Analysis of the titanium ions concentration implanted in low alloy steel

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Abstract. In the surface modification processes obtained by high voltage electric discharges and cathodic arc at low pressures its of great interest to estimate the concentration of ions that are implanted on the surfaces of metallic substrates. The employment of computational tools to estimate the concentrations of implanted ions on the surface of materials as a function of the depth allows to optimize the experimental processes reducing costs and time. In the present research, a software that simulates the mobility, stopping and range of ions in matter by means of the Monte Carlo method is used, in order to obtain the ratio between the concentration and the dose of ions regarding to depth in a titanium ion implantation process on the surface of chromium molybdenum low alloy carbon steel; then, using experimental parameters, the implantation dose is calculated and an estimated profile of ion concentration is obtained as a function of the depth. The results showed that titanium ions implanted at 10 KV for 5 minutes and 10 minutes had projected ion ranges until depths of 250 Å and the highest concentration is located around 50 Å; the concentration of the implanted ions increases with the exposure time of the surface because the implantation dose is proportional to the discharge time. Furthermore, it is observed that the location of the highest concentration region and the range of the implanted ions is invariant.

1. Introduction

Inside material science, surface modification processes have been developed with the objective to improve the properties of a material on the region most exposed to the environment without altering its internal atomic structure. Nowadays there are diverse methods of surface modification that are based on creating a coating with thicknesses of the order of micrometres. However, since the 1960s a technique has been practiced that consists of introducing new elements into the surface of a material to depths of the tenths of a micrometre by means of ion bombardment. This technique is denominated ion implantation and in its beginnings it was mainly aimed at the semiconductor industry. Nonetheless, in the 1970s, Dearnaley [1-3] and Hartley [4] conducted research on metallic materials and observed that ion implantation under certain conditions increases the tribological properties in these materials. Additionally, these researchers promulgated exploring new ion accelerators and versatile ion source designs.

During the years the ion implantation has been growing; new and different techniques have emerged, from ion beam implantation (IBI) [1] and later with techniques based on plasma technology: plasma immersion ion implantation (PIII) and plasma source ion implantation (PSII) [5]. Currently, in the research group of “Física y Tecnología del Plasma y Corrosion” from the Universidad Industrial de
Santander, Colombia, there is the Joint Universal Plasma and Ion Technologies Experimental Reactor (JUPITER) \[6,7\] which is based on the three-dimensional ion implantation technique (3DII) \[8\]. In 3DII a high-voltage discharge is ignited in the left branch of the Pachen curve, in other words, the target material is subjected to pulsed high-voltage discharges at low pressures and under certain parameters, high doses of implanted ions are obtained in short times due to the implantation of quasi mono-energetic ions with an angle of incidence normal to the surface.

Due to the complexity of the phenomena that occur in the penetration of ions in matter, it has been resorted to using numerical models that can reproducing and interpreting an approximation of the real process of the interaction of ions with matter. These days, there are simulation techniques such as Monte Carlo method \[9\], Molecular Dynamics \[10\] and others, that allow a study of ion trajectories and the phenomenology of ion implantation. In the present research, using the implantation parameters from the JUPITER reactor and a simulation software related to the mobility, stopping and range of ions in matter (SRIM/TRIM) \[9\] by Monte Carlo method, the concentration of titanium (Ti) ions implanted in a low-alloy steel is estimated.

2. Methodology
The stages implemented during this investigation process are detailed below.

2.1. Manufacturing and preparation of samples
Disk shape samples of chromium molybdenum low alloy carbon steel were manufactured with diameter of 18.1 mm and thickness of 2.7 mm. Before modifying the surface of the low alloy steel by the ionic implantation process, the surfaces which will be implanted with the Ti ions were ground with silicon carbide abrasive paper from 60 to 600 grit as indicated by ASTM E3-11 standard \[11\]. Then were polished with alumina suspension of 1 μm, 0.3 μm, and 0.05 μm, followed by immersion in an ultrasonic bath in distilled water and pure acetone according to ASTM G1-03 standard \[12\].

2.2. Elemental composition analysis
Using the optical emission spectrometry technique is possible to determine the elemental composition of low-alloy steel. This analysis was performed on a Bruker Q4-TASMAN spectrometer.

