Int. J. Electrochem. Sci., 10 **(2015)** 9408 - 9416

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Assessment of Tribocorrosion Behaviour of Steel 316 LVM Coated with HfN and HfN / Hf.

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Received: 1 September 2015 / *Accepted:* 19 September 2015 / *Published:* 30 September 2015

Monolayers of Hafnium nitride (HfN) and multilayers of hafnium nitride (HfN/Hf) were fabricate with bilayers period of 1, 30 and 50, these were deposited on biomedical level stainless steel AISI 316LVM, using the RF magnetron sputtering reactive method with a source radio frequency (13.56 MHz) and hafnium targets. The electrochemical behaviour simulated the aggressive conditions as presented in the human body applying the tribocorrosión technique (combination of wear and corrosion in aqueous environment), performed with Gamry equipment PCI 4 to which it is adapted a pin on disk tribometer. The test were performed immersed in Hanks solution (Hanks balanced salt solution), the electrochemical cell is composed of a platinum counter electrode, a reference electrode Ag/AgCl and a working electrode (steel with and without coating) at a temperature of 37 ± 0.2 ° C, the test was done by electrochemical impedance spectroscopy (EIS). Regarding the results, was found the multilayer coating of [HfN/Hf]n increases the polarization resistance and decreases the coefficient of friction reported for the substrate and the monolayer of HfN, indicating a good wear and corrosion resistance.

Keywords: Hafnium, hafnium nitride, abrasive wear, corrosion

1. INTRODUCTION

Phenomena such as wear and corrosion are problems that often the industrial machines and devices faced, specially related with pumps that transport fluid as parts of polymer and tackifier [1-2]. This is because some fluids are aggressive substances that also contain suspended particles generating two combined phenomenon, the corrosion and erosion, causing major damage to exposed parts and reduced dramatically the useful life of the elements [3-5].

The monolayers of thin films are materials under study, because with the deposition thereof, can be improved properties such as corrosion resistance and wear, the electrical conductivity, and used as diffusion barriers [6-7]. The deposition of many layers with different mechanical properties between them it can control problems as crack propagation and surface tensions [8].

Hard coatings were design for applications in which traditional steel presents damage, as is the case of the wear produced by the continuous particles impact and the degradation by the contact of the corrosive fluid [9-10]. The advantage of physical vapour deposition coatings in application performance of devices is to provide adequate protection against wear, these coatings can be classified according to the nature of chemical bonding in the following groups: hard ionic materials, metallic and covalent [11]. This classification contributes significantly to the understanding of different crystal structures and the behaviour of materials in the form of simple thin layers [12].

The hard coating have become the solution of problems as corrosion and wear, the physical vapor deposition technique is one of the most used process to obtain hard coating, encompassing any growth process of coatings in a vacuum environment involving deposition of atoms or molecules on a substrate [13]. This technique allows evaporate by physical means and condense the material that will form the coating on the substrate, this process has the advantage of being applicable simultaneously on ensemble or pieces.

The main application of the Hafnium nitride (HfN) is in the area of coatings that function as a thermal barrier to high temperature; additionally it has a higher hardness than other carbides nitrides such as TiN and CrN. For this reason, the HfN thin films it is an excellent protective material for cutting tools at high speed. The stoichiometry of HfN is one of the most stable compounds between mononitruros of transition metals at high temperatures, which makes this an ideal candidate as a diffusion barrier in metallization schemes. The advantage of Hf-N is that present low influence on properties such as hardness and internal stress versus deposition variables as bias voltage [14-15].

The present study aims to evaluate HfN coatings in form of monolayer and multilayer concerning wear resistance against abrasion corrosion, and determining the improvement over these phenomena compared with steels AISI 316LVM, indicating a better performance compared to the synergy of mechanical wear and electrochemical degradation.

2. EXPERIMENTAL DEVELOPMENT

Hafnium nitride monolayers were deposited on substrates of steel AISI 316LVM, which were degreased ultrasonically in a 15 minute sequence of ethanol and acetone. The coatings were obtained by magnetron sputtering technique in RF (13.56 MHz). For the deposition of white coatings 4-inch diameter were used hafnium with having a purity of 99.9%.

