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Short Communication

# **Corrosion Behavior of High-Nitrogen Stainless Steel in NaCl** Solution

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A new high nitrogen nickel free stainless steel (HNSS) was proposed in this paper, which is responsible for the solving the problem of corrosion failure of the heat exchangers. The passivity and semi-conducting behavior of HNSS in 0.5 mol/L NaCl solution have been investigated. The polarization curve of HNSS showed that the material exhibit self-passivation. Mott-Schottky plots indicate that the stability of the passive film decrease with the increase of applied potential. The primary constituents of the passive films formed are iron oxides, manganese oxides and iron oxides. Chloride ions are not incorporated in the oxide layer, but N enrichment appeared in the passive film. The presence of  $NH_3/NH^{4+}$  could accounts for the enhanced protection of the passive film.

Keywords: A. Corrosion, B. High nitrogen stainless steel, C. Passive film, D. XPS analysis

# **1. INTRODUCTION**

According to the related standards, the corrosion rate of stainless steel used in heat exchangers allowed is not less than 0.005 mm/a [1]. Corrosion failures of stainless steel heat exchangers occur at specific times under industrial conditions. Risks occur occasionally and are unpredictable and severe and leading to disastrous consequences. According to a survey about 166 accidents occurred on stainless steel heat exchangers, uniform corrosion accounts for approximately 8.5%, high-temperature oxidation corrosion accounts for 4.9%, and the rest localized corrosion (pitting corrosion, crevice)

corrosion and stress corrosion cracking) [2]. So, it is of great significance to investigate the corrosion properties of stainless steel used as heat exchanger tube, especially the sea water heat exchanger.

The superior corrosion resistance of stainless steel is attributed to the passive film formed on its surface [3]. The results reported indicating that passive films exhibit semi-conductor behavior, and they prevent the metal base from contacting the caustic ions and reduce corrosion rate of metals. Sudesh [4] studied the semiconductor passive films formed on metals and alloys using photocurrent and capacitance measurements. It was found the existence of a large number of localized mid band gap states, consistent with amorphous oxides. However, the flat-band potentials of the austenitic stainless steel passive films were found to be independent of both composition and measuring frequency. The passive films are formed as dual layers, iron oxide outer layer and chromium oxide inner layer. Shintani [5] investigated the composition and structure of passive film formed on 316L SS by X-ray photoelectron spectroscopy (XPS). The results indicated that the passive film possessed a doublelayered structure consisting of a Fe oxide-rich outer layer and a Cr oxide-rich inner layer. Dissolution of the Fe-rich layer and densification of the Cr-rich inner layer were observed, especially at high temperatures. The chloride ions were concentrated in the Fe-rich outer layer, and they penetrated more deeply than that in the aqueous solution into the passive film formed in the methanol solution. Montemor [6] also got the similar results. Fattah-alhosseini[7] investigated the semiconductor properties of passive films formed on AISI 316L and found that the calculated donor density decreases exponentially with increasing passive film formation potential. Also, the results indicated that donor densities increased with temperature. By assuming that the donors are oxygen ion vacancies and/or cation interstitials, the diffusion coefficients of the donors for stainless steels are calculated. Since 1938, nitrogen was used as an alloying element in research on nitrogen-containing stainless steels to improve mechanical properties and corrosion resistance performance without sacrificing ductility and toughness [8-9]. Numerous researchers investigated the effect of nitrogen on corrosion behavior of HNSS and found nitrogen has beneficial effect on the pitting corrosion, crevice corrosion and stress corrosion cracking corrosion of stainless steel [10-16].

The present study focused on the corrosion behavior of a HNSS with nitrogen content approximates 0.75%. The electrochemistry behavior and semi-conducting properties of HNSS in 0.5 mol/L NaCl solutions were investigated based on polarization curve measurement, Mott-Schottky measurement and passive film characterized by X-ray photoelectron spectroscopy (XPS) analysis.

