

High Temperature thermochemical treatment Of 2205 Duplex Stainless Steel to Enhance Corrosion Resistance

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Duplex stainless steel DSS is a corrosion resistance alloy with dual microstructure characteristic of near equal ratio of ferrite and austenite. Its high chromium content has drawn a great interest in application such as oil and gas environment, chlorine environment and generally aggressive environment that needs high corrosion resistance. In spite of good corrosion resistance, DSS is susceptible to certain defect such as stress corrosion cracking, hydrogen Induced cracking and chloride stress corrosion cracking in low pH environment. This work is aim to enhance corrosion resistance by nitriding with a conventional tube furnace. Heat treatment process was conducted at a temperature of 1200°C and at a heating rate of 16.7°C/min for 8 hours. The sample was allowed to cool within the furnace while the gas flow was discontinued to avoid further nitrogen diffusion. Further reheat treatment to 700°C for 1hour was conducted in the absence of nitrogen to minimize sensitization effect and remove residual stress on the sample. The characterization of the sample with the aid of optical Microscope, SEM and EDS showed the formation of expandable austenite precipitation. Corrosion rate test was conducted with FeCl₃ and HCl, it also showed that nitrided sample had a better corrosion resistance than unnitrided sample.

Keyword: Nitriding, corrosion, temperature

1. INTRODUCTION

Nitriding is a diffusion process that involves the movement of ionized nitrogen into vacancy site of a base material. Some characteristic of nitrogen such as ionization power, atomic size and diffusion coefficient has made it relevant element for improving properties of stainless steel. Duplex stainless steel DSS has found great application in oil and gas environment because of its high chromium content which is basically responsible corrosion resistance by the formation of chromium oxide layer know as passivation. (W.Liu, 2014) (Mohammadzadeh, Akbari, & Drouet, 2014) The stability of this layer is thermodynamic dependent on the environment and tribology of base material. DSS which has dual nature of ferrite and austenite microstructure with complex transformation characteristic, this has made thermochemical treatment much challenging especially at certain temperature which my prompt sensitization effect (Pohl, Storz, & Glogowski, 2007) (Lv, liang, Wang, & Guo, 2016). Despite the good corrosion property of DSS, it is vulnerable to certain environment such as high temperature, high chlorine and certain CO₂ / H₂S; this condition might initiate certain defect such as chlorine induced stress corrosion cracking, galvanized independent hydrogen cracking, soft zoning cracking, stress corrosion cracking, sulfide stress corrosion cracking and hydrogen induced cracking (Choi, Nescic, & Ling, 2011) (W.Liu, 2014) This work is focused at producing a hybrid layer which will enhance certain corrosion resistance such as pitting corrosion and inadvertently abrasive –corrosion. In oil sand operation, material selection is pertinent because of oil sand is characterized with aggressive particles from rocks and

presence of chlorine (Lopez, Falleiros, & Tschiptschin, 2011). There is a need to minimize risk by effectively using a suitable material in consideration of operating environment. Comparatively, much work has been done on plasma nitriding than conventional gas nitriding. J.Alphonsa et al, worked on simultaneous improvement of corrosion resistance and hardness of 2205 grade of DSS using plasma nitriding (80%N₂ and 20%N₂) and nitrocarburising (78%N₂, 20%H₂ and 2%C₂H₂) at a low temperature (Alphonsa, Raja, & Muhherjee, 2015) (Chen, Weng, & Yang, 2002). He showed the increase in hardness without impairing on corrosion resistance but increasing in temperature beyond 400°C reduced the corrosion resistance with increase in thickness of surface layer. This present worked is focus on nitriding with pure nitrogen at temperature of 1200°C to enhance the corrosion resistance regarding the possible effect of sensitization which is the precipitation of chromium carbide (Cr₂₃C₆) between a temperatures of 450°C to 950°C which occurs at the grain boundaries (Triwiyanto, Hussain, & Ismail, 2012) (Pohl, Storz, & Glogowski, 2007) (Chen, Weng, & Yang, 2002) (Nilsson, 1992) (Choi, Nescic, & Ling, 2011)

2. EXPERIMENTAL PROCEDURE

2.1 Material Specimen preparation

A pipe of 2205 of DSS with a diameter of 33.4mm, thickness 3.8mm and a length of 1000mm and cut which is perpendicular to the axis of the rod used as specimen in this research. The material composition is given in table 1

