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Short Communication

Improving the Erosion Corrosion Resistance Cavitation of Coatings TiN on Aluminum Exposed to Mixtures Bioetanol

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In the present work is determined, the increase in erosive wear resistance to cavitation, TiN coatings obtained by physical vapour deposition (PVD) on aluminium (99% commercially pure). The wear tests were performed by vibratory cavitation in bioethanol-gasoline mixtures with concentrations of 5% to 30%, in order to study the evolution of erosive wear by cavitation. The characterization after deterioration test was performed by scanning electron microscopy for the different testing times. Because of the cavitation test, the mass loss was determined and, sequential study of the surface appearance of the samples was done to determine the wear mechanisms prevailing in each stage. The results were analysed by atomic force microscopy characterization and scanning electron microscopy of previous form. From the results, it is seen that the highest rate of wear Corresponding to bare aluminium, and with Respect to the further degradation obtained mixture with a high concentration.

Keywords: TiN monolayers, erosion, corrosion, cavitation, bioethanol.

1. INTRODUCTION

Cavitation is caused by the formation of steam bubbles because of the pressure drop associated with a high flow velocity or vibration, which collapse quickly upon the material, creating on them shock waves, this, is caused by erosion [1-2]. Damaged metal parts apart from presenting erosion damage, wear corrosion present, which can be confused with damage caused by the occurrence of vibrations [3-4]. Cavitation corrosion is resulting from the interaction of mechanical and chemical phenomena, leading to accelerated material removal due to the synergy of the two mechanisms are presented together [5]. In the trial of oscillating cavitation energy that causes the formation of holes, formed by steps of pressure pulses in the high frequencies is generated inside the fluid [6]. These pressure pulses are formed by a submergible surface, which vibrates, creating pressure waves in the liquid. Cavitation in fluids generated under special conditions of flow, affects the efficiency of hydraulic systems and produce undesirable problems such as increased noise, vibration and erosion [7].

Currently the new materials have become attractive for many applications in industry. Within these new materials we find hard coatings, these have been developed in order to increase the shelf life of some industrial elements, minimizing production time, cost and maintenance outages. Among the preferred methods, for producing such coatings is physical vapour deposition (PVD), where the material to form the coating is evaporated and subsequently condensed in the form of a layer on the substrate [8]. Wear and corrosion are problems that some useful elements in fluid transport industry, as parts of pumps, in some cases, these fluids are confronted debris that also contain particulate matter, which may be causing two phenomena such as corrosion and erosion, which combined can cause major damage to exposed parts, left here the goal of this article is to present the national scene in the preparation and characterization of hard coatings [9-10].

Hard coatings are applied to various industrial sectors such as automotive, aerospace, fluid transport, mining and the oil industry [11]. By application of hard coatings, to useful products defects may increase hardness, lower coefficient of friction, increase resistance to wear and fatigue, so that an increase in the lifetime of the part is achieved that can mean an increase in the production of a company [12]. Economic losses caused by the phenomenon of corrosion is usually the big problem that some types of businesses face, so what is sought with the use of hard coatings in addition to providing the above properties, is applying them to minimize costs low-value materials that can be used in replacement of others who may have high corrosion resistance but they are usually very expensive [13].

Bioethanol has certain attributes that put it at an advantage compared to fossil; some of these are sulphur-free fuel, aromatic, and non-toxic, biodegradable. Its use greatly reduces the exhaust gas also acts as a fuel additive. The good performance of a gasoline engine with the use of this fuel type depends on its intrinsic properties and product quality [14-16].

Cavitation erosion is due to the damage caused by fatigue processes that form on the surface of the material. The effect of cavitation can result in accelerated phase that existing thin film on the metal, if this mechanism is generated; the rate resulting from the loss of material is called cavitation erosion – corrosion [7]. The surface properties of the material play a significant role in the nature of the interaction with the protective layer; the most important are the passivity of the metal surface, the adhesion of the corrosion product, the metallurgical state of the metal, and the importance of diffusion of dissolved oxygen, the presence of aggressive ions and intensity of cavitation [9]. These factors determine the mode of corrosion and loss rate of erosion – corrosion [10].

