

Study of H₂/N₂ Mixture Plasma Treatment on the AISI 1045

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Abstract In the present work, we analyzed the effect of the plasma treatment of 80% H₂/20% N₂ mixture plasma over the AISI 1045 steel. To produce the plasma, an AC discharge of 0.1 A at 350 V was produced at a total pressure of 3.0 Torr. The mixture plasma was analyzed using optical emission spectroscopy (OES), in the wavelength range of 200 to 1100 nm. The principal species observed in the plasma were NH, N₂, N₂⁺, H₂, and H α . The electron temperature and ion density have been measured using a double Langmuir probe. The samples of steel were treated by plasma at different discharge times, between 3 and 12 h, at the same pressure and AC parameters (0.1 A and 350 V). The treated samples were characterized using X-ray analysis, finding the phases gamma and epsilon of iron nitride. The thickness of the nitrated layers was measured using a scanning electron microscope (SEM). From the images obtained, it is possible to appreciate the interphase between the nitrated layer and the steel matrix. The relationship between the morphology of the surface of nitrated steel and the wetting was analyzed by measuring the contact angle between the surface and a drop of 5 μ L of distilled water. The contact angle of the drop increased with the increase of plasma treatment time. The control sample without treatment presented a smaller angle, and after the treatment the surfaces of the steel became hydrophobic. This may be related to the morphology change of the steel surface produced by plasma treatment.

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1. INTRODUCTION

Due to the low commercial costs of AISI 1045 steel, this is one of the most popular engineering metals used in different industrial sectors. Among its most common applications is the manufacture of machine elements such as arrows, bolts, screws, and crankshafts. AISI 1045 steel is considered a medium alloy; the alloys present give the steel good mechanical properties, such as fatigue behavior and wear and corrosion resistance [2, 4-6, 8]. In spite of the good properties that 1045 steel presents, it is necessary to realize different types of conventional thermal treatments, the most applied on this steel being tempering, to give the alloy better mechanical properties. In recent years, the need to improve steel has experienced a new trend, which is known as surface modification of materials, since the properties acquired by surface modification can provide advantages in specific applications [12]. For steel's superficial modification, one of the most applied techniques is plasma-assisted nitriding. With this modification process, it is possible to harden and improve the mechanical properties in the first superficial atomic layers of the steel by the process of nitrogen diffusion into the inner alloy, resulting in the formation of multilayers with properties other than the metal matrix [5, 10]. The layer known as a nitrided layer is thin and consists of iron nitrides in different phases. The phases that constitute the nitrided layer depend on the present percentage of nitrogen, and its precipitates of second phases are $\text{Fe}_{2,3}\text{N}$ and/or Fe_4N [6, 7]. During the nitriding process, the interaction of plasma and steel, the temperature reached is between 500 and 600°C, so that no phase transformations occur in the steel.

In recent years, the interactions between a solid surface and a liquid have been investigated. Those interactions were investigated by measuring the contact angle between them, which indicates the degree of wettability in the interaction of the solid and the liquid [1]. Knowing the mechanism that prevails in this type of interaction between a flat and a liquid–solid phase is important in certain operations in specific industrial applications, such as lubrication of machine elements and liquid coatings. In order to determine the appropriate application for nitrided steel knowing its contact angle, it is necessary to determine what type of angle is formed: an angle greater than 90° indicates a hydrophobic interface, whereas an angle less than 90° indicates a hydrophilic interface. The behavior of wettability in solids depends mainly on the chemical composition, physical characteristics, interactions between the molecules present in the two substances, and the roughness of the surface [1, 9, 13].

In this work, we analyze the surface modification of the 1045 steel currently used in a local industry, after a nitriding process. The surface modification was

evaluated using X-ray diffraction, measuring the thickness of the diffusion layer by a scanning electron microscope (SEM) and calculating the contact angle of a drop shape of distilled water. Also, the characterization of 80% H₂/20% N₂ plasma was estimated by optical emission spectroscopy (OES) [3, 11] and the electrical properties of the plasma were studied by a Langmuir probe.

1.1 Experimental Setup

The preparation of the samples obtained from the cold-rolled AISI 1045 steel involved the application of a normalized heat treatment on the steel. The conditions at which the treatment was carried out were as follows: temperature of 860°C for a period of 30 minutes inside a muffle of resistors. The cooling process was carried out in air. With the heat treatment, the grain size of the AISI 1045 steel was refined. The standard samples were cut to the following dimensions: 15 × 15 × 5 mm thick. Later, one of the faces was abraded with abrasive sands of silicon carbide of different grain sizes, from 120 to 2000 emery paper. Finally, the surface of the steel was covered with a velvet cloth and 1 μm alumina was used as an abrasive medium, finally obtaining 0.3 μm particle size. The chemical composition of 1045 steel is shown in Table 1, which was obtained by spark spectroscopy.

