Effect of plasma nitriding on corrosion behavior of a high carbon low alloy steel

A. Basu

Department of Metallurgical and Materials Engineering, National Institute of Technology, Rourkela 769008, Odisha, India

basua@nitrkl.ac.in

Abstract

The present study deals with improvement of corrosion resistance of a low alloy–high carbon steel by pulsed direct current glow discharge mode plasma nitriding. During the nitriding, applied voltage was 540–710 V which resulted in 3–6 A current in the temperature range 450–560°C for a time span of 1–5 hours. The phases formed after nitriding and their morphology were characterized by XRD and SEM analysis. Mostly γ'-Fe_4N with a small volume fraction of ε-Fe_3N/Fe_2N was observed on the surface. Nitride fraction was reported to be more with nitriding time and temperature. These nitrides showed improvement in hardness and wear properties of the steel. Corrosion study revealed that plasma nitriding dramatically improves the corrosion resistance of this ferritic steel in terms of corrosion potential, corrosion current density and resistance to polarization. This improvement was attributed mainly to the formation of nitrides on the surface. Quantitative analysis of the nitrides was done with the help of XRD and the obtained value was found to be linked with corrosion data.

Keywords: Plasma nitriding; Corrosion

Extended Abstract

Plasma nitriding of steel compared to conventional gas nitriding or plasma/beam-line ion implantation offers a greater case depth with enhanced kinetics and induces significant improvement in hardness and wear resistance due to both dispersion and solid solution hardening. In the past, several studies were undertaken to determine the mechanism and kinetics of plasma nitriding of ferritic and austenitic steels by Menthe et al., 1995, Lei et al., 1997, Figueroa et al., 1996, Ana et al., 2014 and many others. Main focus was on austenitic stainless steel due to higher solubility of nitrogen in face centered cubic (FCC) γ-iron and studied were made by Berg et al. 2000, Nobuteru et al., 2005, Nikolov at al., 2014 and others. Studies have also been carried out earlier on nitriding of ferritic steel for improving wear resistance property by Jun et al., 1986, Ana et al., 2014 and others. However, corrosion behavior study of plasma nitrided ferritic steel has not been done in details. The present study deals with improvement of corrosion resistance of a low alloy–high carbon ferritic steel by pulsed direct current plasma nitriding technique.

Discs of 20 mm diameter and 5 mm thickness were cut from fully annealed AISI 52100 steel bar. The surface of the samples was ground and polished using 0.25 μm diamond pastes at the final stage and then thoroughly rinsed with acetone before plasma nitriding. Plasma nitriding was carried out with varying (isothermal) time and temperature. After plasma nitriding, both as-received and nitrided samples were polished and etched for a detailed microstructural investigation on the top surface and cross-sectional plane (perpendicular to the top surface) by optical and scanning electron microscopy (SEM). To confirm the microstructural evolution in terms of identification of the phases, samples were studied by x-ray diffraction (XRD) analysis using CoK_α (0.179 nm) radiation. A similar analysis for the near-surface region was done by glancing-angle XRD (GAXRD) at 1, 2, 5 and 10° angles of incidence with a resolution of 0.005° step width. Quantitative analysis of different phases formed were calculated from integrated intensity of x-ray peaks using normalized relative (integrated) intensity ratio (RIR) method or matrix flushing model as described by Chung et al., 1974. The electrochemical characterization was carried out by potentiodynamic polarization test using a PS6 Meinsberger Potentiostat/Galvanostat connected to a standard three electrode cell comprising the sample as the working electrode, a saturated calomel reference electrode and a platinum counter electrode. The electrolyte used was 3.56 wt. % NaCl solution. Post corroded samples were subjected to scanning electron microscopic (SEM) analysis to reveal the severity of corrosion degradation in terms.

XRD profile of the as-received sample shows only α-Fe peak, XRD patterns of plasma nitrided samples record a number of peaks conforming different nitrides. Plasma nitriding at 500°C for 5 hours and 560°C for 3 and 5 hours results in the formation of ε-Fe_2N/Fe_3N along with γ'-Fe_4N. In the sample treated at 450°C, only weak γ'-Fe_4N peaks accompany the strong α-Fe peaks. It may be noted that the relative intensity of Fe_xN peaks increase with increase in nitriding time at a given temperature indicating an increase in weight fraction of the nitride phases at the expense of parent α-Fe matrix as shown earlier by Basu et al., 2007.

To study the evolution of nitrides, GAXRD was carried out at different glancing angle. XRD obtained with very shallow angle incidence (1 – 2°) shows only nitride peaks; whereas, at higher incidence angle ferrite peaks are also visible. As the process is diffusion controlled, formation of higher nitrides at surface is justified (as observed with lower incidence angle).

To quantify this effect, α-ferrite and nitride fraction was calculated at different depth and it shows that there is variation of the fraction of nitrides and α-ferrite phase as a function of nitriding time at different depth of the samples. For a given nitriding time, with increase in distance from surface in the nitrided sample, the amount of nitride decreases maintaining maximum nitride volume fraction at the surface. Similar trend was observed at other temperature of nitriding also.

Potentiodynamic polarization test of the nitrided samples and as received steel was carried out in 3.56 wt. % NaCl solution.. It may be observed that with increase in nitriding time, the corrosion potential (E_{cor}) increases. It was also observed that corrosion current density (I_{cor}) decreases and resistance to polarization (R_p) increases with nitriding time as reported by Basu et al., 2008. This means, nitriding can increase the corrosion resistance of ferritic steel. Same trend was visible at other temperature of nitriding also. Moreover, in some samples short appearance of passivation zone was also observed similar to that of a stainless steel. Reason behind such improvement in corrosion resistance is attributed towards the formation of nitride on the surface which is noble in nature. Moreover, it can also be observed that increase in nitride coverage on the surface leads to betterment of corrosion behavior. Scanning electron micrograph of the corroded surface of nitrided sample revealed that in nitrided surface there was no significant signature of corrosion attack like pits.

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Introduction

BACKGROUND:

- Plasma nitriding is a modern nitriding process having better process control and environment friendly in nature.
- Nitriding of austenitic steel is discussed more due to better solubility of nitrogen in austeninte.
- Apart from surface mechanical properties nitrides are corrosion resistant in nature.
- Amount of nitrides and corrosion has to be correlated.

