Pergamon

Vacuum/volume 51/number 3/pages 385 to 392/1998

0042–207X/98 $19.00+.00

PII : S0042–207X(98)00119–5

Influence of microwave plasma parameters on the nitriding of T-304 stainless steel

Enrique Camps,* Stephen Muhl† and Saúl Romero, *Instituto Nacional de Investigaciones Nucleares, Apdo. Postal 18-1027, 11801 México, D.F. México*

received and accepted 20 November 1997

A microwave (f = $\omega/2\pi$ = 2.45 GHz) electron cyclotron resonance (ECR) plasma source was employed to carry out the nitriding of T-304 stainless steel at low pressures ($\sim 10^{-4}$ torr.) with samples at the plasma floating potential. Even for nitriding times as short as 40 min the surface hardness was found to increase up to 6 × the initial value ; the nitrogen concentration and penetration depth were typically up to 27 at.% and 15 μm, respectively. These quantities were determined by measurements of the nitrogen concentration profiles obtained by Nuclear Reaction Analysis (NRA) and by means of energy dispersion X-ray spectroscopy (EDX) analysis of surface perpendicular to that which received the nitrogen flux. Three different mixtures of N_2/H_2 were used as working gases with an electron plasma density which was greater than the critical value. This density was achieved by lowering the external magnetic field to almost half of its resonant value (B_r = 875 G—resonant magnetic field) ; in this way the samples received enhanced surface ion bombardment during the treatment. The plasma specifications were determined using electric probes.

1. Introduction

The nitriding process for surface hardening of steels has been used in industry for the last 60 years and today has become a highly accepted technology.[1] Traditionally thermochemical processing involving the diffusion of nitrogen using liquid and gaseous mass transfer media has been used and this results in the formation of hard surface layers without substantial modification of the bulk material. However, these processes are not energy efficient and require long treatment times.

The advent of plasma nitriding (or ion nitriding) caused a renewal in the interest in metal processing. By using plasmas it is possible to accelerate the diffusion of nitrogen into the samples, and therefore reduce the treatment times.[2] Moreover, the reactivity of the nitrogen is no longer dependent on the sample temperature[3] and therefore it is possible to fix the temperature according to the sample characteristics and vary the nitrogen activity by changing, for example, the gas partial pressure. Initially, direct current (dc) discharges were used to carry out plasma nitriding.[3,4] In this case, the sample temperature is determined mainly by the electrical power applied to the discharge, so that changes in temperature are closely related with changes in the plasma parameters, leading to results which depend on the experimental conditions in a complicated manner.

The kinetics of nitriding has been the focus of much research since the introduction of the process. The use of plasma processes has meant that the very long treatment times have been considerably reduced ; however the times continue to be high, from a few hours up to several tens of hours for a typical sample.[5–8] The time principally depends on the hardness and the depth penetration of the nitrogen required.[9] Some improvements have been achieved by increasing the ion bombardment of the samples exposed to the plasma. This has been done through the so called Plasma Immersion Ion Implantation technique, which involves the application of a pulsed high voltage bias to samples immersed in a radio frequency (rf) plasma.[10] The process also facilitates the treatment of large samples. Along the same lines considerable progress has been made in the intensification (raising the plasma density) of conventional dc glow discharges, using an auxiliary thermal electron source.[11–13] This variation permits a reduction of the working pressure down to 10^{-2} torr. and shorter treatment times. In particularly, in Ref. 13 it is reported that 2 h of nitriding was sufficient to obtain an increase in the surface hardness of almost 4 × the initial value.

In the case when a microwave ECR discharge is used, low pressure regimes with high plasma density values (i.e. ionization coefficient close to 10%) can be obtained easily. These characteristics, among others, make the use of this kind of approach very attractive for plasma processing and there are various reports of its use in the processing of materials.[14–16] However, there are very few reports of its use in the nitriding of steels (see

* Corresponding author.
† Permanent address : IIM-UNAM, Apdo. Postal 70-360, 04510 México, D.F. México.

