

Corrosion resistance of a carbon-steel surface modified by three-dimensional ion implantation and electric arc.

E.D. Valbuena-Niño^{*1}, L. Gil², L. Hernández² and F. Sanabria¹

¹ Foundation of Researchers in Science and Technology of Materials, Colombia

² Universidad Nacional Experimental Politécnica, Puerto Ordaz, Venezuela

(Received December 13, 2019, Revised February 12, 2020, Accepted February 28, 2020)

Abstract. The hybrid method of three-dimensional ion implantation and electric arc is presented as a novel plasma-ion technique that allows by means of high voltage pulsed and electric arc discharges, the bombardment of non-metallic and metallic ions then implanting upon the surface of a solid surface, especially out of metallic nature. In this study AISI/SAE 4140 samples, a tool type steel broadly used in the industry due to its acceptable physicochemical properties, were metallographically prepared then surface modified by implanting titanium and simultaneously titanium and nitrogen particles during 5 min and 10 min. The effect of the ion implantation technique over the substrate surface was analysed by characterization and electrochemical techniques. From the results, the formation of Ti micro-droplets upon the surface after the implantation treatment were observed by micrographs obtained by scanning electron microscopy. The presence of doping particles on the implanted substrates were detected by elemental analysis. The linear polarization resistance, potentiodynamic polarization and total porosity analysis demonstrated that the samples whose implantation treatment with Ti ions for 10 min, offer a better protection against the corrosion compared with non-implanted substrates and implanted at the different conditions in this study.

Keywords: carbon steel; corrosion; physicochemical properties; plasma technology; polarization resistance; surface treatment

1. Introduction

AISI/SAE 4140 low content carbon steel also contains chromium, molybdenum, and manganese as the main alloying elements. Such an atomic distribution allows it to achieve a relatively high resistance to fatigue, abrasion, impact and torsion, and with an appropriate heat treatment; can reach a high hardness. Additionally, the chromium content provides good penetration resistance, and molybdenum offers high hardness and uniform wear resistance. Because of the previously mentioned properties, AISI/SAE 4140 steel is broadly used in the manufacture of components for automotive, construction, energy, among others industrial sectors (Valbuena-Niño *et al.* 2016, Agüero 2007 and Soares *et al.* 2017).

It is well known that the most common problems that cause the damage of tools and industrial parts, affecting operations, safety, maintenance and therefore costs; are corrosion and wear. For this reason, finding alternatives that increase the performance of surfaces expose to physical and

*Corresponding author, Ph.D., E-mail: deydannv@gmail.com

chemical attack has been a developing subject of interest within the surface science and engineering for materials protection. Enhancing corrosion resistance and wear by modification of the microstructure and surface composition by mechanical, physical or chemical methods; can imply a significant contribution that drives to energy saving by achieving higher efficiency and yield of industrial processes (Winnicki *et al.* 2016, Jothi and Palanivelu 2016).

The surface modification generated by a hybrid of a high voltage pulsed and an electric arc discharges at low pressures, consists in accelerating a flow of metallic and/or non-metallic ions onto the surface of a solid material, where depending on the applied voltage magnitude, the ions are deposited or embedded in the crystalline lattice causing a series of physical interactions that affect the physical and chemical properties of the surface (Mussada and Patowari 2015, 2017, Valbuena-Niño 2012).

This research proposes an evaluation of implanted AISI SAE 4140 steel substrates with metallic (titanium) and non-metallic (nitrogen) species, against the corrosion by electrochemical techniques. Polarization resistance and potentiodynamic polarization allows contrasting the effect of treatment time on the corrosion resistance in implanted samples. Additionally, the changes occurred on the surface structure and composition of the implanted substrates, are identified by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) characterisation techniques. Experiments with a non-implanted reference substrates were also performed for comparison purposes.

2. Experimental methods

The experimental methodology in this work was sequentially developed as follows: Substrates preparation, definition of study conditions, ion implantation treatment and physicochemical and electrochemical characterization.

2.1 Substrates preparation

Disk shape AISI/SAE 4140 steel coupons whose dimensions, 18mm in diameter and 3mm thick, were implemented. Prior the implantation treatment, the surfaces to be expose were ground with silicon carbide abrasive paper from 60 to 600 grit according with ASTM E3-11 Standard (2017), then polished with alumina suspension of 1 μm , 0.3 μm , and 0.05 μm , and subsequently were cleaned in an ultrasonic bath immerse in an ethanol solution for 30min as described by ASTM G1-03 Standard (2017).

2.2 Surface treatment

The surface modification of AISI/SAE 4140 steel samples was carried out in the JUPITER (Joint Universal Plasma and Ion TEchnologies Reactor), by exposing the coupons to Ti and Ti+N atmospheres and activating a hybrid high voltage pulsed (HVP) and an electric arc discharges at low pressure (Khvesyuk and Tsygankov 1997, Dulce-Moreno 2015, Dugar-Zhabon *et al.* 2012). The ion implantation treatment on the substrates were carried out during 5 and 10 min. The discharge parameters such as energy applied, pulse duration and frequency were established at 10 keV, 0.25 ms and 30 Hz respectively. The pulverization of the titanium cathode was performed with an arc current of 140 A at a polarization potential of 19 V. The pressure during the Ti and Ti+N treatment process were maintained at approximately 0.25 Pa and 1.00 Pa respectively. The

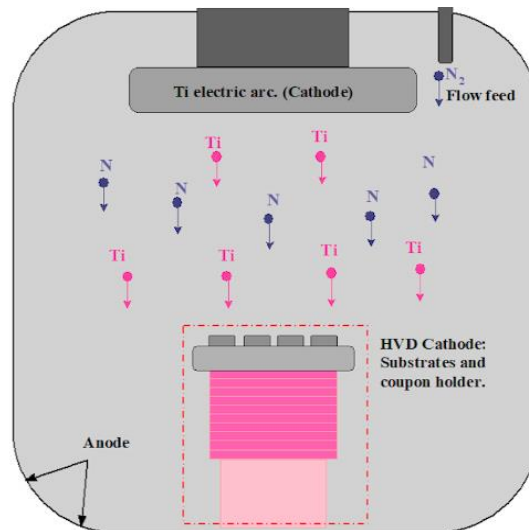


Fig. 1 Scheme of the substrates distributed in JUPITER

substrates, before the implantation treatment, were subjected to a sputtering process (generated with a 5 keV pulsed electric discharge) in an argon atmosphere (Ar) for 15 minutes. Fig. 1 shows the distribution of the arc electric system, whose cathode of Ti (at. 99.96%) was implemented; a piezoelectric valve where the working gas (Nitrogen 99.99% purity) is fed into the chamber and the location of the coupons (upon the HVP discharge cathode) inside JUPITER reactor. It is noteworthy that the walls of the chamber will act as an anode during the ion implantation process. (Dugar-Zhabon *et al.* 2002).