The base pressure inside the vacuum chamber was $2.3x10^{-3}$ mbar. Before starting the deposition the substrates were exposed to a plasma cleaning for 15 minutes under Ar to a bias of -400V on rf during growth, the working gas was a mixture of Ar (93%) and N_2 (7%) with a total pressure of $3.6x10^{-3}$ mbar at a substrate temperature of 400 ° C and an rf substrate bias of -70V and a power of 400W.

The multilayers HfN / Hf were deposited using a system magnetron sputtering technique in multi-rf blank to a substrate temperature of 250 °C. For deposition of multilayer white hafnium, the shutter periodically covered it, while the substrate was kept under circular rotation in front of the targets to facilitate the formation of coatings.

In order to study the influence of the synergy between the abrasive wear and corrosion, fretting corrosion test equipment using an Tribometer NANOVEA MT60 is used at a temperature of 37 ± 0.2 ° C (normal body temperature). Tribometer will be adapted to an electrochemical cell comprising a series of three electrodes, such as reference (Ag / AgCl), the counter electrode (platinum wire) and the work set in a sample holder with an area of exposing the sample of 1 cm^2 and containing the electrolyte [16]. A potentiostat was used for evaluation of corrosion resistance and wear - galvanostat Gamry PCI-4 model using the technique of electrochemical impedance spectroscopy (EIS). Nyquist plots were obtained with frequency sweeping between 0.001 Hz and 100 kHz using an amplitude of the sinusoidal signal of 10 mV [17].

3. RESULTS

3.1 Wear corrosion

The 316LVM austenitic stainless steel is non-magnetic, due to 12% of nickel content allowing to stabilize in the austenitic phase. The good performance in the resistance of corrosion is due of the 17% Cr content, for this is used daily in the medical industry. Multilayers and monolayers coatings are used when the service conditions of 316LVM required a high corrosion resistance due to the pitting phenomena.

The use of monolayers that coat the 316LVM steel substrate has an adequate performance to corrosion phenomena, however the coat have microscopic defects and these damages are paths for conductive ions existing between the monolayer and the reaction sites in the interface, which are generated immediately after contact with the electrolyte. When the electrolyte creates a conductive path in the monolayer, generate macro-defects expanding the routes within the substrate-coating system. In the Nyquist plot (Figure 1), is observed that a protection system generates by the monolayers followed by a ion transportation in the surface due that the corrosion rate depends on transport of Hank´s balanced salt solution for the film to the coating, the diffusion of these ions and their accumulation in the interface generate decrease in adherence and acceleration corrosive processes, due to diffusion effects (Figure 2b) [18].

Due to Fick's diffusion laws, the ions of the electrolyte solution in contact with the coatings tend to enter, due to the zero concentration generated at the interface existing between the substrate and the multilayer coating therefore cannot eliminate the electrolyte of the surface. In Figure 1, it shows that the coatings exhibit excellent corrosion barrier. The proposed study the numbers of multilayers were modified beginning with a multilayer through 30 and ending with 50, indicating that the diffusion rate is lower when a barrier composed of upper multilayer 30 is created by optimizing the process in 50 layers. In the Nyquist plot it indicates that these multilayer coatings protect steel better than the monolayer by a high corrosion resistance which essentially prevents access to ionic coating and between the anodic and cathodic areas which enables a film having little ion-conductive and suitable for this type of protection [19].

