On the stress corrosion cracking of lean duplex steel in chloride environment

Qanita Tayyaba1, Hina Farooq1, Muhammad Shahid1, Ammer Khan Jadoon2, M Shahzad3 and AH Qureshi3
1School of Chemical and Materials Engineering, National University of Sciences and Technology, Islamabad, Pakistan
2British Petroleum Ltd, UK
3Materials Division, ATCOP, Islamabad, Pakistan
E-mail: mshahid@scme.nust.edu.pk

Abstract. duplex stainless steel having attractive combination of austenitic and ferritic properties is being used in industry such as petrochemical, pulp and paper mills. In this study, the corrosion and stress corrosion behavior of duplex stainless steel in 3.5% sodium chloride environment was investigated by weight loss measurements, electrochemical DC testing and slow strain rate test (SSRT). Weight loss data showed no significant corrosion after 1700 hours. Electrochemical polarization test in 3.5% NaCl solution exhibited a uniform corrosion rate of 0.008 mpy (calculated using Tafel analysis) showing passivity in the range of 735–950 mV. A comparison of the slow strain rate test in 3.5% NaCl solution with air shows almost a similar stress strain curve for duplex stainless steel. In comparison, the stress strain curves for 0.15% carbon steel show a loss of about 25% tensile elongation for the same comparison. The excellent corrosion and especially resistance to localized corrosion (pitting) is responsible for no loss of ductility in duplex stainless steel.

1. Introduction
Duplex stainless steels have vast applications in chemical industries, power plants and marine owing to their excellent mechanical properties and high corrosion resistance [1]. These steels consist of a ferrite/austenite volume ratio of about 1:1 placing them amongst good materials against aqueous corrosion along with high strength. However, existence of undesirable phases e.g. intermetallics, nitrides and carbides in the steels profoundly influence on these properties unless controlled during the manufacturing processes [2]. ‘σ’ phase with relatively rapid kinetics for formation is considered to be of particular importance causing a drastic decrease in toughness and corrosion resistance [3].

Nilsson and Wilson [4] investigated the influence of isothermal heat treatment of super duplex stainless steel on toughness and pitting corrosion resistance. They found it to be directly related to the existence of ‘α’ phase due to longer time–temperature regime. Secondary austenite was found to be present at the ferrite/austenite phase boundaries, which can be as detrimental to pitting corrosion as ‘α’ phase.

Pitting resistance of 25% Cr duplex UNS S32550 was investigated as a result of annealing temperature, by Garfias-Mesias et al [5]. Lower annealing temperatures were observed to be favourable to attain higher pitting potentials. Ferrite phase was found to be easy sites for pitting.
Pohl et al [6] studied the effect of intermetallics on corrosion properties of DSS. They had the opinion that the intermetallic precipitations influenced mechanical properties and the corrosive properties rather extensively. Rapid reduction of the toughness of the steel was observed due to precipitation of brittle phases the resultant tertiary austenite makes the alloy prone to corrosion. Sherif [7] studied the corrosion of DSS Alloy 2209 in acidic and neutral chloride solutions and its passivation by ruthenium as an alloying element and found that ruthenium increases its passivity against corrosion. Effect of annealing temperature on pitting corrosion resistance of DSS was investigated by Tan et al [8]. They found that variation in annealing temperature changes the amount of alloying elements in the ferrite and austenite phases and correspondingly affect the critical pitting temperature. In the present investigation, SCC behaviour of DSS has been explored in 3.5% NaCl solution and in air.

2. Experimental

2.1 Metallography and Characterization.
Microstructural characterisation was performed using optical microscope with associated image analysis equipment. This system was used to determine the phase percentages of ferrite and austenite in the duplex stainless carbon steel structures. The material surface was etched using a solution containing 200ml HCl, 200ml water, 200ml HNO₃ and 0.6g Sparbeize (pickling inhibitor) at 40°C to reveal the microstructure of the material. The etching was performed after mechanical grinding with silicon carbide papers (300-1200 grit size), and polished using 6 microns and 1 micron diamond pastes.

2.2 Mechanical Testing.
Hardness was performed using Vicker hardness tester. The minor load of 10kgf and major load of 150kgf (1470N) was applied on specimen surface for a dwell time of 5s. Micro-hardness was performed by a Vickers hardness tester with the load of 1000 gf with a dwell time of 10 seconds using diamond indenter in order to measure the hardness of austenite and ferrite phase. Tensile specimens having gauge diameter 2.5mm and gauge length 11.5 mm were tested under tensile load at strain rate of 0.69mm/min. The load displacement data from the machine was used to plot the stress strain curve for each tested samples.

2.3. General corrosion and pitting corrosion.

2.3.1. Immersion Test.
The 10.0 mm x 8.2 mm x 9.2 mm size and weight of 5.017 grams DSS was first cleaned and polished. A 3.5% NaCl solution (electrolyte) was prepared by taking 7g of NaCl in 200ml of distilled water and was stirred using electronic stirrer. pH of the solution after adding salt was 6.5. Sample of DSS was immersed in this electrolyte. After immersion for a specified time the sample was taken out, washed and cleaned, followed by weighing to determine the weight loss.
The corrosion rate was calculated as: [9]

\[
\text{Corrosion rate (mpy)} = \frac{534W}{DAT}
\]

Where
\[
W = \text{weight loss of the metal} \\
D = \text{density of the metal (in g/cm}^3\text{)} \\
A = \text{surface area of the metal exposed (in}^2\text{)} \\
T = \text{time in hours}
\]

