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Pitting Corrosion Resistance and Repassivation Behavior of C-Bearing Duplex Stainless Steel

Hanme Yoon ^{1,2}, Heon-Young Ha ^{2,*} , Tae-Ho Lee ², Sung-Dae Kim ², Jae Hoon Jang ² , Joonoh Moon ² and Namhyun Kang ^{1,*} 

¹ Department of Materials Science and Engineering, Pusan National University, Busan 46241, Korea

² Ferrous Alloy Department, Korea Institute of Materials Science, Changwon 51508, Korea

* Correspondence: hyha2007@kims.re.kr (H.-Y.H.); nhkang@pusan.ac.kr (N.K.);
Tel.: +82-55-280-3422 (H.-Y.H.); +82-51-510-3274 (N.K.)

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Abstract: The effects of C-substitution for part of the N content, on the pitting corrosion resistance and repassivation tendencies of duplex stainless steels (DSSs) were investigated. For this investigation, normal UNS S32205 containing N only (DSS-N) and the C-substituted DSS (DSS-NC) were fabricated. Microstructural analyses confirmed that the two DSSs had dual-phase microstructures without precipitates, and they possessed similar initial microstructure, including their grain sizes and phase fractions. Polarization and immersion tests performed in concentrated chloride solutions revealed that the DSS-NC was more resistant against stable pitting corrosion and possessed a higher repassivation tendency than the DSS-N. Furthermore, the corrosion pits initiated and propagated to a less corrosion resistant α phase. Polarization tests and corrosion depth measurements conducted in an HCl solution indicated that the DSS-NC exhibited lower galvanic corrosion rate between the α and γ phases than the DSS-N. Therefore, the growth rate of pit embryo was lowered in the DSS-NC, which shifted the potentials for the stable pit initiation and the pit extinction to the higher values.

Keywords: duplex stainless steel; pitting corrosion; repassivation behavior; galvanic corrosion

1. Introduction

The beneficial effects of alloying nitrogen (N) [1–9] and carbon (C) [10–20] on mechanical properties and resistance to the localized corrosion of austenite stainless steels (γ -SSs) are widely investigated, and their mechanistic roles in the performance improvements are well established. N and C are economical and strong γ formers, thus they can be used in the γ -SS in replacement of Ni. In addition, they improve the mechanical strength of γ -SS by solid solution strengthening with a minimal loss of elongation. Moreover, it is reported that alloying N and C enhances the resistance to localized corrosion by strengthening the protectiveness of the passive film. Therefore, various γ -SSs have been modified and newly developed by alloying N and/or C [2,4,5,7,10–12,15]. It is worth mentioning that the advantages of the alloying N and C can be manifested as long as they remain in solid solution state in the matrix. Because the alloyed N and C exceeding solubility limits is prone to form Cr-consuming precipitates, such as Cr_2N [21–23] and Cr_{23}C_6 [19,24], which degrade both mechanical and corrosion properties, thermomechanical processing and welding for N and/or C-bearing γ -SSs should be managed with caution.

Duplex stainless steels (DSSs) are a family of SSs consisting of equal volume of ferrite (α) and γ phases [25–28]. A combination of the α and γ phases exerts beneficial influences on mechanical properties and resistance to corrosion. DSSs are particularly well known for their outstanding resistance to stress corrosion cracking in Cl^- -containing environments [29]. Moreover, DSSs generally contains less Ni content (1–7 wt%) than the commercial 300-series γ -SS (i.e., FeCrNi-based SS contains, generally

8–24 wt% Ni), thus DSSs are known to be more economical than FeCrNi-based γ -SSs. Because of the desirable performances and economic benefits, demand for the DSSs as structural materials shows a continuous increase in various industrial fields requiring high mechanical strength and corrosion resistance.

Alloying N is frequently adopted for DSSs because of its advantages in performance improvement [25,30–34]. Thus, commercial DSSs including UNS S32101, UNS S32304, UNS S32205, and UNS S32750, contain 0.1–0.3 wt% N. However, alloying C to DSSs has rarely been attempted, although C is found to be beneficial to performances of γ -SSs, similarly to N. Generally, C content was carefully controlled to be less than 0.03 wt% for commercial DSSs, because DSSs can provide more sites to Cr_{23}C_6 precipitations such as phase boundaries than the γ -SS [19,35,36]. But as long as C remains in solid solution state, it is expected to take advantages of the alloying C in promoting the physico-chemical properties of DSSs, the possibility of which was supported by the previous studies on C-bearing γ -SSs [10–20].

This study investigated the effects of C on the corrosion properties of DSS. For this study, type UNS S32205 DSS in which some N content was substituted with C, and normal UNS S32205 DSS containing only N, were produced. The resistance to pitting corrosion of the DSSs was assessed, and the role of C-substitution in the corrosion properties was discussed in terms of the repassivation tendency and pit growth rate.

2. Materials and Methods

In the present study, Fe-22Cr-5Ni-3Mo-1Mn-based (in wt%, type UNS S32205) DSSs containing different N and C contents were investigated. The detailed chemical compositions of the DSSs denoted as DSS-N and DSS-NC are given in Table 1.

Table 1. Chemical compositions (in wt%) of the investigated DSSs.

Alloy	Fe	Cr	Ni	Mo	Mn	N	C	S	P
DSS-N	Balanced	22.48	5.17	3.10	1.46	0.24	0.002	0.005	0.005
DSS-NC		22.43	5.18	3.14	1.46	0.13	0.090	0.006	0.004

The DSS ingots of 30 kg were produced by vacuum induction melting in Ar. Then they were homogenized at 1250 °C for 2 h in Ar gas and hot-rolled, followed by water quenching. The hot-rolled plates with a thickness of 2 mm of the DSS-N and DSS-NC were solution treated at 1150 °C and 1130 °C for 1 h, respectively, in order to obtain $\alpha + \gamma$ matrix without precipitates and to control the phase fraction ($\alpha:\gamma$) to be 1:1. The temperatures for the solution treatments were determined based on the equilibrium phase fraction versus temperature diagram (Figure 1), which was calculated using Thermo-Calc software (version 2017b, database TCFE 7.0, Stockholm, Sweden).

