

Ionic Nitriding of an Experimental Microalloy Steel with High Resistance

O. Xosocotla, O. Flores, B. Campillo, H. Martínez

Abstract— A high-resistance experimental microalloyed steel was treated using ionic nitriding at different times—3, 6, 9, 12, and 18 h—with a mixture of gases of 20% N₂ and 80% H₂ at 1 Torr of pressure and at a voltage of 270 V. According to the microhardness tests and the analysis of nitrogen concentration after the ionic nitriding process, it was found that the optimal time is 12 h. The 3.34% weight percentage of alloying elements was not enough to form nitrogen compounds. This fact reduces the formation of the nitrated layer, which is why it is difficult to observe the nitrated layer by means of a chemical attack. The thickness of the nitrated layer was determined using fractography and energy-dispersive X-ray (EDX) spectroscopy analysis.

Index Terms— Microalloyed steel, Ion nitriding, Mechanical properties.

I. INTRODUCTION

Ionic nitriding is a process that uses a direct current discharge for ionizing a mixture of gases enriched with nitrogen. The diffusion of nitrogen toward the nucleus initially forms a diffusion zone enriched with nitrogen. In this region, a compound layer is formed, commonly composed of grains of γ' -Fe-N_(1-x) and ϵ -FeN_(1-x) [1–3, 9]. The process of ionic nitriding improves the surface properties, such as the wear resistance, oxidation, and surface hardness. Ion nitriding is a process that is widely used in the industrial field, since several pieces are in contact with corrosive environments [1, 2, 8]. The mechanical properties of ferrous materials can be modified using their forming process. For example, when steel is rolled, residual stresses form, which can appear as stresses in compression or tension owing to the processing temperature and pressure of the rollers on steel. The latter influences the resulting mechanical properties, and they differ according to the direction in which the test is performed [4]. In recent years, there have been advances in the manufacture of new types of steel to reduce the weight of vehicles and increase their safety [5, 10]. Microalloyed steels were developed to be used in industries such as the automotive industry, since their mechanical properties meet all the requirements. For a steel to be classified as a microalloyed

steel, the content of the alloying elements must be approximately 0.1% by weight, which can be niobium, titanium, or vanadium, which makes the mechanical properties of microalloyed steels superior to those of carbon steels. In this work, an investigation of the performance of a high-resistance experimental microalloyed steel, which contains approximately 3.34% alloying elements by weight, was carried out. This experimental steel was subjected to an ionic nitriding treatment at different times—3, 6, 9, 12, and 18 h—with a mixture of gases of 20% N₂ and 80% H₂ at a pressure of 1 Torr and a voltage of 270 V. In order to monitor the changes in the surface due to the nitriding process, a microdurometer was used, as well as a scanning electron microscope with energy-dispersive spectroscopy.

II. EXPERIMENTAL METHOD

2.1. Materials

Samples of 2.5 × 1.0 × 0.5 cm were cut from a rod of a high-strength experimental microalloyed steel, which had the following chemical composition: 0.0208 wt.% C, 0.2426 wt.% Si, 1.042 wt.% Mn, 0.003 wt.% P, 0.00297 wt.% S, 0.42643 wt.% Cr, 0.17 wt.% Mo, 1.334 wt.% Ni, 0.05147 wt.% Al, 0.00477 wt.% Co, 0.01077 wt.% Cu, 0.0246 wt.% Nb, 0.0154 wt.% Ti, 0.00013 wt.% V, 0.00523 wt.% Pb, and 96.6667 wt.% Fe.

2.2. Ionic Nitriding Treatment

The samples were prepared prior to the nitriding process. A fine polishing procedure was performed with 0.3-micron alumina. Excess alumina was removed using an ultrasonic bath with absolute ethanol. Once the samples were cleaned with absolute alcohol, they were placed in a chamber for ionic nitriding for the durations previously mentioned.

