Analysis of the concentration of nitrogen and titanium ions simultaneously implanted into chromium-molybdenum low-alloy carbon steel

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Abstract. The concentration of nitrogen and titanium atoms that are introduced into the subsurface layers of chromium molybdenum low-alloy carbon steel exposed to the ion implantation surface modification method is estimated in this article using computational tools and the experimental parameters of the process; due to the difficulty of analyzing the trajectories and the distribution of the ions in the matter in an analytical or experimental way, simulation methods were used to effectuate this study. Additionally, experimental tests were carried out with implantation times of 5 minutes and 10 minutes and the behavior of both cases was compared. The results obtained made it possible to characterize the implantation processes through distribution profiles with respect to depth and showed that varying the exposure time did not reach greater depths. However, by increasing the discharge voltage parameter, it is estimated that the projected range increases and the region of greatest concentration are located deeper.

1. Introduction

Increasing the useful life in the service of materials is the main objective of surface modification processes. Nowadays, through different processes such as physical vapor deposition (PVD) [1,2], chemical vapor deposition (CVD) [2,3], anodizing [4], among others, the surface properties of the material are improved without altering the internal atomic structure; so that has sparked the interest of science, engineering, and nanotechnology in the development of new surface modify methods by ion implantation.

On the other hand, around the 1970s, Dearnaley [5-7] and Hartley [8] based on the ion implantation process, which consisted of introducing impurities on the surface of materials by bombarding ions by electric discharges, found that with certain experimental parameters the tribological properties in metallic materials increase. The most representative surface modification techniques are the ion beam implantation (IBI) [5] and the techniques based on plasma technology: plasma immersion ion implantation (PIII), plasma source ion implantation (PSII) [9], and the three-dimensional ion implantation (3DII) [10-12]. In 3DII, the substrate is exposed to high-voltage pulsed discharges at low pressures, where the quasi-monoenergicity of the ions and the normal angle of incidence with respect to the surface provide high ions, density implanted in short times [10-12].
Therefore, owing to the difficulty of studying the trajectories, distribution, and interactions of the ions with the target atoms by analytical or experimental methods, the numerical models have provided a solution to perform this analysis. Currently, two simulation methods stand out that allows estimating the interaction of ions with matter, the Monte Carlo method [13] and the molecular dynamics [13,14]. In the present investigation, the concentration, stopping, and range of nitrogen (N) and titanium (Ti) ions implanted into chromium-molybdenum low-alloy carbon steel is estimated by means of SRIM/TRIM software [15,16].

2. Materials and methodology
The experimental development implemented in this research work is described as follows.

2.1. Samples’ preparation
The surfaces of the cylindrical samples of chromium-molybdenum low-alloy carbon steel, with a diameter of 18.1 mm and height of 2.7 mm, were prepared according to ASTM E3-11 [17] and ASTM G1-03 [18] standards.

2.2. Spectrometry analysis
The chemical analysis of the samples was carried out employing the optical emission spectrometry (OES) method, identifying and quantifying the elemental composition of the steel before the ion implantation.

2.3. Surface modification
First, the samples were introduced into the JUPITER reactor chamber and a sputtering process was made for 15 minutes in an argon atmosphere at 1.7 Pa and a voltage of 5 KV. This process has the purpose of reducing impurities on the surface. After sputtering, an atmosphere of N and Ti was created, evaporating a Ti cathode by a voltage generator installed inside the JUPITER chamber and supplying N gas. The Ti cathode evaporator works with volt-amperic characteristics that ensure the stable operation of the electric arc (see Table 1).

Once the N and Ti atmosphere is generated, the high voltage pulsed discharges at low pressure are ignited according to 3DII [12], producing ionization of the particles in the vacuum chamber and directing them towards the target [19]. Table 1 reports the parameters established in the implantation of N and Ti ions.

| Table 1. Ti+N ion implantation parameters. |
| Parameter       | Magnitude       |
|-----------------|-----------------|
| Implantation time (min) | 5 and 10       |
| High voltage (KV)        | 10              |
| Pulse duration (μs)      | 250             |
| Pulse frequency (Hz)     | 30              |
| Arc current (A)          | 140             |
| Arc voltage (V)          | 16 ~ 18         |
| Pressure (Pa)            | 0.920 ~ 1.080   |

2.4. Dose calculation
The implantation dose in 3DII surface modification processes is estimated from the electrical discharge pulses and experimental parameters [20,21]; therefore, using the treatment conditions, the characteristic values of ionization, the ratio between electric and ionic currents and a web application [22,23] designed with the aim of calculating an approximate value of the total charge in an electric discharge, a considerable implanted ions value was obtained.
2.5. Simulation

SRIM/TRIM [15,16] is a set of programs that calculate the range and stopping of ions in matter using quantum mechanical models of ion-atom collisions. This Monte Carlo simulation software is continuously updated and is based on the monitoring of random trajectories, obtaining histograms that estimate the implantation profiles from statistical algorithms. Additionally, SRIM/TRIM [15,16] provides data files where the interaction phenomena are detailed, facilitating the analysis of the ion implantation process.

2.6. Ions' concentration

The estimated concentration of implanted N and Ti ions is calculated by multiplying the implantation dose and the distribution profile which shows the ratio of the concentration and the dose as a function of depth ($R_{c/d}$). The $R_{c/d}$ profiles are plotted using the data from RANGE_3D.txt file and Equation (1) [24].

$$R_{c/d} = \frac{f_x}{N} \Delta x,$$

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 [24].