Microstructures of the DSSs were examined using light optical microscopy (LOM, Epiphot, Nikon, Minato, Japan), scanning electron microscopy (SEM, IT-300, JEOL, Akishima, Japan), and electron backscatter diffraction (EBSD, HKL Nordlys Channel 5, Oxford Instruments, Abingdon, UK) in a SEM (JSM-7001F, JEOL, Akishima, Japan). For the LOM and SEM analyses, the specimens (10 mm $\times$ 10 mm $\times$ 2 mm) were mechanically polished using suspension containing 1 μm -sized diamond particles. The polished specimens were chemically etched in a mixed acid solution (20 mL HNO_3 + 30 mL HCl + 50 mL deionized water) for 1–3 min [33,35,37,38], which allowed us to measure the phase fractions ($\alpha:\gamma$) of the specimens. Then we electrochemically etched in a 40% HNO_3 solution by applying 4.5 V for 20–30 s [39,40] in order to identify the grain boundaries. Based on the SEM images taken at 5 different locations, the phase fractions ($\alpha:\gamma$ in vol%) of the DSSs were measured by image analysis. For the EBSD analysis, the specimens were polished using colloidal silica with a particle size of 0.02 μm . The EBSD analysis was performed on a scanning area 120 $\times$ 100 μm . with a step size of 0.5 μm , and the grain boundaries were identified with the critical misorientation angle of 10°. Alloying element partitioning in the DSSs was examined by an energy dispersive X-ray spectroscopy

(EDS) equipped on the SEM, and the chemical compositions were quantitatively examined through electron probe micro analysis (EPMA, SX100, CAMECA, Gennevilliers, France).

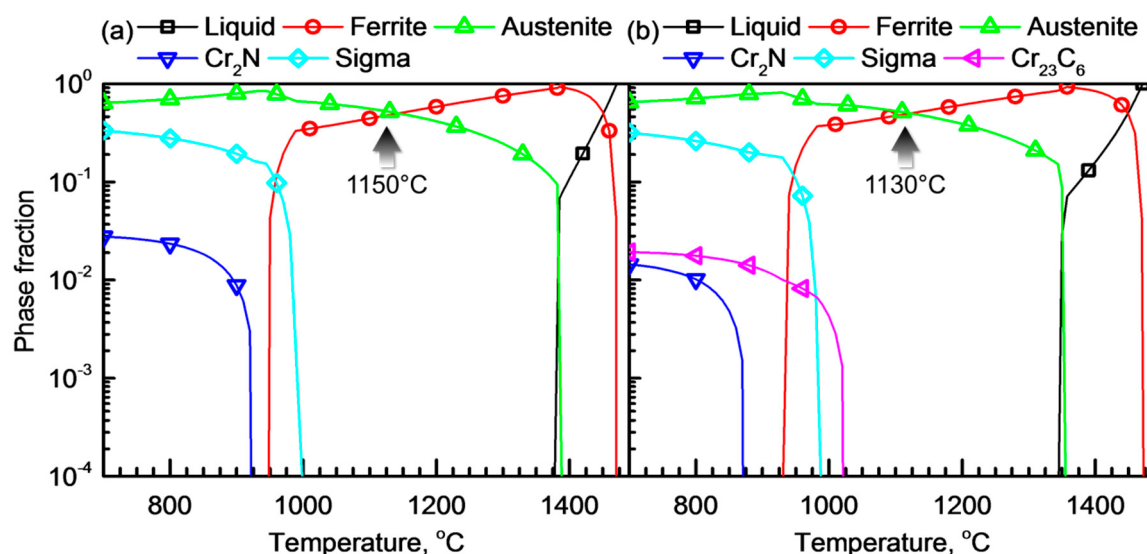


Figure 1. Equilibrium phase fractions of the (a) duplex stainless steel containing N only (DSS-N) and (b) duplex stainless steel containing N and C (DSS-NC) as functions of temperature, calculated using Thermo-Calc software (version 2017b, database TCFE 7.0).

Pitting corrosion resistance and repassivation tendencies of the DSSs were assessed through linear and cyclic potentiodynamic polarization tests in NaCl solutions. The polarization tests were performed in a multi-neck glass cell consisting of a saturated calomel reference electrode (SCE), a Pt plate counter electrode, and a specimen serving as a working electrode. The specimens were mounted in cold epoxy resin and ground using SiC emery paper of up to 2000 grit. The exposed area for the polarization test was controlled to be 0.2 cm² using electroplating tape. The tests were performed with a potentiostat (Reference600+, GAMRY, Warminster, PA, USA). Linear polarization tests were conducted in a 5 M NaCl solution at 50 °C with a potential sweep rate of 2 mV s⁻¹. For the cyclic polarization tests, a 2 M NaCl solution at 50 °C was used, and the potential was elevated from −0.05 V versus corrosion potential (E_{corr}) to the potential value where the current density exceeded 0.15 mA cm⁻², and was then lowered to the repassivation potential (E_{rp}) with a potential sweep rate of 2 mV s⁻¹. Repetitive polarization tests were done at least 5 times, confirming the reproducibility. In addition, immersion tests were employed in order to assess the resistance to pitting corrosion of the DSSs. For the tests, the specimens (30 mm × 30 mm × 2 mm) were mechanically ground using 600 grit SiC paper, and they were immersed in a 6% FeCl₃ + 1% HCl solution at 50 °C for 12 h. Before and after the immersion test, the weight of specimen was measured in order to calculate the weight loss during the tests. Three specimens for each DSS were tested and the average weight loss ratio (weight loss/original weight × 100, %) was calculated.

The sites for the pitting corrosion were observed using the SEM after immersion in a 0.2 M HCl solution (pH 0.62) at 25 °C under the open circuit condition for 4 h. The strong acid containing Cl⁻ was used for the immersion test in order to simultaneously identify the phase boundary and the pit sites.

