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Tribocorrosion Behaviour of Niobium Nitride/ Niobium Multilayer in Contact with Ringer Lactate

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Multilayer coatings with Niobium nitride/niobium were deposited on stainless steel AISI 316 LVM by a multi-target system magnetron sputtering, from Nb targets of high purity (99,99%) in an atmosphere of Ar/N_2, with bilayer periods in the range from 1 to 50, with the purpose to study the variation of the multilayers in function of the mechanical and electrochemical response. The performed tests were corrosion and tribo-corrosion using electrochemical impedance spectroscopy, in both cases the used electrolyte was ringer lactate at 37° C. The corrosion behavior was evaluated by the Bode diagrams, in order to study its effect on the structure and the electrochemical properties. The AISI 316LVM stainless steel is utilized for medical applications due to it is melted under vacuum, generating a high purity grade which is required for the surgical prostheses. Moreover, the 316 LVM steel offers an excellent resistance to the tissues, physiological fluids, intergranular corrosion and the corrosion in general. However, its performance as biomaterial is questioned by its nickel content. Specimens of AISI 316 LVM coated with NbN/Nb were characterized using electrochemical impedance spectroscopy (EIS). It was found a dependence of the bilayers number on the corrosion resistance for the NbN/Nb films.

Keywords: Niobium, biomaterial, friction coefficient, wear, corrosion

1. INTRODUCTION

The niobium nitride, as well as other transition metal nitrides, is refractory and presents great interest to be applied as a coating in the surface engineering owing to it possess excellent mechanical and tribological properties, such as high hardness and high resistance to wear and oxidation [1-2]. These properties are consequence of its complex chemical bonds that combine covalent, ionic and metallic contributions [3-4]. Due to the NbN exists in cubic (c-NbN) and hexagonal (h-NbN) phases, in a reactive sputtering process is necessary a very precise control of parameters such as nitrogen partial pressure and the power spray, with the aim of obtain a high performance coating [5-6].

The niobium nitrides possess interesting properties such as high electrical conductivity, high melting point and chemical inertness. In the last years, its study has focused as coating on metallic surfaces to protect them against wear [7-8]. It was found that the NbN coatings deposited by arc on speed steels enhance the wear resistance in comparison with the TiN coatings [9]. Its chemical inertness, high melting point and low resistivity are properties that make it important in microelectronics for the production of diffusion barriers [10].

The metals are used as biomaterials due to its excellent thermal and electric conductivity and its mechanical properties, owing to the better properties of metals such as niobium, tantalum or titanium and its alloys [11]. Their applications as biomaterials have been subject to much discussion [12]. This competitive situation prompted that a large amount of metallic materials were investigated, with special attention in the development of materials with based already existing, such as the cobalt-chromium alloys free of nickel, the stainless steels with a low carbon content, which avoid the metallic carbides precipitation, and titanium alloys without toxic elements as vanadium (Ti5Al2,5Fe y Ti6Al7Nb), as well as a high fatigue resistance, a Young's modulus even smaller than the titanium [13-15].

Currently, the metallic materials commonly employed in the field of biomedical applications and in particular in orthopedic surgery, are the stainless steels, the alloys based on cobalt and the titanium and its alloys [16]. Each one of them has advantages and disadvantages, result of their different properties, their differences in processing and the chemical nature of the components of the passive layer [17-18].

The purpose of the present article is the evaluation process of the NbN/Nb coatings deposited on AISI 316LVM steel. Initially, the friction coefficient was determined by performing the tribometer test, subsequently it is determined its electrochemical performance by means of electrochemical impedance spectroscopy technique. Finally, the dual performance is evaluated by tribo-electrochemical test.

2. EXPERIMENTAL

The niobium nitride-niobium coatings were grown on AISI 316LVM substrates. For the films deposition, was used the r.f magnetron sputtering technique, intercovamex V.6 reference. Using a Niobium target with a diameter of 10 cm and 99.9% of purity. The deposition parameters were: 400 W of power, -100 V of bias voltage, 300°C of substrate temperature, with a gases mix composed by 82% of Ar and 18% of N_2, at a working pressure of $6x10^{-3}$ mbar.

Atomic force microscopy measurements were taken on coated Steel substrates, with a scanning of 2.5 μm^2 in order to measure the roughness and grain size at nano-metric scale to correlate this with the deposition process variables. The AFM microscope was used in no contact mode on air with a Si cantilever.