OBJECTIVE:

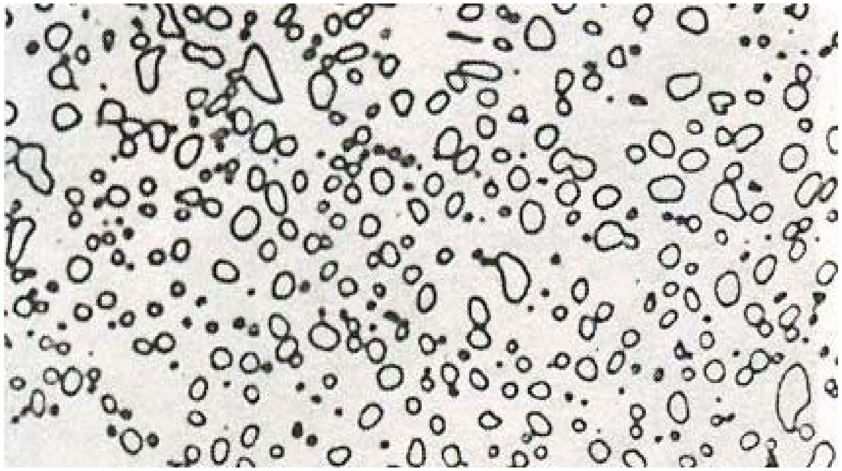
The present study deals with improvement of corrosion resistance of a low alloy–high carbon ferritic steel by pulsed direct current plasma nitriding technique.

Experimental

MATERIAL: AISI 52100 steel

Composition:

Element	C	Si	Mn	Cr	Fe
Wt %	0.95 – 1.05	0.15 – 0.35	0.29 – 0.40	1.50 – 1.65	Rest



As received structure (annealed)

PROCESS ROUTE:

Sample preparation

↓

Sputter cleaning

↓

Plasma nitriding

↓

Characterization (XRD, SEM, Corrosion, hardness, wear)

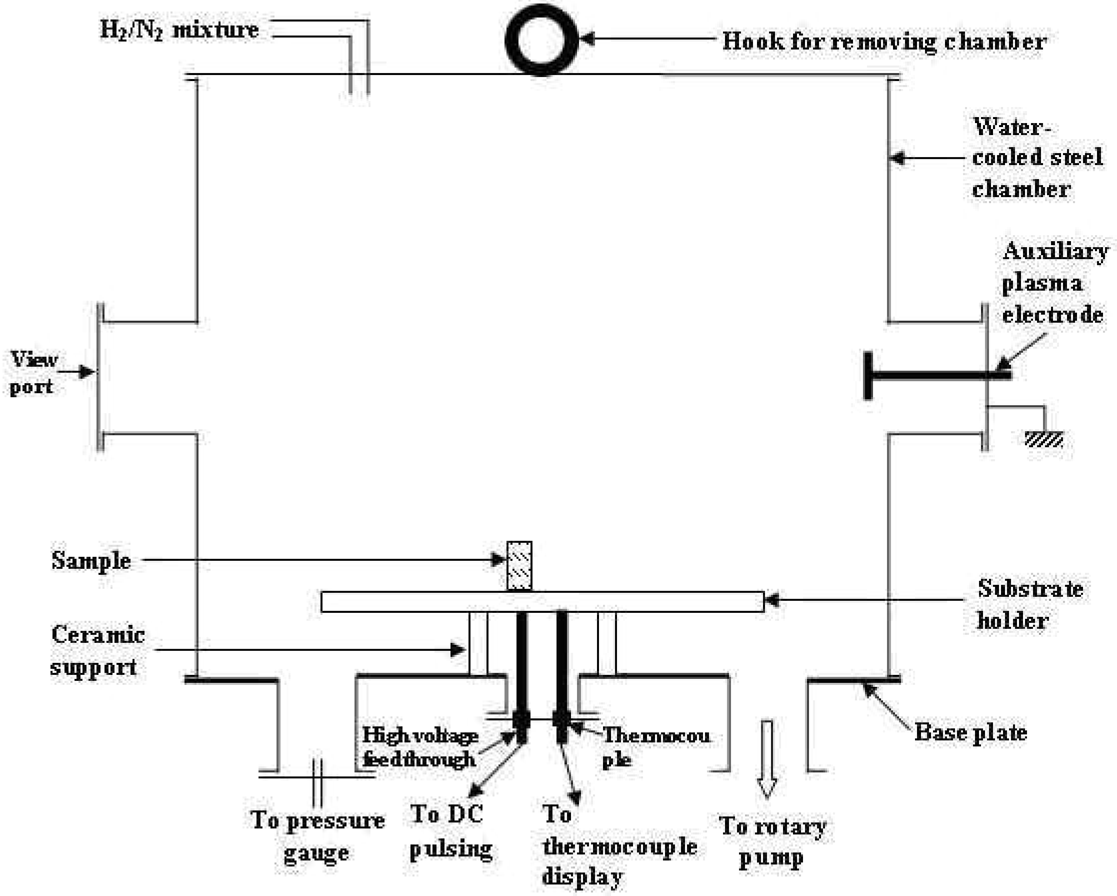
↓

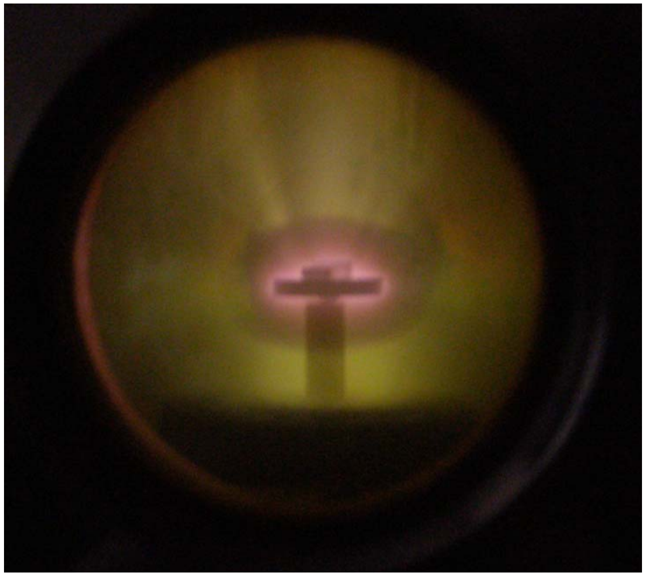
Structure property co-relation

Nitriding parameters:

Precursor :	**H_2/N_2 = 65/35 (Volume)**
Treatment time :	**1, 3, 5 h**
Treatment temp. :	**450, 500, 560^{o}C**
Total gas pressure :	**5 mbar**
Voltage :	**540-710 V**
Current :	**3-6 Amp**
Pulse frequency :	**10 kHz**
Duty cycle :	**66%**

