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Surface Modification of 17-4PH Stainless Steel by Plasma Nitriding

Sangita Jadeja
M tech (Industrial Metallurgy)
Indus University, Rancharda
Ahmedabad – 382115, India

B. Ganguli
Senior Scientist
Institute for Plasma Research
Bhat, Gandhinagar - 382428, India

D. K. Basa
Professor, Metallurgy Department
Indus University, Rancharda
Ahmedabad – 382115, India

Abstract- **Plasma nitriding of 17-4PH martensitic precipitation hardening stainless steels was carried out at 350^0C, 380^0C, 400^0C, 430^0C, 450^0C and 500^0C for 4 hours using a mixture ratio of N_2:H_2 = 1:4. The modified surface was evaluated for micro-hardness as well as characterization tests such as optical microscopy, SEM, and XRD. Corrosion tests were also performed on untreated as well as plasma nitrided samples.**
The micro-hardness tests reveal increase in hardness by a factor of four compared to untreated sample at all temperatures. However, case depths varied from 17 microns (µm) for 350ºC to as high as 52 microns for 500ºC. Optical microscopy and SEM confirm results obtained for micro-hardness, vis-à-vis thickness of the nitrided layer. XRD results show formation of expanded austenite phase (S-phase) below 400ºC and predominantly CrN phase above 400ºC. Corrosion rates evaluated in a electrochemical cell in 3.5% NaCl indicate increase in its value up to 380ºC processing temperature, thereafter it decreases compared to untreated case. The best result is obtained for the case of 500ºC processing temperature.

Keywords- 17-4PH stainless steel, plasma nitriding, microhardness, optical microscopy SEM, XRD, elctrochemical corrosion

I. INTRODUCTION

17-4PH martensitic precipitation hardening stainless steel is attractive for many industrial application sectors (chemical, nuclear, aviation, etc.) due to its desirable property, i.e. combination of high strength, high toughness and good corrosion resistance [1,2,3]. However, their wider applications are restricted by their poor tribological property, which has necessitated the development of advanced surface engineering technologies to address the problem [4,5].

Plasma nitriding is a diffusion process for surface hardening of steel substrates which generates an interface with a graded compositional and hardness profile. The nitrided layer reduces the difference of hardness between the substrate and the coating, improving in this way the tribological behavior and the load capability of the coating [6].

The plasma nitriding method of surface hardening [7-13] uses d.c. glow discharge to impart elemental nitrogen to the surface of steel with subsequent diffusion into the bulk of material. Generally, two layers are created during plasma nitriding process. The compound layer is consisted of ε-$Fe_{2-3}N$ and γ-Fe_4N phases. This type of layer is very hard, but unfortunately brittle with good friction and anticorrosion properties. The thickness and hardness of γ′-Fe_4N depend on quantity and quality of nitride-forming elements. Parameters of plasma nitriding layer are not dependent only on process parameters of nitriding, such as duration, temperature, pressure, voltage and nitrogen potential, but also dependent upon the substrate alloy type as well as its microstructure [14].

A few studies [1,2] have been undertaken to explore the possibility of enhancing the surface hardness of 17-4PH martensitic stainless steel by plasma nitriding; however little or no attention has been paid to the wear and corrosion of plasma nitrided material.

In the present investigation the response of 17-4 PH stainless steel to plasma nitriding over a wide range of treatment temperature (350-500^0C) and fixed duration (4 hours) has been investigated, and experimental results have shown that the nitrided layer characteristics are highly process-conditions dependent. Layer thickness varied from 17µm (350^0C/4hr) to 52µm (500^0C/4hr) in 17-4 PH stainless steels.

Further the paper presents experimental results on the effect of plasma nitriding at 350^0C, 380^0C, 400^0C, 430^0C, 450^0C and 500^0C for process duration of 4 hours on the corrosion behavior of 17-4 PH stainless steel. Based on the experimental results, the mechanisms involved will be discussed.

