

Increase of Salt Fog Corrosion Resistance of Plasma Nitrided Steel by Pulsed Plasma Post-Oxidation

J.C. Díaz-Guillén,¹ J.S. Zamarripa-Piña,² E. E. Granda-Gutiérrez,³
M. A. González-Albarrán,⁴ J.A. Díaz-Guillén,⁵ S.I. Pérez-Aguilar,⁶
J.Candelas-Ramírez⁷

^{1, 2, 3, 4, 6, 7} Corporación Mexicana de Investigación en Materiales S.A. de C.V., Saltillo, Coahuila. México.

⁵ División de Estudios de Posgrado e Investigación. Instituto Tecnológico de Saltillo. Saltillo, Coahuila. México

Abstract: Plasma nitriding has demonstrated to be a good alternative to increase surface hardness, wear and abrasion resistance of AISI 4340 steel. Unfortunately, corrosion resistance of the obtained nitrided layer is poor as a consequence of its high grade of porosity. In the present work, pulsed plasma post-oxidation process is analyzed as an alternative technique to increase corrosion resistance of plasma nitrided AISI 4340. The effect of post-oxidation process duration (15, 30 and 60 minutes) on the corrosion performance of samples when they are exposed to a rich chloride fog under controlled temperature and pressure conditions was evaluated. Results showed that post-oxidized during 15 minutes samples have the best corrosion performance. After 21 h of exposition to 3.5 % NaCl fog, the presence of red rust on post-oxidized during 15 minutes samples was reduced to around 1/16 part of the only nitrided sample. According with scanning electron microscopy and X-ray diffraction analysis, the increase in the corrosion resistance of post-oxidized samples is related to the occurrence of an oxidized thin layer constituted mainly by magnetite kind iron oxide.

Keywords: Plasma nitriding, plasma post-oxidation, salt fog corrosion.

I. INTRODUCTION

Ni-Cr-Mo steel AISI 4340 is a commonly used alloy which is characterized by its remarkable strength, ductility and toughness obtained as a consequence of its good tempering properties [1]. Because of its structural acceptable performance, AISI 4340 is widely used for fabrication of parts and components in automotive, aerospace as well as metal mechanics industries. In this sense, pieces as shafts, bolts, rods, reels, rotors and gears can be fabricated using this alloy. Despite its good mechanical properties, the lifetime of this alloy is not long enough, because of its low corrosion resistance and poor tribological properties [2].

In order to increase the lifetime of pieces and accessories fabricated using AISI 4340 steel, through optimization of corrosion and tribological performance, several coatings [3] and thermochemical treatments [4] have been applied on this alloy. In recent years, it has been demonstrated that ion nitriding, a plasma assisted surface modification thermochemical treatment, is an attractive technique which promotes the increase in hardness, wear and fatigue properties of several iron alloys [5, 6, 7].

Nitriding process results in the formation of a compounds layer followed by a nitrogen diffusion zone. The compounds layer is mainly constituted by a combination of iron nitrides ($\text{Fe}_{2,3}\text{N}$ and/or Fe_4N) and the diffusion zone is composed of nitrogen saturated ferrite together with dispersed precipitates of iron and alloy element nitrides [8]. Both regions are responsible for improvement of previously enounced properties. Nitrided layer improve significantly the tribological surface properties of nitrided pieces but it has a porous structure that limits the corrosion resistance of nitrided steels. In this way, increasing of corrosion properties is still an opportunity area for integral improvement of the surface properties of metal alloys.

In order to increase both, mechanical and corrosion properties of nitrided iron alloys, some complementary processes have been proposed, highlighting oxidation through air furnace process [9] and DC conventional plasma [10]. Post-oxidation treatments produce a thin oxide layer on compounds layer, which covers and seals micro-pores and improves the corrosion resistance of nitrided steel [11,12]. Currently, some researches are focused in the study of the influence of post-oxidation process parameters on properties and performance of these nitrided post-oxidized layers. It has been emphasized the fact that the post-oxidation process has to be controlled to avoid the formation of hematite (Fe_2O_3) and to produce layers with high content of magnetite (Fe_3O_4), a compound of high chemical stability which is highly corrosion resistant [13,14].