This article aims to demonstrate the increase in the lifetime of aluminium alloy after subjecting it to a coating with monolayers of titanium nitride, to determine their protection were exposed to chemical and mechanical wear together in medium electrolyte mixtures of bioethanol.

2. EXPERIMENTAL DEVELOPMENT

Sample Preparation

To determine degradation, samples of aluminum were prepared with an area of 25cm^2, degreasing commercial reference solution SC-66 at a concentration of 20 g/ l was carried out for a time of 10 minutes at a temperature of 46 ± 2 ° C the approximate composition of the alloys are shown in Table 1.

Table 1. Composition of the aluminium alloy used as substrate

Element	Al	Fe	Si	Cu	Ti	Mn	V	Mg	Zn	Ni	Pb	Co	Cr	Sr
%	98.9	0.84	0.142	0.029	0.026	0.011	0.0078	0.0050	0.050	0.002	0.002	0.002	0.001	0.0001

The monolayers of titanium nitride, is deposited on aluminium substrates (Table 1), which were degreased ultrasonically for 15 minutes a stream of ethanol and acetone. The coatings were obtained by the technique of multi-target rf magnetron sputtering (13.56 MHz). For the deposition of white coatings 4 Ti inch diameter were used with a purity of 99.9%.

The base pressure of the inside of the vacuum chamber was 7.0 x10-6 mbar. Before starting the deposition the substrates were subjected to a plasma cleaning for 20 minutes under Ar to a bias of-350V on rf During growth, the working gas was a mixture of Ar (93%) and N2 (7%) with a total pressure of 6x10-3 mbar at a substrate temperature of 400 ° C and an rf substrate bias 0V and a power of 350W.

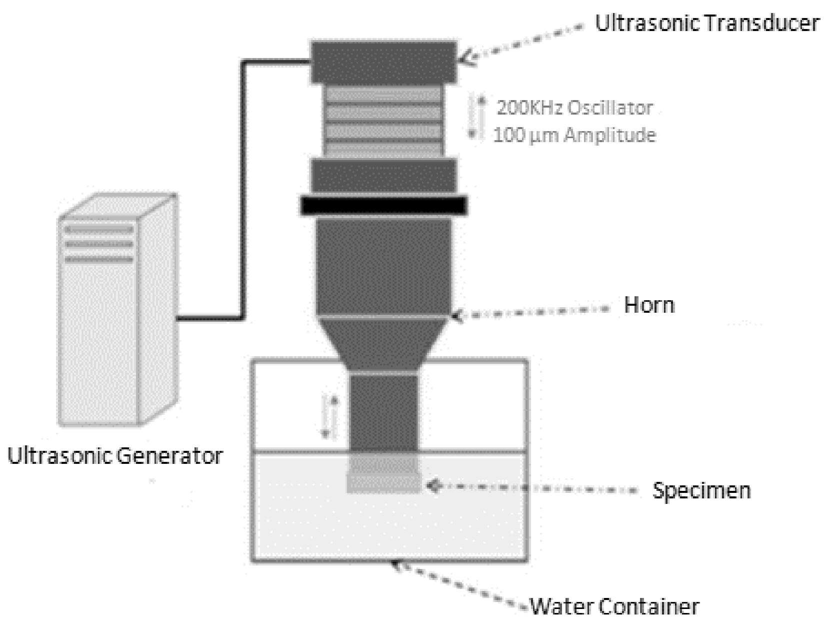


Figure 1. Device for carrying out the tests of cavitation erosion, corrosion, of the coatings subjected to different blends of bioethanol.