Table: Material composition

Element	Cr	N	Mo	Ni	C	Cu	Fe
Wt %	22	0.12	2	7	0.03	1.4	Balance

The sample was placed in the heat zone of the furnace with the aid of a crucible. The grinding was done with Sic Paper with sizes of 400, 600, 800 and 1200grit and polishing with 3µm diamond paste to obtain a mean roughness which will be approximately 0.00 µm. The etchant used in this experiment is kallings solution (5g of CuCl₂ +100ml HCl + 100ml ethanol)

2.2 Gas nitriding

Nitriding process was conducted at a temperature of 1200°C with the pure nitrogen gas. The sample was clean with acetone to remove the oxide layer which might impede diffusion process. The sample is first places inside the furnace with a crucible. The heat treatment was performed with a heating rate of 20°C to attain a temperature 1200°C at which the gas was turned on; the temperature was held for 8 h with a contact flow and pressure of 1 bars. The gas was turned off after 8 h while the sample was allowed to cool in the furnace, this to avoid oxidation process which might be inimical to the mechanical and corrosion properties of the sample.

2.3 Elemental analysis

The microstructure and the chemical composition were performed with the use optical microscope OP, scanning electron microscope SEM. The treated and untreated cross section of the sample was examined. Nickel composition was determined at 3 different spots using with aid of EDS.

2.4 Corrosion rate analysis

A simulated sea water environment was developed at temperature of 40°C using 6% FeCl₃, 1% HCl solution and distilled water (600ml distilled water, 68.72g FeCl₃ and 16ml 1M HCl). The Corrosion rate of the nitrided and untrided sample was determined by immersion process for 48 hours on which the weight and the surface area of the samples were calculated before and after immersion. After immersion, the samples were cleaned with clark solution (stannous chloride anhydrous, hydrochloric acid and antimony trioxide). A five cleaning was performed with ultrasonic bath to determine the average mass loss due to clark solution effect on the sample. The corrosion rate is calculated using the formula as shown

$$Corrosion\ Rate\ (CR) = \frac{KW}{DAT} \quad (1)$$

Where K = constant (87.6mm/yr)

W = weight loss (mg)

D = density ($\frac{g}{cm^3}$)

A = area (cm²)

T = time (hr)

3. RESULT AND DISCCUSION

3.1 Optical microscope and SEM analysis

Duplex stainless has a dual nature of ferrite and austenite of nearly equal ratio. Optical analysis was conducted to aid of abrasive cutter. From fig1a shows the microstructure of untreated sample with nearly equal ratio of austenite and ferrite which is a typical characterization of 2205 grade of duplex stainless steel

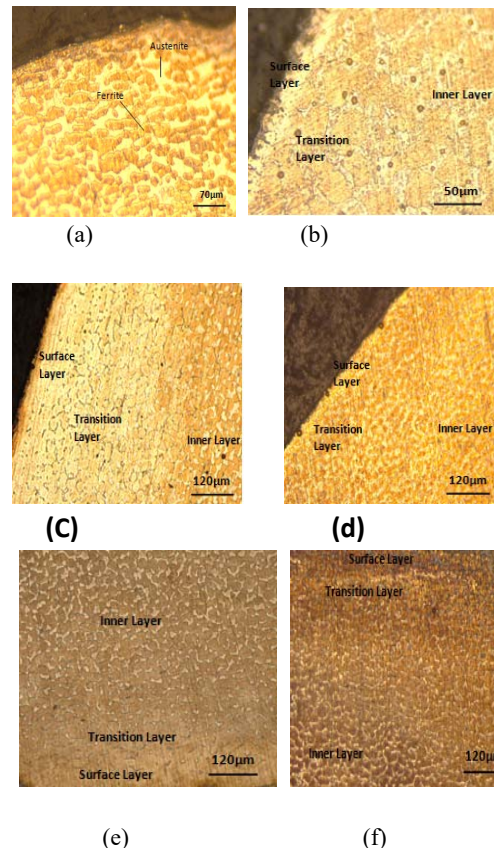


Fig 1: Optical Microscopic Image for (a) untreated sample (b) sample 1 (c) sample 2 (d) sample 3 (e) sample 4 (f) sample 5

It can be seen from fig(1a) that austenite and ferrite are evenly disperse, approximately equal ratio which is a typical character of 2205 grade DSS. Other treated samples have microstructural changes due to nitrogen diffusion which is austenite stabilizer, more expanded austenite phase is

observed in the entire sample which attributed the transformation of ferrite to expandable austenite. It will be observed that there is more morphological changes on the surface layer which might also be attributed as the formation of some other complex compound that will enhance the tribology properties of the treated material.