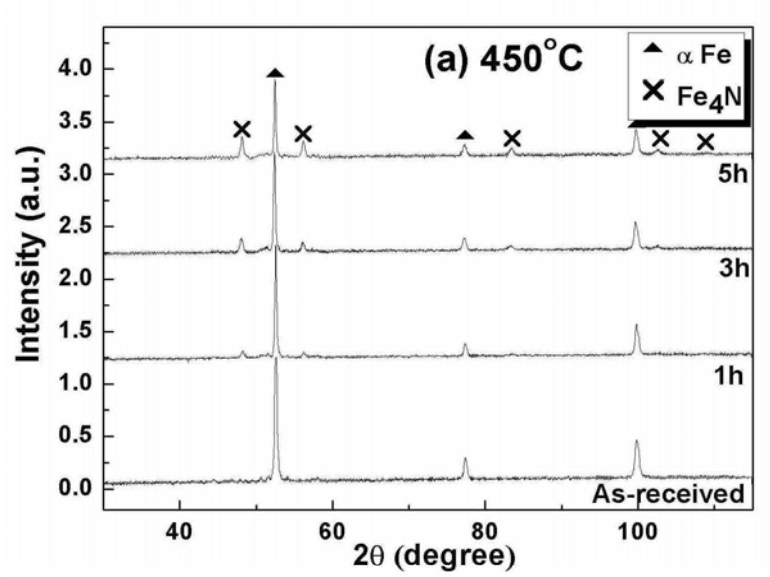
PLASMA NITRIDING
SET UP AND REAL TIME PHOTOGRAPH

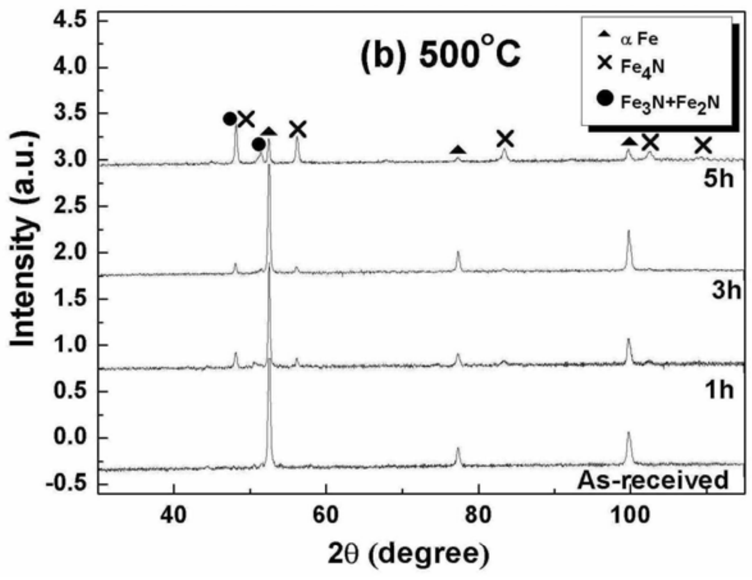


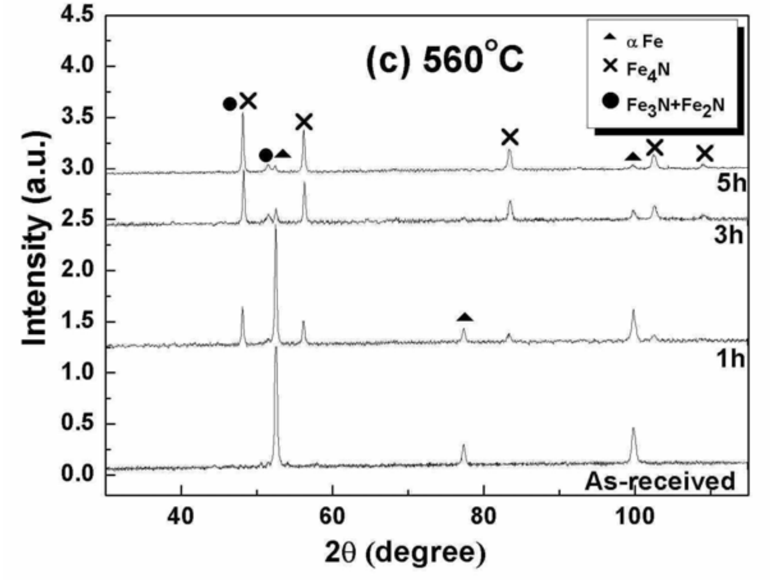


Results

XRD



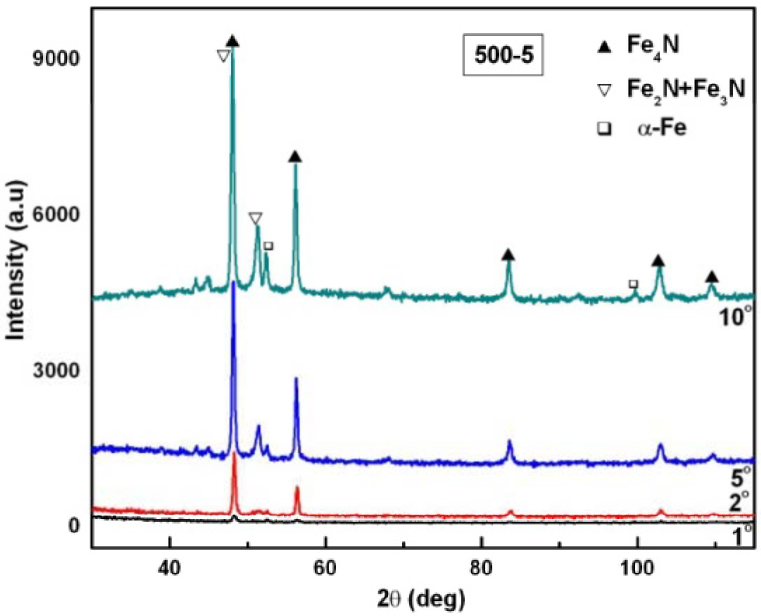


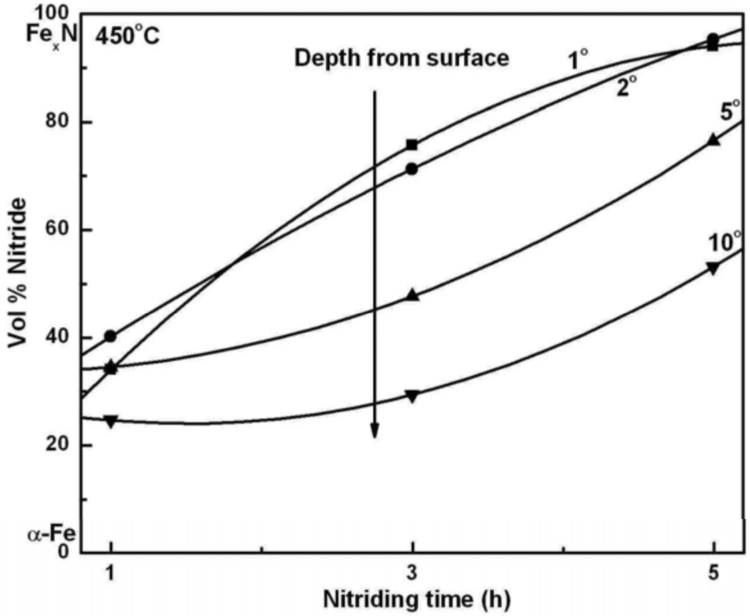


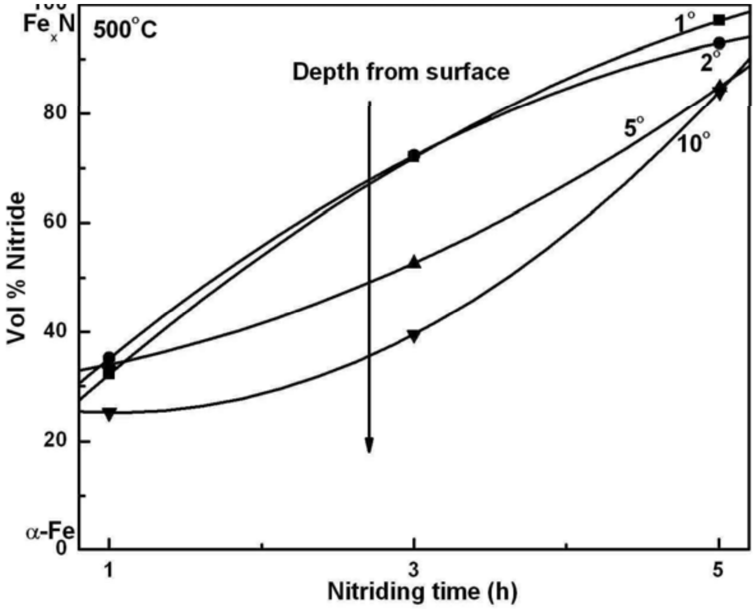
NOTE:

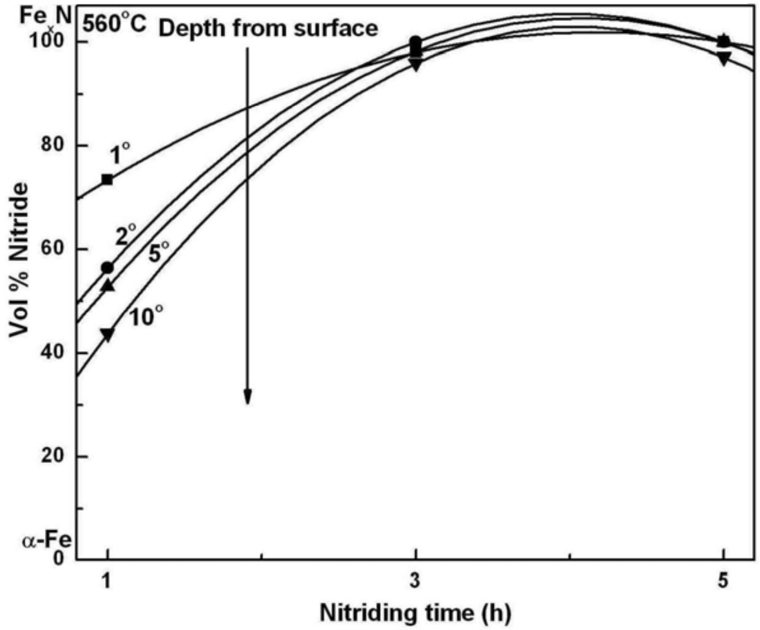
- Fe$_2$N/Fe$_3$N formed only at higher processing time and temperature
- Volume fraction of nitrides increases with nitriding temperature and time