With the aim to contribute to the study of influence of processing parameters during post-oxidation process, on corrosion performance of plasma nitrided low alloy AISI 4340 steel, in the present work it is proposed the pulsed plasma post-oxidation process as an alternative to improve the corrosion performance of this alloy. It is analyzed the influence of plasma post-oxidation process duration, in a pulsed DC glow discharge, on corrosion performance of post-oxidized samples when they are exposed to a 3.5% NaCl fog. (Procedure ASTM B177, Standard practice for operating salt spray apparatus).

II. MATERIALS AND METHODS

AISI 4340 samples (4 x 4 x 0.5 cm) from a commercial source were used in the present study. Table 1 shows the chemical composition of samples which was obtained through infrared detection for carbon and sulfur and X-Ray spectroscopy for the rest of elements.

Table 1. Chemical composition of substrates used in this study

Element	C	S	Mn	P	Si	Cr	Ni	Mo	Cu	Fe
Weight %	0.38	0.017	0.63	0.008	0.19	0.80	1.64	0.20	0.14	Balance

Previous plasma treatment, samples were ground using different grades of SiC emery paper (120, 240, 320, 400, 600 progressively) and polished with a 0.5 μm diamond suspension. After that, samples were subjected to a cleaning stage in an acetone ultrasonic bath, in order to remove dust or oil from the surface.

Pulsed plasma nitriding was carried out using a DC pulsed glow discharge sustained in a 50% N₂ 50% H₂ gas mixture at 2 torr. The next parameters were kept constant: temperature 520 °C, processing time 3 hr, discharge voltage 800V and frequency of 1000 Hz. Pulsed plasma post oxidation process was carried out immediately after nitriding by changing in processing conditions. The DC discharge used during post-oxidation stage was kept using a gas mixture 20% O₂ 80% N₂ at 1.5 Torr using a frequency of 1000 Hz at 400°C. Processing time during post oxidation process was manipulated for values of 15, 30, and 60 minutes.

Both, nitriding and post-oxidizing process were carried out using an own design processing equipment [15] which consists of a vacuum chamber containing a central cathode biased by negative high voltage pulses. Plasma is generated and sustained by an IGBT (Insulated Gate Bipolar Transistor) based DC pulsed power supply unit, which provides precise adjustments of discharge current, pulse frequency and duty cycle. An auxiliary heating system offers full control over the sample temperature, which is measured by a K-type thermocouple directly fastened on the samples. Mass flow controllers allow the precise control of pressure and gas mixture inside the vacuum chamber.

Once duplex nitriding post-oxidizing process was concluded, samples were cross sectioned, polished, and etched with 5% Nital reagent to reveal the modified surface region. Scanning electron microscopy (SEM) was used to analyze morphological changes on surface and cross section of the samples. Crystalline phases occurring on the surface of modified samples were identified by the use of X-ray diffraction technique (XRD). XRD patterns were obtained in a Philips X'Pert diffractometer, using a Cu Kα radiation (λ=1.5406 nm), 45 kV and 40 mA. Scanning was carried out from 34° to 50° 2θ with a step of 0.016° and step duration of 20 s.

Corrosion performance of nitrided post-oxidized samples under influence of a rich chloride fog was evaluated in agreement with procedure specified by standard ASTM B-117. This practice provides a controlled corrosive environment which has been utilized to produce relative corrosion resistance information for specimens of metals and coated metals exposed in a given test chamber. Untreated, nitrided and nitrided post-oxidized samples were exposed to a salt fog for 72 hr. A periodic evaluation of the corrosion grade of surface samples was carried out at 2, 4, 6, 21, 23, 25, 27, 48 and 72 hr. Corrosion performance test parameters are listed at table 2.

Table 2. Salt spray test parameters.

