ISSN: 2277-3754
ISO 9001:2008 Certified
International Journal of Engineering and Innovative Technology (IJEIT)
Volume 2, Issue 11, May 2013

Effect of Temperature on the Plasma Nitriding of Duplex Stainless Steels

Satyapal.M[1], A.S. Khanna[1], Alphonsa Joseph[2]
[1]Dept of Metallurgical Engg &Materials Science, IIT Bombay, [2]Institute for Plasma Research, Gujarat

Abstract*— *Plasma nitriding of duplex stainless steel, grade 2205, was carried out at four different temperatures, keeping other processing parameters constant. The effect of temperature on the surface roughness, hardness, and microstructure was investigated along with their corrosion resistance. The characterization of the plasma nitride samples was carried out using X-ray diffraction, SEM/EDAX. The extent of nitrogen diffusion in the cross section of nitrided layer was also measured. Corrosion analysis was carried out using potentiodynamic polarization in 3.5% NaCl& 1% HCl solutions. The corrosion resistance of the duplex stainless steel decreased with an increase in plasma nitriding temperature, whereas the surface hardness increased with an increase in nitriding temperature.

***Index Terms*— Case-depth, Corrosion, Duplex stainless steel, Hardness, Plasma Nitriding, Polarization.**

I. INTRODUCTION

Duplex stainless steel, grade 2205 combines many beneficial properties of austenitic and ferritic stainless steels. These steels offer excellent mechanical properties and high resistance to uniform corrosion and localized corrosion [1]. The microstructure of these steels consists of nearly equal amounts of ferrite and austenite phases, distributed uniformly in solution annealed condition. These steels find widespread applications in flue gas cleaning systems, chemical industry and sea water applications [2]. Their main usage is for flow lines, process piping lines, and seawater carrying lines [3]. One of the requirements of process flow lines is highly wear and erosion resistant internal surface [4]. However, many surface hardening processes work at temperatures above 500°C, which results in the formation of several deleterious phases such as sigma and chi and other intermetallic phases [5]–[7]. Plasma nitriding is, a low temperature (below 500°C) surface hardening treatment, which avoids the formation of intermetallic phases [8]. Such a treatment can increase the wear and erosion resistance of the material by formation of various phases and compounds such as Fe_4N, Cr_xN. The Υ_N phase, also known as expanded austenite, is formed below 400°C which has a good corrosion and wear resistance [9]. Many of the duplex stainless steels are therefore, used at a temperature less than 300°C, above which there is tendency to form deleterious phases as well as there is a possibility to disturb the composition of ferrite and austenite in the matrix. In this study, the duplex stainless steel 2205 is plasma nitrided at four different temperatures, 350, 400, 450, and 500°C, by keeping all the other processing parameters same, to study the effect of plasma nitriding temperature on the mechanical and corrosion properties.

In an earlier work carried out on AISI 316L austenitic stainless steels, it was shown that the thickness and hardness of nitrided layer increase as the temperature of plasma nitriding increases [10]. Very recently Lee [11] reported that in AISI 304L austenitic stainless steels, precipitation free sub layers are formed with expanded austenitic structure at a plasma nitrocarburising temperature of 400°C, which had excellent corrosion resistance. Above this temperature (430°C), chromium nitrides were formed, leading to an increase in the hardness and thickness and decrease in the corrosion resistance. In case of duplex stainless steels (UNS S31803), the phases formed at a lower plasma nitriding temperature (<420°C) consisted of expanded austenite and ferrites. These resulted in better corrosion resistance [12]. At higher plasma nitriding temperatures (>420°C), precipitation of nitrides occurred, which lowered the corrosion resistance but increased the hardness of the surface.

