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# Microwave plasma characteristics in steel nitriding process

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**Abstract**

We report the plasma parameters of a microwave discharge immersed in a magnetic field (ECR type) studied as a function of the type of gas used to induce the discharge. Plasma diagnostics included a Langmuir probe, an ion energy analyzer and an optical emission spectroscopy system. Results of the diagnostics are discussed in connection with the influence of the plasma parameters on the nitriding of steels. Different $H_2/N_2$ mixtures were used to form the plasma and carry out the nitriding of AISI-316 stainless steel, with samples at the plasma floating potential, so that the energy of the ions hitting the sample surface depends on the difference between the plasma potential and the floating potential. Treatments were carried out in the low temperature regime ($\sim 450°C$), where the steel keeps its anticorrosive properties and its structure corresponds to the so-called expanded austenite according to our X-ray diffraction results. The highest surface hardness was obtained when a 60:40 ($H_2/N_2$) gas mixture was used, corresponding to a 380% hardness increase for a 50-min treatment. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Microwave plasma; Plasma processing; Nitrides

## 1. Introduction

Nitriding is a thermochemical process that generates a gradient of nitrogen in the surface region of metallic samples. This concentration gradient is the result of the formation of nitrided layers with an associated hardness gradient and a compressive stress profile, which produces a notable improvement in the tribological and corrosion properties of the material. Several processes allow us to generate such a nitrogen concentration, for instance, salt nitriding with cyanides, nitriding with gas mixtures that contain ammonia, and plasma nitriding. Nitriding with relatively weakly ionized plasma is particularly important from a technological point of view. Some of the advantages of this process include rapid kinetics of reaction at the surface, homogeneity of the treated surfaces, good control and intrinsic non-toxicity of the process. In plasma nitriding of steels the different types of the nitrided layer that can form and the thickness of the layer depend on the nitrogen concentration at the surface in equilibrium with the gas [1].

In this sense, microwave plasmas are very advantageous, as they are capable of generating high-density plasmas in low-pressure regimes. Low pressures together with the gas composition permit the generation of distinct active species within the plasma. In the present experiment, different concentrations of nitrogen in the gas mixture with hydrogen were used in order to establish the optimal mixture for nitriding of AISI-316 stainless steel. Hydrogen plays two important roles in the nitriding process, one due to its strong deoxidation ability and the other due to the formation of the NH molecule [2], which in the case of the

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microwave discharge is generated in considerably high quantities, being an important source of atomic nitrogen at the surface of the substrates.

It is well known that nitriding of austenitic stainless steel can be carried out at high rates when the sample temperature is sufficiently high [3,4]. Nevertheless, at temperatures above 500°C, precipitation of CrN compounds is favored and a change of structure in the sample occurs. This change of structure seriously damages the corrosion resistance of the steel [5,6]. For this reason, nitriding of AISI-316 in our experiments was carried out in a low temperature regime, so that the determination of the optimal gas mixture is not affected by the high diffusion rates of the high temperature regimes.

## 2. Experimental

The experimental apparatus used to carry out the nitriding has been described in detail elsewhere [7]. The plasma was created by microwave excitation ($f=2.45$ GHz) in an external magnetic field to establish the electron cyclotron resonance. The power used in all the experiments was 350 W. The pressure inside the working chamber was fixed at $4 \times 10^{-4}$ torr for all of the different $H_2/N_2$ ratios used as working gases. The plasma, under these conditions, transfers enough heat to the samples for these to reach a temperature of $450 \pm 30$°C. This temperature value was calculated after obtaining the relationship between the temperature measured by a chrome–alumel thermocouple connected to the back of the sample and that produced on the front face of the sample. Lower values of temperature could be achieved, through a reduction in plasma density, nevertheless, as the nitriding process is a diffusion process this reduction could lead to longer treatment times.

