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Short Communication

Effect of Cavitation on The Corrosion Behavior of Ti(CN)/TiNb(CN) Multilayer in Seawater

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The superficial wear generated by cavitation in an electrolyte as sodium chloride 3.5%, causes damage in steels AISI 4140 by corrosion, it is commonly used in hydraulic machines, therefore suggest to coat with a Ti(CN)/TiNb(CN) multilayer system deposited with a 200 bilayers period, by means of the technique of physical vapor deposition. The combined action of corrosion and cavitation attacks are monitored by the adequacy of an equipment that consists in ultrasonic oscillator, compound by an oscillating ultrasonic transducer that oscillate at 20 kHz with an amplitude of 100um, and conditioned to a galvanostat-potensiostat. The electrochemical characterization was performed by the electrochemical impedance spectroscopy (EIS) and Tafel polarization curves. As for the results, the hard coating of [TiCN/TiNbCN]n, presented a better resistance to the cavitation corrosion in comparison with the substrate owing to in the steels AISI 4140, the cavitation removes the products of corrosion, accelerating the corrosion rate and decreasing the polarization resistance, in contrast to the obtained in the thin films.

Keywords: Cavitation, corrosion, multilayers, ultrasonic.

1. INTRODUCTION

The hard multilayers coating, are materials in study, owing to the deposition thereof can be improve properties such as corrosion resistance and wear, the electrical conductivity, used as diffuse barrier, etc [1]. The deposition of multiple layers with different mechanical properties between them, structure of multilayers can act as an inhibitor of nano-cracks, also increases the fracture resistance [2]. If the monolayers coating are compared with multilayer coating, the latter have a better combination of properties in multiple applications [3]. The hard coating has become the solution to problems like corrosion and wear. The physical vapor deposition technique (PVD), is one of the process more commonly used to obtain the hard coating, encompasses any process of growth of a film in a vacuum environment involving the deposition of atoms or molecules in a substrate. The (PVD) technique was applied with success, to produce different types of multilayer coating, on a wide range of substrates [5].

Some of these coatings that alternated layers are named hetereostructures, exhibit high hardness, and offer potential advantage for drilling, formed and cutting of various materials. In combination of bilayers such as titanium nitride, zirconium nitride [TiN/ZrN] the maximum value of hardness is found in the regimen of hard coating (below 40 GPa) but still are interesting for tribological applications, beside presenting new physicochemical properties such as anticorrosive properties, at present in study [5]. Many recent research points to the study of ternary and quaternary materials, due to their higher mechanical and tribological properties [6]. In the last years, considerable efforts have been made to develop multicomponent as multilayer heterostructure in order to increase the wear resistance and the oxidation of the coating components. Titanium carbonitride monolayers ($TiC_{1-x}N_x$) were deposited onto AISI 4140 steel using the magnetron sputtering technique wherein a 60% increases in hardness and 47% in the modulus of elasticity was obtained [7].

Hard coatings are promising systems for machinery parts that will be subject to cavitation during operation, due to a good performance front of phenomena as wear resistance, having a higher hardness than the base material which usually is martensitic and ferritic steel, additionally the multilayer coating type has the ability to dissipate impact energy generated by the repeated action of the energy generated by continuous collapse of vapor bubbles in the liquid flowing in the system owing to change in the system pressure below and above the steam pressure that the liquid has [8]. The great resistance to indentation can allow that type multilayer coatings resist better the phenomenon.

Multilayer system of $[TiCN/TiNbCN]_n$ were deposited by cathodic pulverization. The research reveals than the period of the double layer (Λ) have a marked influence on the phenomena of wear and adding the electrochemical of the coating; in the system with n=200 y Λ=15 nm, the resistance properties to the erosion by cavitation and corrosion compared uncoated AISI 4140 Steel. In this work the effect of cavitation was studied in the corrosion behavior, therefore was evaluated dynamic corrosion by separately, and subsequently the synergy cavitation erosion-corrosion.

