Hydrogen-assisted stress corrosion cracking of high strength steel

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Abstract

In this work, Slow Strain Rate Test (SSRT) testing, Light Optical Microscopy (LOM) and Scanning Electron Microscopy (SEM) were used to study the effect of microstructure, corrosive environments and cathodic polarisation on stress corrosion cracking (SCC) of two grades of high strength steels, Type A and Type B. Type A is manufactured by quench and tempered (Q&T) method. Type B, a normalize steel was used as reference. This study also supports electrochemical polarisation resistance method as an effective testing technique for measuring the uniform corrosion rate. SSRT samples were chosen from base metal, weld metal and Heat Affected Zone (HAZ). SSRT tests were performed at room temperature under Open Circuit Potential (OCP) and cathodic polarisation using 4 mA/cm² in 1 wt% and 3.5 wt% NaCl solutions. From the obtained corrosion rate measurements performed in 1 wt% and 3.5 wt% NaCl solutions it was observed that increased chloride concentration and dissolved oxygen content enhanced the uniform corrosion for all tested materials. Moreover, the obtained results from SSRT tests demonstrate that both Q&T and normalized steels were not susceptible to SCC in certain strain rate (1×10⁻⁶ s⁻¹) in 1 wt% and 3.5 wt% NaCl solutions under OCP condition. It was confirmed by a ductile fracture mode and high reduction in area. The weld metal of Type A with acicular ferrite (AF), pro-eutectoid (PF) and bainite microstructure showed higher susceptibility to hydrogen assisted stress corrosion cracking compared to base metal and HAZ. In addition, typical brittle intergranular cracking with small reduction in area was observed on the fracture surface of the Type A due to hydrogen charging.
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1 Introduction

High strength steels are widely used in offshore structural applications such as topsides, jackets, jack-ups legs and moorings [1]. Welded tubular assemblies are fundamental structural configurations used in offshore structures. Steel grades used for these applications have to fulfil certain requirements, which are defined in material standards such as Eurocode 3. Ordinary high strength steels, defined in these standards, have typically a yield strength in the range of 350 to 460 MPa [2]. Steels with a yield strength exceeding 460 MPa are nowadays also available on the market. The use of these new steels in structural applications can result in reduced cost for processing and materials, due to the ability to produce steels with good weldability and higher strength.

Besides beneficial physical and mechanical properties, the corrosion resistance of the selected high strength steels grade is of essential importance in offshore applications. These structures are often exposed to severe corrosive environments with high deposition rates of chlorides and wet conditions. Hence, different corrosion protective measures are commonly employed such as e.g. cathodic protection and coating systems to reduce the extent of corrosion. Cathodic protection is achieved, either by using a sacrificial anode, or applying a shifted current to the construction to be protected [3]. Studies have, however, shown that the cathodic protection may increase the risk of e.g. hydrogen embrittlement (HE), hydrogen-induced corrosion cracking and hydride formation [4]. Hydrogen is generated on the steel surface due to the water reduction. Hydrogen can also be formed during welding processes and enhance the possibility of hydrogen-induced corrosion [3].

High strength steel offshore structures are in addition extremely sensitive to stress corrosion cracking (SCC) [5]. Cracking due to the simultaneous presence of hydrogen, the corrosive environment and tensile stresses in a metal or alloy is defined as hydrogen induced stress corrosion cracking (HISCC). Extensive investigations have been conducted to investigate the hydrogen effects on structures failure. However, studies that investigate the combined effect of hydrogen and stress corrosion cracking are more limited.
2 Objective and scope of the thesis

This master thesis is a part of a European project performed between seven participants including research institutes and universities from six European countries. The project is based on the study of mechanical properties, toughness, weldability and performance of high strength steels in tubular structures.

The main purpose of this thesis is to investigate the hydrogen-assisted stress corrosion cracking of high strength steels tubular and joint connections in 1 wt% and 3.5 wt% NaCl solutions.
3 Theoretical background

3.1 High strength steel

A typical high strength steel approximately contains 0.15 wt% carbon, 1.65 wt% manganese and low levels (under 0.035 wt%) of phosphorous and sulphur and additions of other elements. High strength steels, are generally defined as steels with minimum yield strengths of 450 MPa [6].