Table 1: Chemical composition (wt.%) of AISI 1045 steel.

| Steel type | Fe | C | P | S | Ni | Al | Co | Mn | Si |
|------------|----|-------|--------|--------|--------|--------|--------|-------|--------|
| AISI 1045 | 97 | 0.534 | 0.0283 | 0.0079 | 0.0905 | 0.0272 | 0.0108 | 0.942 | 0.1770 |

Prior to the treatment of steel, the samples were washed in an ultrasonic cleaner submerged in acetone for 30 min. The application of plasma-assisted nitriding, discharge monitoring, and measurements of electron density and electron temperature were carried out inside a discharge chamber of our own design (Figure 1). Two stainless steel electrodes, 30 mm in diameter and 3 mm thick, were located in the center of the chamber with a separation distance between them of 5 mm. The chamber was evacuated until a base pressure of 3.6×10^{-2} Torr. The 80% H₂ and 20% N₂ gas mixture is injected and evacuated a couple of times from the inside of the chamber, in order to remove residual gases inside the system and ensure that there is only the desired gas mixture. Subsequently, the gas was injected again until the working pressure of 3 Torr was reached. The conditions for nitriding were as follows: AC discharge was used in the treatment with a voltage of 350V, current of 0.1 A, and treatment times of 3, 6, 9, and 12 h. We ensured that the conditions for generating the plasma were the same for all 1045 steel treatments.

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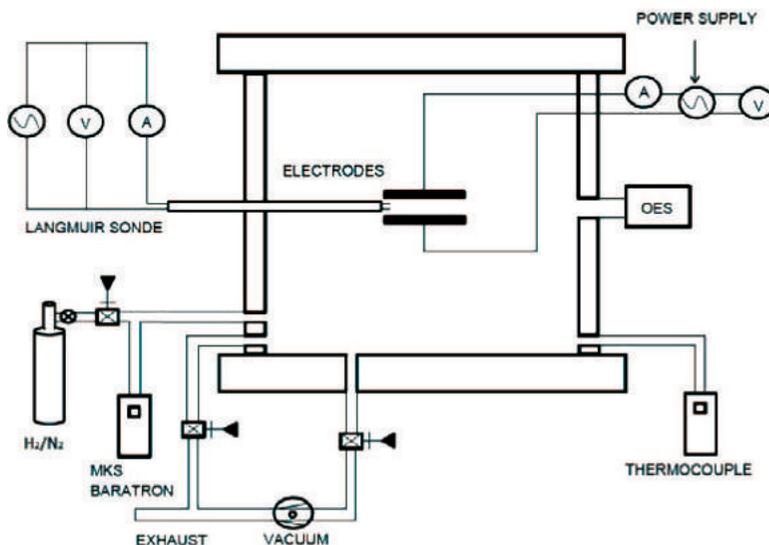


Figure 1: Schematic of the experimental discharge system and data acquisition.

After the plasma-assisted thermochemical treatment, the treated and untreated samples were analyzed microstructurally using a SEM; from this technique, the thicknesses of the nitrated layers were also determined. The nitrated samples were encapsulated in a resin using the Taper Technique, which is useful for preserving thin layers and coatings. Second-phase precipitates were determined using X-ray diffraction with a Bruker D2 PHASER diffractometer using Cu K α radiation with $\lambda = 1.54184 \text{ \AA}$. The sweep angle was between 30° and 100° .

Measurements of the contact angles between the surfaces of the untreated and nitrated samples were performed using a nonstandardized method on a mirror-polished surface. The measurements were carried out immediately after each treatment. Using a micropipette, a drop of distilled water of $5 \mu\text{L}$ was dropped onto the surface of the samples, allowing the drop to stabilize, and an image was captured using a microscope camera. The measurement of the contact angle between the surfaces of each of the samples and their respective drops was measured with software.

An optical fiber (solarization-resistant UV and fiber diameter of $400 \mu\text{m}$) connected to a high-resolution spectrometer (Ocean Optics Inc., spectrometer model HR2000CG-UV-NIR) was used in the plasma monitoring process. The inlet and outlet slots were of $5 \mu\text{m}$ aperture. The process for data acquisition was performed with an integration time of 100 s. The optical fiber was placed in such a way that it could collect the light emitted by H₂-N₂ plasma.