Test parameter	Condition
Cabinet temperature	35 °C
Tower temperature	50 °C
Tower pressure	96.53 kPa (14psi)
Solution pH	6.96
Average of specific gravity	1,040 g/mL
Collection rate	1.68 mL/h
Exposition angle	30° to the vertical
Grade water	ASTM D 1193, Type IV
Exposition time	72 hours

III. RESULTS AND ANALYSIS

Figure 1 shows 2000X SEM surface views of a) Plasma nitrided and b) Plasma nitrided post-oxidized during 15 minutes samples. The surface morphology of pulsed plasma nitrided sample is characterized by edged particles with well-defined boundaries. This morphology has been reported for low alloy steels processed by plasma surface treatment as active screen plasma nitriding [16] and it has been related to sputtering phenomenon intensity [3,17]. However, post-oxidized sample (Figure 1b) exhibits comparatively a more homogeneous appearance with decreased in edged particles quantity leading to a less rough surface which could be related to the formation of an oxides layer resulting from the post-oxidation process. It have been reported for post-oxidation process that an adherent oxide phases fill and seal the holes between particles of nitrided surfaces, which could have a positive effect on corrosion resistance improvement [18].

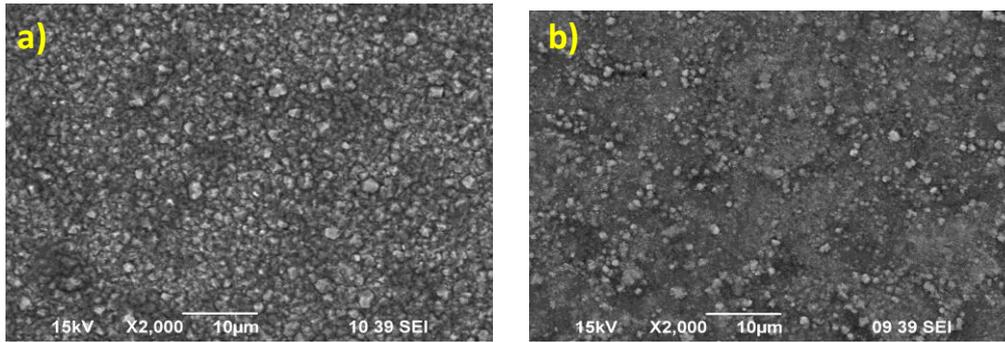


Figure 1. Representative SEM surface views of a) Plasma nitrided and b) Plasma nitrided post-oxidized samples.

Figure 2 shows a SEM cross view of duplex, nitrided post-oxidized during 15 minutes sample. The presence of an oxidized layer on the nitrided surface, which fill and seal the holes of nitrided sample, can be confirmed through this cross view. It can be appreciated a bi-layer arrangement constituted by a thin oxide layer on a thicker nitrided layer. Both, oxidized and nitrided layer are not chemical etched by Nital reagent. This bi-layer arrangement was observed for all evaluated samples; however it was evident the influence of post-oxidation time on oxidized layer thickness: 325 nm (± 28), 431 nm (± 50) and 722 nm (± 118) were measured for samples post-oxidized during 15, 30 y 60 minutes respectively.

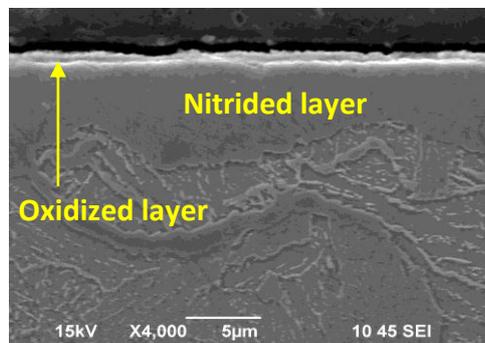


Figure 2. SEM cross view of nitrided post-oxidized sample for 15 minutes.