They have tendency to be used for applications where the design stresses are specifically high, sometimes near the yield stress [7]. These types of steels are conventionally used in jack-ups construction with yield strengths ranging from 480-690 MPa, tankers, navy ships, pipelines, and offshore applications [1, 3, 6, 8]. The development of advanced high strength steels has been motivated by important reasons such as economy, environment, design and safety.

3.1.1 Classification

Steels are classified in different systems such as depending on their composition, manufacturing methods, finishing methods, product form, de-oxidation practice, microstructure, required strength level as specified in EN 10113-7 standard, heat treatment and quality description [9].

According to the European standards, regarding the method of production, steel grades are classified in three groups:

- Normalized steel grades (EN 10113 part 2)

The normalizing of steel is the process of heating the material to partly above transformation temperature range which followed by cooling in air to the ambient temperature. Subsequently, the produced microstructure is a fine, well enough soft structure of pearlite and probably some ferrite. In normalized steel grade compared to the annealed steels (i.e. cooled down in furnace) better machining property and higher hard ability is achieved [2].
- **Thermo-Mechanical controlled Processing steel grades (EN 10113 part 3)**

Thermo-Mechanical Controlled Processing (TMCP) is the most efficient industrial technology for maximizing grain refinement at reasonable costs. TMCP is a procedure, which involves simultaneously controlling both the thermo-mechanical rolling and accelerated cooling. In general, a high quantity of the rolling reduction is performed close to the $Ar_3$ temperature (the temperature at which austenite begins to convert to ferrite upon cooling a steel). Furthermore, the use of TMCP technique results in modifying the microstructure [10-11].

- **Quenched and Tempered (Q&T) high strength steel grade (EN 10137 part 2)**

In order to produce high strength steel with better weldability and mechanical properties than the normalized steels, combination of both controlled rolling and accelerated cooling is necessary. To date, most steel grades with minimum yield strength up to 450 MPa have been produced by TMCP method. Nowadays, regarding the limits in strength and section thickness in TMCP and normalized products; the Q&T method is used to overcome this limit of production of very high strength structural steels [2, 6].

Hardening of low alloy steels is achieved by applying fast quenching in various cooling media (water, salty water, oil etc) from nearly a pure austenitic phase (850-950 °C) to a martensitic structure at room temperature or even below. Martensite is a brittle and hard phase, which hardness increases with the steel carbon content [2].

Tempering almost always must be carried out as an essential second step in aim to reduce the brittleness and increase the toughness. It involves heating the hardened steel to an intermediate temperature in order to release the residual stresses that remain from the quenching (heat gradient). The higher the tempering temperature the higher the tensile strength, toughness (impact), elongation and reduction of area properties [2]. The yield strength level of the high strength steel varies in different production methods. Table 1 shows a number of high strength steels which are commonly used in offshore structures:
Table 1. High strength steels used in offshore [3]

<table>
<thead>
<tr>
<th>Yield Strength (MPa)</th>
<th>Process route</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>Normalized</td>
<td>Structures</td>
</tr>
<tr>
<td></td>
<td>TMCP</td>
<td>&amp; Pipelines</td>
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<tr>
<td>450</td>
<td>Q &amp; T</td>
<td>Structures &amp; Pipelines</td>
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<tr>
<td>550</td>
<td>Q &amp; T</td>
<td>Structures &amp; Moorings</td>
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<tr>
<td></td>
<td>TMCP</td>
<td>Pipelines</td>
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<tr>
<td>650</td>
<td>Q &amp; T</td>
<td>Jack-ups &amp; Moorings</td>
</tr>
<tr>
<td>750</td>
<td>Q &amp; T</td>
<td>Jack-ups &amp; Moorings</td>
</tr>
<tr>
<td>850</td>
<td>Q &amp; T</td>
<td>Jack-ups &amp; Moorings</td>
</tr>
</tbody>
</table>

3.2 Corrosion types

Corrosion could be interpreted in different ways; corrosion commonly is defined as the degradation of the alloy into its constituents in reaction with the environment. It can be classified in different types such as uniform corrosion, crevices corrosion, fretting corrosion, galvanic corrosion, fatigue corrosion, stress corrosion cracking etc [12].

In literature different types of corrosion have been reported for carbon steel structures in contact with corrosive media containing aggressive species such as chloride ion, sulphide ion etc. Uniform corrosion, stress corrosion cracking and hydrogen embrittlement are common corrosion problems for carbon steel structures. Thus, a description of the influence of the different parameters on these kinds of corrosion is given in the following.

