Int. J. Electrochem. Sci., 8 **(2013)** 5275 - 5286

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Determination of the Best Behavior of $[TiCN/TiNbCN]_n$ Multilayer Coating on Erosion–Corrosion Resistance with Varying Particle Angular Velocity

Willian Aperador [1]*, *C. Amaya*[2,3] *J.C. Caicedo*[2]

[1] Departamento de Ingeniería, Universidad Militar Nueva Granada, Carrera 11 No. 101-80, Fax:+57(1) 6343200, Bogotá, Colombia.
[2] Thin Films Group, Universidad del Valle, Cali - Colombia
[3] Research Group in Development of Materials and Products CDT ASTIN SENA, Cali-Colombia.
*E-mail: g.ing.materiales@gmail.com

Received: 12 December 2012 / *Accepted:* 4 March 2013 / *Published:* 1 April 2013

The goal of this work is to study electrochemical behavior under corrosion-erosion conditions for $[TiCN / TiNbCN]_n$ multilayer coatings with periods of 1, 50, 100, 150 and 200 bilayers deposited by a magnetron sputtering technique on AISI 4140 steel substrates. The erosion-corrosion experiments were performed in a test machine in which the impact velocity, impact angle, concentration of solids and pH of the solution were controlled. The multilayers were evaluated compared to corrosion, erosion and erosion corrosion at two impact angles of 30 ° and 90 ° in a solution of 0.5 M NaCl and silica, analyzing the effect of impact angle and the number of bilayers in the corrosion resistance of these coatings. The electrochemical characterization was realized using the Tafel polarization curves technique and microstructural characterization by scanning electron microscopy. The results show a decrease in corrosion rate for multilayer systems tested at 30° with periods of 150 and 200 bilayers.

Keywords: Multilayer, dynamic corrosion, corrosion-erosion, erosion, scanning electron microscopy

1. INTRODUCTION

The erosion-corrosion is an accelerated corrosion of metals due to a combination of a chemical attack and abrasion by physical movement of fluids with suspended solids. Alloys that form film surface under corrosive environment commonly have a corrosion speed limit above which corrosion is accelerated rapidly. Erosion-corrosion is associated with current induced by mechanical removal surface of the protective film that results in further increase of corrosion rate for chemical or electrochemical processes. Surface engineering of metallic substrates with protective film unanimously calls to attention of the industry and researchers, as it produces a host of properties such as wear and erosion resistance, and oxidation and corrosion resistance. However, a coating is highly functional only if the interface between the film and the substrate is stable and strong [1-4]. In recent years, several research has been aimed at developing multilayered structures of nanometric period thickness, also called superlattices, for their use as protective hard coatings. The appeal of such structures rests on their improved mechanical and tribological properties, compared with those of their individual components [5–10].

Hardness enhancements in thin film isostructural superlattices have been successfully modeled by dislocation image forces theories, arising from Koehler's first model [11] based on shear moduli differences, in combination with Chu and Barnett's correction assuming dislocations propagation inside monolayers [12]. Moreover, there have also been reports of mechanical and electrochemical enhancements in isostructural superlattices [12-14]. Among these isostructural systems, metal/ceramic and ceramic/ceramic superlattices have been receiving major attention since this combination can exhibit high hardness values, often increasing it more than a 100% over rule of mixtures, while retaining good ductility and high anticorrosive properties. Several metal/ceramic and ceramic/ceramic superlattices have been studied during the past 10 years including Ti/TiN [13], TiN/V0.3Nb0.7N [14] or the TiN/NbN [15].

