exhibited a higher electropositive corrosion potential and the highest value of R_p . Finally, it can be seen that the values of R_p and E_{corr} increased for binary carbide-titanate coatings, and for the ternary carbide-titanate they decreased.

3.2.2. Electrochemical impedance spectroscopic analysis

The results of the potentiodynamic polarization test showed that among carbides produced through TRD, the ternary carbide had the best corrosion resistance, and for the bilayer coatings, bismuth titanate produced a decrease in this property only in ternary carbide. The impedance spectra of the bare substrate, bilayer, and ternary coatings were analyzed in order to obtain the equivalent circuit. The fit of the EIS data was done through an equivalent circuit for a Randles Cell [19], which is shown in Fig. 4. The coatings were assumed porous, so in this model the electrical elements used were: solution resistance (R_{sol}), pore resistance (R_{por}), coating capacitance (C_{coat}), charge-transfer resistance (R_{ct}), and double-layer capacitance (C_{dl}). In the equivalent circuit of the bare substrate, R_{por} and C_{coat} were not used. In order to obtain a better fit of the EIS data, capacitance was modeled as a constant phase element (CPE), in which the characteristic impedance is represented by the equation [20]:

$$Z_{\text{CPE}} = \frac{1}{Y_0(j\omega)^\alpha} \quad (1)$$

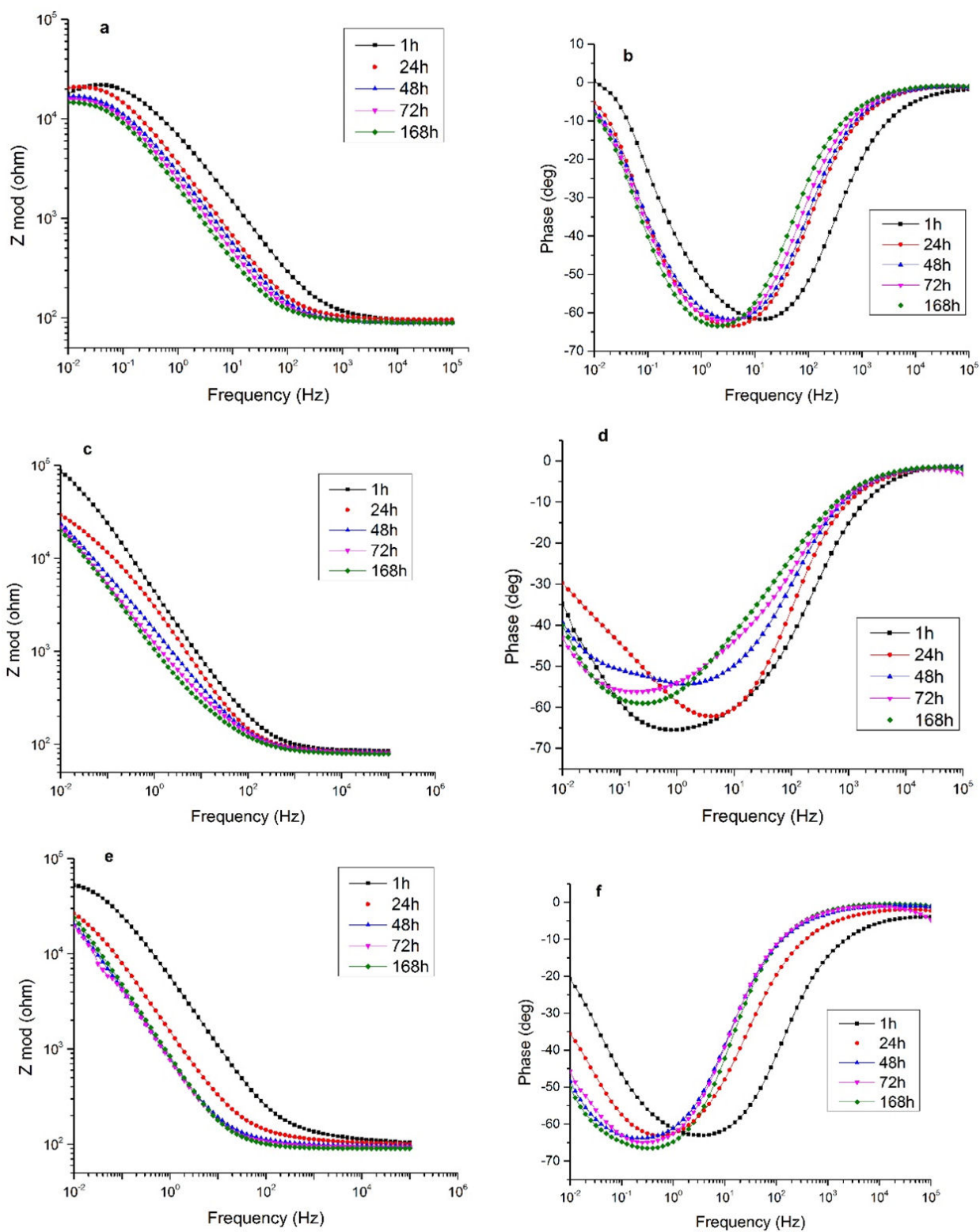


FIGURE 4. Experimental Bode diagrams of impedance and phase angle plots for immersion times of 1h, 24h, 48h, 72h and 168h in 3.5% NaCl test solution: (a), (b) bare D2 substrate; (c), (d) $VNbC_2$ coating; (e), (f) $VNbC_2/Bi_xTi_yO_z$ coating.