2.3 Surface topography

Characterization of the surface morphology of the implanted and non-implanted AISI/SAE 4140 specimens, were analysed by scanning electron microscopy (SEM). The surface topography analysis was carried out by the scanning electron microscope FEI, model QUANTA FEG 650 environmental (ESEM). Likewise, to obtain the chemical composition and also verify the presence of doping particles on the substrate surfaces, an x-ray energy dispersive spectroscopy (EDS) test was performed together with optical emission spectroscopy technique by using a Bruker reference spectrometer Q4 TASMAN.

2.4 Corrosion resistance

The corrosion resistance tests were performed with a Gamry Interface 1000 potentiostat/galvanostat, a standard cell composed of pH and temperature sensors, a nitrogen bubbler and three electrodes. A calomel electrode as a reference, a graphite counter electrode (auxiliary) and implanted and non-implanted AISI/SAE 4140 steel substrates as a working electrode were prepared. A 3% NaCl solution was used as the electrolyte, and the open circuit corrosion potential (E_{corr}) was adjusted for one hour (1h) (ASTM G3 Standard 2014). The corrosion rate (V_{corr}) was obtained by the polarization resistance technique (R_p), with the scanning of a ± 20 mV potential at a scan rate of 0.1mV/s, around the corrosion potential (E_{corr}).

The anodic and cathodic slopes were acquired from potentiodynamic polarization with potential sweep speed of 0.1 mV/s and potential range from -0.250 V to 1.6 V with subsequent Tafel extrapolation at ± 250 mV around corrosion potential (ASTM G5 Standard 014)

3. Results and discussions

The results obtained from the characterizations and electrochemistry test were carried out with the purpose of evaluating the effect of ion implantation on ferrous alloys, identify changes on the AISI/SAE 4140 steel surface and its performance against the corrosion.

3.1 Microstructure and composition of the material

Micrographs of an AISI/SAE 4140 steel surface were obtained from optical microscopy and shown in Fig. 2. The metallographic analysis identified the formation of needle-type martensite (grey phase) and ferrite (white phase) on the surface structure. The presence of such phases are evidence of a quenching and tempering heat treatment during the manufacturing process of the material.

The elemental atomic absorption analysis by arc spark allowed to obtain a percentage composition of the constituent elements of the non-implanted and implanted substrates with Ti and N ions. The results obtained in the Table 1 indicate that the samples correspond to alloy steel whose chemical composition is similar to the values reported by ASTM A322 (2013). It is evident that the implanted surfaces present an increase in the concentration of titanium and nitrogen compared with the reference sample. Additionally, a direct correlation between the time of treatment, the type of species or treatment and the composition of doping particles was identified.

3.2 Surface modification.

The superficial modification of AISI/SAE 4140 steel substrates were performing with Ti, and N ions, where the surface modified with Ti exhibits a silver-coloured metallic shine, characteristic of titanium while that treated with Ti+N ions present a golden metallic shine, indicating the precipitation of titanium nitrides into the surface (see Fig. 3).

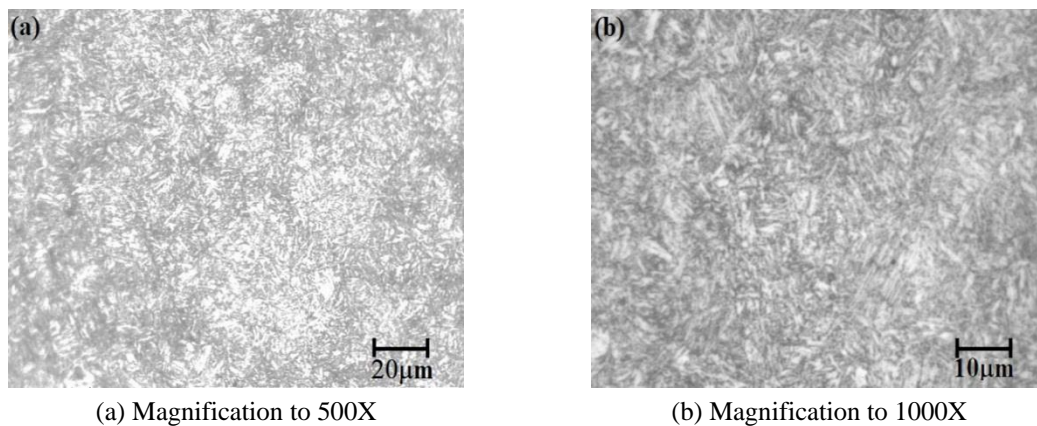


Fig. 2 Surface of a AISISAE 4140 steel revealed with 2% nital

Table 1 Elemental chemical composition of implanted and non-implanted substrates

Element	AISI/SAE 4140	Ti (5 min)	Ti (10 min)	Ti+N (5 min)	Ti+N (10 min)
C	0.452	0.451	0.435	0.456	0.442
Cr	0.963	0.935	0.889	0.922	0.909
Mo	0.193	0.196	0.199	0.201	0.213
Mn	0.687	0.667	0.639	0.650	0.605
Si	0.293	0.319	0.542	0.317	0.928
Cu	0.080	0.079	0.077	0.076	0.067
Bi	0.048	0.056	0.070	0.051	0.073
Ta	0.064	0.058	0.031	0.044	0.030
V	0.0097	0.019	0.055	0.019	0.100
W	0.021	0.014	0.010	0.010	0.012
S	0.150	0.150	0.150	0.150	0.150
P	0.016	0.017	0.017	0.016	0.016
N	0.025	0.040	0.156	0.482	0.981
Ti	0.0026	0.832	2.120	1.004	1.035
Fe	96.90	96.06	94.50	95.95	95.23



Fig. 3 Ion implantation: Post-treatment substrates

3.3 Surface analysis

The photomicrographs and spectra obtained by SEM and EDS illustrate the substrates surface modified with Ti and N ions. The comparison between a non-implanted sample and Ti and Ti+N implanted coupons are presented in Figs. 4, 5 and 6 respectively.

