Superficies y Vacío 9, 290-293, Diciembre 1999

Microwave plasma steel nitriding using different H_2-N_2 gas mixtures

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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 done in the low temperature regime (~ 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.

PACS: 52.58Q, 52.75.R, 81.65
Keywords: Microwave plasmas, plasma processing, optical spectroscopy, 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 selective generation of distinct active species within the plasma. In the present experiment, different concentrations of nitrogen in the gas mixture were used in order to establish the optimal mixture for nitriding of AISI-316 stainless steel.

2. Experimental

The experimental apparatus used to carry out the nitriding has been described in detail elsewhere [2]. The plasma is 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 350W. The pressure inside the working chamber was fixed at 4 x 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 ± 30 C.

The plasma specifications were determined by means of a single Langmuir probe, an ion energy analyzer of the Faraday cup type [3] and by optical emission spectroscopy. In the present experiments, machined and mirror-polished AISI-316 steel samples, 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

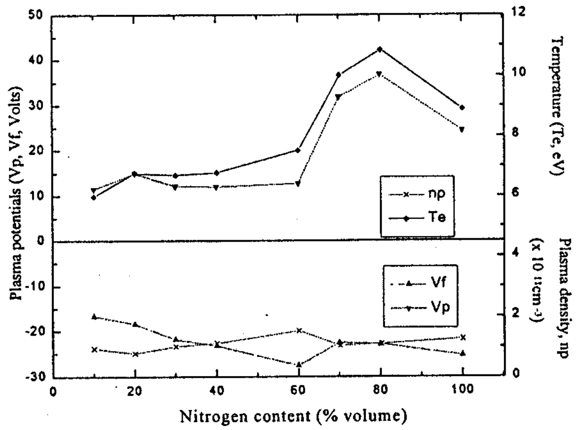

Fig. 1. Variation of the plasma parameters as a function of the nitrogen content in the working gas.

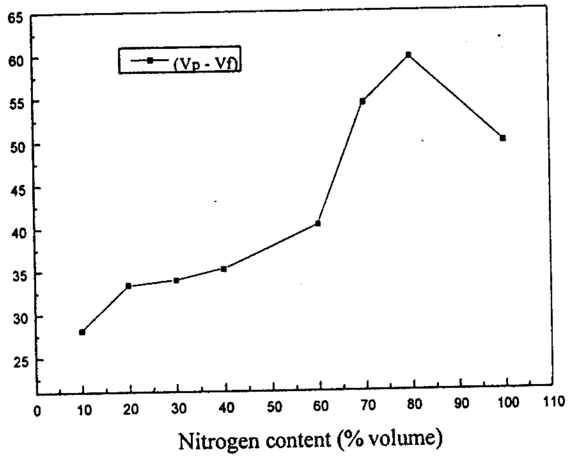

Fig. 2. Difference between plasma and floating potentials (Vp and Vf) as a function of the nitrogen content in the gas.

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 the nitrogen depth penetrations were measured. Surface hardness was measured using a Vickers's microindentor and the depth profile by means of nuclear reaction analysis. The structural details of the nitride layers formed were investigated by X-ray diffraction 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 [4], as our results showed.

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 (Te) and density (np), as well as the floating (Vf) and plasma potentials (Vp) were determined as functions of the type of gas used. Parameters such as the incident (used) power and magnetic field also influence the plasma parameters, but in our experiments these were kept constant. In the range from 300 to 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 is ignited, a value close to half of the resonant one was chosen because it provided an overdense plasma (i.e. plasmas with density greater than the critical value, which for the case of f = 2.45 GHz, is 7.5 x 10^{10} cm^{-3}. At this value of density the electromagnetic wave is reflected, as the dielectric constant becomes zero, and plasma waves can be excited), and moreover with this magnetic field the reflected power was a minimum (~ 15 %).

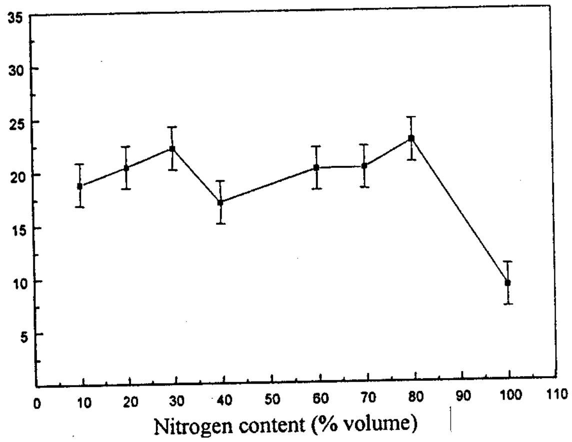

Fig. 3. Ion energy as a function of the nitrogen content in the gas.

Fig. 1 shows the variation of the plasma parameters as a function of the nitrogen content in the working gas. As it can be seen, the plasma density is practically unaffected, but the rest of parameters do change. The plasma density had a value close to 1 x 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 the 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 figure 2 where the difference of potentials as a function of the nitrogen concentration is shown. This difference of potentials establishes the maximum value of energy that ions can achieve inside the plasma flux. Inside the sheath electrons are repelled, as the samples are maintained at the 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 ions are accelerated towards the sample due to the difference of potentials [5], 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 about 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 of the difference of 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 H_2 – N_2 mixtures as working gases. In both