The nitride coatings, which are characterized by high hardness, wear resistance, and corrosion resistance, are obtaining ever wider use for strengthening and protection of constructional steels from wear and corrosion. A significant disadvantage of such coatings limiting their use is their thickness, which in many cases does not exceed 5 μm. In connection with this, broadening of the use of the Physical Vapor Deposition (PVD) magnetron sputtering technology for strengthening of machine parts is possible with the development of multilayer coatings having a higher combination of properties. One of the most important parameters determining the service properties of nitride coatings is the size and quantity of the pores, which as the result of the thinness of the protective layer pierce it all the way through to the base and serve as origins of corrosion. It is known that PVD coatings have significantly less porosity in comparison with coatings obtained by other methods of vacuum technology and also by methods of gas thermal spraying. In some cases magnetron sputtering makes it possible to obtain porosity-free coatings mainly in multilayers with a thickness on the order of 1 μm, which is the result of the high packing density of the atoms being concentrated. However, according to the data of some works, the porosity of nitride coatings may reach 5% which differs from the multilayer nitrides where the porosity decreases to 1% [15]. Therefore the corrosion resistance of multilayer nitride coatings is higher than that of single-layer ones, which may be explained by their greater thickness and features of their microstructure, including the absence of circular crystals characteristic of single layer coatings, moreover failure of nitride coatings under the action of a corrosive medium occurs at structural defects, which determine their corrosion resistance and electrochemical properties [11].

The aim of this paper is to study the electrochemical character based on multilayer coatings [TiCN / TiNbCN] n, in order to analyze their chemical response in aggressive media, the phenomenon of erosion and corrosion-erosion synergism. This study will contains enough information from the multilayer $[TiCN / TiNbCN]_n$, in order to determine the influence of the angle of impact and the number of bilayers in wear phenomena.

2. EXPERIMENTAL

$[TiCN/TiNbCN]_n$ multilayers were deposited on AISI 4140 steel substrates by using a multitarget magnetron reactive sputtering technique, with an r.f. source (13.56 MHz) and two stoichiometric TiC and Nb targets with purity of 99.9%. The deposition parameters for obtaining high-quality coatings were sputtering power of 400 W for TiC and 350 W for the Nb target; substrate temperature of 300 ºC; under circular rotation substrate with 60 RPM, to facilitate the formation of the stoichiometric quaternary film. The sputtering gas was a mixture of Ar 76% and N_2 24% with a total working pressure of $6x10^{-3}$ mbar. An unbalanced r.f. bias voltage, which generates a constant voltage offset of -50V was applied. Moreover our magnetron sputtering device has a substrate positioning substrate system in relationship to target spot, this parameter permits varying the bilayer number ranging from 1, 50, 100, 150 and 200; changing the bilayer period. The measured total thickness deposited [TiCN/TiNbCN]n multilayers was found to be approximately 3 μm for all them. The individual thickness varied in function of bilayers number from n = 1 to n = 200 producing layers with thicknesses from 1.5 μm to 15 nm, respectively.

For the analysis of the erosive–corrosive effect a device built for the evaluation of chemical attack in metallic materials and coated materials was used. Fig. 1 shows the erosive–corrosive test device that consists of a tribometer with a glass container for erosive–corrosive storage, an acrylic cover that is available in the sample holder and electrodes an impelling of High Ultra Molecular Weight Polyethylene (HUMWPE) which rests on a Teflon shaft that is attached to the main shaft motor which provides fluid motion. The lid of the container allows locate the sample exposure under two impact angle of 30° and 90º for corrosive fluid action, as well as the reference electrode and counter-electrode. The last one angle leads to locate the sample perpendicular with respect to the fluid flow. On the other hand, the fluid movement is caused by a shaft driver motor. The tangential speed applied to the fluid with erosive particles was fixed to 13 m/s, this take into account that the impeller radius is 0.055 m and the motor speed was fixed to 2250 RPM. The electrochemical study was carried out with a Gamry PCI 4 300™ Potentiostat, which has a Gamry Framework Version 4.21/DC corrosion software, Tafel polarization curves techniques, these curves were realized at room temperature using a cell that support one working electrode ($[TiCN/TiNbCN]_n$) within an exposed area (1 cm^2), a reference electrode (Ag/AgCl) and graphite counter electrode under a 0.5M NaCl solution with distilled water. The resting potential was measured during 30 minutes. Measurements were carried out on a set of three different replicate samples. The Tafel curves were taken about 1 hour in the test, this time was necessary for the anodic and cathodic sweep potentials. Tafel polarization curves were obtained at a sweep speed of 0.16 mV/s within a voltage range from -0.3 V to 0.3 V. In this work, silica (SiO_2) was used as an abrasive agent with a particle size between 210 μm and 300 μm. This chemical solution was chosen since it has been shown that it can be used to study steel as it facilities the observation of chemical attack at defined anodic region and chloride addition guaranteed the effective attack. The weight of the work electrode (E_w) for all test was around 55.847g/mol taking into account the Fe (pure) as reference since this material (Fe) present low carbon content.