Fig. 4(a) shows the surface of the reference substrate (non-modified), where some irregularities and small pitting are observed due to the surface sensitivity achieved by the decrease of the surface area generated in the metallographic preparation. From the composition spectrum acquired by EDS, the presence of the elements on the untreated surface, are shown in Fig. 4(b). As expected, a high content (atomic percentage) of iron (88.77%) and the concentration values of other alloy elements

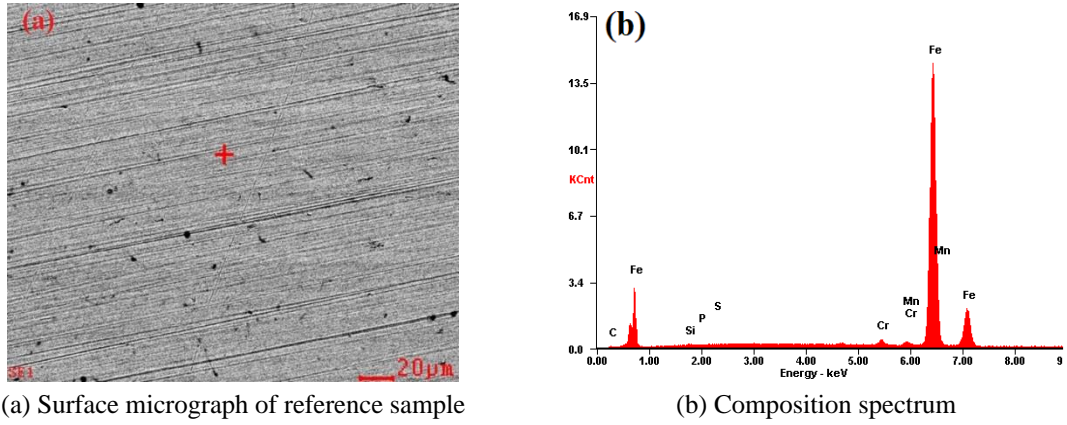


Fig. 4 Photomicrograph and spectrum of AISI SAE 4140 surface obtained by EDS

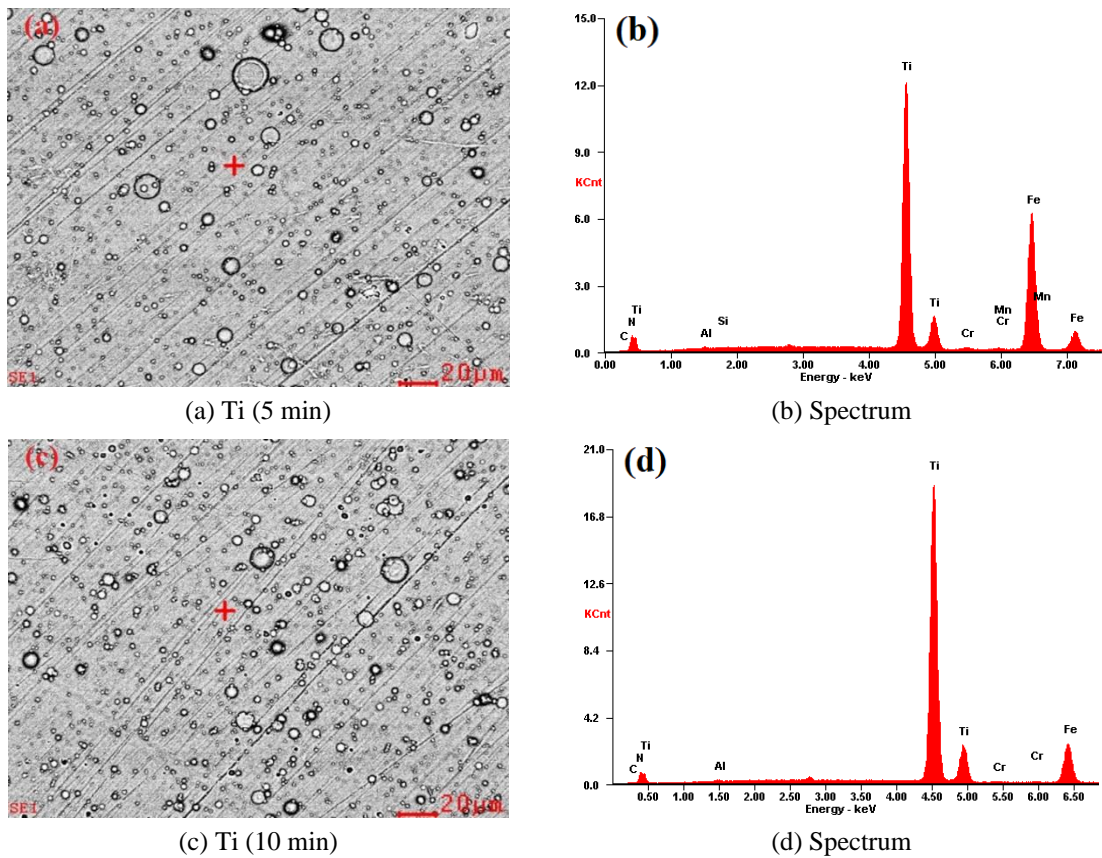


Fig. 5 SEM images and EDS Spectrums upon the implanted substrates

such as C (5.21%), Cr (1.41%), Mn (1.24%), Si (1.62%), S (0.93%) and P (0.82%) are in agreement with those present in an AISI/SAE 4140 steel.