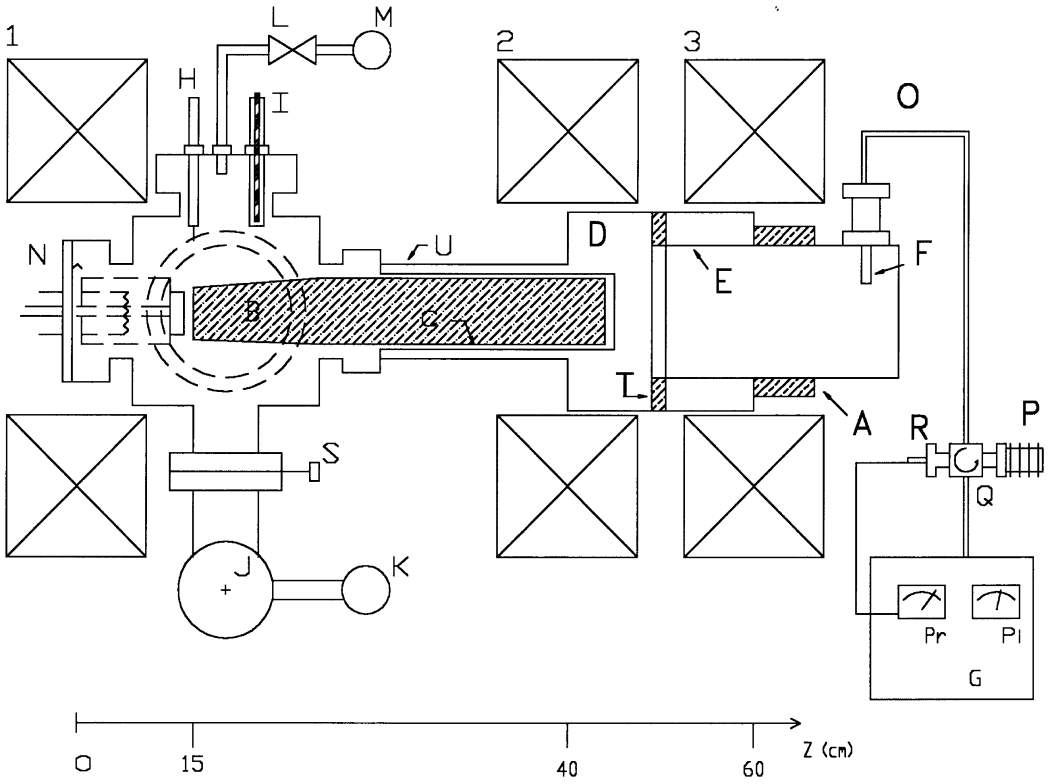

Figure 1. Schematic drawing of the experimental equipment.

for example[17]). Therefore, the aim of the present paper is to study the characteristics of this type of plasma and the influence of these characteristics on the nitriding of steels. We restrict our study to the description of those regimes in which it is possible to obtain the maximum surface hardness and layer thickness, for comparatively short treatment times

2. Experimental setup

The microwave ECR source is shown schematically in Fig. 1, a complete description of the device was given earlier.[18] Briefly, the microwave system consists of a Micro Now 420B1 microwave power oscillator (G in Fig. 1) of fixed frequency of ($f = \omega/2\pi = 2.45$ GHz) and variable output, 500 W maximum, denoted as incident power P_i. In the experiments described a constant power of 320 W was used. The microwave power is applied through a cylindrical TE_{11} waveguide (E in Fig. 1) to a cylindrical TE_{111} resonant cavity (D in Fig. 1). It is possible to adjust the inner wall of the resonator and the antenna length (F in Fig. 1) in the waveguide to match the impedance of the cavity to that of the plasma.

The external magnetic field is generated by three solenoids. These are used to create the resonant condition in the central part of the resonator and to extract the plasma into the reaction chamber (B in Fig. 1). The resonant condition exists when the electron cyclotron frequency (ω_{ce}) equals the pump frequency (ω), and this corresponds to a magnetic field of 875 G. In this work we refer to the magnetic field values as the ratio ω_{ce}/ω in the center of the resonator. Magnetic field variations were found to significantly influence the plasma density and its uniformity. As was shown previously,[18] in our system the highest values of plasma density are obtained when the magnetic field values are reduced to $\omega_{ce}/\omega \sim 0.6$. In the experiments we describe here the magnetic field value was kept constant at 0.6.

The gases used flowed through a quartz tube (C in Fig. 1), which is located inside the resonant cavity and limits the plasma radius to approximately 3 cm. The ultimate pressure of 5×10^{-6} torr. was obtained using a 200 l/s vacuum diffusion pump. The nitriding treatments were carried out in this equipment, using different values of pressure in the 10^{-4} torr. range, and the corresponding total gas flows are shown in Table 1. It should be noted that in our present setup the gas flow determines the pressure in the reactor, since there is no variable conductance valve between the chamber and the diffusion pump. Three different hydrogen/nitrogen mixtures (80/20, 85/15 and 90/10) were used as feed gases. The purity of the gases was 99.99%.

Table 1. Processing parameters used in plasma nitriding

Incident power	320 W
Magnetic field ω_{ce}/ω	0.6
Pressure	$2–8 \times 10^{-4}$ torr.
Gas flow	4–20 sccm
Gas composition H_2/N_2 (vol.%)	90/10, 85/15, 80/20
Nitriding time	40 min
Initial hardness ($HV_{0.5}$)	260 ± 25

A single Langmuir probe (H in Fig. 1) was used to take radial profiles of the plasma parameters (electron temperature T_e and density n_e, floating (V_f) and plasma (V_p) potentials) in a region of the reaction chamber close to the sample holder. The radius of the probe was 0.15 mm and the length 5 mm.

