Electrochemical Properties of TiWN/TiWC Multilayer Coatings Deposited by RF-Magnetron Sputtering on AISI 1060

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Abstract: Nitride and carbide ternary coatings improve the wear and corrosion resistance of carbon steel substrates. In this work, Ti-W-N and Ti-W-C coatings were deposited on AISI 1060 steel substrates using reactive radio frequency (RF) magnetron sputtering. The coatings were designed as monolayers, bilayers, and multilayers of 40 periods. The coatings were obtained with simultaneous sputtering of Ti and W targets. The microstructure, composition, and electrochemical properties were investigated by techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), atomic force microscopy (AFM), electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization. XRD results showed a mix of binary TiN and W2N structures in the Ti-W-N layer, a ternary phase in Ti-W-C layers, and a quaternary phase of Ti-W-CN in the multilayers. The analysis of the XPS demonstrated that the atomic concentration of Ti was more significant than W in the Ti-W-N and Ti-W-C layers. The lowest corrosion rate (0.19 mm/year) and highest impedance (~10 kΩ·cm²) out of all coatings were found in n = 40 bilayers. In the simulation of equivalent electrical circuits, it was found that the Ti-W-N coating presented three processes of impedance (Pore resistance + Coating + Inductance). However, the multilayer (n = 40) system presented a major dielectric constant through the electrolyte adsorption; therefore, this caused an increase in the capacitance of the coating.

Keywords: hard coatings; monolayer; bilayer; forty-periods; corrosion

1. Introduction

In the last few decades, transition-metal nitride and carbide coatings have been extensively used to enhance the life and performance of cutting tools and mechanical components. Conventional binary hard coating such as TiN, CrN, and TiC can improve the wear and corrosion resistance of metallic substrates, such as carbon steels [1]. These coatings are applied to cutting, surface finishing, and other manufacturing processes to increase wear resistance, improve finishing [2], reduce friction, and improve chemical resistance in components exposed to corrosive environments [3,4]. In tribological applications, the brittleness of some transition-metal nitrides is a drawback. Furthermore, the porosity of coatings can weaken the corrosion resistance of the composite coating-substrate since the electrolyte forms a galvanic pair with the noble coating and active substrate [5].
In order to increase the oxidation resistance at high temperatures, improve the tribological performance and increase the corrosion resistance of conventional binary coatings, ternary nitride and carbide coatings, such as TiAlN, Ti-W-C, and Ti-W-N, have been investigated, while Ghufran et al. [6] and Akito et al. [7], registered a patent invention (#US20200156213A) denominated “Super-Abrasive Grain and Super-Abrasive Grinding Wheel”, grinding ternary nitride and carbide-based on Ti. The industrial sector of polymer petrochemistry has demanded improvement in the cutting of poly-vinyl chloride (PVC) profiles. The main problems presented in these systems are the deterioration and corrosion in the cutting devices. There are different methods to reduce these problems, such as modifying the tools’ surface [8,9], and through the use of hard carbide and nitride coatings deposited by reactive RF-magnetron sputtering. Tungsten-nitride (W-N) deposited on steel tool substrates improves their hardness and deterioration resistance [10]. Coatings of TiN and W\textsubscript{2}N have been successfully deposited on steel tools [11]. In order to improve adherence between the coating and the substrate, a metal interface has been included in the systems, for example, the deposition of a titanium (Ti) buffer layer in a titanium nitride (TiN/Ti) coating [12]. Another benefit of using pure Ti as an interlayer is the improvement of the corrosion behavior of the n = 40 nanostructured Ti/TiN [13]. With this, the corrosion rate decreases even further since the interface provides lower permeability to the coating, diminishing the defects and pores between the columns that reach the substrate [14,15]. The presence of many interfaces between individual layers of a multi-layered structure results in a drastic increase in hardness and strength [16]. Thus, multilayer coatings have also gained the interest of researcher due to their advantages over single coatings. Additionally, multicomponent coatings based on different metallic and non-metallic elements combine the benefits of different individual components, leading to a further refinement of coating properties.

Carbon steel 1060 is used in the cutting process of PVC, in which the steel is in contact with the chloride polyvinyl polymer matrix, which produces abrasive deterioration [17]. In addition to this, the high temperatures in the system ease the detachment of hydrogen chloride, promoting generalized corrosion of the metal due to the steel depassivation process [18]. The use of metal nitrides has been suitable for industrial applications, thus a comparison between nitrides has been established; for example, between Ti-W-N and Ti-W-C, being determined that the latter have better electrochemical properties [16]. Considering the above, Ti-W-N/Ti-W-C coatings are expected to present better mechanical properties, as well as other properties relevant to applications of elements subjected to high wear conditions [17]. Unfortunately, the literature presents little research focused on studying the electrochemical properties of Ti-W-N/Ti-W-C multilayers in aggressive environments. Although some authors [18,19] have studied the physical properties of steel substrates coated with single Ti-W-N layers, these studies do not relate to the Ti-W-N/Ti-W-C coating’s performance in aggressive environments. Therefore, the present work aimed to study the structural, morphological, and electrochemical behavior of Ti-W-N/Ti-W-C multilayer coatings on AISI steel substrates, in aggressive environments, with potential applications in the metal-mechanic industry. To this end, four different coating systems were deposited by the reactive RF- magnetron sputtering technique, specifically two monolayer coatings of ternary Ti-W-N and Ti-W-C, one bilayer coating of Ti-W-N / Ti-W-C (period n = 1), and a forty-bilayer coating of Ti-W-N/Ti-W-C (n = 40).