The ion nitriding system is shown in Fig. 1, which uses two stainless-steel circular plate electrodes, with a thickness of 1 mm and a diameter of 30 mm. These electrodes are positioned horizontally at the center of the chamber, with a 4 mm gap between them. The gas mixture was injected into the chamber by means of a flowmeter; the same gas connection was used for the pressure sensor. During the installation process, a voltage of 280 V and a current of 0.27 A were maintained. The base pressure of the chamber was maintained at 3.0×10^{-2} Torr using a mechanical pump (LAV-3; Fischer Technical Company, Roselle, IL, USA), performing several purges with N₂ at 1 torr to remove the residual gases. The nitriding process was carried out with a mixture of 20% N₂ and 80% H₂ for 3, 6, 9, 12, and 18 h. Figure 2 shows the plasma formed by the ionized gas due to a discharge on a sample of experimental microalloyed steel.

Oscar Xosocotla is a master's degree student at the Faculty of Chemistry, National Autonomous University of Mexico, Mexico City, Mexico

Oswaldo Flores, Dr. in Chemical Metallurgical Engineering, graduated from the National Autonomous University of Mexico. Currently in the Institute of Physical Sciences and professor of postgraduate of the Faculty of Chemistry of the UNAM

Bernardo Campillo, Dr. in metallurgical chemistry, graduated from the National Autonomous University of Mexico

Horacio Martínez Valencia received the Ph.D. degree from Facultad de Ciencias, Universidad Nacional Autónoma de México (UNAM), México City, México

2.3. Microhardness Tests

Microhardness was measured on the nitrided surface and on a cross-sectional area of the nitrided surface (microhardness profile), with a load of 300 and 10 g, with a penetration time of 20 s (see Fig. 3).

2.4. Fractography

The samples were fractured with liquid nitrogen (-195.8°C) in the transverse direction (TD) in relation to the nitrided layer. In addition, the microhardness profile was used to estimate the thickness of the nitrided layer, since with the chemical attack, it could not be revealed.

2.5. Mechanical Tests

The test specimens were machined according to ASTM-08 [11] in order to perform tension tests. These tests were performed in the longitudinal direction (LD) and transverse direction (TD) of the experimental microalloyed steel, in relation to the rolling process in the samples without treatment (see Fig. 4).

2.6. Nitrogen Concentration (EDX)

A line scan was performed to obtain the nitrogen concentration profile at $50\ \mu\text{m}$ from the nitrided surface toward the nucleus (see Fig. 5).

2.7. Metallography

A chemical attack was performed using Nital 3% in order to obtain the phases present in the experimental microalloyed steel without treatment. Images were taken with an Olympus PMG3 optical microscope (Olympus, Tokyo, Japan).

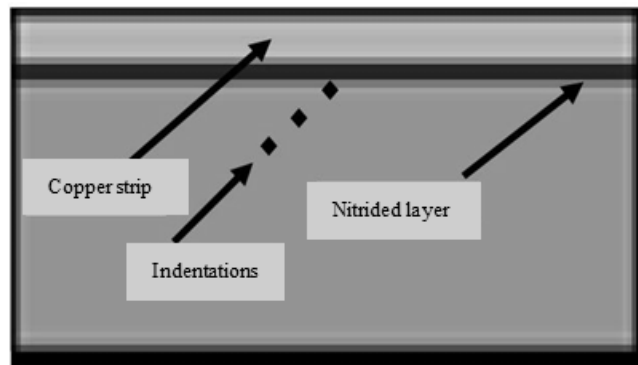


Fig. 3. Microhardness profile.

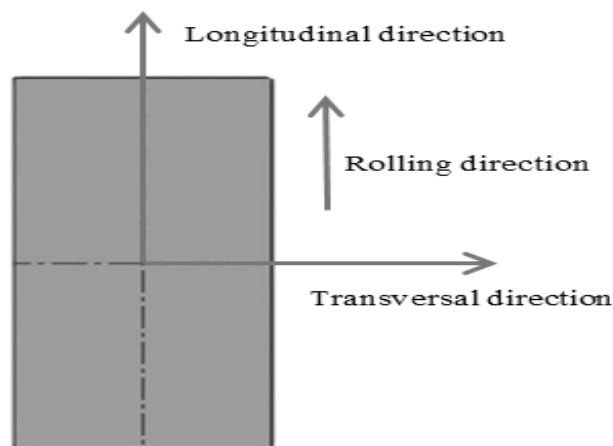


Fig. 4. TD and LD in as-rolled steel.