The samples were subjected to wear due to erosion during 24 hours and a temperature of 25 °C. For the purpose of determining the weight loss due to erosion, during an immersion test in a solution of NaCl 0.5 M in the presence of particles of silica (SiO_2), samples were removed from the solution in intervals of 15 minutes, cleaned with water, dried with hot air, and weighed on a balance with a precision of 0.1 mg. The erosive phenomenon was evaluated using cathodic protection of 1V cathodic in respect to open circuit potential of both the steel and the coating respectively, according to the ASTM G 119-93 [16]; this cathodic protection ensures surface damage only by effect of erosive particles.

Finally, the effect of surface corrosion as well as the superficial morphology were analyzed and characterized by using a High-Resolution Scanning Electron Microscope (SEM) (Philips XL 30 FEG).

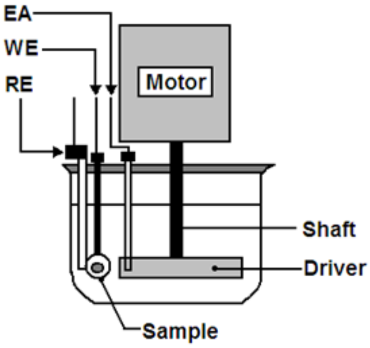


Figure 1. Schematic for device used at corrosion-erosion wear testing. In the figure, the acronyms EA, WE and RE are the auxiliary electrode, working electrode, reference electrode, respectively [1-3].

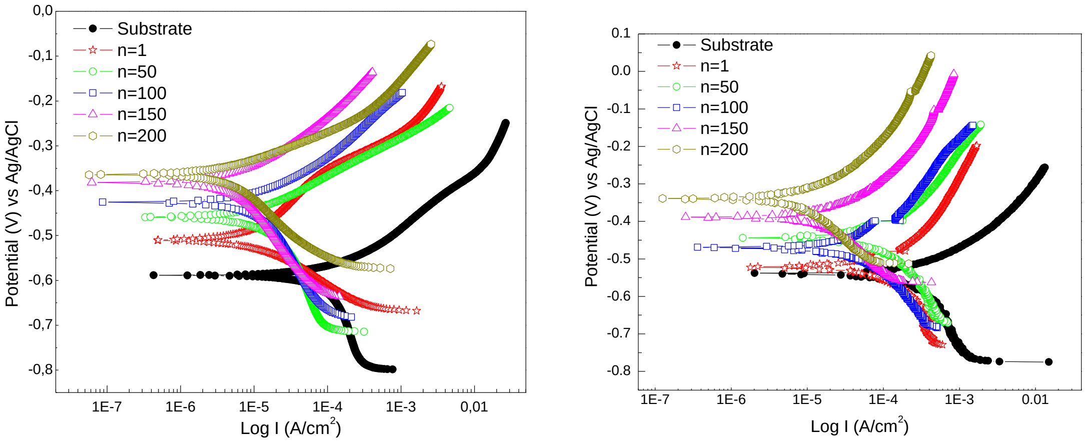
3. RESULTS AND DISCUSSION

3.1 Dynamic corrosion

In the figures 2a and 2b are shown the anodic polarization curves of samples tested at 30° and 90°, respectively. For substrates and [TiCN / TiNbCN]n multilayers are emphasized that the potentials of these coatings are moved to anodic zones (protection). Therefore can be established a bi-dimensional distribution of the influence of increased of the multilayers in the increased of the potential of corrosion. Setting up a relation represented by a linear regression (Table 1).