Commercial 304 austenitic stainless steel was used as the substrate material. The chemical composition of the material is : 0.08 wt% C, 18 wt% Cr, 8 wt% Ni, 1 wt% Si, 2 wt% Mn and 0.15 wt% S. Prior to nitriding the specimens were machined into a square shape (approximately 15 mm $\times$ 15 mm) with a thickness of about 8 mm, and annealed at 1050°C for 30 min. This procedure was used in order to homogenize the samples and to avoid an increase in hardness due to heating during the treatment. In this way we attempted to guarantee that any increase in sample hardness was a result of the plasma treatment and hardness measurements of heat cycled but untreated samples showed this to be correct. All samples were mirror polished using 600 grit silicon carbide sandpaper and then 1 μm alumina paste, with a final ultrasonic clean in methanol. The Vickers microhardness measurements were carried out using a Matsuzawa MXT30-UL tester and the average value before the plasma nitriding was 260 ± 25 Hv for 50 and 10 g loads.

The surface concentration and maximum penetration of the nitrogen was measured by nuclear reaction analysis (NRA) and energy dispersion X-ray spectroscopy (EDX), which also was used for the studies of penetration vs treatment time. A Tandem Van de Graaff accelerator was used to carry out the NRA measurements, by irradiating the samples with 1800 and 2200 KeV deuterons. The detection angle was 150° and the sample surface was perpendicular to the ion beam. The study was made on the basis of the $^{14}N(d, p_0)^{15}N$ and $^{14}N(d, \alpha_0)^{12}C$ nuclear reactions. The analysis of the experimental and simulated spectra allowed, in some cases, the calculation of the nitrogen depth penetration and in others to establish a minimum for this value, at the same time estimations of the relative surface concentration for most of the samples were obtained. The maximum detectable penetration for the NRA work is determined by the energy of the incident beam and the limitations of the simulation process. The EDX measurements were carried out using a Phillips XL30 equipped with an EDAX microprobe.

Plasma nitriding was performed with externally heating of the samples to a temperature of 350°C for the treated surface. This value of temperature was calculated after obtaining the relationship between the temperature measured by a chromel-alumel thermocouple connected to the back of the sample and that produced on the front face of the sample. The temperature of 350°C was chosen from a series of optimization experiments. For these experiments the plasma conditions were kept constant and the temperature was varied from 500 to 300°C. The greatest increment of surface hardness was found for a temperature of 350°C. These experiments could not be conclusive and a more complete study of the effect of the sample temperature is necessary, taking into account that the plasma can heat the sample to greater than the initial temperatures; but for the purpose of the present paper, the selected value is considered to be adequate to study the influence of the plasma parameters.

The samples were electrically isolated from the chamber and attained the floating potential of the plasma. This procedure takes advantage of the naturally established difference between the plasma and floating potential to cause bombardment of the substrate. In these conditions, etching of the sample is avoided, as no high voltages are applied; and at the same time, as it will be shown, an enhancement in the nitriding process is obtained, using this simple and cheap technique.

3. Plasma parameters

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 total pressure and the type of gas used. Parameters such as the incident power and magnetic field also influence the plasma parameters, but in our experiments they were kept constant. In the range from 300 to 500 W, the P_i 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, the value $\omega_{ce}/\omega = 0.6$, was chosen because it provided an overdense plasma (i.e. plasmas with density greater than the critical value, which for the case of $\omega = 2.45$ GHz, is 7.5×10^{10} cm^{-3}); moreover, with this magnetic field the reflected power is minimum ($\sim 15\%$).

Figure 2 shows the variation in electron density along plasma radius for various pressures, for the 80/20 (H_2/N_2) mixture. There is a resonant behavior in the plasma density, the maximum being at 4×10^{-4} torr. This kind of behavior is typical for plasmas with densities greater than the critical value and is related to the transformation of the incident electromagnetic wave into plasma waves via linear or nonlinear effects, which are known to be of the resonant type.[19] This value of pressure was chosen to be the mid point of the range of pressures used for the nitriding studies. The plasma potentials and electron temperature are shown in Fig. 3. In this graph, the average values near the center of the plasma tube are plotted, since this is the area occupied by the samples to be nitrided. The results show a decrease in both the electron temperature (T_e) and plasma potential (V_p) with increasing pressure, but no consistent variation in floating potential (V_f) as a function of gas pressure is seen. It is important to note that although V_f does not change in the same manner with this variable, the difference between V_p and V_f systematically decreases with increasing pressure. Table 2 shows the results of the plasma measurements for the three mixtures. For the case of the 80/20 mixture, there are shown two more values of pressure, in which the plasma density decreases affecting considerably the nitriding. Furthermore as these features are observed for all the gas mixtures used, nitriding with the other gases was carried out only in the pressure range within which the plasma keeps its highest values of density. The numbers correspond to the average values for the center region of the plasma. The values of plasma density indicate an ionization of close to 10%, when the values of the working pressure are taken into account. These plasma regimes were those that were used to carry out the nitriding of the steel.