Uniform (or general) corrosion behavior of the DSSs was examined through linear polarization tests in the 0.2 M HCl solution (pH 0.62) at 25 °C with a potential sweep rate of 2 mV s⁻¹. In addition, galvanic corrosion rate between the α and γ phases in the DSSs were quantified by measuring the corrosion depth of the α phase as compared by the γ phase. The DSS specimens were polished using a suspension with 1 μm -sized diamond particles, and then the specimens were immersed in the 0.2 M HCl solution (pH 0.62). After the 40 min of immersion, the three-dimensional corroded

morphology and the corrosion depth was investigated using a surface optical profiler (Wyko NT8000, Veeco, Plainview, NY, USA). The corrosion test conditions employed in this study are listed in Table 2.

Table 2. Experimental conditions for the corrosion tests.

Purpose		Experiment	Test Condition
Evaluation of resistance to pitting corrosion	Measurement of E_{pit}	Linear potentiodynamic polarization test	Solution: 5 M NaCl (50 °C) Potential sweep rate: 2 mV s ⁻¹
	Measurements of E_{pit} and E_{rp}	Cyclic potentiodynamic polarization test	Solution: 2 M NaCl (50 °C) Potential sweep rate: 2 mV s ⁻¹
	Measurement of weight loss	Immersion test	solution: 6% FeCl ₃ + 1% HCl (50 °C) Immersion time: 12 h
	Observation of pit initiation sites	Immersion test	Solution: 0.2 M HCl (25 °C) Immersion time: 4 h
Evaluation of resistance to uniform corrosion	Measurement of E_{corr} , i_{corr} , and i_{crit}	Linear potentiodynamic polarization test	Solution: 0.2 M HCl (25 °C) Potential sweep rate: 2 mV s ⁻¹
	Evaluation of galvanic corrosion rate	Immersion test	Solution: 0.2 M HCl (25 °C) Immersion time: 40 min

3. Results

3.1. Microstructure

Figure 1a,b shows the equilibrium phase fraction versus temperature plots of the DSS-N and DSS-NC, respectively. Figure 1a informs that precipitates including sigma (σ) phase and Cr₂N can be formed in the DSS-N below 1000 °C, and Figure 1b indicates that, in addition to the σ and Cr₂N, Cr₂₃C₆ can be formed below 1020 °C in the DSS-NC. Based on Figure 1, the temperatures for solution treatments were determined as 1150 °C for the DSS-N and 1130 °C for the DSS-NC.

Figure 2a,b shows the microstructures of the DSS-N and DSS-NC, respectively. LOM images (Figure 2a-1,b-1) and SEM images (Figure 2a-2,b-2) show that the two DSSs have typical dual-phase microstructures, and non-metallic inclusions are rarely observed in both DSSs. The high-resolution SEM images (Figure 2a-3,b-3) show that the precipitates, including Cr₂₃C₆, Cr₂N, and σ are not formed. Elemental distribution maps in Figure 3 indicate that Ni being a γ -stabilizer, it is enriched in the relatively bright phase, whereas Cr and Mo being α -stabilizers are concentrated in the dark phase. Therefore, the relatively bright phase in the SEM image was found to be the γ and the matrix phase was the α . The image analyses on the SEM micrographs revealed that the two DSSs had the mostly same α volume fractions; specifically, those of the DSS-N and DSS-NC were 51.5 ± 3.2 and 52.6 ± 2.2 vol%, respectively. The grain boundaries were identified in the electrochemically etched specimens in a HNO₃ solution by applying 4.5 V (Figure 2a-4,b-4). Image analysis on the Figure 2a-4,b-4 showed that the two DSSs were similar in grain size with a diameter of 7.5–8.5 μm . The EBSD analysis gave more precise analysis results. Figure 4 shows the phase maps measured through EBSD analysis, in which the green phase is the α phase and the red phase with annealing twin is the γ phase. For the DSS-N and DSS-NC, the average grain sizes of the α phases were 7.71 and 6.97 μm , respectively, and those of the γ phases were 8.05 and 8.20 μm , respectively.

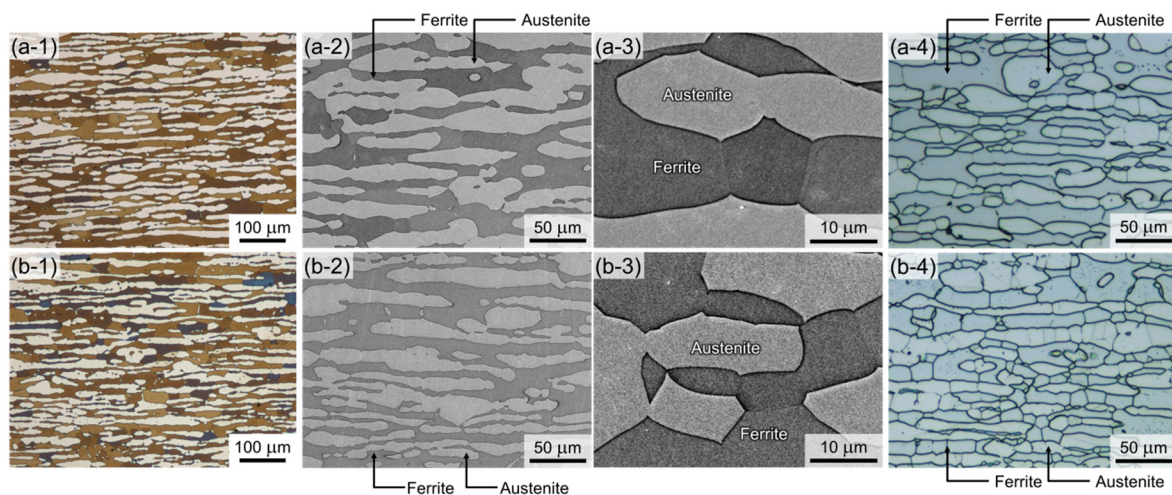


Figure 2. Microstructures of the (a) DSS-N and (b) DSS-NC: (a-1,b-1) Light optical micrographs and SEM micrographs taken at (a-2,b-2) low and (a-3,b-3) high magnifications of the specimens etched in a mixed acid solution (20 ml HNO_3 + 30 ml HCl + 50 ml deionized water). (a-4,b-4) Light optical micrographs of the specimens etched in a 40% HNO_3 solution by applying 4.5 V.