DEPTHWISE PHASE FRACTION



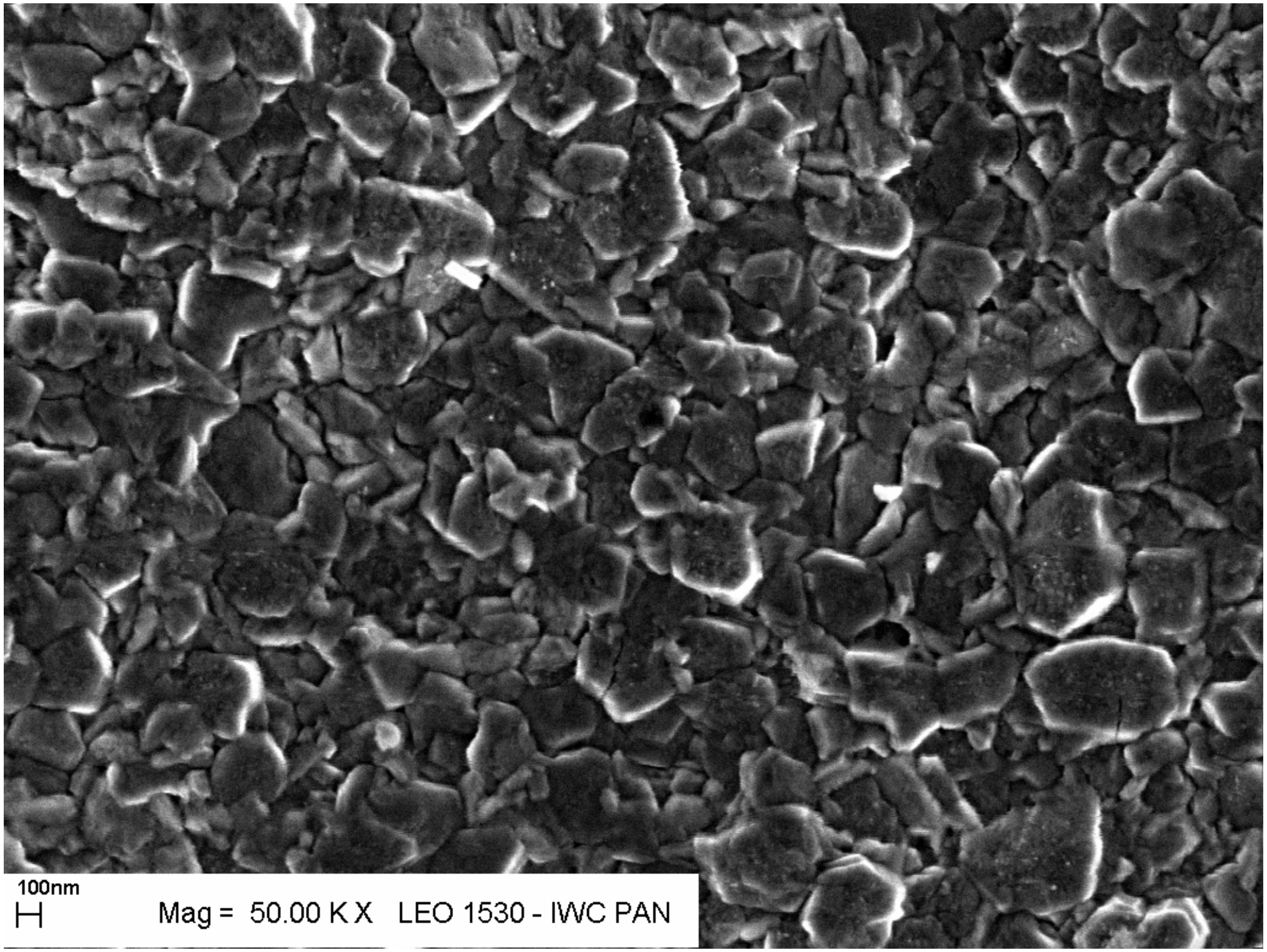






NOTE: Nitride fraction decrease slowly from the surface

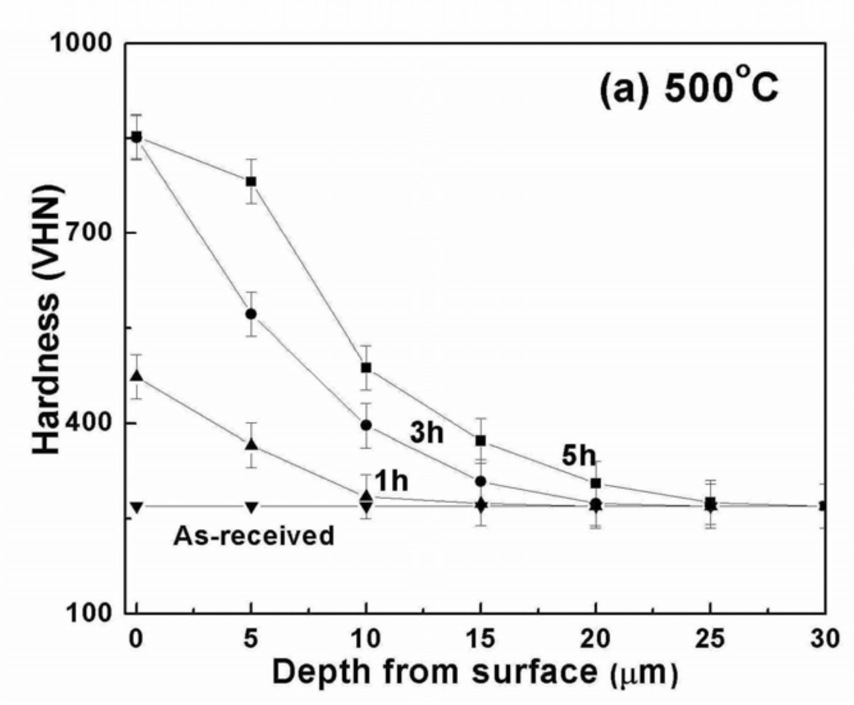
SEM MICROGRAPGH

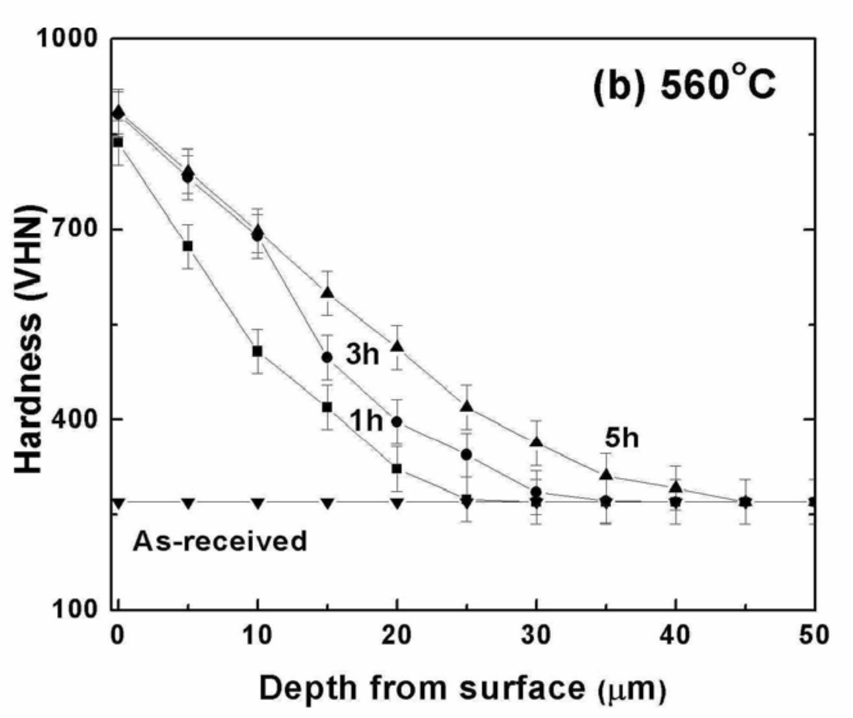


