

Corrosion Resistance of the [TiN/CrN]_n Coatings Deposited on Steel AISI 4140

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Received: 4 June 2013 / Accepted: 28 June 2013 / Published: 1 August 2013

In this paper is presented the improvement against corrosion of the multilayer coatings [TiN/CrN]_n with periods of 20, 50, 100 and 200 bilayers deposited by the PVD magnetron sputtering technique on carbon steel AISI 4140. The electrochemical evaluation was performed by electrochemical impedance spectroscopy (EIS) and the polarization curves techniques in a solution of 3.5% wt. of NaCl. The corrosion resistance increased gradually in function of the bilayer number in comparison with the substrate; finding corrosion velocity values of 1225 $\mu\text{m/y}$ for the substrate without coating and 72.75 $\mu\text{m/y}$ for the specimen with 200 bilayers. The electrochemical results reveal the positive effect regarding the superficial protection of the 4140 steel with the increase of the period in the multilayers of [TiN/CrN]_n.

Keywords: [TiN/CrN]_n multilayers, corrosion velocity, EIS, Tafel.

1. INTRODUCTION

The hard coatings have been converted in the solution of problems such as corrosion. The physical vapor deposition technique (PVD), is one of the process more used for the obtention of hard coatings, that encompasses any growth process of a film in a vacuum environment that involves the deposition of atoms or molecules on a substrate [1][2], that consists of evaporating by physical means the material, which forms the coating and its subsequent condensation on the substrate, this process has the possibility to be applied simultaneously to sets or parts.

The first coating to be used in the machining industry and the actual recognition is TiN. This coating combines the high hardness with properties of low friction coefficient, ensuring greater service life therefore it is used mainly to coat cutting tools. In 1986 the TiN coatings were modified

implementing the TiAlN coatings [3][4][5]. The incorporation of aluminum atoms (Al) within the crystalline structure of titanium nitride (TiN) not just increases the oxidation resistance by formation of a stable layer and compact the surface, but also contributes to a significant increase in the hardness in comparison with the simple binary nitride [6][7]. Other of the used materials used to migrate superficial damages in the chromium nitride CrN, owing to its excellent mechanical properties (hardness around the 20 GPa), tribological (friction coefficient comparable to the TiN when is in contact with steel), high chemical and thermal stability with oxidation temperature about 700°C, that make this coating useful in a wide variety of industrial applications, such as the automotive industry [8] [9]. However, despite the excellent properties exhibited by both coatings, the corrosion resistance of these materials has been conditioned by the presence of structures defects inherent such as micropores, valleys and crevices that appear during the deposition, from this reason the focused effort by the researchers in the optimization of the deposition parameters. The presence of these defects is an important factor to take into account, since influence the integrity of the coating, not just in terms of corrosion resistance, in tribological and mechanical properties as well [10] [11]. In the last years, considerable efforts have been done to develop multicomponent coatings such as heterostructures in multilayers with the purpose to improve the wear and oxidation resistance of the coated components.

The improvements are presented in the alternating deposition of two (or more) chemical layers and/or mechanically different, such the tension concentration and the propagation conditions of nano-cracks can be controlled. Therefore the multilayer structure can acts as inhibitor of nano-cracks, in addition increases the fracture toughness [12].

The aim of this work is study the multilayers electrochemical nature, of the coatings multilayers type based on [TiN/CrN]*n* exposed to an aggressive medium in static conditions, comparing that behavior with the presented by the substrate.