II. EXPERIMENTAL WORK

A. *Materials Used*

Duplex stainless steel grade 2205 was procured as a bar of 25mm diameter in solution annealed condition, whose chemical composition is given in table.1. The bar was cut into 4mm thick discs, polished using various grades of emery papers, followed by diamond polishing and finally using alumina paste until a scratch free, mirror like surface finish was obtained. These polished samples were loaded into the plasma nitriding chamber in such a way that the polished surface of the sample faced plasma of the nitrogen. The initial microstructure of the sample was observed using Kalling's waterless reagent (100ml HCl + 100ml C_2H_5OH + 5gm $CuCl_2$) as an etchant for about 30 seconds.

Table. I Chemical Composition of Duplex Stainless steel 2205

.

Element	C	Ni	Cr	Si	Mn	S & P	Mo	Fe
Wt%	0.026	4.6	22.06	0.69	1.74	<0.02	2.580	Rest

B. *Plasma Nitriding Process*

Plasma nitriding was carried out in a large working volume (1meter diameter and 1 meter height) with necessary arrangements of vacuum system and auxiliary heating. After evacuation, when the pressure was about 9 mbar, plasma of hydrogen was obtained at a voltage of 410V and a current of 1.1A. Plasma sputtering in pure hydrogen gas atmosphere was carried out at a pressure of 1 mbar with gas flow rate of 250 ml/min and temperature > 250^{O}C for 1h. Temperature was increased with the help of heaters until the required temperature for plasma nitriding was obtained. As soon as the required temperature was reached, the heater was switched off and the temperature required was maintained by the heat dissipated from the nitrogen ions striking the surface of the substrate.

Plasma nitriding was carried out for 4hr at a pressure of 5mbar and the gas composition was maintained as 80%N_2 + 20%H_2 by adjusting the mass flow meter. Temperature was the only parameter which was varied, keeping all the other parameters constant and its effect was studied on the hardness and corrosion resistance of the duplex stainless steel 2205. The four temperatures, at which the nitriding was carried out, were 350, 400, 450 and 500^{o}C and the corresponding coated samples were designated as PN350, PN400, PN450 and PN500 respectively.

C. *Characterization of Plasma Nitrided*

The detailed surface characterization of the nitrided samples was carried out by using SEM/EDAX and X-ray diffraction. Surface morphology and surface composition was determined using SEM/EDAX and exact compound formed using X-ray diffraction (Cu K_α radiation (λ = 1·5418 Å)). The cross section of the nitrided samples was also analysed by SEM/EDAX for characterising the nitrided layers, white layer/compound layer with their thickness.

The surface roughness parameter R_a of the untreated and treated samples was measured by a Mitsutoyo SJ 201 surface roughness tester. The effect of temperature on R_a values was determined.

Surface hardness was measured using Leitz vicker's hardness tester with a load of 100 gm (0.981N). The hardness values were taken from the centre of the disc samples.

Grazing incidence X Ray Diffraction of the plasma nitrided sample was performed to determine various phases formed at different plasma nitriding temperatures.

Electrochemical studies were carried out in by potentiodynamic polarizing technique in 3.5 wt% deaerated NaCl solution as well as in 1% HCl solution. The scan rate was 1mV/sec with saturated calomel electrode as the reference electrode and platinum as the counter electrode. The analysis was done using the Chemdraw software.

Nano Indentation of the cross section of plasma nitrided samples was carried out at a load of 10,000µN. Indents were made along the X-axis after keeping the Y coordinate constant. The hardness value along the cross section of plasma nitrided samples was calculated using the formula [13].

Hardness (M Pa) = Max. Load / Contact Area.
Where the maximum load applied is in µN and the contact area is in nm^2.

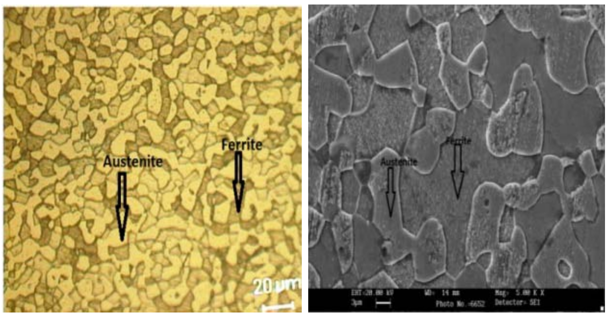
III. RESULTS & DISCUSSION

A. *Characterization of untreated sample*

Fig. 1 shows the microstructures of the Duplex Stainless Steel, using optical microscope and SEM, after etching with Kalling's reagent. Ferrite phase appears dark whereas the austenite phase is represented in white, in the optical micrograph. In the SEM micrograph, the smooth and shinier phase is austenite. There is almost an equal amount of distribution of both the phases.

