Nitriding of Duplex Stainless Steel for Reduction Corrosion and Wear

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Abstract Duplex stainless steel (DSS) which has a dual nature of ferrite and austenite with nearly equal ratio has found a good application in oil and gas industries because of its excellent corrosion resistance, high yield strength, good weldability, and relative low life cycle costing from reduced operating cost. Dual phases of DSS or combination of two-phase existence to be more characterize with better mechanical properties than a single-phase metal of ferrite or austenite. Nitrogen is a good strengthening alloy for DSS because it forms a solid solution of $(Fe, Cr)_2N$ which is responsible for the hardness and wear resistance in DSS. Spontaneous formation of oxide or passivated layer is responsible for shield and direct exposure of surface of stainless steel to corrosive medium though is susceptible to depletion and deterioration in high chlorine water and low pH level in production environment. Total damage of passivated region on the surface of DSS prompts initiation of localized defect such as pit which grows over a time to form crack. Oil and gas environment is characterized with high H_2S content which is a constraint in application of DSS in this environment because of its insignificant resistance to sulfide stress corrosion cracking (SSCC) and hydrogen-induced cracking (HIC).

Keywords Nitriding · Stress corrosion cracking · Pitting corrosion H_2S · CO_2

1 Introduction

Nitriding is an act of bombarding nitrogen atom into lattice or interstices of a parent material to form solid solution. Nitriding is a diffusion process that involves ionized nitrogen gas from high-concentration region to low-concentration region. It is a

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thermochemical process that requires high activation energy from temperature and pressure to overcome barrier since is a nonspontaneous reaction.

Nitriding of stainless steel and other nonferrous material has found much benefit such as in improvement mechanical hardness, increase corrosion resistance, wear resistance, and yield strength. The importance of nitriding on duplex stainless steel (DSS) to increase corrosion resistance in oil and gas environment can never be overemphasized.

Duplex stainless steel is a dual-phase material which comprises approximately 50 % ratio of ferrite and austenite. Dual nature of duplex stainless steel has made it relevant in many application, especially in oil and gas environment (pipes, tubes, valves, storage tank, and Christmas tree) because its properties like yield strength, pitting resistance equivalent number (PREN), high resistance to chloride environment, good corrosion, and wear resistance and weldability. Its excellent resistance to corrosion is attributed to high chromium and molybdenum contents which are responsible for passivation layer. In oil and gas environment, molybdenum enhances resistance to localized corrosion by forming film layer MoS_2 which could prevent further dissociation of Fe on the surface of DSS. Subsequently, spontaneous formation of chromium oxide which is the most active film layer on stainless steel acts as barriers from attack on material though can be depleted by low pH level and presence of chlorine water from production system in oil and gas environment. Pitting resistance equivalent number (PREN) is a numerical guide for estimating the localized corrosion resistance of steel in chloride environment (Francis et al. 1997). In sour and CO_2 environment in the presence of chlorine water, DSS is more vulnerable to SSCC and chloride stress corrosion cracking. Other type of cracking that can occur in hydrogen sulfide environment are stress corrosion cracking (SCC), hydrogen-induced cracking (HIC), stress-oriented hydrogen-induced cracking, soft zone cracking, galvanized independent hydrogen stress cracking. Operating limits have been provided in NAEC MR1075 for corrosion resistance alloy CRA in sour environment to minimize the susceptibility of SSCC and other sulfide-related cracks.

2 Corrosion Problems in Oil and Gas Environment

Natural gas and crude oil do carry high impurity substance which are very corrosive and hence attack materials. Their inherent corrosive nature which constitutes H_2S, CO_2, and chlorine water has been the major catalyst that facilitates the degradation of steel material in oil and gas environment. For corrosion to occur, there must be an anode (corroded site), a cathode (unaffected sites), and an electrolyte (crude oil). Pipeline is used in transportation of crude from oil well to gathering site with a high-pressure-exposed steel material to resist wear and corrosive attack. Corrosion resistance alloy is oil and gas environment are still susceptible to certain corrosion such as sweet corrosion, sour corrosion, oxygen corrosion, microbiological corrosion, pitting corrosion and erosion corrosion. Destruction of passive film on stainless steel to form either localized site for corrosion propagation, corrosion is been controlled by velocity of gas flow in the pipe, partial pressure ratio of H_2S/CO_2, chlorine content, operating temperature. When the internal surface of a pipeline is exposed to direct contact with the crude, it is then susceptible to electrochemical reaction as below:

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{1}$$

On exposure to corrosive attack, the metals loss electron to become positively charged, these create a localized site in form pit. For corrosion to occur, there must be an anodic and cathodic reaction. In oil and gas environment, there are various possibles of cathodic reactions (Popoola et al. 2013)

$$O_2 + 4H^+ + 4e^- = 2H_2O \tag{2}$$

$$2H^+ + 2e^- = H_2 \tag{3}$$

$$H_2O + 2e^- = H_2 + 2OH^- \tag{4}$$

Equations 2, 3, and 4 are cathodic reactions by using different solutions either acidic or basic. The processes in Eqs. 1–4 are good promoters of corrosion, as they decrease the pH level of crude oil making material to be more susceptible to degradation and sudden failure. Hydrogen gas evolved can penetrate on degraded surface of a material causing hydrogen embrittlement.

3 Effect of Treating Temperature on Microstructure of Steel

Temperature is a relevant factor in thermochemical treatment of stainless steel. High chromium and molybdenum contents in stainless steel make it very sensitive at a temperature between 650 and 950 °C which affects the mechanical properties (Poph et al. 2006). Intermetallic phases are detrimental to the inherent good mechanical properties of steel because of their brittle nature, low corrosion resistance, low yield strength, and toughness. This effect has given restriction in application of duplex stainless steel and stainless steel in high-temperature device (Fig. 1).

Various investigators in the past had proposed a methodology to overcome inimical morphological changes that occur on the surface of stainless steel on thermochemical treatment because of the formation of chromium oxide and molybdenum oxide, nickel oxide but with little progress in establishing simultaneous improvement in hardness, wear, and corrosion resistance. J.W. Simmons in 1994 analyzed the effect of Cr_2N precipitation on austenitic stainless steel. It was observed that Cr_2N reduced the ductile strength in austenitic stainless steel (Poph et al. 2006; Simmons 1990; Uggowitzer and Harzenmoser 1989; Simmons and Atteridge 1993). The three major intermetallic phases that precipitate in stainless

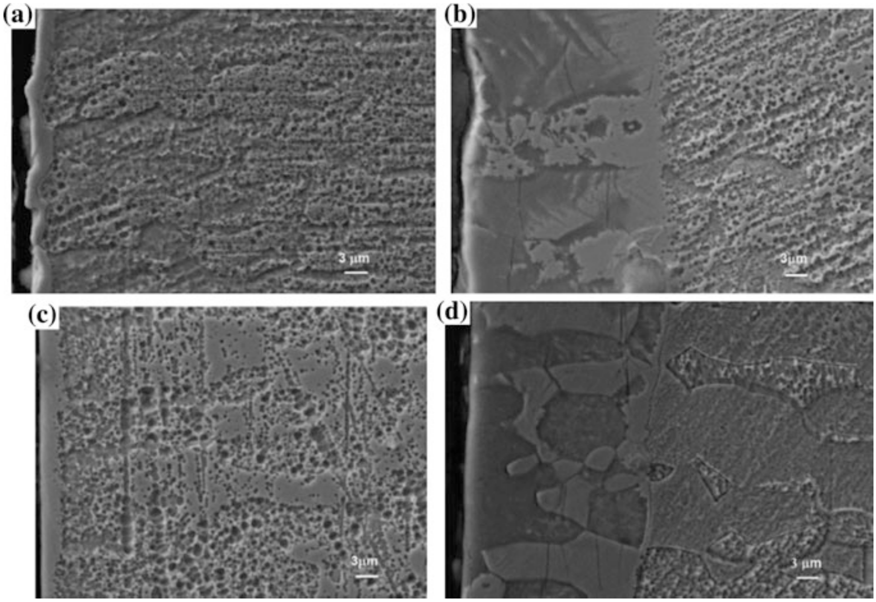


Fig. 1 Cross-sectional SEM images of duplex stainless steel, plasma nitrided at **a** 400 °C, **b** 500 °C and plasma nitrocarburized at **c** 400 °C and **d** 500 °C (Alphonsa et al. 2015)