The plasma specifications were determined by means of a single Langmuir probe, an ion energy analyzer of the Faraday cup type [8] and by optical emission spectroscopy. In the present experiments, AISI-316 steel samples machined and mirror-polished, were exposed for 50 min to the $H_2/N_2$ plasma, with nitrogen concentrations being varied from 10 to 100%. The samples were electrically isolated from the chamber, in this way attaining the plasma floating potential; no bias voltage was applied to the samples.

In order to determine the optimal gas mixture in the plasma to carry out the steel nitriding, the surface hardness and nitrogen depth penetrations were measured. Surface hardness was measured using a Vickers microindentor and the depth profile by means of nuclear reaction analysis. The microstuctural details of the nitride layers formed were investigated by X-ray diffraction using CuK$\alpha$ radiation in order to assure the presence of the so-called expanded austenite structure. In this way the corrosion resistance of the material is not spoiled and can even be improved [9], as our results showed. Roughness and surface morphology were analyzed by atomic force microscopy (AFM). Chemical composition in function of the $H_2/N_2$ ratio was determined by electron dispersion spectroscopy (EDS) at 20 keV.

## 3. Results and discussion

As the ionization characteristics of the plasma sources are known to be crucial to their effectiveness in the nitriding process, it is of interest to study the influence of the plasma parameters on the results of the treatment. In the experiments described below using the microwave ECR discharge, the electron temperature and density, as well as the floating and plasma potentials, were determined as functions of the type of gas used. Parameters such as the incident power and magnetic field also influence the plasma parameters, but in our experiments these were kept constant. In the range 300–500 W, the incident power has only a slight influence on the plasma density. On the other hand, there is a strong dependence of plasma parameters on the magnetic field. Once the plasma was ignited, a value close to half of the resonant one was chosen because it provided an overdense plasma (i.e. a plasma with a density greater than the critical value, which for the case of $f=2.45$ GHz is $7.5 \times 10^{10}$ cm$^{-3}$). At this density value the electromagnetic wave is reflected, as the dielectric constant becomes zero, and plasma waves can be excited, moreover with this magnetic field the reflected power was minimum ($\sim 15\%$).

Fig. 1 shows the variation of the plasma parameters as a function of the nitrogen content in the working gas. As can be seen, the plasma density is practically

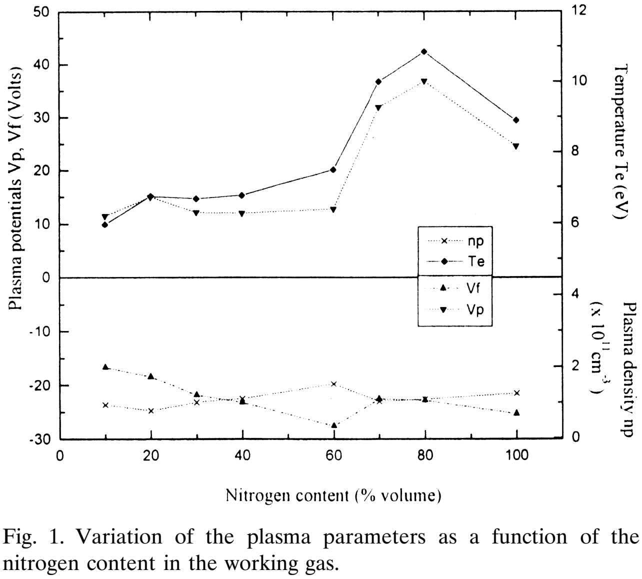

Fig. 1. Variation of the plasma parameters as a function of the nitrogen content in the working gas.

