Chemical characterization of 4140 steel implanted by nitrogen ions

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Abstract. AISI SAE 4140 steel samples of different surface roughness which are implanted with 20 keV and 30 keV nitrogen ions at a dose of 1017 ions/cm² are studied. The crystal phases of nitrogen compositions of the implanted samples, obtained with help of an x-ray diffraction method, are confronted with the data reported by the International Centre for Diffraction Data (ICDD) PDF-2. The implantation treatment is realized in high-voltage pulsed discharges at low pressures. The crystal structure of the implanted solid surfaces is analyzed by the x-ray diffraction technique which permits to identify the possible newly formed compounds and to identify any change in the surface structure of the treated samples. A decrease in the intensity of the plane (110), a reduction of the cell unity in values of 2-theta and a diminishing of the crystallite dimensions in comparison with non-implanted samples are observed.

1. Introduction

It is well known that the plasma immersion methods of ion implantation which do not change the sample geometric dimensions are used to modify the physical and chemical properties of solid surfaces [1]. One of these methods is the 3DII method reported by Khvesyuk and Tsygankov [2]. In this method, the high voltage low pressure discharge is ignited without a pre-discharge [3]. It is important that the cathode drop zone of the 3DII discharge should be very stable to guarantee a small energy dispersion of the ions accelerated in the cathode zone and their normal incidence on the treated surface. This suggests that the electron emission remains constant during the treatment process due to the ion bombardment of the surface, thus simplifying the implanted ion dose calculations [4]. In the Industrial University of Santander (Colombia), the 3DII method is implemented in the JUPITER (Joint Universal Plasma and Ion Technologies of Experimental Reactor) [5,6] equipment which is used for modifying the superficial metal layers.

In this paper, the surface characteristics of the AISI SAE 4140 steel samples exposed to a high voltage pulse discharge in the JUPITER reactor are presented. Their study includes four stages. The first step consists in choosing the sample material, designing, manufacturing and sample preparation. On the second stage the chemical composition of the substrate material is analyzed. The third stage is devoted to the sample implantation treatment. On the fourth stage the chemical characteristics of the
sample surface phases and compounds are qualitatively analyzed by comparing the obtained diffraction profiles with those reported in the PDF-2 database of the International Centre for Diffraction Data (ICDD).

2. Chemical composition of the samples

The chemical composition analysis of samples is made through an optical emission spectroscopy (EOS) technique which permits to determine precisely the sample material type. The spectroscopy results indicate that the sample material correspond to an AISI SAE 4140 alloy steel whose chemical composition corresponds (see table 1) to the data reported in ASTM A 322 standard [7]. The steel AISI SAE 4140 [8,9] is chosen because it is widely used in industry.

| Table 1. Chemical composition of the simple tested AISI SAE 4140 steel. |
|--------------------------|--------------------------|
| Element | % | Element | % |
| C | 0.40 | Cu | 0.17 |
| Cr | 0.85 | Sn | 0.019 |
| Mo | 0.14 | V | 0.026 |
| Mn | 0.85 | Al | 0.002 |
| Si | 0.24 | Ni | 0.09 |
| S | 0.018 | Nb | 0.007 |
| P | 0.012 | Cu | 0.17 |

3. Sample preparation

The samples of a cylindrical geometry of 1.8 cm in diameter and 0.5 cm thick are polished with abrasive SiC paper of numbers of 320, 600, 1200 and 6µ and with a 1µ cloth according to ASTM E 3-95 standard [10,11]. This procedure also eliminates the surface impurities which are formed because of the contact with the environment.