2.3. Surface modification process
The surface modification of the low alloy steel samples was carried out in the JUPITER; prior to implantation of Ti ions, the samples are subjected to a sputtering treatment in an argon atmosphere and a potential difference of 5 KV for 15 minutes at 1.7 Pa to complete the surface preparation. Then, a source of Ti ions must be created; this is achieved through the evaporation of a Ti cathode that is connected to a voltage generator with volt-ampere characteristics that guarantee the stable operation of the evaporator. Simultaneously the Ti particles are ionized by high voltage pulsed discharges under high vacuum conditions complying with the three-dimensional ionic implantation technique \[8\]; with the purpose of comparing the Ti concentrations at different exposure times, two implantation processes were accomplished for 5 minutes and 10 minutes. The implantation parameters used in the JUPITER are reported below (see Table 1).

| Parameter       | Magnitude          |
|-----------------|--------------------|
| High voltage (KV) | 10                 |
| Pulse frequency (Hz) | 30               |
| Pulse duration (μs) | 250              |
| Discharge time (min) | 5 and 10         |
| Arc voltage (V)     | 22                 |
| Arc current (A)      | 140                |
| Pressure (Pa)        | 0.250-0.260        |
2.4. Ion implanted dose calculation

Using a web application [13,14] developed from experimental parameters established in a 3DII process as in the JUPITER, it estimates the total charge in an electric discharge, which allows knowing the approximate value of the dose of ions implanted on the surface of the material [15,16].

2.5. Simulation with SRIM/TRIM software

The SRIM/TRIM simulation code [9] is a collection of software packages that calculates the transport, stopping and range of ions in matter, which has been continuously updated since its introduction in 1985. This Monte Carlo simulation software consists in following a great amount of randomly selected trajectories, obtaining a statistical histogram of the desired implantation profiles using the experimental implantation parameters. Besides, SRIM/TRIM software generates different data files that describe the interaction of the ions in the target material.

2.6. Estimation of implanted ions concentration

RANGE_3D.txt data file contains in detail the final three-dimensional location of all ions that are implanted into the target during simulation in the SRIM/TRIM software. With this data file, the profiles of the ratio between ion concentration and dose are plotted as a function of depth \( \frac{R_{c/d}}{d} \) applying the Equation (1).

\[
R_{c/d} = \frac{f_{x}/\Delta x}{N},
\]

where \( f_{x} \) is the frequency of implanted ions in a depth differential, \( \Delta x \) is the depth differential and \( N \) is the total number of ions; finally, by multiplying the \( R_{c/d} \) profile with the implantation doses calculated for 5 minutes and 10 minutes, the estimated concentration profiles as a function of depth are obtained for each exposure time.

3. Results and discussions

The results obtained in this research work are shown below.

3.1. Elemental composition analysis

The results obtained from the analysis of elemental composition by optical emission spectrometry (OES) corroborate that the specimens were manufactured from a chromium molybdenum low alloy carbon steel and mostly complies with the ASTM A29/A29 M-15 standard [17] for an AISI/SAE 4140; from the results of the chemical composition, 20 representative elements are selected to model the target material in the simulation software (see Table 2).

| Element | %   | Element | %   | Element | %   | Element | %   |
|---------|-----|---------|-----|---------|-----|---------|-----|
| C       | 0.4520 | Cr      | 0.5630 | As      | 0.0055 | Sb      | 0.0100 | S    | 0.1500 |
| Si      | 0.2930 | Mo      | 0.1930 | Bi      | 0.0480 | Ta      | 0.0640 | Al   | 0.0050 |
| Mn      | 0.6870 | Ni      | 0.0320 | Co      | 0.0077 | V       | 0.0097 | Pb   | 0.0110 |
| P       | 0.0160 | Cu      | 0.0800 | Mg      | 0.0061 | W       | 0.0210 | Fe   | 96.9000 |

3.2. Web application to calculate the ion implanted dose

Figure 1 and Figure 2 show the web application interface where the dose of implanted ions is calculated for discharge times of 5 minutes and 10 minutes respectively; not only the implantation parameters are required, but it is also necessary to find the values of the number ion charge [18,19] and the secondary emission coefficient [20]. However, secondary emission coefficients of Ti ions in low alloy steels have not yet been reported, so the values of the behavior of Ti ions in another metal material were chosen [19].
Figure 1. Calculation of the implanted dose for 5 minutes exposure time by the web application.