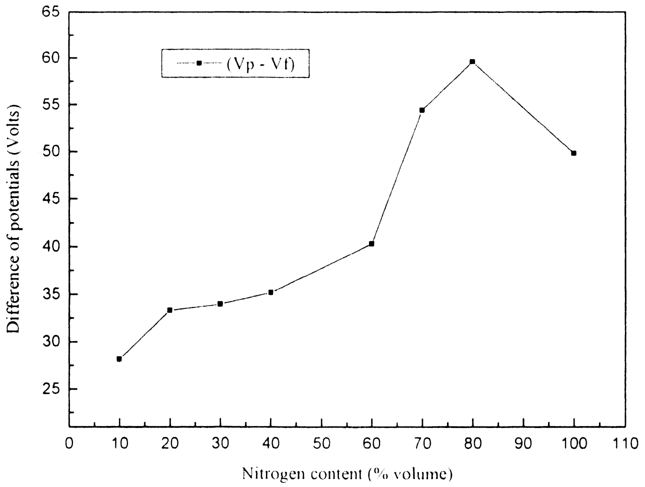

Fig. 2. Difference between the plasma and floating potentials ($V_p$ and $V_f$) as a function of the nitrogen content in the gas.

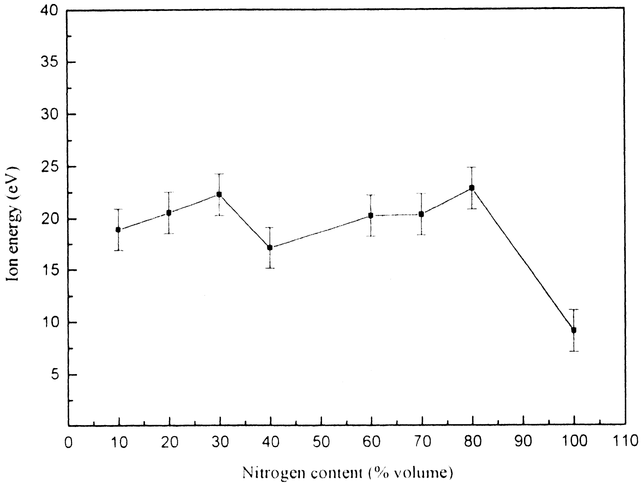

Fig. 3. Ion energy as a function of the nitrogen content in the gas.

unaffected, but the rest of parameters do change. The plasma density had a value close to $1 \times 10^{11}$ cm$^{-3}$. Higher densities are undesirable as they can excessively heat the samples. The electron temperature shows a tendency to increase as the amount of hydrogen reduces, although it decreases when 100% nitrogen is used. The rise in electron temperature causes the floating potential to be more negative and the plasma potential to increase in order to compensate for losses to the walls. Thus the sheath potential at the plasma edges, as well as at the sample surface, tends to increase. This can be seen in Fig. 2, where the difference of the potentials as a function of the nitrogen concentration is shown. This difference of the potentials establishes the maximum energy value that ions can achieve inside the plasma flux. Inside the sheath electrons are repelled, as the samples are maintained at the

