

# XC48 nitriding by Plasma Immersion Ion Implantation

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In this work, Nitrogen plasma immersion ion implantation (PIII) treatment of (XC48) Carbon steel was performed in a plasma reactor with an inductive RF source (13.56 MHz) at low pressure in order to investigate the influence of the process conditions on the chemical and mechanical properties of this studied material. The X-rays diffraction analysis revealed the presence of several nitride phases ( $\text{Fe}_3\text{N}$ ,  $\text{FeN}$  and  $\text{Fe}_4\text{N}$ ) formed onto implanted samples. The mechanical characterization of the processed samples showed an increase of 300 % in the nano-hardness. A low corrosion rate is obtained denoting an improvement in the corrosion resistance behavior. These results are particularly interesting since they were obtained for relatively low bias voltages and processing time.

## 1. Introduction

Plasma immersion ion implantation (PIII) is a relatively new surface treatment process which offers considerable flexibility to modify the properties of a very wide range of materials[1-5]. Plasma immersion ion implantation is a surface modification technique used for improving wear, corrosion and fatigue resistance of steels and metallic materials. As its name suggests it is to modify the properties of a material by ion insertion in its bulk. This process, developed in 1988 by Conrad et al[6]. In this study, we are interested to highlight the effect of self\_heating by the high negative DC voltage applied to the substrate. The DC voltage is known to be able to rapidly heat the samples, on the contrary to the pulsed polarization which necessitates more elevated bias voltages. Thus, the DC polarization enables us to avoid the heat treatment ex-situ to diffuse the implanted ions, which means that this type of treatment requires no oven. To avoid the breakdown and arcs problem caused by the DC bias voltage. This work aimed at improving the micro-hardness and corrosion resistance of XC48 Carbon steel.

## 2. Experimental details

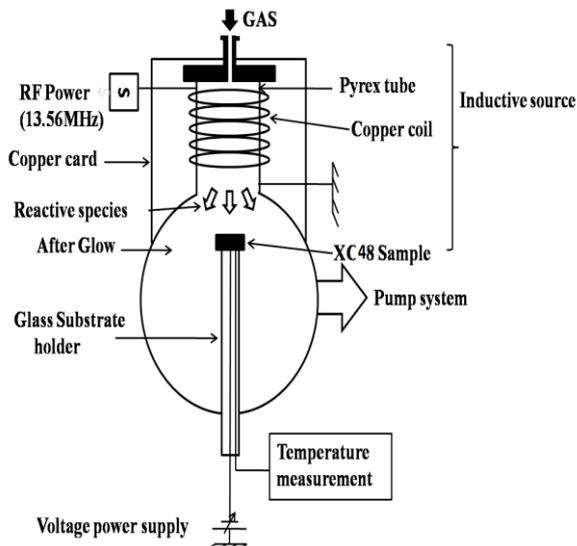
The experimental setup of the PIII system used for the surface treatment of the material is shown in Fig.1. It consists of a spherical chamber of 930 mm diameter which is connected to a pumping unit designed to evacuate air until a vacuum of  $10^{-6}$  mbar. The pumping unit involves a primary pump which allows achieving a primary vacuum of about  $10^{-3}$  mbar and a secondary oil diffusion pump in order to achieve a high vacuum of the order  $10^{-6}$  mbar. To create the plasma, we used an inductive excitation system. The inductive excitation consists of a Pyrex tube surrounded by a Copper coil polarized by an RF generator (13.56 MHz). A glass substrate holder with a length of 1500 mm and 13 mm of a diameter has been used. In order to bias our samples, we used an HCN 2800\_6500 high negative voltage power supply to reach values of the order 400 mA/6.5kV.

## 3. Results and discussion

### 3.1 X-Rays Diffraction Analysis

The results of the X\_ray diffraction analysis are given in the Fig.4. The sweep range in  $2\theta$  Was limited to the range between  $25^\circ$  and  $88^\circ$ , since no peak was detected outside that range for treated substrates. The XRD patterns of the

untreated XC48 Carbon steel (Fig.2 (a)) shows only two peaks related to the crystallographic planes (110) and (200) of  $\alpha$ -Fe phase (100) denoted as *ferrite* located at  $44.67^\circ$  and  $65.02^\circ$ , respectively. Concerning the diffraction pattern of implanted XC48 (Fig.2 (b)), even if the diffraction peaks of  $\alpha$ -Fe is strongly observed, the diffractogram exhibits the characteristic peaks of iron nitride:  $\text{Fe}_3\text{N}$  (i.e.  $\epsilon$ - $\text{Fe}_2\text{N}_{1-x}$ ) and  $\gamma$ - $\text{Fe}_4\text{N}$ .