The estimation of the damage, which can occur due to the cavitation in a corrosive fluid, was performed using equipment comprising an ultrasonic oscillator consisting an ultrasonic transducer, which oscillates at 20 kHz with an amplitude of 100µm, and a sonotrode, and is shown in Fig. 1. The device configuration is performed taking into account the guidelines indicating the ASTM G32-03 standard. The test method was indirectly, which provides the location of the sample to 0.5 mm from the tip of the oscillator. Oscillator team has adapted the reference electrode - ER (Ag / AgCl), the counter-EA (platinum wire) and the specimen-ET with a display area of the sample of 1 cm^2, the electrodes are immersed in a ethanol-gasoline comprises at concentrations of 5% to 30% and connected to a potentiostat solution - Gamry galvanostat model PCI-4 using the techniques of electrochemical impedance spectroscopy and Tafel polarization curves. Diagrams for Tafel polarization curves were obtained at a scan rate of 0.125 mV/s in a voltage range of −250 to 250 mVAg/AgCl; this voltage range was defined with respect to the open circuit potential (OCP). To determine the weight loss due to erosion by cavitation, the samples were subjected to wear due to cavitation erosion corrosion - for a total exposure time of 480 minutes at 23 ° C, the samples were removed from the solution at time intervals of 30 minutes, cleaned with a jet of water, dried with hot air and weighed on a precision balance (0.1 mg). Degradation phenomena were observed with an electron microscope (SEM), the surface characteristics were determined with JEOL SEM NeoScope JCM-5000 equipped with an electron optics with magnification range from 50 to 40.000 X and microscope and atomic force microscopy (AFM), the surface morphology was recorded by AFM using a nanosurf easy scan 2.

3. RESULTS

3.1 Surface Analysis.

Fig 2 present the morphology of the layer of single-layer coating of titanium nitride deposited on the aluminium plate before a process of corrosion cavitation process, the surfaces were observed by scanning electron microscopy, a uniform layer is obtained with low imperfections (pores or microcracks), performing spectroscopy analysis by X-ray energy, the compositional analysis is obtained which allowed a semi quantitative determination of the atomic concentration of the films obtained values of Ti and 42.8% to 54.2 % of N in the TiN layer, the oxygen concentration was 3% [17].

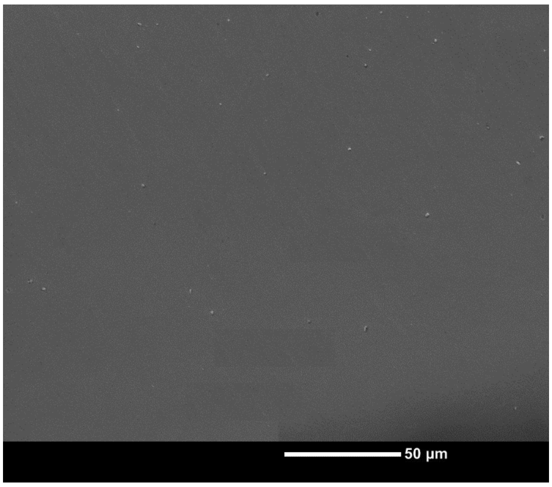


Figure 2. Surface micrograph of the titanium nitride coating deposited on the aluminium alloy.

Fig 3, shown the surface morphology of the thin film of TiN, made by the technique of atomic force microscopy (AFM) technique was used in the non-contact method, the area analysed for both samples was 2.5 µm x 2.5 µm, from these AFM images were extracted values of grain size and roughness using statistical analysis software (SPIP ®) for these coatings the values of grain size of about 67 ± 2 nm was found, respectively, for furthermore, the values of roughness measurements yielded values of 5.4 ± 0.3 nm from these results we can infer that the surface has a regular appearance and show low values of surface roughness, this is due to the amount of nitrogen found in the stoichiometry of the coating, allowing an improvement in the mechanical properties by increasing the hardness of the coating, which increases the lifetime against cavitation corrosion [18].