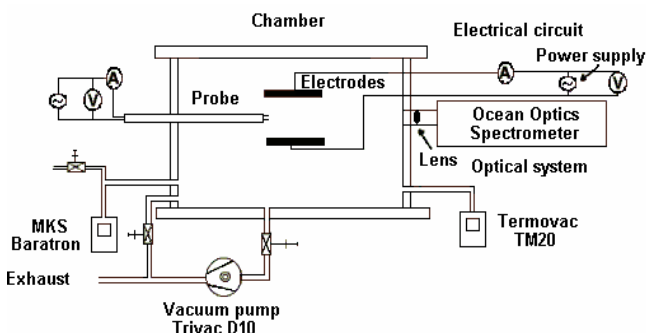


Fig. 1. Diagram of the system of the ionic nitriding process.

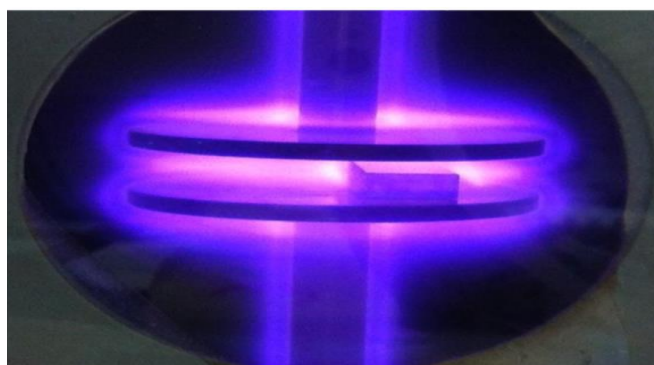


Fig. 2. The plasma nitriding process.

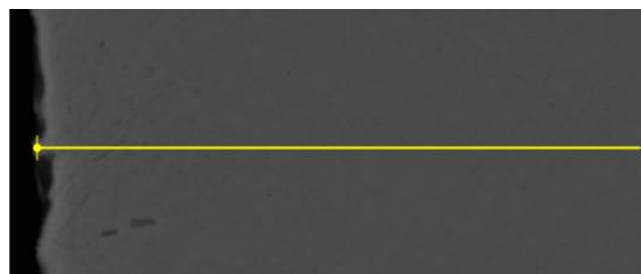


Fig. 5. Nitrogen concentration profile (scan line).

III. RESULTS AND DISCUSSION

Figure 6 shows elongated needles of a bainite phase, surrounded by a martensite phase in a ferrite matrix in the sample without treatment in the microalloyed experimental steel in the as-received condition. Bainitic–martensitic steels are hard and resistant because they have a fine structure with particles of carbides in these phases. These fine particles, known as second-phase particles, are characteristic of this type of microalloyed steel, and they infer a combination of mechanical properties. In Fig. 7, some precipitates with cuboidal shapes can be observed, which are characteristic and related to titanium nitrides (TiN) [12], which are very hard. The formation of titanium nitrides depends on the composition and the casting process.

Table 1 shows the mechanical properties of steel samples obtained without treatment in both directions, which have a

higher strength compared to low-carbon alloyed steels. The experimental microalloyed steel shows better mechanical properties in the TD than in the LD, because during the rolling process, residual stresses are generated either from the thermomechanical process or from the cooling procedure.

Table 1: Traction test in the LD and TD.