Figure 2. Calculation of the implanted dose for 10 minutes exposure time by the web application.

Table 3 reports the results of the calculation and shows that the dose implanted for 10 minutes is twice the dose implanted for 5 minutes. This can be explained by the fact that the only parameter that is modified is the discharge time, and the implantation dose depends directly on this parameter [15,16].

| Discharge time (min) | Ion implanted dose (ions/cm²) |
|----------------------|-------------------------------|
| 5                    | 1.3204e+22                    |
| 10                   | 2.6408e+22                    |

3.3. Profiles of concentration and dose relation

With the data provided in the RANGE_3D.txt file, the $R_{cd}$ profiles can be plotted as shown in Figure 3(a) and Figure 4(a) using Equation (1); therefore, it is possible to identify the estimated region of greatest concentration in an ion implantation process. Table 4 reports the depth where the estimated region of highest concentration in the implantation of Ti ions at 10 KV and 20 KV is located. Moreover, the final location of the implanted ions at the target also can be plotted with respect to the point of incidence on a two-dimensional plane as shown in Figure 3(b), Figure 3(c) and Figure 4(b).
Figure 3 and Figure 4 allow to identify in a simpler way the maximum ion range projected, that is, the maximum depth reached by an ion until it stops. Table 5 reports the maximum ion range projected in the implantation of Ti ions at 10 KV for 5 minutes and 10 minutes, and Table 6 reports the maximum ion range projected in the implantation of Ti ions at 10 KV, and 20 KV.

![Figure 3](image1.png)

**Figure 3.** (a) $R_{\text{cl}}$ profile of Ti ion-implanted at 10 KV; The final position of Ti ions implanted for (b) 5 minutes, and (c) 10 minutes.

![Figure 4](image2.png)

**Figure 4.** (a) $R_{\text{cl}}$ profiles of Ti ion-implanted at 10 KV and 20 KV. The final position of Ti ions implanted at (b) 10 KV and 20 KV.
Table 4. The maximum concentration of Ti ion-implanted at 10 KV and 20 KV.

| High voltage (KV) | Highest concentration depth (Å) |
|-------------------|---------------------------------|
| 10                | 50                              |
| 20                | 80                              |

Table 5. Maximum range projected of Ti ion-implanted at 10 KV for 5 minutes and 10 minutes.

| Discharge time (min) | Maximum ion range projected (Å) |
|----------------------|---------------------------------|
| 5                    | 250                             |
| 10                   | 250                             |

Table 6. Maximum range projected of Ti ion-implanted at 10 KV and 20 KV.

| High voltage (KV) | Maximum ion range projected (Å) |
|-------------------|---------------------------------|
| 10                | 250                             |
| 20                | 435                             |

3.4. Concentration profiles

Figure 5 shows that the estimated concentration magnitude is greater for longer exposure times, but the higher concentration region locations are the same; these values are reported in Table 7.

![Estimated profiles of Ti ions concentration implanted at 10 KV for 5 minutes and 10 minutes.](image)

Table 7. Location and magnitude of the highest concentration in Ti ions implanted at 10 KV.

| Exposure time (min) | Maximum concentration (Atoms/cm³) | Highest concentration region depth (Å) |
|---------------------|-----------------------------------|----------------------------------------|
| 5                   | 1.6181e+28                       | 50                                     |
| 10                  | 3.2363e+28                       | 50                                     |

4. Conclusions

The concentration of titanium ions implanted in a low alloy steel at a determined discharge voltage increases with the exposure time of the surface due to the implantation dose depends directly on the discharge time. The location of the highest concentration region and the implanted ion ranges increase with the discharge voltage but are invariant with the exposure time at a determined discharge voltage. The Rc/d profiles show that the location of the highest concentration region and the implanted ion ranges are greater for higher discharge voltages but do not guarantee the concentration values will have the same behavior.
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