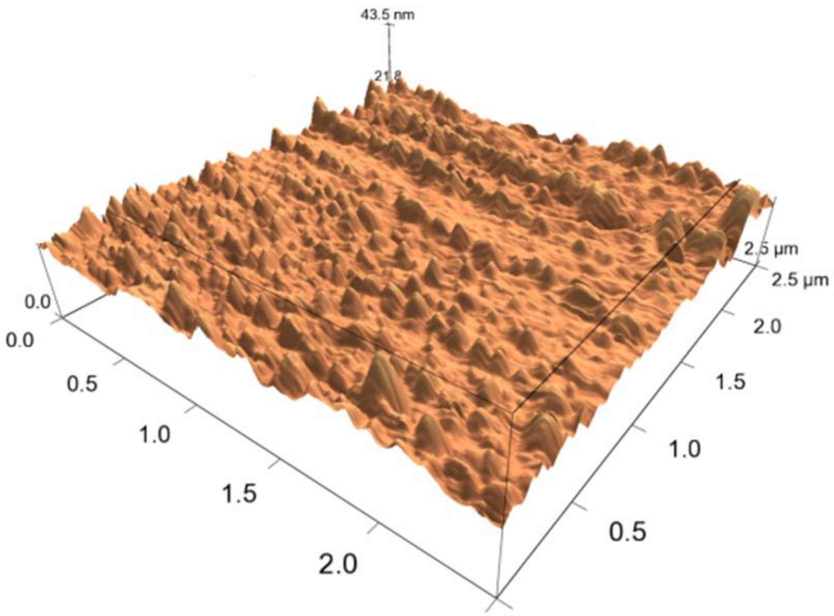


Figure 3. Image of atomic force microscopy of single-layer coating of titanium nitride.

3.2 Electrochemical evaluation

Fig. 4 Nyquist diagrams is observed where samples of coated aluminium are exposed to 480 minutes to the combined cavitation corrosion, the variation of the mixtures used as electrolyte was made as a percentage of volume, ie that for 5% to 95% of gasoline is used 5% ethanol which is produced by yeast fermentation of the sugars contained in the juices extracted from sugar cane, for 10% to 90% gasoline 10% ethanol, for 20% to 80% of gasoline and 20% ethanol and 30% with 70% gasoline and 30% ethanol. To simulate what is happening at the interface of the coating in contact with fuel mixtures obtained with the various blends the circuit corresponding to Figure 5, which indicates that the double layer capacitance is in parallel with the used impedance due to ion transfer reaction, then shows that there is a second interface that corresponds to the interface between the coating and the aluminium. The resistance value of the solution is decreased according to the increase in percentage of mixture of ethanol, this is due to the lower calorific value to be found in mixtures of 10 to 30%, which generate a decrease in the conductivity of the values of polarization resistance and observed that decrease as the mixing ratio is increased. The values of the polarization resistance, encountered with impedance spectroscopy diagrams were used to investigate the corrosion generated by the polarization curves. The values of | Z | shows that the thin films generate impedance module of the same order of magnitude for different percentages of mixtures, with the exception of the mixture with 30%, which showed a | Z | value of an order of magnitude less. This suggests that the conductivity of the medium increased probably due to the presence of degradation products and the effect of erosion caused by cavitation.

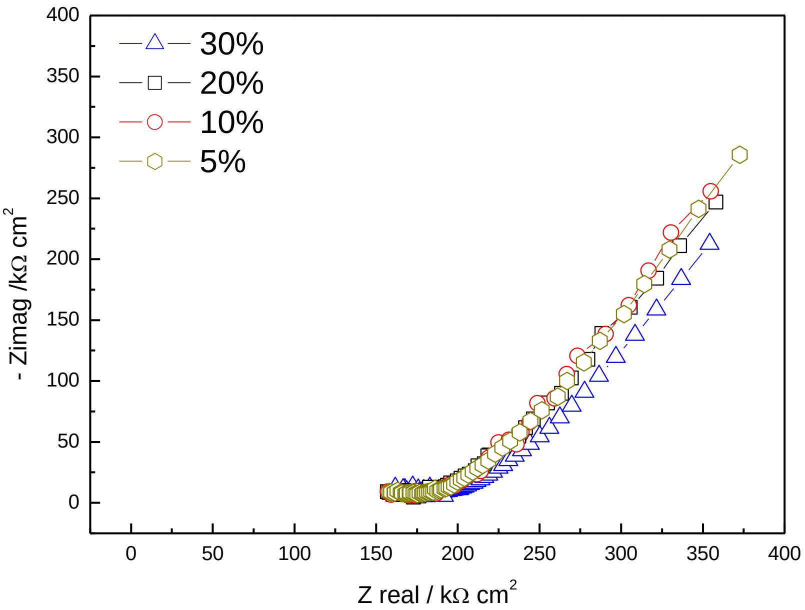


Figure 4. Nyquist diagram of TiN coatings deposited on aluminium and evaluated by varying the concentration of ethanol from 5 to 30%.