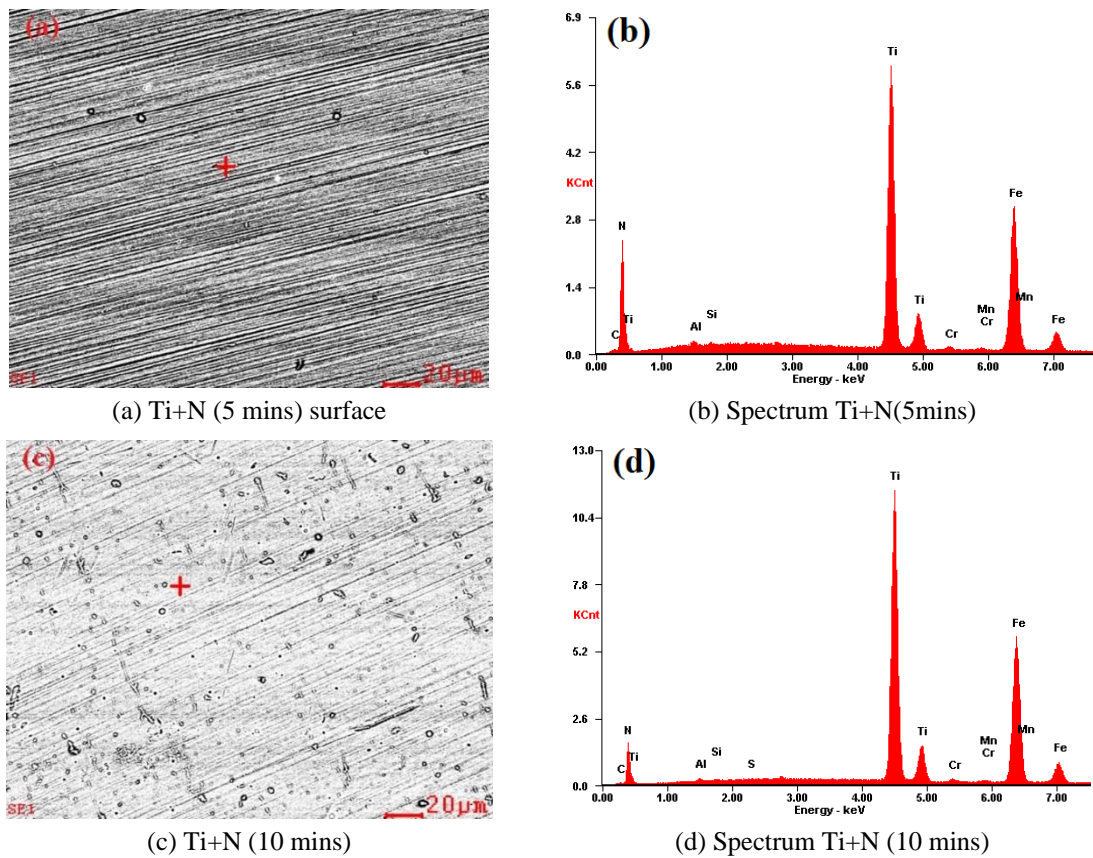


Fig. 6 SEM images and EDS Spectrums upon the implanted substrates

From the photomicrographs of the surface of AISI/SAE 4140 steel modified with Ti (5 min) and Ti (10 min) (Figs. 5(a) and 5(c) respectively) can be seen deformations (multiple micro-drops) that appears due to the solidification of the evaporated material and the non-ionized Ti species (clusters formed during the evaporation of the Ti cathode). This physical process could be attributed to the operation conditions of the cathodic arc system implemented in the JUPITER reactor for the evaporation of metals. The production of micro-droplets may be attributed to the electric arc discharge does not ignite all over the surface of the cathode, which causes instability of some spots called bright spot or cathodic spot which can be controlled from experimental parameters such as the electric current. (Valbuena-Niño *et al.* 2011).

Elemental spectra obtained by EDS on the surface of the specimens treated with Ti (5 min) and Ti (10 min) detected a titanium atomic percentage of 49.32% and 75.89% respectively, in addition to the typical alloy elements presents in this type of carbon steel (see Figs. 5(b) and 5(d)). Such a direct increase in the Ti concentration may be attributed to a longer exposition (for dose depends on implantation time among other parameters) hence enabling more time to longer Ti ionized particles to penetrate and then incorporate into the bulk, which profoundly disturbs the original lattice (Sanabria *et al.* 2019).

The photomicrographs of the substrate surface of AISI/SAE 4140 steel surface modified with Ti+N (5 min) and T+N (10 min) ions respectively, are presented in Figs. 6(a) and 6(c). The laminar

shape that is appreciated in the structure, depends on the surface state obtained in the metallographic preparation of the substrates. Additionally, a decrease of micro-droplets is shown in comparison with that presented in Fig. 5 (surface modified with Ti ions). The decrease of microdroplets present on the surface is due to the hybrid treatment involves the interaction of both titanium and nitrogen particles by an electric arc discharge and a high voltage pulsed discharge respectively with the substrate. The activation of these discharges with nitrogen ionized particles, reduces the formation of Ti clusters produced by the electric arc discharge (Tsygankov *et al.* 2016).

As for the EDS results, the elemental composition spectra obtained on the modified specimen surfaces with Ti+N for 5 min and 10 min are illustrated in the Figs. 6(b) and 6(d) respectively. From the treatment with Ti+N (5 min), titanium composition were identified with 29.36% and Nitrogen with 39.60% (in atomic percentage); while the treated substrates with Ti+N (10 min), the atomic percentage of Ti and N detected was 30.43% and 30.73% respectively, results that are in agreement with those reported in other works (Correa *et al.* 2008, Vladescu *et al.* 2004 and Manory 1987).

3.4 Electrochemical tests

Table 2 presents the results obtained from the electrochemical tests of potentiodynamic polarization and polarization resistance (R_p).