2. EXPERIMENTAL DETAILS

Multilayers of Ti(CN)/TiNb(CN) were deposited on AISI 4140 steels substrates (diameter 15.86 mm; thickness 4 mm), which was cleaned in an ethanol and acetone bath by ultrasonic in a sequence of 15 minutes. The coatings were obtained by the technique of multi-target RF magnetron sputtering (13.56 MHz). For the deposition of the coating were used targets of 4 inches diameter of TI and Nb with a 99.9% purity. In order to study the influence of the synergy between dynamic corrosion, cavitation erosion and cavitation erosion and corrosion, systems of Ti(CN)/TiNb(CN) were deposited with periods of 200 bilayers controlling the time of the open and close for the shutter. The thickness of the coating was obtained by a DEKTAK 8000 perfilometer with a tip diameter of 12.00±0.04 μm a sweep length of 1000 μm – 1200 μm. For the 200 bilayer sample, the thickness was 3.00 ± 0.04 μm.

For the evaluation of the dynamic corrosion resistance and erosion-corrosion by cavitation was used a Gamry potentiostat-galvanostat PCI-4 model, using the technique of electrochemical impedance spectroscopy (EIS). The specimens were located immersed in a NaCL 3.5% solution prepared with distilled water. The cell composed of a counter-electrode (Platinum), an Ag/AgCl reference electrode and AISI 4140 steel with and without multilayer coating as working electrode. The polarization curves was obtained with a scan rate of 0.5 mV/s in a voltage range of -0.25V to 0.25V, the Nyquist diagrams were obtained performing frequency sweeps in the range of 0.001 Hz until 100kHz, using an amplitude of the sinusoidal signal of 10 mV using an exposed area of 1 cm^2, the electrochemical behavior was evaluated after 45 minutes, time necessary to stabilize the open circuit potential.

The evaluation of the damage which can be produced owing to the effect of cavitation in a corrosive fluid was performed in a ultrasonic oscillator equipment that consist mainly of an ultrasonic transducer oscillating at 20 kHz with an amplitude of 100μm, and a sonotrode. The configuration of the equipment was made taking into account the guidelines indicating the standard ASTM G32-03. The test method was directly, which includes the location of the sample at 0.5 mm from the oscillator tip, to determine the weight loss due to the erosion, the specimens were removed from the solution at intervals of 30 minutes; cleaned with a jet of water, dried with hot air and weighed on a precision balance (0.1 mg). The microstructural observation was made through a scanning electron microscope of high resolution, which has a resolution of 1nm to 30kV.

3. RESULTS AND DISCUSSION

3.1 Erosion

The evaluation of the erosive phenomenon was performed using cathodic protection cathodic 1V with respect to open circuit potential of the coating. Cathodic protection was provided by a potentiostat this protection was generated because the assembly is immersed in a solution of 3.5% by weight NaCl, simulating an aggressive condition [9]. The erosive wear is evaluated in this paper is due to moving fluids that commonly cause sudden changes in pressure creating bubbles that implode and generate shockwaves that damage the surface of the elements causing the wear phenomenon. The rate of cumulative erosion was estimated by the measurements described in the experimental development, and shown in Figure 1, the dynamic curves indicate that the substrate has a greater mass loss as a function of time, because its ductility suffers proportionally greater wear exposure time. When assessing multilayer systems $[TiCN / TiNbCN]_{200}$ a decrease in the inclination of the curves to lower values of mass loss versus time for evaluation is obtained, displaying the beneficial effect of coating the AISI 4140 steel [10]. It has been determined that the cavitation erosion in NaCl was completely dominated by the mechanical strength, so that the evaluation of synergism is performed by electrochemical techniques.