The Langmuir probe that was used for the measurements of the electron density and temperature consisted of two tips of tungsten wire of 0.25 mm diameter. The tips of the double probe were aligned parallel to the electrodes where the discharge was generated. The probe was connected to a DC power source; the voltage applied to the probe was supplied manually, performing a scan from +50 V to -50 V. The current supplied to the probe was monitored with a multimeter and the scanning time for each measurement of the I-V curve was between 10 and 15 minutes. The final I-V curve was the average of five measurements. Finally, the temperature and the density of the plasma were calculated from the curve.

2. RESULTS

2.1 Metallographic Characterization

In Figure 2, a micrograph obtained by the SEM, which corresponds to the cross section of the 1045 steel, is displayed. The image shows the effect of the chemical attack on the surface by Nital 2 reagent (2% nitric acid in methyl alcohol). In this figure, the microconstituents of steel 1045 can be observed.

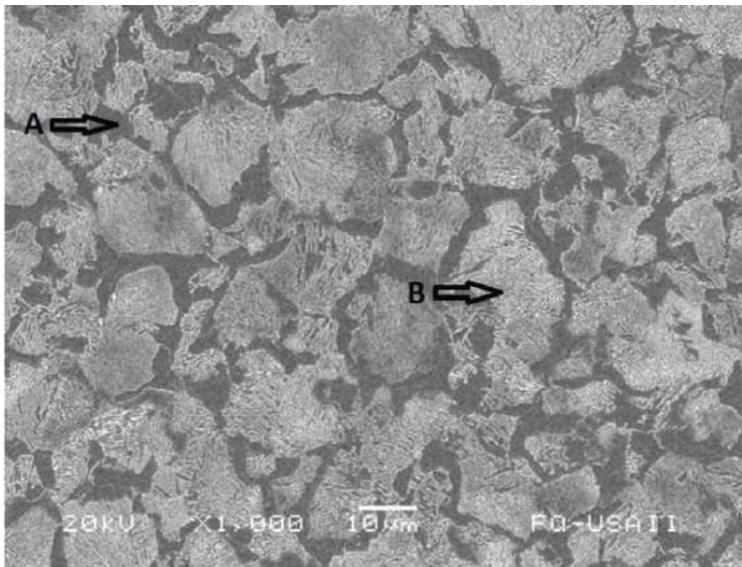


Figure 2: SEM micrograph of AISI 1045, in which the pearlite phases (lighter areas) (B) and ferrite (the darker parts) (A) as microconstituents of steel are presented.

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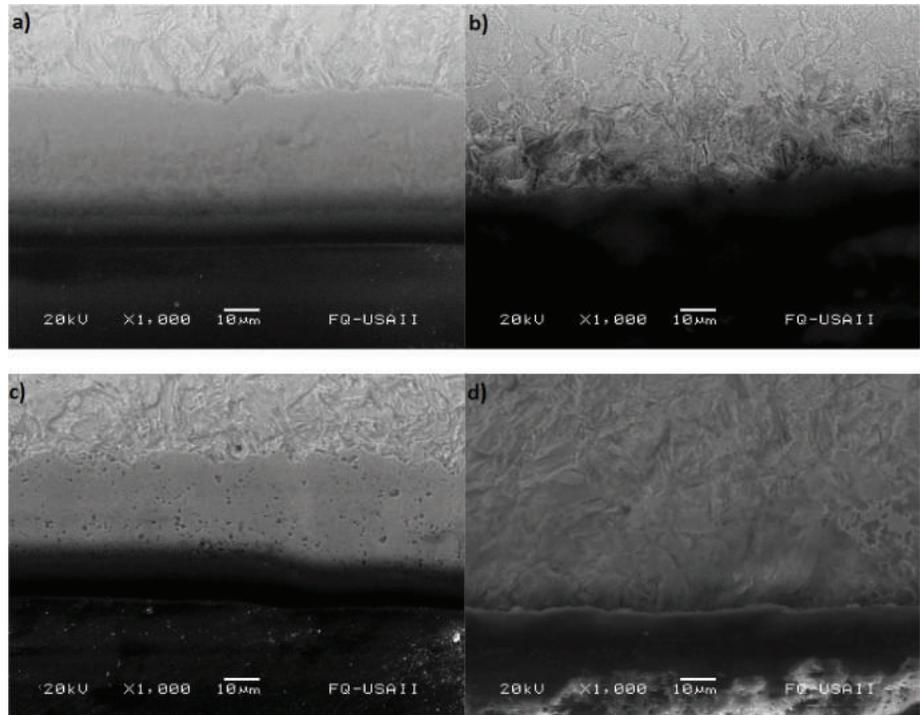


Figure 3: SEM micrographs of the different thicknesses of the layers nitrided at different times: (a) nitrided for 12 h, (b) nitrided for 9 h, (c) nitrided for 6 h, and (d) nitrided for 3 h.