2. Materials and Methods

2.1. Materials

For the deposition of the Ti-W-N and Ti-W-C coatings, high purity target discs of Ti (99.99%) and W (99.95%) with a 10 cm diameter and 5 mm thickness were used. For the plasma formation, argon (Ar) was used as the working gas for the carbides, and a mixture of Ar (40%) and high purity nitrogen gas (60%) was implemented for the nitrides. For the carbide compounds, methane (CH\textsubscript{4}) was used as a reactive gas. The dimensions of the carbon steel samples used as substrates were 28 mm in length, 28 mm in width, and 3 mm
in height, consisting of 0.65% carbon content. For a cross-section analysis, silicon wafers (100) with an approximate area of 1 cm² were also coated. The metallic substrates were sanded with 100, 220, 400, and 600 grit sandpapers and later washed with industrial soap and dried in a forced-air (Thermo Fischer Scientific, Waltham, MA, USA) stove at 100 °C for 30 min. All substrates were cleaned by immersion in an acetone/isopropyl alcohol ultrasonic bath for 10 min. Electrochemical analyses were performed using a 3.5 wt.% aqueous solution of sodium chloride (NaCl) in distilled water.

2.2. Coating’s Deposition

The coatings were deposited via reactive RF-magnetron sputtering in a vacuum system using a power supply of 13.56 megahertz (MHz) of frequency and applying a negative bias of −10 V on the substrate. The substrates were placed on a rotatory system in the middle of both magnetrons with the Ti and W targets. The distance between the targets and the samples was 10 cm, with the substrate being heated to a temperature of 300 °C. The baseline pressure before the deposition process was 4 × 10⁻⁴ Pa. Samples were cleaned before the deposition process by plasma etching in the vacuum chamber for 20 min. The adhesion coating interlayers of pure Ti were deposited applying 450 watts of RF power and voltage bias of −10 V on the substrates for 10 min at 300 °C; and injecting Ar gas at a mass flow of 50 standard cubic centimeters per minute (sccm). The work pressure of the sputtering chamber was kept constant at 1.46 Pa for all deposited layers. For the deposition of the coatings, a RF-power of 350 and 420 W were applied to the Ti and W targets during the three hours of deposition. The n = 1 and n = 40 multilayer coatings were deposited by alternating the nitride and carbide monolayers’ parameters, as shown in Table 1.

Table 1. Deposition parameters and coating thicknesses for each coating: adhesion layer, monolayers, n = 1 bilayer and n = 40 bilayers.

| Parameter | Ti       | Ti-W-N   | Ti-W-C   | n = 1     | n = 40    |
|-----------|----------|----------|----------|-----------|-----------|
| Power (W) | Ti       | Ti-W-N   | Ti-W-C   | n = 1     | n = 40    |
| Ti        | 450      | 350      | 350      | 350       | 350       |
| W         | –        | 420      | 420      | 420       | 420       |
| Flux (sccm)| Ar   | 50/50    | 50/50    | 50/50     | 50/50     |
| N₂        | 0        | 12/0     | 12/0     | 12/0      | 12/0      |
| CH₄       | 0        | 16/0/16  | 0/16     | 0/16/0/16 | 0/16/0/16 |
| Deposition time (min.) | 20 | 180/180 | 180/180 | 90/90 (2.25/2.25) |
| Total Thickness (µm) | 0.21 | 2.81 | 3.54 | 1.57 + 1.20 = 2.77 | 3.57 |