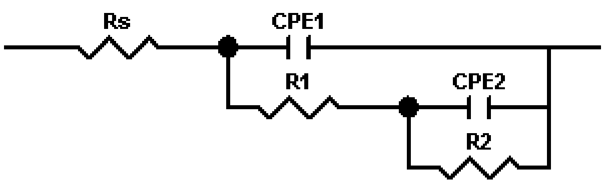
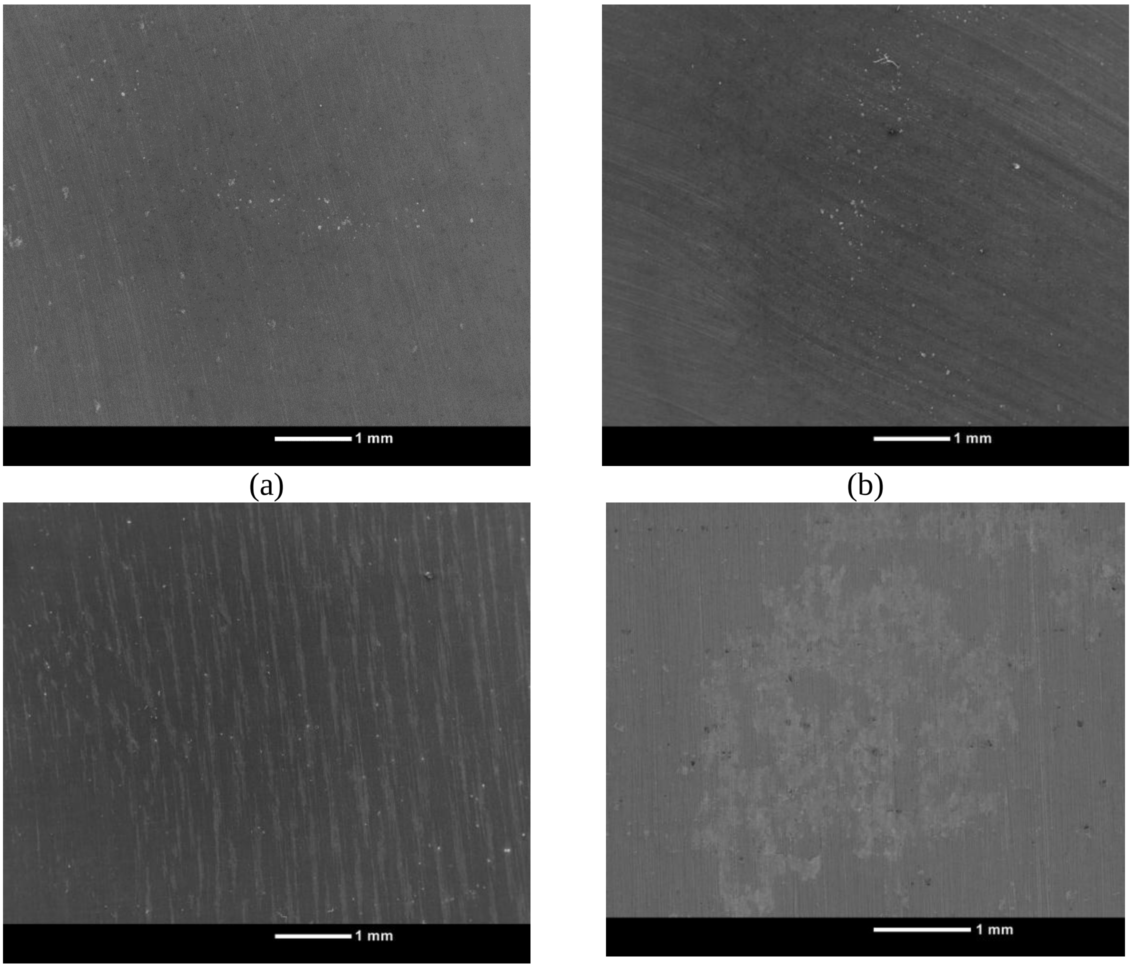


Figure 5. Circuit to fit the impedance data of the coatings with the changes of the solutions.