# **2. EXPERIMENTAL**

The HNSS used in this study was made by the dissolution of the raw materials in high vacuum furnace, followed by forging, hot rolling, cold rolling and then air cooling to room temperature. The HNSS was in the form of sheet with thickness of 8 mm. The chemical composition of HNSS used in the present study is listed in Table 1. The HNSS used was solution annealing as fllow: HNSS was heated to 1150  $^{\circ}$ C and holding for 60 min then quenched with water to room temperature. HNSS plate was cut into samples with dimensions of 10×10×5 mm. Samples were then mechanically polished with

a series of silicon carbide abrasive papers of variable grades to a finish grit of 1000#. Before the experiment, samples were washed by ultrasound with acetone and then air-dried. The specimen used for microstructure examine was mechanical polished with 1.5  $\mu$ m diamond then electrolytic etched in 10% oxalic acid reagent at 12 V for 60 s.

 Table 1. Chemical composition of tested HNSS (wt %)

С	Si	Mn	Ν	Cr	Mo	S	Р	Fe	
0.048	0.22	19.68	0.75	19.71	2.23	0.003	≤0.03	Bal.	

The experiments were performed in 0.5 mol/L NaCl. Reagent grade NaCl and distilled water used. To prevent crevice corrosion, working surface with an exposed working area of 1 cm<sup>2</sup> was immersed in 30 % (wt) nitric acid at 50 °C. Non-working surface was sealed with epoxy. All electrochemical tests were conducted in a standard three-electrode system in a 1.5 L glass cell using Corrtest CS350 potentiostat/galvanostat with a Pt counter electrode and saturated calomel reference electrode. All electrochemical tested were carried out in open air without stirring at room temperature. Prior to testing, working electrodes were initially polarized to -1.2 V<sub>SCE</sub> for 180 s to remove passive films formed in air and then polarized at 0.1, 0.2, 0.3, 0.4 and 0.5 V<sub>SCE</sub> for 300 s to form a passive film. Excitation voltage with sine wave modulated signal of 10 mV was employed in tests. Polarization curves were measured at a sweep rate of 0.333 mV/s. A step rate of 20 mV/s and frequency of 1000 Hz were applied [17].

The microstructures of HNSS were observed by using XL20 scanning electron microscopy (SEM) with acceleration voltage of 20 kV. The crystal structure of HNSS were studied by XRD (Philips PW3710), using Cu K<sub>a</sub> radiation generated at 40 kV and 35 mA. Surface analyses of passive films were conducted by conventional angle-resolved X-ray photo-electron spectrometry ESCALAB250. Alloying elements, such as O, Cl, and N were detected after reaching vacuum settings at  $10^{-7}$  Pa. Depth profiling was performed by argon ion bombardment at an ion energy of 0.5 keV. During depth profiling, sample current measured 0.5 mA, and bombardment area totaled 2×2 mm<sup>2</sup>. Peak identification was performed by referring to an XPS database.

## **3. RESULTS AND DISCUSSION**

#### 3.1 Microstructure of HNSS

Fig. 1 shows microstructure of tested HNSS after solution annealing. As shown in Fig. 1, HNSS is a single-phase austenite with annealing twins existing in the grain. Fig. 2 depicts the X-ray diffraction (XRD) profile of HNSS.



Figure 1. Microstructure of the tested HNSS after solution annealing



Figure 2. XRD profiles of HNSS after solution annealing

As shown in Fig. 2, HNSS comprised austenite phase ( $\gamma$ ) in XRD analysis, which is consistent with metallographic structure analyses as shown in Fig.1.

#### 3.2 Polarization Curves

Fig. 3 depicts potentiodynamic polarization curve of HNSS in 0.5 mol/L NaCl solution. As shown in Fig. 3, corrosion potential HNSS measured  $-0.35 V_{SCE}$  in 0.5 mol/L NaCl solution. HNSS exhibited a passive state in the potential region, which ranged from  $-0.10 V_{SCE}$  to 0.55  $V_{SCE}$ . In this region, the passive film remained stable without evident pitting potential. When potential reached higher than 0.55  $V_{SCE}$ , the passive film was unstable and pitting occurred. Five potentials (0.1, 0.2, 0.3, 0.4, and 0.5  $V_{SCE}$ ) were selected to investigation of semiconducting properties of passive film.