2.3. Coatings’ Characterization

Structure analysis of the coatings was performed by X-Ray Diffraction (XRD) using a Malvern Panalytical X-ray diffractometer (Almelo, The Netherlands) with a Cu Kα (λ = 1.5406 Å), and the Bragg-Brentano configuration with a 2θ scanning scale from 20° to 80°. Chemical analysis was accomplished using the X-ray photoelectron spectroscopy (XPS) SAGE HR 100 (SPECS, Berlin, Germany) system. Samples were placed in an ultra-high vacuum (8 × 10⁻⁸ mbar.) previous to the XPS characterization. Following this, the binding energy was centered according to the location of the main peaks with 1.0 eV of full width at half maximum (FWHM). Coating thickness cross-section analyses were obtained by scanning electron microscopy (SEM, JEOL Ltd., Tokio, Japan) operating at 20 keV and on the secondary electron’s mode. Also, the sample preparation for the cross-section observations using transmission electron microscopy (TEM, JEOL Ltd., Tokio, Japan) was carried out using a focused ion beam (FIB) with a JEOL JEM-9320FIB equipment (JEOL Ltd., Tokio, Japan). The high-resolution (HR-TEM) images were acquired in scanning-TEM (STEM) mode with a JEOL JEM 2200Fs + Cs equipment operating at 200 keV.
The roughness and topography analyses of the coatings were carried out using atomic force microscopy (AFM, Nanosurf, Liestal, Switzerland) in contact mode through an Asylum Research equipment model MFP-3D (MFP-3D-Stand Alone, Asylum Research, Abingdon-on-Thames, UK) on an area of 45 µm x 45 µm. A review of the images was executed using the Gwyddion 2017 version software (Czech Metrology Institute, Brno, Czech Republic). The roughness profile analysis of the coatings was obtained with a Tesa-Rugosurf 90G Surface Profilometer (Tesa, Bugnon, Switzerland).

2.4. Electrochemical Evaluation

Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization tests were used to evaluate the electrochemical behavior of the coatings. The dynamic corrosion evaluation was conducted using a Gamry potentiostat-galvanostat (Gamry Instruments, Warminster, PA, USA), Model PCI4. These tests were carried out in environmental conditions at a room temperature of 25 °C, using an acrylic rotatory cell that consists of a glass recipient where the solution (3.5% NaCl) that was used as the electrolyte was contained, and an acrylic covering which supported the electrodes. The test electrode (coating on steel) had an exposed area of 1 cm² submerged under the sodium chloride solution; the reference electrode (silver /silver chloride (Ag/AgCl)) was submerged in a saturated potassium chloride (KCl) solution at 3.33 molar, using a platinum wire as a counter-electrode.

2.5. Considerations for Electrochemical Evaluation

2.5.1. Open Circuit Potential

Before the electrochemical measurements were performed, the working electrode was subjected to a surface cleaning pretreatment with distilled water and then dried with air. Subsequently, it was subjected to an ultrasonic bath in acetone for 1 min followed by 1 min in ethanol to ensure complete cleaning of the surface. After the pretreatment, the metal was depolarized. The working electrode was positioned together with the reference electrode and the counter electrode, while the open circuit potential was monitored until it reached a stationary value. The potentiostatic polarization curves were performed by scanning discrete potential values. The evolution of the open circuit potential was carried out during 120 min, and in all cases, it presented a typical curve, exhibiting a rapid decrease in the initial period and then diminishing its slope until it stabilized. The evolution of the OPC towards more negative values was observed in each case, indicating a cathodic control in the metal dissolution process. This is observed in the polarization curves obtained by Tafel.

The term Corrosion Potential, $E_{corr}$, is related to the potential in an electrochemical experiment in which no current flows. In the cases evaluated the values of $E_{oc}$ and $E_{corr}$ were identical. The equations used to convert from one form of potential to the other is Equation (1):

$$E_{vs. \ E_{ref}} = (E_{vs. \ E_{oc}}) + E_{oc}$$

In the case of corrosion reactions, an electrochemical reaction under kinetic control obeys the Tafel equation, Equation (2):

$$I = I_0 e^{(2.3(E-E^0)/\beta)}$$

where $I$ = the current resulting from the reaction, $I_0$ = a reaction-dependent constant called the Exchange Current, $E$ = the electrode potential, $E^0$ = the equilibrium potential (constant for a given reaction), $\beta$ = the reaction’s Tafel Constant (constant for a given reaction). Beta has units of volts/decade.
2.5.2. Corrosion Current Density

According to ASTM G102-1994 [20], corrosion current values are obtained by Tafel Extrapolation through the conversion of the measured current value to current density, Equation (3):

\[ \textit{i}_{\text{corr}} = \frac{I_{\text{corr}}}{A} \]  

where:

- \( \textit{i}_{\text{corr}} = \) corrosion current density (\( \mu A/cm^2 \))
- \( I_{\text{corr}} = \) total anodic current, \( \mu A \)
- \( A = \) exposed specimen area, cm².

2.5.3. Corrosion Rate

Calculate the corrosion rate (CR) in terms of penetration rate, Faraday’s law is used [20,21], Equation (4):

\[ \text{CR} = K_1 \frac{\textit{i}_{\text{corr}}}{\rho A} \text{EW} \]  

where:

- \( \text{CR} = \) Given in mm·year⁻¹
- \( \textit{i}_{\text{corr}} = \) Corrosion current in amperes
- \( \text{EW} = \) Equivalent wight in grams/equivalent
- \( K_1 = 3.27 \times 10^3, \text{ mm g/} \mu A \text{ cm} \cdot \text{year} \)
- \( A = \) Area of the sample in cm².