2. EXPERIMENTAL DEVELOPMENT

[TiN/CrN]*n* multilayers were deposited overs substrates of AISI 4140 steel, which were cleaned by ultrasound in a sequence of ethanol and ketone during 15 minutes each one. The coatings were obtained by the magnetron sputtering multi-target technique in r.f (13.56 MHz). For the deposition of the coatings, were used targets with diameters of 4 inches of Ti and Cr with a purity of 99.9%. The base pressure at the interior of the vacuum chamber was 7.0×10^{-6} mbar. Before of initiate the deposition, the substrates were subjected to a cleaning by plasma during 20 minutes in Ar atmosphere at a bias of -400V in r.f. During the growth, the working gases were a mixture of Ar (92%) and N₂ (8%) with a total working pressure of 2×10^{-3} mbar, at a substrate temperature of 250°C. For the deposition of the multilayers, the aluminum target was periodically covered by the obturator, while the substrate was keeping under circular rotation in front the targets to facilitate the formation of the coatings [13].

With the purpose of study the influence on the electrochemical behavior of coatings multilayers type, were deposited systems of [TiN/CrN]*n* with periods of 20, 50, 100 and 200 bilayers controlling the opening and closing time of the obturator. The thickness of the coatings was obtained using a

profilometer DEKTAK 8000 with a tip diameter of 12 μm at a scanning length among 1000 – 1200 μm . For the specimen of 20 bilayers, the thickness was $2.96 \pm 0.04 \mu\text{m}$, and given that the coatings were obtained under the same parameters of growth and total deposition time, it is possible to state that multilayers systems have a thickness around this value.

For the evaluation of the static corrosion resistance was used a potentiostat - galvanostat, Gamry PCI-4 model; using electrochemical impedance spectroscopy (EIS) and polarization curves techniques, at room temperature, the specimens were placed under immersion in a solution 3.5 in weight of NaCl prepared with distilled water, using a cell composed by a counterelectrode of platinum, a reference electrode of Ag/AgCl and as a working electrode was used the AISI 4140 steel with and without coating in multilayers form. The Nyquist diagrams were obtained performing frequency scanning in a range of 0.001 Hz to 100 kHz, using amplitude of the sinusoidal signal of 10 mV. The Tafel diagrams were obtained at a scanning velocity of 0.5 mV/s in a range of -0.25 V to 1 V using an exposed area of 1 cm^2 .

3. RESULTS AND DISCUSSION

3.1 Surface analysis by SEM

The figure 1a and 1b show the surface of the films of $[\text{TiN/CrN}]_n$ con $n=20$ and 200 at 2000X, respectively. In these can be observe that the surface of $n=20$ presents an agglomerate type morphology, distribute in all the area of the micrography with some big grains, while the $n=200$ presents a uniform surface with more refined grains. This indicates that under the selected deposition parameters, the growth form is in a disorderly way for $n=20$ comparing with the $n=200$, indicating that a rougher coating implies a different behavior versus the corrosion resistance.