4. Nitriding

The results of the nitriding of the specimens held at a fixed temperature and with a plasma exposure time of 40 min, are also shown in Table 2. The HV values correspond to the 15 g load microhardness measurements on the treated surfaces. From these results, the 90/10 mixture can be seen to given somewhat lower values compared to the 80/20 and 85/15 mixtures. Furthermore, the values correspond to an increase of between 450 and 600%

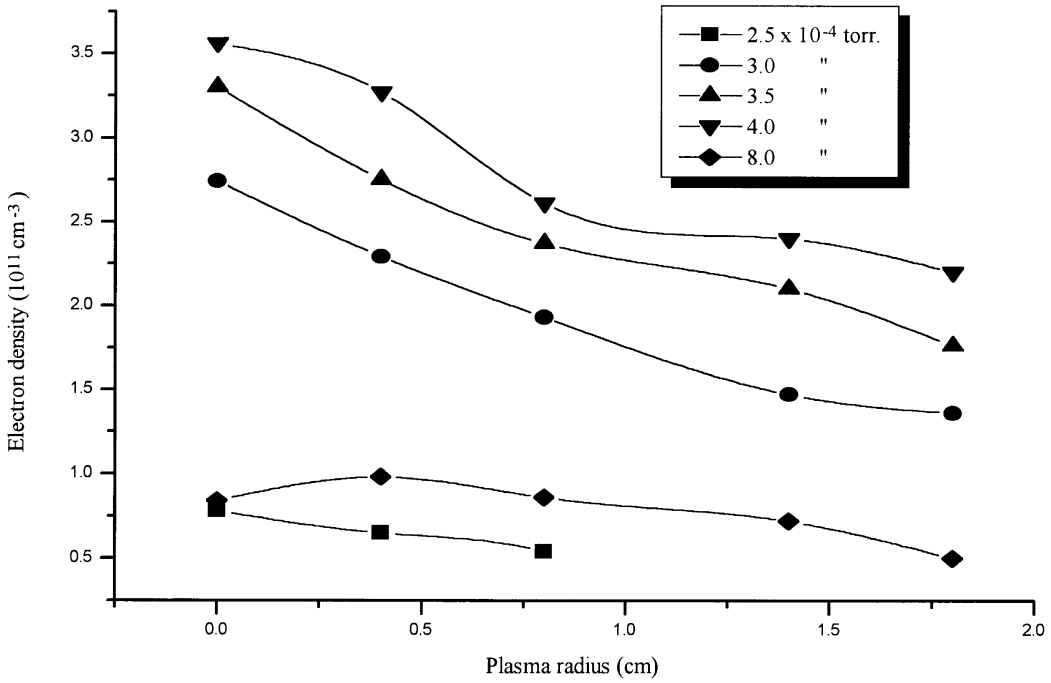

Figure 2. Radial electron density distribution, for different working pressures of the mixture 80/20 (H_2/N_2) with fixed magnetic field $\omega_{ce}/\omega = 0.6$ and $P_i = 320$ W.