2.5.4. Porosity Factor

The permeable defects are detrimental to the substrate due to the propagation of the corrosion, caused by promoting direct ways that allow the corrosive electrolyte to reach the substrate. The evaluation of porosity by an electrochemical method is based on the correlation of the current density, but it takes into account the indirect potentiodynamic measurement of the electrochemical behavior and the current density, which is indirectly proportional to the resistance of polarization [22]. The polarization resistance is experimentally determined from the impedance measurements according to Tato’s equation [23]:

\[ P (\%) = \left( \frac{R_{p,u}}{R_{p,r-u}} \right) \]  

where:

- \( P = \) the porosity factor, if it’s near to 0%, it indicates that the coatings act as an inert barrier against the corrosive solution. If the factor of porosity is close to 100%, it indicates that the coating does not act as a barrier for corrosive diffused Cl⁻ ions that are attributed to creating coating defects such as pores, cracks, delamination, material dissolution, etc.
- \( R_{p,u} = \) total resistance (kΩ·cm²) of the bare substrate
- \( R_{p,r-u} = \) total resistance (kΩ·cm²) of the coating.

3. Results and Discussion

3.1. X-ray Diffraction Analysis

Diffractograms of the monolayers, \( n = 1 \) bilayer and the multilayered coating are shown in Figure 1. The XRD spectra of the Ti-W-N (green line) consisted of five peaks, corresponding with two crystalline phases of Ti₂N and W₂N respectively reported by different authors [10,11,19]. The peaks diffracted at 2θ angles 36.8°, 43.9°, and 76.5° by planes (111), (200), and (311) [24] corresponded to the typical simple cubic (SC) W₂N, indexed by ICDD PDF No. 00-025-1257 database [25]. The Ti₂N phase was identified as a tetragonal crystal structure (ICDD PDF No. 01-080-3438), corresponding to the peaks at 36.8°, 41.5°, 57.1°, and 69.9° originated by planes (112), (004), (105), and (301) respectively.

It is considered that the crystal structure is a mixed phase of W₂N/Ti₂N [11]. Furthermore, it was calculated that a pseudobinary mix of cubic TiN and hexagonal WN (as WC) phases
were thermodynamically favored in Ti-W-N [26]. The spectra of the Ti-W-C monolayer coating (blue line) had four peaks, where an intense peak related to the orientation plane (111) at 49.8°, corresponding to the titanium dicarbide (TiC\(_2\)) cubic type structure [27], according to chart PDF 04-007-2539. While the peaks located at 43° and 73° correspond to a W\(_2\)C hexagonal structure (PDF 04-014-5679). The atomics radius of tungsten and titanium are similar, thus are easily formed into the Ti-W-C ternary system [28]. The spectra of the n = 1 bilayer (orange line) showed an intense peak with a preferential plane (111) is observed corresponding to the TCC structure. The Ti-W-C-N (red line) multilayer (n = 40) had peaks that belong to Ti-W-N and Ti-W-C, plus a quaternary phase of Titanium Tungsten Carbide Nitride (Ti\(_{0.75}\)W\(_{0.25}\))(C\(_{0.75}\)N\(_{0.25}\)), which has a cubic structure according to the ICDD 01-081-8122 database, considering a phase stability domain [29]. The formation of the quaternary phase could possibly be due to the diffusion between the carbide and nitride layers, as it has been found for Ti-N/Ti-C multilayers, by means of XRD [30], SEM cross-section [31], and Glow Discharge Optical Emission Spectroscopy (GDOES) analysis [32,33]. XRD results indicate the formation of a quaternary compound, meaning that, when taken into consideration with the presence of mixed binary phases for W-Ti-N and W-Ti-C layers, and the evidence of the coexistence of multiple crystalline phases in the multilayer with 40 periods, it can be supposed that there is a graded zone along with the interfaces of multilayer. It would be interesting to investigate the phase distribution by transmission electron microscopy (TEM), as well as through compositional depth profiling, but this is beyond the reach of this paper.

3.2. Microstructural Analysis

Cross-section micrographs of Ti-W-N, Ti-W-C monolayers, n = 1, and n = 40 multilayers are shown in Figure 2a–d. As seen in Figure 2a, the thickness of the Ti-W-N coating was 2.81 ± 0.27 μm with a buffer layer of 200 to 240 nm deposited in all coatings; the thickness average was similar to the obtained by the profilometry method, which was 3.29 ± 0.06 μm. The evolution of the microstructure was the typical columnar growth of PVD processes, similar to those reported in [34,35]. In the case of the Ti-W-C coating (Figure 2b), the thickness was 3.54 ± 0.04 μm, however, when measured by the profilometer it was 2.95 ± 0.08 μm. The microstructure obtained was of columnar growth typical of WC and TiC monolayer coatings deposited at low temperatures between 200 to 500 °C by sputtering [36]. Figure 2c evidenced that the thickness of the upper Ti-W-C coating was 1.56 ± 0.02 μm and the thickness of the lower Ti-W-N coating on the substrate was 1.20 ± 0.03 μm (total thickness of 2.76 μm); the thickness average obtained was 2.06 ± 0.03 μm. The upper dark grey layer corresponded to the presence of carbon atoms in the formation of Ti-W-C, and the
light grey layer is the Ti-W-N [37]. Figure 2d exhibits the n = 40 multilayers, showing a thickness of 3.57 ± 0.06 μm; this value was similar to that obtained by the profilometer (3.29 ± 0.12 μm).