In Figure 3, the micrographs of the nitrided steel obtained by SEM are shown, in which the nitrided layer obtained at different treatment times can be observed. In Figure 3(d), it is observed that, for a treatment time of 3 h, the nitrided layer (darkened zone) was not completely formed; however, the steel reacted chemically with the nitrogen, to form some nitrides. In Figure 3(c), it is observed that, in the sample nitrided for 6 h, the nitride layer was formed. In the sample nitrided for 9 h (Figure 3(b)), two distinct phases of steel are observed, one slightly darker (nitride layer) and the other in a lighter gray tone, which corresponds to the steel matrix. Finally, Figure 3(a), corresponding to treatment for 12 h, also shows the nitrided layer. In this sample, we can observe three phases, the diffusion zone of N, in which the nitrides were formed, with a combined layer of oxides (Fe_3O_4) and nitrides in the phases ϵ and γ , whose presence will be corroborated by X-ray diffraction analysis. The thicknesses of the obtained layers are listed in Table 2.

Table 2: Nitrided layers' thicknesses.

| Treatment time | Thickness (μm) |
|----------------|----------------|
| 3 h | ---- |
| 6 h | 34.75 |
| 9 h | 25.06 |
| 12 h | 35.14 |

2.2 X-Ray Diffraction Analysis

The diffraction patterns of the second-phase precipitates formed in the nitrided samples of AISI 1045 steel obtained for each sample at different treatment times are shown in Figure 4. For the sample without treatment, two main peaks of the α phase, corresponding to the element Fe, can be observed. For the samples treated by plasma, the diffraction patterns confirm the surface modification of the samples. As the first phase of the process, a nitrogen-rich phase (FeN) is formed; this condenses on the surface of the metal. This phase undergoes disintegration, releasing nitrogen that diffuses into the matrix of the sample, with some N returning to the plasma. As N increases in concentration on the surface of the steel and with its subsequent diffusion, nitrides are formed, which

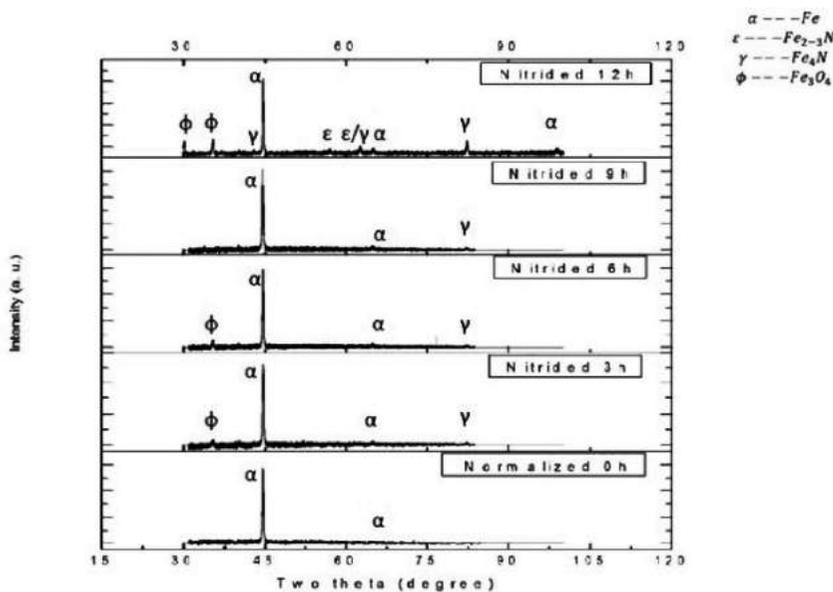


Figure 4: X-ray patterns of the AISI 1045 steel at different times of plasma treatment.