Structure after nitriding at 560^{o}C for 5 hours

Note: Maximum nitride size is ~ 400 nm

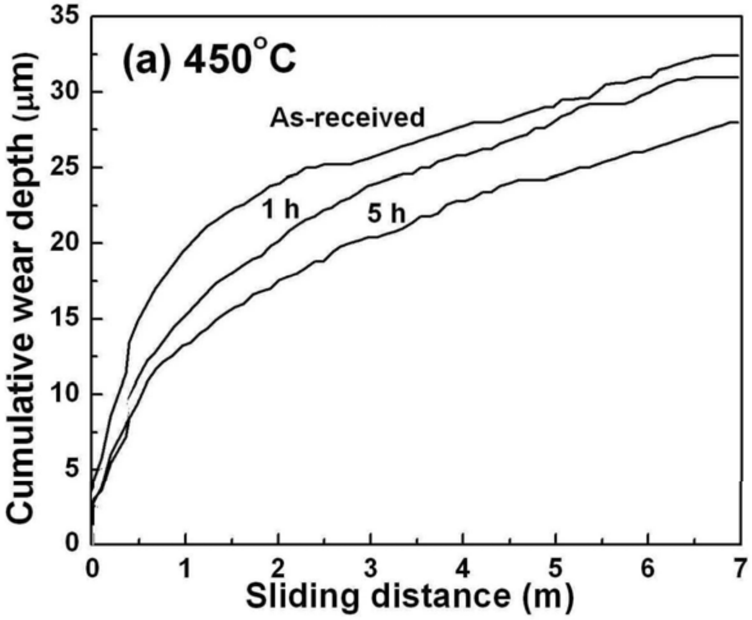
MICROHARDNESS

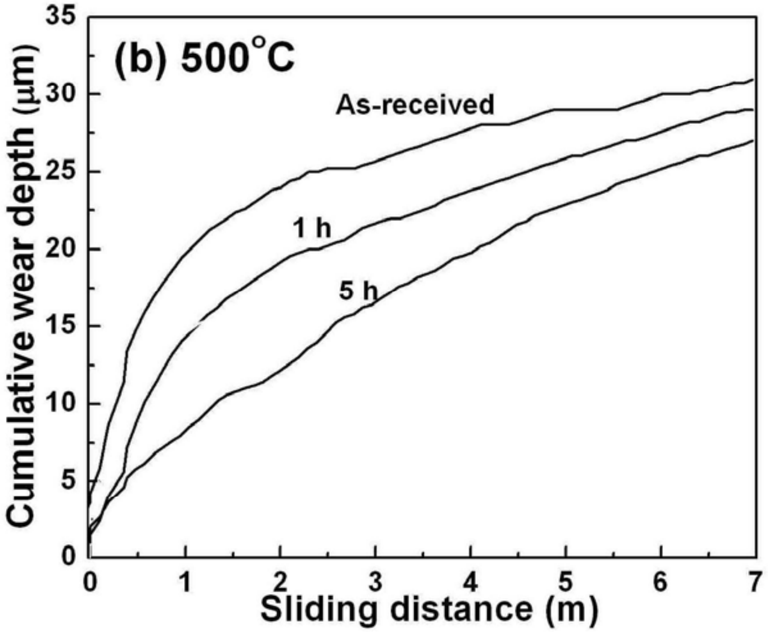


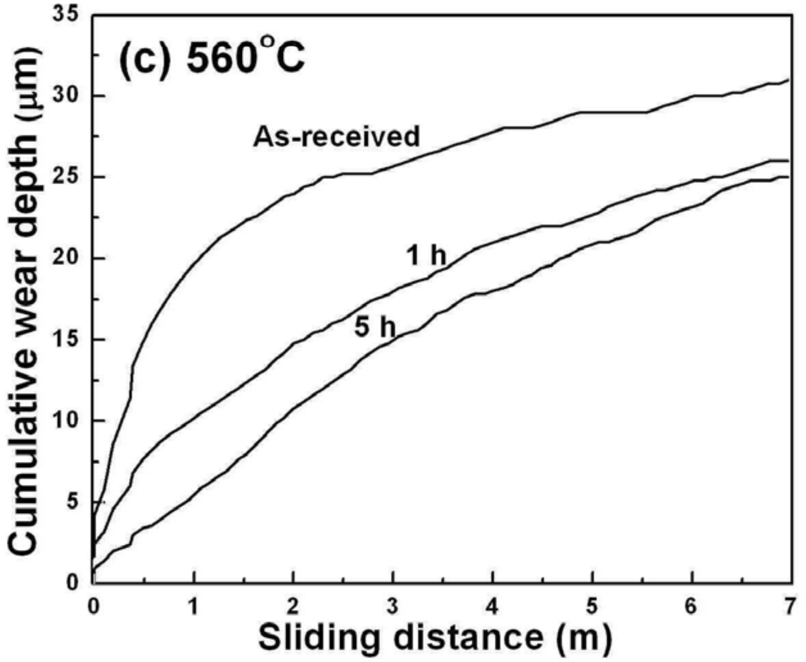


Note: Maximum hardness 890 HV,