3. Results and discussions

Following was reported the results obtained and discussions:

3.1. Spectrometry analysis

Table 2 shows 20 representative elements and the respective percentage of the chemical composition of the chromium molybdenum low alloy carbon steel samples, selected from the OES analysis, and it was confirmed that were manufactured with AISI/SAE 4140 because they comply the ASTM A29/A29M-15 standard [25].

| Element | %   | Element | %   | Element | %   | Element | %   |
|---------|-----|---------|-----|---------|-----|---------|-----|
| C       | 0.4520 | Mo     | 0.1930 | Co     | 0.0077 | W      | 0.0210 |
| Si      | 0.2930 | Ni     | 0.0320 | Mg     | 0.0061 | S      | 0.1500 |
| Mn      | 0.6870 | Cu     | 0.0800 | Sb     | 0.0100 | Al     | 0.0050 |
| P       | 0.0160 | As     | 0.0055 | Ta     | 0.0640 | Pb     | 0.0110 |
| Cr      | 0.9630 | Bi     | 0.0480 | V      | 0.0097 | Fe     | 96.9000 |

3.2. Dose calculation by a web application

Figure 1, Figure 2, Figure 3, and Figure 4 show the estimated N and Ti dose calculation with exposure times of 5 minutes and 10 minutes. Web application requires inputting the implantation parameters, the value of the ionic charge number [26,27] and the secondary emission coefficient [27,28] to get the results. Nevertheless, it is relevant to consider that the most abundant ion in nitrogen ionization is N$^+$ [27]; therefore, the nitrogen estimated dose by the web application is multiplied by a factor of 2 because the ion is diatomic. On the other hand, the coefficients of secondary emission of Ti ions in low-alloy steels have not yet been reported, then, to estimate the dose, the values of the behavior of Ti ions in another metallic material were chosen [24,29].
Figure 1. Estimation by web application of dose of N ions implanted for 5 minutes.

Figure 2. Estimation by web application of dose of Ti ions implanted for 5 minutes.

Figure 3. Estimation by web application of dose of N ions implanted for 10 minutes.
Table 3 shows that the results of surface dose implanted during 10 minutes is twice the surface dose implanted during 5 minutes [23,24].

| Implantation time (min) | \( D_N \) (ions/cm\(^2\)) | \( D_Ti \) (ions/cm\(^2\)) | \( D_{N+Ti} \) (ions/cm\(^2\)) |
|-------------------------|-----------------------------|-----------------------------|-----------------------------|
| 5                       | \( 2.8125 \times 10^{22} \) | \( 1.3204 \times 10^{22} \) | \( 4.1329 \times 10^{22} \) |
| 10                      | \( 5.6250 \times 10^{22} \) | \( 2.6408 \times 10^{22} \) | \( 8.2658 \times 10^{22} \) |

3.3. Concentration-dose profiles

Figure 5(a) and Figure 6(a) show the \( R_{c/d} \) profiles plotted using RANGE_3D.txt data files and Equation (1) [24]; these distribution profiles make it possible to locate the estimated region of highest concentration in ion implantation processes (see Table 4).

Further, another use of the data contained in the RANGE.txt file was found; by plotting the final location of the implanted ions with respect to the point of incidence on the target, two dimensional planes of distribution are obtained (Figure 5(b) and Figure 6(b)) [24]. Table 4 shows the maximum projected ion range in the N and Ti ion implantation at 10 KV and 20 KV.

Figure 5. Ion distribution profiles at 10 KV. (a) \( R_{c/d} \) profile; (b) Final location of ions in 2D plane.
Figure 6. Ion distribution profiles at 20 KV. (a) $R_{cd}$ profile; (b) Final location of ions in 2D plane.

Table 4. N and Ti ions.

| High voltage (KV) | Highest concentration depth (Å) | Maximum projected range (Å) |
|-------------------|---------------------------------|----------------------------|
| 10                | 50                              | 495                        |
| 20                | 80                              | 423                        |

3.4. Concentration profiles

Figure 7 shows that longer implantation times produce greater concentrations, but the highest concentration regions are located at the same depth (see Table 5).

Figure 7. N+Ti Estimated concentration. (a) 5 minutes; (b) 10 minutes.

Table 5. N+Ti ions maximum concentration vs location.

| Implantation time (min) | Concentration (Atoms/cm$^2$) | Depth (Å) |
|-------------------------|-------------------------------|-----------|
| 5                       | $2.65 \times 10^{28}$         | 51        |
| 10                      | $5.30 \times 10^{28}$         | 51        |
4. Conclusions
It is estimated that the concentrations of nitrogen and titanium atoms implanted simultaneously in chromium molybdenum low-alloy carbon steel increase with respect to the implantation time; nonetheless, the ions do not reach greater depths even if the material is exposed for a longer time to the surface modification process.

On the other hand, the distribution profiles of ion implantation at a higher discharge voltage estimate that the region of greater concentration is located in deeper regions and that the projected range of ions is greater.

Acknowledgments
The authors greatly acknowledge the research group of “Fisica y Tecnologia del Plasma y Corrosion” and to the “Laboratorio de Espectroscopía Atómica Molecular” from the Universidad Industrial de Santander, Colombia, for supported this research work. This research project was partially financed by the Colombian agency Colciencias through doctoral scholarship 617.

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