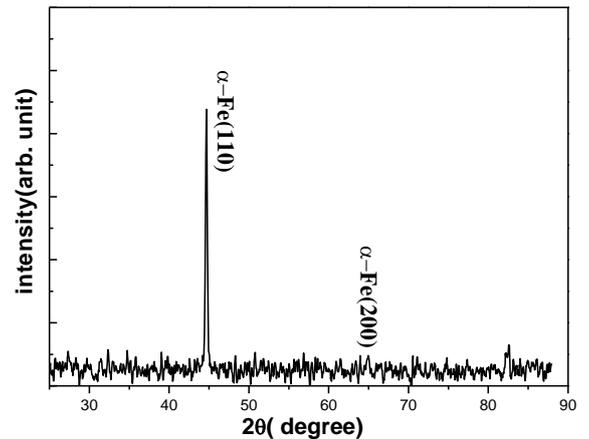


**Fig. 1:** Experimental setup

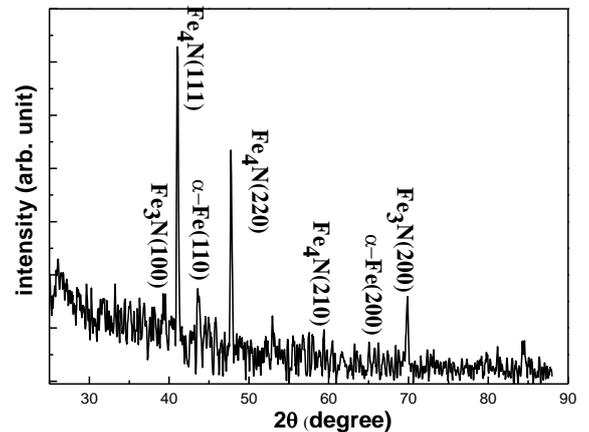
These results are in good agreement with the binary phase diagram of Fe-N proposed by Perrot [7] which gives the presence of the iron nitride  $\text{Fe}_3\text{N}$  and  $\text{Fe}_4\text{N}$  at the temperature of  $400^\circ\text{C}$ . These phases were also observed in  $\alpha$ -Fe PIII implanted at 5 to 20 kV with respect to low temperatures range of  $366$  to  $591^\circ\text{C}$  [8, 9].

### 3.2 Nano-hardness

The mechanical properties such as nano-hardness of the treated XC48 were measured and the influence of the implantation conditions on the nano-hardness are presented in Fig.3 and 4. We note that all treated samples exhibit an evident increase in the nano-hardness compared to the untreated samples (roughly around 150 HV). Fig. 3 gives the influence of the power on the nano-hardness for 4 kV bias voltage,  $8 \times 10^{-2}$  mbar pressure and 120 min of treatment time. The nano-hardness increases from 440 HV (160 Watt) to 700 HV (400 Watt).



**Fig.2(a):** X-rays diffraction patterns of XC48 steel, untreated sample



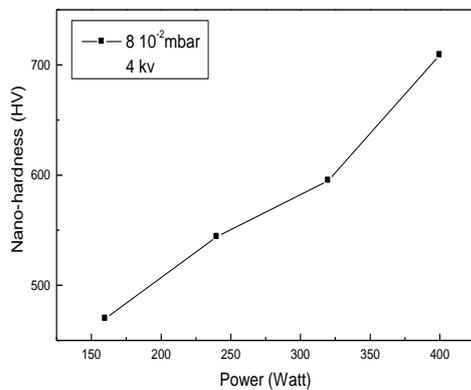
**Fig.2(b):** X-rays diffraction patterns of XC48 steel

Nitrogen-implanted sample for experimental conditions 4KV, 240Watt,  $4 \times 10^{-2}$  mbar and 120min.