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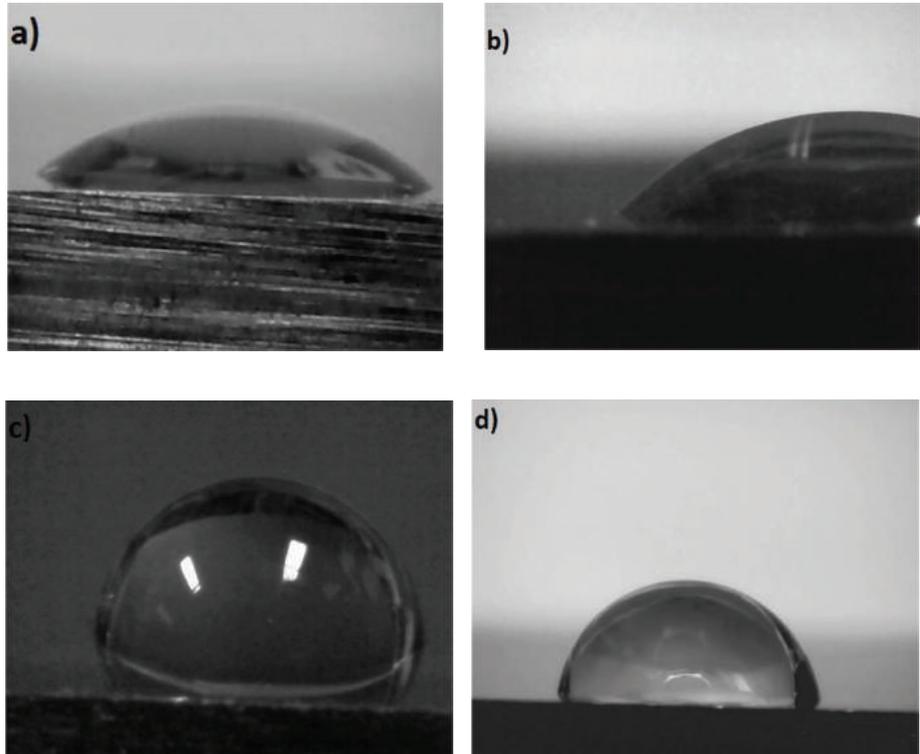
is confirmed by the peaks corresponding to second-phase precipitates, formed by the addition of nitrogen ions from the plasma that reacts thermochemically with Fe to form γ -Fe₄N and ϵ -Fe_{2,3}N phases. In Figure 4, it can be observed that the intensity of the different Fe phases (nitrides), as well as the γ phase, increases as the treatment time increases. The phase ϵ -Fe_{2,3}N can be attributed to the duration of the treatment that favored the formation of these phases of Fe nitrides, as well as the N content present on the surface of the sample. FeO was also observed in the treated samples.

2.3. Water Contact Angle Measurements

The contact angles were measured on the untreated and treated samples by the plasma. The angles calculated from Young's equation (1) are shown in Table 3.

$$\gamma_{SV} = \gamma_{LS} + \gamma_{LV} \cos\theta \quad (1)$$

The calculated angles indicate that there was a surface change in the AISI 1045 steel due to the thermochemical interaction with the plasma.



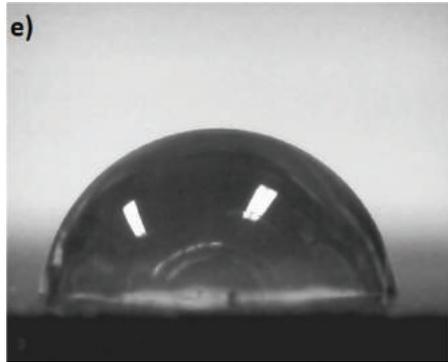


Figure 5: Angle of contact of the drop of distilled water on the surface of plasma treated AISI 1045 steels at different times: (a) sample without treatment, (b) 3 h treatment, (c) 6 h treatment, (d) 9 h treatment, and (e) 12 h treatment.

The contact angles [1] present a decreasing behavior after treatment with plasma, indicating a more hydrophobic behavior on the surfaces of treated steels. It can be explained by the change in the surface of the steel produced by the treatment that the formation of the second-phase precipitates (γ and ϵ) produces physical and chemical changes on the surface, which were confirmed by X-ray diffraction.