The curves obtained in figure 2a and 2b generate an active corrosion zone behavior in the anodic zone being more prominent for the substrates. The multilayers create zones of less electro-dissolution (250mV vs E_{corr}), subsequently, the active corrosion zone of the multilayers increased due to the increase of the corrosion density. The steels (substrates) in a NaCl 0,5 M medium show a change in the behavior on the anodic branch when potential is close to -510 mV vs. Ag/AgCl, for evaluation at 90 ° and -400 mV vs. Ag / AgCl. For a 30° angle approximately, this change can be distinguished as the start of the formation of a stable general corrosion due to a further increase in the density of corrosion, indicating the regeneration of a products corrosion layer which lets stabilize the current density around this potential and prevent increasing the dissolution of the steel velocity. The multilayers show a similar behavior to the substrate, owing to the appearance of a passive layer on the material cannot be evidenced, which allows for the active state generation caused by lack of passivity of the material, for this reason diffusion of the NaCl electrolyte can occur generated by the creation of anodic and cathodic zones. The dissolution of the coating is generated by anodic zones due to the diffusion which is presented in the coating; once the passivity is destroyed there is corrosion by sting increasing, whereby the shape of the curves is modified; this characteristic can be appreciated for the full range of potentiodynamic curves.

By and large, it is observed that in a NaCl 0,5 M medium, the corrosion potential which represent the multilayers is more positive with the decrease of the impact angle. This event provides a clear indication that the electrochemical behavior of this parameter depends mostly to the conditions of the electrolyte and the interaction with the material instead of the mechanic effect of agitation, therefore there is less tendency to suffer corrosion in a saline medium at an angle of 30 ° compared to 90 °.



(a) (b)

Figure 2. Polarization curves of AISI 4140 steel substrates and [TiCN / TiNbCN]n multilayers tested at a) 30° and b)90° in a 0,5 M NaCl solution.

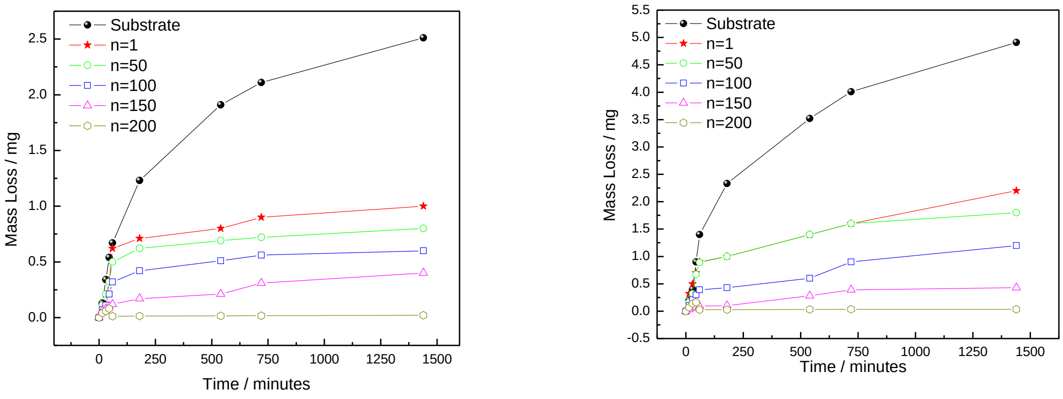
The table 1 shows the velocity and density decrease of corrosion current in [TiCN/TiNbCN]n multilayer coatings, for the angles 30° and 90° this decrease can be attributed to the degree of porosities present in the thin films, indicating that porosity decreases when the number of multilayer increase. The porosities in the multilayers can be produced on the coating by nucleation phenomenons during the growth of the layers generating paths of least resistance for the passage of ion Cl [16-20]. The displacement of Tafel curves to positive potentials according the number of applied layers increase resides in the nature of the multilayer type structures, inasmuch as increasing the number of multilayers increases the number of interfaces between the both monolayers TiCN and TiNbCN. The interfaces are zones, where structural disorders generate a change in crystallographic orientation which act like dispersion points hampering the migration of Cl ion from the surface to the metal substrate and delay the corrosive processes initiation [4]. This entails that the energy required for the ions of the solution to migrate freely from the surface to the interface film / substrate increases with the increase of multilayers, this behavior is reflected in the decrease of the corrosion current density and the corrosion velocity (table 1) [6].

Table 1. Obtained parameters through polarization curves for substrates and [TiCN/TiNbCN]n multilayers subjected to dynamic corrosion.