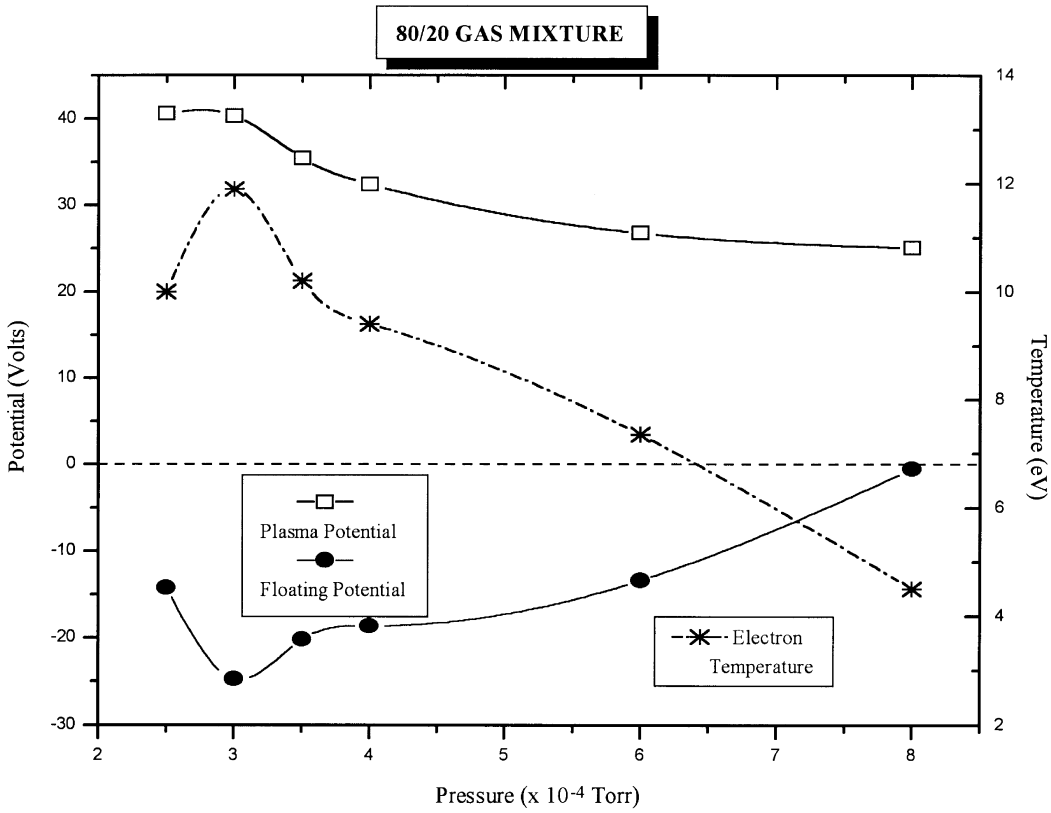

Figure 3. Electron temperature, plasma and floating potentials as functions of pressure.

Table 2. Measured plasma parameters

H_2/N_2	Pressure 10^{-4} torr.	T_e (eV)	Density 10^{11} cm^{-3}	V_p (V)	V_f(V)	$V_p - V_f$	μ Hardness ($HV_{0.015}$)
90/10	3	12.5	2.8	44.6	−25	69.6	1230 ± 150
90/10	3.5	10.9	3.5	38.6	−21.2	59.8	1070 ± 150
90/10	4	8.2	4.6	29.5	−15	44.5	1220 ± 150
85/15	3	14.0	2.7	48.7	−27.8	76.5	1410 ± 200
85/15	3.5	13.2	2.6	45.1	−26.8	71.9	1520 ± 200
85/15	4	8.9	3.7	31.2	−17.5	48.7	1630 ± 200
80/20	2.5	10.0	0.7	40.6	−14.2	54.8	355 ± 25
80/20	3	11.9	2.3	40.3	−24.7	65.0	1780 ± 200
80/20	3.5	10.2	2.8	35.4	−20.2	55.6	1450 ± 200
80/20	4	9.4	3.2	32.4	−18.6	51.0	1550 ± 200
80/20	8	4.5	0.9	25.1	−0.5	25.6	880 ± 100

in the hardness of the steel. Apparently this is the maximum value achievable even if longer treatment times or biasing of the substrate is employed. These last aspects are discussed later.

Microhardness measurements were performed at different loads in order to estimate the penetration depth of the nitrogen. Figure 4 shows a typical plot of the indentation depth vs hardness for the 80/20 mixture at different pressures. The x axis of the plot is the indentation depth (d_i) calculated from the relation

$$d_i = (d/2) \tan 22,$$

where d is the average value of the diagonal of the indentation, and tan 22 arises from the geometry of the indenter. From this type of graph we have estimated the penetration depth of the indenter for a microhardness 100% greater than the initial value of the untreated steel.

