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# Elevated temperature plasma nitriding and effects on electrochemical properties of steel

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## ABSTRACT

Surface modification of tool steel had been performed by utilizing plasma nitriding at elevated temperature by varying the exposure time. The nitrided steel had shown significantly enhanced corrosion resistance properties.

X-ray diffraction (XRD) had revealed the presence of Fe<sub>x</sub>N (x = 2–3, 4) in the surface modified microstructure after nitriding. In an environment of NaCl potentiodynamic polarization and impedance (EIS) tests of steel with and without nitriding had been performed. Both these tests had shown the improved resistance to corrosion of the steel after nitriding.

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## 1. Introduction

Surface microstructural and the crystal lattice modifications had been proved to be the main reasons for the improvement of surface hardness, resistance to fatigue, wear and corrosion. The improvement of these properties has recently been realized in tool industries where the premature failure caused by the wear and corrosion in the service conditions demands the early replacement of the tools. Though the other processes like physical/chemical vapour deposition has been practiced to overcome these for a long time but the poor adhesion and delamination of the deposited layer had been the subject of concern [1–4]. Among the various surface modification methods plasma mediated nitriding has already been recognized as an environmental friendly and efficient process which has circumvented these limitations.

Formation of desirable nitride phases and the modification of surface microstructure, generation of stresses in the crystal lattice are well controlled and hence the process is successful and widely accepted for mechanical properties, corrosion and biocompatibility [5–15]. In the plasma nitriding process, the samples to be nitrided are polished to mirror finish and cleaned ultrasonically to remove the dirt on the surface. Samples are placed on the sample holder inside the nitriding chamber then evacuated to around 10<sup>-6</sup> mbar. A mixture of nitrogen and hydrogen at certain ratio is then fed into

the chamber then triggered the plasma. Samples are biased negatively to attract the positively charged ions from the plasma towards itself. Sample temperature is raised to the desired level by auxiliary heater.

Nitrogen and hydrogen ions accelerate towards the surface, adsorb on the surface, diffuse towards the bulk of the sample and form the nitrides.

Though several works have been reported so far in the literature on nitriding of steel, however very less is known about the nitriding and corrosion of wood machining CrMoV martensitic steel. Previously, Corinne et al. shown an improvement of hardness similar steel and shown a significantly higher hardness of around 1150 H<sub>v</sub> than steel without nitriding which had ~655 H<sub>v</sub> [9]. So far there is no sufficient literature on the electrochemical characterization of this steel after nitriding. Hence, an attempt has been made in the present work to understand the electrochemical corrosion this steel after nitriding in an environment of 3.5% NaCl. From the previous studies [9] it is understood that the hardness improvement is significant after nitriding at 500 °C but reduced when nitrided at 520 °C. Hence in the present studies the nitriding temperature was kept at 500 °C.

## 2. Experimental details

Austenitized steel was quenched in a bath of oil followed by tempering. Samples of dimension of 8 × 8 × 4 mm<sup>3</sup> were cut from this steel then polished to mirror finish and cleaned with ultrasonic

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bath. The composition of the steel is given as: Carbon (0.5%), Silicon (1%), Manganese (0.5%), Chromium (8.0%), Molybdenum (1.5%), Vanadium (0.5%) and balance iron.

### 2.1. Method

Then samples were kept on the sample holder inside the nitriding chamber. By using rotary and diffusion pump vacuum to a pressure of 0.05 Pa was created in the chamber. Sample was negatively biased and with Ar<sup>+</sup> sputtering nitriding cycle initiated. Nitrogen and hydrogen at a ratio of 80:20 fed into the chamber. Nitriding was followed at 500 Pa when the temperature reached to 500 °C. After nitriding the samples with bare sample were exposed to detailed X-ray diffraction studies.

Bare and nitrided steel samples then subjected to corrosion tests by following potentiodynamic polarization and subsequently impedance spectroscopic tests (EIS) in an environment of 3.5% NaCl. The electrochemical testing was followed by using the system Model SI 1287-Solatron Analytical, U.K. The cell was consisting of nitrided sample, a saturated calomel (SCE) and Pt electrodes in 3.5% NaCl already purged with nitrogen. The tests were conducted when once the equilibrium attained. The sample was scanned through ±1 V at free atmosphere at the rate 1 mV/s.