	UTS	E	σ_y	σ_{fract}	ϵ	RA
	MPa	GPa	MPa	MPa	%	%
TD	1,135.5	208.0	931.5	749	13.9	52.6
LD	1,018.5	183.5	860.5	565	17.8	60.6

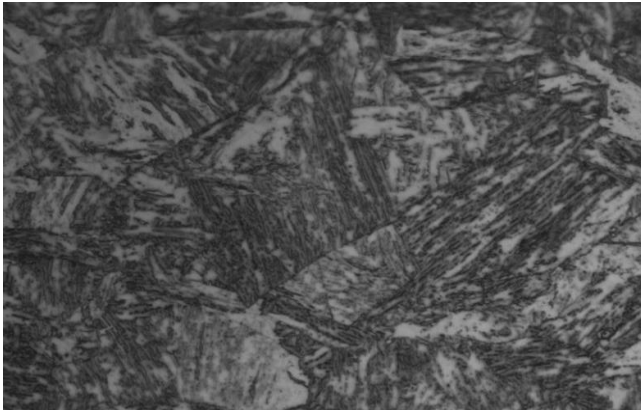


Fig. 6. Bainitic–martensitic phases observed in a matrix of ferrite of the experimental microalloyed steel (100x).

The results of the Vickers microhardness tests, performed with a load of 300 g (HV 0.3), showed a decrease in hardness over time (9 h) during the nitriding process, which then again increases as a function of time (12 and 18 h). This behavior is associated with the increment of the compound layer and its thickness. In the sample nitrided for 9 h, the thickness of the nitrided layer was not thick enough for the impact in the microhardness tests, whereas in the samples nitrided for 12 and 18 h, the layer was thick enough to observe the increase in surface hardness.

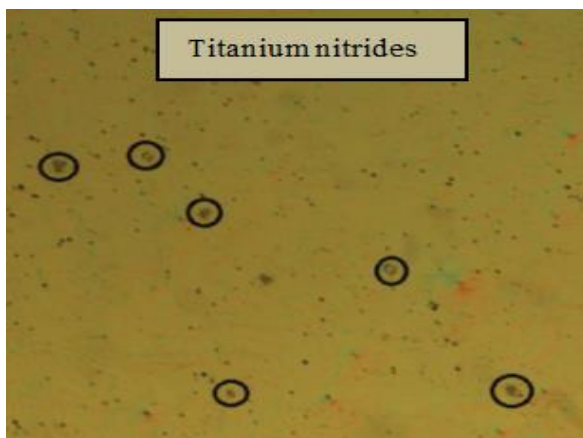


Fig. 7. The titanium nitrides observed (circles, 10x).

The estimated thickness of the compound layer was determined using fractography (see Fig. 8). The sample was fractured at liquid nitrogen temperature. Fig. 9 displays the

layer thickness of the fractured nitride samples as a function of the treatment time. It was observed that the thickness of the nitrided layer is proportional to the nitriding duration, obtaining a maximum thickness at 18 h of treatment [6, 7]. The fractography test was carried out because it was difficult to observe the nitrided layer through chemical etching (see Fig. 10). The fractures are widely distinguished between the superficial nitrided layer and the transition to the matrix, showing a fragile fracture and a ductile fracture [6, 7].

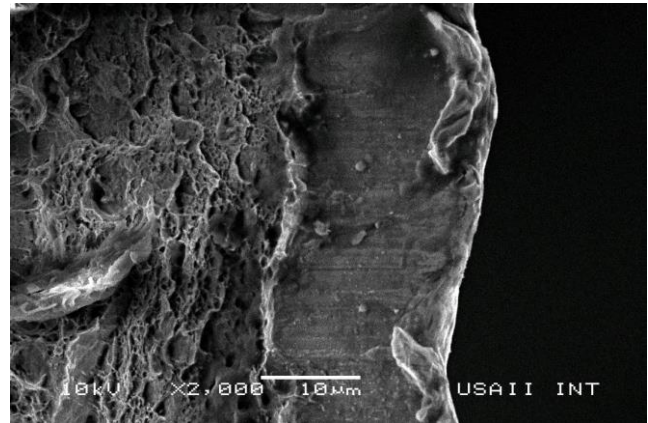


Fig. 8. Fracture of the nitrided layer at liquid nitrogen temperature.