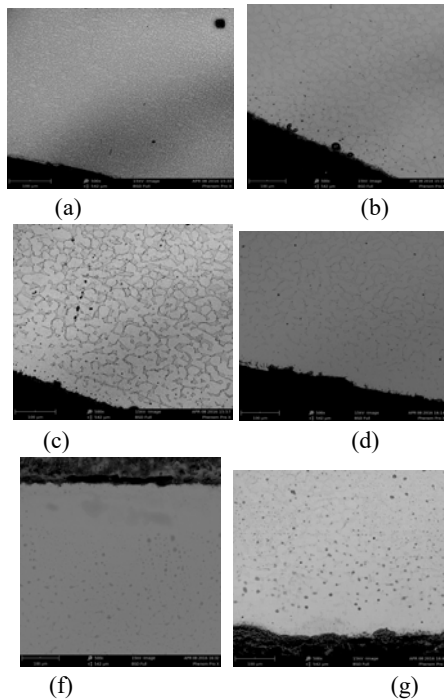


Fig 2: Scanning Electron Microscopic Image for (a) untreated sample (b) sample 1 (c) sample 2 (d) sample 3 (e) sample 4 (f) sample 5

Fig 2a which the unnitrided layer shows no substrate layered formed and the clears show the phase of austenite and ferrite are of approximately equal ratio while other sample which have undergone heat treatment process have morphological changes due to temperature, treating time and diffusing element which in the case is nitrogen. It will be observed that the hybrid formation on all the nitride material which will be responsible for providing a shielding against aggressive attack.

Uniform diffusion

Nitrogen diffusion within the horizontal axis of the furnace from inlet to outlet point of the furnace was studied.

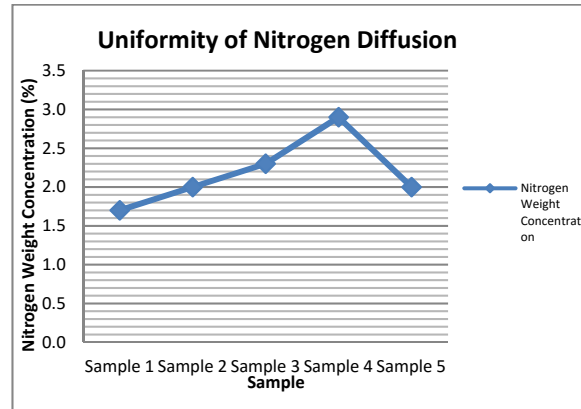


Fig 3: Uniformity of Nitrogen Diffusion

Samples which were placed in the same direction of gas flow, was studied after nitriding. Samples one in this study is considered as unnitrided sample. Nitrogen concentration along the flow direction was studied with sample 2,3,4 and 5 which was longitudinally placed within the heating chamber of the furnace. From EDS, Nitrogen concentration on the sample gave a tolerance of $\pm 1.2\%$. This can be considered uniform diffusion within the chamber of the furnace.

3.2 Nickel Composition

Nickel which is austenite former like nitrogen was carefully studied with the aid of EDS, Dark spot, light spot and the surface layer were focus points. This was done to identify the phase produced after nitriding process.

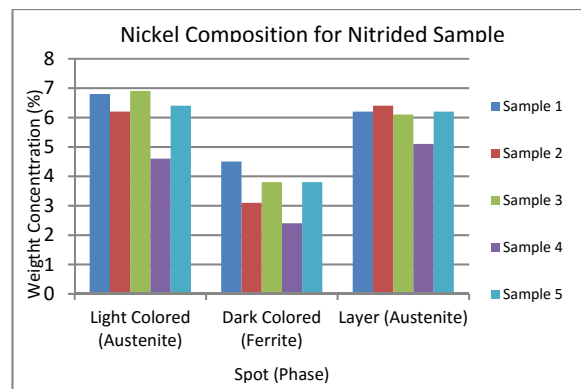


Fig 4: Nickel composition for nitrided samples

From fig 4, it can be seen that nickel weight percent concentration is more on the light spot for all the samples which is between 4.7 wt% to 6.8wt % compared to dark spot with nickel composition between 2.5 wt% to 4.5 wt%. The surface layer is suggested to be austenite from the nickel composition, these is envisaged based on that nickel has enhanced the formation of expandable austenite and on its characteristics as austenite reformer. From iron pseudo binary

phase diagram, weight concentration between 3 to 8% of nickel consists of austenite and ferrite phase when subjected

