

Surface evaluation of carbon steel doped with nitrogen ions

Evaluación superficial del acero al carbono implantado con iones de nitrógeno

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Abstract

This study proposes by means of analytical characterization techniques, a structural evaluation of the surface modification of a ferrous material by three-dimensional ion implantation plasma technology. Carbon steel substrates immerse in a gaseous atmosphere, were surface-implanted with nitrogen ions via high voltage pulse discharges activated at a low-pressure range (“high vacuum”). The effect of the surface treatment on the structure, composition, and morphology of the substrates was verified by microscopy and spectroscopy techniques. From the micrographs obtained by scanning electronic microscopy and the analysis elemental by energy dispersive spectroscopy the morphology and nitrogen concentration of the treated and non-treated samples were analyzed and compared. As for the elemental analysis by energy dispersive spectroscopy, nitrogen concentration in the implanted substrates were detected and determined at a relatively low amount. In regard to the x-ray diffraction results, a decrease in the intensity of the (110), (200) and (211) planes of the treated substrate compared with the reference substrate, was observed. The analysis of phases-formation on the surface material performed by Raman spectroscopy, identified mainly ferric oxy-hydroxides typical uniform corrosion products.

Keywords: ferrous alloys; superficial treatment; ion implantation; physicochemical characterization.

Resumen

El presente trabajo de investigación propone mediante técnicas analíticas de caracterización, evaluar la estructura de materiales ferrosos modificados superficialmente mediante la tecnología plasma de implantación iónica tridimensional. Substratos de acero al carbono, inmersos en una atmósfera gaseosa, fueron implantados sobre la superficie con iones de nitrógeno por medio de la activación de una descarga pulsada de alto voltaje a bajas presiones. Se verificó el efecto del tratamiento superficial sobre la morfología, estructura y composición de las superficies implantadas con nitrógeno mediante técnicas microscópicas y espectroscópicas. Los resultados obtenidos por microscopía electrónica de barrido y espectroscopia de rayos X de energía dispersa muestran las morfologías y concentraciones de las especies presentes en la superficie de los substratos implantados y no implantados con iones

de nitrógeno. Los espectros de difracción de rayos X muestran una disminución en la intensidad de los planos (110), (200), (211) del sustrato implantado con nitrógeno respecto al sustrato no implantado. Los espectros Raman muestran la formación de compuestos sobre los sustratos implantados con iones de nitrógeno, encontrándose principalmente fases de óxidos e hidróxidos de hierro, típicos productos de corrosión uniforme.

Palabras clave: aleaciones ferrosas; modificación superficial; implantación iónica; caracterización fisicoquímica.

1. Introduction

During the last two decades of the 21st century, some interest has been highlighted in the application of technologies associated with surface modification and / or protection of the surfaces of materials. The surface is considered the most susceptible region and prone to develop various phenomena that at the time of interacting with the surrounding environment, being it either solid or fluid (liquid or gas), impacts to some degree its characteristics. Hence the importance of its study and analysis as a singular element in the materials field [1].

In effect, the recent technological advancement and development of new materials are focus on the search for modification techniques that allow the improvement of their surface properties when those are exposed in aggressive environments [2]. Likewise, in the study of the science and engineering of the materials surface (especially of metallic type), surface treatments should be considered as an alternative of choice when present solutions of less complexity in structures, equipment, parts or mechanical components that comply the operating conditions demanded by modern industry.

Research on surface modification of materials has presented the method of ion implantation as an alternative to enhance its properties. The implantation technology consists in modifying the surface and subsurface layers of the materials by influencing high-energy ions upon their surface, without altering the geometric dimensions or their internal properties [3-5].

The first studies on ion bombardment date back to the 60s and 70s, mainly aimed at doping in semiconductors. However, the production and innovation of equipment destined for this type of process was scarce due to the skepticism and limitations that the investigations carried out during this period were supported [6,7].

Subsequently, and as a result of a greater understanding of the ion implantation phenomenon, scientists were interested in the search for new applications by discovering valuable results in the enhancement of surface or tribological properties (hardness, wear resistance, abrasion and corrosion resistance) of the

materials, mainly of a metallic nature. The inlay of ions and associated stresses can inhibit the movement of dislocations and increase the packing density of the crystal, increasing the hardness and resistance to fracture (See figure 1) [8].