The obtained values of d_i are considered to be representative

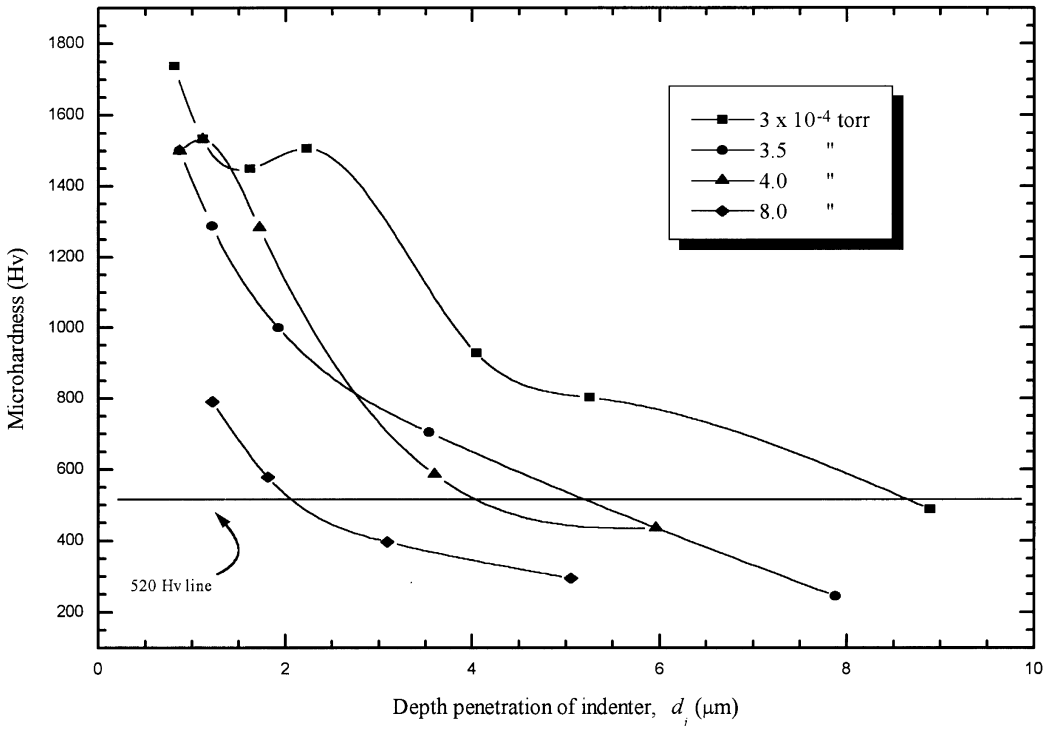

Figure 4. Microhardness measurements performed with different loads for samples treated with the 80/20 mixture at different pressures, the errors related with these measurements are shown in Table 2. The intersection of the 520 HV line with the curves were used in the estimation of the nitrided layer thickness.

of, but not necessarily equal to, the thickness of the nitrided layer. The values of this representative depth for all of the samples are shown in Table 3.

The results of these measurements show that although there is no large difference in the surface hardness for the different mixtures, the penetration of the nitrogen into the samples is strongly dependent on which mixture is used. Table 3 also includes the values of the difference of the plasma and floating potentials, and it can be seen that for the lower gas pressure—and hence the larger potential difference—the deeper the penetration of the nitrogen. This data shows that the dependence of the penetration on the difference of potentials is maintained as long as the plasma density does not vary greatly. However, a reduction in both parameters also results in a reduction in the penetration, as shown in the data for the 80/20 mixture. In general, the data demonstrates that changes in the plasma parameters play an important role, and therefore changes in external parameters (such as input power, magnetic field, total pressure or gas flow) must be considered through the changes they produce in the plasma parameters. In particular, alteration of the external conditions may lead to nitriding results which are radically different to those expected.

As mentioned, the depth of nitrogen penetration from the indenter data is only a representative value, and more precise measurements were performed using Nuclear Reaction Analysis (NRA) and EDX. However due to the limitations of the NRA technique in determining large depths, in some cases it was only possible to obtain a minimum value of the penetration.

The EDX measurements were carried out on a face cut perpendicular to the nitrided surface. For this work each sample was analyzed in successive 2 μm steps from the edge of the cut and nitrided surface, until the nitrogen signal was seen to decrease to the background level, the results are listed in Table 3. In this way it was possible to obtain the maximum depth of penetration of the nitrogen and also corroborate the depth profiles from the NRA measurements. A comparison between the different methods to determine the depth penetration of nitrogen, shows that the representative depth from the indentation depth gives a low value, particularly when the penetration is large, i.e. when high loads (1 kg for example) are needed. Nevertheless the method can give a quick and confident estimation of the nitrogen penetration up to approximately 8 μm.

A combination of data obtained from NRA and EDX, allowed the calculation of the absolute nitrogen concentration in the surface of the samples. Except for the extremes of the pressure range used this concentration was constant, within the calculation error, and was approximately equal to 27 at.%. A slight reduction was observed (22.13 at.%) when the plasma density was reduced, and under these conditions the surface hardness only increased by 50% and the nitrogen penetration was very low. Although the accelerating potential for this case is only slightly reduced, the quantity of particles hitting the sample surface is severely affected by the decrease in the plasma density, and this leads to the inclusion of less nitrogen.[20] Table 3 shows that the highest values of N concentration are related with the highest values of surface hardness and the N penetration depth is proportional to the accelerating potential.

An additional aspect demonstrated by the NRA analysis was that the penetration depth of the nitrogen, the maximum surface concentration of nitrogen and the concentration profile can vary independently. In particular, the samples treated with the 80/20 mixture at 2.5 and 8×10^{-4} torr., show similar nitrogen penetrations and surface concentrations, but the concentration profile for the lower pressure sample decreases much more rapidly, and this is reflected in a lower surface hardness. Similarly, the 90/10 3.0×10^{-4} torr. and 80/20 3.0×10^{-4} torr. samples have similar nitrided layer thicknesses, but the 80/20 sample has a higher nitrogen surface concentration, and this again gives a larger surface hardness value.

In general, the results of the nitrogen depth penetration show that for short treatment times it is possible to form a relatively thick nitrided layer with high surface hardness, when an adequate difference of potentials (between V_p and V_f) is established. Our experiments indicate that an accelerating potential of 76 V is sufficient to increase nitrogen penetration up to approximately 15 μm, in 40 min. As can be seen from Figs 2 and 4, and Table 3, a reduction in the plasma density leads to a decrease in the surface hardness and the nitrogen penetration, independent of whether the potential is reduced or not. Similarly, a reduction in the accelerating potential greatly affects the effectiveness of the treatment, even if the density is only slightly reduced.