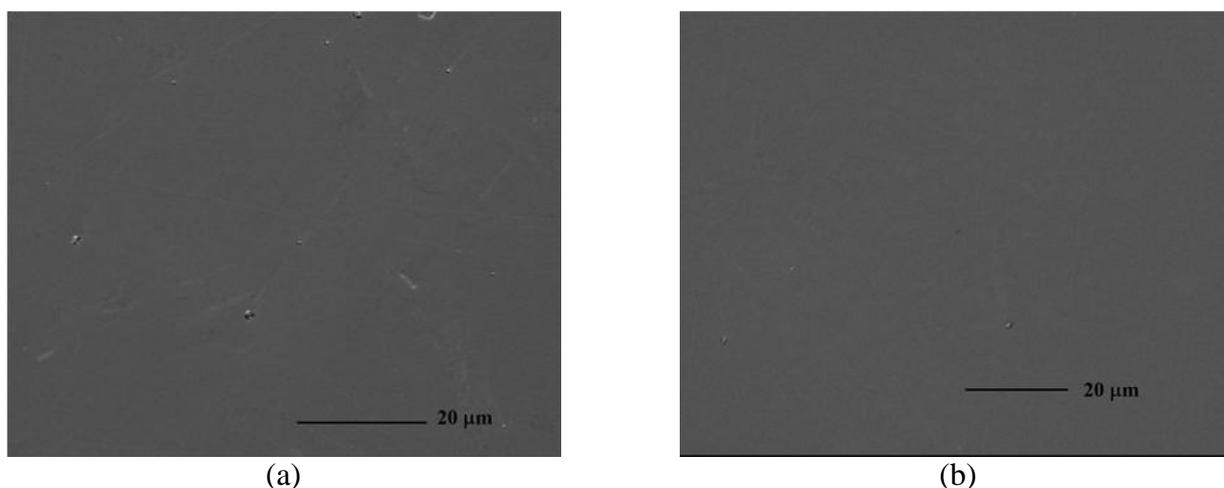


Figure 1. SEM micrograph of (a) $n=20$ (b) $n=200$ at 2000X

3.2 Electrochemical evaluation

In the figure 2 is shown the Nyquist diagrams corresponding to the substrate and the [TiN/CrN]_n. The values of those parameters had been obtained using a non linear program of least squares complex. The Nyquist for the bilayers show two time elements, the first is the semicircle found in the region of high frequencies, this correspond to the passive layer and/or the dielectric properties of the coatings, the second semicircle is associated to the interphase between the bilayers and the substrate, this corrosive process is found for the low frequencies [14].

For the substrate, it just has a semicircle due to the oxide layer that forms the steel with the contact of the aggressive solution at which is subjected. The from total impedance data better known as the summation of the resistance R₁+R₂ is obtained, that are increasing according the number of bilayers increase (Table 1), additionally it is observed that are superior than the found in the substrate due to the electrolyte is enough aggressive generating a higher reaction velocity on the steel without coating.

The figure 2 shows the Nyquist diagrams of the substrate and the coatings submerged in a solution of NaCl at 3.5%. In all the Nyquist diagrams of the figure 2 are observed a capacitive behavior at high frequencies, in which is defined a flattening semicircle and its center is located below of the real axis.

This flattening phenomenon of the semicircle is associated with a dispersion process in the frequency, due to the electrode surface is not homogeneous. In addition, it is observed a diffusion process which aims to define a second semicircle at low frequencies. The figure 2 also includes the simulation results using the electric circuit indicated in the figure 3. As can be seen, there are good concordance among the experimental and simulated results [15].

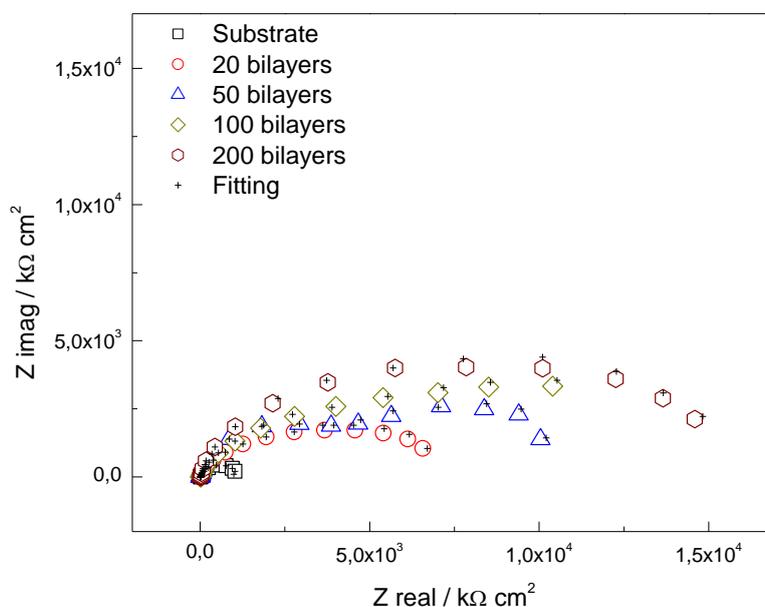


Figure 2. Nyquist plots experimentation for multilayers [TiN/CrN]_n.