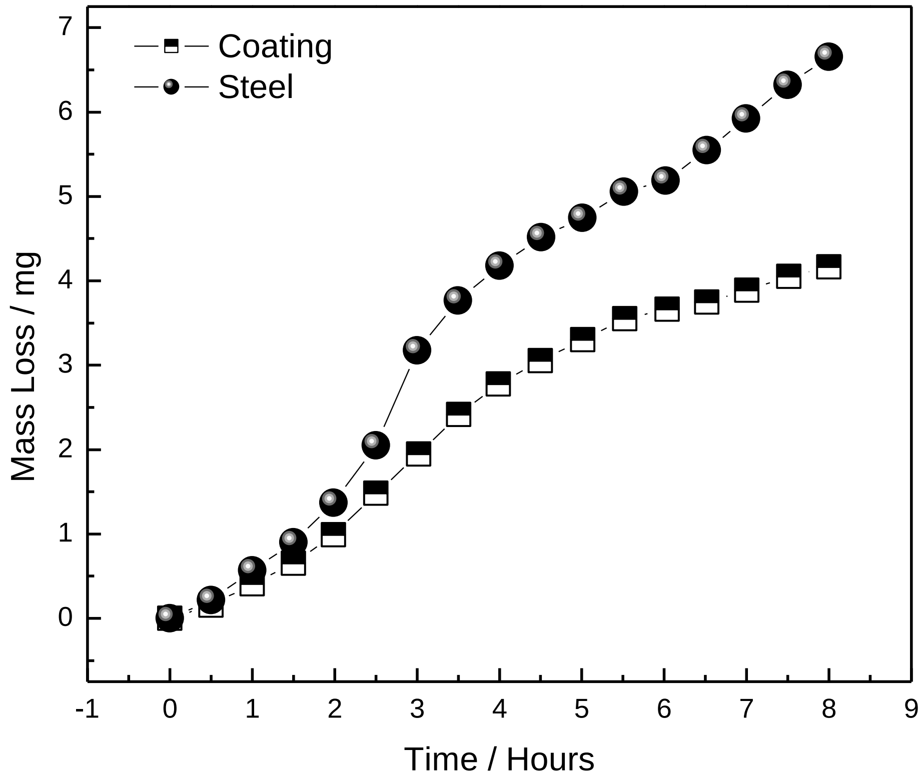

Figure 1. Erosion wear curves of the coatings and the substrate for 8 hours evaluated wear.

3.2 Electrochemical Evaluation

Fig. 2, potentiodynamic polarization curves of the substrate and coating [TiCN / TiNbCN] $_{200}$, evaluated at 30, 180 and 480 minutes for both systems are presented. The coated materials have a lower corrosion current density and corrosion potentials with more noble values, compared with uncoated metals assessed at 480 minutes. The corrosion current density of coated and immersed in the electrolyte sample of NaCl, increases as the evaluation time progresses (table 1). This is because the coatings show improved resistance to cavitation erosion, compared with 4140 steel, as shown in Figure 1. Additionally it was found that the protective film to produce an adequate performance when exposed to a corrosive medium as the effect observed is dissolved in all cases evaluated, generating an adequate performance in coatings such as adhesion film is not affected, and therefore the loss of mass of the combined system in minimum [11]. Because the quaternary coatings deposited in multilayer form can combine the improved properties such as increased hardness and chemical stability.

The corrosive effect by itself is relatively small and the synergism of corrosion and erosion has a strong effect on the surface damage of the coating and the substrate [12]. This result suggests that corrosion coatings and steel has significant damage due to the dissolution observed in the anodic region in the polarization curves, in addition it was found that the combination of corrosive factors and mechanical action produces far more damage than if each were generated separately, so we can say that it is corrosion-induced erosion [13].

