Performance in saline environment of a carbon steel surface modified by three-dimensional ion implantation

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Abstract. The three-dimensional ion implantation method is presented as a new plasma-ion technology for advanced surface treatment. It is based on a high voltage pulsed discharge activated in the low-pressure range and applicable to solid surface immersed in a gaseous atmosphere. This process is carried out in the joint universal plasma and ion technologies experimental reactor and is widely used to improve the tribological properties and corrosion resistance of metallic materials, specially steels. In this study, the performance in a corrosive environment of a carbon steel surface-modified was evaluated. High-energy nitrogen ions were implanted on the surface of the material at different discharge voltages and times. Treated and non-treated substrates were exposed to saline solution for 35 days, where the effect of the surface modification was shown to decrease the corrosion rate and degradation of the implanted material surface compared to untreated substrates. The estimation of the nitrogen concentration from experimental parameters were calculated by a novel web application. Additionally, the effect of the implantation process of the modified steel structure was analyzed by optical emission spectroscopy, whose results detected mainly an increase of the nitrogen concentration at the surface of the modified substrates.

1. Introduction
The three-dimensional ion implantation (3DII) is presented by V. Khevsyuk and P. Tsygankov as a new plasma-ionic alternative for advanced surface treatments, allowing other traditional ion implantation technologies to be adapted without major costs and a significant enhancement in equipment capacity [1]. It is based on a high voltage pulsed discharge activated in the range of low pressures ("high vacuum") generating a self-sustaining high energy ion flux that are implanted perpendicularly and at a quasi-stationary character on the surface of the desired implanted material [2]. Compared with other traditional ion implantation methods, 3DII allows to obtain acceptable concentrations of implanted species, achieve an exceptional adhesion of the layer on the substrate, avoid the usage of sample handling devices, which guarantees a correct incidence of the ions and homogeneity of the layer formed on irregular pieces; and neither requires a pre-generate plasma or a beam formation system to produce a monoenergetic ion flux. It is also noteworthy that the heating in the material to be treated is not significant, thus avoiding phase transformations and deformation of the piece. A detailed review on this technology was reported by [3]. Recent studies have demonstrated interesting results in the enhancement of the physicochemical properties of carbon steels and ferrous alloys Cr-Mo implementing 3DII [4-7]. From the ion implantation of several species such as nitrogen (N), titanium (Ti) and simultaneously N-Ti on the surface of these materials, while applying voltages between 5 keV - 30 keV at different
implantation times, the effects in protection against corrosion in electrolytic environments, biological corrosion and hydrogen permeation; reported favorable results by decreasing the rate of physicochemical and microbiological corrosion by electrochemical tests [8]. Additionally, other authors have already suggested that the implantation of nitrogen ions decreases the mobility of hydrogen and its diffusion in ferrous metals, avoiding problems of embrittlement, blistering and corrosion by exfoliation [9]. With the aim of improving the functionality of low-carbon steels widely used in engineering applications, this work proposes to evaluate the effectiveness of the 3DII technique as a corrosion protection method by gravimetric tests (in saline solution) and other characterization techniques. The surface of the substrates was implanted with nitrogen ions by a high voltage pulsed discharges activated at low pressures, at different potentials and established exposure times. These modifications were made in the joint universal plasma and ion technologies experimental reactor (JUPITER) located in the laboratory of Física y Tecnología del Plasma y Corrosión (FITEK) of the Universidad Industrial de Santander (UIS), Bucaramanga, Colombia.

2. Methods and materials

2.1. Substrate material
Gravimetric carbon steel coupons with different morphologies were implemented. Dimensions are shown in Figure 1 and chemical characterization will be given in the results section. Prior the surface modification treatment, the coupons were ground and then polished consecutively with silicon carbide papers down to 1200 grit according with ASTM E3-95 Standard [10], followed by immersion in pure acetone and distilled water in an ultrasonic bath as described by ASTM G1-03 Standard [11].

![Figure 1. Geometry of the carbon steel substrates.](image)

2.2. Surface modification by three-dimensional ion implantation
The surface modification of carbon steel coupons by nitrogen ion bombardment was carried out in the JUPITER reactor illustrated in Figure 2.