steel during the high-temperature operation are σ-, χ-, and Laves, but the propensity of their precipitation depends on the alloy composition and temperature above 500 °C. Duplex stainless steel with high chromium composition is very susceptible to sensitization effect though most of relevant intermetallic precipitation occurs at the ferrite phase because it has a higher diffusion rate than austenite (Simmons and Atteridge 1993; Alphonsa et al. 2015). σ is associated with binary system of Fe–Cr, χ is associated with ternary system (Fe–Cr–Mo) and quaternary of Fe–Cr–Ni–Ti and Fe–Cr–Ni–Mo (Simmons 1990; Uggowitzer and Harzenmoser 1989; Simmons and Atteridge 1993). The precipitation of the phases is time and temperature dependent; the formation of nuclei in each phase can be analyzed with the aid of time–temperature–transformation (TTT) as in Fig. 2.

Intermetallic formation such as sigma phase which starts with nuclei precipitation that apparently transform to a core-like structure depending on diffusion rate and distance. This intermetallic phase is responsible for loss in toughness and ductility in DSS though increases the hardness. It is paramount to note that high-diffusion velocity gives rise to higher local supersaturating and subsequently high density precipitation. From Fig. 3, the fastest precipitation of sigma phase occurred between 720 and 800 °C. Literature has showed that the sigma affects some mechanical properties such as toughness and varies with temperature (Poph et al. 2006). There is some literature of low-temperature gas nitriding and high-temperature gas nitriding (HTGN) of stainless steel. J.H. Sung in 2007 performed HTGN of ferritic stainless steel between a temperature of 1050 and 1100

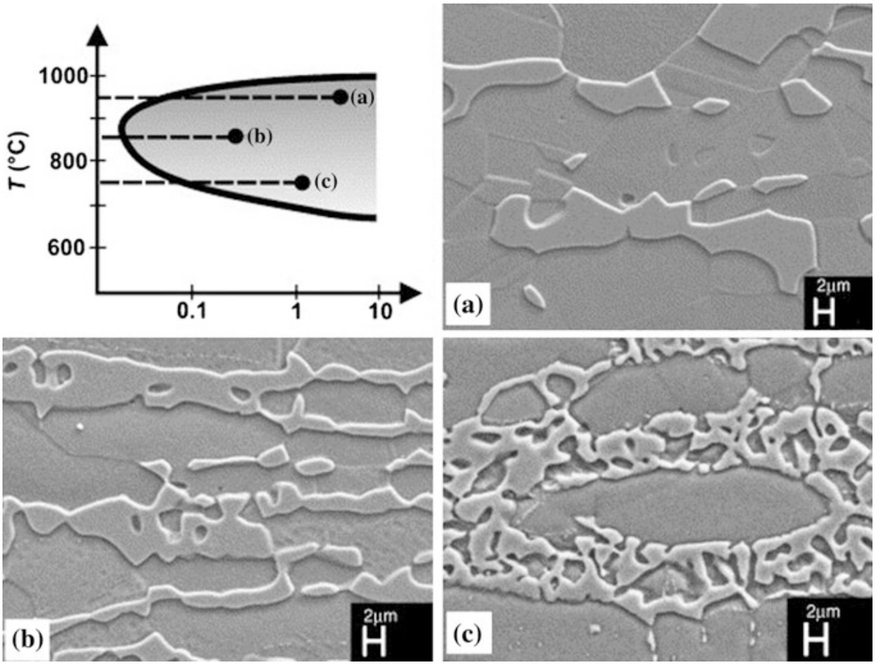
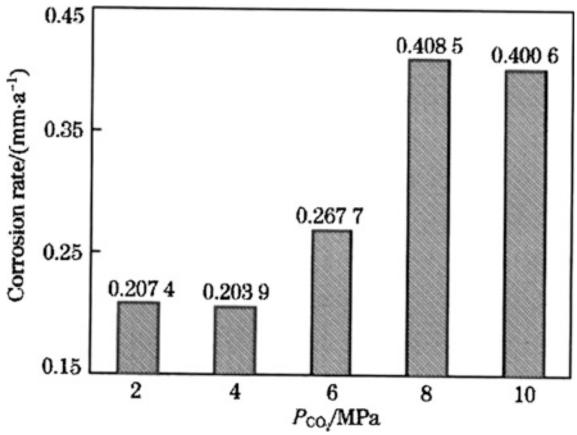