B. *Surface morphology of plasma nitrided samples*

Fig. 2 shows the SEM micrographs of duplex stainless steel 2205 after plasma nitriding at various temperatures. The visibility of various nitrides and other phases formed, improves with increase in temperature. Higher the nitriding temperatures, better is the etching by plasma. The surface appears to be smooth in the PN 350 sample and the smoothness decreases with an increase in temperature. As the temperature is increased from 400^{o}C to 450^{o}C, there is a drastic transition in the surface morphology due to the formation of nitrides after the lattice is completely saturated with nitrogen. At 500^{o}C, precipitation of nitrides is visible at the interface of the two phases as shown in the PN 500 sample. Table.2 shows the EDX analysis data in which the surface nitrogen content, which gradually increases with an increase in temperature, due to higher diffusion rate of nitrogen at higher temperatures.



(a) (b)

Fig. 1 (a) Optical micrograph and (b) SEM micrograph of the untreated duplex stainless steel 2205

Table. II EDX analysis of surface of nitrided samples

Element	Nitrogen	Chromium	Iron	Nickel
PN 350	1.44	21.78	66.59	4.43
PN 400	2.43	21.98	64.96	4.53
PN 450	3.13	22.73	64.48	4.63
PN 500	3.86	21.8	63.85	4.45

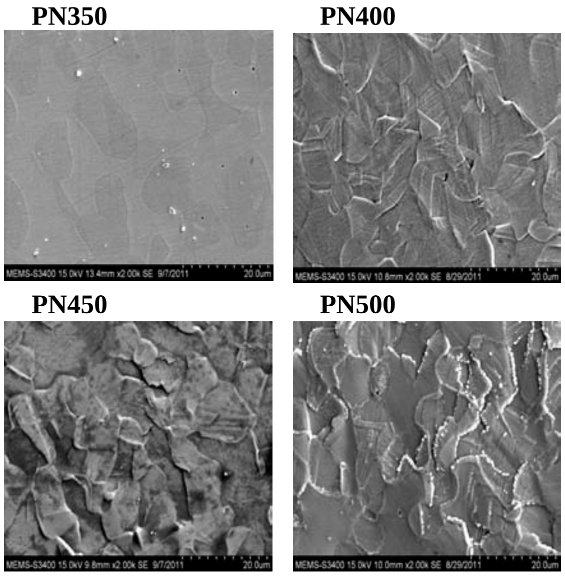

PN350 PN400 PN450 PN500

Fig. 2 SEM micrographs of the surface after plasma nitriding at different temperatures

C. *Cross sectional analysis of plasma nitrided samples*

Fig. 3 shows the SEM micrographs of the cross section of plasma nitrided samples. There is no formation of the white layer or the compound layer below 400^{o}C. The solubility of nitrogen in both ferrite and austenite phases is different. Nitrogen has higher solubility in the austenite phase. Therefore, the solubility limit of nitrogen in ferrite is reached before that of the austenite and this result in the formation of needle like precipitates at the grain boundaries of the ferrite.

When the nitriding temperature is further increased, the nitrogen ions diffuse much faster in the surface of the substrate and result in the saturation of lattice of both the phases. The PN 450 sample shows a 4.5µm thick uniform white layer formation, whereas a 2.4µm thick white layer is formed on the PN 500 sample.