![Figure 2. JUPITER reactor.](image)
Once the specimens were prepared, they were mounted on a SAE 4140 steel coupon holder acting as a cathode. Then, inserted in the cathodic drop region of the discharge chamber of the reactor (region where practically all the applied potential drops) ready to receive the implantation process. This experiment was performed from a flux of gaseous nitrogen fed into the vacuum chamber. The atoms of this flow pass into an ionization state when they are exposed to the discharge conditions; then, the ionized particles are implanted quasi-stationery onto the cathode at an energy and for a previously established time. All the electrical signals were measured by a two-channel digital oscilloscope and the study variables and discharge parameters were adjusted from the control panel, see Table 1. The frequency and duration of the pulse of the discharges were maintained at 30 Hz and 25x10\(^{-5}\) s respectively; the pressure range indicates the values at which the corresponding discharges were activated [3-9].

| Table 1. Discharge parameters and operation conditions. | Time (min) | Voltage (keV) | Pressure (Pa) |
|------------------------------------------------------|------------|--------------|---------------|
|                                                       | 60         | 10           | 0.7 - 2.7     |
|                                                       |            | 20           | 0.3 - 1-3     |
|                                                       | 120        | 10           | 0.7 - 2.7     |
|                                                       |            | 20           | 0.3 - 1-3     |

2.3. Dose
The process of ion implantation on solid surfaces is usually characterized by the dose (ions/cm\(^2\)), which relates the number of implanted ions at a certain depth per surface area of the cathode [7]. It is essential to know the dose of ions that is supplied to the metal substrates, since research have indicated that high doses could become detrimental to the performance against corrosion and other properties such as electrical conductivity, limiting the range of application of this technology. The calculation of the dose of ions implanted in some metallic materials depends mainly on factors such as: Duration of treatment, ion current density, repetition frequency, pulse duration, ion-electron secondary emission coefficient of the material and the cathode area [2]. The method used to calculate the implanted dose was that reported by [12-14]; it method consists in the design of a web application that allows estimating the implanted dose based on the parameters described above [14].

2.4. Optical emission spectroscopy
The elemental chemical composition of the substrates was obtained from the evaluation and analysis of implanted and non-implanted surfaces by the atomic emission or arc spark spectroscopy technique, using a Q4 TASMAN spectrometer.

2.5. Gravimetric analysis
The gravimetry test was carried out in order to determine the performance of the implanted samples against the non-implanted samples, allowing quantification of the damage caused by corrosion. For each implantation treatment the samples were immersed in a saline solution at 3.5% NaCl. The exposure in the solution was established for 35 days by conducting inspection at 0, 28, 56, 84, 112 and 140 hours; then at 7, 14, 21, 28 and 35 days; recording at each time the loss of weight of the material. The assembly of the gravimetry test was performed as reported in ASTM G1-03 [11] and NACE Standard RP 0775-2005 [15].

3. Results
Once the image and the data of the pulse of the discharge extracted from the oscilloscope are input, the application calculates the area under the curve of the rectangular pulse which correspond to the total charge of said pulse. Likewise, other experimental parameters are entered to obtain the value of the implantation dose. Theoretical parameters such as the secondary emission coefficient $\gamma$ depend on the
nature of the penetrating ion, the target material and the applied voltage. Shamin, et al. reported \( \gamma \) values for different materials and voltages applied in a gaseous discharge with nitrogen ions [16].

Table 2 shows the doses values obtained from each experiment, observing a direct relationship between the dose with the exposure time and inverse with the applied voltage. The latter is due to the secondary emission coefficient increases with the applied voltage, obtaining higher values in the 10 keV discharge compared to the 20 keV discharge.

| Discharge conditions | Dose (ion/cm\(^2\)) |
|----------------------|----------------------|
| Voltage (keV) | Time (min) | Value |
| 10 | 60 | 4.22 x 10\(^{-23}\) |
| 10 | 120 | 8.44 x 10\(^{-23}\) |
| 20 | 60 | 3.75 x 10\(^{-23}\) |
| 20 | 120 | 7.50 x 10\(^{-23}\) |

