Stress corrosion cracking behavior of welding joint of high strength steel

R Sepe¹, F Bollino², F Caiazzo¹ and F Berto³

¹Dept. of Industrial Engineering, University of Salerno, Via Giovanni Paolo II, 132 - 84084 – Fisciano (SA) - Italy
²Dept. of Engineering, University of Campania “Luigi Vanvitelli”, via Roma 29, 81031, Aversa (CE), Italy
³Dept. of Mechanical and Industrial Engineering, Norwegian University of Science and Technology, 7034 Trondheim, Norway

E-mail: rsepe@unisa.it

Abstract. Nowadays, high-strength steel structures are increasingly being used in marine or soil environments, but low attention has been paid on the corrosion and stress corrosion cracking problem. In this paper, the susceptibility to stress corrosion cracking (SCC) of butt-welding joints of Strenx® 700 (S690QL high strength steel) both in marine and acid-polluted marine atmospheres was studied, by using slow strain rate tensile (SSRT) test. The seawater corrosion environment was considered and it was prepared following the ASTM D1141. To study the influence of the environment pH, NaOH 0.1M solutions and pure H₂SO₄ were used to adjust the pH of the simulated seawater solution to 8 and 4, respectively. The slow strain rate tensile tests (SSRT) with a crosshead speed of 0.000017 mm/s were carried out at room temperature (approximately 25 °C). After failure, the SCC susceptibility was evaluated acquiring the elongation loss rate and the reduction-in-area loss rate. The fracture surfaces were analyzed by SEM observation.

1. Introduction

Nowadays, although the introduction of advanced materials, the metals remain the materials of choice in structures and machinery for their strength, stiffness, toughness, and resistance to high temperatures.

However, most metals are susceptible to corrosion phenomena. The corrosion can occur in several forms. When it takes place in conjunction with mechanical stress can lead to a failure by cracking, which is named stress corrosion cracking (SCC). This event was responsible for several disasters which caused significant economic losses throughout the world, such as the rupture of high-pressure gas transmission pipes, the explosion of boilers, and the destruction of power stations and oil refineries. The onset of such catastrophic failures generally occurred without any prior warning [1, 2]. SCC, indeed, can cause high and fast loss of mechanical strength with little metal loss causing the fracture and, thus, the failure of components and structures. Fortunately, the development of such cracks on a structure is relatively rare, because requires the simultaneous achievement of three conditions: a specific corrosive environment able to promote the crack formation, metallurgic features of the material making it susceptible to SCC, and tensile stress higher than a specific threshold value inducing SCC [1]. The SCC failure can take place at a stress intensity factor below the fracture toughness, $K_{IC}$, and stress below the yield stress [3].
The need for avoiding catastrophic failures of structures and machinery due to SCC has induced many research groups to address their efforts towards the study of the mechanisms driving the phenomenon and the identification of the factors that affect it as well as the strategies for its hindering.

High-strength steels (HSSs) are highly susceptible to SCC. The process involves electrochemical reactions that take place at the crack tip. In the aqueous environment, the most likely reactions occurring are the following [3]:

Anodic reaction: \[ M \rightarrow M^{n+} + ne^- \] (1)

Cathodic reactions: \[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \] (2)

\[ 2H^+ + 2e^- \rightarrow H_2 \] (3)

The electrochemical conditions at the crack tip (e.g. electrochemical potential, pH, oxygen concentration, etc.) favour one of the two cathodic reactions, determining the mechanism leading to the onset of the SCC. To date, two main mechanisms have been identified: The anodic dissolution (AD) and the hydrogen embrittlement (HE) [3]. The first is due to the occurring of the anodic reaction at the grain boundaries.

The AD can take place when the repeated rupture of the passive film covering the crack sides occurs, leading to its advancement with a speed related to the metal dissolution rate at the crack tip [3]. This mechanism is favoured by a high pH, while a near-neutral or low pH values, together with a low concentration of oxygen, induce the occurring of the second mechanism additionally to AD [4]. HE, indeed, induces a failure due to the transport and location of the hydrogen produced by the cathodic reaction (Equation (2)) into the material. This causes a reduction in ductility and strength of the alloy and results in a nonductile fracture [3].

In addition to the pH of the environment, the microstructure of the steel plays an important role in the occurrence of the SCC [5, 6]. The literature, for example, proves that ferrite is the phase more resistant to HE whereas the martensite and bainite are susceptible to HE [6, 7]. The dependence on microstructure contributes to explain the high susceptibility of the welded joints of HSS to the SCC.

The welding microstructure in the heat-affected zone (HAZ), indeed, is different from that one of the base material. Generally, the HAZ has a complex microstructure where more phases (mainly granular bainite, upper bainite, lath bainite, acicular ferrite, quasi-polygonal ferrite, martensite/austenite) coexist and, thus, the welding can show a different SCC behaviour compared to the structures [8]. The high susceptibility of the welding to the SCC is also due to the stress concentration in such areas of the structure [8]. Therefore, when the external passivation coating of the structure in the HSS is disbanded putting the material in contact with the corrosive environment, the coupling with the tensile stress can engender SCC failure. The HSSs are widely used in structures such as ocean engineering equipment (e.g. offshore platform, infrastructure construction in coastal regions, etc.) or buried high-pressure and long-distance oil/gas transmission pipelines, where such materials are exposed to aggressive environments, such as soils with several chemical compositions or the seawater, that is one of the most corrosive environment due to the high chlorides concentration. Moreover, welding is an essential process in the application of the materials for most structures. Therefore, the SCC issue has high relevance.