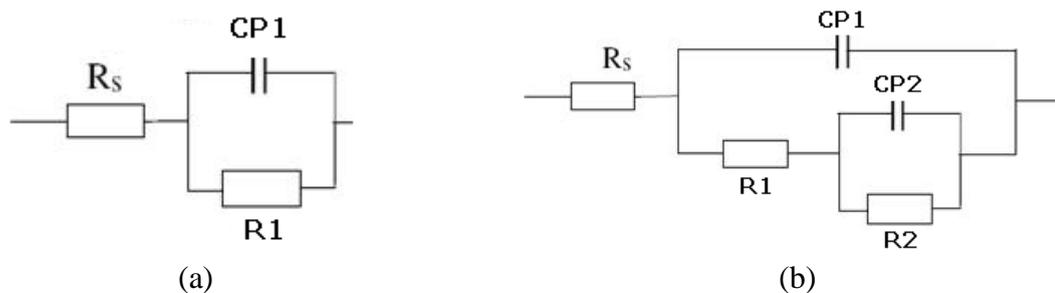


Figure 3. (a) Equivalent circuit used to fit substrate impedance data. (b) Equivalent circuit used to fit multilayer impedance data.

In the table 1 indicated the values of the used parameters in the simulation. In the figure 3 is observed the equivalent circuit corresponding to the Nyquist diagrams for the coatings, which show a capacitance denominated “constant phase element of double phase” (CPE), which is independent to the faradic reactions, that contribute with a pseudocapacitance (CPE2+CPE1) to the total impedance of the system. On the other hand, in this electrochemical cell exists an electric resistance as well, associated to the electrolyte resistance (R_s), which likewise will become manifest in the total impedance of the system. The values of α (table 1), correspond to the exponential coefficient of the phase angle shift ($n/2$).

The total impedance data better known as the summation of the resistance R_1+R_2 are increasing according the number of bilayers increase (Table 1), furthermore it is observed that are superior than the found in the substrate due to the electrolyte is enough aggressive generating a higher reaction velocity on the steel without coating.

Table 1. Parameters used in the fitting of impedance data for substrate and multilayers [TiN/CrN]_n.

	R_Ω	CPE_1	α_1	R_1	CPE_2	α_2	R_2
200 bilayers	45.21 (0.5%)	12.15 (3%)	0.92 (0.4%)	7.24 (5%)	45.23 (4%)	0.85 (0.5%)	14.09 (6%)
100 bilayers	42.3 (0.5%)	5.12 (1.4%)	0.84 (0.3%)	6.12 (5%)	34.24 (6%)	0.87 (0.3%)	13.14 (5%)
50 bilayers	39.5 (0.7%)	4.14 (2.9%)	0.74 (0.4%)	5.21 (3%)	24.25 (3%)	0.72 (0.6%)	10.24 (5%)
20 bilayers	45.2 (0.8%)	3.98 (2.4%)		4.19 (3%)	13.54 (2%)	0.68 (0.7%)	7.42 (3%)
Substrate	49.1 (0.7%)	3.84 (2.9%)	0.82 (0.6%)	1.45 (5%)			

The Tafel polarization curves are shown in the figure 4, in where is observed that the corrosion potentials are displaced towards cathodic zones (protection), as the number of bilayers increase, furthermore the current corrosion density decrease in comparison with the obtained in the substrate.

Otherwise it was observed that the coated steel with [TiN/CrN]_n which contents 200 bilayers, shows a wide displacement towards lower current corrosion densities, indicating a lower corrosion susceptibility in the analyzed solution, that can be attributed to the level of porosities present, which

can be produce in the coatings by nucleation phenomena, during the growth generating a trajectory of lower resistance for the passing of the Cl ion. Coatings of [TiN/CrN]_n owing to its greater Cr content, are passivated generating a protector layer; it makes better behavior against to corrosive phenomena in contrast with the AISI 4140 steel [5]. Moreover, the Tafel curves displacement as increase the period, lies in the nature of the multilayers type structures, inasmuch as increasing the bilayers number are increase the interphases number among the monolayers of TiN and CrN, due to the interphases are zones where are present structural disorders given that is generated a crystallographic orientation change which acts as dispersion points, that difficult the migration of the Cl ion from the surface to the metallic substrate, delaying the begging of the corrosive process [16].