The electrochemical characterization was carried out in a Gamry PCI 4 equipment using the electrochemical impedance spectroscopy (EIS) technique, at a 37°C temperature, utilizing a cell composed by the working electrode with an exposed area of 1 cm^2, a reference electrode of Ag/AgCl and a platinum wire as counter-electrode in a solution of Ringer lactate. The Bode diagrams were obtained by frequency sweeps in a range of 100 kHz to 0.001 Hz, using amplitude of the sinusoidal signal of 10 mV.

With the purpose of study the influence of the synergy between the abrasive wear and corrosion, were used a tribo-corrosion equipment. The tests were carried using a Tribometer MT60 NANOVEA, at a temperature of 37±0.2°C (Normal body temperature). To the tribometer was adapted an electrochemical cell composed by a series of three electrodes, the reference electrode (Ag/AgCl), the counter-electrode (Platinum wire) and the working electrode placed in a sample-holder with an exposition of the specimen of 1 cm^2 and contents the electrolyte. For the corrosion and wear resistance evaluation, a potenciostat-galvanostat was used with the same specifications used in corrosion.

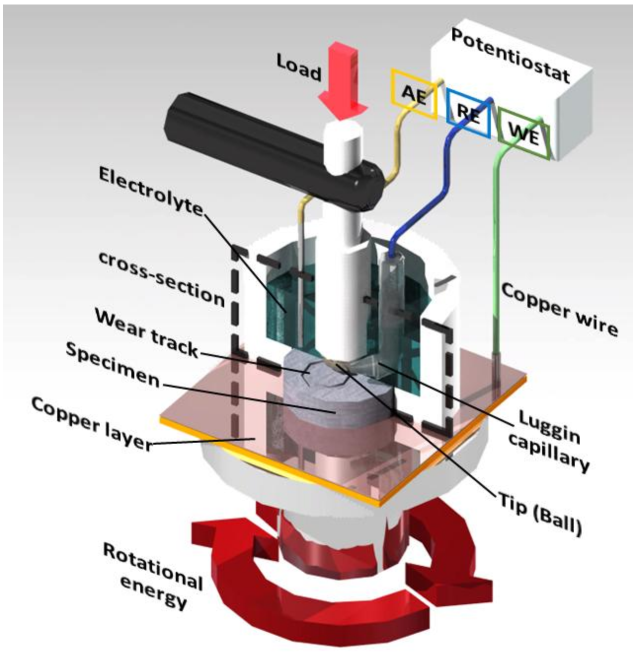
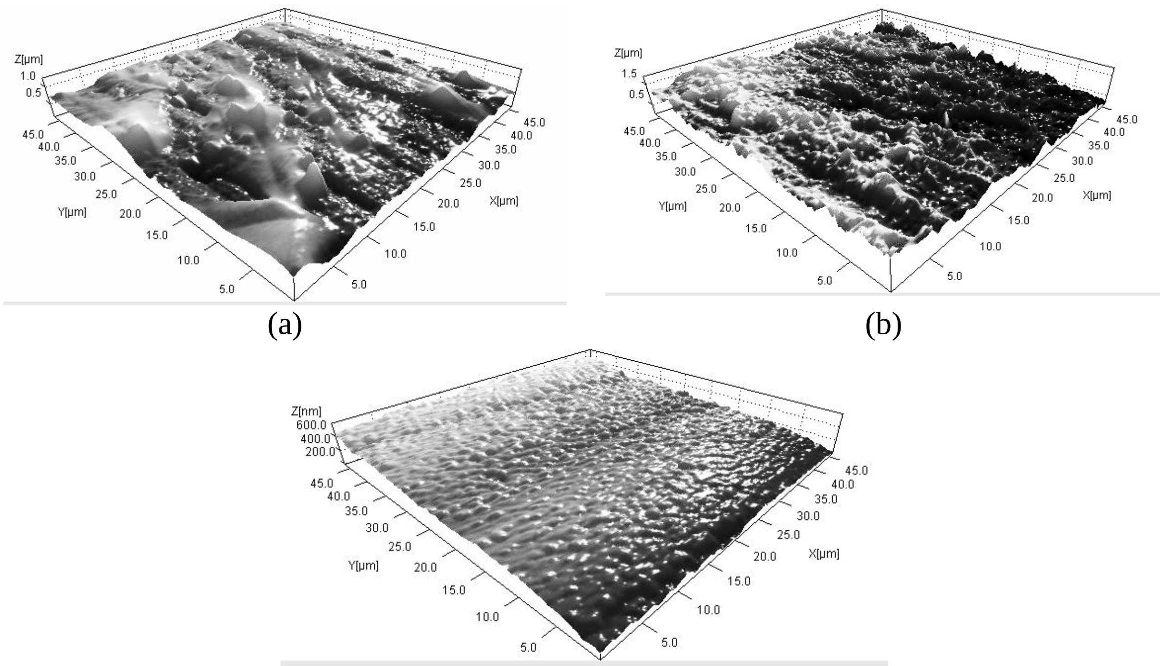