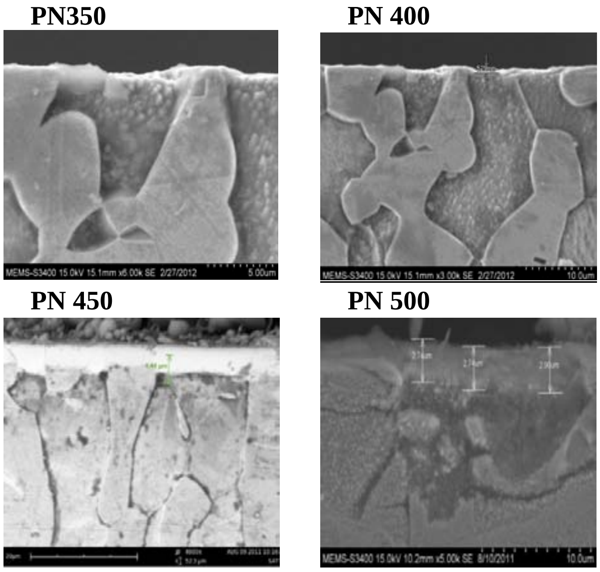

PN350 PN 400 PN 450 PN 500

Fig. 3 SEM micrographs of cross section of nitrided samples

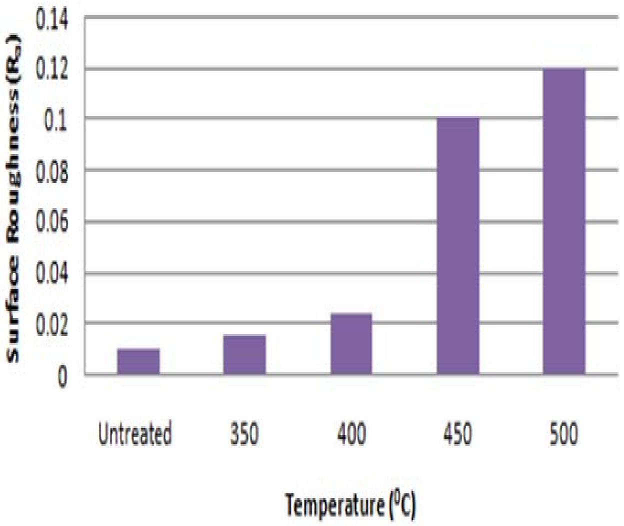


Fig. 4 Effect of plasma nitriding temperature on surface roughness (Ra in µm)

D. *Surface Roughness*

Surface roughness of the plasma nitrided samples increased with an increase in nitriding temperature as shown in Fig. 4. The increase in surface roughness at temperatures above 400^{o}C is 10 times more than below 400^{o}C. The reason for this sharp increase in surface roughness is due to the formation of compound layer on the surface after the solubility limit of nitrogen in the solid solution has reached. This is also evident from the SEM images of the cross section as well as the grazing angle X-ray diffraction results

E. *Surface Hardness & Cross Sectional Hardness*

Fig. 5 shows that the increase in surface hardness with an increase in nitriding temperature. It is due to the formation of a thicker nitride layer at higher temperatures. The case depth is more at higher temperatures because of faster diffusion of nitrogen. The Hardness of the compound layer is much higher than the diffusion zone and it is clearly observed from the SEM micrographs of cross section of treated samples (Fig. 3). There is formation of compound layer only above 400^{o}C. Thus the hardness values of samples above 400^{o}C are 3 times higher than the untreated samples.

In order to know the hardness in the case depth of plasma nitride layer, which comprises of two layers i.e. the white/ compound layer (top layer) and the diffusion zone (next to base material). Thickness of the compound layer formation depends on the amount of nitrides precipitating from the substrate. Nano indentation test of the cross section of plasma nitrided samples reveals that PN 500 sample has the highest case depth and PN 350 sample has the lowest case depth. Higher case depth in the PN 500 sample is due to the fact that at higher nitriding temperature the rate of nitrogen diffusion is high. This is shown in the Fig. 6 which shows the hardness (load/surface area) in MPa as a function of case depth.