Within the evolution of traditional ionic implantation schemes, it was found the classic design of ionic beam implantation (IBI) whose complex assembly requires ultra-vacuum conditions, the additional installation of an extraction of particles unit, focus systems and a sample handling component [8]. Further, methods based on plasma technologies such as ion implantation by plasma source (PSII) and ion implantation by plasma immersion (PIII), require of low vacuum conditions and a combination of direct current DC or radio frequency RF sources for the preparation of a *pre-generate* plasma and, a high voltage pulsed (HVP) power supply that guarantees the flow of ions onto the surface. Finally, the three-dimensional ion implantation (3DII) that operates in a high vacuum regime and activates at a HVP discharge, is presented; generating a high-density plasma and simultaneously attracting the ions to the substrate that in this case acts as a cathode.

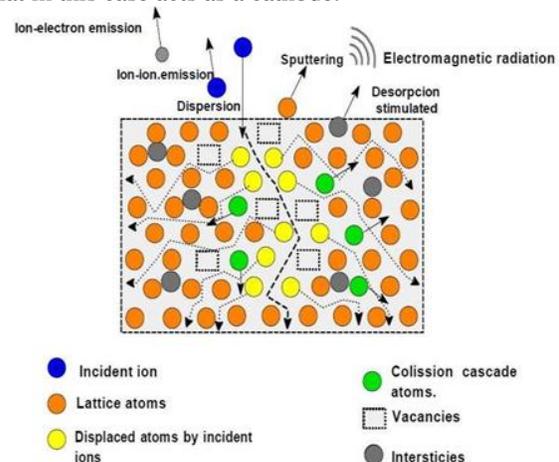


Figure 1. Ion implantation phenomena. Source: H. J. Dulcé [8].

Recent studies have demonstrated that 3DII technique, a form of plasma technology, is a simple, yet effective, ion implantation method to enhance the physicochemical properties of ferrous and other alloys [9-12]. It is

noteworthy that 3DII inexpensively allows adapting and resolving some limitations from other plasma technologies, achieving an acceptable quality of surface treatment by guaranteeing a sufficient concentration of implanted species, quasi-monoenergetic ions flux, and impressive homogeneity and adherence upon the exposed surface. Furthermore, the heating in the material to be treated is not significant, thus avoiding phase transformations and deformation of the piece. More details of this topic can be found in [13].

The aim of this work is to examine the effect and changes that occurred on carbon steel surfaces when implanting N^+ by the 3DII method, at different durations of treatment and potential differences applied. Following the ion implantation process, the microstructure and composition of the treated surfaces are characterized by scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDS), x-ray diffraction (XRD), and Raman spectroscopy.

2. Materials and methods

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

2.1. Substrate Material

Gravimetric carbon steel coupons with a square shape and whose dimensions are 19x19 mm and a thickness of 3 mm, were implemented. Chemical composition is given in Table 1.

Table 1. Carbon steel substrates chemical composition

Element	%	Element	%
C	0.180	Ni	0.040
Si	0.277	Cu	0.097
Mn	0.751	Bi	0.027
P	0.021	Ta	0.030
S	0.150	Zn	0.036
Cr	0.133	Fe	98.16

Source: F. Sanabria [14].

Prior to the surface modification treatment, the coupons were ground and then polished consecutively with silicon carbide papers down to 1200 grit according to ASTM E3-95 Standard [15], followed by an ultrasonic

bath in pure acetone and distilled water as described at ASTM G1-03 Standard [16].

2.2. Surface treatment

The coupons were surface modified by implanting nitrogen ions in the Joint Universal Plasma Ion Technology Reactor (JUPITER) (see Figure 2). Once the samples were prepared, they are mounted on a SAE 4140 steel coupon holder, exposing the largest surface area. Then, the coupon holder (as a cathode) was inserted along with the coupons in the cathodic drop region of the JUPITER reactor discharge chamber (region where practically all the applied potential falls), ready to receive the process of implantation.

Under high vacuum conditions, a controlled flux of nitrogen gas is fed to the JUPITER chamber. In the cathodic drop region, a high voltage pulsed discharge is applied, ionizing the particles present in the gaseous atmosphere, then implantation on the target material at a previously established potential difference and duration (see table 2) is done. The frequency and duration of the pulse of the discharges were maintained at 30Hz and 25x10⁻⁵s respectively. The pressure range indicates the values at which the corresponding discharges are activated.