Figure 1. Schematic diagram of the adequate potenciostat for the tribometer, to perform abrasive wear test and the corrosion erosion synergy.

3. RESULTS

3.1 Atomic force microscopy (AFM)

In the figure 2, is observed the topographic images of the coated specimens with multilayers, in the figure 2a is obtained the micrograph with n=1, where the surface has heterogeneous structure since it has regions with different hardness and friction coefficient. As the microscope tip scans the surface, the interaction of the probe with the surface changes when it moves from a region to other [19]. These changes in the forces give a constant generating a difference of the materials on the heterogeneous surface [20]. In the figures 2b and 2c, are observed the grain size value for the coating with n=20, that is around 89± 3 nm and for n=50 the value is 28 ± 3 nm. On the other hand, the values of roughness were 2.35 ± 0.1 nm for n=20 and 0.5 ± 0.1 nm for n=50. From these results are possible to infer that the surface of both layers are very regular and show low roughness values in relation to n=1. This fact is attributed to an energy increase of the absorbed atoms on the substrate surface, generating a large numbers of nucleation sites which lead to a reduction of the grain size, decreasing the roughness of the total surface as well as an increasing of the film density [21]. Owing to the n=50 system has a smooth surface and adequate homogeneity (figure 2c), so it can help reduce the susceptibility to corrosion when these films are exposed to aggressive environments. For industrial applications as biomaterials, the rugosity grade of the surface is important, it is intended that the surface of the finished product has a minimum roughness, because this reduces the friction of the surface when is in contact with other, reducing the wear phenomena and corrosion of these materials.



(a) (b)

(c)

Figure 2. Atomic force micrograph of the niobium nitride/niobium coatings. a) multilayer, b) 20 multilayers and c) 50 multilayers.

3.2 Corrosion

In the figure 3, is evidenced the evaluated multilayer systems in a electrochemical cell without being subject to mechanical wear phenomena, its response is observed by the Bode curves [22]. For each multilayers exist a different response due to the corrosion mechanism is different for each evaluated system. The coatings have a porosity level, however the n=1 possess the greater value.

Therefore, it is obtained the lower opposition of the passage of ions that are in the Ringer lactate, the effect of the electrolyte is the dissolution of the protecting layer after an exposure time.

The corrosion mechanisms for the multilayers has schematized in the figure 4. In the part (a) of such figure is shown the deposited multilayer before being exposed to the electrolyte, it can be seen that the niobium nitride/niobium multilayers have pores which cross them, these defects are generating during the deposition process, the way to control them is with the deposition parameters which are the same for the three studied multilayers. The figure 4 is schematized when the multilayers with n=1 are exposed to the electrolyte action, the additional pores are due to the creation of cathodic and anodic zones around the pores which interconnected after the reaction.