	Ecorr (V vs Ag/AgCl)	*Icorr (μA/cm^2)*	*Vcorr (μmy)*
90°			
Substrate	-0.538	309.1	436.96
n=1	-0.520	94.21	132.78
n=50	-0.441	64.54	90.38
n=100	-0.468	41.13	58.59
n=150	-0.389	18.41	25.39
n=200	-0.339	9.31	12.94
30°			
Substrate	-0.588	221	251.94
n=1	-0.511	15.2	21.31
n=50	-0.457	12.7	17.21
n=100	-0.423	9.04	12.74
n=150	-0.384	5.17	7.28
n=200	-0.361	4.08	5.66

3.2 Erosion

In the figures 3a and 3b are shown the different dynamic curves of the wear steels AISI 4140 and [TiCN / TiNbCN]n multilayer coatings exposed to wear, in an erosive fluid constituted with hard particles of SiO_2. The severity that presents the wear with respect to the variation of the angle of impact is clearly differentiable, where the normal angle condition represents greater material thickness losses in comparison with the grazing angle. This type of wear is a result of successive impact of abrasive particles on a material surface in an average linear velocity of 13 m/s, it shows a clearly dependence with the impact angle due to energetic conditions which involve the particle impact over the material surface, nevertheless dominant wear micromechanisms in each case are different. The figure 3 shows the loss of mass over time in the substrates due to their low ductility, suffering a great wear when they are exposed to impact angle of 90° in comparison with the 30°. The [TiCN / TiNbCN]n multilayer coatings generate a decrease in the mass loss. The sample with 1 multilayer reduce the mass loss in a 53% for a normal angle and 64% for a grazing angle of (30°) with respect to the substrate without coating, showing the beneficial effect of the application of the films to the AISI 4140 steel. The coating sample with 200 multilayers for the two tested cases (30° and 90°) presented the lowest value of mass loss. This behavior can be attributed to the increase in the number of multilayers provides a improvements of mechanical properties such as hardness and elastic modulus, therefore diminishes the mass loss and improving the wear resistance. Increasing the number of interphases enhacement the capability of the coating to absorb and distribute impact energy generated by the abrasive particles in a better way. [13] [14] [15].



(a) (b)

Figure 3. Mass loss in function of the [TiCN/TiNbCN]n multilayers without a corrosive effect at a) 30° and b)90° in an erosive fluid with hard particles of SiO_2.

The figures 4a and 4b, shown the wear phenomenons associated to repetitive impacts of solid particles after 24 hours of test. Such behavior can be associated with the removal forms of material in each situation, since in the grazing angle is expected processes of micro-cutting and micro-plowing, while in the normal angle the wear is ruled by surface fatigue (figures 4a and 4b). These behaviors can be easily distinguished for substrates due to the AISI 4140 steel exhibit greater volume loss with a wear kinetic that tends to be lineal for the normal angle and a grazing angle condition.