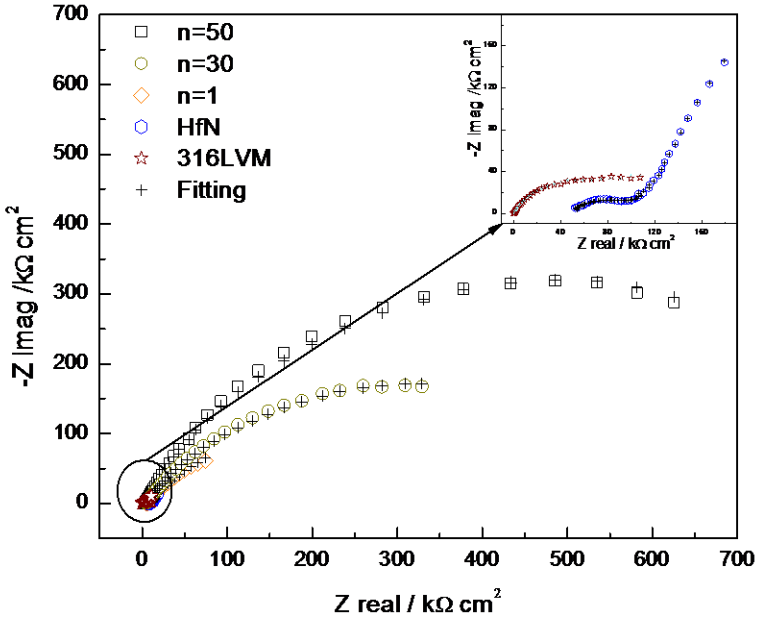

Figure 1. Diagram of Nyquist of the different systems analysed in mixed form assays electrochemical degradation and abrasive wear.

The multilayer design is made taking into account the mechanical properties indicating that as the number of layers increases its ability to absorb and distribute energy in the system causing increased mechanical performance, the HfN / Hf systems have a high hardness value, which places them in the group of hard coatings, and is generated due to the level of layers, to analyse the system of dual form abrasive wear and corrosion; as shown in Figure 1, it is obtained that systems generate better tribocorrosion performance are multilayers with layers 30 and 50, because of its superior mechanical and corrosion resistance [20]. These coatings have complex electronic system which links includes a predominantly ionic character form (51.44%), followed by covalent and metallic bonds. The multilayer coatings are polycrystalline type forming a metal layer consisting of hafnium and a nitride ceramic generated hafnium, successfully reducing the permeability of electrolyte of Hanks the coating [21].

The equivalent circuits (Figure 2) generated from implementing the technique of electrochemical impedance determine the behaviour of steel, monolayers and multilayers. In Figure 2a, the equivalent circuit of the substrate is shown, the impedance data are analysed experimentally found by Randles circuit, where there is a resistance which opposes the passage of ions into the metal surface, thereafter is located a polarization resistance in parallel with an element of constant phase corresponding to the irregularities in the substrate, after the surface preparation.

In Figure 2b, corresponding to the monolayer HfN equivalent circuit shown, this is divided into three areas, the first area is corresponding to the interaction of the electrolyte with the system, the second is due to the reaction generated by the film thin and absorption of ions in this region is due to the electrolyte saturation. In this phase a simple circuit polarization resistance and capacitance of double layer coating in contact with the electrolyte is observed, relates that the coating functions as a perfect barrier. After some time exposure to ions and oxygen, due to Fick's second law can arrive at the interface substrate coating generating the formation of sites electrochemical corrosion at the interface, this is represented in the equivalent circuit by a constant phase element and a resistance of charge transfer later is located intensive attack may occur in the final stage of corrosion products, which is represented in the equivalent circuit as an element of electrochemical diffusion diffuser Warburg corrosive products [22].

In figure 2c is obtained a third equivalent circuit, which fits the experimental values, these elements are similar to those used in the monolayer in the first two stages, as each element is associated with a physical phenomenon that is happening in the substrate / coating system in contacting a working solution. Rs is termed as a solution resistance, considered in this way by means of ionic conduction in the system.