**Figure 3.** Potentiodynamic polarization curve of HNSS in 0.5 mol/L NaCl solution in open air without stirring at room temperature

#### 3.3 Semiconducting Behavior of Passive Film

Passive films formed on most metals and alloys exhibit semiconducting behavior, which related to the corrosion resistance of tested materials. The semiconductor type and doping density of passive films can be determined according to Mott–Schottky analysis. Mott–Schottky equation can be expressed as follows [15]:

$$\frac{1}{C^2} = \frac{1}{C_H^2} + \frac{1}{C_{SC}^2} + \frac{2}{\varepsilon \varepsilon_0 eAN_d} (E - E_{fb} - \frac{kT}{e})$$
(1)

where  $C_H$  refers to Helmholtz layer capacitance,  $C_{SC}$  represents space charge capacitance,  $N_d$  denotes donor/acceptor density in passive film,  $\varepsilon$  indicates dielectric constant of oxide (15.6 for passive film on steel),  $\varepsilon_0$  corresponds to vacuum permissive constant ( $8.85 \times 10^{-12} Fm^{-1}$ ) [18], e depicts electron charge ( $1.6 \times 10^{-19}$  C), k is Boltzmann constant, T stands for absolute temperature, A represents sample area, and  $E_{fb}$  is flat band potential, which is determined from E intercept. For p-type semiconductors, Eq. (1) yields a positively sloped curve. Inversely, for n-type semiconductors, Eq. (1) implies a negatively sloped curve.

Fig. 4 plots Mott–Schottky curves of HNSS in 0.5 mol/L NaCl at various formation potential. From the Mott–Schottky curves, the passive film showed electrochemical behavior of n-type semiconductors at potentials between 0 and 0.5  $V_{SCE}$ , whereas it exhibited electrochemical behavior of p-type semiconductors when potential measured higher than 0.5  $V_{SCE}$ . Mott–Schottky curves indicate p-n junction-type semiconductors at various formation potentials. These semiconductors feature high corrosion resistance. Studies showed that passive films formed on Fe–Cr alloys feature a double structure [19]. The inner layer consists of Cr oxides, indicating p-type semiconductor property. The outer layer comprises Fe oxides, indicating n-type semiconductor property with defect types consisting of oxygen vacancies.



**Figure 4.** Mott–Schottky plots for HNSS in 0.5 mol/L NaCl at various formation potential in open air without stirring at room temperature

Oxygen vacancies represent the dominant species in passive films. Fig. 5 presents physicochemical processes that occur within passive films based on the Point Defect Model (PDM) [20-22]. Formation and dissolution of passive film include five chemical reactions [23]:

$m + V_m^n \rightarrow M_m + ne$	(2)
$m \rightarrow M_m + \frac{n}{2} V_o^{\cdot \cdot} + 2e$	(3)
$M_m \to M^{n+} + V_m^{n'}$	(4)
$V_o^+ + H_2 O \rightarrow O_o + 2H^+$	(5)
$M_2O_n + 2nH^+ \rightarrow nH_2O + 2M^{n+}$	(6)

where m represents a metal atom,  $V_m^{n'}$  corresponds to metal vacancies in passive film,  $M_m$  refers to metal atoms in passive film,  $V_o^{"}$  depicts oxygen vacancies in passive film,  $M^{n+}$  stands for metal ions in solution,  $O_o$  indicates oxygen atom in passive film, and  $M_2O_n$  represents the general expression of passive film.