X-Ray diffraction patterns for untreated, nitrided and nitrided post-oxidized during 15 minutes samples are showed at figure 3. Plasma nitriding promoted a high attenuation of the reflections related to α -Fe giving rise to appearance of reflections located at 41.09° and 47.74° 2 theta associated to γ' - Fe_4N monophasic layer. Similarly, the post-oxidation treatment promotes the clear appearance of reflection located at 35.90° and 43.64° 2 theta, which are characteristics of kind magnetite iron oxide. It is important to remark that, for iron alloys oxidation process, the presence of high content of magnetite layers instead of hematite is preferred, mainly due to the well-known high corrosion performance of magnetite phase [13, 14]. In this sense, this work shows optimal processing condition for getting rich magnetite layers.

Both crystalline phases, γ' - Fe_4N and Fe_3O_4 , occur for all evaluated post-oxidation periods. However, additional to appearance of magnetite as a consequence of oxidation process, there is evident the occurrences of Fe_3N iron nitride. This phenomenon has been reported previously and it has been related to Fe_4N decomposition chemical reaction, because the presence of oxygen, to produce kind magnetite iron oxide through the reaction $3\text{Fe}_4\text{N} + 2\text{O}_2 = 3\text{Fe}_3\text{N} + \text{Fe}_3\text{O}_4$ [14].

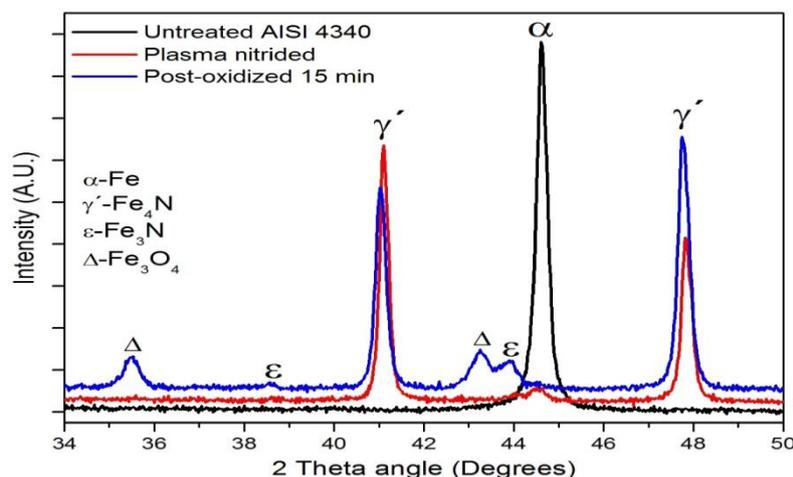


Figure 3. X-ray diffraction patterns for untreated, nitrided and nitrided post oxidized during 15 minutes samples.

Figure 4 shows the influence of post-oxidation process duration on samples corrosion performance, tested under rich chloride fog in agreement with procedure ASTM B117 and under conditions previously described. It can be seen that both, nitrided and nitrided post-oxidized samples show lower corrosion rate that untreated sample (evaluated through red rust presence on the surface of the samples). Moreover, it is evident that corrosion susceptibility of nitrided post-oxidized samples is considerably lower than only nitrided sample, which is much more evident after 21 hour test. Thus, after 21 h exposed to rich chloride fog, untreated and plasma nitrided samples showed presence of red rust on 90 and 80% of their surface respectively. However, for nitrided post-oxidized samples after 21 h test, presence of red rust on 5, 40 and 45% of the samples surface was detected for oxidation periods of 15, 30 and 60 minutes respectively. Figure 5 shows surface views of the samples: untreated, nitrided and nitrided post-oxidized during 15, 30 and 60 minutes.

