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Electrochemical and Tribological and Mechanical Performances Coatings Multilayer Type NbC / CrN

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Niobium nitride / Chromium nitride multilayer coatings deposited by unbalanced magnetron sputtering system, with two cathodes in alternate positions (Nb/Cr). Four multilayer NbN/CrN coatings were produced with different periodicities (1100 nm, 440 nm, 220 nm and 110 nm) with total thickness from 2.2 µm in all cases. Mechanical and tribological characterization was conducted by microhardness measurements and tests pin-on-disk; according to ASTM G99-05 standard to 25 ° C, in order to evaluate and compare the wear resistance of the multilayers study, increased hardness and reduced coefficient of friction with the content of more layers from low to high periodicity was determined, indicating a potential better performance of the lower periodicity multilayer coating systems in service. Also is conducted the study of the electrochemical behavior coatings analyzed under a corrosive environment by Tafel polarization curves, determining the protection generated by the thin films.

Keywords: Multilayer, Niobium nitride, Chromium nitride, wear, corrosion.

1. INTRODUCTION

Hard coatings resistant to corrosion, have increasing application in the protection of industrial components, especially the deterioration of metallic materials, equipment, tools that are put in operation to wear processes, friction, electrochemical corrosion and aggressive environments every day requirements are more severe in service and to prolong the its lifecycle, been developed surface coating processes [1-2]. The corrosion resistant coatings have increasing application in the protection of industrial components metal which they are subjected in operation to wear processes in aggressive environments causing corrosion of such components, such that the development of coatings which not only resist wear and that inhibit the attack from the environment to which they are subjected [3].

It has been used methods of physical vapour deposition (PVD) that do not modify the mechanical or structural features, because low deposition temperatures are used. An example of this are the austenitic steels which when subjected to temperatures above 400 ° C, present intergranular corrosion. It is noteworthy development that have different types of materials, with the chromium nitride one of the most important, because it has a high resistance to oxidation (above 800 ° C) [4], decorative finish, high hardness, which makes it a very effective coating for cutting tools, injection moulds and extrusion tools for metal forming among others [5]. The main feature CrN is its high resistance to corrosion compared to other coatings.

Specifically they have been used methods of physical vapour deposition that do not modify the mechanical or structural characteristics of the substrate at low temperatures in this case at room temperature. For coatings have been used as metallic elements as chromium nitride to form ceramic composites dramatically increase the surface hardness, improving tribological performance [6-7]. Niobium nitrides have been studied for many years, due to its mechanical and tribological properties, properties CrN and NbN obtained by this material corrosion is a major characteristic where resistance is high [8].

Various types of coatings have been obtained in order to increase the corrosion resistance of metal elements used in corrosive atmospheres [9]. To this end, hard coatings such as aluminium nitride, CrN, the properties of good thermal conductivity have attracted considerable research interest of this material in recent years, being applied in such a demanding industry as it is microelectronics, because of its heat resistance and anticorrosion properties [10]. Other materials used to mitigate surface damage is niobium nitride (NbN), due to its excellent mechanical properties, tribological, high chemical and thermal stability with oxidation temperature around 800 °C, which make this useful coating a wide variety of industrial applications, such as the automotive industry [11]. Besides other interesting properties such as high electrical conductivity and high melting point, making it important for use in microelectronics production diffusion barriers found. In recent years the study has focused on metal surfaces coated to protect against wear [12]. It has been found that coatings deposited on high speed steels NbN using electric arc system increased wear resistance compared to niobium nitride coating [13].

However, despite the excellent properties exhibited by the nitrides of niobium and chromium, the corrosion resistance of these materials has been conditioned by the presence of inherent structural defects such as micropores [14], valleys and cracks appearing during deposition of Hence the effort by researchers focused on optimizing the deposition parameters [15]. The presence of these defects is an important factor to consider influence as coating integrity, not only in terms of corrosion resistance but also in mechanical and tribological properties [16].

In this paper they specimens with NbN / CrN were coated steels AISI 4140 steel ferritic - pearlitic, mainly used in the manufacture of axles and parts under friction conditions and fatigue. The tests performed were dual wear condition assisted corrosion, corrosion tests and dry wear were performed.