II. EXPERIMENTAL

A. Material and Treatments

The material used in present work is 17-4PH stainless steel with the following composition (wt%): 0.041% C, 0.355% Si , 0.908% Mn, 0.019% S, 0.022% P, 15.395% Cr, 4.354% Ni, 0.450% Mo, 3.328% Cu, 0.003% Ti, 0.043% V, 0.183% Nb, 0.027% W and Balance Fe. Cylindrical samples were cut from 9.7mm diameter with thickness of 8mm. They were mirror polished by using SiC abrasive papers of different grit size and disc polishing machine. The samples were cleaned thoroughly with petroleum ether to remove the impurities prior to plasma nitriding. Plasma nitriding was carried out in a DC glow discharge reactor using a mixture of N_2 and H_2 (1:4) at a total pressure of 5 mbar at process temperatures of 350^{0}C, 380^{0}C, 400^{0}C, 430^{0}C, 450^{0}C and 500^{0}C for a fixed duration of 4 hours. Temperature was monitored using a K-type thermocouple and controlled by adjusting the bias voltage on the cathode (sample).

B. Characterization

After plasma nitriding, the specimens were characterized by a variety of analytical techniques, including metallography for transverse sections for layer morphology and X-ray diffraction for phase identification.

The XRD of all the samples was carried out with the help of "Bruker" X-ray diffractometer with Cu-Kα radiation (λ=1.5406 Å), 40 kV, 40 mA with 0.05 step size using Bragg-Brentano powder mode. The 2 Theta scan range was from 30° to 90°.

SEM and optical microscopy were used to observe surface morphology of plasma nitrided samples. Thickness measurements were undertaken using SEM of LEO Corp., model s440i.

A Vickers micro hardness tester (Leitz, model no. RZD-00) was used to measure the hardness on the as-treated surface and as a function of depth on cross-section of the treated specimen. Loads of 100gm and dwell times of 20s were employed.

The corrosion properties of plasma nitrided layers were evaluated using Digi-ivy, model DY2300 Potentiostat in 3.5% NaCl to measure the corrosion rates with the help of Tafel plots.

III. RESULTS AND DISCUSSION

A. Physical Appearance

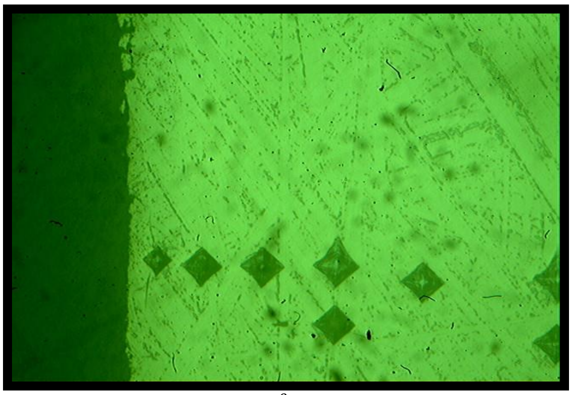
The difference between the untreated and nitrided samples can be seen from Fig 1. The untreated sample has a plain polished mirror like surface shown Fig. 1(a), whereas the nitrited sample has grey colour (Fig. 1 (b)).