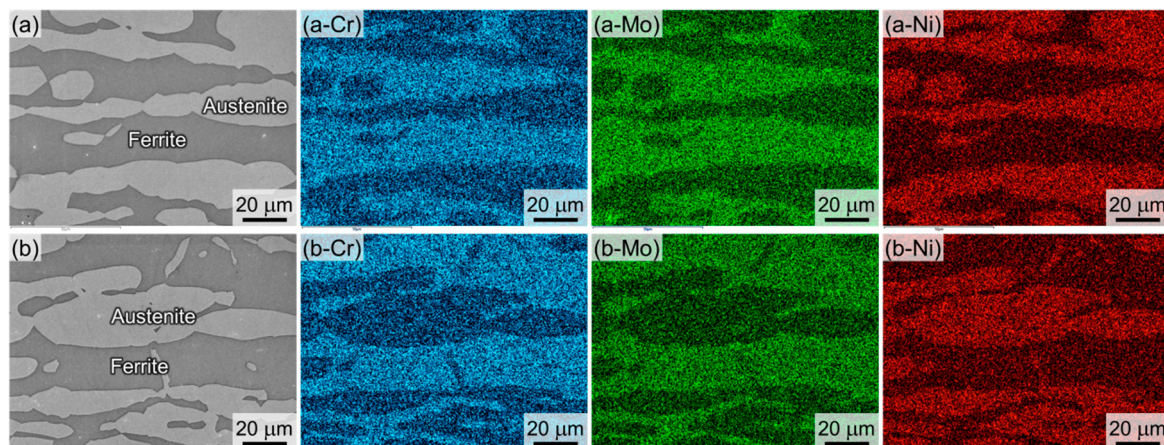


Figure 3. SEM micrographs of the (a) DSS-N and (b) DSS-NC with EDS maps (Cr, Mo, and Ni).

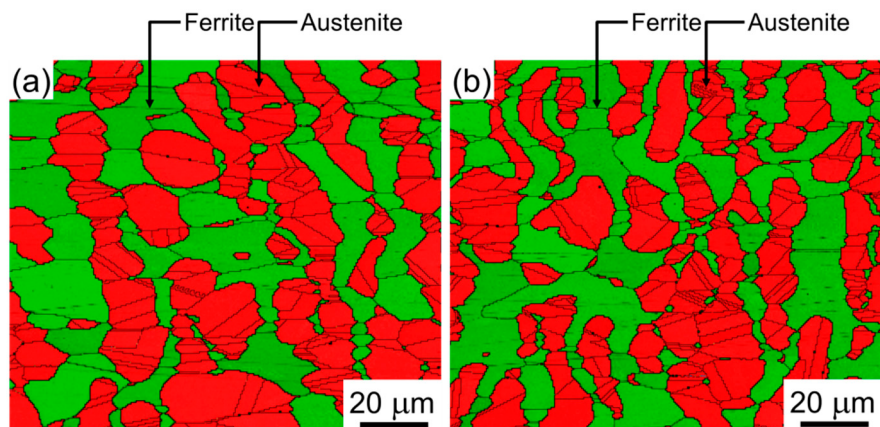


Figure 4. Electron backscatter diffraction (EBSD) phase maps of the (a) DSS-N and (b) DSS-NC. The grain boundaries were identified with the critical misorientation angle of $>10^\circ$. (red: Face-centered cubic (γ) and green: Body centered cubic (α)).

3.2. Partitioning of Alloying Elements

Individual chemical compositions of the α and γ phases of the DSSs were measured using the EPMA and they were indicated in (Figure 5). The α phases of both DSSs contained only 0.05 wt% N (Figure 5a), which was the solubility limit of N in the α phase [38,41–43]. Most of the alloyed N was concentrated in the γ phase, whose concentration was 0.40 wt% for the DSS-N and 0.26 wt% for the DSS-NC (Figure 5a). Ni contents of the γ phases of the two DSSs were 6.44–6.53 wt%, and those of the α phases were 4.14–4.16 wt% (Figure 5b). The γ -stabilizing elements, i.e., N and Ni, were enriched in the γ phases. However, the α -stabilizing elements, i.e., Mo and Cr, were concentrated in the α phase. The two DSSs contained 3.71–3.77 wt% Mo in the α phases and they had approximately 2.3 wt% Mo in the γ phases (Figure 5c). The Cr contents of the α phases were 23.81 wt% for the DSS-N and 24.07 wt% for the DSS-NC, and those of the γ phases were 21.00 wt% for the DSS-N and 20.74 wt% for the DSS-NC. Figure 5b,c indicates that the partitioning of Ni and Mo was not significantly affected by the C-substitution for N in the DSSs. In contrast, the C-substitution for N notably affected Cr partitioning in the DSSs (Figure 5d). Regarding C contents (Figure 5e), C partitioning of the DSSs was estimated through thermodynamic calculation using Thermo-Calc. Since the DSS-N contained only 0.002 wt% C, the C partitioning could be negligible. However, for the DSS-NC, the C contents calculated in the α and γ phases were significantly different: 0.031 wt% and 0.153 wt%, respectively.

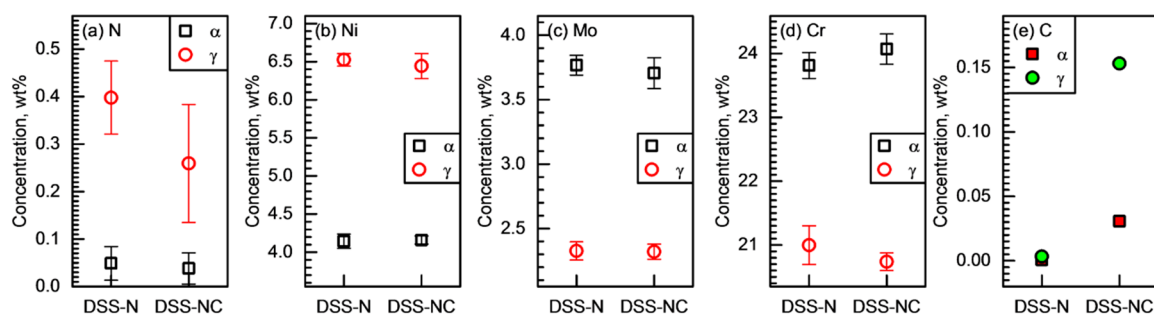


Figure 5. Chemical compositions of (a) N, (b) Ni, (c) Mo, and (d) Cr of the α and γ phases in the DSS-N and DSS-NC measured using the EPMA. For each phase of each DSS, 10 points were analyzed using an EPMA, and the averages and the standard deviation values (scatter band) were calculated. (e) C contents of the α and γ phases of the DSSs calculated by Thermo-Calc software.