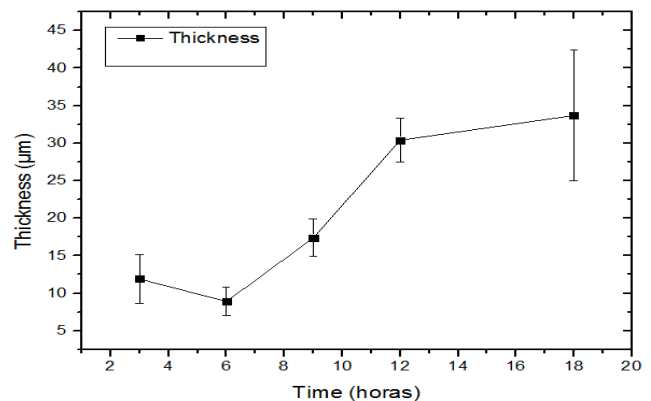


Fig. 9. The layer thickness of the fractured nitride samples as a function of the treatment time. The standard deviation is also shown.

Table 2: Vickers microhardness of the surface of the nitrided samples and the estimated thicknesses by fractography of the nitrided region.

Time (h)	HV 0.3	Thickness (μm)
0	360 ± 10	—
3	331 ± 23	11.9 ± 3.2
6	323 ± 8	8.9 ± 1.9
9	303 ± 16	17.4 ± 2.5
12	318 ± 13	30.4 ± 2.9
18	344 ± 9	33.7 ± 8.7

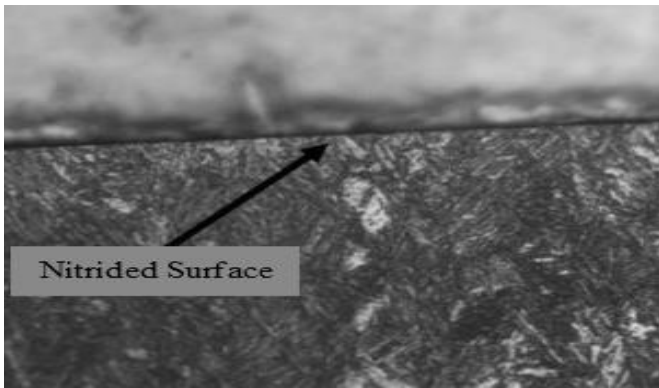


Fig. 10. Chemical etching on the cross-sectional area of the nitrided layer (9 h).

Figures 11 and 12 show the hardness profiles obtained for nitrided samples at 12 and 18 h treatment. The lower hardness values were close to the edge of the sample, since part of the penetration energy is absorbed by the edge. The hardness value in the matrix was 220 HV 0.010; this value remained almost constant for depths greater than 50 μm . The hardness profile was obtained only for the samples nitrided for 12 and 18 h, because the thickness of the samples nitrided for 3, 6, and 9 h was relatively small and it was not possible to perform the test.

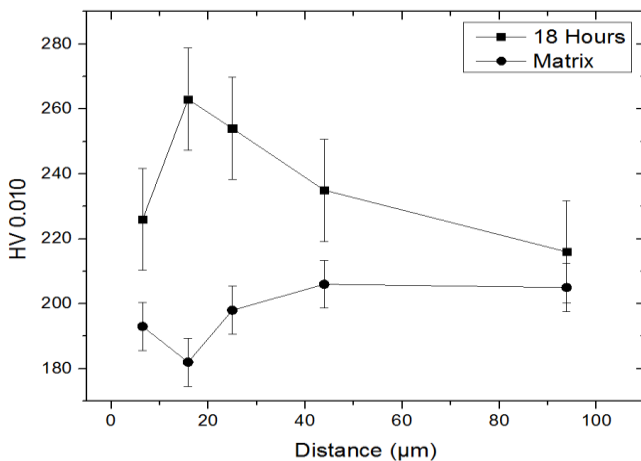


Fig. 11. Hardness profile of the sample nitrided for 18 h.