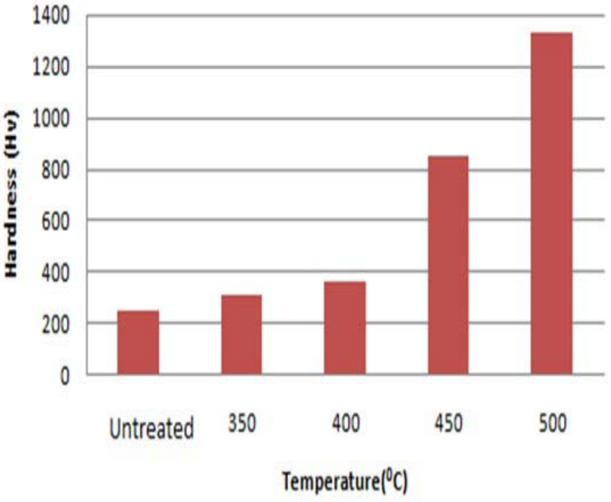


Fig. 5 Effect of plasma nitriding temperature on surface hardness (H_V)

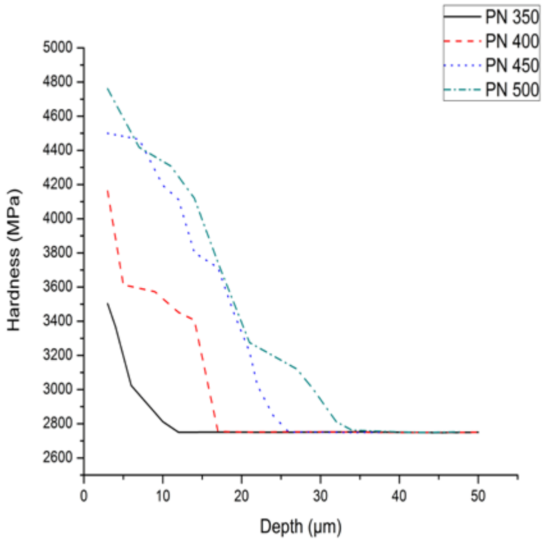


Fig. 6 Nano-indentation hardness as a function of case depth of plasma nitrided samples at different temperatures.

F. *XRD Analysis*

Grazing incidence XRD analysis on the treated and untreated samples shows the formation of different phases at various temperatures. The untreated sample showed peaks of both austenite and ferrite as shown in fig. 7. PN 350 sample showed a shift in peaks of austenite and ferrite due to the diffusion of nitrogen in the lattice of the substrate and leading to an expansion of the lattice. Thus, there is a formation of expanded austenite and ferrite phases. As the temperature is increased further, there is a shift in the peaks due to higher nitrogen diffusion until finally it results in the formation of nitrides of chromium and iron (CrN, Fe_3N) which are formed at 450°C and 500°C.