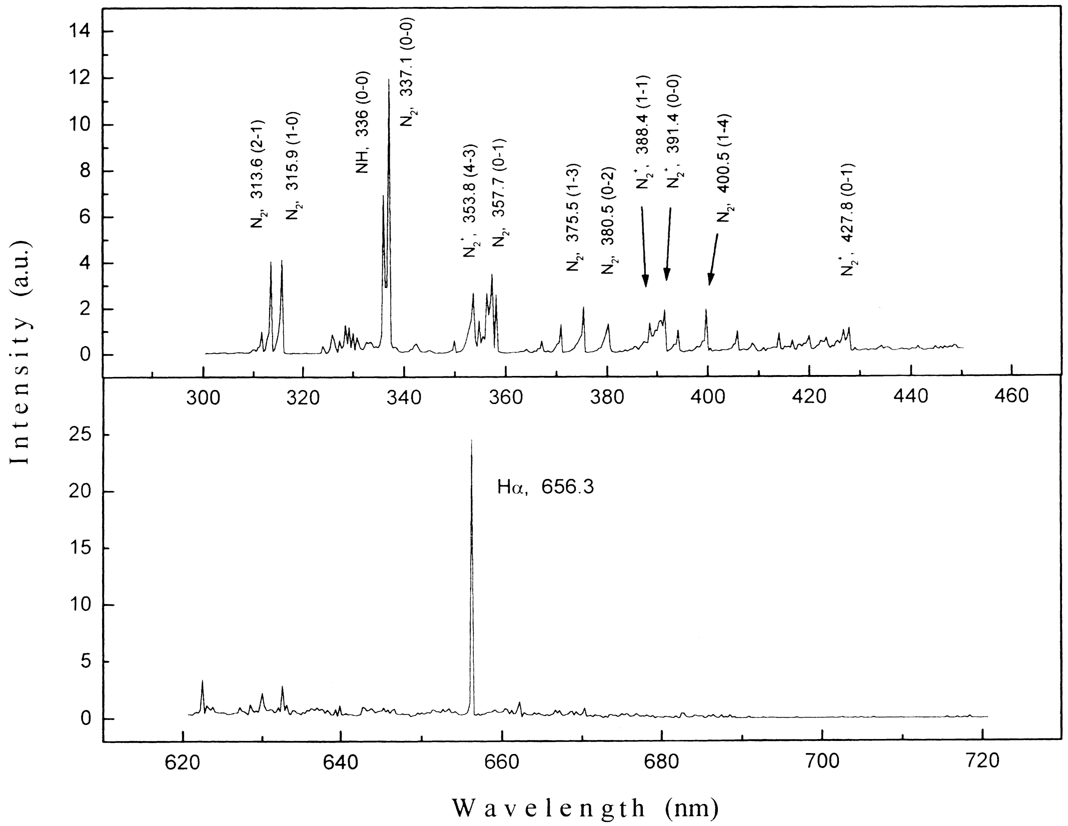

Fig. 4. Optical emission spectra from a plasma formed in a 60:40 $H_2/N_2$ mixture.

floating potential since this is negative with respective to the plasma potential, so that although the electron temperature increases with the nitrogen concentration they are repelled from the samples, avoiding excessive heating.

Though the ion energy within the plasma is known to be less than 1 eV, some are accelerated towards the sample due to the difference of the potentials [10], as shown in Fig. 2. Fig. 3 shows the variation of the ion energy, measured using the ion analyzer, as a function of the gas mixture. As can be seen, the energy was almost constant at a value of approximately 20 eV, except when the gas used was 100% $N_2$, when the value decreased to 10 eV, which can be explained by the reduction in the difference of the potentials (see Fig. 2). Reducing the magnetic field from the first coil can increase the ion energy. Nevertheless this variation is accompanied by a reduction in plasma density near the substrate, so that as the ion energy increases the ion flux is reduced, with this leading to longer treatment times.

Nitriding in the microwave discharge was carried out using 100% $N_2$ or mixtures of $H_2/N_2$, as the working gas; in both cases neutral and excited species are involved. The majority of the species are vibrationally excited at a fundamental level. These molecules are adsorbed onto the iron surface and subsequently dissociate and dissolve into the steel matrix. Due to the low pressures of the microwave discharge, there is little probability of the formation of atomic nitrogen, as this process requires a high excitation of the gas and a three-body recombination process. This is accompanied by the formation of molecular nitrogen with a photon emission corresponding to the first positive system of $N_2$ (i.e. with wavelengths in the range 540–750 nm). Optical emission measurements showed that no emission in this range was observed. On the other hand, as Fig. 4 shows, the most intense peak in the emission spectra came from the second positive system, corresponding to the excitation of the nitrogen molecule by electronic collisions. Together with these peaks, an intense peak corresponding to the emission of the NH molecules was present (when using gas mixtures with hydrogen). These peaks are the most important in our experiments, so that from the spectroscopic point of view the excitation ion mechanism in the microwave discharge is due to electronic collisions, contrary to the case of discharges working at higher pressure and lower frequencies.