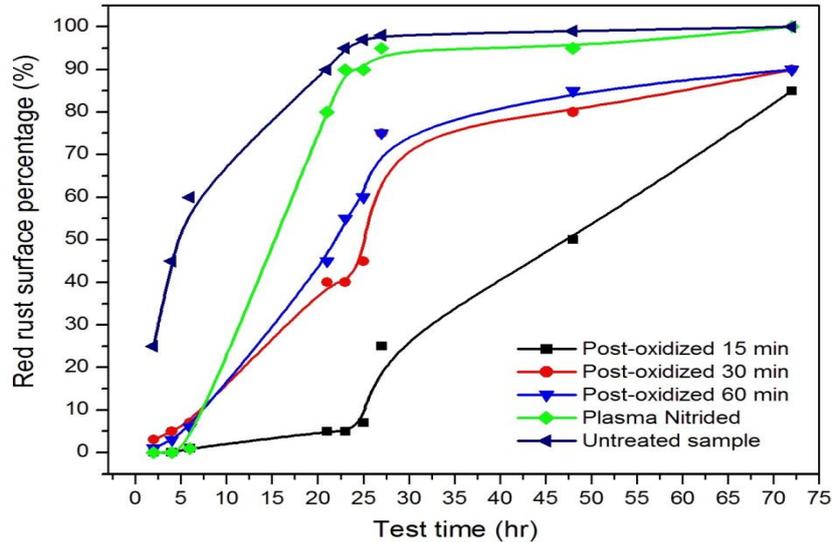


Figure 4. Influence of post-oxidation process duration on corrosion performance of evaluated samples.



Figure 5. Surface pictures of samples after 21h exposed to rich chloride fog. a) Untreated, b) nitrided, and post-oxidized during c) 15, d) 30 and e) 60 minutes.

In a previously work we reported that for the case of nitrided post-oxidized AISI 1045 steel, after 30 minutes of oxidation at 400°C, oxidized layer shows a cracking phenomenon which could be attributed to its thicker thickness and to the embrittlement of oxidized layer due to oxygen oversaturation [19]. In this sense, samples exhibiting any superficial cracking could be result in the exposition to fog of little surface sections without oxidized layer, which would result in the evident decrease in the corrosion performance.

Corrosion performance results show that show that 15 minutes of post-oxidation process is enough time to reduce the corrosion rate to around 1/16 part of the only nitrided sample corrosion rate. This fact represents a considerable increase in corrosion resistance of samples post-oxidized during 15 minutes respect samples processed during 30 and 60 minutes, which can be directly translated to an important energy and time saving.

It is important to emphasized that after 72 hour test, the better corrosion performance of post-oxidized samples respect untreated and nitrided samples is still evident. Thus, after 72 h test, untreated and nitrided samples shown presence of red rust on 100% of its surfaces while post-oxidized samples showed presence of this red rust on 85, 90 and 90% of its surface for samples post-oxidized during 15, 30 and 60 minutes respectively.

IV. CONCLUSION

In the present work the influence of pulsed plasma post-oxidation process on crystalline phase's composition and corrosion performance of plasma nitrided AISI 4340 steel was evaluated. Results analysis let us to conclude that:

Pulsed plasma nitriding promotes the modification of surface morphology from mirror polished (untreated sample) to a surface characterized by edged particles and well defined boundaries. As a consequence of the post-oxidation process, the quantity of edged particles was reduced leading to a less rough surface; the latter could be related to the formation of a homogeneous oxidized layer. Plasma post-oxidation process of nitrided AISI 4340 steel promotes the occurrence of a surface constituted by a magnetite thin layer on a thicker nitrided layer. The oxidized layer is characterized by presence of kind Fe_4N and Fe_3N iron nitrides.

The corrosion performance of the samples exposed to a salt fog was significantly better in the case of the oxidized samples compared with nitrided samples. After 21 h test, plasma nitrided sample showed red rust on 80% of its surface while samples post oxidized during 15 minutes showed only 5% of its surface with the occurrence of this red rust. This fact represent a decrease in corrosion rate of sample post-oxidized during 15 minutes to 1/16 part respect only nitrided sample.