Fig. 2 Morphology of the sigma phase with respect to the isothermal annealing temperature; **a** 950 °C, **b** 850 °C, and **c** 750 °C (Poph et al. 2006)

Fig. 3 Average corrosion rates of 110S tube steel under different CO_2 partial pressures (Li et al. 2012)



followed by a tempering process. An improved surface hardness after tempering was observed and improved corrosion resistance in $1NH_2SO$ (Kasper 1954). There are various methods of thermochemical treatment such as ion beam implantation, plasma nitriding, plasma immersion ion implantation, and plasma nitrocaburizing which is a recent development that involves a single-cycle process of nitrogen and carbon. Recent development has adopted a methodology of using single-cycle process with different alloying composition of gases such as nitrogen, methane, and ammonia to achieve better surface layer with increase in hardness and wear resistance. The effect of gas ratio has been a contributing factor in determining the effective diffusion for solid solution formation and precipitation of phases. Different pretreatment processes sputtering with hydrogen have proved a great relevance because they eradicate oxide layer for better diffusion which is a barrier on the surface of a stainless steel that acts as protective shield for in-depth penetration of alloying component. Expected precipitates on treated DSS are $(Fe, Cr)_2N$, expandable austenite (responsible for wear resistance), and sigma phase, χ-, and Laves, and the characterization is done by field-emission scanning electron microscope (FESEM), X-ray diffraction XRD, and conversion electron. Characterization of DSS is peculiar to their grades also subjective on thermo-chemical treatment because variation in chemical composition by weight% (Sung et al. 2008; Hughes and Llewelyn 1959; Escriba et al. 2009; Saithala et al. 2014; Rolinski 1987) (Table 1).

4 Possible Corrosion Type on Duplex Stainless Steel in H_2S and CO_2 Environment

Duplex stainless steel has an excellent corrosion resistance to uniform corrosion, but it is susceptible to corrosion into certain operating condition and environment. In oil and gas environment, H_2S and CO_2 are the major constituents that directly affect the stability of material because of their oxidation rate on stainless steel. The combination effect of chlorine water and low pH level, in oil and gas environment, facilitates certain corrosion on DSS such as, SSCC, SCC, and HIC. In flow lines such as tubes and pipes, DSS is susceptible to erosion corrosion and cavitation. However, wellheads and valves, DSS is susceptible to crevice corrosion (Popoola et al. 2013).

Table 1 Classification of some duplex stainless steel

Grade	Cr (wt%)	Ni (wt%)	Mo (wt%)	Mn (wt%)	N (wt%)
UNS S32205/S32803	22.5	5.6	2.8	2	0.17
UNS S2304	23	4	–	–	–
UNS S32750	25	7	3.5	2	0.25
LDX 2101	21.5	1.5	0.3	5	0.22
S32760	25	7	3.5	–	0.30
S31260	25	6.5	3.0	–	0.3