Formula	$K \times W$	$A \times T \times D$	$(K \times W) / (A \times T \times D)$
corrosion rate (mm/yr)	1.27×10^5	6.34×10^3	20.099
Area ,A		15.728	cm^2
density ,D		7.81	g/cm^3
K		8.76×10^4	

to 1200°C. Below 3% is ferrite phase and higher than 8% of nickel weight concentration is austenite phase. From fig4, the light colored has a higher nickel weight concentration and is attributed to be austenite while the dark color is ferrite. The surface weight concentration of nickel is has a very high nickel concentration. Hence the surface layer can be extrapolated to contain expandable austenite which will be responsible for higher corrosion resistance compared to untrided sample. Expanded austenite has a good corrosion resistance property which is responsible to for corrosion resistance of nitride corrosion resistance alloy.

Corrosion test which was calculated using weight loss method by immersion of nitride and untrided sample in a saturated solution of FeCl₃ and five cycle cleaning with clark solution. Fig 6 shows a plot of mass loss against cleaning cycle.

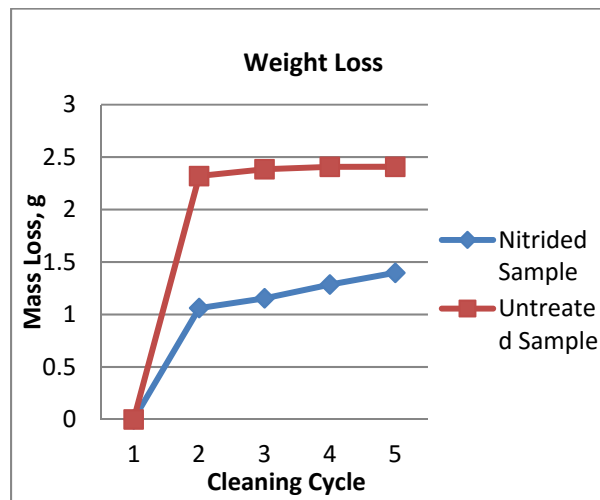


Fig 6: Weight Loss per Cleaning Cycle for Untreated

Formula	$K \times W$	$A \times T \times D$	$(K \times W) / (A \times T \times D)$
corrosion rate (mm/yr)	2.11×10^5	5.89×10^3	35.797
Area ,A		15.728	cm^2
density ,D		7.81	g/cm^3
K		8.76×10^4	

Sample

It can be seen from fig6 at the first cleaning both nitride and untrided sample have the same mass loss while subsequent cycle showed that mass loss was more on the untrided layer than the nitride layer. This suggest higher that nitride sample has a better corrosion resistance than untrided after immersion in FeCl₃ for 48 hours.

Table 2: corrosion rate calculation of untrided sample

Table 3: corrosion rate calculation of nitride sample

From table 2 and 3 will be seen that the corrosion rate is higher on the untrided sample than nitride sample. The average weight used in calculating the corrosion rate.

4. CONCLUSION

Nitriding of duplex stainless steel using a conventional gas tube furnace can enhance the corrosion resistance by treating it at a high temperature between 1100°C and 1200°C. From the microscopic and SEM analysis, the phase of nitrided and untrided were apparently differently with the formation of hybrid layer on the surface of the nitride sample which is a thermochemical effect. EDS also suggested that the formation of expanded austenite which is responsible for enhanced corrosion resistance. Increased in nickel weight percent concentration in nitride sample indicated that diffusion of nickel reaffirmed nickel as austenite former which inadvertently promoted the formation of austenite layer on the surface of the nitride material. Subsequently corrosion test was conducted in a simulated sea water environment also showed that there is a higher corrosion resistance in nitride sample than untrided sample (Lopez, Cid, & Puiggali, 1999).

Hence is it can be logically concluded that corrosion resistance of 2205 grade of duplex stainless steel can be enhanced at high temperature which is beyond the sensitization temperature without practically precipitating inimical phase such sigma phase and S phase which are prime phase that exacerbates the statutory property of corrosion resistance alloy.

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