TABLE IV. Impedance parameters obtained for bare and coatings for immersion time of 168h in 3.5% NaCl solution.

Sample	R_{sol} (Ω)	R_{por} (Ω)	CPE_{coat}		R_{ct} (Ω)	CPE_{cdl}		$R_p = (R_{por} + R_{ct})$ (Ω)
			Y_{coat} ($S^* s^a$)	A		Y_{Cdl} ($S^* s^a$)	α_{Cdl}	
D2	90.23	-	-	-	1.63×10^4	1.09×10^{-5}	0.792	1.63×10^4
VNbC ₂	79.01	4.63×10^2	1.78×10^{-4}	0.696	4.51×10^4	9.27×10^{-5}	0.756	4.56×10^4
VNbC ₂ /Bi _X Ti _Y O _Z	90.71	1.41×10^4	2.9×10^{-4}	0.792	2.43×10^5	2.61×10^{-5}	0.140	2.48×10^5

TABLE V. Impedance values for different immersion times and low frequency (0.01 Hz).

Sample	Z_{real} (Ω)				
	1h	24h	48h	72h	168h
D2	1.8×10^4	2.0×10^4	1.7×10^4	1.6×10^4	1.5×10^4
VNbC ₂	8.5×10^4	2.9×10^4	2.4×10^4	2.2×10^4	2.0×10^4
VNbC ₂ /Bi _X Ti _Y O _Z	5.2×10^4	2.6×10^4	2.0×10^4	1.9×10^4	2.4×10^4

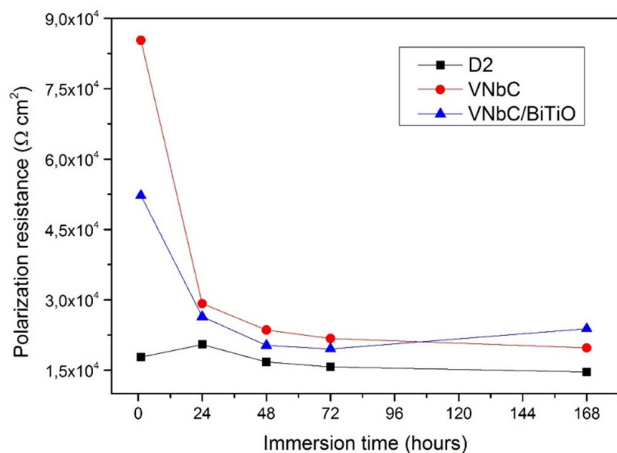


FIGURE 5. Polarization resistance as a function of immersion time for bare substrate, ternary, and bilayer coatings.

where, Y_0 is the admittance and the value of α determines if the behavior of the CPE is an ideal capacitor ($\alpha = 1$) or a resistance ($\alpha = 0$) [20].

The results obtained from analysis of Bode and phase diagrams of the bare substrate and the bilayer coatings are shown in Table IV. The fitting data show that the ternary coating exhibits a capacitive behavior ($\alpha = 0.696$) and a low value of R_{por} . Moreover, the bilayer coating has a resistive behavior ($\alpha_{dl} = 0.14$) and a high value of R_{por} . The polarization resistance decreases with increasing immersion time for the ternary coating, as shown in Fig. 5, indicating that the ternary coating is porous, and the electrolyte has penetrated the coating through the pores, producing a localized corrosion. This can also explain the low value of R_{por} . However, the bilayer

coating shows improvement of the resistance polarization for a long immersion time, showing that the titanate had barrier effects over the ternary coating defects, which is reflected in a high value of R_{por} . Finally, at low frequency (0.01 Hz) and long immersion time (168h), the coatings exhibited better electrochemical behavior with respect to steel. This is reflected in a higher impedance value (see Table V).

4. Conclusions

Coatings of NbC, VC and VNbC were produced through the TRD process, and on them amorphous BiTiO layers were grown.

The corrosion behavior was studied using potentiodynamic polarization curves and modeling of EIS spectra. The results obtained allow establishing that these coatings were chemically less reactive than substrate and can be used as a protective layer on steel used for fabricating cutting tools. The values of polarization resistance decreased with assay time, likely to due to increased pores in the coating, which promotes an increase of corrosive electrolyte on the substrate surface.

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