As a result of increasing the number of alternating layers of TiN and CrN, for a constant total thickness of the multilayer [5]. This leads to the required energy for the film/substrate is higher with the increase of the bilayers number, which is reflects in the increase in the polarization resistance and the decrease of corrosion velocity.

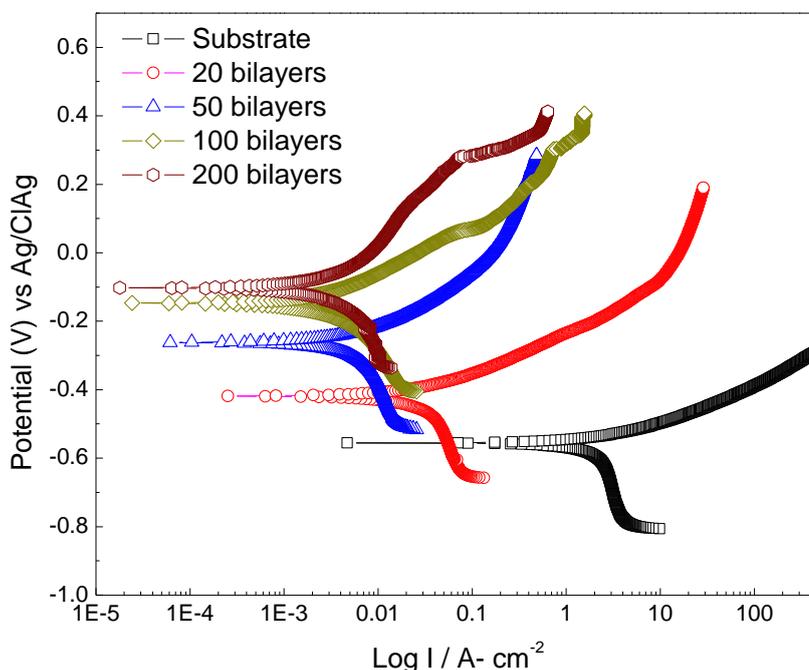


Figure 4. Polarization curves Tafel for multilayers [TiN/CrN]_n.

In the figure 5, is observed the behavior of the corrosion velocity and the polarization resistance, in function of the bilayers number, can be seen clearly that the lowest value of resistance to the corrosive effect is presented in the substrate usually the highest corrosion velocity (1225 μmy), as increasing the bilayers number is generated a increase in the polarization resistance, which indicates a significantive in corrosion velocity, reaching values of 72.75 μmy in the 200 bilayers.

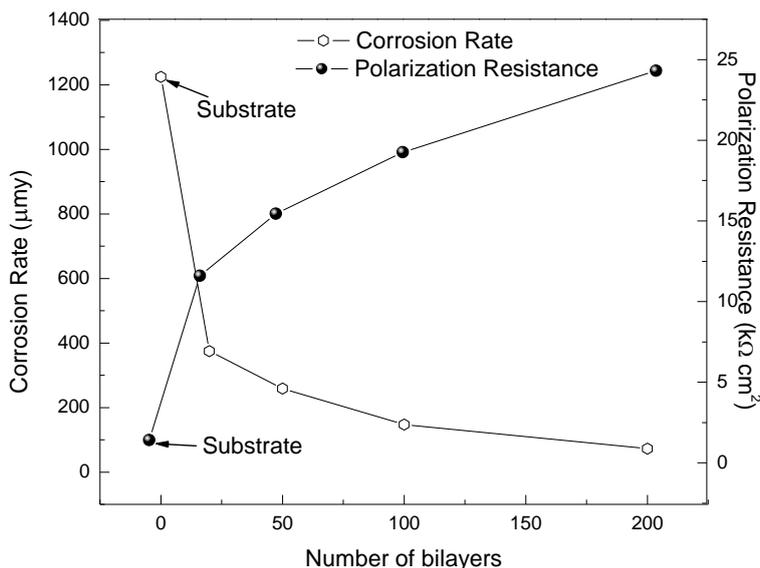
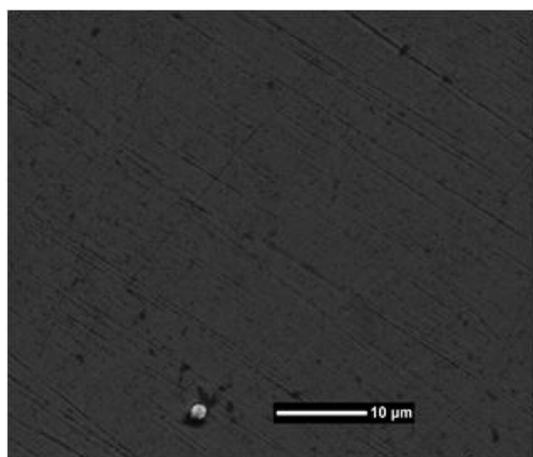