On the basis of these results, the use of high potentials together with high plasma density is the best combination. In order to confirm these ideas, a dc bias was applied to the sample holder,

Table 3. Nitrided layer thickness, nitrogen surface concentration and difference of potentials for different experimental regimes

H_2/N_2	Pressure 10^{-4} torr.	d_i (μm)	NRA (μm)	EDX (μm)	Max. N at.%	$V_p - V_f$ (V)
90/10	3	7.4	9.7	11.0	25.23	69.6
90/10	3.5	5.1	$\geqslant$7.1		28.33	59.8
90/10	4	4.8	$\geqslant$7.1		24.34	44.5
85/15	3	9.6	$\geqslant$10.8	15.0	27.5	76.5
85/15	3.5	7.4	7.1	12.0	29.5	71.9
85/15	4	8.0	$\geqslant$7.3	10.0	32.2	48.7
80/20	2.5	0.5	4.15		22.1	54.8
80/20	3	8.6	9.7	14.0	29.0	65.0
80/20	3.5	5.3	$\geqslant$7.1		25.9	55.6
80/20	4	4.7			28.3	51.0
80/20	8	2.3	4.15		21.5	24.6

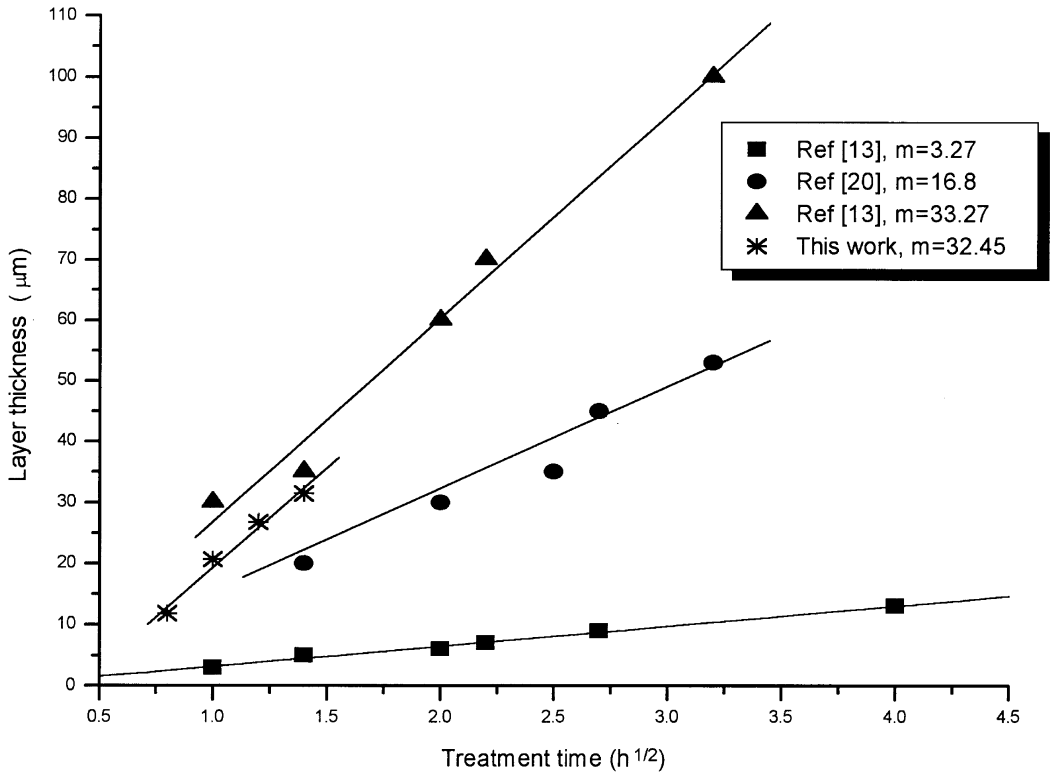

Figure 5. Nitrided layer thickness as function of processing time (m is the slope of the fitted lines).

while the rest of the experimental conditions were maintained as for the case of the mixture 85/15 and the pressure 3.5×10^{-4} torr. Two values of dc bias were used -100 and -50 V. In this case, the accelerating potential is the difference between V_p and the applied bias.