3.2.1 Uniform corrosion

Uniform corrosion carries on at approximately the same corrosion rate over the whole exposed metal surface. Carbon steels are most often corroded uniformly when it is exposed to open offshore atmosphere and natural seawater, leading to the rusty appearance. Figure 1 shows a picture of the created electrochemical cell which causes corrosion of the surface steel under the seawater droplet. The most accepted corrosion reactions of carbon steels exposed to the water drop are:

Anodic reaction: \( \text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^- \)  \hspace{1cm} (1)

Cathodic reaction: \( 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \rightarrow 4\text{OH}^- \)  \hspace{1cm} (2)
In high strength low alloy steels, lack of alloy elements such as Cr, Ni makes these types of steel susceptible to uniform corrosion. Uniform corrosion of high strength steels is strongly influenced by sodium chloride concentration in solution [12-13]. The corrosion rate increases by the adsorption of some aggressive ions such as Cl\(^-\) on the surface metal. Therefore, the addition of sodium chloride increases the corrosion current density \(i_{\text{corr}}\) and shifts the corrosion potential to the positive direction, which reduces the corrosion resistance. Additionally, the corrosion products on the steel surface are extremely porous and loose and chloride ions can easily diffuse from the corrosion products layer to the bare surface of the steel [13].

Significant information is obtained regarding corrosion mechanisms, corrosion rate and susceptibility of specific materials to different corrosion types in different aqueous environments [12]. In this connection, there are several methods to measure the corrosion rate such as electrochemical impedance spectroscopy (EIS), corrosion potential, Electrochemical Noise (EN), Thin Layer Activation (TLA) and Gamma radiography. Normally, electrochemical test is employed to investigate the impact of the accelerating corrosion processes on the corrosion. For example, polarisation resistance \((R_p)\) is one of the well-organized methods [4]. In other words, electrochemical corrosion rate measurements provide results in terms of electrical current. By Faraday’s law, the corrosion current values can be converted into corrosion rate (\(\mu m/\text{year}\)) by the equation 3 [14]:

\[
r = 0.00327 \frac{ai}{D}
\]

\(i =\) corrosion current density \(a =\) atomic weight of the reactant
\(r =\) corrosion rate in \(\mu m/\text{year}\) \(D =\) density of the metal

\(\text{Figure 1. Schematic structure of uniform corrosion of steel under seawater droplet [4]}\)
3.2.2 Hydrogen damages

3.2.2.1 Hydrogen cracking

Practically, to protect the high strength steels structure from the uniform corrosion some techniques such as cathodic protection and coating are simultaneously employed [12]. Cathodic protection is achieved, either by using a sacrificial anode, or by applying a shifted current to the material (i.e. direct current produced by the power supply is transferred to the material). During the cathodic protection process, hydrogen is generated on the steel surface due to the water reduction. Hydrogen diffuses into the metal and usually increases the risk of hydrogen damages [2]. The susceptible materials such as high strength steels undergo brittle fracture as a result of accidental introduction of hydrogen (internal and/or external sources) to the steel surface during the operation or manufacturing process. Hydrogen can also be generated by corrosion products or the presence of H₂S species [1, 3, 15]. Hydrogen embrittlement cracking is referred to the process of loss of ductility of metals which is caused by reduction of hydrogen ions to atomic hydrogen followed by uniting of hydrogen atoms and formation of solid solution of hydrogen and hydrogen molecules, in the metal matrix [16]. In the presence of the hydrogen recombination poisons (S, P, As, Sn), hydrogen atoms cause hydrogen embrittlement cracking whereas in the absence of these elements molecular hydrogen is formed from combination of hydrogen atoms [16].

High strength steels are extremely sensitive to cold cracking phenomenon such as hydrogen embrittlement cracking, particularly when their strength exceeds a specific level, YS > 550 MPa [2]. In laboratory tests, the embrittlement degree of the specimen is shown by a decrease in area reduction, elongation and time to failure. The mechanism of hydrogen transportation from the environment to crack tips considerably influences the hydrogen embrittlement cracking mechanism [15].

Several different mechanisms have been proposed for hydrogen embrittlement cracking in literature such as reduction of cohesive force in lattices, interaction of hydrogen with dislocations, reduction in surface energy and formation of H₂ bubbles between grain boundaries and inclusions [12, 16]. Concentrated H₂ bubbles in the grain boundaries give rise to increased local high-pressure, which subsequently makes the material more susceptible to hydrogen embrittlement cracking [17-18]. Moreover, both the microstructure
and the strength of the base metal, welded joints have large effects on the materials resistance to hydrogen embrittlement cracking [3].