2. MATERIALS AND METHODS

The films were made using magnetron sputtering technique on a laboratory-AJA Orion 5 Scaled unbalanced magnetron sputtering system. The shutter was controlled in the deposition system of coatings with alternating layers of chromium nitride and hafnium nitride. Four-inch chromium and niobium targets (99.5%) were used and powered in dc, mixture with a flow-rate at a substrate temperature of 200 °C and a pressure system of 0.4 Pa. The substrates set for 5 min in an Ar glow discharge at a total pressure of 5 Pa, and a process time of 180 minutes to produce an average thickness of 2.2 μm. During deposition a -50 V rf-biasing of the substrates was used to ensure a dense coating morphology. The multilayer arrangement was kept similar for all depositions, with NbN as the starting layer at the substrate interface and also as the top layer.

To measure the coefficient of friction is used a Nanovea Pin-On-Disk Tribometer Equipped with the lubrication module was used with an area of alumina (Al_2O_3) of 5 mm diameter test speed 5 cm / s, 3mm radius, distance of 80 m and a load of 5N, the tribometer has software that controls the computer and also allows to calculate the wear rate, using the average cross-sectional area in μm^2 and the radius of the worn tread (r) in mm, load in Newton and the distance test in meters.

The hardness and Young's modulus were measured in a nanoindenter Nanovea in gigapascals. The indenter used was Berkovich diamond tip three-sided pyramidal shape with the same depth-area ratio of the Vickers indenter. This indenter was used for several reasons for having a good finish to be sharp tip better resolution in very small contact areas it is achieved also better uniformity is achieved in the contact area.

Electrochemical tests of hard coatings was analyzed by a potentiostat - Gamry galvanostat model PCI-4 using potentiodynamic technique Tafel curves. The specimens were immersed in a 0.5M NaCl solution, prepared with distilled water. Tafel plots were obtained dynamically to a scan rate of 0.125 mV / s with potential between -0.3V - 0.3V, and 1 cm^2 area exposed. The electrochemical behaviour was evaluated after 45 minutes; allowing the stabilization of the open circuit potential. The standards applied in the measurement criteria and calculations corresponded to ASTM G 5 and G 59.

3. RESULTS AND DISCUSSION

3.1 Coefficient of friction and wear

The conditions of the trials of pin-on-disc they maintained at equal conditions with regard to the distance used, the applied load and temperature for the multilayers with a total thickness varying the total period in 1100 nm (2 bilayers), 440 nm (5 bilayers), 220 nm (10 bilayers), 110 nm (20 bilayers), with respect to the coating it is observed that initially the friction coefficient is constant over the first 10 meters then rises possibly due to trapped particles between the tribological pair to steady state [17].

In Figure 1, the graph of friction coefficient versus distance of travel is obtained for the first system analyzed bilayers n = 2, it can be determined that the friction coefficient is larger for this multilayers since presented the highest rate of wear [18-19]. What it can be associated with fractures obtained on the coating due to cyclic loads applied during the test, in Figure 1 shows the process of plastic deformation type this is observable at baseline in the 20 meters, since there is increased friction coefficient after causing various deformation processes, then it presents a constant behavior but the loosened particles generate third bodies that influence the tribological pair presenting a very inconsistent coefficient of several ups and downs [20-21]. With respect to coating with 5 bilayers; a representation of a lower wear rate is obtained because the friction coefficient is low at the beginning due to the homogeneity of the film this is also related to the hardness where the difference in hardness of the tribological couple of ball Alumina (Al_2O_3) with respect to the coating is removed and adheres, the experimental adhesion is related to the effort of basic adherence but other extrinsic values, which have to do with the conditions of the test and the intrinsic physical properties affecting the measurement [22].

The value of coefficient of friction for the 10 and 20 bilayers are similar however these curves show two distinct regions. In the first regions the friction coefficient starts with low values this area is called start-up period and is associated with interferential friction mechanism due to contact between the tips of the asperities of both counterparties, Alumina ball and the coating surface [23]. By increasing the sliding distance increases friction coefficient in the tribological pair, this due to the formation of wear particles generated by the breakup of the tips of the asperities because there are two systems input from both of the coatings thus the asperities of both bodies are softened thereby reducing the coefficient of friction. The region is called steady-state friction period; and starts after about 20 -70 m sliding. This station is generated a stabilization of the friction coefficient associated with the coexistence and competition between the mechanisms and interferential adhesive friction due to the elastic-plastic properties and surface roughness [24].