![Cross-section SEM images of the coatings](image)

**Figure 2.** Cross-section SEM images of the coatings, (a) Ti-W-N monolayer, (b) Ti-W-C monolayer, and (c) n = 1. HR-TEM micrographs (d) n = 40 deposited on Si (001)/Ti by RF magnetron sputtering.

This thickness exhibited a progressive increase in the interface roughness with the rise of the number of stacked layers; however, the thickness of each bilayer remained unchanged [34]. This zig-zag-like interface roughness is attributed to the application of negative substrate bias during the deposition process, which produces ion bombardment on the TiWC/TiWN layers while the add-atoms reach the substrate surface [38]. Järrendahl et al. [39] found that sputtered layers display, a cupola-like microstructure with a working pressure of 0.67 Pa and without substrate bias. Conversely, Cancellieri et al. [40], reported waving patterns due to the kinetic energy of the incident ionic species by the rf-bias, increasing the velocity and surface mobility of the add-atoms, thus, affecting the crystalline quality.

3.3. XPS Analysis

The X-ray photoelectron broad spectra obtained in the range of 0–1000 eV for the Ti-W-N coating are depicted in Figure 3a–d. The quantification of the atomic concentration (%) corresponding to Ti-W-N is shown in Table 2. The photoelectron peaks of O (KLL), Ti (2s), O (1s), Ti (2p3), N (1s), Si (2p), and W (4f) are revealed (Figure 3a–d). Figure 3a puts on display the high-resolution W (4f) peak of the Ti-W-N coating. These peaks were found at 38.31 and 34.42 eV, corresponding to the tungsten bonded with N (W-N) and Ti (W-Ti), respectively. Figure 3b shows the two N (1s) bonding energies of N-Ti with 396.97 eV and of N-W-O with 400.38 eV [41]; this binding energy N(1s) corresponds to the N-Ti bond according to Restrepo et al. [42]. Figure 3c, shows the photoelectron peak of Ti (2p) was at 457.59 eV (Ti-N) and 462.79 eV (N-Ti-N) [43].
Figure 3. High resolution XPS spectra of the Ti-W-N coating deposited by RF magnetron sputtering.
(a) W (4f), (b) Ti (2p), (c) N (1s).
On the other hand, Figure 4a–d discloses the X-ray photoelectron wide spectra obtained for the coating Ti-W-C. The quantification of atomic concentration (%) corresponding to the Ti-W-C coating is shown in Table 2. The photoelectron peaks of O (KLL), Ti (2s), O (1s), Ti (2p3), N (1s), Si (2p), and W (4f) have been shown. Figure 4a, shows the line of the photoelectron of W 4f, identifying two bond energies corresponding to W-C (34.37 eV) and W-Ti (38.85 eV). In Figure 4b, the peak of C 1s is due to the formation of carbide titanium C-Ti with a bond energy of 284.73 eV. Moreover, it presents a bond energy of W-C-O (289.06 eV) [44]. Finally, Figure 4c indicates the peak of photoelectron Ti 2p, which presents two bond energies of Ti-N (457.31 eV) and W-Ti-O (463.26 eV). The presence of residual oxygen on coatings is due to the typical desorption in PVD deposition processes [45].

### Table 2. Chemical composition in atomic concentration (%) using XPS.

| Material Type | Element | C  | N  | W  | Ti  |
|---------------|---------|----|----|----|-----|
| Ti-W-N        |         |    | 24.16 | 35.72 | 40.12 |
| Ti-W-C        |         | 20.30 |    | 36.97 | 42.72 |

3.4. Roughness Analysis

Roughness by AFM

AFM images of the Ti-W-N, Ti-W-C monolayers, and \( n = 1, n = 40 \) multilayers are shown in Figure 5a–d. In Figure 5a, the Ti-W-N coating shows the topography of regular texture, exhibiting certain homogeneous formations with similar dimensions, in which not more than three or four isolated cone-type crests were observed on the surface. These
cone-types crests are produced by an intermixing process of columns that occurs during the coating’s growth at the interfaces with the substrate [46]. The surface roughness Ra (average) was 15.5 ± 0.1 nm and the top of the columns were 132.3 ± 3.9 nm. In Figure 5b, the monolayer coating of Ti-W-C presents similar topography in the surface; it also presents some isolated crests, a few small sharp pyramid-type crests with an increase in their height profile, with an average roughness of 12.6 ± 0.9 nm, and formations of 128.5 ± 3.8 nm. Figure 5c reveals the most significant texture, the roughness of the material, which was 8.1 ± 0.1 nm with domes of 115.6 ± 3.5 nm. Figure 5d shows an uniformly smooth texture with bulk grains; it also indicates a decrease in roughness of 4.7 ± 0.3 nm, and a 96.4 ± 2.9 nm grain size. These roughness values are in agreement with those previously reported by Petrović et al. [47]. The n = 40 multilayer’s smoother surface can be explained by the reduced width of the column growth (see Figure 2d), evidenced in the morphology of the cross-section observed by SEM. The n = 40 multilayer’s repeated nucleation processes impeded the columns’ widening [48,49].