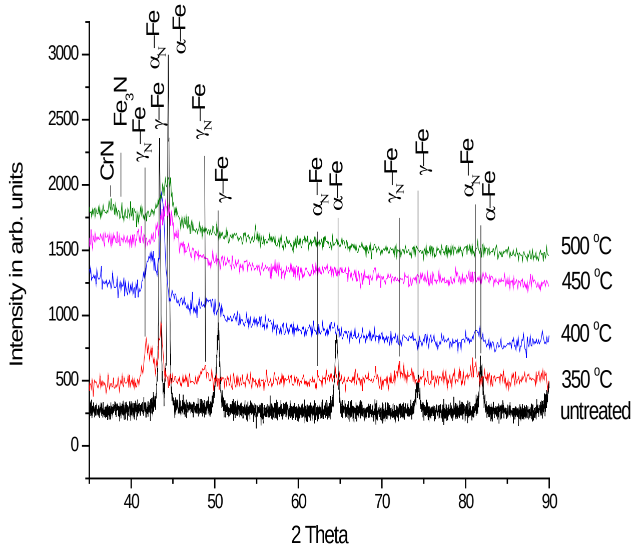


Fig. 7 GIXRD plot of untreated & plasma nitrided samples

G. *Potentiodynamic polarization study in 3.5% NaCl*

The potentiodynamic polarization results of both untreated and treated samples, carried out in the 3.5 wt% NaCl, solution are shown in Fig. 9. The corrosion current density of PN350 sample was the lowest and PN400 showed the next lowest values compared to the other samples, including the untreated sample. From this study, it can be concluded that the ´Υ_N phase formed during nitriding at 350°C and 400°C is the most corrosion resistant in this environment. Whereas the samples treated at 450 and 500°C are more susceptible to corrosion. This is due to the formation of chromium nitride phase, as confirmed by XRD results. These phases have no free Cr available to form the passive oxide layer. Therefore, these samples have a corrosion rate 10 times more than the untreated samples than those treated below 400°C. The SEM micrograph in Fig. 8 shows the phase which is being dissolved in the 3.5wt% NaCl environment. The PN500 sample showed severe tendency for the formation of corrosion products during the polarization test.

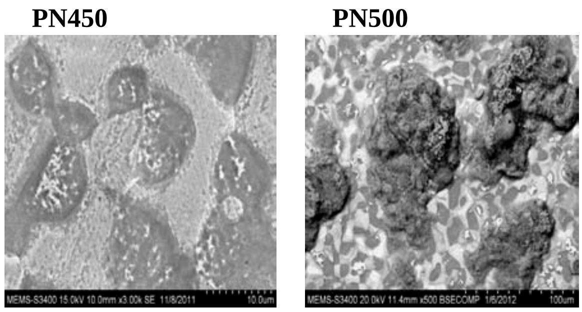

PN450 **PN500**

Fig. 8 SEM of the plasma nitrided samples after potentiodynamic polarization study in 3.5 wt% NaCl

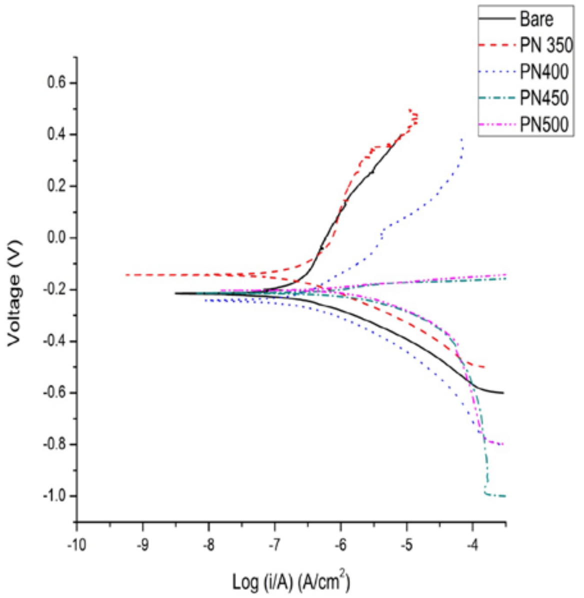


Fig. 9 Potentiodynamic polarization in 3.5 wt% NaCl

H. Potentiodynamic polarization study in 1% HCl

Potentiodynamic polarization tests in 1% HCl (Fig. 11) show that the PN 400 sample has the lowest E_{corr} and i_{corr} values, when compared to the treated and untreated samples. The reason for this behavior can be explained from the phases formed at nitriding temperature of 400°C. The phase present in the PN400 sample is identified as the expanded austenite Υ_N, which has excellent corrosion resistance. The nitriding temperature above 400°C led to the formation of chromium and iron nitrides. The chromium nitride formation resulted in loss of chromium from the solid solution instead of forming stable passive oxide film. Thus these samples showed poor corrosion resistance in the 1% HCl environment. The phase dissolved during the corrosion study is analyzed by SEM as shown in Fig. 10. The CrN phase on the surface of PN450 and PN500 dissolves in 1% HCl solution. After its dissolution, the Cr from the sub surface forms the protective layer to passivate the sample which can be seen in the potentiodynamic plot of both PN450 & PN500 samples.