To further understand the corrosion behaviour of the nitrided and bare steel, electrochemical impedance spectroscopic analyses in 3.5% NaCl was followed by using A.C. signals.

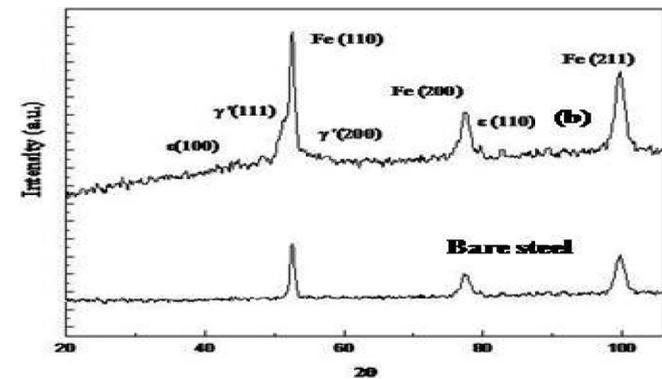


Fig. 1. X-ray diffractograms of (a) bare steel (S0) and nitrided samples at 500 °C for 8 h (b).

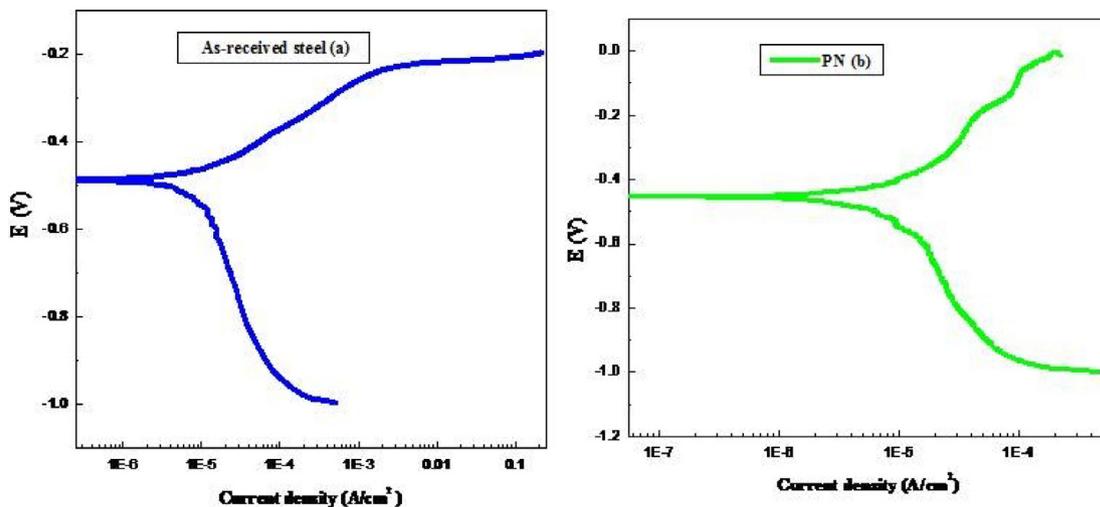


Fig. 2. Potentiodynamic polarization curves of (a) bare steel and (b) the nitrided steel at 500 °C for 8 h.

## 3. Results

### 3.1. Phase evolution

The nitrided and bare samples were exposed to detailed XRD analyses. Fig. 1 reveals the phases of bare and nitrided steel samples. From these XRD patterns it is found that the bare sample has only the Fe (1 1 0), Fe (2 0 0) and Fe (2 1 1) phase (Fig. 1a). The samples nitrided at 500 °C for 8 h (b) modified to the surface containing Fe-nitrides Fe<sub>x</sub>N (x = 2–3, 4). These peaks are γ' (Fe<sub>4</sub>N) along with ε N.

ε N shows a good corrosion resistance. γ' (Fe<sub>4</sub>N) contributes to the hardness of the surface but the not so beneficial to corrosion resistances. Similarly, sample nitrided for 10 h shows both these nitrides.

### 3.2. Electrochemical characterization

For the samples before and after plasma nitriding corrosion tests were conducted in an electrolyte NaCl at room temperature. The electrochemical system Model SI 1287 ELECTROCHEMICAL INTERFACE-Solatron Analytical, U.K. was used for the tests.

