Vol. **123** (2013) *ACTA PHYSICA POLONICA A* No. 5

Proceedings of the IX International Conference ION 2012, Kazimierz Dolny, Poland, June 25–28, 2012

Nitriding of 4140 Annealed Low Alloy Steel in RF Plasma

A. de la Piedad-Beneitez[a], A.E. Muñoz-Castro[b], R. Valencia-Alvarado[b],
R. López-Callejas[a,b,*], A. Mercado-Cabrera[b], R. Peña-Eguiluz[b],
B. Rodriguez-Mendez[b] and S.R. Barocio[b]
[a]Instituto Tecnológico de Toluca, Av. Tecnológico S/N, A.P. 890, Toluca, Mexico
[b]Instituto Nacional de Investigaciones Nucleares, Plasma Physics Laboratory
A.P. 18-1027, C.P. 11801, Mexico D.F., Mexico

The annealed low alloy 4140 steel samples have been nitrided for different treatment periods (1–6 h) in an RF inductive plasma discharge with very low bias voltage ($\approx$ 400 V). The resulting nitrided layer has been observed by means of an optical microscope whereas the nitride phases have been characterised by X-ray analysis. The corrosion response, assessed by the potentiodynamic tests in the 3.5% NaCl solution, presents both higher noble potential values and lower corrosion rates when compared with the untreated sample. The Vickers microhardness tests values show an appreciable increment compared to that of the untreated sample. The process is characterized by a high overall efficiency because similar average Vickers tests values were obtained, no matter for how long the treatment was extended. Likewise, the scanning electron micrographs confirmed no appreciable size evolution of the compound layer microstructure at different times of treatment.

DOI: 10.12693/APhysPolA.123.904

PACS: 52.77.Dq, 52.80.Pi, 62.20.Qp, 81.40.Pq, 81.70.Cv

1. Introduction

Ion nitriding is an effective technique to improve some surface properties by using different plasma discharges, with or without a bias voltage on the working piece. In both cases, the diffusion of nitrogen is a process dominated by temperature. The outcome is a modified layer with better surface performance as for: corrosion, hardness, wear, etc. The surface layer of ion nitrided steels is formed by two layers, a thinner compound layer constituted by the intermetallic γ'-Fe_4N and/or ε-$Fe_{2-3}N$ phases and a nitrogen diffusion layer with the interstitial atoms and coherent nitride precipitates.

The ion nitriding is vastly used in the industrial manufacture of: tools, forging pieces, engine spares, bearings, etc. for the benefits of both the enhanced mechanical surface properties and the relatively low cost. In comparison with gas and salt bath nitriding, the ion process has proved to be a time and energy saving technique.

Several authors have investigated the influence of various treatment parameters on the surface properties of low alloy steels. It should be observed that, while the compound layer provides a better corrosion resistance [1, 2], the diffusion zone concentrates the load bearing capacity and fatigue strength [3, 4]. Then long treatments weaken the surface hardness and a deeper diffusion layer the wear [5]. The wear rate is a function of the surface hardness and layer depth but some amount of the diffusion layer thickness is needed to support the thin surface layer [6]. The thin monophase γ'-Fe_4N compound layer becomes more wear resistant compared to the ε-$Fe_{2-3}N$ monophase one because of its ductility [6]. However, the situation is reversed when corrosion is an issue showing the ε-$Fe_{2-3}N$ is more corrosion resistant than γ'-Fe_4N as a consequence of its crystalline structure and higher nitrogen content [7]. The effects of a maximised content of nitrides have also been studied [2]. The aim of the present work is to investigate the effects of ion nitriding on corrosion and microhardness in the 4140 annealed low alloy 4140 steel when treated in an RF discharge at a very low bias voltage ($\approx$ 400 V).

2. Experimental

Annealed low alloy 4140 steel whose chemical composition is given in Table I has been chosen for the purposes of this study. A series of 3 mm thick disc specimens of 9.3 mm diameter were cut off a rod of 0.5 inch diameter. The samples were machined, polished to a mirror finish and ultrasonically cleaned in acetone before being placed into the nitriding reactor.