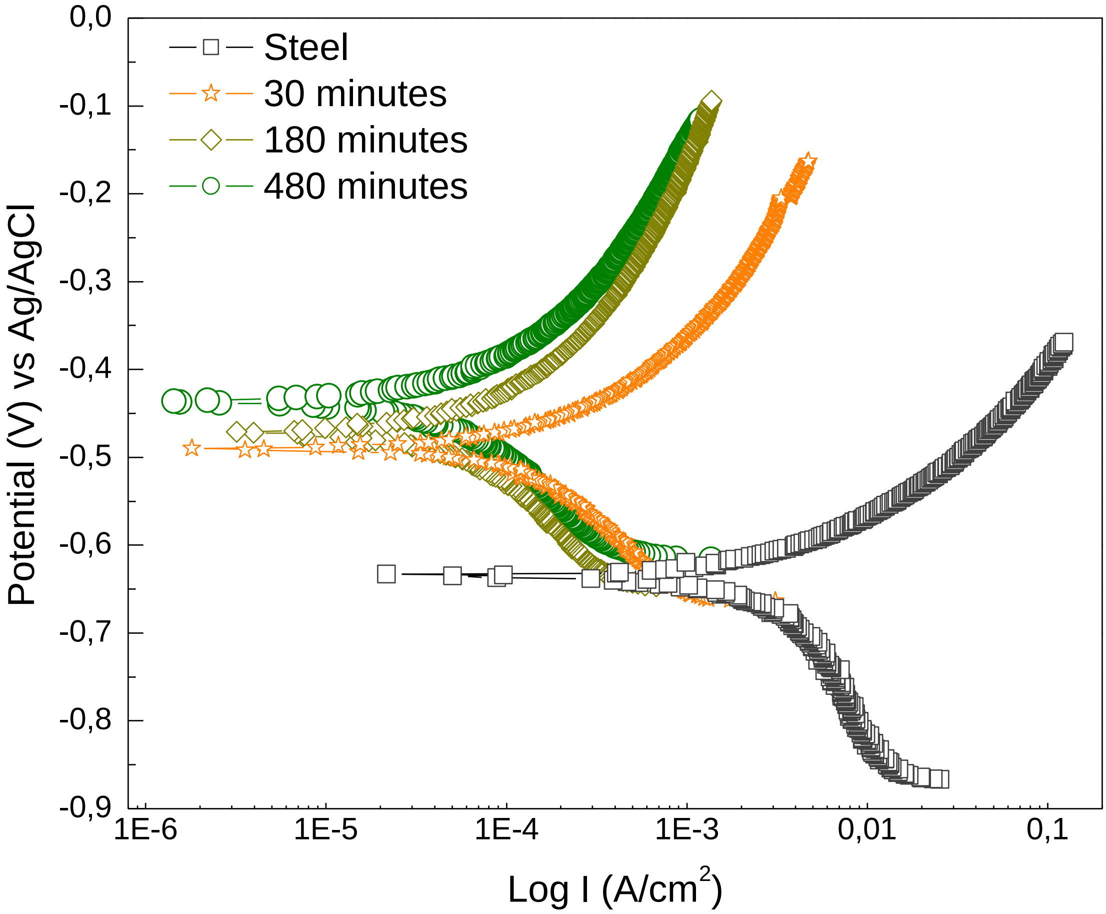

Figure 2. Polarization Tafel curves for the substrate and the coatings evaluated after 30, 180 and 480 minutes.

Table 1. Electrochemical parameters of the substrate and the coating, to determine the rate of deterioration.

	Steel	30 minutes	180 minutes	480 minutes
Corrosion current, icorr (A/cm^2)	$34*10^{-3}$	$24*10^{-4}$	$8.5*10^{-5}$	$4*10^{-5}$
Open circuit potential (mV) vs Ag/AgCl	- 650	- 490	- 480	- 440

Fig. 3 shows the impedance spectra evaluated under the effect of cavitation erosion corrosion at 30 and 180 (for coating) and 480 minutes for both coating and substrate. In Nyquist substrate is observed for a semicircle connected with the protective layer caused by the corrosive effect. For coatings two related semicircles are obtained the first relates to the evaluation at higher frequencies, where it interacts aggressive solution with the coating is subjected to cavitation, it follows that the coupling resistor and capacitor which are connected in parallel decreases considerably for the estimate to 480 minutes, while at 30 and 180 minutes these values are similar because the front of corrosive phenomena featuring multilayers [TiCN / TiNbCN]$_{200}$, protection is not affected , the effect is mechanical wear due to erosion generated for this same system rated to 480 minutes for submitted wear is higher due to that obtained in the Tafel polarization curves, wherein the coating solution was higher for this time evaluation due to the increased corrosion current. The second semicircle corresponding to low frequencies and this is because adhesion between the coating and the substrate. The important contribution that exists in obtaining multilayer coatings because it generates multiple interfaces that stops the advance of corrosion since having 200 bilayers and get in touch with ions Cl- change direction every time meet a new interface thus allowing that the electrochemical potential which promotes corrosion resistance is increased, also the interfaces promotes increased porosity reduction in the multilayers, however as erosion corrosion progresses the porosity increases due to micro cracks generated by the erosive effect, this increase increased dominant corrosion process was accelerated by chloride ion transport.