REFERENCES

- [1] ASM International. ASM International Handbook Volume 1. Properties and selection: irons steel and high performance alloys. 10 th edition USA
- [2] R.C. Souza, H.J.C. Voorwald and M.O.H. Cioffi. Fatigue strength of HVOF sprayed Cr3C2–25NiCr and WC-10Ni on AISI 4340 steel. *Surface and Coatings Technology*. 203, 2008, 191-198.
- [3] H.J.C. Voorwald, L.F.S. Vieira, M.O.H. Cioffi. Evaluation of WC-10Ni thermal spraying coating by HVOF on the fatigue and corrosion AISI 4340 steel. *Procedia Engineering*. 2, 2010, 331-340
- [4] Sule Yildiz, Kahraman Sirin, Erdinc Kaluc. Effect of the ion nitriding surface hardening process on fatigue behavior of AISI 4340 steel. *Materials Characterization* 59, 2008, 351-358
- [5] Asadi Z.S., Mahboubi F. Effect of component's geometry on the plasma nitriding behavior of AISI 4340 steel. *Journal of Materials and Design* 34, 2012, 516-521
- [6] A. Akbari, R. Mohammadzadeh, C. Templier, J.P. Riviere. Effect of the initial microstructure on the plasma nitriding behavior of AISI M2 high speed steel. *Surface and Coatings Technology*, 204, 2010, 4114-4120
- [7] J.C. Stinville, P. Villechaise, C. Templier, J.P. Riviere, M. Droue. Plasma nitriding of 316L austenitic stainless steel: Experimental investigation of fatigue life and surface evolution. *Surface and Coatings Technology*, 204, 2010, 1947-1951
- [8] K. Ozbaysal, O. T. Inal. Thermodynamics and structure of solidification in the fusion zone of CO₂ laser welds of 15-5 PH stainless steel. *Materials Science Engineering*. 78, 1986, 179-191.
- [9] Yucl Birol. Effect of post-oxidation treatment on thermal fatigue behaviour of plasma nitrided hot work tool steel at elevated temperatures. *Surface and Coatings Technology*. 205, 2011, 2763-2769
- [10] N. Yasavol, F. Mahboubi. *Materials and Design* 38, 2012, 59-XX
- [11] M. Zlatanovic, N Popovic, Z. Bogdanov, S.Zlatanovic. Pulsed plasma-oxidation of nitrided steel samples. *Surface and Coatings Technology*. 174-175, 2003, 1220-1224
- [12] F. Borgioli, E. Galvanetto, A. Fossati, T. Bacci. Glow-discharge nitriding and post-oxidising treatments of AISI H11 steel. *Surface and Coatings Technology*. 162, 2003, 61-66
- [13] F. Mahboubi, M. Fattah. Duplex treatment of plasma nitriding and plasma oxidation of plain carbon steel. *Vacuum*. 79, 2005, 1-6
- [14] Yang. Li, Liang Wang, Dandan Zhang, Lie Shen. Improvement of corrosion resistance of nitrided low alloy steel by plasma post-oxidation. *Applied Surface Science*. 256, 2010, 4149-4152
- [15] Díaz Guillén J C, Campa Castilla A, Pérez Aguilar S I, Granda Gutiérrez E E, Garza Gómez A, Candelas Ramírez J, Méndez Méndez R. Effect of duty cycle on surface properties of AISI 4340 using a pulsed plasma nitriding process. *Superficies y Vacío*. 21, 2009, 1-4
- [16] Z.Sotani Asadi, F. Mahboubi. Effect of component's geometry on the plasma nitriding behavior of AISI 4340 steel. *Materials and Design*. 34, 2012, 516-521
- [17] H.J.C. Voorwald, L.F.S. Vieira, M.O.H. Cioffi. *Procedia Engineering* 2, 2010, 331-340
- [18] Zhao C, Li C.X, Dong H, Beel T. Study on the active screen plasma nitriding and its nitriding mechanism. *Surface and Coatings Technology*. 201, 2006, 2320-2325
- [19] Alireza Esfahani, Mahmoud Heydarzadeh Sohi, Jafar Rassizadehghani, Farzad Mahboubi. Effect of treating atmosphere in plasma post-oxidation of nitro carburized AISI 5115 steel. *Vacuum*, 82, 2008, 346-351
- [20] Díaz Guillén J. C., Granda Gutiérrez. E. E., Campa Castilla A., Pérez Aguilar S. I., Garza Gómez A., Candelas Ramírez J. Modificación superficial de un acero AISI 1045 mediante un proceso dúplex nitruración y post- oxidación en un plasma CD pulsado. *Superficies y Vacío* 25(3), 2012, 166-170.