base hardness 270 HV

WEAR STUDY



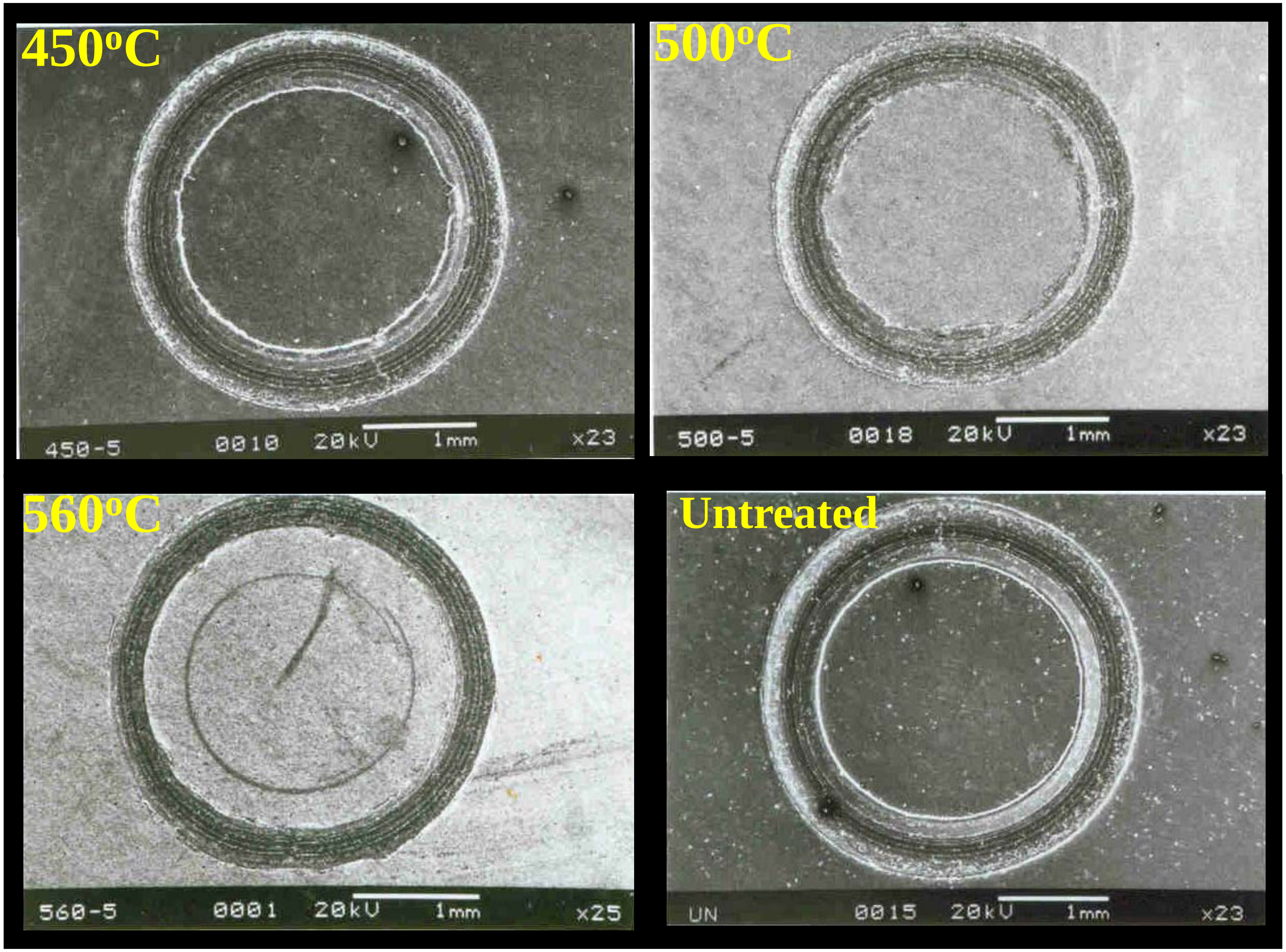




Wear testing load: 4 kg

Note: Wear rate is slow in samples with higher nitriding time

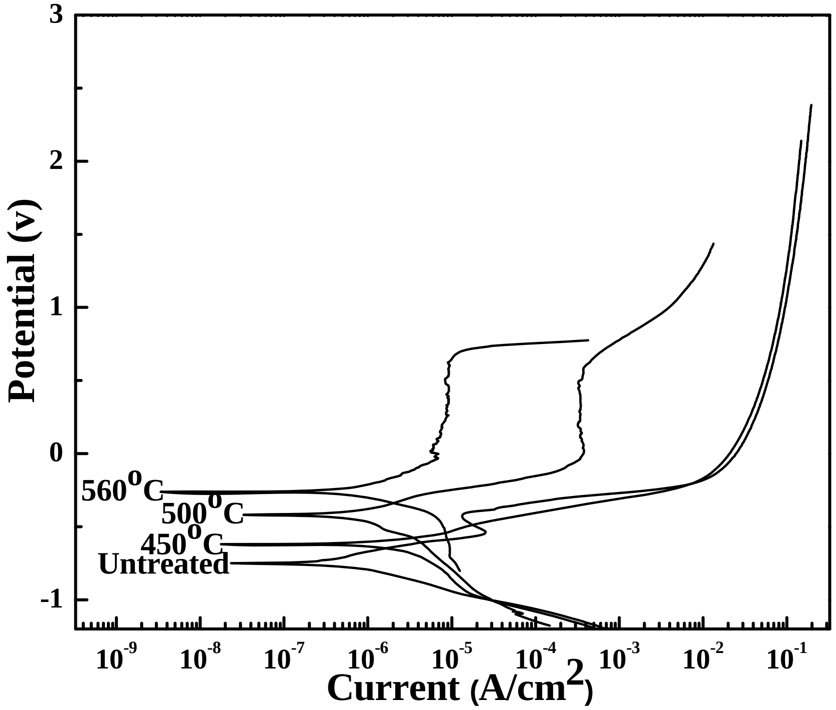
WEAR TRACK (SEM MICROGRAPH)