TABLE I

Chemical composition of the 4140 steel.

C	Mn	P	S	Si	Cr	Mo	Fe
0.40	0.90	0.03	0.03	0.25	0.95	0.20	Bal.

The ion nitriding on the samples was achieved by an RF inductive discharge in the 75% H_2 and 25% N_2 atmosphere at 10 Pa working pressure, after being evacuated down to a 5×10^{-2} Pa base pressure. Before their treatment, the samples were finally cleansed by a 20 min bombardment with Ar ions. The specimens were biased at $\approx$ 400 V DC when nitrided in the RF inductive discharge reactor (Fig. 1) for 1, 3, 4.5 and 6 h at the

---

[*] corresponding author; e-mail: regulo.lopez@inin.gob.mx

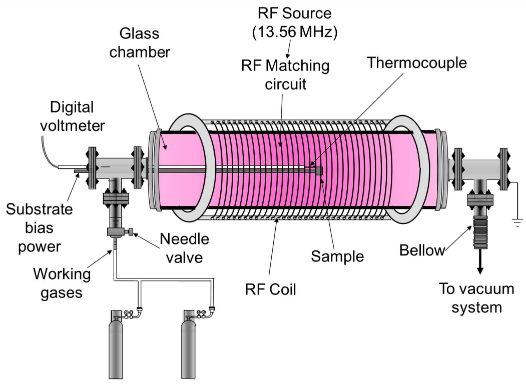

Fig. 1. Diagram of the inductive discharge reactor.

temperatures ranging within 500–530 °C, which was measured by a commercial *K*-type thermocouple. The compound layer was observed and measured with an optical microscope. For that purpose, the samples were previously cross sectionally cut, metallographically prepared and etched with the 2% Nital solution. In order to follow up the microstructure evolution, a scanning electron microscope was used while the energy dispersive spectroscopy (EDS) technique was applied in order to evaluate the nitrogen content. X-ray diffraction of Cu K_α radiation (1.5405 Å) determined the phases in the compound layer. The surface microhardness was assessed with a Vickers tester using a 500 g load by averaging every six measurements. Potentiodynamic tests in the 3.5% NaCl solution were carried out at room temperature with the potentials ranging from −300 mV (with respect to the corrosion potential) to 1200 mV (with respect to the saturated calomel electrode) at a scan rate of 1 mV/s so as to determine the corrosion performance.

3. Results and discussion

The optical micrograph in Fig. 2 depicts the typical compound nitrided layer, a few μm thick, of one sample of the lot. It reflects the compound layer stability due to this type of treatment. The EDS technique with a scanning electron microscope was used in order to evaluate the nitrogen content, which was around 20% at due to the well nitrided compound layer.

In the diffractogram corresponding to the typical treated sample, seen in Fig. 3, there appear the phases: ε-Fe$_{2-3}$N(ε), γ'-Fe$_4$N(γ') and Fe$_3$O$_4$. The notorious presence of Fe$_3$O$_4$ in the samples treated for 1 h (1) and 4.5 h (3) but scarcely found in the 3 h (2) and 6 h (4) ones could be attributed perhaps to a small leakage in the gas mixture admission system. It exhibits a relatively high content of the ε and γ' phases in samples (1) and (3) whereas (2) and (4) maintain almost the same content. As the treatment time extends from 3 h to 4.5 h the γ' increases, as found by the other authors [8, 9] but reverses at 6 h, along with the ε phase, indicating a relatively high sputtering [8] and/or nitride saturated content in the compound layer.