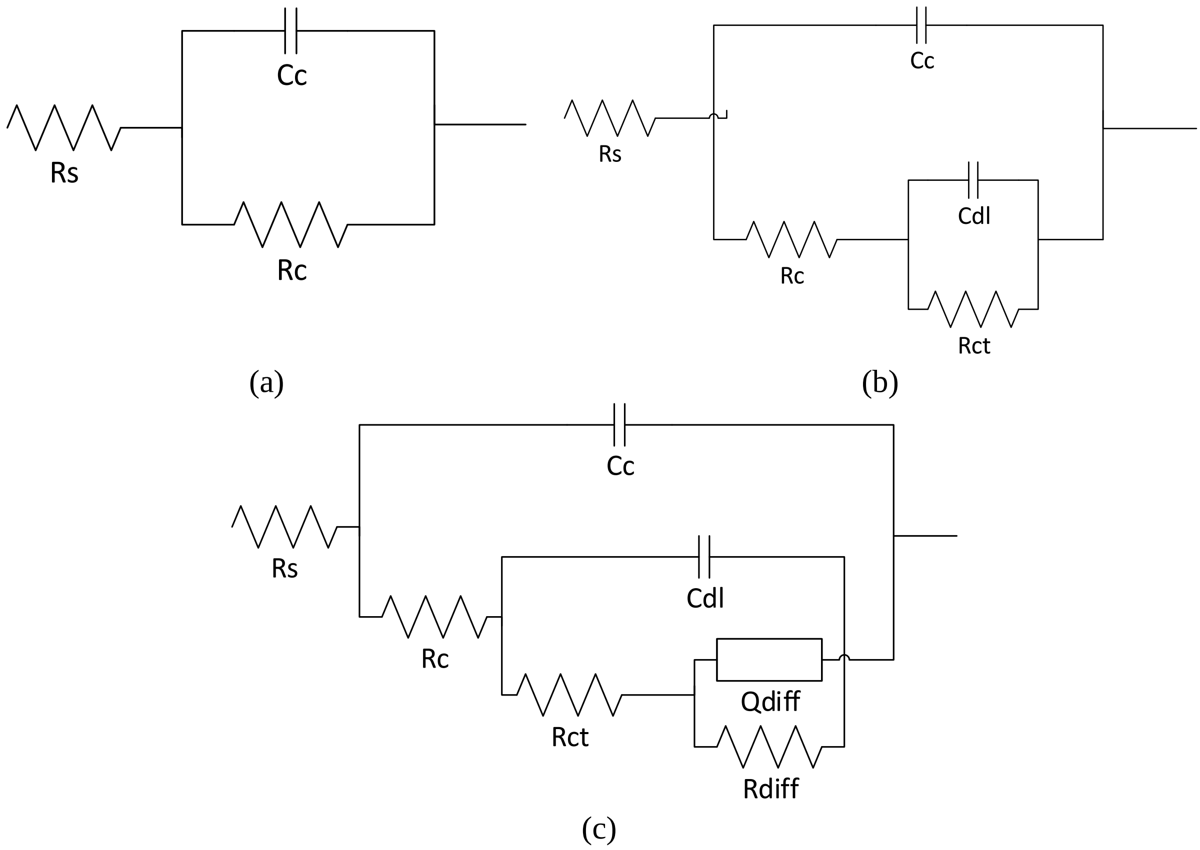

Figure 2. Equivalent circuit's multilayer, a) substrate, b) monolayer corresponding to diffusive phenomena c) multilayers where corrosive processes is evident.

Polarization capacitance is associated with the contact of the solution with external multilayers. The polarization resistance is the resistance of the surface of the multilayer contacting the ion conduction route of; in the second stage of the equivalent circuit is obtained parallel capacitance corrosion, corresponding to contact of the first multilayer and the substrate interface, the value of n CPE, has a resistive component due to a distribution occurs heterogeneous ions that have gotten through the upper layers, the corrosion resistance occurs in the same area of the capacitor, and its value depends on the respective response generated by the interface steel - multilayer.

In Table 1 are reported the values generated after setting the equivalent circuits, an important element with impedance spectroscopy studies is that it could be rated for various types of coatings thanks to the resistance value as you can obtain the impedance measurements and serves as an indicator of behaviour. Coatings with values above 300 kΩ.cm^2 resistance can be classified as excellent protection while those with values below 300 kΩ.cm^2 are categorized as good protection. In the specific case the monolayer has a value of 287 kΩ.cm^2 and the multilayer with n = 50 has a value of 824 kΩ.cm^2, indicating the good performance of the multilayer and the process optimization achieved [22-23].