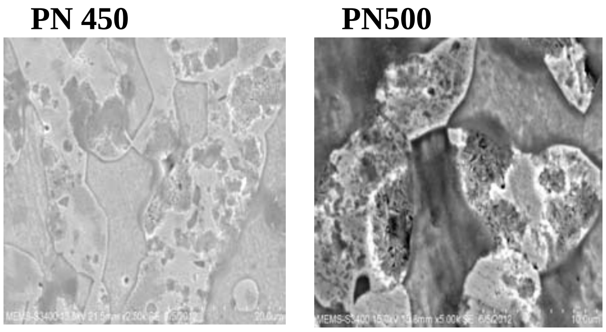

PN 450 **PN500**

Fig. 10 SEM analysis of the plasma nitrided samples after corrosion study in 1% HCl

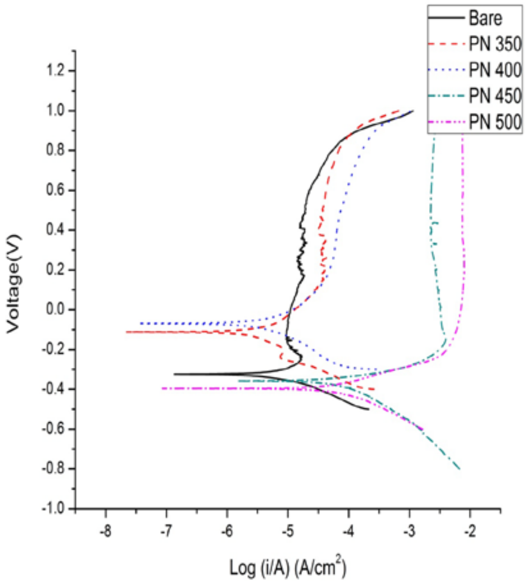


Fig. 11 Potentiodynamic polarization study in 1% HCl

IV. GENERAL DISCUSSION

The Grade 2205 is the most widely used duplex stainless steel in oil and gas industry for sea water pipelines. These systems require a wear resistant surface to withstand the abuse of the aggressive flowing environment. However, duplex stainless steels are susceptible to the formation of detrimental intermetallics, when exposed to higher temperatures (>500°C) which leads to the degradation of the mechanical properties. Thus, there is need to use a low temperature surface hardening method such as plasma nitriding without compromising the loss of other structural properties of the materials.

The surface hardness, surface roughness and plasma etching of the nitrided surface of duplex stainless steel 2205, improved with an increase in the plasma nitriding temperature. This resulted due to the faster diffusion of nitrogen at higher temperatures, leading to the formation of thicker nitride layers. The phases formed after plasma nitriding at different temperatures showed a shift in the peaks with an increase in temperature due to the diffusion of more amount of nitrogen into the lattice. The formation of expanded austenite and expanded ferrite phases appears below 400°C. As the temperature increased above 400°C, peaks of nitrides of Fe and Cr appeared.

The potentiodynamic polarization of the samples plasma nitrided at 350°C and 400°C showed better corrosion resistance than the 450°C and 500°C samples. At high temperatures, chromium nitrides are formed which leads to the depletion of chromium from the solid solution. Protective layers of chromium oxide cannot be formed due to the non availability of free chromium on the surface. The expanded austenite phase which is formed below 400°C is the most corrosion resistant phase in these environments.

The surface hardness and roughness increases with an increase in temperature. But the corrosion resistance decreases with an increase in temperature above 400°C. In order to withstand the aggressive environment, optimum combination of both the properties has to be taken into account. Possibility of further increase in hardness and corrosion resistance could be obtained by increasing the exposure time at 400°C.

V. CONCLUSION

The present work is an attempt to demonstrate that plasma nitriding is an important technique to enhance the surface hardness of duplex stainless steels, especially when used in flowing fluids as tubes and pipes. The biggest problem is the temperature of plasma nitriding and the changes in the microstructure of the duplex stainless steels. The process conditions are chosen so that a good case depth of the nitrided layer is formed without affecting the composition and microstructure of the base duplex stainless steels. The work has demonstrated that at higher temperature, especially around 500°C, but it has been found that above 400°C, the corrosion resistance decreases, as part of the chromium is used up in the nitride formation. Thus one has to look for optimum temperature may be 400°C, where slightly lower hardness is obtained but corrosion resistance still remains acceptable.