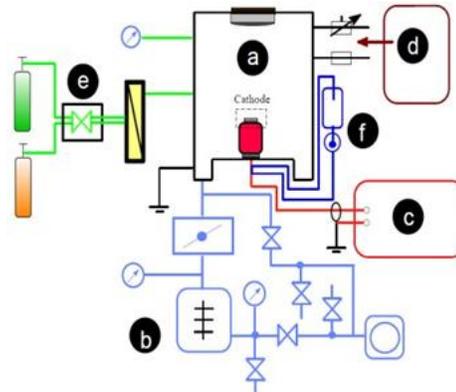


Figure 2. Schema of the JUPITER reactor. Discharge chamber (a), vacuum system (b), high voltage power supply (c), control panel (d), gas supply (e), and cooling system (f). Source: Own elaboration.

Table 2. Discharge parameters and operation conditions

Time (min)	Energy (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

Source: Own elaboration.

2.3. Scanning electronic microscopy and energy dispersed spectroscopy

Characterization of the morphology, finishing, and elemental analysis of the material was carried out in a scanning electron microscope and dispersed FEG Quanta 650 spectroscopy using an Auto Defect Classification (ADC) detector at 10kV voltage. It was possible to obtain black and white images of the surveyed surface topography.

2.4. X-ray diffraction analysis

The structural characterization of the sample surfaces is fulfilled with the x-ray diffraction on polycrystals XRD method. The samples were mounted directly on a polymethylmethacrylate (PMMA) sample holder using the frontal filling technique. X-ray diffraction measurements were performed on a BRUKER model D8 ADVANCE powder diffractometer with DaVinci Geometry. The working conditions are presented in Table 3. The qualitative analysis of the phases present in the samples was performed by comparing the profile observed with the diffraction profiles reported in the PDF-2 database of the International Center for Diffraction Data (ICDD).

Table 3. Operation conditions XRD

Parameter	Value
Voltage	40 V
Current	40mA
Slit DS	0.6mm
Slit RS	2.5 ^o
Sampling	0.02035 ^o 2-Theta
Measuring range	5-90 ^o 2-Theta
Radiation	CuK α 1
Filter	Niquel
Detector	Linear LynxEye
Type of measure	Steps
Sampling time	0.6s

Source: Own elaboration.

2.5. Raman spectroscopy

This technique is used to identify and verify the presence of compounds present on the surface of the implanted and non-implanted substrates. The operating conditions are presented in Table 4.

Table 4. Raman operation conditions

Parameter	Value
Radiation wavelength	785 nm
Zoom	100%
Diffraction Slit	600 g
Target	100X
Acquisition time	60 s
Accumulation	5

Source: Own elaboration

3. Results

Following the ion implantation process, the appearance of the samples generated by the surface modification was visually verified. Implanted and non-implanted coupons at different energies and duration of treatment are observed in Figure 3. In the bottom of each specimen, with the exception of the non-implanted substrate (see figure 3(a)), a seemingly non-implanted portion of surface is identified that corresponds to the edge where it was supported on the coupon holder or cathode during high voltage discharge, validating the fact that the entire surface exposed to the gaseous discharge inside the chamber will present the formation of a homogeneous layer.

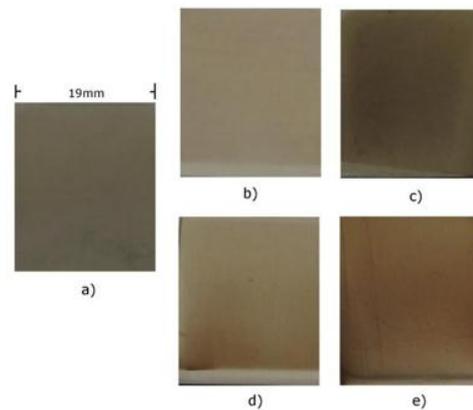


Figure 3. Carbon steel substrates. Non implanted (a); implanted with nitrogen ions by 3DII at 10 keV/60min (b), 10keV/120min (c), 20 keV/60 min (d), and 20 keV/120min (e). Source: Own elaboration.

On the other hand, in most of the surface of the treated substrates (figure 3(b) to figure 3 (e)) there is a change in the coloration and hue of the implanted surface proportional to applied voltage and implantation time. The samples turn a certain golden color due to the interaction of species present in the gaseous atmosphere during the electric discharge, possibly generating the

formation of iron nitride phases. The change in the tonality is produced by the difference in the depth of implantation, that is, the incorporation of nitrides particles is more superficial at 10 keV voltages, therefore the nitrogen concentration will be higher in the outermost surface layers compared to the discharge at 20keV [8,17].