The present work aims to investigate the SCC behaviour of welded joints of S690QL HSS subjected to the corrosion action of the marine atmosphere by conducting slow strain rate tensile (SSRT) tests. Further, to study the effect of pH value on SCC behaviour of such materials, the tests were carried out exposing the specimens to simulated seawater solutions prepared according to ASTM D1141 and adjusting the pH to 8 (for simulating the marine environment) and 4 (for simulating an acid-polluted marine atmosphere) with 0.1M solutions of NaOH and pure \( H_2SO_4 \) respectively.

2. Materials and methods

2.1 Specimens preparation

Strenx 700 of SSAB (S690Q) HSS was employed in the present study. The typical chemical composition of the material used in the experimental tests and the mechanical properties at room
temperature are reported in Tables 1 and 2, respectively, where $\sigma_s$ is yield stress, $\sigma_u$ is tensile strength and $A_s$ is the elongation at break.

Table 1. Chemical composition (wt%) of the Strenx 700 of SSAB.

| C | Si | Mn | P | S | Cr | Cu | Ni | Mo | B | Ceq |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.2 | 0.6 | 1.60 | 0.020 | 0.010 | 0.80 | 0.30 | 2.0 | 0.70 | 0.005 | 0.34 |

Table 2. Mechanical properties of the Strenx 700 of SSAB.

| $\sigma_s$ [MPa] | $\sigma_u$ [MPa] | $A_s$ [%] |
|---|---|---|
| 700 | 780÷930 | 14 |

Two butt joints were made using 8 mm thick S690Q HSS plates by means Metal Inert Gas (MIG) welding process. Two plates with sizes 150x100x8 mm×mm×mm were welded in double multipass welding, with welding parameters reported in Table 3.

Table 3. Welding parameters.

| Pass | Current [A] | Voltage [V] | Welding Speed [mm/s] | Wire diameter [mm] |
|---|---|---|---|---|
| 1 | 192 | 19.3 | 2.32 | 1.2 |
| 2 | 180 | 19.4 | 2.5 | 1.2 |

Both weld passes have been carried out at uniform speed and under room conditions, using a 1.2 mm diameter metal-cored wire LNM MoNiVa Lincoln Electric (AWS A5.28 ER110S-G). The typical chemical composition and mechanical properties of the filler material are reported in Table 4.

Table 4. (a) Chemical composition (wt%) and (b) mechanical properties of filler material.

(a)

| C | Si | Mn | Cr | Cu | Ni | Mo | V |
|---|---|---|---|---|---|---|---|
| 0.08 | 0.44 | 1.7 | 0.23 | 0.25 | 1.35 | 0.3 | 0.08 |

(b)

| $\sigma_s$ [MPa] | $\sigma_u$ [MPa] | $A_s$ [%] |
|---|---|---|
| 710 | 790 | 20 |

After that, the welding joints were milled on opposite side and their thickness was reduced to 5.6 mm to obtain specimens with a uniform cross-section. According to ASTM E8, specimens with the shape showed in figure 1, were obtained. Afterword, the tensile specimens were cut out from butt joints for direct tensile test. Three specimens were tested for each environment evaluated.
Figure 1. Shape and size of the tested specimens, according to ASTM E8.

2.2 Corrosive environment
Before the tensile tests, the specimens were immersed in solutions simulating the seawater for 7 days. The artificial seawater was prepared according to ASTM D1141-98 standard to obtain the chemical composition reported in Table 4. All used reagents were provided by Sigma Aldrich (Milan, Italy).

Table 5. Chemical composition (g/L) of the artificial seawater testing solution, according to ASTM D1141-98 standard.

| NaCl       | MgCl$_2$·6H$_2$O | Na$_2$SO$_4$·H$_2$O | CaCl$_2$·6H$_2$O | KCl     | NaHCO$_3$ | KBr     |
|------------|------------------|---------------------|------------------|---------|-----------|---------|
| 24.5300    | 5.2000           | 4.6087              | 2.2898           | 0.6950  | 0.2010    | 0.1010  |

The suitable amount of each salt was weighed with an analytical balance (KERN, ABJ 120-4NM) and solubilized in deionized water under magnetic stirring. Afterwards, the solution was brought to the final volume with the addition of water within a volumetric flask. Moreover, the pH value of the solution was adjusted to 8 and 4 by adding some drops of 0.1 M NaOH solution and pure H$_2$SO$_4$ (95±97%) respectively.