(a) Untreated *(b) Plasma nitrided sample*

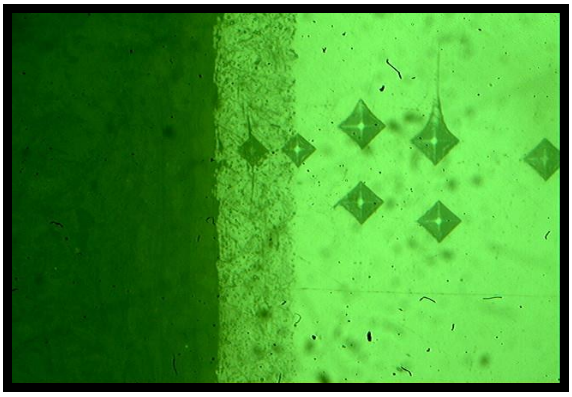
Fig.1. Physical Appearance

B. Optical microscopy

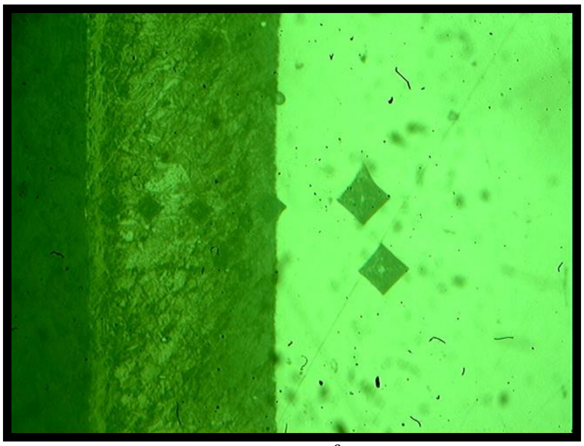
We observed thick layer of nitrogen diffusion on the nitrided sample by optical microscopy. We can see thick layer shown in Fig.2(c). Maximum 52 micron thick nitrited layer can be seen between the mould material and core material of 17-4PH SS.



(a) 400^{0}C



(b) 430^{o}C



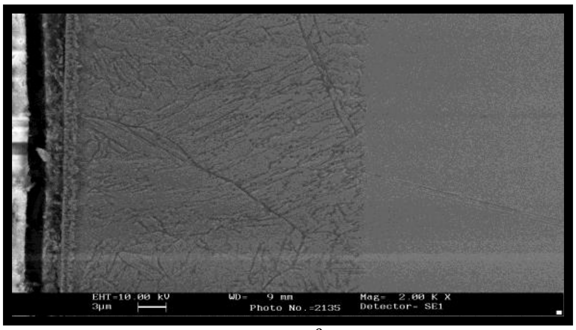
(c) At 500^{0}C

Fig.2. Comparison of nitrided layers for various process temperatures by optical microscopy

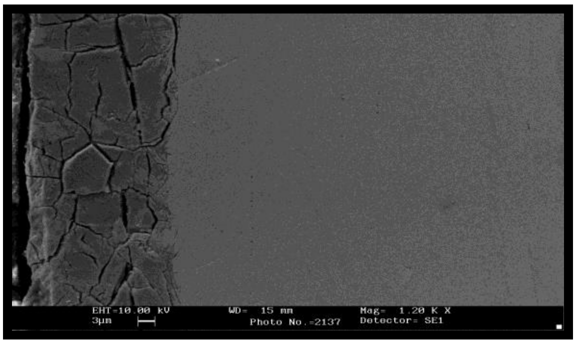
Fig. 2 (a) & (b) shows the comparison of 400^{0}C and 430^{0}C treated 17-4PH after nital etching by optical microscopy. In this observation at 400^{0}C temperature dark layer was not observed though high hardness was measured close to the surface. This hardness is due to S Phase and not by CrN. Nitrogen does not react with Cr at low temperature, so does not form CrN. At low temperature (350-380^{0}C) corrosion resistances is decreased which implies that S Phase is detrimental for corrosion resistance. At 430^{0}C S Phase disappears due to nitrogen reacting with Cr above 400^{0}C temperature forming CrN.

C. SEM Analysis

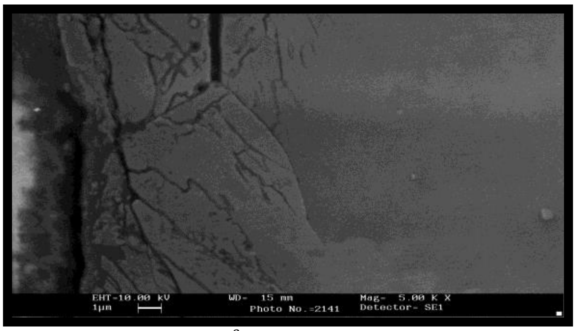
In SEM analysis shown in Fig.3, nitrided layers are observed for various temperatures (350-500^{0}C). Maximum thickness of nitrided layer is observed at the highest processing temperature (500^{0}C). The microstructure of the modified surface is clearly visible. At lower temperatures (350^{o}C and 380^{o}C) it is due to S-phase while at higher temperatures (430^{o}C and 500^{o}C) it is due to CrN precipitates.