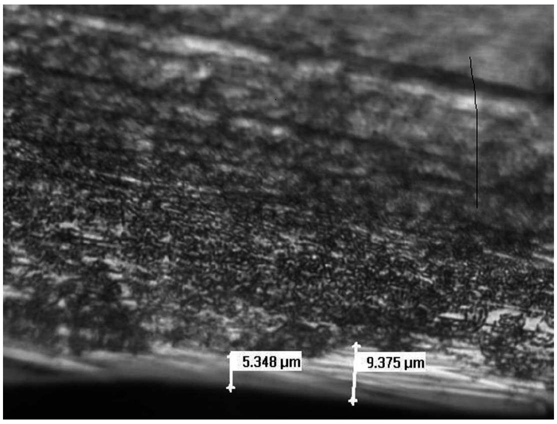

Fig. 2. Compound layer of 4140 steel revealed by the 2% Nital solution.

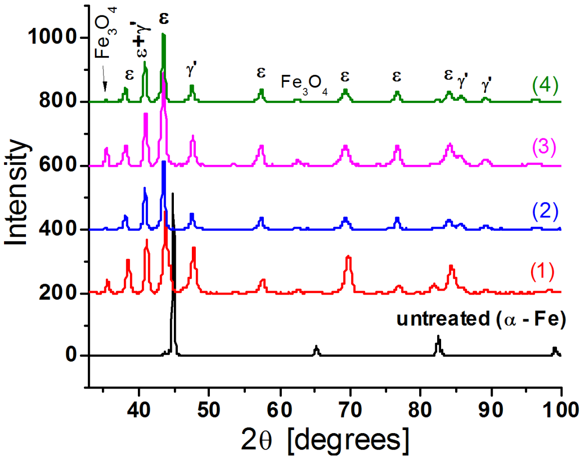

Fig. 3. Diffractogram of: untreated, and treated for 1 h (1), 3 h (2), 4.5 h (3) and 6 h (4) of nitriding time.

The surface hardness of the nitrided specimens remained practically constant, around 818 HV at a 500 g load. In contrast with 300 HV at the same load in the case of the untreated sample, this means an increment of more than 2.5 times, entailing better results than those obtained by the other authors using plasma nitriding [10, 11] or thermochemical treatment of gases nitriding [12]. The reason for this outcome has not been the formation of large nitride precipitates, as pointed out by [8, 9]. The SEM micrographs (Fig. 4) do not show any appreciable size evolution of microstructure of the precipitates in the samples (2) and (4), corresponding to 3 and 6 h treatment, respectively. Nevertheless, these micrographs depict small microformations determined by the intensity of sputtering and redeposition [8].

The potentiodynamic tests displayed in Fig. 5 present a shift to higher, noble potential (E_{corr}) values and lower corrosion currents (i_{corr}), considering the Tafel slopes of

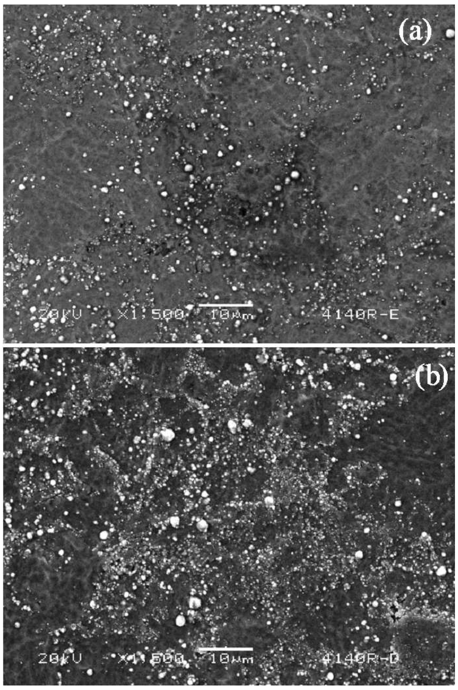

Fig. 4. SEM micrographs of the samples treated for: (a) 3 h and (b) 6 h.