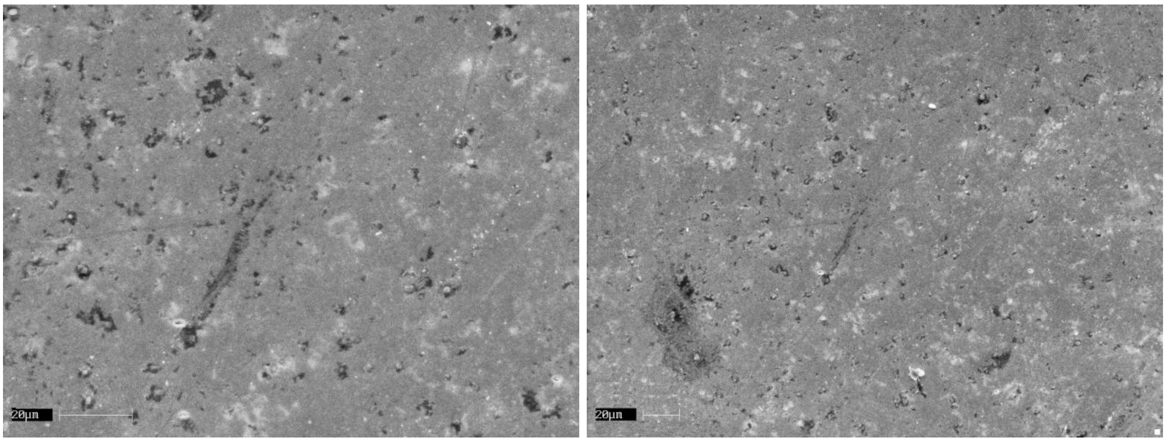
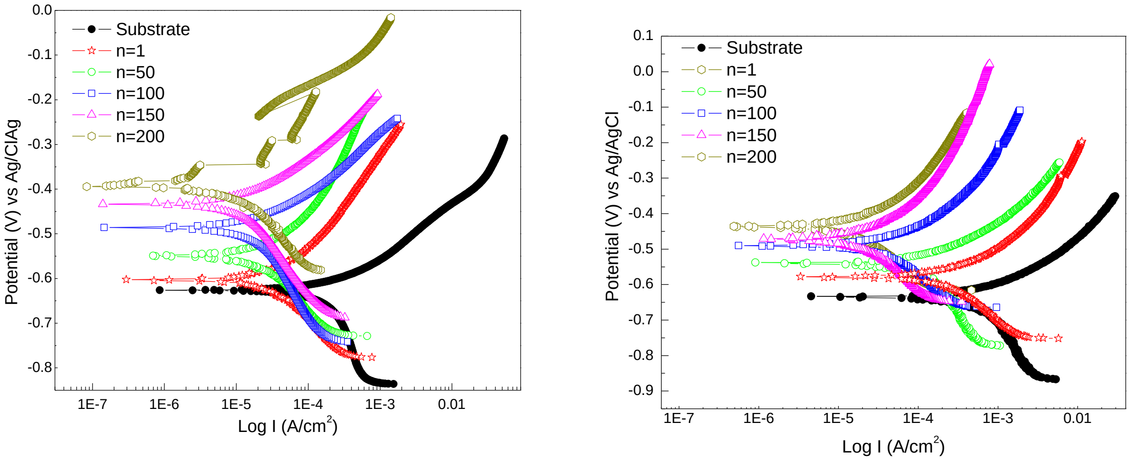


Figure 4. Top view SEM micrographs for samples subjected to erosion without corrosive effect: a) substrate at 90° impact, multilayers with b) n=200 at 90° impact.

3.3 Corrosion erosion

In the figures 5a and 5b are presented the polarization curves of the substrate and the multilayers under both attack angles in a medium with dynamic conditions, adding the particle action. Comparing the corrosion behavior adding the wear by erosion is presented an increase of the activity, especially in the corrosion current density, moreover in a medium with dynamic conditions in particular under abrasive particle action is observed that the modifications of the mechanical conditions of the medium , such as fluid impact and erosive particles in some attack angles lead to a slight change of the corrosion potential, the agitation effect of the medium by the energy dissipation in it; at the same time is noticed an increase of the corrosion current density caused by the particles attack and the generating subsequent of the localized corrosion points and afterwards the generation of a widespread corrosion phenomenons especially in all multilayers, however the difference of the corrosion velocity values should that the reaction kinetic depend of multilayers number, being faster for the 1 bilayer, followed by the 50, 100, 150 and 200 bilayer in decreasing order. In qualitative form is possible group the Tafel polarization curves, being the curves of coating steel with 150 and 200 similar to each other. The [TiCN/TiNbCN]n multilayers show a material dissolution moderately, this behavior is found in all coatings in 120mV vs. Ag/AgCl indicating the regeneration of the products corrosion layers which allow to stabilize the current density around this potential and prevent the increase of the dissolution metal velocity. Starting from 200 mV vs. Ag/AgCl, the processes kinematic is dominated for diffusion which modifies the curves shapes; this characteristic can be appreciated in the entire set of potentiodynamic curves and accords with the effect observed when the current density increases in function of the potential.