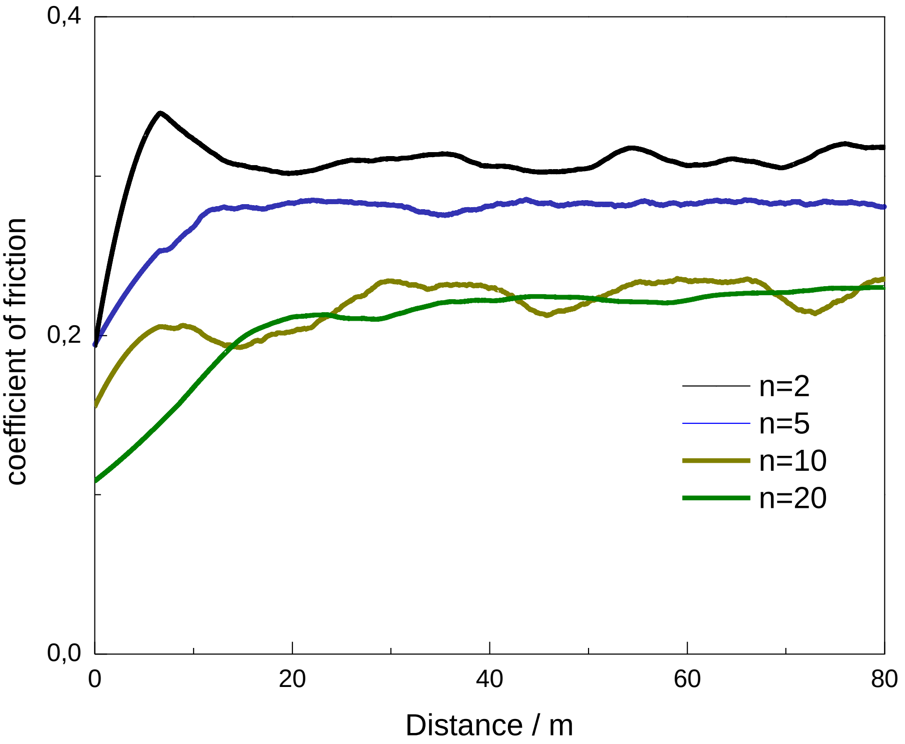

Figure 1. Results of the tribological tests analyzed for four systems corresponding to the multilayer NbN / CrN with n = 2, 5, 10 and 20 bilayers.

3.2 Hardness

Figure 2, displayed varying the hardness of the thin films measured at a scale of 10 nm in length using loads depending on the period of the multilayers of NbN / CrN, It shows that the maximum value (32.45 GPa) of this property is achieved with a multilayer whose period is 20 bilayers, the other multilayers evaluated have a lower value corresponding to 29.97 GPa for n = 10, 26.02 GPa for n = 5 and 24.9GPa for n = 2, the latter values have been reported as coatings hardnesses CrN / NbN type, deposited by reactive magnetron sputtering [25].

As can demonstrate the period influences in the Nano hardness of the multilayers, Nano hardness in the multilayers is increased by effect of decreasing the period, this may be due increase when efforts to change stress to compression [26]. The difference in elastic modulus value found in the analyzed cause a differential value Nano hardness systems, that is to say layers whose elastic modulus is low are not able to resist crack growth and generation and therefore Nano hardness around the coating is affected this is the case for the 2 and 5 bilayers, these results demonstrate that there is no appreciable difference in the moduli of elasticity, increased hardness for multilayers 10 and 20 is the microstructure, when the thickness of the individual layers is small diffusion of atoms makes the interface between the same is well defined, therefore, the composition shows a gradient, these phenomena allow dislocations dissipate between the layers after that hardness increases [27].