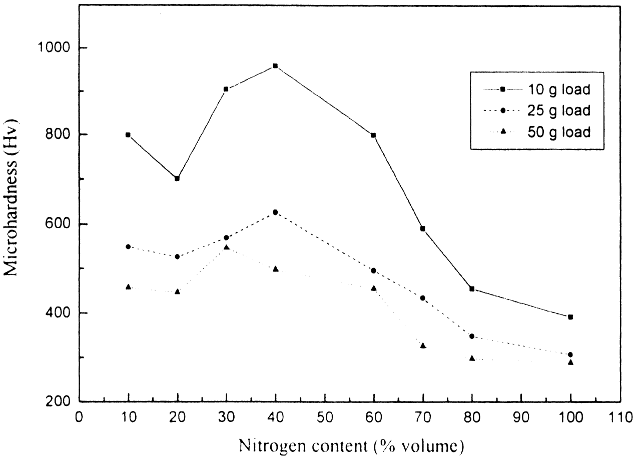

Fig. 5. Microhardness measurements performed with different loads for samples treated with different nitrogen content in the gas.

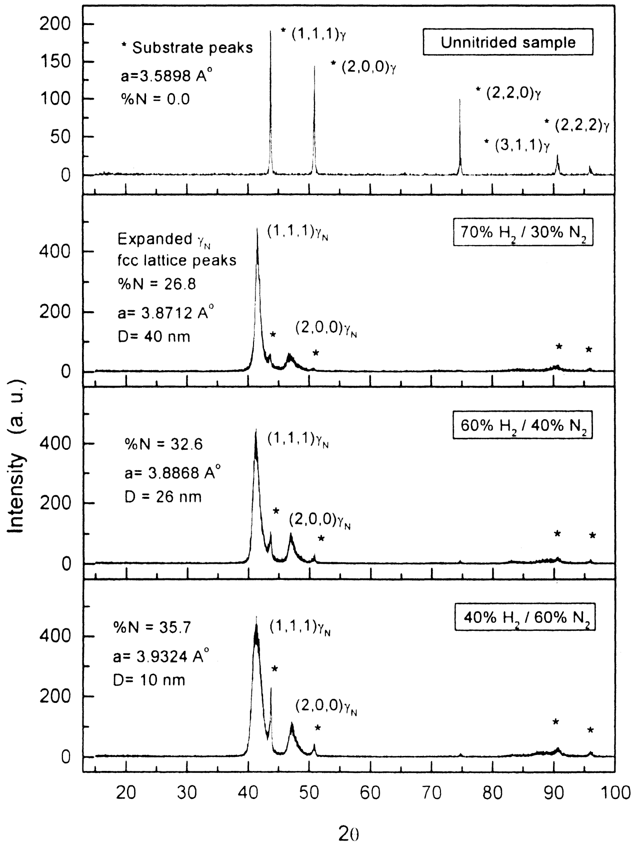

Fig. 6. Comparison of X-ray diffraction patterns of an untreated sample with samples treated with three different gas mixtures used to form the plasma.

The results of microhardness measurements with different loads as a function of the nitrogen concentration in the working gas are shown in Fig. 5. The highest hardness was observed for samples treated in the 60:40 $H_2/N_2$ plasma. A value of 1000 ± 150 Hv was obtained for a 10-g load. The initial hardness value was 260 ± 20 Hv, so that almost a 380% increase in hardness was achieved. The rapid decrease in hardness with increasing load is due to low thickness of the nitrided layer.

The nuclear reaction analysis allowed us to determine the nitrogen depth penetration for samples treated with different gas mixtures in the plasma. The

60:40 $H_2/N_2$ sample showed the thickest constant nitrogen layer (approx. 1.6 μm). Although the 70:30 $H_2/N_2$ sample had a smaller constant nitrogen layer (approx. 1.3 μm); its concentration decreases more slowly, achieving a greater final penetration of almost 3.5 μm. More data are required to adequately explain this effect. The results obtained show that the optimal nitrogen concentration in the gas used to form the plasma in a microwave discharge is close to 60:40 $H_2/N_2$.