3.3. Resistance to Pitting Corrosion

The resistance to pitting corrosion of the DSSs was assessed by linear potentiodynamic polarization tests in a 5 M NaCl solution at 50 °C, and the polarization curves were presented in Figure 6a. In this environment, both DSSs exhibited passive behavior at the E_{corr} of $-0.33 V_{\text{SCE}}$, and as the applied potential increased, stable pitting corrosion occurred in both DSSs at certain potentials. The pitting potential (E_{pit}) of the DSS-N was $0.06 V_{\text{SCE}}$, and that for the DSS-NC was $0.15 V_{\text{SCE}}$ (Figure 6b and Table 3). From the repetitive polarization tests in the 5 M NaCl solution, the average E_{corr} , E_{pit} and passive current density (i_{passive}) were measured as given in Table 3.

The E_{pit} and E_{rp} were measured through cyclic potentiodynamic polarization tests in a 2 M NaCl solution at 50 °C (Figure 7a). A more dilute NaCl solution compared with that for the linear polarization test (Figure 6) was used in order to extend the passive potential range for the measurement of E_{rp} . Additionally, in this solution, both DSSs exhibited passivity from E_{corr} to E_{pit} . The E_{pit} of the DSS-NC was $0.21 V_{\text{SCE}}$ and that of the DSS-N was $0.16 V_{\text{SCE}}$, which also confirmed that the DSS-NC exhibited a higher E_{pit} than the DSS-N. It is noted that the E_{rp} of the DSS-NC was also higher than that of the DSS-N: The E_{rp} of the DSS-NC was $0.05 V_{\text{SCE}}$ and that of the DSS-N was approximately $0 V_{\text{SCE}}$ (Figure 7b and Table 3). In Table 3, the average E_{corr} , E_{pit} , E_{rp} , and i_{passive} obtained from the cyclic polarization curves in a 2 M NaCl solution at 50 °C were summarized.

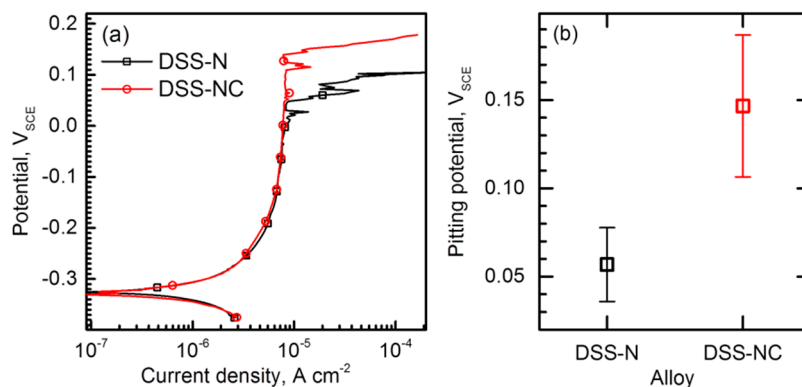


Figure 6. Resistance to pitting corrosion of the DSSs: (a) Linear potentiodynamic polarization curves of the DSSs measured in a 5 M NaCl solution at 50 °C with a potential sweep rate of 2 mV s $^{-1}$ and (b) the average and standard deviation values (scatter band) of the pitting potentials obtained from 5 repeated polarization tests.

Table 3. The corrosion characteristics of the DSS-N and DSS-NC measured through polarization tests in 5 M NaCl (Figure 6) and 2 M NaCl solutions (Figure 7) at 50 °C.

Test Condition	5 M NaCl at 50 °C			2 M NaCl at 50 °C			
Alloy	E_{corr} , V $_{SCE}$	E_{pit} , V $_{SCE}$	$i_{passive}$ at -0.1 V $_{SCE}$, μ A cm $^{-2}$	E_{corr} , V $_{SCE}$	E_{pit} , V $_{SCE}$	E_{rp} , V $_{SCE}$	$i_{passive}$ at -0.1 V $_{SCE}$, μ A cm $^{-2}$
DSS-N	−0.326	0.057	6.997	−0.192	0.164	0.001	2.696
DSS-NC	−0.324	0.147	6.875	−0.189	0.211	0.048	2.471

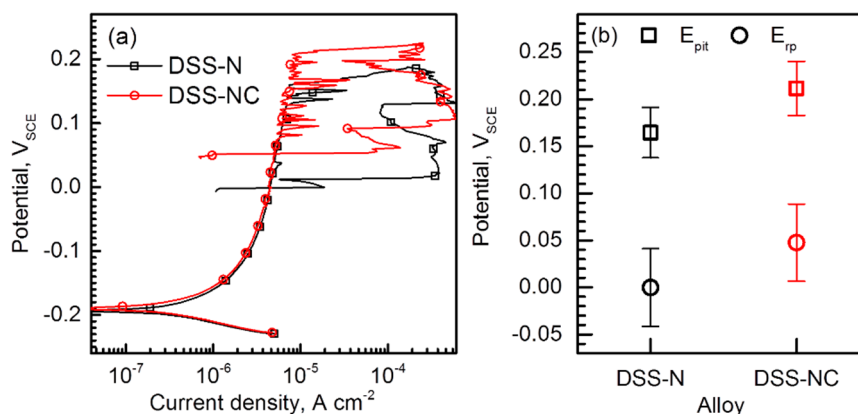


Figure 7. Resistance to pitting corrosion and repassivation behavior of the DSSs: (a) Cyclic potentiodynamic polarization curves of the DSSs measured in a 2 M NaCl solution at 50 °C with a potential sweep rate of 2 mV s $^{-1}$ and (b) the average and standard deviation values (scatter band) of the pitting and repassivation potentials (E_{pit} and E_{rp} , respectively) obtained from five repeated polarization tests.