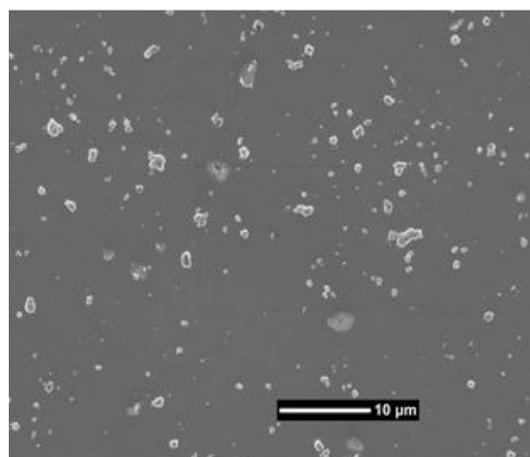
Figure 5. Behavior of the rate corrosion and polarization resistance of multilayer coatings [TiN/CrN]*n*.

3.3 Scanning electron microscopy.

In the figure 6 is evidenced by scanning electron microscopy, the degradation process of the coatings as function of the chloride ion attack. In these images ia noticed clearly the superficial attack that suffered the substrate of AISI 4140 without coating (figure 6a) and the coated substrate with each one of the variations of the multilayers (figures 6b, 6c, 6d an 6e). The corrosive attack originates a elevated damage in the substrate surface. Furthermore, generates damages by pitting and breakage of the continuity of the fimls, as is shown in the figures 6b and 6c, which increase drastically the corrosion velocity, that was demostrated in the polarization curves and the Nyquist diagrams. Finally, it is observed that the the deposited film with *n*=100 and 200 (figures 6d and 6e) offers higher resistance to the attack, due to the growth in ordenated way, that generated a coating with lower rugosity.



(a)



(b)