As for the micrographs in figure 4, it can be seen the surface of the coupons non-implanted in figure 4(a) and implanted with nitrogen ions in figure 4(b) by 3DII without significant effects on the structure of the material. A possible explanation for these results is that implanted species are placed at the range of the 10^{-10} m which makes it difficult to unequivocally identify them. Also, the surface roughness for the type of carbon steel in question, which is widely accepted in the industry, was not appropriate for this experiment. Nonetheless, the identification of the structural arrangements and atomic distribution profiles may be determined by using surface sensitive characterisation techniques or doing a much more specialised surface preparation [13, 18, 19]. Despite this, the images allowed to identify convenient zones for the eventual elemental composition analysis upon the surface of the substrates.

In effect, from the elemental analysis (see Table 5), the typical elements of carbon steel were detected in the non-implanted substrates. Additionally, in the implanted substrates, the incorporation of nitrogen on the surface of the material was identified (see table 6), however, this element was found at a very low concentration compared to the other alloy elements present.

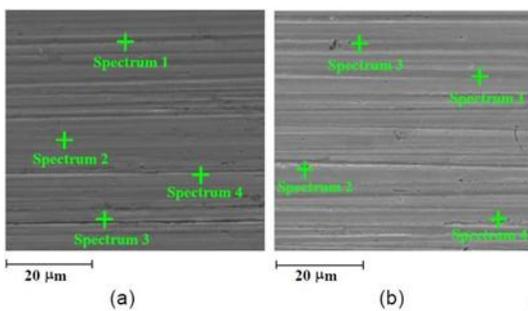


Figure 4. Morphology of the implanted and nonimplanted substrates: (a) nonimplanted, and (b) implanted. Source: Own elaboration.

In spite of having modified the surface of the material, the formation of iron nitrides compounds was not identified by the obtained diffract grams (see Figure 5). This can be attributed to a low implanted nitrogen

concentration. Another possible explanation for this is that nitrogen atoms may lie in the crystal interstice spaces, being screened or overlapped by other elements or compounds. Nevertheless, the superposition of the (110) plane shows that the diffraction peak intensity decreased and the peak slightly shifted towards bigger angles sides with the voltage applied, which could be occurred due to the implantation of larger N^+ ions on the treated substrate structure (See figure 6) [20].

Table 5. Elemental analysis by EDS. Non-Implanted substrates

Element	Spectrum			
	1	2	3	4
	At%	At%	At%	At%
Fe	84.08	95.79	58.52	86.97
C	7.78	1.41	12.85	4.86
O	8.14	2.8	28.63	8.17
N	-	-	-	-

Source: Own elaboration.

Table 6. Elemental analysis by EDS. Implanted substrates with nitrogen ions

Element	Spectrum			
	1	2	3	4
	At%	At%	At%	At%
Fe	86.72	79.12	82.37	83.79
C	5.11	14.31	5.99	5.66
O	4.90	1,8	6.85	6.54
N	3.27	4.77	4.79	4.01

Source: Own elaboration.

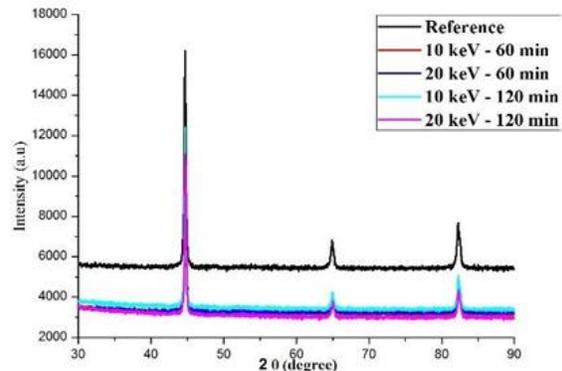


Figure 5. X ray diffraction. Implanted and nonimplanted substrates with nitrogen ions. Source: Own elaboration.

The Raman spectra of figure 7 correspond to the reference and surface modified samples to the different study conditions. Although nitrides compounds were not presented in the profiles, iron oxyhydroxides phases such as Lepidocrocite (L), Goethite (G), Akaganeite (A), Hematite (H) and Magnetite (M); typical products of uniform corrosion in carbon steels, were identified. The spectrums show the presence of a very intense peak at 390 cm^{-1} (the strongest peak) which effectively indicates that this is the lepidocrocite phase [21-24]. It is also possible to see in the spectrum two peaks of less intensity at $250, 260,$ and 310 cm^{-1} also referring to lepidocrocite according to other authors [26-28]. The second strongest peak at 380 cm^{-1} , has been broadly referred to as the goethite phase. Goethite forms by the transformation of the lepidocrocite phase [24-26].