Figure 5. AFM images in 2D of the coatings, (a) Ti-W-N monolayer, (b) Ti-W-C monolayer, (c) n = 1, and (d) n = 40 coatings.

3.5. Electrochemical Behavior
3.5.1. Potentiodynamic Curves

Corrosion tends to happen in the most reactive points of the surface, considering factors as emerging dislocations, high index face grains, inclusions, grain limits, particles, second phases, and cracks [50]. The behaviour of the potentiodynamic curves using the 3.5% NaCl solution as the electrolyte is revealed in Figure 6. All polarization tests evidenced typical zones of anodic-cathodic activation. However, the monolayer of Ti-W-N (green curve) indicated a primary passive potential (Epp) and critical current density [51]. These are results of the kinetic reactions satisfying the equation for i (total) = 0 [52], promoting the formation and development of a passive coating on the surface. The passive protective coating may act as a barrier layer to prevent the metal of the metal ion [53]. The current limit (i_{lim}) is increased in the anodic region. The intersection curve for the cathodic reaction of the anodic polarization is the passivation region, which is due to the spontaneous coating
passivation [54]. For the case of the coating with carbides (blue curve), the corrosion resistance decreased when the carbon contained in the material increased [55].

![Figure 6](image)

**Figure 6.** Potentiodynamic curves of the substrate and coated samples in 3.5 wt.% NaCl solution.

The n = 1 (orange line) coating presented spontaneous symmetry in the anodic and cathodic regions. The $E_{corr}$ value of $-0.55 \text{ V}$ tends to be positive, and the $i_{corr}$ of $2.0 \times 10^{-6} \text{ A cm}^{-2}$ decreased compared to the bare substrate. For the n = 40 coating (red line), the $E_{corr}$ was $-0.26 \text{ V}$ and the $i_{corr}$ was $9.2 \times 10^{-6} \text{ A cm}^{-2}$. Thus, it can be considered that the material tends to become noble (electropositive potential), improving the decrease of the anodic current density around two scales of magnitude compared with the bare substrate. This behavior was similar to that obtained by Alves et al. [56]; though was better than the one obtained by Caicedo et al. [25]. The potential and current increased due to the dissolution of active metal generated by the galvanic coupling between the substrate and the coating [57]. Coating passivation (active-passive) can be attributed to the presence of Ti, considering the chemical property of this transition metal which inhibits corrosion. The increase of corrosion resistance in the materials was attributed to the compact microstructure, and density of the coating [58]. The low corrosion current was influenced by the chemical composition close to the surface, due to the formation of the passive layer of oxide (TiO$_2$) on the surface [59].

### 3.5.2. Corrosion Rates

In Table 3, the $i_{corr}$ of each system was taken, and the corrosion rates (CR) were calculated. The n = 40 coating presented a significant decrease in the CR, specifically 0.19 mm·year$^{-1}$; this is significantly more than 16 times less than the bare steel substrate. This behavior is characteristic of the n = 40 layered structure due to the increased number of multilayers (n), density, and the number of interfaces while maintaining a uniform thickness in the multilayered system [60].

| Material Type  | $E_{corr}$ (V vs. Ag/AgCl) | $i_{corr}$ (A·cm$^{-2}$) | CR (mm·year$^{-1}$) |
|----------------|-----------------------------|--------------------------|---------------------|
| AISI 1060      | $-1.13$                     | $4.2 \times 10^{-5}$     | $3.12$              |
| Ti-W-N         | $-0.86$                     | $5.7 \times 10^{-6}$     | $0.58$              |
| Ti-W-C         | $-0.69$                     | $2.2 \times 10^{-6}$     | $0.42$              |
| n = 1          | $-0.55$                     | $2.0 \times 10^{-6}$     | $0.35$              |
| n = 40         | $-0.26$                     | $1.08 \times 10^{-6}$    | $0.19$              |

Table 3. Electrochemical parameters of the potentiodynamic curves of the monolayers, n = 1 and n = 40 coatings.
3.5.3. Electrochemical Impedance Spectroscopy

Nyquist Diagram

Figure 7 shows the Nyquist diagram for all the systems evaluated, including both monolayers, \( n = 1 \), and \( n = 40 \) multilayers. The bare substrate presented less impedance value due to its high reactivity compared with the coatings; this is because the measurement of impedances is between 0.001 Hz and 100 kHz. The real axis \((Z')\) presented a decrease in the electrical resistance \((k\Omega \cdot m^2)\) of the electrolyte \((R_s)\), and greater resistance of the transference of the charge \((R_p)\), the double layer \((R_2)\), the polarization of capacitance \((CPE_1)\) and the double layer \((CPE_2)\). Thus, the real impedance \(R_{sol} + R_1 + R_2\) presented the same behavior in the imaginary axis \((Z'')\), that is, it presented high resistance of polarization compared with the other systems (see results in Table 4).