2.3.2 Electrochemical Corrosion Test. Electrochemical studies were conducted using DC corrosion testing technique, in a 3-electrode electrochemical cell; a silver/silver chloride reference electrode in saturated potassium chloride (KCl), and a working electrode. The potentiodynamic polarization response of the DSS was recorded in 3.5% NaCl solution. Tafel Plots were determined at a scan rate of 1 mVs⁻¹ starting from -0.30V to +0.60V with respect to open-circuit potential.
2.3.3 Slow Strain Rate Test. Stress corrosion cracking behaviour of DSS samples was conducted by slow strain rate test (SSRT). The gauge length of each tensile specimen was polished to 1000 grit paper finish and cleaned with acetone before using them for SSRT. These specimens were then uni-axially loaded in a modified slow strain rate testing machine with autoclave in an environment containing 3.5% NaCl solution at room temperature and at atmospheric pressure. The specimens were then subjected to an initial strain rate of $1 \times 10^{-6}$s$^{-1}$ and loaded until fracture occurred. Samples were electrically isolated from the test rig by making use of ceramic washers. Stress-strain curves were obtained from each test. Fractured surfaces were examined in SEM to examine the mode of fracture while EDS helped to obtain chemical composition of the fractured surface and performing phase analysis.

3. Results

3.1 Metallography and Scanning Electron Microscopy. The microstructural analysis shows approx. 70:30 ($\alpha$: $\gamma$ volume ratio) duplex microstructure with ferrite grains elongated in the rolling direction. The point count method was used to estimate the volume fractions of microstructural constituents. The optical micrographs show dark phase (elongated phase) as ferrite and light phase (matrix) as austenite. The micrographs are shown in figure 1.

![Micrographs showing Ferritic & Austenitic phases.](image)

The ferrite contained chromium content in higher percentage compared with the matrix (austenite). The matrix contained nickel content in higher percentage than ferrite. The composition of the two phases is summarized in table 1.
Table 1. EDX analysis of Ferrite phase and Austenite phase.

| Elements (Ferrite) | Mass % |
|-------------------|--------|
| Iron              | 62.36  |
| Chromium          | 27.08  |
| Nickel            | 4.57   |
| Molybdenum        | 3.55   |

| Elements (Austenite) | Mass % |
|----------------------|--------|
| Iron                 | 63.20  |
| Chromium             | 24.45  |
| Nickel               | 8.13   |
| Molybdenum           | 1.67   |

3.2 Mechanical Testing

3.2.1 Hardness testing
Measurements of macro-hardness were performed by a Rockwell hardness tester using diamond indenter on scale C gave 21.0 HRC. Measurements of micro-hardness were performed by Vickers hardness tester showed that elongated phase (ferrite) was harder than austenite (matrix). The results showed that Ferrite phase is 37% harder than Austenite. Table-2 shows the hardness values of DSS.

Table 2. Hardness values of DSS.

| Bulk hardness of DSS                                      | 290 HV |
|----------------------------------------------------------|--------|
| Micro hardness of ferrite (elongated) phase              | 361 HV |
| Micro hardness of austenite (matrix) phase               | 262 HV |

3.2.2 Tensile Testing
Stress-strain curve for DSS in air is given in figure 2. From the graph UTS was found to 750 N/mm², elongation 6.7% and reduction in area was observed as 3.4%.
3.3 Testing for corrosion behavior

3.3.1 Immersion Test

Immersion Corrosion Test in 3.5% NaCl solution showed no significant corrosion after 1700 hr. The graph in figure 3 shows no change in weight with the passage of time.

![Figure 2](image1.png)

**Figure 2.** Graph showing stress-strain curve of DSS.

![Figure 3](image2.png)

**Figure 3.** Corrosion rate vs. time of DSS in 3.5% NaCl solution.
3.3.2 Electrochemical Corrosion Testing
‘E-log i’ diagram of DSS in 3.5% NaCl solution is given in figure 4. Tafel analysis exhibited a corrosion rate of 0.008 mpy using a built-in software of Gamry® framework. The data obtained from the figure is summarized in table 3.

![E-log i diagram](image-url)

**Figure 4. ‘E-log i’ diagram for DSS in 3.5% NaCl Solution**

| Property             | Value          |
|----------------------|----------------|
| $E_{\text{corr}}$ (mV) | -106.0 mV      |
| $I_{\text{corr}}$ (nA) | 55.80 nA       |
| $\beta_c$            | $85.30 \times 10^{-3}$ (mV/dec) |
| $\beta_a$            | $267.7 \times 10^{-3}$ (mV/dec) |
| Corrosion Rate       | $8.439 \times 10^{-3}$ (mpy) |

**Table 3. Corrosion data from Tafel analyses**

3.3.3 Slow Strain Rate Test
Slow strain rate Stress-Strain curves for mild steel in seawater and air are shown in figure 5. The graph shows that air and seawater has almost similar UTS point and Strain to failure which indicating that no stress corrosion cracking took place in the allowed time. Figure 6 shows SSRT curve for mild steel in similar environments. Comparison of the two figures reveals that mild steel had a substantial effect of environmental conditions whereas it was not significant in case of DSS. Mild steel exhibited a loss of about 25% in elongation in seawater compared with air. The excellent corrosion and especially resistance to localized corrosion (pitting) is responsible for no loss of ductility in duplex stainless steel.
3.3.4 Fractography
Figure 7 reveals the fractured surface of DSS exposed to SSRT in seawater. The detailed examination of the fracture morphology showed a ductile fracture showing dimpled pattern.
4. Conclusions

- A higher volume fraction of ferrite increases hardness and gives a good uniform corrosion resistance as well as pitting.
- The DSS under investigation had about 60% higher UTS compared with mild steel.
- During slow strain rate testing in seawater, in comparison with DSS mild steel showed a loss of about 25% tensile elongation in seawater. The excellent corrosion resistance to localized corrosion (pitting) was presumably responsible for no loss of ductility in duplex stainless steel.

5. References

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