The polarization tests in the concentrated NaCl solutions indicated that the DSS-NC exhibited better resistance to localized corrosion than the DSS-N. Twelve hours of immersion tests in 6% FeCl $_3$ + 1% HCl solution at 50 °C confirmed the finding. Figure 8 shows the corrosion morphologies of the DSSs after the immersion tests. Multiple pits are shown in the DSS-N (Figure 8a), while only one or two pits are observed in the DSS-NC (Figure 8b). The average weight loss ratio of the DSS-N was $3.46 \pm 0.50\%$, and that of the DSS-NC was $1.93 \pm 0.42\%$.

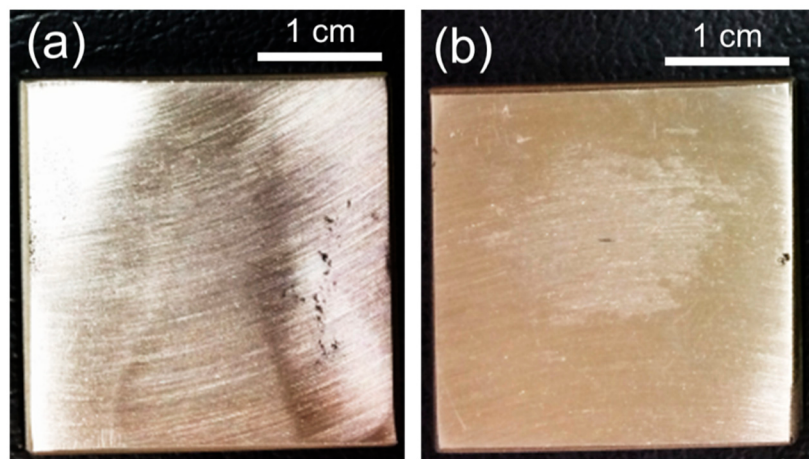


Figure 8. Corrosion morphologies of (a) DSS-N and (b) DSS-NC after immersion in 6% FeCl_3 + 1% HCl solution at 50 °C for 12 h.

The sites for the pitting corrosion were examined. After immersion in the 0.2 M HCl solution, it was possible to simultaneously identify the pit initiation sites with the phase boundaries. Figure 9a,b exhibits the pit morphologies of the DSS-N and DSS-NC, respectively. After 4 h of immersion, the stable pits with a size of several μm were observed at the α side of the phase boundary for both DSSs.

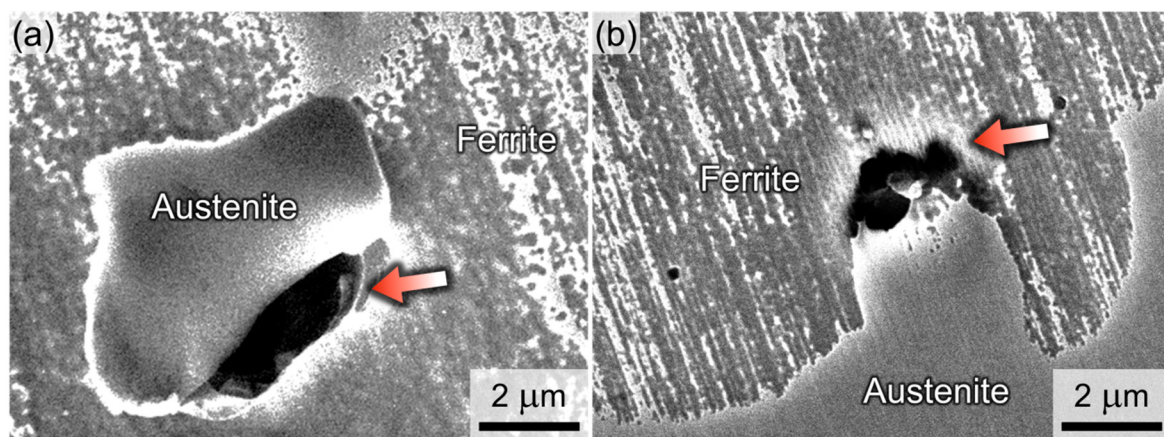


Figure 9. Pit morphologies of (a) DSS-N and (b) DSS-NC after immersion in a 0.2M HCl solution at 25 °C for 4 h.

3.4. Resistance to Uniform Corrosion

The resistances to uniform corrosion of the two DSSs were evaluated by measuring the E_{corr} and the dissolution rates from the linear polarization tests performed in a 0.2 M HCl solution (Figure 10a). Once the pit is initiated by the passive film breakdown, the electrolyte confined inside the pit cavity becomes acidified because of the hydrolysis reaction of metal ion [44,45]. Thus the evaluation of the uniform corrosion behavior in the acidified chloride solution can provide important information about the pit growth reaction inside the pit. In this acid solution, both DSSs exhibited typical active–passive transition behavior in the potential range from the E_{corr} to approximately $-0.15 \text{ V}_{\text{SCE}}$, and passive behavior was observed within the potential range from $-0.15 \text{ V}_{\text{SCE}}$ to $0.80 \text{ V}_{\text{SCE}}$. Although passive behavior of both DSSs was similar to each other, the differences were distinguishable in the active–passive transition behavior. Figure 10b enlarged the active–passive transition curves. E_{corr} of the DSS-N was $-0.41 \text{ V}_{\text{SCE}}$ and that of the DSS-NC was $-0.38 \text{ V}_{\text{SCE}}$. The difference in the E_{corr} values was small but it was consistently observed in the repetitive polarization tests. Moreover, the corrosion rate (i_{corr}) and critical anodic current density (i_{crit}) of the DSSs were obviously reduced

by substitution of C for N. As shown in Figure 10c and Table 4, the average i_{corr} of the DSS-N was $117.3 \mu\text{A cm}^{-2}$ and it decreased to $61.4 \mu\text{A cm}^{-2}$ for the DSS-NC. Moreover, the i_{crit} of the DSS-N was $158.3 \mu\text{A cm}^{-2}$ (at $-0.29 \text{ V}_{\text{SCE}}$), and that of the DSS-NC also decreased to $104.9 \mu\text{A cm}^{-2}$ (at $-0.26 \text{ V}_{\text{SCE}}$). The corrosion characteristics, including E_{corr} , i_{corr} , polarization resistance, corrosion rate (milli-inches per year, MPY), and i_{crit} which were obtained from Figure 10 are given in Table 4. The MPY was calculated in accordance with the following equation; $\text{MPY} = 0.13 \times i_{\text{corr}} (\mu\text{A cm}^{-2}) \times \text{equivalent weight (g)}/\text{density (g cm}^{-3}\text{)}$.