The reaction in Eq. (3) plays a key role in chemical reactions at metal-film interface. Eq. (3) indicates passive film formation. The reaction in Eq. (5) plays a leading role in chemical reactions at film-solution interface, reflecting chemical dissolution of passive film. The relationship between acceptor density and formation potential can be expressed as follows:

$$N_d = \omega_1 \exp(-bE_f) + \omega_2 \tag{7}$$

where  $\omega_1$ ,  $\omega_2$ , and *b* can be obtained from fitted curves of  $N_d$ – $E_f$ . Figure 6 shows variation in acceptor density with formation potential based on Mott–Schottky curve in Fig. 4. Figure 6 also shows that acceptor density N<sub>d</sub> increased with formation potential. The relationship can be fitted with Eq. (7). The fitting equation is as follows:

$$N_d = 1.24 \times 10^{19} \exp(8.16 V_{\text{SCE}}) + 3.85 \times 10^{20} \text{ cm}^{-3}$$
 (8)

Eq. (8) indicates that stability of passive film decreases with increasing formation potential.



**Figure 5.** Schematic diagram of physicochemical processes occurring within passive films according to PDM [24-25]



Figure 6. Changes in  $N_d$  of passive film formed on HNSS in 0.5 mol/L NaCl solution at various potentials in open air without stirring at room temperature. Solid lines indicate fitted results.

3.4 XPS Results

Fig. 7 presents XPS spectra depth profiles of main elements detected from passive films of HNSS in tested solution at 0.3  $V_{SCE}$ . The passive film mainly comprised of Fe, Cr, and Mn oxides. Cl<sup>-</sup> was detected in passive film surface, the concentration of which decreasing with the etching time indicating that Cl<sup>-</sup> was involved in film formation. *N* refers to maximum concentration of element observed in surface of the passive film, and its concentration decreased with sputtering time. Consequently, this condition leads to enrichment of N in passive film, implying that N participated in film formation. Cr concentration is richer than that of Fe in passive films. Mo and Fe contents

increased during sputtering period, as caused by dissolution of Mo and Fe contents in acid. N concentration stabilized after sputtering for 50 s due to puncturing of passive film. According to test parameters in XPS analysis, thickness of passive film is about 4 nm.



**Figure 7.** XPS spectra depth profiles of main elements detected in passive films of HNSS in 0.5 mol/L NaCl solution at 0.3 V<sub>SCE</sub> in open air without stirring at room temperature

Fig. 8 shows XPS spectra of Cr, Fe, Mn, Mo, and O recorded from passive film on HNSS in 0.5 mol/L NaCl solution at 0.3 V<sub>SCE</sub> and etching time of 30 s. The figure also displays three constituent peaks of Cr, which represent metallic states of the element, namely,  $Cr^0$ ,  $Cr(OH)_3$  and  $Cr_2O_3$ . Similar results were obtained by Liu [26] and Singh [27]. Fe in passive film exists mainly in the form of Fe<sup>3+</sup>. According to XPS spectra, the studied passive film comprised Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>. Mn existed mainly in the form of MnO and Mn<sub>2</sub>O<sub>3</sub>, and Mo mainly existed as MoO<sub>2</sub> and Mo(OH)<sub>3</sub>



**Figure 8.** XPS spectra of Cr, Fe, Mn, Mo, and O recorded from passive film on HNSS in 0.5 mol/L NaCl solution at 0.3 V<sub>SCE</sub> in open air without stirring at room temperature



Figure 9. XPS spectra of N recorded from passive film on HNSS in 0.5 mol/L NaCl solution at 0.3  $V_{SCE}$  in open air without stirring at room temperature

Fig. 9 illustrates XPS spectra of N recorded from the passive film on HNSS in tested solution at 0.3  $V_{SCE}$  and poling time of 30 min. Passive film surface was rich with N, which existed in the form of NH<sub>3</sub> and NH<sup>4+</sup>. These molecules can protect the base against Cl<sup>-</sup> corrosion [28]. Fig. 7 provides the evidence that the passive film contained low levels of Cl<sup>-</sup>. Some references showed that H<sup>+</sup>

decreases due to chemical reaction of N atoms at solid-solution state, forming  $NH_4^+$  and leading to decreased pH value and improved stability of passive films.

# 4. RESULTS

1) The material used was a single-phase austenite with twins existing in grains and with nitrogen content of 0.75%

2) HNSS exhibited excellent passivity behavior in tested solution. Moreover, the protective ability of passive film decreased with the increase of formation potentials.