### 3.2.2.2 Hydrogen-induced cracking

Hydrogen-induced cracking (HIC) is a mechanism which absorbed hydrogen atoms (diffused hydrogen atoms into the metal) can destroy the unit of manufactured low strength steel structures. HIC has been mainly observed in low strength steels which generally takes place at low temperatures, typically less 90 °C [16, 19].

It is recognized that HIC starts from inclusions such as aluminium oxides, titanium oxides and ferric carbides in the steel matrix [19]. Due to the difference of the thermal expansion coefficients between the metal lattice and the inclusion cavities, metal hydrides are usually created at the interface [20]. Moreover, the entrapping of adsorbed hydrogen atoms as H$_2$ molecules in these cavities (inhomogeneous places) or local voids leads to an increase in internal pressure and thus causes HIC and blister formation [16].

It is acknowledged that the entrapped hydrogen is responsible for crack initiation while the mobile hydrogen is responsible for loss of ductility during straining [3, 20]. HIC morphology is most often parallel with the rolling plane and surface [16, 21].

### 3.2.2.3 Stress corrosion cracking

Stress corrosion cracking (SCC) is the cracking induced from the simultaneous action of a corrosive environment and external and/or internal tensile stress [15, 22-23]. These tensile stresses originate from residual stresses (e.g. thermal stresses) or applied tension. Failures always take place under tensile stresses lower than the macroscopic yield strength of the material [24]. The occurrence of SCC depends on the coincident of three prerequisites, susceptible material, tensile stress and a corrosive environment Figure 2.

According to the microscopic mechanism of crack propagation, SCC is classified in two basic categories as shown in Figure 3:
**Figure 2. Prerequisite factors for Stress Corrosion cracking phenomenon**

**Figure 3. Main variant of SCC phenomenon**

- **Active path dissolution**
  In this model, the crack propagates by a localized corrosion (e.g. preferential dissolution) at the tip of the crack where metal is locally corroded [17]. Anodic dissolution can result in formation of active paths in the material, internal stresses at the growing crack tip due to the formation of corrosion products and interaction of chemical–mechanical behaviour of the metal. The active path dissolution normally occurs along the grain boundaries. This process is therefore called intergranular cracking as demonstrated in Figure 4.a. In addition, the presence of applied stress opens the crack tip and increases the anodic dissolution rate. So, the anodic dissolution model in this case can be characterized as stress assisted intergranular corrosion.

- **Hydrogen degradation**
  Opposed to the anodic dissolution, in hydrogen attack mechanism, there is no need of metal dissolution for the cracks to propagate. In other words, the crack grows very fast
through the grain boundaries and the fracture does not need to lose much material as corrosion products. Besides, the fracture surfaces display a shiny and brittle feature. In this respective, the hydrogen atoms diffuse into the metal and precipitate as hydrogen molecules at the interfaces of matrix-inclusion and subsequently reduce cohesive energy of the solid, as depicted in Figure 4.b. Hydrogen is generated on the metal surface from electrochemical reactions during cathodic protection [21].

![Figure 4. SCC crack propagation mechanism: a) Anodic Dissolution b) Hydrogen Embrittlement [16]](image)

- **Crack propagation types**
  The stress corrosion cracks are more likely to form in anodic areas where the metallic material starts corroding. Cracks usually have clean, sharp, and branching form. Figure 5 shows two different categories of metallurgical crack propagation:
  
  i. **Intergranular SCC (IGSCC)** refers to cracks propagating along grain boundaries Figure 5.a. IGSCC is most often attributed to the corrosive solution with high pH value. In such environment the anodic dissolution at the grain boundaries and the rupture of the passive film on the crack tips is the dominant factor which leads to SCC [25].
  
  ii. **Transgranular SCC (TGSCC)** refers to crack propagation through the grains in the direction of particular crystallographic planes Figure 5.b [16]. However, there is not enough substantial information on the mechanism of SCC under near-neural pH condition to distinguish the initiation and growth rate of the crack.
Studies have shown that low strength steels are not very sensitive to SCC under static load in sodium chloride solution (i.e. seawater) [2, 12]. However, high strength steels are susceptible to SCC due to material properties such as the steel composition, environmental conditions, geometry of the crack, stress state, interaction of dislocations, grain size, orientation of the grains, production history, distribution of the precipitates etc [15-16]. Carbon content and its distribution in the material matrix decreases required stress for initiation of the crack due to the formation of the carbides so that strongly affects the materials resistance to SCC [16].