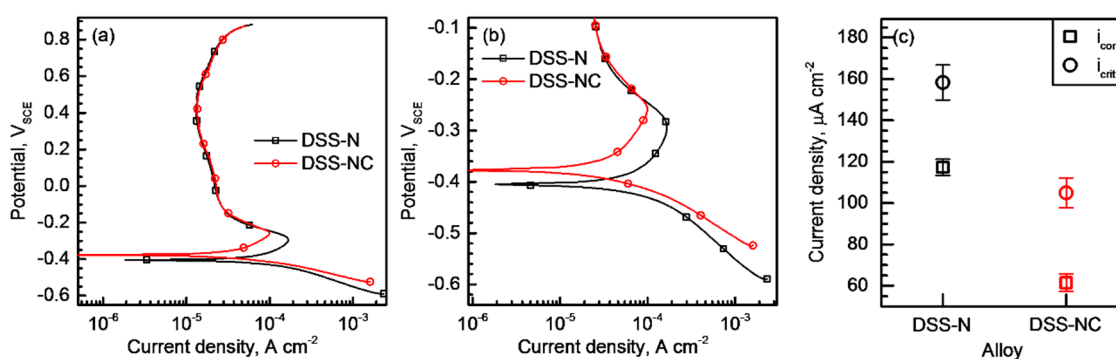


Figure 10. Resistance to general corrosion of the DSSs: (a) Linear potentiodynamic polarization curves of the DSS-N and DSS-NC measured in a 0.2 M HCl solution at 25 °C with a potential sweep rate of 2 mV s^{-1} , and (b) the enlarged polarization curves showing active–passive transition behavior. (c) The average and standard deviation values (scatter band) of the corrosion rate (i_{corr}) and critical anodic current density (i_{crit}), which were obtained from five repeated polarization tests.

Table 4. The corrosion characteristics of the DSS-N and DSS-NC measured through polarization tests in a 0.2 M HCl at 25 °C (Figure 10).

Alloy	$E_{\text{corr}}, \text{V}_{\text{SCE}}$	$i_{\text{corr}}, \mu\text{A cm}^{-2}$	Polarization Resistance, Ohm cm^{-2}	Corrosion Rate, Milli-Inches per Year	$i_{\text{crit}}, \mu\text{A cm}^{-2}$
DSS-N	−0.405	117.29	355.35	54.18	158.32
DSS-NC	−0.377	61.44	517.25	28.38	104.94

3.5. Galvanic Corrosion Between the Two Constituent Phases

The dissolution rate of the dual-phase matrix is related to the galvanic corrosion rate between the two constituent phases. Thus, for the DSSs, the galvanic corrosion rate was quantified by measuring the corrosion depth between the α and γ phases [38,43,46]. The polished DSS specimens were immersed in the 0.2 M HCl solution and the corrosion surface was examined using a surface profiler. Figure 11a,b shows three-dimensional images of the corroded surfaces of the DSS-N and DSS-NC, respectively. A towering structure composed of the α (bluish color) and γ (golden-red color) phases was observed, showing that the α and γ phases exhibited different corrosion rates in the strong acid. In both DSSs, the more corroded phase was the α , suggesting that the α phase was more active than the γ phase. Therefore, the dissolution depth of the active phase (i.e., α phase), as compared to that of the noble phase (i.e., γ phase), can be correlated with the galvanic corrosion rate of the dual-phase matrix. Analysis on the contour maps revealed that the corrosion depth for the DSS-N was $0.131 \mu\text{m}$ and that for the DSS-NC was $0.114 \mu\text{m}$ (Figure 11c).

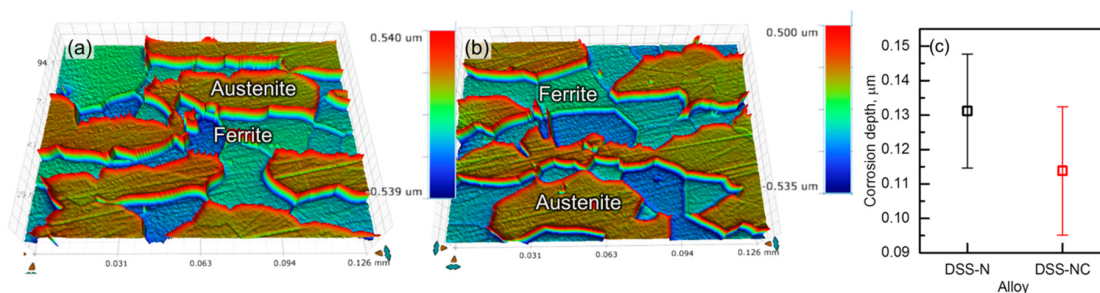


Figure 11. Three-dimensional images of the corroded surfaces of the (a) DSS-N and (b) DSS-NC. The images were obtained after immersion in a 0.2 M HCl solution at 25 °C for 40 min. (c) Variation in the corrosion depth of the two DSSs.

4. Discussion

This study examined the microstructure and alloying element partitioning for the DSS-N and DSS-NC. Then for the two DSSs, the E_{pit} and E_{rp} were measured through polarization tests in 2–5 M NaCl solutions. Weight loss ratio was obtained from immersion tests in a 6% FeCl_3 + 1% HCl solution, and the E_{corr} , i_{corr} , and i_{crit} were measured by the polarization tests in a 0.2 M HCl solution. In addition, the galvanic corrosion rate was quantified by measuring the corrosion depth between the two constituent phases after immersion in the HCl solution.