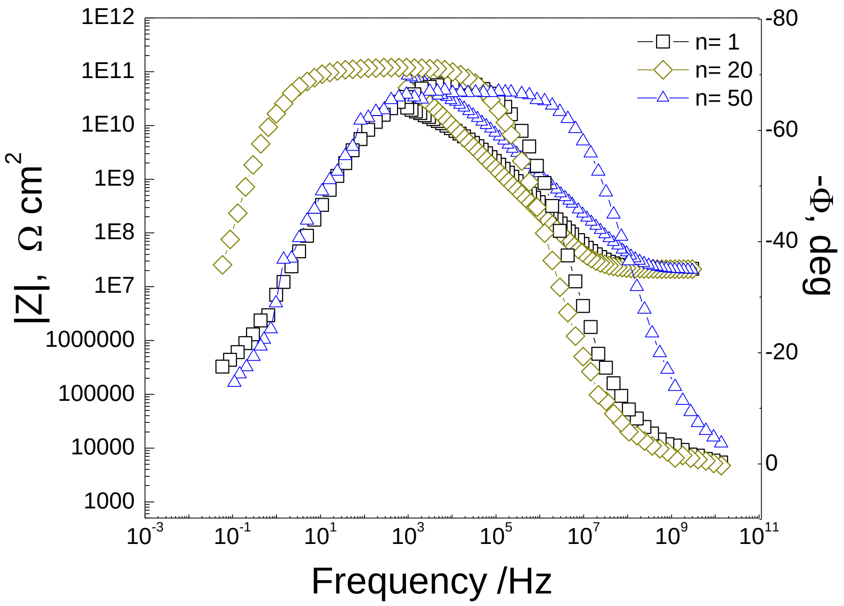
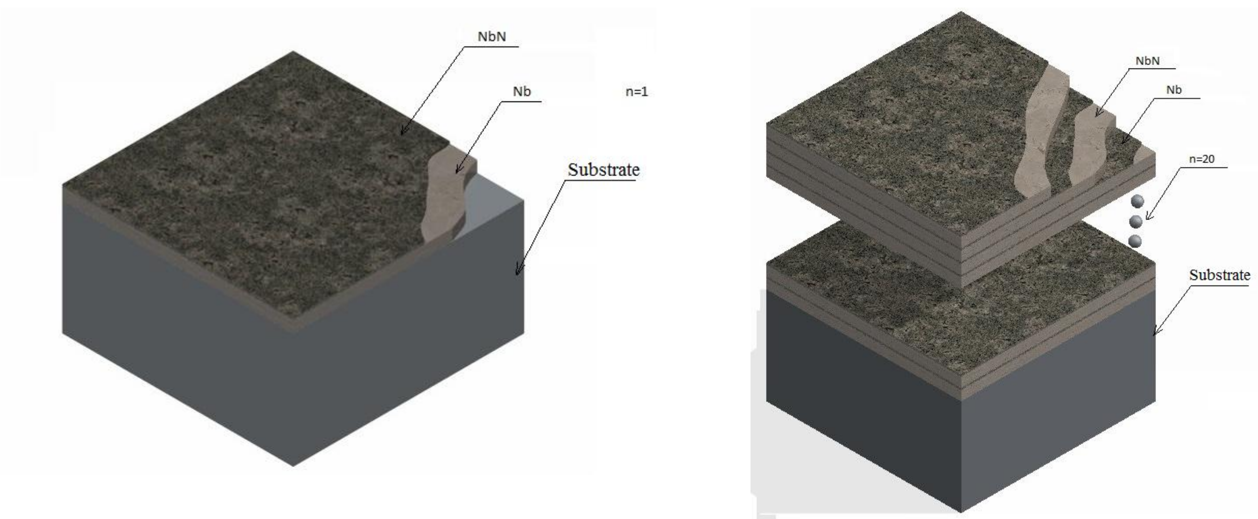
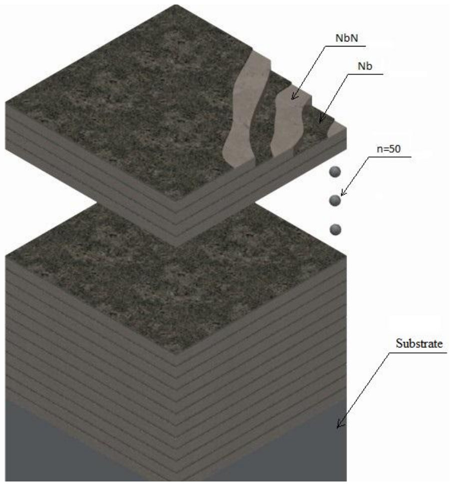


Figure 3. Bode diagrams of the multilayers after being evaluated in static corrosion and subjected in a fluid that simulates the human body conditions.



(a) (b)



(c)

Figure 4. Corrosion attack schemes of the coatings, a) n=1; b) n= 20 y c) n=50.

In the figure 4b is shown the corrosive process of the multilayers with n=20, the layers of niobium nitride have dissolved by action of the electrolyte, while the niobium layers have formed a stable films of niobium oxides, consequently it takes into account the number of niobium nitride-niobium layers when the n=50 is observed (figure 4c). Due to the quantity of NbN layers is greater in the multilayer, the electrolyte will take more time to dissolve the multilayer, and thus they are more resistant to corrosion. Additionally, a greater Nb layers enhance the corrosion resistance given that generates an oxides layer which retard the action of the electrolyte [23].