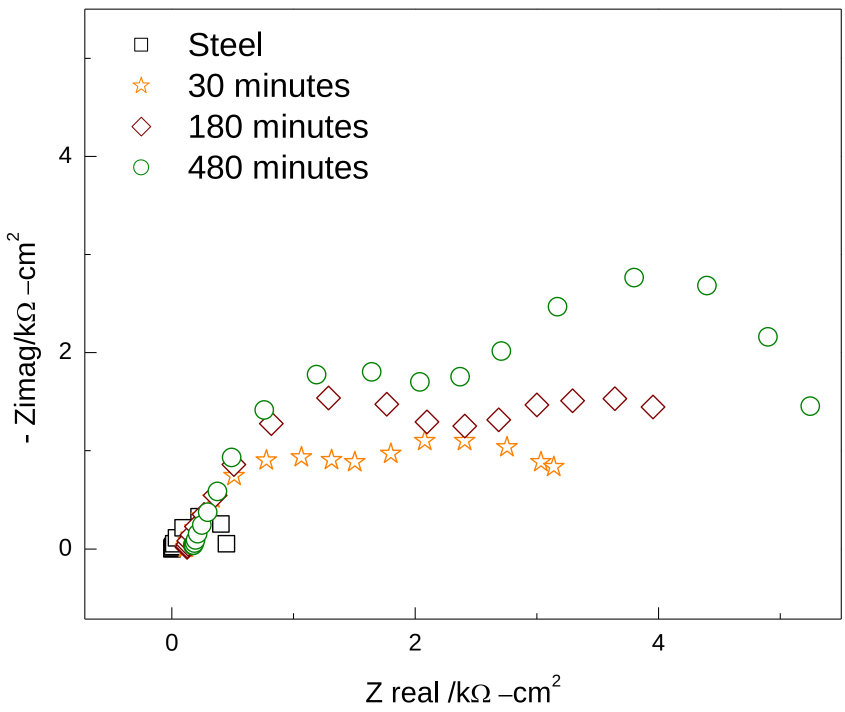

Figure 3. Nyquist plot corresponding to the assessment of corrosion erosion, to the substrate and the coatings.

4. MICROGRAPH OF EROSIVE–CORROSIVE WEAR RESISTANCE

Fig. 4 the micrographs of the multilayer after the cavitation erosion test and corrosion to 30 minutes (Figure 4a) and 480 minutes for both the multilayer and the substrate (Figure 4b and 4c respectively) are shown. It is noted that in the multilayers were damaged after 30 minutes of the test run assisted cavitation corrosion. The trial at 480 min sample surface damage in the area where erosion generates a surface damage to compare this result with respect to the substrate is observed that steel generates numerous deep cavities.In Figure 4, the micrographs of the multilayer after the cavitation erosion test and corrosion to 30 minutes (Figure 4a) and 480 minutes for both the multilayer and the substrate (Figure 4b and 4c respectively) are shown. It is noted that in the multilayers were damaged after 30 minutes of the test run assisted cavitation corrosion. The trial at 180 min sample surface imperfections in the area where erosion generates defects. Comparing this result with respect to the substrate is observed that steel generates numerous deep cavities and the coating generate wear abrasive type.