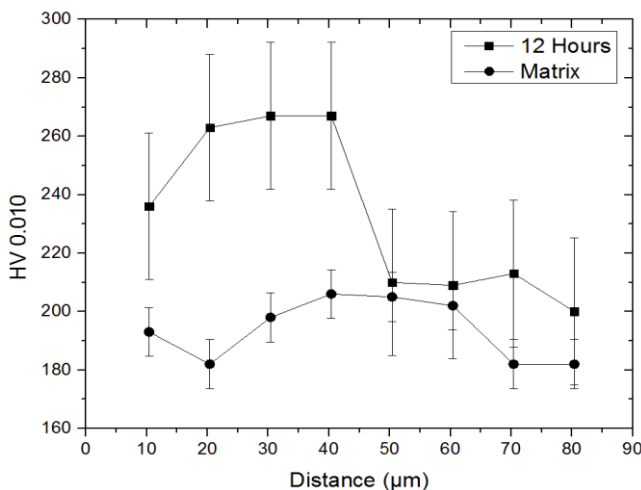


Fig. 12. Hardness–distance curve for the sample nitrided for 12 h.

Figures 13–15 show the profiles of nitrogen concentration in the samples nitrided for 3, 9, and 18 h. In the concentration profiles, it is possible to see the process of diffusion of nitrogen into the matrix. In general, it is observed how the concentration of nitrogen is reduced to the matrix and remains constant when the depth is greater than that estimated in fractography (see Table 2), with its corresponding nitriding time.

In order to obtain the coefficient of diffusion or diffusivity, the experimental results are adjusted with a mathematical solution of the partial differential equation that describes non-steady-state diffusion under the condition where D is assumed to be constant, which is obtained by the mathematical solution to the profile of the Gaussian function (GF):

$$c(x) = \frac{c_0}{\sqrt{4\pi Dt}} e^{\left(-\frac{x^2}{4Dt}\right)}$$

where $c(x)$ is the concentration, x is the distance from the surface, c_0 is the concentration on the surface, and t is the treatment time.

From Figs. 13–15, it can be seen that the GF profile fits the experimental data (dotted and solid lines), because the fitted GF profile has a free parameter, that is, the diffusion coefficient (D), whose value can be obtained from the adjustment. The fitted data were found to agree with the experimental data. Table 3 shows the values of the diffusion coefficients obtained from the experimental results.

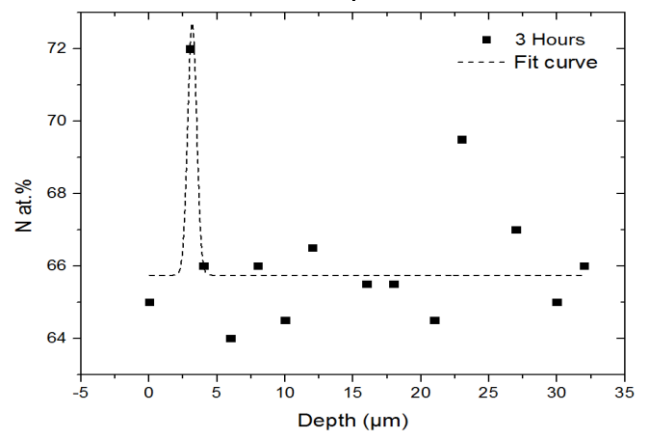


Fig. 13. Concentration profile of nitrogen at 3 h of treatment.

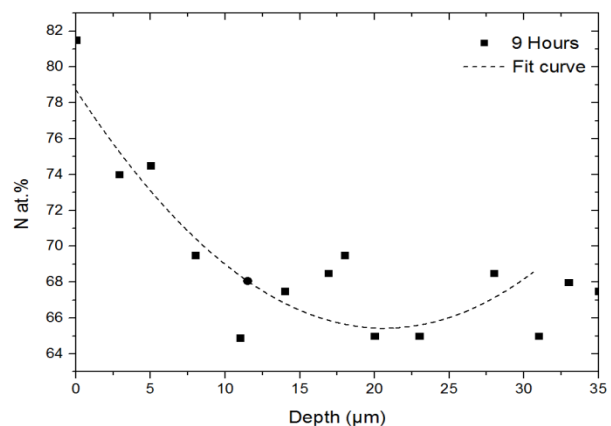


Fig. 14. Concentration profile of nitrogen at 9 h of treatment.