3.3 Wear

The wear on the biomaterials implemented in the body is undesired, since is important to keep the shape of the replacing part, as well as the integrity on the device surface. The first tests were performed without lubrication, applying a normal load using a pin on disk equipment. The used specimens are flat and rotate at a constant speed of 47.12 m/min. The tribological pair corresponding to a bone pin and the coated specimens with the niobium nitride-niobium multilayers. The tests were done at 37° C of temperature that represents the working temperature of the specimens.

In the figure 5 is registers the friction force in function of the distance (100 meters), during this path is observed different zones interpreted as follows. At the beginning of the test, is observed an increase of the friction coefficient to its maximum values. Consequence of the inertia that occurs between the body and counter body, due to the topography of the coatings with n=1 and n=2 multilayers that present a higher value of roughness in comparison to the n=50 coating that does not present asperities owing to the homogeneity achieved in the manufacturing process, subsequently to this removal process is obtained a series of film deformation due to is found an increase and then a decrease of the coefficient as a consequence of the oxides and particles present. For n=1 and n=20, the stability is achieved after the 15 and 30 meters respectively, generating stable films. Regarding the n=50 sample, it can be indicate mainly that has the best elastoplastic properties (H, Er) and lower roughness presenting the lower friction coefficient.

The corresponding analysis of the corrosion wear phenomena indicates that in the three studied cases is demonstrated a decrease of the friction coefficient, due to the lubricant composition which reaches a balance among the corrosive and adhesive wear providing a minimal wear rate; given that the pin on disk test is generating by multiple runs, the state of the coated material after the beginning of the mix test of corrosion degradation is the following; the wear losses in the niobium nitride-niobium film is generated by the periodic removal of the sacrificial film, then is formed a film that protects the system against the abrasive wear. This generated film is removing slowly due that is adherent providing superficial hardness; the contact zones are deformed and not removed generating a lower quantity of displaced material. By comparing the different multilayers, there is no evidence a difference among the n=1 and n=20 systems, due to the curves are similar and the friction value for the both cases is 0.22 in average. For the case of the greater quantity of multilayers is obtained an average value of 0.12, corresponding to the half of the wear rate generated by the other multilayers (n=1 and n=20), due to there is a lower abrasion, therefore the formation of the passivating film is immediate, generating a delay in the corrosive and wear processes simultaneously.

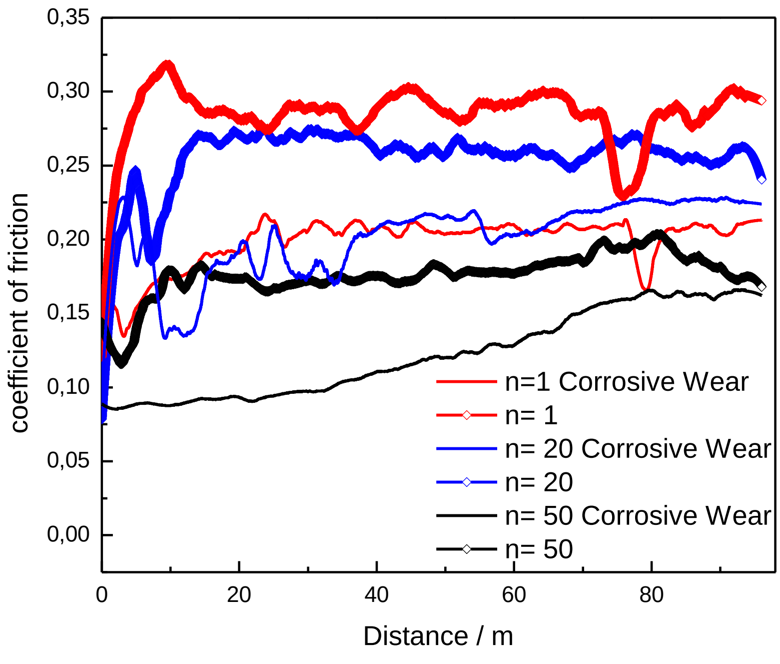


Figure 5. Variation of the friction coefficient in function of the wear and corrosion-wear tests