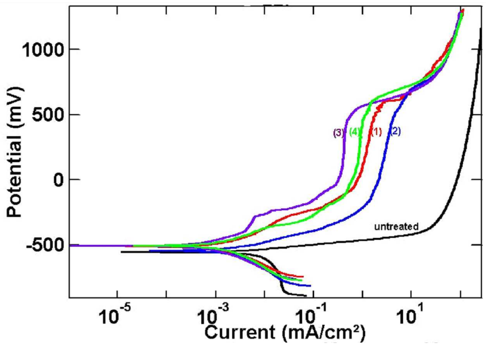

Fig. 5. Corrosion test in 3.5% NaCl of samples: untreated, (1) 1 h, (2) 3 h, (3) 4.5 h and (4) 6 h.

the nitrided pieces compared with those untreated (see Table II) calculated with the software incorporated into the work station. It should be noted that the better electrochemical performance obtained in sample (1) is due to a higher content of the ε phase compared to other nitrided samples according to [7]. These figures are in good agreement, though, to these published about 4140 low alloy steel [13]. On its part, all nitrided samples exhibit a passive behaviour between −500 mV and 500 mV as observed in all specimens showing very low anodic current. The sample treated for 4.5 h makes evidently much lower passive currents than its counterparts. Around 600 mV, the breakdown occurs in all treated specimens. These parameters indicate an enhanced corrosion performance because of nitriding.

TABLE II
Polarization test results.

Sample	Treatment time [h]	E_{corr} [V]	i_{corr} [A/cm^2]
untreated		−556	2.55×10^{-6}
(1)	1	−510	1.82×10^{-6}
(2)	3	−544	1.41×10^{-6}
(3)	4.5	−505	2.12×10^{-6}
(4)	6	−522	2.04×10^{-6}

4. Conclusions

Effective RF discharge nitriding has been achieved, proving that it is a time saving process with notorious increase in the Vickers hardness during only one hour of treatment. Potentiodynamic tests show an improved electrochemical behaviour compared to that of the untreated samples. The RF discharge nitriding process shows saturation or/and high sputtering after 4.5 h of treatment due to the removal of ε and γ' phases simultaneously although without demerit of the hardness. A compromise has to be established between the nitriding time and the corrosion parameters obtained.

Acknowledgments

This project has been partially funded by CONACyT, México. The authors are grateful to Jorge Pérez for their technical support in the XRD and EDS diagnostics. The technical assistance received from Pedro Ángeles Espinoza, María Teresa Torres M. and Isaías Contreras Villa is much appreciated.

References

[1] Dong Cherng Wen, *Appl. Surf. Sci.* **256**, 797 (2009).
[2] A. Basu, J. Dutta Majumdar, J. Alphonsa, S. Mukherjee, I. Manna, *Mater. Lett.* **62**, 3117 (2008).
[3] A. Alsaran, M. Karakan, A. Celik, *Mater. Charact.* **48**, 323 (2002).
[4] S.Y. Sirin, K. Sirin, E. Kaluk, *Mater. Charact.* **59**, 351 (2008).
[5] M.B. Karamiş, E. Gerçekcioğlu, *Wear* **243**, 76 (2000).
[6] M.B. Karamiş, *Wear* **147**, 385 (1991).
[7] S.D. Oliveira, A.P. Tschiptschin, C.E. Pinedo, *Mater. Design.* **28**, 1714 (2007).
[8] P. Corengia, G. Ybarra, C. Moina, A. Cabo, E. Broitman, *Surf. Coat. Technol.* **200**, 2391 (2005).
[9] A. Çelik, S. Karadeniz, *Surf. Coat. Technol.* **72**, 169 (1995).
[10] S.Y. Sirin, E. Kaluc, *Mater. Design* **36**, 741 (2012).
[11] M.S. Shah, M. Saleem, R. Ahmad, M. Zakaullah, A. Qayyum, G. Murtaza, *J. Mater. Proc. Technol.* **199**, 363 (2008).
[12] S. Weber, T. Werner, *Int. J. Mater. Res.* **102**, 17 (2011).
[13] M. Fattah, F. Mahboubi, *Mater. Design* **31**, 3915 (2010).