![Nyquist Diagram](image)

**Figure 7.** Nyquist diagram of all the coatings after AC impedance testing in 3.5 wt.% NaCl solution.

**Table 4.** Electrochemical behavior by EIS of the monolayers, \( n = 1 \) and \( n = 40 \) coatings.

| Material Type | \( R_p \) (k\(\Omega\) \(\cdot\) cm\(^2\)) | \( CPE_1 \) \( S \times s^n \) | \( n_1 \) | \( CPE_2 \) \( S \times s^n \) | \( n_2 \) |
|---------------|-----------------|-----------------|--------|-----------------|--------|
| AISI 1060     | 0.32            | \( 1.87 \times 10^{-9} \) | 0.72   | \( 26.09 \times 10^{-9} \) | 0.92   |
| Ti-W-N        | 12.15           | \( 8.70 \times 10^{-7} \) | 0.84   | \( 119.7 \times 10^{-6} \) | 0.85   |
| Ti-W-C        | 16.48           | \( 0.74 \times 10^{-6} \) | 0.94   | \( 133.6 \times 10^{-6} \) | 0.86   |
| \( n = 1 \)   | 32.02           | \( 6.66 \times 10^{-6} \) | 0.82   | \( 177.9 \times 10^{-6} \) | 0.86   |
| \( n = 40 \)  | 56.82           | \( 8.70 \times 10^{-6} \) | 0.92   | \( 20.97 \times 10^{-6} \) | 0.92   |

\( S \) is siemens (=1/ohm), \( s^n \) is second-to-the-power-\( n \).

The dissolution resistances obtained at 100 kHz are considered high frequencies and the data is acquired in the range between 100–0.0001 Hz, while low frequencies provide information about reaction kinetics. All proposed systems had a better resistance compared with the bare steel substrate. The response to impedance in the semi-circle is attributed to the controlled process of energy activation. However, the repressed semi-circles can be found in these coatings since the systems are not ideal, and therefore, the application of a resistor-capacitor pair \((R_1\text{-}CPE_1)\) would not be enough to model that impedance response [61]. The \( n = 40 \) multilayer system formed the symmetrical semi-circle (loop) where the limit of low frequency \((\omega \rightarrow 0)\) was without any defect in the semi-circumference. The element of constant phase CPE is accompanied by a parameter denominated as \( n \), which is independent of the frequency when its value is near to 1. When this occurs, it behaves like an ideal capacitor and represents the capacity of the interface; when it takes a value close to 0, it associates it to an element resistor. Additionally, the system describes the behaviour of the surface heterogeneity; hence, the values close to \( n = 1 \) are associated with a decrease in surface roughness or coating homogeneity.
Table 4 shows how $R_p$ changes as a function of the coated materials and the different multilayers. With respect to the AISI 1060 steel substrate, as the multilayers increase, there was an increase in $R_p$, possibly attributed to the fact that the corrosion products had blocked the pores, increasing the resistive path. But a better indicator of the corrosion resistance of coatings is the polarization resistance. At higher $R_p$ values, increased corrosion protection is achieved, and fewer defects are present in thin films; it is also inversely proportional to the corrosion rate. This parameter is observed to take higher values in multilayers than in bare AISI 1060 steel, confirming that these coatings offer better protection against corrosion. In relation to the change experienced by $R_p$ through time, it can be appreciated that the multilayers were evaluated at different times. After the second hour of immersion, the polarization resistance presented an average value of 3 kΩ higher; however, at 72 h a constant value of $R_p$ was appreciated, which is recorded in Table 4. These results can be explained by the relationship between $R_p$ and the evolution of porosity through time; an increase in polarization resistance and consequently a decrease in porosity, which can be related to the accumulation of corrosion products in the defects. Another parameter obtained by modeling the electrical circuits and used to analyze the corrosion resistance is the capacitance of the coatings (CPE2). The decrease of this parameter indicates that the coating’s porosity increased, and this greater number of pores allowed the electrolyte to penetrate and affect the substrate. The value of the AISI 1060 steel substrate corresponds to the passive layer on its surface, specifically the iron oxide film. This layer has the lowest capacitive properties compared to the multilayers and it is due to the fact that this layer dissolves.