3.4 Tribocorrosion

In the figure 6 is observed the Bode diagrams of the evaluated steel and the coatings in the Ringer´s solution, with the modifications on the multilayers is possible identify the prevalence of the electrochemical wear mechanism in each case. The coatings with one multilayer show a difference in the polarization resistance, obtaining a greater degradation for the coating in comparison with the n=20 and n=50 systems, due to a diminution in the electrochemical parameters as a consequence of the abrasive effect and the detachment of the thin film. By observing the corrosion behavior is obtained on the evaluated systems a general corrosion, owing to the dissolution effect existing on such coatings. However, the layers with n=20 and n=50 the passive layer of protection is diluted by the synergistic effect. Therefore, the degradation effect is more accelerated for n=1, which indicates that the protective effect is adequate using the coating with n=50.

These coatings present a behavior of increase the total impedance on each one of the evaluated multilayers. By observing the capacitive behavior of the n=1 multilayer at high frequencies, is defined a flattened semicircle. This flattening phenomenon of the semicircle is associated with a dispersion process in the frequency, due to the electrode surface has a greater value of roughness. Regarding the coatings with higher number of multilayers is observed a capacitance denominated "constant phase element" (CPE) that is independent of the faradic reactions, which contribute with a pseudo capacitance to the total impedance of the system. This system has a value with higher capacitive component than resistive, which indicates the effect of the roughness diminution, generating a low friction coefficient and a lower degradation of the coatings.

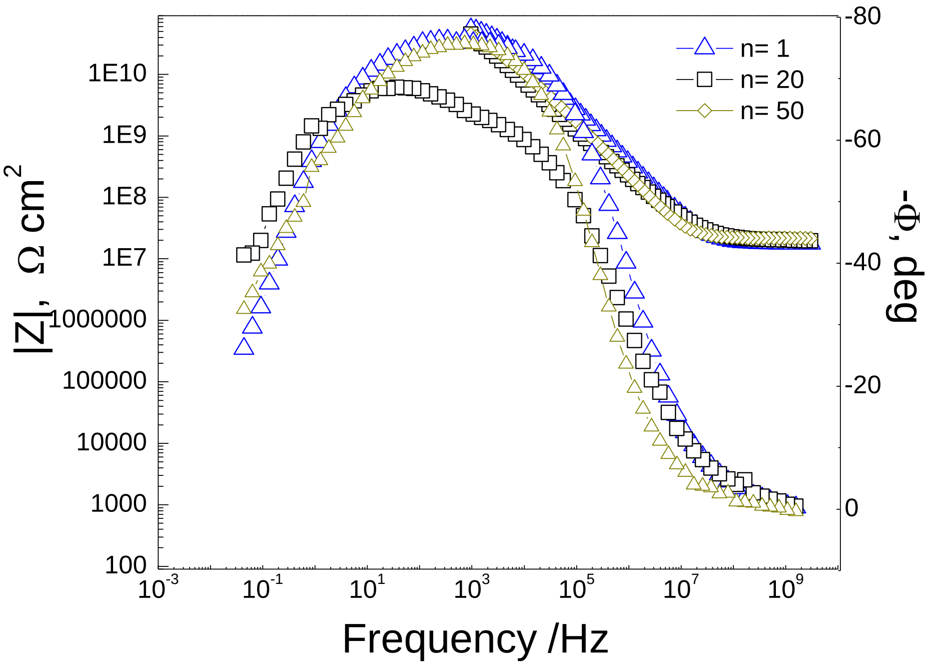


Figure 6. Bode diagrams corresponding to the multilayers which were evaluated at corrosion and abrasive wear synergistically.

4. CONCLUSIONS

The niobium nitride coatings - niobium have excellent performance against corrosive phenomena, by the Bode plot it is set the kinetic behavior of the charge transfer through the 3 different interfaces present in the system the first corresponding to n = 1, the second n = 20 and n = 50 it was established that each has a different interfacial property due to the interaction of the multilayer system with the electrolyte. The surface coatings indicates a difference in the protective layers, if the system generated the best performance against tribocorrosion phenomena corresponds to a greater quantity of multilayers and is due to appropriate accommodation of atoms on each of the layers.

The abrasive effect evaluated separately, is more intense than the corrosive effect, therefore it was determined that mechanical abrasion speed is greater than the corrosion rate, so it follows that the corrosion resistance of a low-abrasion material depends on the corrosion resistance of the material.

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