3.4.1 Potentiodynamic polarization

The potentiodynamic polarization is a very versatile technique, which gives information about the active-passive behaviour of the system under study and also allows obtaining the Tafel (β_a , β_c) slopes. Fig. 7 shows the curves of the anode and cathode branches of the non-implanted and implanted substrates with Ti and Ti+N ions. It is important to emphasize that the corrosion potential (E_{corr}) provides the thermodynamic tendency of the system to corrode and that the more positive the value, the lower the thermodynamic tendency to corrosion. In the potentiodynamic polarization curves of the surface modified substrates only with Ti during 5 min and 10 min, the E_{corr} is found to be more positive than the corrosion potential of the non-treated and treated samples with hybrid (Ti+N) treatment. On the other hand, the corrosion current density (i_{corr}) gives information about the kinetics of the corrosive process; the same can be related to the rate of corrosion through Faraday's law, the higher the i_{corr} system, the higher the corrosion rate. In this work, it was found that the i_{corr} of systems surface modified with Ti (10 min) and Ti (5 min) is smaller per an order of magnitude than the i_{corr} of the non-modified substrate and the system modified superficially with Ti+N (Table 2), indicating that the surfaces modified with titanium are the most resistant to corrosion. Remarkably, the modified surfaces with Ti (10 min) are the most resistant to corrosion followed by Ti (5 min), Ti+N (5 min), Ti+N (10 min) and those used as

Table 2 Potentiodynamic polarization and polarization resistance results

Treatment type	i_{corr} ($\mu A/cm^2$)	E_{corr} (mV)	R_p (Ω)	β_a (mV/decade)	β_c (mV/decade)	V_{corr} (mpy)
Ti+N (10min)	3.7E+02	7.1E+02	5.4E+01	8.4E+01	1.5E+02	1.6E+02
Ti+N (5min)	3.0E+02	6.9E+02	5.7E+01	4.2E+01	1.5E+02	1.3E+02
Ti (10min)	3.4E+01	6.3E+02	1.2E+03	1.5E+02	7.2E+02	1.8E+01
Ti (5min)	1.3E+02	6.7E+02	1.7E+02	5.6E+01	1.3E+02	5.9E+01
No treatment	2.2E+03	6.4E+02	9.7	6.4E+01	1.0E+02	9.6E+02

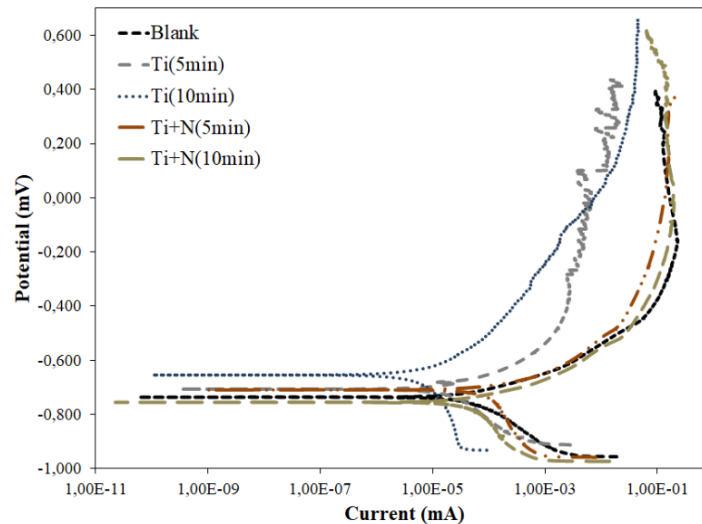


Fig. 7 Curves of potentiodynamic polarization

a reference (see Table 2 and Fig. 7). A reason for this result is that Ti and the hybrid system Ti+N, act as a diffusion barrier to prevent the transference of oxygen (among other oxidising agents) during the oxidation process. Turning to the best corrosion resistance achieved in the Ti (10 min) system by this electrochemical technique, it is interested to mention a correlation found between the implantation time and the corrosion resistance where, as previously discussed, higher doses of dopant particles reached in longer times will offer a better protection upon the surface of the material as long as such a dose remain within the admissible range for this type of surface treatment.

The anodic branch of the potentiodynamic polarization curve of the system surface modified with Ti+N behaves similarly to the anodic branch obtained on the non-modified surface substrate, which means that the treated surface with Ti+N was permeated by the corrosive medium with greater ease compared to that modified with Ti. In Fig. 7, it is evidenced that the anodic curves of all the evaluated surfaces did not present passive behaviours

3.4.2 Linear polarization resistance (LPR)

It is noteworthy that the larger the value of R_p , the lower the corrosion rate of the evaluated surface. Considering that by increasing the total resistance of the system, is not easy to determinate which of the contribution increases, but either the coating resistance generated by the layer of ions implanted or by the charge transference, it is rising its anticorrosion protection. The obtained results in Fig. 8(a) show that the surfaces implanted with Ti (10 min) seem to have the best polarization resistance (R_p) with two orders of magnitude higher than the non-treated substrate, and an order of magnitude greater than the surface modified system with Ti+N and Ti (5 min) species. As for Fig. 8(b), it shows the E_{corr} obtained by means of the R_p test, from which the thermodynamic trend of the evaluated systems can be derived qualitatively. The results agree with those obtained by the potentiodynamic polarization technique, i.e., the surface modified system with Ti (10 min) has less tendency to corrode compared to the other evaluated surfaces.

The corrosion current density was calculated using Eq. (1) of Stern-Geary (Stern and Geary 1957).