5 Effect of H_2S and CO_2 Partial Pressure Ratio on Corrosion of DSS

Internal corrosion in tube and pipes is more predominate than external corrosion because of flowing pressure and velocity with the internal region of the flow line. Currently, oil field production is characterized with increasing H_2S contentment, making the most significant challenge in corrosion study. High operating velocity and pressure destabilize the oxide file DSS, making it susceptible to erosion corrosion. Available literature has showed that in oil and gas environment, the presence of H_2S can inhibit or accelerate the corrosion in carbon steel depending on H_2S/CO_2 partial pressure. The pressure ratio of H_2S and CO_2 has been of great relevance in prediction of corrosivity of stainless steel in oil and gas environment. High partial pressure of H_2S generally increases the corrosion by increase in the dissociation rate of H_2S which lowers the pH level. Z.F. Yin et al. in his consideration analyzed that increase of S^{2-} formation could result in formation of sulfides which will inhabit corrosion. From literature, K. Masamura et al. presented a critical ratio of P_{CO_2}/P_{H_2S} in identifying corrosion mechanism and susceptibility of carbon steel in H_2S/CO_2 environment. He suggested that when $P_{CO_2}/P_{H_2S} > 200$, CO_2 plays a dominating role in the environment, and he subsequently stated that $P_{CO_2}/P_{H_2S} < 200$ FeS layer will be formed on the surface on carbon steel material which will act as an inhibitor. B.F.M. Pot et al. showed that when $P_{CO_2}/P_{H_2S} > 500$ the corrosion mechanism is controlled by CO_2 while $P_{CO_2}/P_{H_2S} > 20$, the corrosion mechanism is led by H_2S (Li et al. 2012). In DSS, the surface layer is controlled basically by chromium oxide and P_{CO_2}/P_{H_2S} that favors the formation of FeS which destabilizes the adherence of chromium oxide to the base material. Figure 3 shows that increase in partial pressure of CO_2 is directly related to corrosion in carbon steel. No intensive works have been done recently on the analysis of CO_2/H_2S partial pressure ratio on DSS after heat treatment.

6 Effect of Gas Composition on Surface Morphology

The surface change of nitride stainless steel is also dependent on the composition of nitride gas which precipitates or contributes in solution formed. Untreated stainless steel characterized with this is inherent attribute of passivated layer made of oxide film as a protective shield or coat that prevents direct aggressive environmental attack. Every nitriding process is aimed at achieving a better surface layer which will improve the corrosion and wear resistance without compromising the other mechanical properties if relevant in intended application. Recent development has proved that composition of other gas such as hydrogen, ammonia, or methane gas in nitriding of stainless steel has better and improved mechanical properties than single gas nitriding. This effect is attributed to be the change in surface microstructure which advertently initiates a tribological change. Efficient nitriding of steel can be achieved with high density of reactive nitrogen such as ions N^+ or ridicule (N). Hydrogen plays a role of removing oxide layer that might impair in-depth of nitrogen. The reactive nitrogen is enhanced by mixture with hydrogen; this due to dissociation (8.8 eV) and ionization (13.1 eV) energy of hydrogen is smaller than that of nitrogen which has 24-eV dissociation and 15.58-eV ionization energy. Increase in nitrogen composition increases the case depth, hardness, and the surface roughness of treated material (Mohammadzadeh et al. 2014).

7 Possible of Increase of Surface Roughness After Nitriding

It has been discovered that after nitriding of steel material, there is tribological change due to surface microstructural change which lead to increases in surface roughness. XRD analysis, optical microscope, and scanning electron microscope (SEM) can be used in the study of surface morphology and tribology. After gas nitriding or thermochemical treatment of steel material, there is an increase in thickness layer due to microstructural changes effected by diffusion of gas such as nitrogen. Under the same treating condition, plasma nitriding produces a higher thickness layer than the use of conventional gas nitriding because plasma nitriding completely removes passivated layer that can be an encumbrance to efficient diffusion rate. Figure 4 shows increase in surface roughness with increase in time. It also shows increase in hardness with respect to time.

Some of the possible causes of change or increase in surface roughness are the following:

- Reposition of the sputtered material on the surface,
- Sputtering that is caused collision of particles which is induced by energetic nitrogen bombardment,
- Different lattice expansion of the grains of polycrystalline material.