As for the elementary analysis of the implanted substrates, the Table 3 summarizes the results obtained. Experiment with blank substrates was also performed for comparison.

| Element | Blank | 60 min | 120 min |
|---------|-------|--------|---------|
| C       | 0.180 | 0.183  | 0.190   |
| Si      | 0.277 | 0.273  | 0.277   |
| Mn      | 0.751 | 0.749  | 0.758   |
| P       | 0.021 | 0.020  | 0.021   |
| S       | 0.150 | 0.150  | 0.150   |
| Cr      | 0.133 | 0.133  | 0.134   |
| Ni      | 0.040 | 0.040  | 0.040   |
| Cu      | 0.097 | 0.097  | 0.098   |
| Bi      | 0.027 | 0.028  | 0.028   |
| Ta      | 0.030 | 0.030  | 0.030   |
| Zn      | 0.036 | 0.036  | 0.036   |
| Fe      | 98.16 | 98.16  | 98.14   |
| N       | 0.025 | 0.036  | 0.043   |

According to the results, the chemical composition of the steel used was verified, where the percentage values obtained for each of its main alloying elements are located within the compositional ranges of low carbon steel AISI-SAE 1018, as reported in ASTM A29M [17]. Additionally, an increase in the concentration of N correlated with the applied potential and the treatment time on the analyzed surfaces is evidenced, possibly due to the exposure in the nitrogen atmosphere and the conditions of implantation of the gas discharge.

The risks associated with corrosion were quantified by means of the corrosion rate (Vcorr), which allows estimating the lifetime, or the speed with which the thickness of the metallic material per year is lost per exposed area. Calculations were supported under ASTM G1-03 [11], ASTM G31-72 [18] and NACE Standard RP0775-2005 [15]. The values obtained from the average Vcorr for either flat and perforated coupons are summarized in Table 4.

The behavior of the corrosion rate for both treated and nontreated coupons during the exposure time in saline solution is illustrated in Figures 3 and Figure 4, analyzing the effect of the operation conditions. Figure 3 compares the performance of the blank and 60 minutes treated coupons without significant differences between the average corrosion values. The effect of the voltage applied to each treated sample is not evident. However, after 35 days of exposure into the brine, the treatment at 10 keV demonstrated more comprehensive results reaching average corrosion rates with an additional 8% corrosion protection.
Table 4. Corrosion rate.

| Substrate | Voltage (keV) | Corrosion Rate (mpy) |
|-----------|--------------|----------------------|
| Blank     | -            | 3.230±0.057          |
| Flat      | 10           | 3.153±0.099          |
| Perforated| 10           | 2.811±0.063          |
| Flat      | 20           | 3.187±0.121          |
| Perforated| 20           | 2.938±0.385          |

In the Figure 3, the difference between the values obtained in the average corrosion rate for the specimens treated for 120 minutes and the blank can be seen more clearly. The effect caused by the duration of treatment and the applied voltage can be attributed to an increase in the dose of N ions on the surface of the treated substrate, validating the calculations obtained in the dose estimation (Table 1). On the other hand, the difference between voltages is not noticeable, however, the 10 keV discharge achieves remarkable results, managing to enhance the protection of carbon steel against corrosion by up to 33%.

Figure 3. Corrosion rate. Flat substrates at 60 minutes.

Figure 4. Corrosion rate. Flat substrates at 120 minutes.
The findings regarding perforated coupons, whose performance is similar to that described above for flat coupons, validate that the substrate geometry is inherent to the implantation treatment in this study, providing protection even on irregular surfaces. In general, the same behavior of the corrosion rate is maintained, decreases in time tending to be constant due to the reduction in the kinetics of electrochemical reactions by repassivation of the material.

4. Conclusions
The performance of the implanted substrates with nitrogen ions at 10 keV for 120 minutes achieve up to 33% of additional protection against corrosion in saline environment and is due to a greater incorporation of ions on the surface, validating the results obtained in the dose calculation. The elemental composition analysis performed by the optical emission spectroscopy technique showed an increase in the nitrogen composition of the implanted substrates, which means there is a correlated with the applied voltage and the treatment time.

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