Impedance spectra indicate that the effect of cavitation erosion and corrosion was evident on the surfaces tested, however it is obtained that the corrosion rate increases as the content of the mixture is increased. After an inspection, oxides and mechanical degradation are observed, due to the erosive effect is generated on the surface; the degree of oxidation of the surface was also increased slightly as the ethanol content increases. The surface oxidation was caused by a reaction between the oxide layer and the fuel mixture. The fuel mixture causes more surface corrosion as expected, since the effect of erosion on each of the surfaces (Fig. 6) is evident. By observing the surface of the coated aluminium and exposed to the mixture of aggressive fuel was observed that corrosion only affected the surface and appeared to be uniform, the other type of wear observed is mechanical which generates a gradual loss coating occurred in the 480 minutes of assessment. What is evident in each of the micrographs of Figure 6 is that the surface layer produces a surface layer that aims to increase its resistance to abrasion, friction, impact and corrosion.

Nyquist plots, which were taken for the different fuel blends in contact with the coatings of titanium nitride generated a modulus of the impedance (| Z |) of the monolayer in contact with the electrolyte of 5% at low frequencies has a value of about two orders higher than that of the coating in contact with the biodiesel to 30% magnitude, it indicates that the polarization resistance of these coatings was increased after the aforementioned mixing ratio of ethanol and a smaller percentage thus the increased corrosion resistance [19]. On the other hand it is observed that the period of monolayers influences the impedance module, for varying this, it also does so, but not in direct connection; low frequency | Z | [20].



(a) (b)

(c) (d)

Figure 6. Micrographs of the thin films after test them against cavitation corrosion. a) TiN in contact with a mixture of 5% of ethanol, b) 10%, c) 20% and d) 30%.

In the micrographs of Figure 6, the surface characteristics of the monolayers with the mixture ratio variation are observed. After the process of cavitation erosion corrosion. In Figures 6b, 6c and 6d of the single-layer coating has been deteriorated due to the erosive effect, the interactions of the particles and generate wear track grooves on the surface are observed. This has generated parallel grooves in the direction of motion, similar to a sanding. In Figure 6d. A central area, characterized by the action of the corrosion and cracking of the coating generated by the impact energy of the bubbles that have impacted the surface differs. In addition, seen in Figure 6a, a homogeneous protection zone generated defence mechanisms under cracking zones and high dissolution; these areas show a fracture free surface representing the protective action afforded by the process of reducing the percentage of mixture of bioethanol.

Fig 7 are observed Tafel polarization curves; in which can be calculated the corrosion rates which show that protection made by the thin film that is appropriate since the values of corrosion densities were not significant in all cases. The corrosion rates are higher for the system subject to the 30% bioethanol, which has a value of 0.404 mils per year, corresponding to excellent corrosion resistance typical on for these types of coatings (table 2). For the case of monolayers exposed to percentages from 5 to 20%, a good performance as shown observe widespread displacement towards lower corrosion current densities, indicating less susceptibility to corrosion in the solution mixture analysed. This can be attributed to the degree of porosity present in the coatings produced by sputtering at high bias voltages.