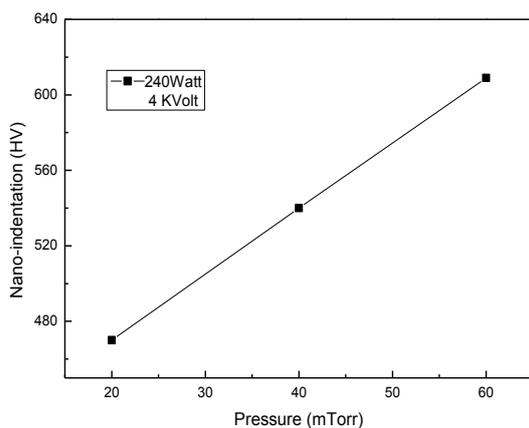
This trend seems obvious because it is due to implantation-induced defects. Also, an increase in the power has a direct effect on the plasma characteristics. Indeed, the plasma contains more ionic species density ( $\text{N}^+/\text{N}^{2+}$ ) due to the increased electronic density with increasing incident power [10], and those species will be accelerated and implanted into the sample to form the new hard phases nitrides, as revealed by XRD.

Fig.4 shows the micro-hardness as a function of pressure for 4 kV bias voltage, 240Watt and 120 min of treatment time. The nano-hardness

increases with pressure, and this is due to the increasing ionic species density ( $N^+/N^{2+}$ ), induced by increased number of collisions between particles; which enhances the diffusion of these species in the sample.



**Fig.3:** Micro-hardness of the implanted sample XC48 versus the injected power.



**Fig.4:** Micro-hardness of the implanted sample XC48 versus the pressure.

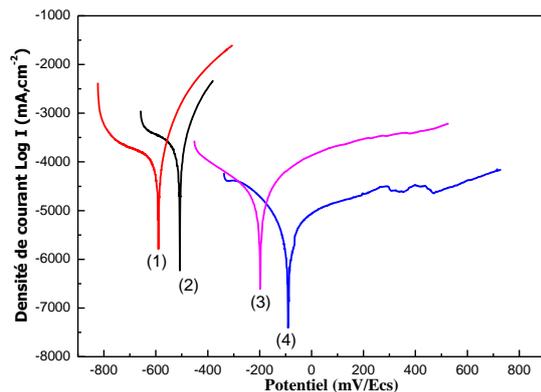
### 3.3 Potentiodynamic polarization characterization

Fig.5 shows potentiodynamic curves recorded after immersion in a saline solution of 3.5 wt. % NaCl at room temperature (25°C), for untreated and Nitrogen-implanted XC48 surfaces treated with different negative bias voltage (2.5, 3, 3.5, 4KV) under the following operating conditions; power: 240Watt, pressure:  $2 \times 10^{-2}$  mbar and treatment time: 120 min. From

the curves (Fig.5), it is clear that the displacement of treated samples curves to lower values of the corrosion current and higher values of polarization voltage is the main indicator of the enhancement in corrosion performance of the treated samples. The corrosion current density ( $I_{corr}$ ) was significantly decreased after nitriding compared to the un-nitrided substrate, which indicated that the nitrided case impeded the anodic dissolution resulted in a very low corrosion current. The corrosion potential ( $E_{corr}$ ) was shifted to higher values, e.g. from  $-507\text{mV}$  for the untreated XC48 to around of  $-197\text{mV}$  for the nitrided samples. However the current densities were decreased from the untreated sample to the nitrided one. The corrosion current densities ( $I_{corr}$ ) of all nitrided samples were decreased in the range between 66.62 and 10.18  $\text{mA}/\text{cm}^2$  respectively for 3.5 and 4KV of negative bias voltage. It is well established that the best corrosion performance of nitrided samples is related to the preferred formation of  $\text{Fe}_3\text{N}$  crystalline phase; where the preference of nitrided sample with a  $\text{Fe}_3\text{N}$  nitride content and  $\text{Fe}_4\text{N}$  nitride because of their good corrosion performance [11, 12].