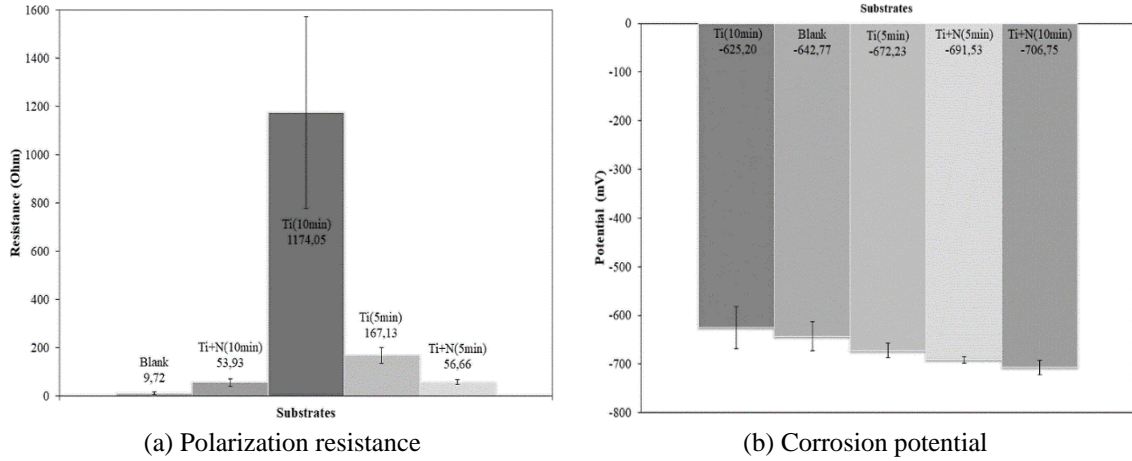


Fig. 8 Polarization electrochemical

$$i_{corr} = \frac{\beta_a \beta_c}{2.303 (\beta_a + \beta_c) R_p} \quad (1)$$

From Eq. (1) β_a and β_c are the Tafel slopes obtained from potentiodynamic polarization tests. The i_{corr} presents the same behaviour as that found by the potentiodynamic polarization technique. The implanted surface with Ti (10 min) demonstrated the best corrosion resistance. The corrosion current density of the surfaces with Ti (10 min) is two orders of magnitude smaller than the i_{corr} of the non-treated substrate, and an order of magnitude smaller than the i_{corr} of the surface modified with Ti+N and Ti (5 min) (see Fig. 10(a)). In conclusion, all AISI/SAE 4140 steel samples surface modified by ion implantation with metallic and non-metallic species, have higher corrosion resistance compared to the non-treated reference substrate, revealing the beneficial effect of the plasma-ion implantation technique in question.

The corrosion rate was calculated with the following Eq. (2).

$$V_{corr} = \frac{0.13 i_{corr} \cdot \text{equivalent weight}}{\text{Density}} \quad (2)$$

From the Fig. 10(b), it can be seen how the corrosion rate of the non-implanted AISI/SAE 4140 steel substrate exceeds the corrosion rate of the other surface modified substrates with Ti and Ti+N species, where the lowest corrosion rate was obtained by the surfaces modified with Ti (10 min). Therefore, we can state that the surface modification performed by pulsed hybrid voltages of high voltage and electric arc at low pressures in a Ti and Ti+N atmosphere is a technique capable of improving the corrosion resistance of AISI/SAE 4140.

Titanium only surfaces have a better corrosion resistance compared to Ti+N treated specimens, which is attributed, in the former, to the protective double layer (deposition and implantation) that is formed on the surface of the substrate during the surface modification process, where much of the titanium material evaporated by the cathodic arc discharge was deposited in the controlled atmosphere during the ignition of the high voltage electric discharge. In the case of the Ti+N modified system, it is possible that titanium nitride precipitation acts as a cathode and the steel matrix as an anode, promoting micro galvanic corrosion, and as a consequence, the surface of the

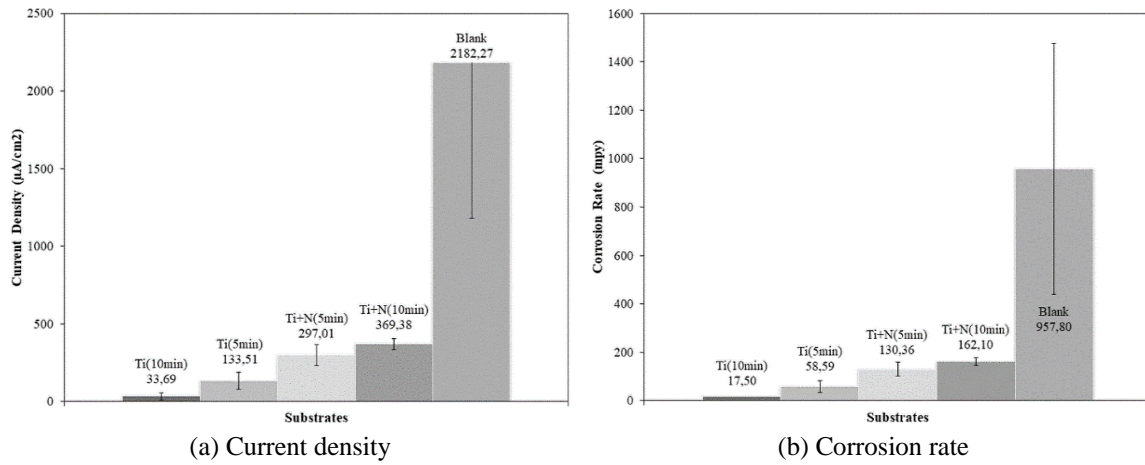


Fig. 9 Corrosion parameters

substrate will preferentially corrode (Chang *et al.* 2016, Vasilescu *et al.* 2015). Additionally, despite of offering a better protection than pristine samples, it has been reported that the effect of nitrogen with titanium promotes the oxidation process by the presence of unbonded nitrogen. These unbonded nitrogen atoms may accumulate at defect sites to form bubbles which are prone to burst and therefore expose the surface to the chemical attack. (Karimi *et al.* 2002).

3.4.3 Total porosity

The porosity of a surface or coating is an important parameter studied in the corrosive processes. The evaluation of the porosity by electrochemical methods is based on the ratio of the current densities through the pores of the surface or layer under study (Liu *et al.* 2003). In the present investigation, the total porosity (P) is obtained with Eq. (3), in agreement with the study by Escobar *et al.* (2013) in layers of VN and HfN modified on AISI/SAE 4140 steel.

$$P = \frac{R_{p,substrate}}{R_{p,layer}} \quad (3)$$

Where $R_{p,substrate}$ is the polarization resistance of the substrate without surface modification, and $R_{p,layer}$ is the polarization resistance of the modified layer-substrate. Table 3 shows the total porosity coefficient in each of the evaluated surfaces.