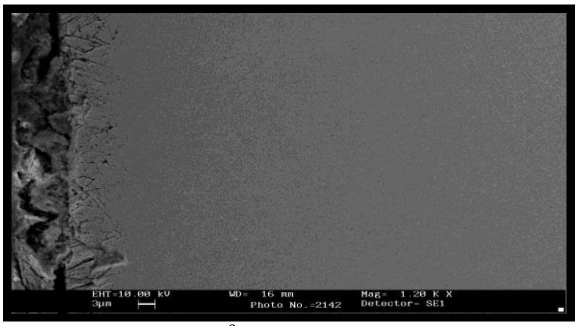
a) 500^{0}C



(b) 430^{o}C



(c) 380^{0}C



(d) 350^{0}C

Fig.3. Nitrided Layer Observation by SEM of a) 500^{0}C (b) 430^{0}C c) 380^{0}C (d) 350^{0}C temperatures

D. XRD analysis

The phase composition in the nitrided layer was analyzed with XRD using Cu-Kα radiation. The XRD diffraction patterns of phase structure of the layers are shown in Fig.4. It can be clearly observed that α' peak for untreated sample is sharp. XRD analysis revealed the overlapped peaks and gradual changes in phase constituents of nitrided layers as the nitriding temperature is increased. High temperature (≥430^{0}C) treated samples show peaks of CrN, α', Fe_4N. S phase is observed at low temperature (≤400^{0}C). Therefore, at 350^{0}C, 380^{o}C and 400^{0}C, a broad peak at the diffraction angle, i.e. 2 theta equaling 43.650 is observed, which has been associated with a metastable phase called 'S phase' (expanded austenite). S phase peak disappears above 400^{0}C temperature due to formation of CrN precipitates.

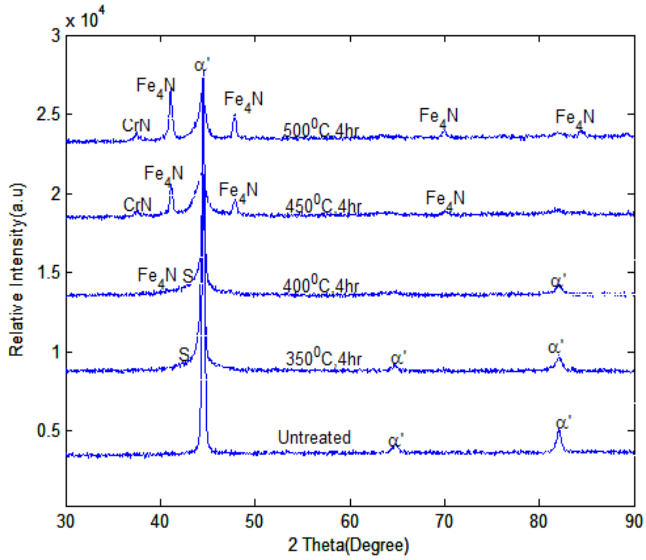


Fig.4. XRD analysis

E. Micro-Hardness

The micro-hardness of nitrided layer as a function of depth from surface for various processing temperatures is shown in Fig.5. It is clearly observed that the thickness of the hard nitrided layer depends mainly on the nitriding temperature. The maximum thickness is observed at temperature of 500^{0}C. Hardness increases above 400^{0}C due to formation of CrN. Increasing the nitriding temperature increases the nitrided layer thickness.