### 4. Conclusion

In this study, Nitriding-PIII XC48 steel was investigated under different operating conditions (pressure, power and negative bias voltage). Different techniques of characterization were used: X-ray diffraction, micro-hardness and the potentiodynamic polarization tests. The micro-hardness increased up to 400% for the Nitrogen-implanted samples compared to the untreated one (150HV). The highest surface hardness value (700 HV) was obtained when Nitriding PIII process was carried out at 400°C using at 4 KV, 400Watt, 120 min and  $8 \times 10^{-2}$  mbar.



**Fig.5:** Potentiodynamic polarization curves of untreated and treated XC48 samples different negative bias voltage (2.5, 3, 3.5, 4KV), in 3.5 wt.% NaCl at room temperature (25°C).

The XRD analysis revealed the presence of nitride  $\text{Fe}_3\text{N}$  and  $\text{Fe}_4\text{N}$  phases which were formed into implanted samples using our inductive plasma reactor. Corrosion resistance of XC48 Carbon steel is improved by plasma immersion ion implantation of Nitrogen.

## 5. References

- [1] T. Balusamy, T.S.N. Sankara Narayanan, K. Ravichandran, Il Song Park, Min Ho Lee, Plasma nitriding of AISI 304 stainless steel: Role of surface mechanical attrition treatment, *materials characterization*, 2013, **85**, p 38–47.
- [2] Wang Jun, Lin Yuanhua, Fan Hongyuan, Zeng Dezhi, Peng Qian, Shen Baoluo, Effects of Temperature on Microstructure and Wear of Salt Bath Nitrided 17-4PH Stainless Steel, *J. Mater. Eng. Perform.*, 2012, **21**, p 1708-1713.
- [3] Y Zhao, B Yu, L Dong, H Du, J Xiao. Low-pressure arc plasma-assisted nitriding of AISI 304 stainless steel. *Surf. Coat. Technol.*, 2012, **210**, p 90–96.
- [4] Wang J, Xiong J, Peng Q, Fan H, Wang Y, Li G, et al. Effects of DC plasma nitriding parameters on microstructure and properties of 304L stainless steel. *Mater Character*, 2009, **60**, p197–203.
- [5] Laleh M, Kargar F, Velashjerdi M. Low-temperature nitriding of nanocrystalline stainless steel and its effect on improving wear and corrosion resistance. *J. Mater. Eng. Perform.*, 2012, **22** (5), p1304–1310.
- [6] J.R. Conrad, R.A. Dodd, F.J. Worzala, X. Qiu, New, cost-effective, non-line-of-sight technique for ion implantation of materials, *Surf. Coat. Technol.*, 1988, **36**, p 927-937.
- [7] M.P. Fewell, J.M. Priest, M.J. Baldwin, G.A. Collin, K.T. Short, Nitriding at low temperature, *Surface and Coatings Technology*. 2000, **131**, p 284–290.
- [8] André Anders, Plasma and ion sources in large area coating: A review, *Surface & Coatings Technology*, 2005, **200**, p 1893 – 1906.
- [9] Z.J. Wang, X.B. Tian, C.Z. Gong, J.W. Shi, S.Q. Yang, Ricky K.Y. Fu, Paul K. Chu, Plasma immersion ion implantation into cylindrical bore using internal inductively-coupled radio-frequency discharge, *Surface & Coatings Technology* 2012, **206**, p 5042–5045.
- [10] M.M. Alim, M.Zekara, L. Henni, R. Tadjine, K. Henda, *Advence. Mater.Reseac.*, 2011, **227**, p 185-188.
- [11] J. Alphonsa, G. Sinha, A. Kumar, G. Jhala, S. K. Tiwari, S. Gupta, P. A. Rayjada, N. Chauhan, P. M. Raole, S. Mukherjee. Effect of frequency on the properties of plasma nitrided AISI 4340 steel, *J. Metall. Mat. Sci.*, 2008, **50** (2), p 119-125.
- [12] Díaz-Guillén J.C., Díaz-Guillén J.A., Granda-Gutiérrez E.E., Díaz-Guillén M.R., González-Albarrán M.A. Electrochemical Corrosion Performance of AISI D2 Tool Steel Surface Hardened by Pulsed Plasma Nitriding, *Int. J. Electrochem. Sci.*, 2013, **8**, p 973 – 982.