Tribo-electrochemical characterization of hafnium nitride/vanadium nitride multilayer systems deposited on AISI 4140 steel

M Mora¹, E Vera² and W Aperador³
¹ Fundación Universitaria Juan de Castellanos, Tunja, Colombia.
² Universidad Pedagógica y Tecnológica de Colombia Tunja, Colombia.
³ Universidad Militar Nueva Granada, Bogotá, Colombia.

E-mail: g.ing.materiales@gmail.com

Abstract. In this work is presented the synergistic behaviour among corrosion/wear (tribocorrosion) of the multilayer coatings hafnium nitride/vanadium nitride [HfN/VN]n. The multilayers were deposited on AISI 4140 steel using the technique of physical vapor deposition PVD magnetron sputtering, the tests were performed using a pin-on-disk tribometer, which has an adapted potentiostat galvanostat with three-electrode electrochemical cell. Tribocorrosive parameters such as: Friction coefficient between the coating and the counter body (100 Cr6 steel ball); Polarization resistance by means of electrochemical impedance spectroscopy technique and corrosion rate by polarization curves were determined. It was observed an increase in the polarization resistance, a decrease in the corrosion rate and a low coefficient of friction in comparison with the substrate, due to an increase on the number of bilayers.

1. Introduction
Various investigations have been made about wear of different materials with or without lubrication, similarly it has analysed the behaviour of corrosion when materials are exposed to aggressive environments [1-2]; however these analyses were carried out separately, and according to experimental observations, the most materials are subjected to the combined effect of corrosion and wear (tribocorrosion), therefore it is necessary to study the synergy, because it allows at real time the characterization of the electrochemical surface condition of a material and its evolution during friction tests [3-9]. Considering; these statements, the development of this work contributes to the assessment of the tribocorrosion properties of [HfN/VN]n multilayer coatings, which exhibit similar properties to titanium nitride under static conditions of corrosion and wear, such as high hardness, wear and corrosion resistance, among others [10-14]. Likewise, it will serve as a reference for application of these coatings, in improving the tribological and electrochemical properties of different steels for industrial use.

2. Experimental procedure
The sample preparation of AISI 4140 steel was performed using metallographic techniques, which consisted of passing the samples on an abrasive silicon carbide paper, and observe the process of polishing in the optical microscope. This process was repeated with different grain papers (80-1500) and a cloth using alumina as an abrasive solution. Then, the multilayer coatings of [HfN/VN]n were obtained by the PVD magnetron sputtering technique multi-target rf (13.56 MHz). The coatings were
deposited on AISI 4140 steel substrates; (2cm diameter, thickness 4mm); with a total coating thickness 0.04 microns ± multilayer for each system. The substrates were subjected for 15 minutes to a bias voltage of -400V (rf), with a power of 60W (rf) and a plasma of argon (Ar) to remove the oxide layer. Similarly, an intermediate layer of V and Hf films were deposited for the VN and HfN respectively for the four deposited multilayer systems. In order to increase adhesion between the coatings and the substrate, it was used a low power rf 350W and 400W respectively, in an argon atmosphere for 5 minutes. Thereafter, the samples were subjected to tribocorrosion tests using the system shown in Figure 1, which consisted of a pin-on-disk tribometer with a galvanostat potentiostat and a three electrode electrochemical cell, that has as reference electrode a Silver/Silver Chloride (Ag/AgCl), a platinum as counter electrode; and as working electrode the samples AISI 4140 steel with and without coating, immersed in a solution of NaCl 3.5% at room temperature (25°C).

Figure 1. Experimental system used for evaluation of corrosion-wear (fretting corrosion) of the [HfN/VN]n multilayer coatings synergy deposited on AISI 4140 steel.

3. Results and discussion

In each of the graphs in Figure 2, are observed the results of the synergy between corrosion and wear (tribocorrosion), both the substrate and the [HfN/VN]n multilayer coatings (n=1, 30, 50 and 80 bilayers). For the accomplishment of the tests it was used as a pin (counterbody) a steel sphere of 100Cr6 with 6mm of diameter. The applied load was 5N with a travel distance of 80m. Also, the Figure 2 shows that at the begging of the test the coefficient of friction has increased because at this point the force of static friction is overcome between the two contact surfaces, but once you start the relative movement is reduced this ratio reaching a point in which it is approximately constant, this reduction is attributed to the lubricating effect of the corrosive environment that softens the contact between the pin and the surface of the coating, furthermore, due to the movement generated by the solution makes tribometer wear particles ejected out of the contact zone. In addition, it can be see that as the number of bilayers increases, the coefficient of friction decreases, being smaller for n =80 bilayers, due to the function or contribution of each layer that constituting the coating, providing, either as hardness, adhesion, particle size and other surface properties, which help to improve the wear resistance.

The electrochemical impedance spectroscopy assays were performed in a frequency range of 100kHz to 0.001Hz, as a result of these tests, in Figure 3 the shows Nyquist plots for the substrate and the multilayer coatings [HfN/VN]n. As increases the number of bilayers the semicircles of Nyquist plots have increased amplitude as compared to uncoated steel diagram, this also indicates a significant increase in polarization resistance increase being higher for the system with n=80 bilayers. Therefore wear in the multilayer coatings [HfN/VN]n decreases; improving the protection of AISI 4140 steel, corrosion caused by the NaCl solution.
Figure 2. Coefficient of friction as a function of distance; for AISI 4140 steel and multilayer coatings [HfN/VN]n, in presence of NaCl 3.5% saline.

Figure 3. Diagrams Nyquist AISI 4140 steel and multilayer coatings [HfN/VN]n.

In Figure 4 are observed the polarization curves in a potential range of -0.25mV to 1V, with the cathodic and anodic slopes was determined corrosion rate of the coated and uncoated steel. After analyzing the results in Figure 4, it can be seen that as the number of bilayers increase, the coating have a better performance against degradation phenomena, because they exhibit noble corrosion potential (positive) and low density, indicating that the corrosion rate is less for multilayer coatings especially for n=80 bilayers; in comparison with the uncoated steel which has a higher value.

This value is related to the friction coefficient obtained in Figure 2, since it could generate a greater amount of wear particles; and when they are in contact with saline medium increases the corrosion rate significantly.
4. Conclusion

The multilayer coatings [HfN/VN]n (n = 1, 30, 50 and 80 bilayers); give to the AISI 4140 industrial steel an enhancement in its properties. An improved resistance to polarization and a lower corrosion rate, ensuring their use in mechanical systems exposed to the phenomena of tribocorrosion.

The number of bilayers has great influence on the tribo-chemical properties of the [HfN/VN]n coatings and which give suitable tribological and electrochemical properties; creating good corrosion barrier between the substrate and the corrosive medium.

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