Table 3: Contact angles.

| Treatment time | Contact angle |
|----------------|---------------|
| 0h | 23.26° |
| 3h | 41.47° |
| 6h | 88.15° |
| 9h | 72.31° |
| 12h | 73.22° |

2.4 OES

The OES of the 80% H₂/20% N₂ plasma at a pressure of 3 Torr was investigated. The spectrum obtained from the plasma is shown in Figure 6. It can be observed that the main species were NH ($A^3\Pi - X^3\Sigma^-$) at 336.10 nm; N₂ ($C^3\Pi_u - B^3\Pi_g$) at 357.69 nm; N₂⁺ ($B^2\Sigma_u^+ - X_2\Sigma_g^+$) at 391.44 nm and 427.81 nm; N₂ ($B^3\Pi_g - A_3\Sigma_u^+$) at 562.11 nm; H₂ at 487.30 nm, 519.64 nm, 561.25 nm, and 563.48 nm; and H α at 656.28 nm.

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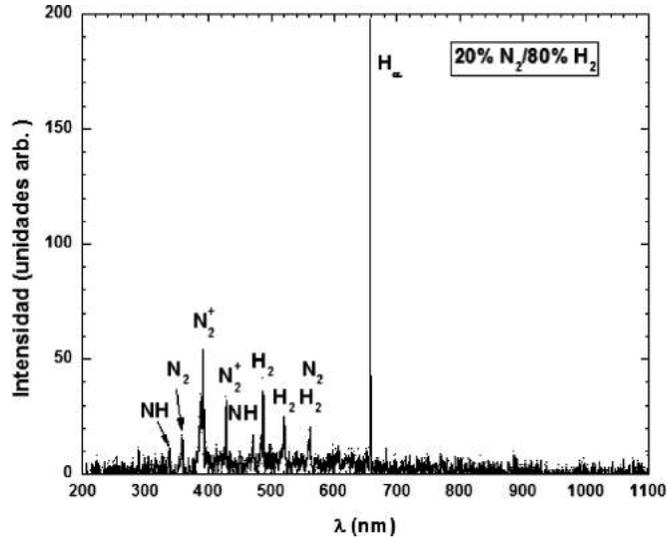


Figure 6: The OES of 80% H₂/20% N₂ plasma at 3 Torr.

2.5 Electrical Characterization

The electron temperature (T_e) and ion density (n_i) of the H₂-N₂ plasma at 3 Torr were measured by a double Langmuir probe. T_e and n_i were obtained by adjusting the I-V experimental curve with the theoretical curve. Using the Saha's equation (2) and Boltzmann's equation (3) to obtain T_e and n_i .

$$\frac{n_i^2}{n_N} = 2\pi m_e k T_e^2 e^{\left(\frac{-I}{kT}\right)} \quad (2)$$

Where:

I = potencial de ionización,

$n_i = n_e$ = ion density

n_N = density of neutral atoms

h = Planck's constant

k = Boltzmann's constant

$$T_e = \frac{E_2 - E_1}{k} \left[\ln \frac{I_1 \lambda_1 g_2 A_2}{I_2 \lambda_2 g_1 A_1} \right]^{-1} \quad (3)$$

Where:

I = Intensity of radiation.

A = Probability transition for spontaneous emission of Einstein (S^{-1}).

g = Statistical weights.

k = Boltzmann's constant.

T_e = Electronic temperature.

The adjustment procedure yielded the following results: $T_e = 13.51$ eV and $n_i = 3.98 \times 10^9$ cm⁻³.

CONCLUSIONS

The AISI 1045 steel samples treated by H₂/N₂ mixture plasma presented surface modification, which was confirmed by X-ray diffraction spectra. The spectra showed the surface change of the samples, which are the ϵ -Fe_{2.3}N and γ -Fe₄N second-phase precipitates of the iron nitrides. In the sample treated for 12 h, the ϵ phase is observed with a higher intensity than at the other treatment times, which can be attributed to the duration of the treatment and the concentration of nitrogen on the surface.

The contact angles measured on the surface of nitrated steels were reduced by plasma treatment, turning them into a hydrophobic surface. The sample nitrated for 6 h (88.15°) was the one that showed a greater hydrophobicity behavior than the rest. The samples nitrated for 9 and 12 h had a contact angle less than that of the sample treated for 6 h; this can be attributed to the change in the chemical compounds present on the surface of these samples, mainly to the ϵ phase and the formation of FeO.

The main species observed in a glow discharge H₂/N₂ plasma, using OES, were H₂, N₂, and the molecular bands of NH. By the technique of double Langmuir probe, the electron temperature and the ion density were found to be $T_e = 13.51$ eV and $n_i = 3.98 \times 10^9$ cm⁻³, respectively.

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