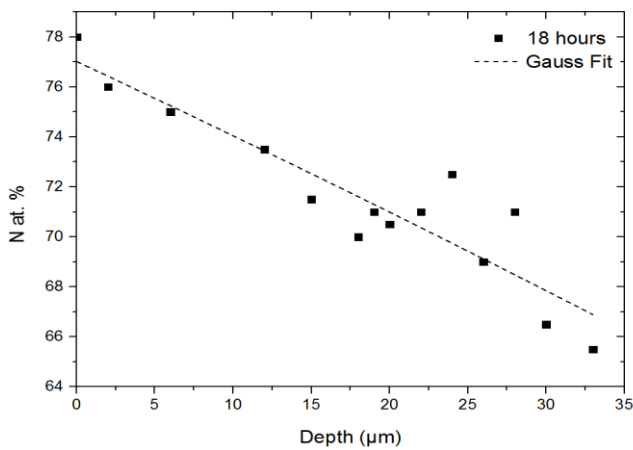


Fig. 15. Concentration profile of nitrogen at 18 h of treatment.

Table 3: Values of the diffusion coefficients

Time (h)	$D \left[10^{-13} \frac{m^2}{s} \right]$
3	1.99×10^{-3}
9	9.54
18	48.20

From Table 3, it can be observed that there is stronger nitrogen diffusion as a function of the treatment time, which is promoted by diffusion plasma treatment.

IV. CONCLUSIONS

- (1) The surface hardness of the experimental high-resistance microalloyed steel increased during the nitriding process, obtaining a maximum hardness in the sample that was nitrided for 12 h.
- (2) A minimal difference was found in the hardness obtained from the nitrided layers in the samples nitrided for 12 and 18 h.
- (3) The thickness of the nitrided layer increases with the increase of the duration of the nitriding process.
- (4) The nitrogen concentration profile corroborates the thickness of the nitrided layer estimated by fractography.
- (5) The nitrogen diffusion coefficients showed a strong correlation with the treatment time, which is promoted by diffusion plasma treatment.

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Oscar Xosocotla is a master's degree student at the Faculty of Chemistry, National Autonomous University of Mexico, Mexico City, Mexico. He is currently developing scientific research on surface modifications of polymers by means of an atmospheric plasma process.



Osvaldo Flores, Dr. in Chemical Metallurgical Engineering, graduated from the National Autonomous University of Mexico. Currently in the Institute of Physical Sciences and professor of postgraduate of the Faculty of Chemistry of the UNAM. Some areas of interest: materials science, plasma at low temperature, hydrogen in metals, intermetallic materials, thermal treatments, spectroscopic techniques, additive technology to the biomechanical area and energy, and design of prosthetic materials.



Bernardo Campilo, Dr. in metallurgical chemistry, graduated from the National Autonomous University of Mexico. Current researcher of the Institute of Physical Sciences and postgraduate coordinator of the Faculty of Chemistry of the UNAM in the Institute of Physical Sciences. Some areas of interest: materials science, plasma at low temperature, intermetallic materials, thermal treatments and spectroscopic techniques.



Horacio Martínez Valencia received the Ph.D. degree from Facultad de Ciencias, Universidad Nacional Autónoma de México (UNAM), México City, México, in 1987. He is currently a Researcher in the Instituto de Ciencias Físicas, UNAM. He leads the spectroscopy laboratory of the Instituto de Ciencias Físicas. His Research fields are basic plasma phenomena, Low temperature plasma, Plasma surface interactions, Spectroscopy of cold plasma, Plasma diagnostics and Atomic, molecular and optical physics