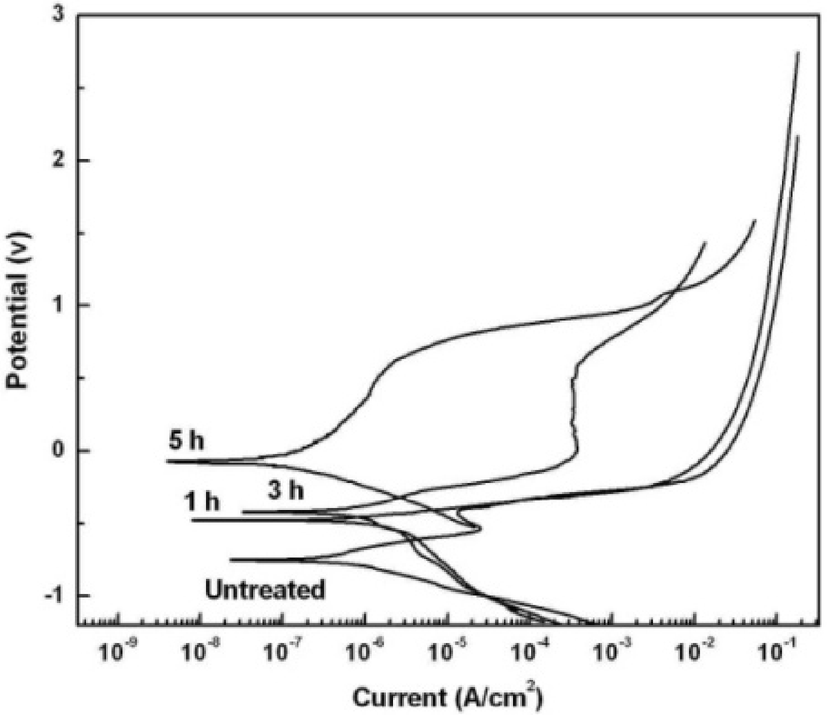


Wear track of untreated and plasma nitrided (5 h) samples

Note: At 560ºC, wear track is visibly narrow

POTENTIODYNAMIC POLARIZATION BEHAVIOR





Nitriding time = 3 h

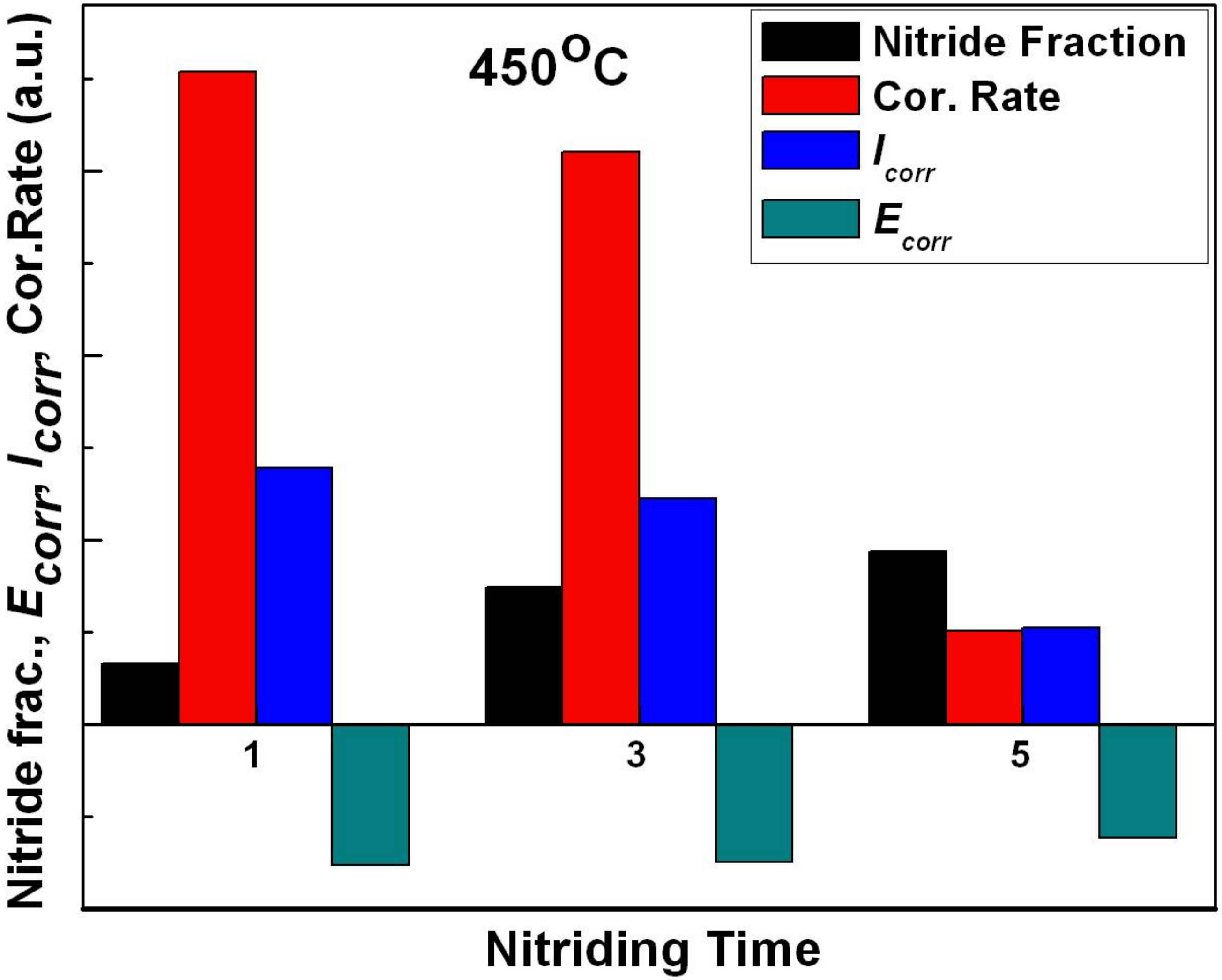
Nitriding temp.= 500°C

Noticeable improvement in corrosion resistance is achieved

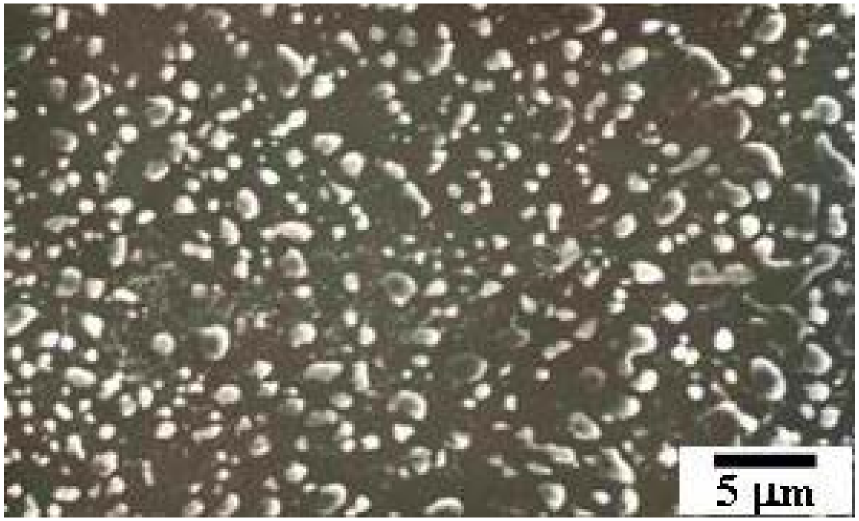
CORROSION DATA

Sample History (temperature and time)	I_{corr} **(A/cm^2) (x 10^{-8})**	R_p **(Ohm) (x 10^4)**	E_{corrr} ***(mV)***	***Corrosion rate (mm/year)(x 10^{-3})***
Untreated	**1390**	**0.89**	**-765**	**550.2**
Nitrided at 450°C for 1 h	**1389**	**0.54**	**-750**	**353.6**
Nitrided at 450°C for 3 h	**1220**	**0.79**	**-619**	**310.5**
Nitrided at 450°C for 5 h	**519**	**1.91**	**-26**	**50.1**
Nitrided at 500 °C for 1 h	**479**	**1.08**	**-477**	**121.9**
Nitrided at 500 °C for 3 h	**410**	**2.14**	**-419**	**91.1**