The XRD patterns of Fig. 6 can be interpreted as indicated, with both substrate $\gamma$ peaks and the expanded $\gamma_N$ fcc lattice peaks. The positions of the peaks are consistent with thicker layers and an increasing expansion of the fcc lattice as a function of the nitrogen content. This confirms that the treatment temperatures were correctly chosen and that there is no precipitation of CrN phases, which is normally accompanied by decomposition of the $\gamma_N$ phase [11]. The average nitrogen content was determined by EDS at 20 keV

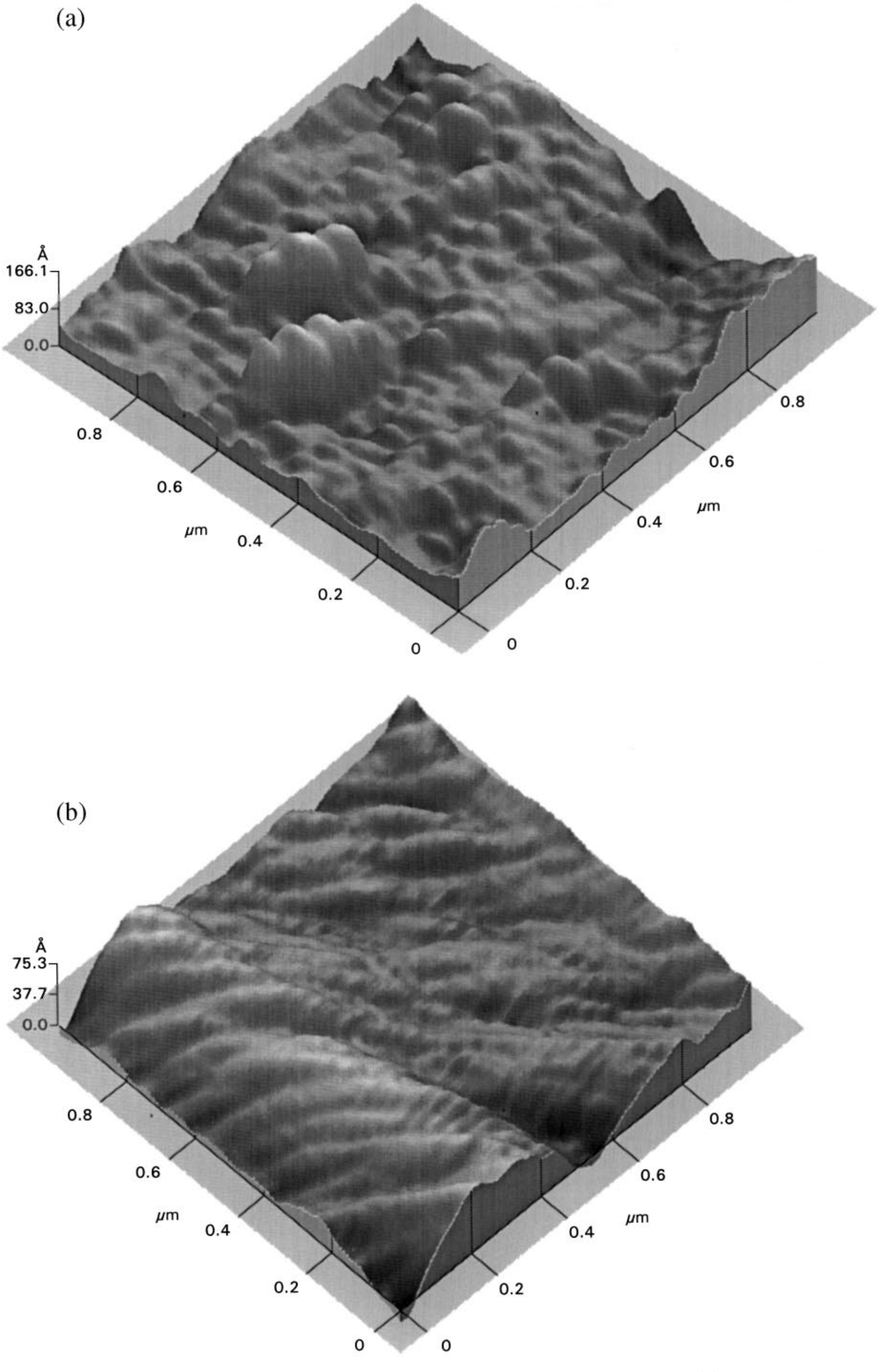

Fig. 7. Atomic force micrographs of AISI-316 steel surface nitrided with different gas mixtures: (a) 70:30 $H_2/N_2$; and (b) 40:60 $H_2/N_2$.

electron energies with 200 s measurement time. The measured nitrogen content in the samples of Fig. 6 increases from 26.8% to 35.7%, which induces the increase in lattice parameters for the different samples. The XRD analysis showed that the nitrogen-containing layer has a (111) preferential orientation and that the diffraction peaks broaden as the nitrogen content in the layer increases. Examination of this broadening indicates that the lattice parameter, *a*, increases from 3.87 Å to 3.93 Å, and the grain size changes from 24 nm to 10 nm as the nitrogen content increases.

Fig. 7 shows a sequence of three-dimensional surface images obtained on an area of 1.0 $\mu m^2$ by atomic force microscopy. As indicated by the vertical scale, the sample prepared at 70:30 $H_2/N_2$ (Fig. 7a) shows surface modulations with an amplitude of approximately 44 Å (roughness) due to the granular morphology of the surface. The surface of the sample prepared at 40/60 $H_2/N_2$ (Fig. 7b) shows modulations with a decreased amplitude of approximately 31 Å with surface features like rod-globular grains. Notice that the rod agglomerates have longitudinal dimensions, with a ratio of