REFERENCES

[1] A.M.Kliauga, and M.PohI, Effect of plasma nitriding on wear and pitting corrosion resistance ofX2 CrNiMoN 22 5 3 duplex stainless steel, Surface & Coatings Technology 1998, 1205-1210.

[2] L. Scoppio, and M. Barteri, Proceedings of the Applications of Stainless Steel1992, Stockholm, Sweden, 1992, 260–269.

[3] C.-J. Maderud, J.-O. Andersson, and M. Liljas, Proceedings of the Applications of Stainless Steel, Stockholm, Sweden, 1992, 370–378.

[4] D.H. Mesa, C.E. Pinedo, and A.P. Tschiptschin, 'Improvement of the cavitation erosion resistance of UNS S31803 stainless steel by duplex treatment' Surface & Coatings Technology 2010, 205, 1552–1556

[5] L. Karlsson, Proceedings of the Duplex Stainless Steels 1997, Maastricht,The Netherlands, 1997, 43–58.

[6] L. Karlsson, S. Rigdal, and F. Lake, Proceedings of the Duplex America 2000, Houston, USA, 2000, 257–272.

[7] J.-O. Nilsson, A. Wilson, B. Josefsson, and T. Thorvaldsson, Proceedings of the Applications of Stainless Steel 1992, Stockholm, Sweden, 1992, 280–289.

[8] Z. L. Zhang and T.Bell, "Structure and corrosion resistance of plasma nitrided stainless steel" Surface Engineering, 1985, 1, 131-136~~.~~

[9] Kimiaki Nagatsuka, Akio Nishimoto, and Akamatsu, 'Surface hardening of duplex stainless steel by low temperature active screen plasma nitriding' Surface & Coatings Technology 2010, 205, S295-299.

[10] A.M. de Oliveira, R.M. Muñoz Riofano, L.C. Casteletti, 'Effect of the temperature of plasma nitriding in AISI 316L austenitic stainless steel' Revista Brasileira de Aplicações de Vácuo, vol. 22, no. 2, 63-66, 2003.

[11] Insup Lee, 'Influence of Temperature and Time on Low-Temperature Plasma Nitrocarburizing of AISI 304L Austenitic Stainless Steel' Journal of the Korean Physical Society, Vol. 54, No. 3, March 2009, pp. 11311135.

[12] L. H. Chiu, Y. Y. Su, F. S. Chen, H. Chang, 'Microstructure and Properties of Active Screen Plasma Nitrided Duplex Stainless Steel' Materials and Manufacturing Processes, Vol. 25: 316–323, 2010.

[13] C. Tromas, J.C. Stinville , C. Templier, and P. Villechaise, "Hardness and elastic modulus gradients in plasma-nitrided 316L polycrystalline stainless steel investigated by nanoindentation tomography" Acta Materialia 60 (2012) 1965–1973.

Mr. Satyapal did his Masters in Corrosion Science & Engineering from IIT Bombay and Bachelors in Metallurgical & Materials Engineering department from IIT Roorkee. He worked for Cheers Interactive Ltd as a subject matter expert with the patent licensing department.

Prof. A.S.Khanna is from Indian Institute of Technology. He has experience of a reputed Research Institute such as IGCAR Kalpakkam for 15 years after which he joined IIT Bombay in 1991. He has more than 15PhD's and 100 Master's to his credit. He has published 250 papers, written two books and edited several. He is widely travelled and had several international assignments, Fellow of Humboldt Foundation, Fellow Norwegian Science and Technology, Japan Key Centre and visiting Prof. in Germany and France. He is distinguished Fellow of ASM International and NACE International, two well known bodies for Materials and Corrosion protection.