The information on the structure characteristics of the tested material is obtained with the metallographic analysis which is fulfilled using an Olympus microscope OBM X3. In order to compare the pre- and post-nitrogen ion implantation surface roughness, the roughness of every prepared surface is measured thrice with the help of a T500 Hommel roughness tester [12,13]. Table 2 reports the roughness parameters $R_a$, $R_z$ and $R_{max}$, which evidence that the nitrogen ion dose rise reduces the roughness significantly due to the pickling effect that occurs in the sputtering process and the collisions of the incident ions with the crystal structure of the material [12,13].

| Table 2. Roughness for implanted and without implant samples. |
|--------------------------|--------------------------|
| Voltage Discharge | Finish Superficial | $R_a$ (µm) | $R_z$ (µm) | $R_{max}$ (µm) |
|--------------------------|--------------------------|
| 30kV | Cloth 6µ | 0.48 | 0.15 | 0.08 | 0.02 | 1.12 | 0.21 |
| 20kV | Cloth 6µ | 0.48 | 0.36 | 0.08 | 0.03 | 1.12 | 0.82 |
| 30kV | Cloth 1µ | 0.51 | 0.31 | 0.03 | 0.03 | 1.73 | 0.73 |
| 20kV | Cloth 1µ | 0.51 | 0.46 | 0.03 | 0.05 | 1.73 | 1.00 |
4. Surface treatment samples

The data obtained in this work together with the previous studies results[14-16] permit to establish the range of discharge voltages, the dose of implanted ions and the gas pressures for optimal condition for the 3DII implantation technology. The samples are located in the discharge chamber (see figure 1) on the surface of the cathode that renders the sample into cathode part. The chamber walls act as the anode. In the high voltage discharge, the sample is surrounded by the cathode drop zone where the ions are accelerated and incident onto the surface sample. The potential which accelerates the ions is almost equal to the applied cathode-anode voltage. The nitrogen ion implantation is performed in pulsed discharges of 20 kV and 30 kV, at pulse duration of 0.40 ms, pulse repetition frequency of 30 Hz and a 60-minute exposure treatment time at pressures of 0.40 Pa and 0.45 Pa.

![Figure 1. Container with a sample holder on the cathode surface.](image)

The implanted dose was determined by taking into account the value of the secondary ion-electron emission coefficient ($\gamma$) and the total current value obtained during the sample surface treatment. The secondary emission coefficient for a discharge of 30 kV is taken $\gamma = 1$, taking into consideration that the sample holders are made of 304 stainless steel [17]. In table 3, the total current values for the samples polished with the clothes of 1µ and 6µ and at discharge voltages of 20 y 30 kV are presented.

| Voltage Discharge | Polished Surface | Total Current [A] |
|-------------------|-----------------|-------------------|
| 20kV              | Cloth 6µ        | 0.359             |
| 20kV              | Cloth 1µ        | 0.324             |
| 30kV              | Cloth 6µ        | 0.678             |
| 30kV              | Cloth 1µ        | 0.648             |

With the data on total current and secondary emission coefficient values, the total ion flow incident on the sample surfaces are obtained. The dose of nitrogen ions implanted into the surface is calculated in accordance with the following equation [12,13]

$$D = 2\Phi \int dt \left[ \text{ions/cm}^2 \right]$$

where $D$ is the dose of implanted ions, $\Phi$ is the ion flux incident on the sample, $f$ is the pulse repetition frequency, $d$ is the pulse duration, $t$ is the time of implantation and number two is due to the fact that
the ions in the nitrogen discharge are molecular ions $N_2^+$ which are dissociated into two atomic ions $N^+$ being penetrated into a solid.