approximately 7:1. This effect may be due to an increase in the surface mobility of the nitrided grains, favoring phase segregation and junction formation of a stable rod-like crystalline structure with small individual grains as observed by X-ray diffraction measurements. As a result, the surface roughness decreases as the nitrogen content is increased in the plasma gas and in the nitrided coating.

A corrosion test was performed on the 60:40 $H_2/N_2$ sample in a 3.5% NaCl solution. The results showed an improvement in the corrosion properties of the material of approximately 90% of the corrosion rate: from $588.6 \times 10^{-3}$ to $309.6 \times 10^{-3}$ mpy. This result confirms that the X-ray measurements correctly show the formation of the $\gamma_N$ phase, and that the value of the treatment temperature is adequate for the formation of this phase.

## 4. Conclusions

Nitriding of AISI-316 stainless steel was carried out in a microwave discharge with different gas mixtures of $H_2/N_2$ used as the working gas to form the plasma. It was determined that a mixture close to a 60:40 $H_2/N_2$ ratio produced the best mechanical properties of the steel. Nitriding was performed at low temperatures, where the formation of the so-called nitrogen expanded austenite phase ($\gamma_N$) takes place. The formation of this phase guarantees that the corrosion properties of the material are not altered, which was confirmed by a corrosion test.

The main effects on the material due to the increasing nitrogen content in the working gas are:

1. Enlargement of the lattice parameters from 3.5898 Å to 3.9324 Å.
2. Decrease of the crystal size from 40 nm to 10 nm.
3. The surface features change from globular-spherical grains to rod-globular grains.
4. Decrease of the surface roughness from approximately 44 Å to 31 Å, i.e. a smoother surface.

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