Table 1. Values of fit of the substrate, coatings monolayer and multilayer type.

	R_s Ω cm^2	C_c F cm^{-2} s$^{-(1-\alpha_1)}$	α_1	R_c kΩ cm^2	C_{dl} F cm^{-2} s$^{-(1-\alpha_2)}$	α_2	R_{Ct} kΩ cm^2	W_{diff} kΩ cm^2
Substrate	365.1	4.67×10^{-12}	0.89	128.043	-	-	-	-
HfN	371.9	1.20×10^{-6}	0.70	12.29	377.4×10^{-12}	0.91	187.122	115.212
n=1	366.1	79.38×10^{-9}	0.71	33.42	7.25×10^{-13}	0.85	345.002	
n=30	391.2	11.02×10^{-9}	0.79	193.244	8.38×10^{-13}	0.94	556.883	
n=50	372.3	897×10^{-9}	0.62	203	8.57×10^{-14}	0.79	824.422	

3.2 Porosity of the Monolayer and Multilayer

In Figure 3, the porosity of the coatings was measured quantitatively, since the porosity corresponds to the relationship between the polarization resistance of the substrate and the coating as shown in equation (1)

$$P = \frac{R_{p-s}}{R_{p-r}} \qquad (1)$$

Where P is the total porosity of the coating, R (p-s) is the polarization resistance of the substrate and R (p-r) the polarization resistance of the coating [23]. These porosity values are presented in Figure 3 depending on the number of bilayers. This is because the deposition of thick layers of hafnium nitride / hafnium, by sputtering technique allows obtaining a dense structure free of pores, and electrochemical characteristics.

The low porosity value found in the coatings is due to the generation of interfaces in coatings through the multilayer formation, since the interfaces in these types of systems are energy dissipating sites and deflection of fissure. The presence of interconnected porosity that can generate microcracks that achieve greatly influence the service performance of the coatings and modifying mechanical properties.

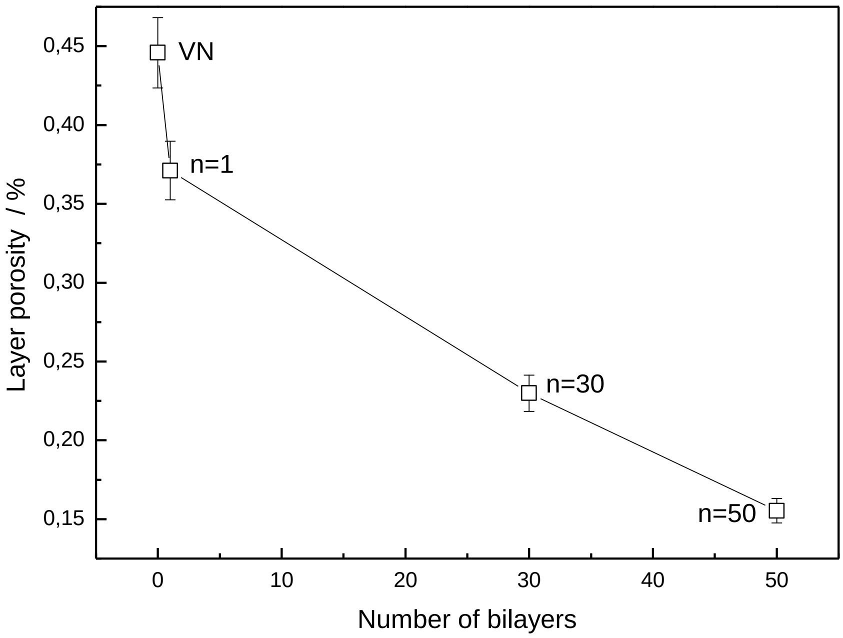

Figure 3. Calculation of porosity depending on the coating and the number of bilayers for coating HfN / Hf.