### 3.3. Stability of potential (O.C.P.)

The bare and the nitrided steel samples were exposed to the electrolyte 3.5% NaCl for a duration until a stable equilibrium state was attained. The steel nitrided at 500 °C had shown the decreased susceptibility towards corrosion. Initially a variation in corrosion potential was noted which ultimately reached to a stable state.

#### 3.3.1. Potentiodynamic polarization

Potentiodynamic polarization tests were performed after equilibrium attained in 3.5% NaCl electrolyte (Fig. 2).

From the polarization diagrams as shown in Fig. 3 the as-received sample (a) has faster dissolution kinetics as compared to the nitrided steel (b). It has also been found that the other steel nitrided for longer time 10 h at the same temperature has similar dissolution kinetics. The rate of corrosion of as-received sample was found to be 3.6597 MPY much higher than the nitrided steel 1.8071 MPY.

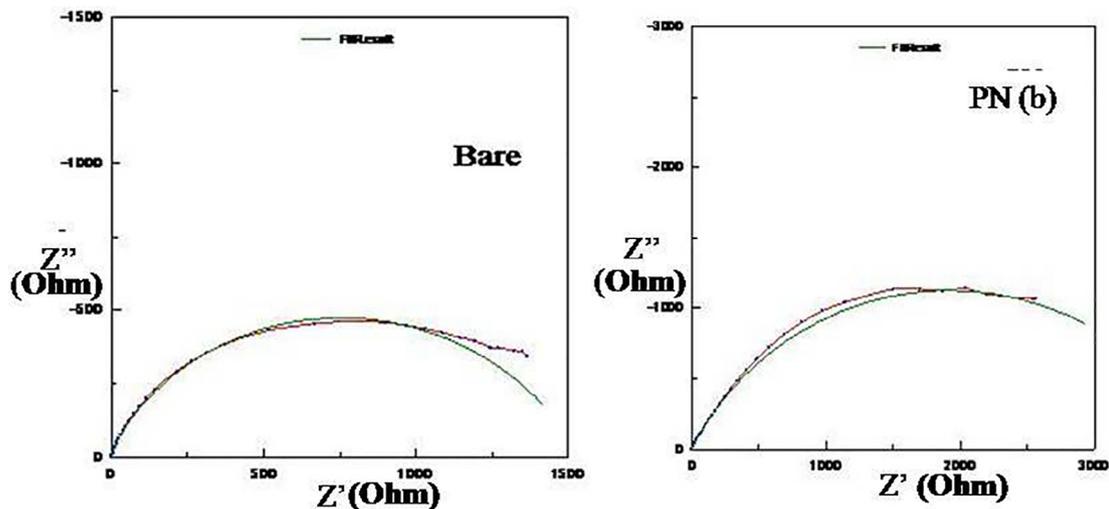


Fig. 3. Nyquist diagram of steel before and after 8 h nitriding 500 °C.

### 3.3.2. Corrosion tests by electrochemical impedance spectroscopy (EIS)

Bare and nitrided samples were exposed to further tests by electrochemical impedance spectroscopic method in the electrolyte 3.5% NaCl, by using the system Model SI 1287 ELECTRO-CHEMICAL INTERFACE-Solatron Analytical, U.K.

In the above Nyquist plots the  $Z'$  represents impedance real and  $Z''$  represents imaginary values. The  $Z_{real}$  represents the resistance to corrosion. Higher the  $Z_{real}$  value more will be the corrosion resistance i.e., the larger the diameter of the semicircle the greater will be the corrosion resistance. From the above Fig. 3 the plasma nitrided steel shows corrosion resistance more than the bare steel. From the XRD studies it is understood that after plasma nitriding the microstructure contains  $Fe_xN$  ( $x = 2-3, 4$ ). The modified microstructures of the nitrided steel containing mainly the  $\epsilon$  N and  $Fe_4N$  nitrides are responsible for the corrosion resistance properties.

## 4. Conclusions

Martensitic tool steel after elevated temperature plasma nitriding shows the enhancement of resistance to corrosion significantly.  $Fe_xN$  ( $x = 2-3, 4$ ) phases were found on the surface microstructure after nitriding.  $\epsilon$  N phase in the modified microstructure is responsible for the resistance to corrosion. Both the nitrided sample treated for 8 and 10 h show better corrosion resistance when compared to bare steel. However, the improvement of corrosion resistance of both these steels was found to be almost similar. The tool life in the harsh corrosive atmosphere can be prolonged after nitriding. This would be beneficial for machining and tool industries.

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