2.3 SSRT Testing
To investigate the SCC susceptibilities of HSS steel, slow strain rate tensile test (SSRT) with a crosshead speed of 0.000017 mm/s was conducted with Zwick Roell testing machine equipped with a load cell of 250 kN. The gauge section of each specimen, with the dimension of 32x6x5.6 mm×mm×mm, was ground sequentially to 1500 grit with the last grinding along the axial direction. Then the specimens were cleaned with acetone and dried in air. An extensometer with a length gage of 25 mm was used. The SCC susceptibility was evaluated acquiring the elongation loss rate ($I_\delta$) and the reduction-in-area loss rate ($I_\psi$) by the following formulas:

$$I_\delta = \left(1 - \frac{\delta_s}{\delta_0}\right) \times 100$$

$$I_\psi = \left(1 - \frac{\psi_s}{\psi_0}\right) \times 100,$$

where: $\delta_0$ and $\psi_0$ are the elongation and area reduction of specimens in air environment, while $\delta_s$ and $\psi_s$ are the elongation and area reduction of specimens in the corrosion solutions respectively.

3. Results and discussion
The exposure to corrosive artificial seawater for 7 days led the formation of a precipitate on the surface of all specimens. Its typical orange-brown colour allows to identify it as rust (Fe$_2$O$_3$·nH$_2$O) formed starting from the products of the anodic reaction (equation (1)) and the cathodic reaction reported in the equation (2). The amount of precipitate is greater on the surface of the specimens exposed to alkali environment. In acid solution, indeed, the reduction of the oxygen molecules
(equation (2)) competes with the reduction of the hydrogen ions (equation (3)) which leads to hydrogen molecules formation. Therefore, a lower amount of products are available for rust formation. After soaking, all samples were washed with deionized water and dried, before to perform the tensile tests. In Figure 2, some photographs of the cleaned specimens after soaking in the seawater solutions, and in particular an enlargement view of the welding joints, are reported.

![Photographs of specimens after soaking in seawater solutions](image)

**Figure 2.** Photographs of specimens after 7 days of soaking in artificial seawater (enlargement on welding).

To evaluate the susceptibilities of HSS steel to the SCC, SSRT tests were carried out. Figure 3 shows the photographs of the specimens after the tests. In Table 6 the elongation loss rate ($I_\delta$) and the reduction-in-area loss rate ($I_\psi$) are reported. The maximum strength value was for all tests was about $700 \pm 10$ MPa. Data analysis shows that the SCC susceptibility of (S690Q) steel is higher in acid artificial seawater (pH = 4). This can be due to synergic effect of anodic dissolution (AD), due to the oxidation of the metal atoms (equation (1)), and hydrogen embrittlement (HE), caused by the hydrogen molecules formed in the acid environment by the hydrogen ions reduction (equation (3)).

![Specimens after SSRT tests](image)

**Figure 3.** Specimens after SSRT tests.

| Corrosion environment | $A$[%] | $I_\delta$[%] | $I_\psi$[%] |
|-----------------------|--------|--------------|-------------|
| Air                   | 7.03   | --           | --          |
| pH 8 seawater         | 6.25   | 11.11        | 2.24        |
| pH 4 seawater         | 5.47   | 22.22        | 92.14       |

**Table 6.** SSRT tests results.
In figure 4 are shown the fracture surfaces obtained by SEM observation. As it is possible to observe the fracture surfaces are different and depend on corrosion environment.

![Fracture Surfaces](image)

**Figure 4.** Surfaces of fracture of specimens subjected to different corrosion environments: (a) and (d) air, (b) and (e) pH 8 seawater, (c) and (f) pH 4 seawater.

4. Conclusions
In the present work, stress corrosion cracking behaviour of (S690Q) steel in artificial seawater with different pH are investigated. The results showed that (S690Q) steel is more susceptible to SCC in acid artificial seawater (pH=4) probably because in such environmental conditions both the anodic dissolution (AD) and hydrogen embrittlement (HE) mechanisms drive the failure event.

Acknowledgements
This work was supported by the Programma VAnviteLli. pEr la RicErca -V:ALER 2017.

5. References
[1] Koch G H 2001 *Adv Mater Process* **159**(8) 36 - 8.
[2] International A. ASTM D1141-98, Standard Practice for the Preparation of Substitute Ocean Water. West Conshohocken, PA 2013.
[3] Ramamurthy S and Atrens A 2013 *Corros Rev* **31**(1) 1.
[4] Liu Z Y, Li X G, Du C W, Zhai G L and Cheng Y F 2008 *Corros Sci* **50**(8) 2251-7.
[5] Liu Z Y, Li Q, Cui Z Y, Wu W, Li Z, Du C and Li X G 2017 *Constr Building Mater* **148** 131-9.
[6] Ma H, Liu Z, Du C, Wang H, Li C and Li X 2015 *Mater Sci Eng A* **642** 22-31.
[7] Park G T, Koh S U, Jung H S and Kim K Y 2008 *Corros Sci* **50**(7) 1865-71.
[8] Li X, Liu J, Sun J, Lin X and Li C 2019 *Corros Sci* **160** 108167.