Nitrided at 500 °C for 5 h	**369**	**3.20**	**-47**	**4.2**
Nitrided at 560 °C for 1 h	**358**	**3.01**	**-469**	**92.5**
Nitrided at 560 °C for 3 h	**364**	**2.89**	**-261**	**58.9**
Nitrided at 560 °C for 5 h	**350**	**3.37**	**-42**	**2.1**

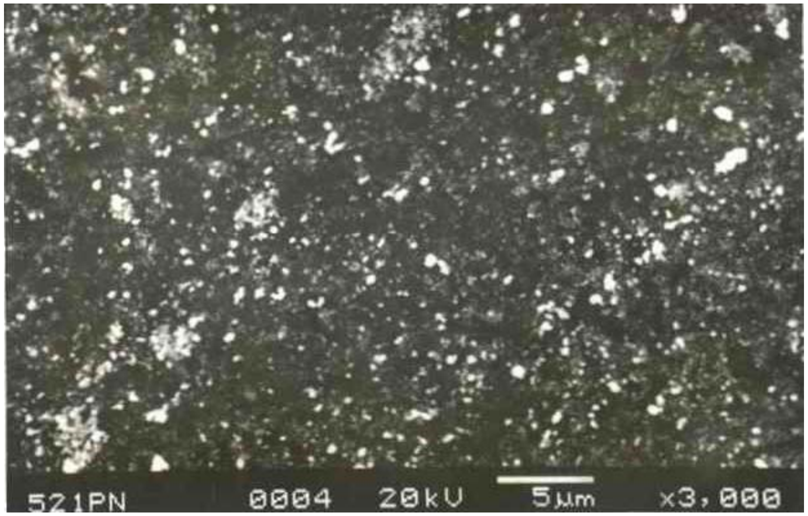
RELATION WITH NITRIDE FRACTION



POST CORROSION MICROGRAPH



Untreated steel



Nitrided at t = 5 h, T = 500^{o}C

Conclusion

- **Nitride fraction of increases with increase in nitriding time and temperature.**
- **γ'-Fe_4N forms at all temperatures and ε-Fe_3N/Fe_2N forms mainly at 500 and/or 560^{o}C.**
- **At higher depth from the surface the amount of nitride decreases gradually.**
- **Increase in corrosion resistance was observed and it can be linked directly to the increase in nitride volume fraction at the surface.**
- **Noticeable improvement in hardness and wear property was also observed**