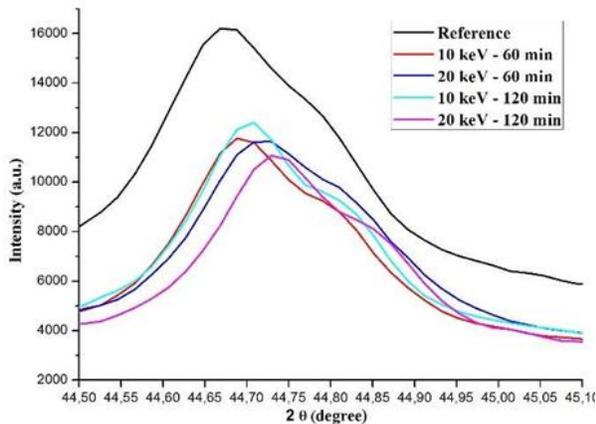


Figure 6. Superposition of the diffraction profiles. Implanted and non-implanted substrates with nitrogen ions. Source: Own elaboration

Therefore, the similarity between their characteristic Raman peaks. Weaker peaks are also seen at $410\text{--}430\text{ cm}^{-1}$, and a broad band at $1110\text{--}1120\text{ cm}^{-1}$ which is also a characteristic of this phase [27]. The presence of Akaganeite, a typical corrosion product, was observed at 310 and 330 cm^{-1} . [23,25]. Magnetite shows broad band identified at 670 cm^{-1} being in a good agreement with the reported values in [21-24]. Hematite shows that the peaks in the given spectrums agree with those obtained in [26-28]. Based on these peaks, it is possible to identify hematite on the basis of four peaks at $210, 230, 270\text{ cm}^{-1}$ and a broad band at 1270 cm^{-1} .

Finally, it is worthy to mention that different works have obtained interesting results regarding the study and understanding of the phenomena that occur on the surfaces of ferrous alloys when modified by 3DII. In [29], a correlation between the applied voltage and the treatment time with the concentration of nitrogen implanted on carbon steel surfaces was reported by means of the optical emission spectroscopy analysis. Likewise, in [5], position and concentration profiles of doping species were obtained by computational simulation together with the identification of its structural arrangements when subjected to the bombardment of metallic and nonmetallic ions. The findings obtained in this research validates will serve as a base for future works on interaction ion-solid and plasma technology processes, making it of great promising and interest to various applications, especially for the enhancing of tribologic properties in metallic materials.

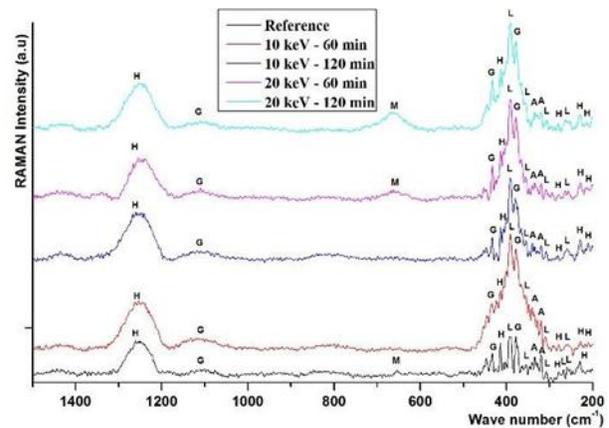


Figure 7. Raman spectra. Implanted and nonimplanted substrates with nitrogen ions. Source: Own elaboration.

Conclusions

Carbon steel samples were surface modified by means of the 3DII at different duration of treatment and applied voltages. Some modifications on the metal surface such as a change in the color and tonality due to the incorporation of nitrides identified by visual inspection were observed.

The methods of characterization studied in this work presented some limitations and unexpected results due to the operating conditions or the sensibility of the techniques. The formation of nitrides layers was not detected by neither DRX nor Raman spectroscopy. Only

the formation of ferrous oxyhydroxides, typical corrosion products of carbon steel were identified.

Nevertheless, the effects of the 3DII treatment on the surface structure of carbon steel such as a decrease in the intensity of the planes (110), (200) and (211) and a relatively low nitrogen concentration, were found by DRX and SEM-EDS techniques respectively.

Acknowledgments

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