The two DSSs had dual-phase microstructures without non-metallic inclusions and precipitates, as indicated in Figures 2–4. In addition, the two DSSs possessed similar grain sizes and phase fractions. The investigation on the alloying element partitioning (Figure 5) indicated that C-substitution brought a slight deviation in the Cr-partitioning in the DSS, and the γ of DSS-NC contained N with meaningful amount of C (0.26N-0.15C wt%), while that of the DSS-N had N only (0.40 wt%). Thus, it could be concluded that the only variable to determine the corrosion behavior was chemical compositions of the constituent phases.

The pitting corrosion resistance of the DSSs was quantified by E_{pit} and E_{rp} obtained from the polarization tests in 2–5 M NaCl solutions at 50 °C. The solutions with Cl^- concentrations higher than 2 M were required for these tests, in order to provoke the stable pitting corrosion in the investigated alloys. Higher E_{pit} indicates higher resistance to the stable pit initiation, and higher E_{rp} means greater tendency for the pit extinction (i.e., repassivation) [47,48]. Figures 6 and 7 revealed that the DSS-NC exhibited higher E_{pit} and E_{rp} than the DSS-N. In addition, the immersion tests (Figure 8) also indicated that the DSS-NC was more resistant against pitting corrosion than the DSS-N. Therefore, it was concluded that the DSS-NC possessed higher resistance to stable pitting corrosion and repassivation tendency than the DSS-N.

The sites for pitting corrosion were observed (Figure 9) and it was found that the pits grew to the less corrosion resistant phase (i.e., α phase). The bare surface of the matrix in the pit cavity is exposed to the acidified solution that is locally confined within the occluded pit, and hence uniform corrosion takes place upon the matrix. For this reason, the uniform corrosion rate of the matrix is directly correlated with the pit growth rate. Slower growth of the pit embryo implies less probability of stable pit formation and higher tendency for pit extinction. In the case of dual-phase matrix, the uniform corrosion occurred in the form of galvanic corrosion, as supported by the pit propagating behavior shown in Figure 9. Therefore, it was concluded that the galvanic corrosion rate of the DSS matrix was associated to the pit growth rates of the two DSSs.

From the polarization (Figure 10) and the immersion tests (Figure 11) in the 0.2 M HCl solution, quantitative information about the galvanic corrosion rates of the matrices of the two DSSs was obtained. The strong acid with Cl^- was required for these tests to simulate the locally confined solution inside the pit cavity. As shown in Figure 10, rise in the E_{corr} and decreases in the i_{corr} and i_{crit} were observed in the DSS-NC in comparison with those of the DSS-N. This observation firstly indicated that the C-substitution for part of N made the DSS matrix noble. Furthermore, the i_{corr} of the

DSS-NC ($61.4 \mu\text{A cm}^{-2}$) was only half of that of the DSS-N ($117.3 \mu\text{A cm}^{-2}$), which implied that the C-substitution lowered pit growth rate.

Uniform dissolution of the dual-phase matrix inside the pit cavity occurred in the form of galvanic corrosion between the two constituent phases, as shown in Figure 11. In the DSSs, the less noble phase was the α , and the dissolution rate of the α relative to the γ of the DSS-NC was lower than that of the DSS-N (Figure 11c). Therefore, it was concluded that the DSS-NC exhibited lower galvanic corrosion rate than the DSS-N, and hence the growth rate of the pit embryo was lowered in the DSS-NC, which consequently shifted the potentials for the stable pit initiation (i.e., E_{pit}) and the pit extinction (i.e., E_{rp}) to the higher values.

The observations in Figure 11 implied that the difference in the E_{corr} values of two constituent phases was reduced in the DSS-NC in comparison with the DSS-N. The difference in the nobility between the α and γ was caused by the element partitioning (Figure 5). It was noted that the C-substitution particularly changed the N, C, and Cr partitioning in comparison with the DSS-N, which resulted in decrease in the galvanic corrosion rate between the two constituent phases. In order to understand the difference in the galvanic corrosion rate between the two DSSs, estimating the respective E_{corr} values of the α and γ phases for each DSS from the alloying element combination needs to be done. For this, the abilities of alloying elements, including N and C, to change the nobility of the SS matrix should be separately quantified. Further work on this topic is now underway, and if the roles of the various alloying elements for SSs in making matrix noble are quantitatively established, it would be helpful to design new DSSs with well-balanced nobility between the two constituent phases, leading to high corrosion resistance.

5. Conclusions

The effects of C-substitution for part of N on the pitting corrosion resistance and repassivation behavior of type UNS S32205 DSS (Fe-22Cr-5Ni-3Mo-1Mn-based DSS, in wt%) were investigated. For this investigation, normal UNS S32205 DSS containing N only (DSS-N) and the C-substituted DSS (DSS-NC) was fabricated. The followings summarize the findings of this study.

- (1) The microstructural analyses revealed that the two DSSs after solution treatments had dual-phase microstructures without non-metallic inclusions and precipitates. They had similar initial microstructure, such as grain sizes and phase fractions. Cr partitioning was promoted by C-substitution for N in the DSS, and the γ phase of DSS-NC contained N with a meaningful amount of C (0.26N-0.15C wt%) while that of the DSS-N had N only (0.40 wt%).
- (2) Polarization tests performed in 2–5 M NaCl solutions and immersion tests in a 6% FeCl_3 + 1% HCl solution revealed that the DSS-NC possessed higher resistance to stable pitting corrosion and repassivation tendency than the DSS-N. Furthermore, the corrosion pits initiated and propagated to less a corrosion resistant phase (i.e., α phase).
- (3) Polarization tests and corrosion depth measurements conducted in a HCl solution indicated that the DSS-NC exhibited a lower galvanic corrosion rate between the α and γ phases than the DSS-N. Therefore, the growth rate of pit embryo was lowered in the DSS-NC, which shifted the potentials for the stable pit initiation and the pit extinction to the higher values.

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