3) The Mott-Schottky plot indicated that the surface films of HNSS have both p-type and n-type electronic characteristics. Oxygen vacancy was the dominant species in passive film. The concentration of acceptor density  $N_d$  in the passive film increased with the increasing of formation potentials and following.

4) The passive film consisted of Fe, Cr, and Mn oxides. The formed passive film surface was enriched with N, which N existed in the form of  $NH_3$  and  $NH_4^+$ , thus improving stability of passive film.

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# References

- 1. F.L. Huang, K. Li, M. Yang and X.L. Wang, Petro & Chemical Equipment, 11 (2008) 45.
- 2. D.Y. Ying, Chemical Equipment and Piping, 3 (1980) 56.
- 3. E. Sikora and D.D. Macdonald, *Electrochimica Acta*, 48 (2002) 69.
- 4. T.L. Sudesh, L. Wijesinghe and D.J. Blackwood, Journal of Physics, 28 (2006) 74.
- 5. D. Shintani, T. Ishida, H. Izumi, T. Fukutsuka, Y. Matsuo and Y. Sugie, *Corrosion Science*, 50 (2008) 2840.
- 6. M.F. Montemor, R. Pinto and M.G.S. Ferreira, *Electrochimica Acta*, 54 (2009) 5179.
- 7. A. Fattah-Alhosseini, M.A. Golozar, A. Saatchi and K. Raeissi, Corrosion Science, 52 (2010) 205.
- 8. M. Janik-Czachor, E. Lunarska and Z. Szklarska-Smialowska, Corrosion, 31 (1975) 394.
- 9. E.A. Cho, S.J. Ahn and H.S. Kwon, *Electrochimica Acta*, 50 (2003) 3383.
- 10. G. Rondelli, B. Vicentini and A. Cigada, Materials and Corrosion, 46 (2015) 628.
- 11. Y.X. Qiao, S. Wang, B. Liu, Y.G. Zheng, H.B. Li and Z.H. Jiang, Acta Metallurgica Sinica, 52 (2016) 233.
- 12. H.J. Grabke, Transactions of the Iron and Steel Institute of Japan, 36 (1996) 777.
- 13. R.F. A. Jargelius-Pettersson, Transactions of the Iron and Steel Institute of Japan, 36 (2007) 818.
- 14. S. Ningshen, U.K. Mudali, V.K. Mittal and H.S. Khatak, Corrosion Science, 49 (2007) 481.
- 15. Y.X. Qiao, Y.G. Zheng, W. Ke, P.C. Okafor, Corrosion Science, 51 (2009) 979.
- 16. H.Y. Ha, H.J. Jang, H.S. Kwon and S.J. Kim, Corrosion Science, 51 (2009) 48.
- 17. M.H. Dean and U. Stimming, Corrosion Science, 29 (1989) 199.
- 18. C.O.A. Olsson and D. Landolt, *Electrochimica Acta*, 48 (2003) 1093.

- 19. Y.X. Qiao, X. Cai, J. Cui and H.B. Li, *Advances in Materials Science and Engineering*, 2016, 6065481.
- 20. C.Y. Chao, Journal of the Electrochemical Society, 129 (1981) 1874.
- 21. C.Y. Chao, Journal of the Electrochemical Society, 128 (1981) 1194.
- 22. C.Y. Chao, Journal of the Electrochemical Society, 128 (1981) 1197.
- 23. E. Sikora, J. Sikora and D.D. Macdonald, *Electrochimica Acta*, 41 (1996) 783.
- 24. D.D. Macdonald, Journal of Nuclear Materials, 379 (2008) 24.
- 25. M. Metikoš-Huković and Z. Grubač, Journal of Electroanalytical Chemistry, 556 (2003) 167.
- 26. C.T. Liu and J. K. Wu, Corrosion Science, 49 (2007) 2198.
- 27. V.B. Singh and M. Ray, Journal of Materials Science, 42 (2007) 8279.
- 28. C.R. Clayton, G.P. Halada and J.R. Kearns, Materials Science & Engineering A, 198 (1995) 135.

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