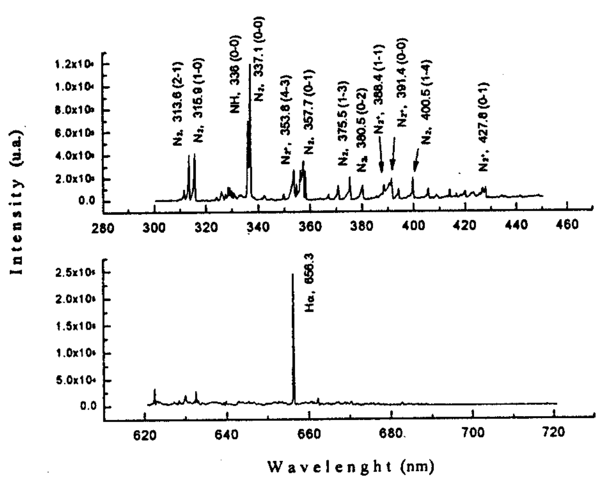

Fig. 4. Optical emission spectra from a plasma formed in a mixture 60% H\-(2) / 40%N\-(2).

cases neutral and excited species are involved. The majority of the species are vibrationally excited at a fundamental level. These molecules are adsorbed on 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 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 in the with wavelength range of 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 come 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 is 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.

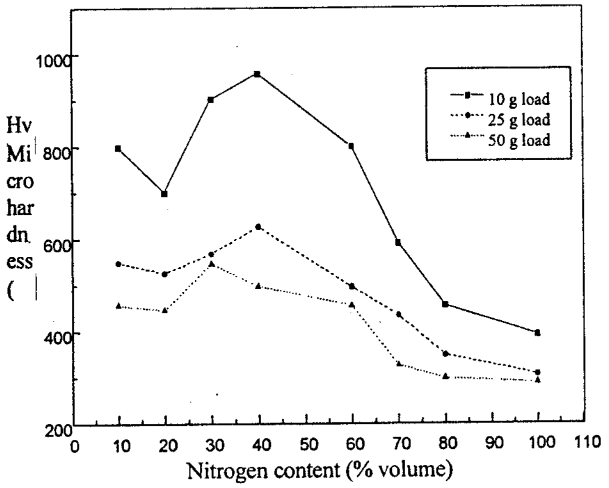

Fig. 5. Microhardness measurements performed with different loads for samples treated with different nitrogen content in the gas.

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 10g load. The initial hardness value was 260 ± 20 Hv, so that almost a 380% increase in hardness is achieved. The rapid decrease of hardness with increasing load is due to the small thickness of the nitrided layer.

The nuclear reaction analysis allowed us to determine the nitrogen depth penetration for the samples treated with the different gas mixtures in the plasma. The 60 – 40 $H_2 – N_2$ sample showed the thickest constant nitrogen layer (about 1.6 μm). Although the 70 – 30 $H_2 –N_2$ sample had a smaller constant nitrogen layer (about 1.3 μm) its concentration decreases gradually finally achieving a greater final penetration of almost 3.5 μm. More data is required to adequately explain this effect.

The results obtained showed that the optimal nitrogen concentration in the gas, used to form the plasma in a microwave discharge, is close to 60 – 40 $H_2 – N_2$.

Figure 6 shows the XRD pattern for the sample treated in the 60/40 H_2/N_2 plasma mixture. This was a typical result in which it is possible to see the peaks corresponding to the γ_N phase (or expanded austenite), located at 2θ values 41 and 46, meanwhile the less intense peaks located at 67 and 83, are not detectable to be detected in our XRD system. This confirms that the treatment temperatures were correctly chosen and that there is no precipitation of CrN phases, which normally is accompanied by decomposition of the γ_N phase [6]. The γ phase peaks seen result from the stainless steel. 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. The steel matrix has a grain size of about 100 μm. The nitrided layer growths with a granular

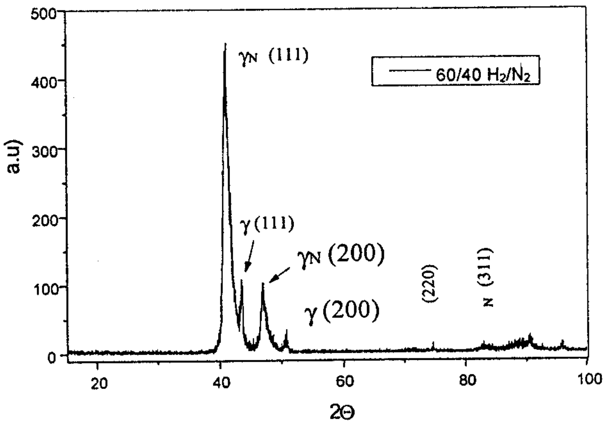

Fig. 6 X-ray diffraction pattern of the sample treated in the 60/40 H_2/N_2 plasma.

shape with a small crystalline grain, whose size depends on the dissolved nitrogen content in the steel matrix. Examination of the position of the peaks and the broadening indicates that the lattice parameter, *a*, increases from 3.87Å to 3.93Å, and the crystallite grain size changes from 24 nm to 10 nm as the nitrogen content increases. A corrosion test was performed on this sample in a 3.5% NaCl solution. The results showed an improvement of the corrosion properties of the material of about 90% in the corrosion rate; 588.6×10^{-3} to 309.6×10^{-3} mpy. Corrosion tests for all the samples treated with different working gases used to form the plasma are now in process.

The results show that it is possible to carry out the nitriding of AISI-316 at low temperatures in a microwave discharge which results in an enhanced surface hardness without causing damage to the corrosive properties of the material, and this for relative short treatment times.

Acknowledgements

The authors would like to thank Mr. Caballero, José Guzmán, E. Martínez and M. García from IIM-UNAM and Sabino Hernández from ININ, for their technical support. This work was partially supported by CONACYT, contract No. 29250E

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