Due to the presence of cracks in the monolayers and multilayers a result of the deposition parameters, and they affect the mechanical properties, considering that cracks affecting abrasion and cracks in the surfacing are as the trials involve corrosive phenomenon should be monitored internal microcracks which originate in the layers of the interface coating / substrate.

The quantity of multilayers can generate microcracks better control of proliferation and decreased by comparing the number of multilayer is obtained that the system decreases when higher porosity are obtained multilayer 30, optimizing and generating the least amount of imperfections when obtained 50 multilayers [24].

3.3 Wear

In Figure 4, the combined effect of wear and corrosion to the steel used as the substrate, the monolayer and multilayer, the effect of corrosion wear in all cases was evaluated in a hostile environment composed by the solution of hanks at 37 °C. In the case of steel, evidenced a high coefficient of friction generated by the abrasion that accelerates corrosion due the repeated removal of the passive film. In the graphic two zones are observed: the first corresponding to the effect of coefficient of static friction, it is measured when the two surfaces are at rest, then an increase because the tribological pair and starts the rotational movement and the displacement is generated [25]. The maximum coefficient values are due to the removal of corrosion product, which are assisted by adhesive wear. The wear coatings is less due to its high hardness, since the deformation is very low because there is plastic deformation type additionally the wear material that generates has a low adhesion with the coating decreasing the contact areas, additionally because the pin is a ceramic wear coming from the bone, the adhesion can be low with the coating since there is formation of primary bonds required for increased wear simultaneously both mechanical and electrochemical.

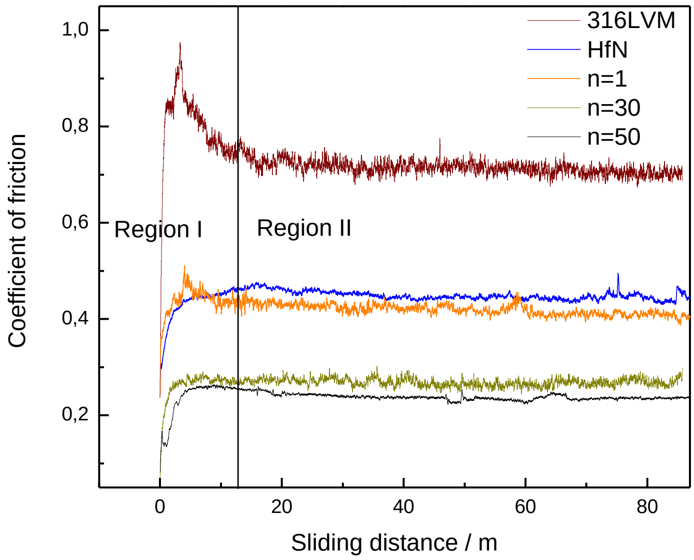

Figure 4. Coefficient of friction as a function of distance, steel 316LVM, HfN monolayer and multilayer of HfN / Hf, where the wear is decreased, with increasing form the multilayer system.

4. CONCLUSIONS

The use of monolayers and multilayers coatings are suitable systems for protection of steel 316LVM, because they improve adhesion, friction coefficient, and anticorrosive properties. The coatings analysed influence properties such as increased hardness, decreased porosity, increased corrosion resistance. Measurements through electrochemical impedance spectroscopy have shown that can be increased up to six times the charge transfer resistance of the substrate with the multilayer.

This study also showed that the porosity is not distributed evenly in the coating but varies from layer to layer depending because of the composition thereof, so that the multilayer reduce the value as the ratio increases.

Given the evolution of all these parameters, we conclude that the multilayer coatings of HfN / Hf have great potential to resist the strict conditions in the human body. Also within the structures we studied, it was found that structures with a certain type and amount of evenly distributed porosity reduce residual stresses in the layers and thus increases system integrity.

ACKNOWLEDGEMENTS
This research was supported by "Vicerrectoría de investigaciones de la Universidad Militar Nueva Granada" under contract ING 1775.

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