The sample treated with a -100 V dc bias showed a $d_i = 10$ μm nitrogen depth penetration and a surface hardness of 1270 ± 150 HV (15 g load). This surface hardness was practically the same as for the floated sample. However, the nitrogen penetration is higher by at least two-fold; unfortunately, an exact determination of the penetration is not possible as the sample suffered considerable etching. Similarly, the characteristics of the plasma could not be recorded as the probe was contaminated by the sputtered material a few minutes after the treatment was begun. In the experiment with -50 V dc bias, no etching was observed, the surface hardness and nitrogen penetration were slightly reduced (1100 HV and 6.5 μm respectively) but the plasma was also highly perturbed by the bias. A comparison with the experiments with floated samples is difficult, as the plasma was significantly different. Nevertheless, some conclusions can be made. Firstly, that a negative bias voltages as high as 100 V, with plasma densities in the mid of the 10^{11} cm^{-3}, causes sputtering of the sample surface, which is undesirable. Secondly, the dc bias is highly perturbative to the plasma, indicating that an rf induced bias may be preferable to carry out these kind of experiments in an ECR microwave plasma.

In order to establish the layer growth kinetics an experiment was run under the same conditions as for the sample treated with the 85/15 mixture at 3.5×10^{-4} torr., but the sample was divided into four regions which were exposed to the plasma for different intervals of time, 30, 60, 85 and 120 min each. EDX measurements were performed on a face cut perpendicular to the nitrided surface, in order to determine the nitrogen depth penetration in each of the treated regions. Figure 5 shows the kinetics of the layer growth; in this plot we include results from other authors. It can be seen that the process is very rapid compared to conventional plasma nitriding (for example in comparisons with ammonia nitriding see Ref. 20) and has basically the same velocity as for the case of the so called intensified glow discharge.[13]

The ECR microwave discharge used in the described experiments is useful to carry out the nitriding of steels. Its effectiveness is a direct consequence of the high ionization coefficients close to the 10% which are possible in these kind of devices. On the other hand, for the gases used it is possible to find regimes in which the difference between plasma and floating potentials is suitable (of the order of 75 V, in our case) to cause sufficient bombardment of the sample and in this way increase the efficiency of the nitriding process, but at the same time not too large to cause sputtering. The reported experiments in this paper were focused on the problem of hardness enhancement and nitrogen depth penetration, in order to study the role of the plasma parameters in the discussed treatments. Problems related with the structure changes in the steels and the chemical processes that take place in the plasma are in progress at present in our laboratory.

Acknowledgements

The authors would like to thank Ing. Leticia Carapia and M. C. Jesús Arenas for their technical support in SEM measurements.

We also thank Pedro Alonso Jiménez and Juana Medina Rodríguez for preparing samples and performing microhardness measurements. This work was partially supported by CONACYT under contract No. 3325P-A9607.

References

1. American Society for Metals, *Metals handbook*, *Heat treatment*, Vol. 4, 1981.
2. Edenhofer, B., *Heat Treat. Met*., 1974, **1**, 23.
3. Petitjean, L. and Ricard, A., *J. Phys. D* : *Appl. Phys*., 1984, **17**, 919.
4. Staines, A. M. and Bell, T., *Thin Solid Films*, 1981, **86**, 201.
5. Chung, M. F. and Lim, Y. K., *Scripta metallurgica*, 1986, **20**, 807.
6. Menthe, E., Rie, K. T., Schultze, J. W. and Simson, S., *Surf. Coat Technol*., 1995, **74–75**, 412.
7. Robino, C. V. and Inal, O. T., *Mat. Sci. and Engineering*, 1983, **59**, 79.
8. Hannula, S. P., Nenonen, P. and Hirvonen, J. P., *Thin Solid Films*, 1989, **181**, 343.
9. Williamson, D. L., Ozturk, O., Wei, R. and Wilbur, P. J., *Surf. Coat Technol*., 1994, **65**, 15.
10. Kenny, M. J., Weilunski, L. S., Tendys, J. and Collins, G. A., *Nucl. Instrum. Methods*, *B*, 1993, **80-81**, 262.
11. Matthews, A., *J. Vac. Sci. Technol*., 1985, **A3**, 2354.
12. Brokman, A. and Tuler, F. R., *J. Appl. Phys*., 1981, **52**, 468.
13. Meletis, E. I. and Yan, S., *J. Vac. Sci. Technol*., 1993, **A11**, 25.
14. Chang, J. J. and Mantei, T. D, 1992, **71**, 5724.
15. Matsuo Seitato and Kiuchi Hikiho, *Jap. J. Appl. Phys*., 1983, **22**, L210.
16. Shapoval, S. Y., Petrashov, V. T. and Popov, O. A., *J. Vac. Sci. Technol*., 1991, **9**, 3071.
17. Lei, M. K. and Zhang, Z. L., *J. Vac. Sci. Technol*., 1995, **A13**, 2986.
18. Camps, E., Olea, O., Gutierrez-Tapia, C. and Villagrán, M., *Rev. Sci. Instrum*., 1995, **66**, 3219.
19. Popov, O. A. and Westner, A. O., *Rev. Sci. Instrum*, 1990, **61**, 303.
20. Ozbaysal, K. and Inal, O. T., *J. Mater. Sci*., 1986, **21**, 4318.