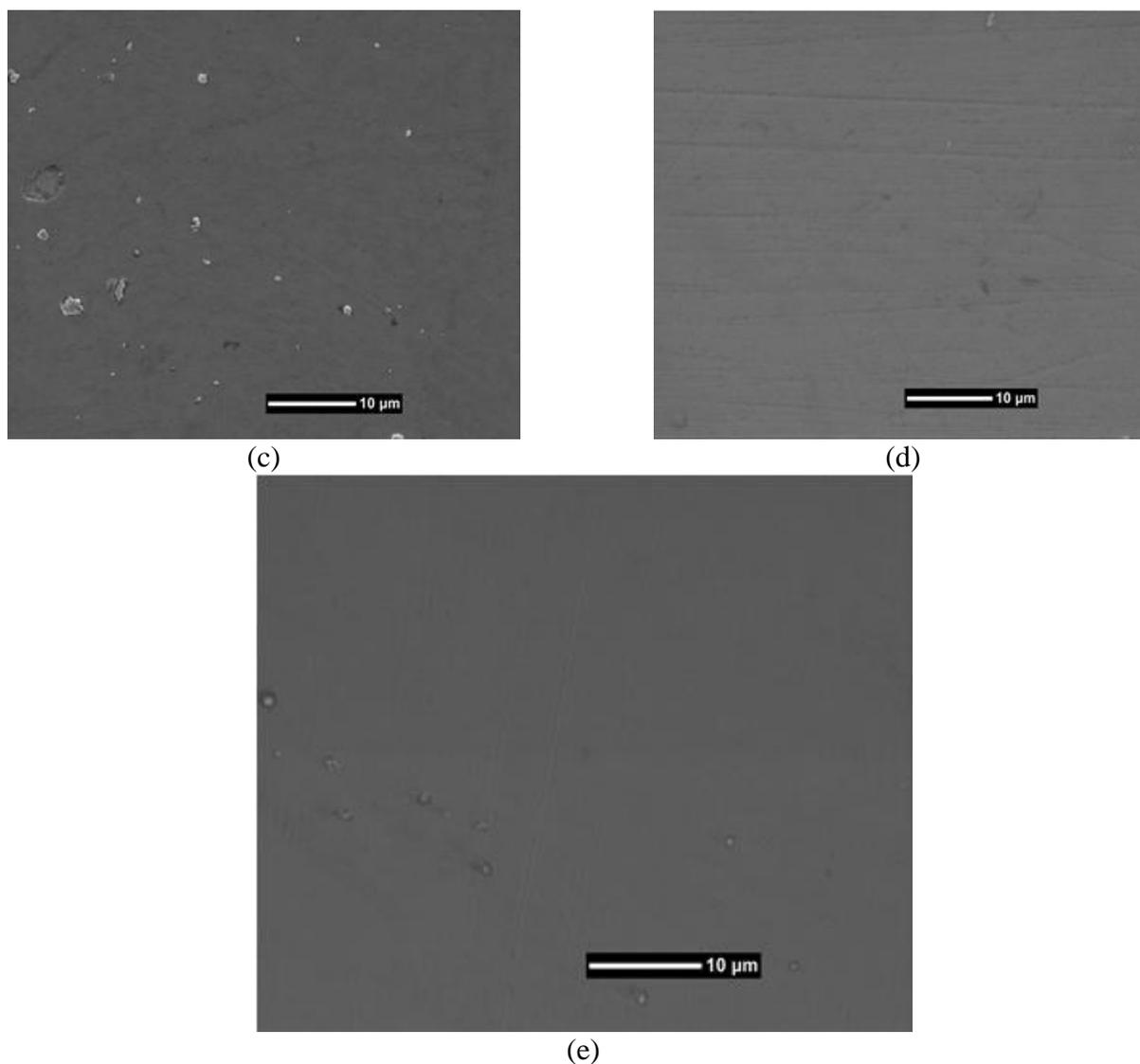


Figure 6. SEM micrographs for samples with degradation a) substrate of AISI 4140, b) $n=20$, c) $n= 50$, d) $n= 100$, e) $n=200$.

4. CONCLUSIONS

Thin films of $[\text{TiN}/\text{CrN}]_n$ were deposited on substrates of AISI 4140 steel by a radio frequency system varying the bilayers number. From the EIS analysis were obtained two types of equivalent circuits; Randles type that describes the behavior of the substrate without coating and the other with two elements of constant phase, which describes the behavior of the substrate-thin film system.

The obtained electrochemical behaviors were modeled with the substrate and the multilayers, allowing find the total impedance relation of the researched systems. The electrochemical impedance spectroscopy and Tafel polarization curves results, indicate the good performance of the multilayers due to increase its protection against the highly corrosive phenomena, furthermore it was observed that the trend is to increase its protector value as the bilayers number is increasing.

ACKNOWLEDGEMENTS

The authors of the work express their gratitude to the Universidad Militar Nueva Granada.

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