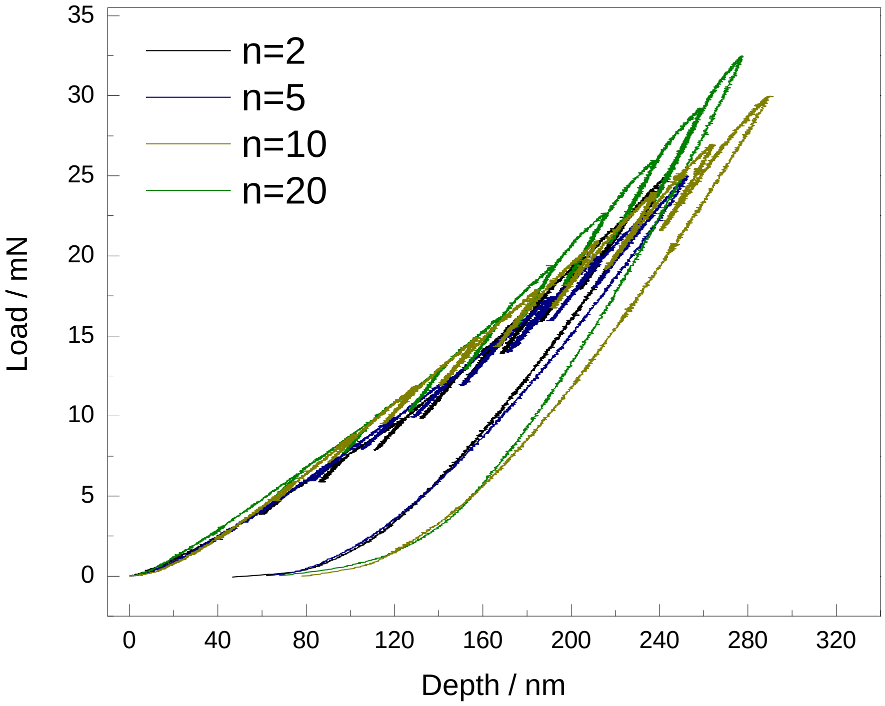

Figure 2. Measurement of hardness and Yield Stress of thin films NbN / CrN type by nanoindentation tests.

The thickness of the interface is critical to define the value of the Nano hardness of the multilayers, the thickness average value of the interface for 20 bilayers is 110 nm, and this number when compared to the thicknesses of the individual layers of the multilayer becomes more significant inasmuch as the period of the bilayer is reduced. In a multilayer of 1100 nm period interface equivalent to 50% of the thickness of the individual layers, whereas for a multilayer of 110 nm period interface mean 5% of the thickness and a multilayer of 220 nm period, interface occupy 10% of the thickness of the individual layers, this comparison shows that the spread between the layers would be considerable what it in turn would affect the nanohardness obtained [28]. The latter results indicate that the interface is well defined and this is the fundamental factor for the nanohardness of the multilayers increase with the decrease of the bilayer period.

3.3 Polarization curves

In Figure 3, the polarization curves are presented Tafel which they were obtained to contact the electrolyte sodium chloride on coated samples where overpotential of 300 mV around, applies in anodic and cathodic corrosion potential sense, the value of corrosion current density is obtained by extrapolating the linear portion of the polarization curve to the corrosion potential, Extrapolating a line segment in the anodic and cathodic curves, of this linear region is found the corrosion resistance, the results of the coatings indicate that the corrosion potential are similar for the four systems tested because its fluctuation is 20 mV, additionally, there is no relationship between the amount of multilayers and thermodynamic potential, this is due to the reaction is set by the elements of the coatings such as Niobium, Chromium and Nitrogen [29]. The difference in electrochemical terms are generated with respect to the corrosion current density and this is because the microstructure generated where it was found that for n = 2 has a current density of 2.19 μAcm^{-2}, for n = 5 the value is 1.29 μAcm^{-2}, n = 10 corresponds to 0.27 μAcm^{-2} and finally of n = 20 is 0143 μAcm^{-2}, this decrease in density of corrosion as the number of bilayers is increased is generated due to the barrier properties of the coatings and the interfacial adhesion, because in all cases observed in anodic dissolution so generally, avoiding the creation of micro cracks permit diffusion of electrolyte to the other layers, the decrease in density of corrosion current generates an obstruction to the passage of ions and thus the corrosion rate is decreased and coating delamination [30]. The potential difference in multilayers is because thermodynamics of the system, as can be inferred surface imperfections where it is generated concentrators current density in defects. With respect to the anode zone it can indicate that the multilayers n = 2, has a region called a general solution, where there is a proportional increase in current versus applied overpotential in the anodic branch to -310 mV vs. SCE potential approximately, this change can be distinguished as the start of the dissolution of the passivating layer with weak stability because when you reach that potential gradual increase of the current density is observed. Accompanied by this phenomenon is the plateau in the range of -200 mV vs. to -310 SCE [31]. Which may indicate regeneration of a layer of corrosion products that provide a stable current density around this range of potential and prevent the increase of the dissolution rate of the multilayer coating, in the case of n = 10 a change is observed in the corrosion current in this variation it is close to a decade, finally to n = 20 is obtained no detectable changes in the polarizations is obtained which is stable system relative to other coatings analyzed.