(a) (b)

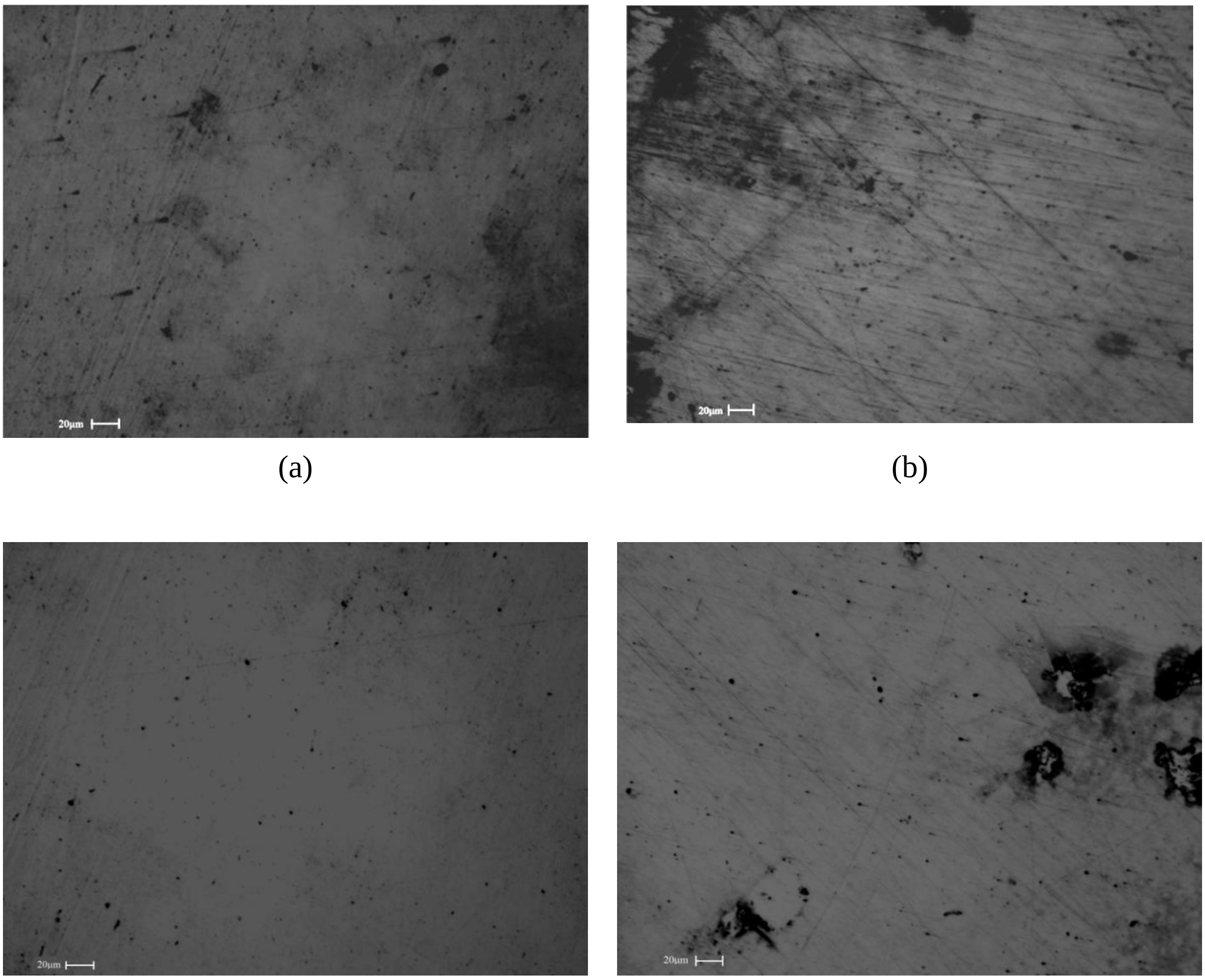
Figure 5. Polarization curves of the substrates and multilayers subjected to a dynamic corrosion erosion in a 0,5 M NaCl solution at a) 30° and b)90° impact angles.

The data in the table 2 indicates effectively, a smaller electrochemical performance in comparison with the dynamic corrosion (figures 2a and 2b and table 1) facing the corrosion erosion, which shows a reduction in corrosion potential and densities relatively acceptable for multilayers with 1 multilayers and even slightly better than the multilayers 50 and 100, and good conditions for the multilayers 150 and 200. All in all, the data (table 1) shows a good behavior of all test coatings in comparison to the base material when is subjected to corrosive phenomenons. However, when it is under to corrosive-erosive flow (table 2) the passive film formed on the surface normally is eliminated and removed by the action of hard particles, leading to the loss of anticorrosive protection. Corrosion in turn, reduces the resistance of these coatings on the surface and promotes an increase in the corrosion rate compared to the dynamic corrosion.