8 Carbide Precipitation and Its Effect

Precipitation of carbide upon thermal treatment of stainless steel is described as sensitization effect. These processes are the temperature-dependent processes which occur at a temperature between 425 and 870 °C. When a thermochemical treatment is performed within these temperatures, stainless steel is susceptible to precipitate carbide at the grain boundaries which weakens the mechanical properties of the material. The most inimical is carbide, i.e., $Cr_{23}C_6$, because of the depletion of chromium alloy which is the chief corrosion-resistant alloying element in stainless steel. Some alloying elements in stainless steel are responsible for impairing the

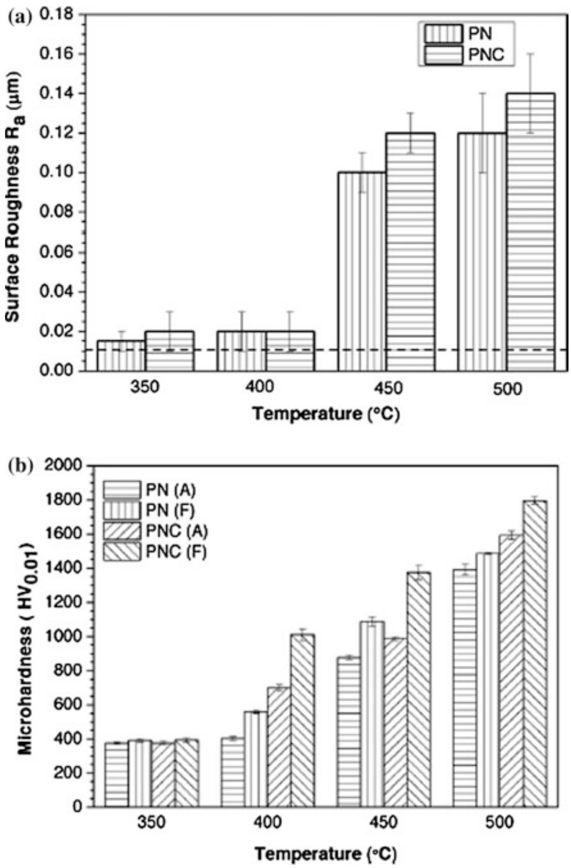


Fig. 4 **a** Surface roughness (the *dashed line* indicates that the initial surface roughness). **b** Microhardness values obtained on austenite and ferrite phases after plasma nitriding and plasma nitrocarburizing treated at different temperatures (Alphonsa et al. 2015)

sensitization effect, such as nitrogen and titanium niobium. Some of them, which have high affinity carbon, deter the precipitation of chromium and molybdenum carbide. The quantity of carbon in stainless steel has an effect on sensitization process; because of high affinity, it can diffuse very fast with the grain boundaries altering the microstructure and enhances the precipitation of carbide. Nitriding of stainless steel is also a good chemical treatment process which might form a solid solution $(CN)_2$ thereby locking up the diffusion rate of carbon at the grain boundaries.

9 Conclusion

Duplex stainless steel has played so much roles in oil and gas environment but still operates in a very close boundary between its acceptability in oil and gas environment. There is a need to further reduce the life cycle cost of DSS material used in oil and gas environment by improving the corrosion and wear resistance of DSS which will reduce the operating cost. Nitrogen thermochemical treatment with conventional tube furnace has significant advantage over plasma nitriding which is on commercial application of pipe and tubes. Plasma nitriding is limited to size that cannot be applied on commercially. Since every engineering process ought to be sensitive to cost-effectiveness, conventional tube furnace which utilizes nitrogen from the atmosphere makes it relative cheaper than plasma nitriding. Literature has shown that nitriding of stainless steel can improve the corrosion and wear resistance by formation of thicker surface layer and expandable austenite layer within the matrix and ferrite and austenite. Nitrogen, which is an austenite former, stabilizes and enhances austenite precipitation from ferrite.

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