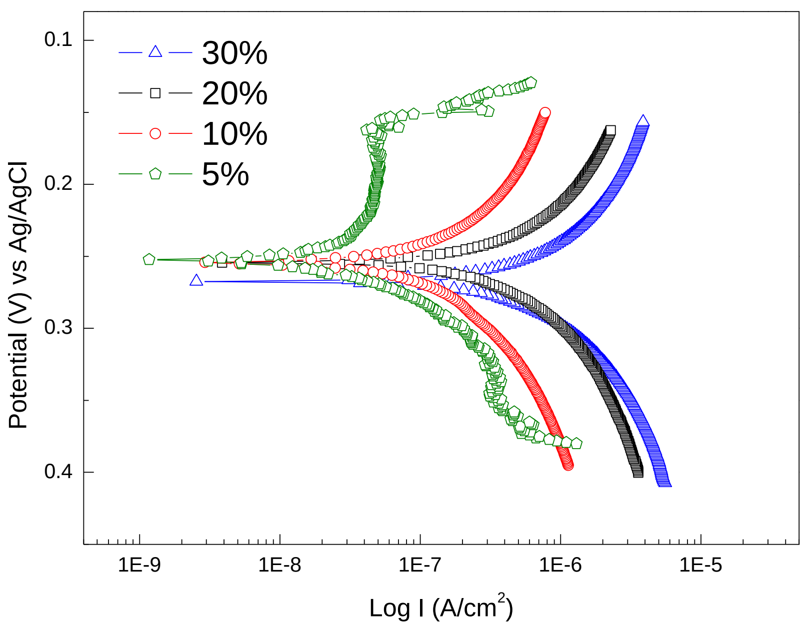


Figure 7. Potentiodynamic curves corresponding to the monolayer coatings undergo corrosion cavitation tests, varying the ethanol content.

With respect to the corrosion potential toward areas of increased cathodic region (protection) is appreciated, the noble value of the potential are presented for coatings with lower content of bioethanol. This is because it is only a partial corrosion. Due to increased acidity, since the dehydrated ethanol generates moisture absorption when in contact with the environment, bioethanol has in its composition, a rate close to 0.5% water; this is because of distillation process. The density of corrosion current (Table 2), is the parameter that was more variation in function of the content of the mixture, this is because that increasing the ethanol content in the mixture gas causes an increase in impurity content chlorides, generating an increase in the corrosion rate. Another variable that increases the corrosion current density is the high water content (0.5%), as recommended limits are around 0.2%, this percentage promotes dissolution of the passive film, thereby increasing the kinetics of corrosion, as can decrease the value of the surface hardness of the coating resulting in losses of mechanical properties, which leads to increasing the cavitation corrosion.

Table 2. Parameters calculated by Tafel polarization technique, wherein a parameter variation is obtained after the evaluation of corrosion assisted cavitation.

Parameter	30%	20%	10%	5%
β_a (mV/decade)	3947	806.1	219.3	1.081
β_c (mV/decade)	939.9	758.1	117.9	12.9
i_{corr} ($\mu A/cm^2$)	0.771	0.236	0.104	0.032
Ecorr (mV)	269	252	252	252
Corrosion velocity (mpy)	0.404	0.123	0.0545	0.0167

In all cases, the polarization curves generate uniform corrosion behaviour, in which the anode region describes the tendency to maintain the current flow as the potential increases. The values of the polarization resistance, calculated using EIS, vary in relation to different values of corrosion current. The corrosion rate is calculated using the current values of corrosion due to the direct relationship between these two quantities, so that the values of the polarization resistance are inversely proportional to the values of the corrosion rate. The results show that the current density has great influence on the corrosion rate due to the high current density to obtain coatings with fine grain size and very low porosity. The values of current density and show corrosion rate of titanium nitride coating a passivating oxide layer. However, the passive film is unstable as deduced from anodic polarization curves in part upon dilution to attain H_2O decomposition zone.

4. CONCLUSIONS

Metallic materials such as aluminium exposed to the mixture of ethanol and gasoline creates problems of degradation; however the monolayer coating of titanium nitride is generated as an alternative coating of parts subjected to contact such mixtures; this because the titanium nitride film increases the mechanical properties of the material because it increases the hardness of the coating.

Mixtures of ethanol decrease the resistance of TiN coatings, due to the decreasing values of the polarization resistance. Thin films generated conductivity increases due to the presence of degradation products and the effect of erosion caused by cavitation; for the case of monolayers exposed to different percentages indicating less susceptibility to corrosion. Impedance spectra indicate that the effect of cavitation erosion and corrosion, on the surfaces evidenced evaluated and a faster corrosion is obtained as the content of the mixture is increased. Impedance spectra indicate that the effect of cavitation erosion and corrosion, on the surfaces evidenced evaluated and a faster corrosion is obtained as the content of the mixture is increased.

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