Table 2. Parameters obtained by polarization curves for substrates and [TiCN / TiNbCN] n multilayers under to erosion corrosion.

	Ecorr (V vs Ag/AgCl)	*Icorr ($\mu A/cm^2$)*	*Vcorr (μmy)*
90°			
Substrate	-0.633	706	995.46
n=1	-0.579	374	527.34
n=50	-0.538	186	262.26
n=100	-0.490	51	71.91
n=150	-0.469	26	33.26
n=200	-0.438	17	21.65
30°			
Substrate	-0.627	216	304.56
n=1	-0.602	35.4	49.35
n=50	-0.550	27.10	37.05
n=100	-0.486	20.11	28.2
n=150	-0.431	13.38	19.54
n=200	-0.395	3.04	4.23

The micrographs in figure 6 show the corrosive erosive attack results. These micrographs are taken in the substrate surface and the multilayer with 200 multilayers after the corrosion erosion process at impact angles of 30° and 90°. In the figures 6a and 6b are observed the zones of the substrate which has been deteriorated due to the effect of the dynamic corrosion and the erosion generated by the particles at angles of 30° and 90°. In the figures 6c and 6d are noted the damage at an angle of 30° and 90° respectively. It is visualized how the coating has suffered wear mechanisms by cracking, it is distinguished different zones: 1) evidence of degradation process due to general corrosion shown in polarization curves 2) harmful effect generated by the action of corrosion and cracking of the coating generated by the impact energy of the abrasive particles of silica. Furthermore, grey zones are observed where the protector effect has generated defense mechanisms that produce zones of low cracking. These areas show a surface without fracture whose protection has been provided by the multilayers; it is observed on the 200 multilayers coating surface, focus of located corrosion, which can be associated with the generated respond using anodic polarization curves, where at -135 mV vs. Ag/AgCl is produced attack by pitting.



(a) (b)

(c) (d)

Figure 6. Top view SEM micrograph of samples exposed to corrosion – erosion at two impact angles. Substrate a) 30° and 90° b) [TiCN / TiNbCN] n with n = 200 c)30° and d)90°, in a 0,5 M NaCl solution.

4. CONCLUSIONS

In general, we can affirm that the dominant mechanism is the erosive wear, followed by the synergism, and the electrochemical after. In addition, it was observed that the electrochemical component is benefited by dynamic changes of the medium and even more by the impact action over the surface thus leads or not to the hardening of it, because the impact removes or deforms external layers of the material, increasing the superficial area exposed and the reaction capability with the surrounding medium, also the agitation promotes the limit layer diminution of the electrolyte on the material surface which conducive a dominant mechanism of overpressure by oxygen diffusion and ionic species onto the material surface. According to this dinamica of ideas, in a marine environment the erosive condition contributes the greatest electrochemist wear of the material. In the corrosion erosion synergy mechanism was evident the simultaneity in processes: mechanical material removal (substrate and multilayer) via erosion and electrochemical corrosion process.

The corrosion erosion magnitude indicates that the wear mechanisms performance is related implicitly with the aggressiveness or the medium effect on the material, owing that in the NaCl medium the values are positives to this parameter. Making a detailed analyze of the mechanisms performance in a marine environment was observed that the material with the greatest synergetic effect is the carbon steel in a normal angle condition, while the multilayers present decreased values in function with the multilayes growth. This effect should be basically to the chloride ion action, in as much as the polarization generated on the system promotes localized corrosion phenomenons that advance to the depth of material without expanding the affected areas, which is work of the mechanical removal by impact and at normal angle the generated ridges by chopping are flattened, decreasing the amount of electrolyte contained therein. This result indicates that the wear micromechanisms are the responsible of the presence and advance of localized corrosion and benefit a greater removal of the external layers of the multilayers.

ACKNOWLEDGEMENTS
The authors wish to thank the Universidad Militar Nueva Granada for financially supporting this work.

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