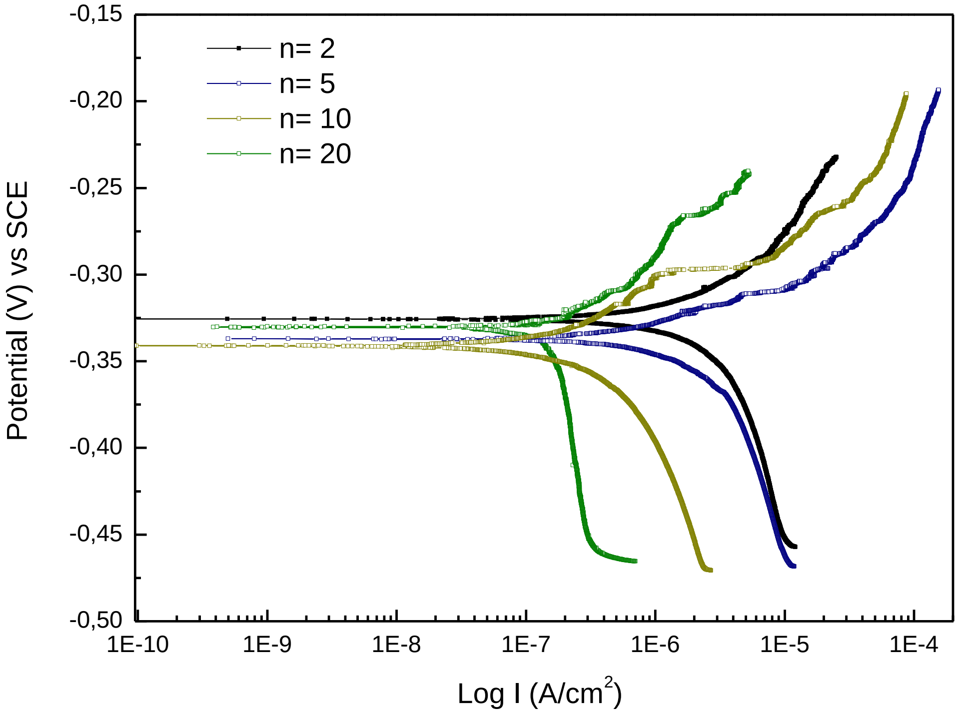

Figure 3. Polarization curves in the dual system of dynamic corrosion and abrasive wear corresponding to the multi-layer type coatings

4. CONCLUSIONS

Coatings NbN / CrN were deposited on substrates of AISI 4140 steels ferritic-pearlite, with the purpose of studying the tribo-corrosive behavior. From the analysis of the tribological part it was determined that the parameters in the form of multilayer deposition will influence the mechanical behavior coatings and therefore on the part of corrosion thereof, The parameters influencing the tribological behavior of the coatings have effects on the hardness, thickness, adhesion, so the elastoplastic properties and lower friction coefficient are obtained. The tribological properties are related to the morphological properties of the surface of the tribological pair (steel-hard layer), the mechanical properties and the results multilayers NbN / CrN Multilayer, finish at higher hardness much higher is obtained, showing the benefits of the materials obtained.

The current values for the coatings are smaller as the number of layers is increased which ensures sputtering magnetron technique provides very good growing conditions movies with smaller pore size, which improves the behavior of a multilayer system when exposed to aggressive media as it is sodium chloride.

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