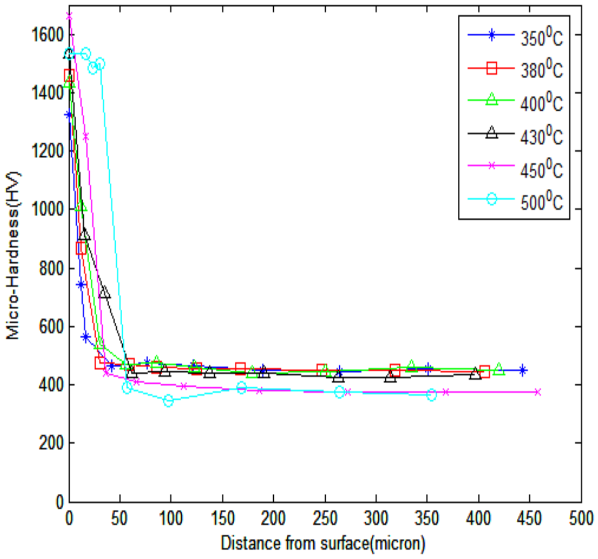


Fig.5. Micro-Hardness comparison

Table 1. Nitrided case depths at different process temperatures

Sample No.	*1 (500°C)*	*2 (450°C)*	*3 (430°C)*	*4 (400°C)*	*5 (380°C)*	*6 (350°C)*
Case Depth (microns)	*52*	*36*	*33*	*29*	*21*	*17*

F. Corrosion performance

The corrosion behavior of plasma nitrided 17-4PH stainless steel in 3.5% NaCl solution has been examined using linear sweep voltammetry (log I vs. V) in an electrochemical cell. Tafel plots were obtained which provided the corrosion rates. Fig. 6 shows the results. At higher temperature corrosion performance is better than untreated, however at lower temperatures (≤ 380°C) corrosion resistance decreases. Above 400^0C corrosion resistance is improved due to formation of Fe_4N confirmed by X-ray diffraction analysis.

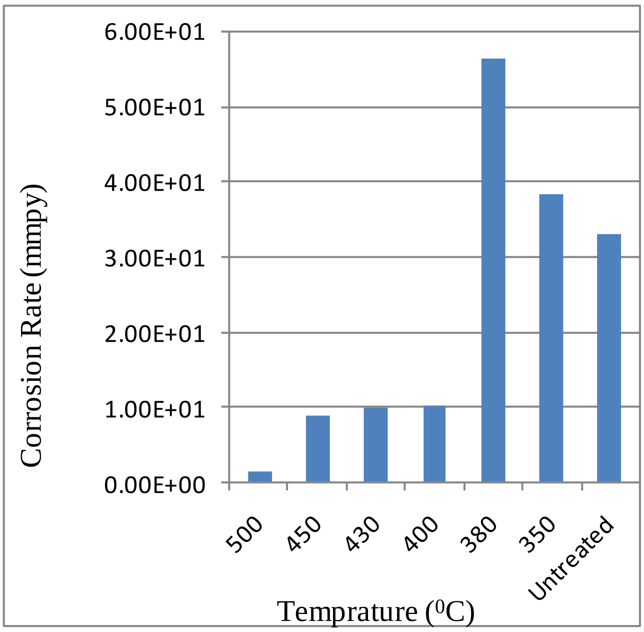


Fig.6. Corrosion behavior of plasma nitrided 17-4PH stainless steel

IV. CONCLUSIONS

Plasma nitriding of 17-4 PH stainless steel increases surface hardness by a factor of four (~1600HV compared to 370HV for the untreated sample) for all process temperatures starting from 350°C to as high as 500°C (for a fixed N_2:H_2=1:4, duration = 4 hours). However case depths range from a low of 17μm for 350°C to as high as 52μm for 500°C. XRD, optical microscopy and SEM confirm presence of S phase in the temperature range from 350^0C to 400^0C. Above 400^0C S phase disappears. As nitriding temperature increases nitrogen diffusion also increases leading to more depth of the nitrided layer. From the XRD results it can be concluded that CrN and Fe_4N form only at higher temperatures (≥430). Electrochemical corrosion rate measurements carried out in 3.5% NaCl reveal that the performance of plasma nitrided 17-4 PH steel is better at higher temperature (≥400°C) leading us to conclude that it is due to formation of Fe_4N at the top of the surface.

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