When the value of the porosity is equal to the unit "1", it means that there is no type of barrier between the corrosive medium and the substrate. When the porosity value is equal to zero "0", it means that the modified layer acts as an effective barrier, with no porosity or defects. Table 3 shows that the value of the total porosity of the surface modified system with Ti (10 min) is in the order of 10^{-3} , that is, an order of magnitude lower than in the system modified Ti (5 min) and two orders of magnitude below the porosity found on surfaces modified with Ti+N ions, which

Table 3 Porosity of the evaluated surfaces

Reference	Ti (10 min)	Ti (5 min)	Ti+N (10 min)	Ti+N (5 min)
1,0	8.3E-3	5.8E-2	1.8E-1	1.7E-1

Table 4 The efficiency of evaluated surfaces in function of i_{corr} and R_p .

Reference	Ti (10 min)	Ti (5 min)	Ti+N (10 min)	Ti+N (5 min)
i_{corr}	0.0	98.5	93.9	83.1
R_p	0.0	99.2	94.2	81.8

means that the behaviour of the porosity is consistent with that obtained in the corrosion tests on the evaluated surfaces. The less porous system presented better corrosion behaviour due to the barrier effect that prevents the penetration of the corrosive electrolyte towards the substrate structure.

3.4.4 Surface modification efficiency

The efficiency of the modified surface corresponds to the superficial and electrochemical differences that exist between the treated and non-treated surfaces. Eqs. (4)-(5) calculated the efficiency of the modified surfaces concerning the non-modified as a function of the i_{corr} and the R_p , in agreement with Escobar *et al.* (2013).

$$\%E = \frac{i_{corr\,substrate} - i_{corr\,modified}}{i_{corr\,substrate}} \times 100 \quad (4)$$

$$\%E = \frac{R_{p\,substrate} - R_{p\,modified}}{R_{p\,substrate}} \times 100 \quad (4)$$

Table 4 shows the values of efficiency percentage of the evaluated surfaces as a function of i_{corr} and R_p . The surface modified substrates with Ti ions, present better efficiency than those surface modified with Ti+N. The results indicate that surface modification with Ti and Ti+N ions provide corrosion protection efficiency greater than 81%.

The efficiency values reported in Table 4, although maintaining the same trend, show that those calculated as a function of R_p are slightly greater than those obtained from i_{corr} . Therefore, the difference presented between the two methods is due to possible alterations which are manifested in the substrate of the modified systems when being polarized.

4. Conclusions

- The treatments with Ti and N species by a hybrid high voltage pulsed and electric arc discharges at low pressures, offered a surface protection against corrosion on AISI/SAE 4140 steel substrate with an efficiency between 81% and 99%. Therefore, surface modification with Ti ions provides higher corrosion resistance in comparison with the surface modified samples with Ti+N ions and the reference substrate without any treatment.
- The lower porosity ($P = 8.3 \times 10^{-3}$) was obtained in the implanted samples with Ti ions for 10 mins, which was two orders of magnitude inferior to the porosity achieved by the hybrid surface treatment with Ti+N ions.
- The linear polarization resistance and potentiodynamic polarization results indicated that the AISI/SAE 4140 steel surface modified with Ti ions during 10 min is the most effective corrosion resistant treatment compared with the other treatments in this study.

- The surface characterization by SEM showed that the existence of microdroplets on the surface of AISI/SAE 4140 steel modified Ti ions, is more appreciable compared to those treated with Ti+N ions. Elemental composition spectra obtained from EDS analysis, detected the presence of Ti and N particles on the surface of AISI/SAE 4140 steel samples, validating the effect of the metallic and non-metallic ions implantation on the microstructure of ferrous alloys surfaces by the plasma-ion technique used in this study.

Acknowledgments

The authors acknowledge the “Física y Tecnología del Plasma y Corrosión” research group, Laboratorio de Espectroscopía from Universidad Industrial de Santander and DIM-ETSI Industriales from Universidad Politécnica de Madrid for the generous collaboration in the acquisition of data and results.

References

- Agüero, A. (2007), “Ingeniería de superficies y su impacto medioambiental”, *Rev de Metal.*, **43**(1), 63-75.
- American Society of Testing Materials (ASTM) (2013), Standard specification for steel bars, alloy, standard grades; ASTM International, Standard No. ASTM A322-13, West Conshohocken, PA, USA.
- American Society of Testing Materials (ASTM) (2014a), Standard practice for conventions applicable to electrochemical measurements in corrosion testing; ASTM International, Standard No. ASTM G3-14, West Conshohocken, PA, USA.
- American Society of Testing Materials (ASTM) (2014b), Standard reference test method for making potentiodynamic anodic polarization measurements; ASTM International, Standard No. ASTM G5-14, West Conshohocken, PA, USA.
- Chang, M., Su, J., Hu, G., Zhai, B., Meng, D., Sun, L., Chen, Y., Li, Y. and Cui, Y. (2016), “Enhancement of corrosion resistance of a biomedical grade NiTi shape memory alloy by cyclic potentiodynamic polarization in PBS solution”, *Int. J. Electrochem. Sci.*, **11**, 1092-1098.
- Correa Ballesteros, F., Caicedo Angulo, J.C., Aperador Chaparro, W.A., Rincón Castro, C.A. and Bejarano Gaitán, G. (2008), “Mejoramiento de la resistencia a la corrosión del acero AISI 4140 utilizando multicapas de titanio/nitruro de titanio”, *Rev. Fac. Ing. Univ. Antioquia*, **46**, 7-14.
- Dugar-Zhabon, V.D., Moreno, H.J.D., Villamizar, H.A.G. and Niño, E.D.V. (2002), “High voltage pulse discharge for ion treatment of metals”, *Rev. Sci. Instrum.*, **73**(2), 828-830.
<https://doi.org/10.1063/1.1429785>
- Dugar-Zhabon, V.D., Moreno, H.J.D., Villamizar, H.A.G. and Niño, E.D.V. (2012), “A new method for surface modifications of carbon steels and alloys”, **15**(6), 969-973.
<https://doi.org/10.1590/S1516-14392012005000133>
- Dulce-Moreno, H.J. (2015), “Descargas eléctricas y sus aplicaciones”, *Ecomatematic*, **6**(1), 6-21.
<https://doi.org/10.22463/17948231.447>
- Escobar, C., Caicedo, J.C., Aperador, W., Delgado, A. and Prieto, P. (2013), “Improve on corrosion resistant surface for AISI 4140 steel coated with VN and HfN single layer films”, *Int. J. Electrochem. Sci.*, **8**, 7591-7607.
- Jothi, K.J. and Palanivelu, K. (2016), “Praseodymium oxide modified hybrid silane coatings for anti-corrosion applications”, *Surf. Eng.*, **32**(1), 47-52. <https://doi.org/10.1179/1743294414Y.0000000333>
- Karimi, M.V., Sinha, S.K., Kothari, D.C., Khanna, A.K. and Tyagi, A.K. (2002), “Effect of ion implantation on corrosion resistance and high temperature oxidation resistance of Ti deposited 316 stainless steel”, *Surf. Coat. Technol.*, **158-159**, 609-614. [https://doi.org/10.1016/S0257-8972\(02\)00319-5](https://doi.org/10.1016/S0257-8972(02)00319-5)
- Khvesyuk, V.I. and Tsygankov, P.A. (1997), “The use of a high voltage discharge at low pressure for 3D ion