Table 4 data show the 20 keV and 30 keV nitrogen ion doses [12,13] (with the accuracy not worse than 0.0015) obtained for the samples of different roughness.

| Voltage | Discharge Polished Surface | Nitrogen Doses [ions/cm²] |
|---------|-----------------------------|---------------------------|
| 20kV    | Cloth 6µ                   | 4.409*10^{17}             |
| 20kV    | Cloth 1µ                   | 4.0089*10^{17}            |
| 30kV    | Cloth 6µ                   | 7.5501*10^{17}            |
| 30kV    | Cloth 1µ                   | 7.1269*10^{17}            |

5. XRD characterization

The structural characterization of the sample surfaces is fulfilled with the method of x-ray diffraction on polycrystals (XRD PD) by using Bragg-Bentano geometry equipment. The samples are mounted on its aluminum sample holder of a Rudaku diffractometer, model D/MAX IIIB, and the tests are fulfilled under the working conditions reported in table 5. The qualitative and comparative analysis of phases and compounds of the implanted and non-implanted samples of different roughness is made by comparing the diffraction profiles obtained experimentally with the profiles registered in PDF-2 data of the International center for Diffraction Data (ICDD). In the process of nitrogen implantation into steel, the formation of iron nitride Fe$_x$N is theoretically possible, but in the obtained spectra the peaks corresponding to this compound have not been observed, which can be attributed to a relatively low content of the nitrogen atoms in the steel substrate. The nitrogen atoms may reside in the crystal interstice spaces and are screened or are overlapped by some element or compound.

Table 5. Working conditions of the XRD.

| Parameter       | Value                |
|-----------------|----------------------|
| Voltage         | 40kV                 |
| Current         | 20mA                 |
| Slit DS         | 1º                   |
| Slit RS         | 0.3mm                |
| Slit SS         | 1º                   |
| Sampling        | 0.02º 2-Theta        |
| Measuring Range | 30º-120º 2-Theta     |
| Radiation       | CuK$_{α1}$           |
| Monochromator   | Graphite             |
| Type of measure | Continuous           |
| Scanning speed  | 1.2º/min             |

Nevertheless, the superposition of the obtained profiles for each of the samples (implanted and non-implanted) evidences that nitrogen causes some changes in the AISI SAE 4140 steel surface: the crystal cell size decreasing, some increase in the 2-theta positions of the diffraction maxima and diminishing of the intensity of the (110) diffraction plane. The higher deformation is observed in the samples which get a higher nitrogen dose; these are the samples with 6 µ polishing and implanted by
30 keV ions. In this sample, the cubic crystal structure is transformed into a pseudocubic (see figures 2(a) and 2(b)). The crystallite dimensions for each of the samples are calculated in accordance with the Braker TOPAS program [18] which determines that the small displacements of the (110), (200), (211), (220) and (310) are generated by micro-tensions provoked by the implanted ions. The values presented in table 6 show that the crystallite dimensions are reduced by implantation due to the nitrogen ions collisions with the crystal structure.

6. Conclusions and recommendations
In this article, it is demonstrated that the high voltage pulse discharges excited at very low pressures are well suited to implantation treatment of steels. It is observed that the implantation of 20 keV and 30 keV nitrogen ions into the AISI SAE 4140 steel sample decreases significantly the superficial roughness. It is determined that the implantation of high energy nitrogen ions also causes some decrease in the (110) plane intensity, reduces the cell in 2-theta values and diminishes the crystallite dimensions in respect to the cases without implantation.

![Figure 2(a)](image)

**Figure 2(a).** Overlapping XRD pattern. Superposition of the diffraction profiles for the implanted and non-implanted samples of different roughness.
Figure 2(b). Overlapping XRD pattern. Enlargement of superposition of the diffraction profiles for the implanted and non-implanted samples of different roughness in the plane (1 1 0).

Table 6. Crystallite size calculated for the plane (1 1 0).

| Sample surface smoothing     | Plane(1 1 0) Crystallite Size (nm) |
|------------------------------|-----------------------------------|
| No Implanted                 | 90.0                              |
| 6µ cloth, implanted, 30kV    | 58.6                              |
| 6µ cloth, implanted, 20kV    | 68.7                              |
| 1µ cloth, implanted, 30kV    | 66.5                              |
| 1µ cloth, implanted, 20kV    | 69.9                              |

Acknowledgments
This work was carried out with financial support under the Colciencias code 1102-06-17623.

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