3.5.4. Determination of Porosity

The percentage of porosity calculated from Equation (3) indicates that the coatings had a high homogeneity, which is due to their low percentage of porosity value. The coatings obtained by PVD associate this effect to the continuous bombardment of energetic ions of argon gas in the deposition of the coatings, increasing the movement of absorbed atoms on the steel substrates. This generates a coated surface that is more compact compared to the bare substrate. In Figure 8 shows the best system was the $n = 40$ multilayer, that multilayers because of its low porosity value, which is related to the grain size, whose measurement was obtained by AFM; showing a significant quantity of grain boundary, and hence a more homogeneous surface. The effect of increasing the number of multilayers also allowed the relaxation of residual stress; thus, the symmetry in the interfaces relates with the sinkhole of energy that prevents the propagation of cracks inside the coating and the reduction in porosity.

![Figure 8](image_url)

Figure 8. Percentage of porosity as a function of the coatings.

3.5.5. Equivalent Electrical Circuits

Randle’s equivalent electrical circuits, which are the physical model’s representation to understand the EIS mechanism of the monolayers, $n = 1$, and $n = 40$ multilayer coatings are
displayed in Figure 9a,b. Figure 9a, reveals that the circuit consisted of a double capacitance (CPE₁) which was connected in parallel with the charge resistance (R₂), also known as resistance polarization; both connected in series with the solution resistance (R₁) between the working electrode (WE) and reference electrode (RE). This circuit model represents the simple corrosion system, which is completely in control of the charge transference. The double-layer capacitance provides information on the polarity and the quantity of charge of the AISI 1060/electrolyte interface. When the coating was in direct contact with the electrolyte, it provided a direct diffusion path to the corrosive medium. In this process, the galvanic cell corrosion was formed and its domain was localized as well. In such a case, the interface was divided into two sub-interfaces: electrolyte/coatings and electrolyte/AISI 1060. The equivalent circuits R₁ and CPE₁ are related to the coating’s properties and reactions between the electrolyte and the coating. R₁ and CPE₁ are related to the reaction of the charge-transference in the electrolytes/AISI 1060 interface [62]. When an alternate potential was applied to the system (electrolyte + coating + substrate), a condenser was formed, known as the capacitance of the coating (CPE₁). In addition, the capacitor was formed when the coating began to be defined, and the electrolyte penetrated the space between the layer and the metallic substrate. The electrolyte and the substrate formed two condenser plates, while only one layer of water molecules (Helmholtz plane) separated the two plates that formed the dielectric [61]. This capacitance is well known as the double layer capacitance (CPE₂). For the case study of the coatings, the n = 40 multilayer system presented a major dielectric constant through the electrolyte adsorption; therefore, it caused the increase in the coating’s capacitance. In the Ti-W-N coating, the dielectric constant decreased, which indicates that the electrolyte penetrated to the metal through pores or cracks (as Figure 9b) [63].

![Figure 9](image-url)

Figure 9. Schematic of a standard equivalent circuit model (Randles circuit) (a), and impedance simulated of the coating system (b).
4. Conclusions

In this study, Ti-W-N and Ti-W-C monolayers as well as (TiWC/TiWN)\(_n=1\) and (TiWC/TiWN)\(_n=40\) multilayers were successfully synthesized by RF magnetron sputtering in order to examine the phase formation, microstructure, roughness, and electrochemical behavior in a NaCl solution.

- The Ti-W-N film structure consisted of a mix of two phases corresponding to Ti\(_2\)N (tetragonal crystal structure) and W\(_2\)N (typical simple cubic). For the n = 1 the diffraction peaks were identified as a sum of their respective phases for each layer. In the case of n = 40, the appearance of new intense peaks was observed, which were attributed to a quaternary compound Ti-W (CN) that could have been formed by the diffusion between nitride and carbide layers or the co-deposition of the used reactive gases: N\(_2\) and CH\(_4\). This quaternary compound, with the presence of mixed binary phases of WTiN and WTiC, could indicate that there is a graded zone along with the interfaces, which would be interesting to investigate by transmission electron microscopy and by small angle x-ray diffraction in future research.

- The microstructure was of the columnar growth type in all films, and the multilayers showed the smoothest surface because of the repeated nucleation processes that occurred in their growth. The same defects as cone-dome were observed in the monolayers.

- In the quantification of atomic concentration by XPS, a significantly larger presence of Ti in comparison to W was found in all the films.

- The results of the potentiodynamic prove were \(-0.26\) V for \(E_{corr}\), and \(9.2 \times 10^{-6}\) (A·cm\(^2\)) for \(i_{corr}\). The corrosion rate (CR) was 0.19 mm·year\(^{-1}\). Also, n = 40 exhibited the best protection and excellent dielectric resistance (~52.86 KΩ·cm\(^2\)). This behavior can be correlated to the interruption of the pores and defects that reach the substrate by the multilayer interfaces, making the coatings less permeable.

- In the equivalent electrical circuits, the n = 40 system presented a major dielectric constant throughout the adsorption of the electrolyte; hence, they have a greater capacitance. However, the simulation through the equivalent electrical circuits showed that in the TiWN system, the material presented three processes of impedance (pore resistance + film + inductance).

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