- implantation”, *Surf. Coat. Technol.*, **96**(1), 68-74. [https://doi.org/10.1016/S0257-8972\(97\)00117-5](https://doi.org/10.1016/S0257-8972(97)00117-5)
- Liu, C., Bi, Q., Leyland, A. and Matthews, A. (2003), “An electrochemical impedance spectroscopy study of corrosion behavior of PVD coated steel in 0.5N NaCl aqueous solution: Part II. EIS interpretation of corrosion behavior”, *Corr. Sci.*, **45**(6), 1257-1273. [https://doi.org/10.1016/S0010-938X\(02\)00214-7](https://doi.org/10.1016/S0010-938X(02)00214-7)
- Manory, R. (1987), “Effects of deposition parameters on structure and composition of reactively sputtered TiNx films”, *Surf. Eng.*, **3**, 233-238. <https://doi.org/10.1179/sur.1987.3.3.233>
- Mussada, E.K. and Patowari, P.K. (2015), “Characterisation of layer deposited by electric discharge coating process”, *Surf. Eng.*, **31**(10), 796-802. <https://doi.org/10.1179/1743294415Y.0000000048>
- Mussada, E.K. and Patowari, P.K. (2017), “Post processing of the layer deposited by electric discharge coating”, *Mater. Manuf. Process.*, **32**(4), 442-449. <https://doi.org/10.1080/10426914.2016.1198021>
- Sanabria, F., Viejo, F. and V-Niño, E.D. (2019), “Performance in saline environment of a carbon steel surface modified by three-dimensional ion implantation”, *J. Physics: Conf. Ser.*, **1403**, 012015. <https://doi.org/10.1088/1742-6596/1403/1/012015>
- Soares, M.E., Soares, P., Souza, P.R., Souza, R.M. and Torres, R.D. (2017), “The effect of nitriding on adhesion and mechanical properties of electroless Ni–P coating on AISI 4140 steel”, *Surf. Eng.*, **33**(2), 116-121. <https://doi.org/10.1080/02670844.2016.1148831>
- Stern, M. and Geary, A.L. (1957), “Electrochemical Polarization: a theoretical analysis of the shape of polarization curves”, *J. Electrochem. Soc.*, **104**(1), 56-63.
- Tsygankov, P.A., Becerra, F.P., Dugar-Zhabon, V.D., Plata, A. and V-Niño, E.D. (2016), “Artificially modulated hard coatings produced with a vacuum arc evaporator”, *J. Phys. Conf. Ser.*, **687**(1), 1-4. <https://doi.org/10.1088/1742-6596/687/1/012005>
- Valbuena-Niño, E., Tsygankov, P., Plata, A., Ochoa, C., Parada, F., Chacón, C. and Dugar-Zhabon, V. (2011), “Study of volt-ampere characteristics and functioning peculiarities of a vacuum arc sprayer”, *Rev. Col. de Fís.*, **43**(2), 458-462.
- Valbuena-Niño, E., Pinto, J.L., Dugar-Zhabon, V. and Henao, J.A. (2012), “Chemical characterization of 4140 steel implanted by nitrogen ions”, *J. Phys. Conf. Ser.*, **370**(012031), 1-7. <https://doi.org/10.1088/1742-6596/370/1/012031>
- Valbuena-Niño, E.D., Gil, L., Hernández-Molina, L., Barba-Ortega, J.J. and Dugar-Zhabon, V. (2016), “Characterization of the low alloy steel modified superficially with ions of titanium and nitrogen”, *CT&F*, **6**(3), 135-146.
- Vasilescu, C., Drob, S., Calderon J., Osiceanu, P., Popa, M., Vasilescu, E., Marcu, M. and Drob, P. (2015), “Long-term corrosion resistance of new Ti-Ta-Zr alloy in simulated physiological fluids by electrochemical and surface analysis methods”, *Corros. Sci.*, **93**, 310-323. <https://doi.org/10.1016/j.corsci.2015.01.038>
- Vladescu, A., Cotrut, C., Braic, V., Balaceanu, M. and Braic, M. (2004), “Biocompatible thin films deposited by cathodic arc method”, *Roman. Rep. Phys.*, **56**(3), 460-465.
- Winnicki, M., Baszczuk, A., Rutkowska-Gorczyca, M., Małachowska, A. and Ambroziak, A. (2016), “Corrosion resistance of tin coatings deposited by cold spraying”, *Surf. Eng.*, **32**(9), 691-700. <https://doi.org/10.1080/02670844.2016.1190064>