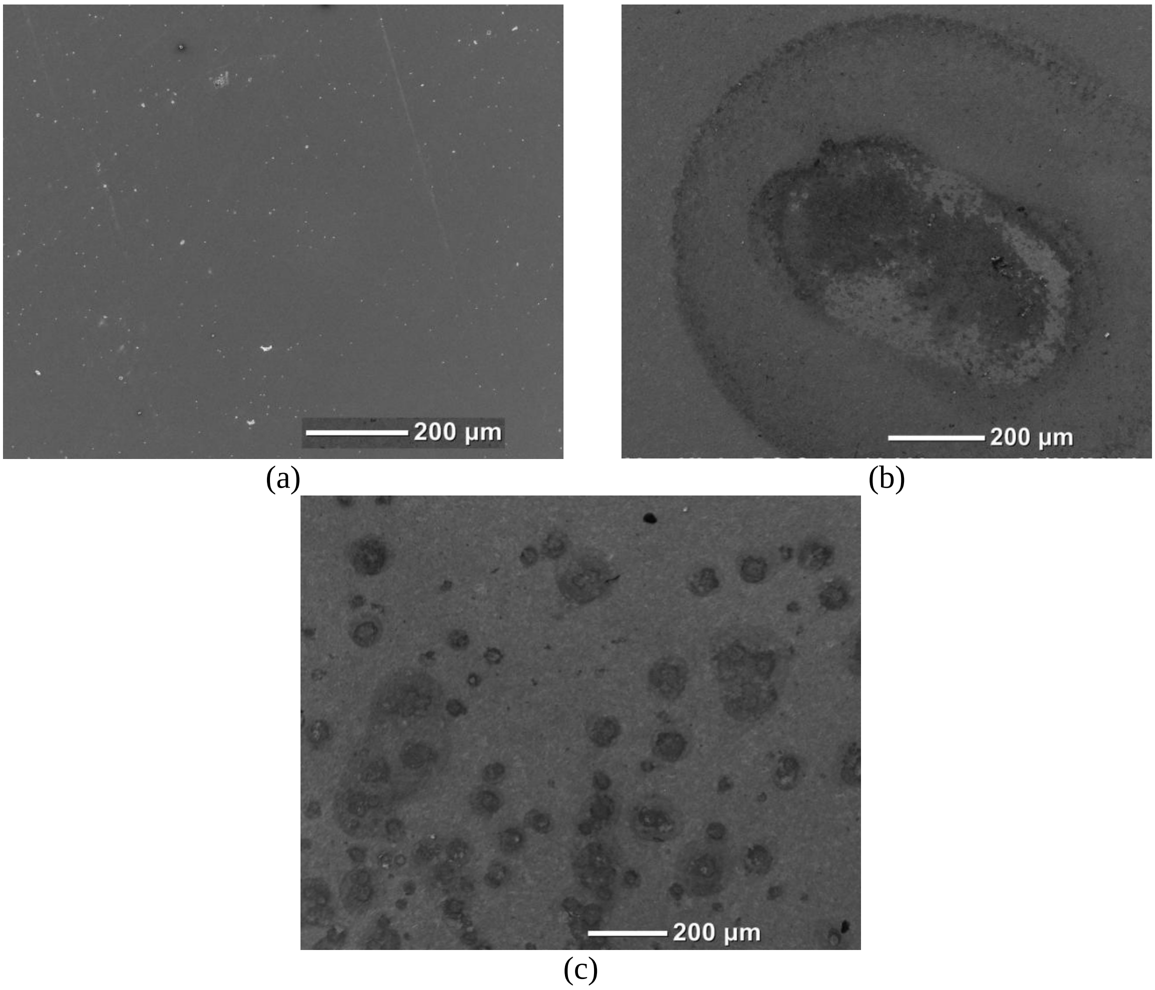

Figure 4. SEM micrograph of the coating and substrate evaluated under the combined effect of cavitation erosion corrosion) 30 minutes of evaluation of multilayer b) 480 minutes, the end time of evaluation of multilayer (c) 480 minutes of assessment of steel

5. CONCLUSIONS

Multilayers of [TiCN / TiNbCN] 200, subject to erosion by cavitation and assisted by corrosion generated a phenomenon which involves the interaction of mechanical, chemical and electrochemical factors. The mass loss indicates that as time progresses of evaluation is generated the start and spread of cracks. With respect to the corrosion potential was determined to have a tendency towards active region and the corrosion current density is increased, because the mass loss produced by the electrolytic solution. By the technique of electrochemical spectroscopy impedance, is determined separately, the interaction of the electrolyte (chloride ion) with the coating, additionally permitted thus the 200 bilayers generate a barrier of chloride ion, thus allowing to reduce the effect of increase in corrosion rate.

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