3.3 Effect of environmental and metallurgical parameters on SCC

Investigations show that chemical composition, microstructure, welding heat input, temperature and pH have considerable influence on high-strength steels resistance to HIC, SCC and sulphide stress corrosion cracking (SSCC) in offshore engineering structures [11]. A number of effects of these factors are summarised in the following:

- **pH**

Phelps and Bhatt showed that SCC occurred quite rapidly at high pH values due to formation of relatively a thin condensed and protective oxide layer in the concentrated carbonate-bicarbonate environment. The lower the pH value and the corrosion potential, the higher the hydrogen concentration in the steel is. However there is still a lack of information concerning the susceptibility to SCC in near-neutral pH solution [7].
- **Composition**

Perry found that Mo, V, Nb have significant influence on carbon steel resistance to SCC. For instance, by adding Mo austenitic steels susceptibility to SCC will decrease in seawater and increase in contact with caustic solutions [16]. He also observed higher resistance to SCC for specimens which contained Mo and V compared to samples with only one of these alloying elements [7]. Presence of trace elements and inclusions have also important role in enhancing the susceptibility of the high-strength steels to SCC by accelerating hydrogen atom absorption [7]. The beneficial or harmful role of the alloying elements on the susceptibility to SCC depend on how they affect carbide segregation (e.g. the segregation of the cementite at the grain boundaries) [16]. In order to improve mechanical properties, hardenability and weldability, alloying elements such as Ti and Ni, may be added up to 0.10 weight percent to the steel composition.

- **Microstructure**

Different mechanical properties of steels are ascribed to different microstructures such as bainite, ferrite, martensite, pearlite and austenite [26-27]. However, a complete definition of the effect of the specific microstructure on the SCC has not yet been entirely understood, the predominant effect of the hardness is clear. The distribution of carbide particles in the microstructure affects the mechanical and the SCC susceptibility. For instance, the presence of carbide particles in ferrite grain boundaries is responsible for intergranular cracking of carbon steels with carbon concentration > 0.1 wt% [16].

In Q&T method, during tempering the precipitating of fine dispersions of copper/carbide alloy is normally desired to obtain highest level of strength. Materials with untempered martensite structure are not appropriate to employ in engineering applications because of poor ductility before tempering owing to the existence of internal stresses. The internal stresses originate from quenching and can be released during a tempering procedure [27].

The untempered zone in welded joints generally has weak mechanical properties and low toughness (i.e. the ability of a material to absorb energy and plastically deform without fracturing) and is therefore most susceptible to hydrogen embrittlement [28]. The fracture surface in this region is more brittle than that of the other parts [1]. Normally, normalized and rolled steels both with ferritic and pearlitic microstructure showed greater susceptibility to sulphide stress corrosion cracking (SSCC). The results show that refined and homogeneous Q&T bainite/martensite microstructures have the best resistance to HIC.
and SSCC [11]. A coarse-grained structure increases the HE susceptibility of the materials [29]. In addition, in order to achieve high-deformability of pipelines up to 100 times a specific control of the ferrite-bainite microstructure is necessary [30]. The higher the temperature during Q&T process the greater the average diameters of the grains size of prior-austenitic are. Thus the larger the grain size, the more quickly is the critical stress reached at which slip is initiated in the neighbouring grain. Increased in grains size results in increasing the cleavage fracture stress so that enhanced the risk of intergranular fractures [31].

- **Heat input during welding process**

Increasing the heat input during the welding process escalates the susceptibility to hydrogen embrittlement of the acicular ferrite in grain-refined HSLA-80, whereas it is indicated that in low heat input condition further ductility deterioration did not occur in grain-refined HSLA-80. The HE resistance comes up with the existence of predominant acicular ferrite and/or lath martensite or a mixture of both in grain-coarsened HSLA-100 and for the low heat input grain-refined HSLA-80 steels [32]. Ideally, a low hydrogen welding electrode should be chosen for welding of this type of steel because even low hydrogen content leads to catastrophic failure during operation. Furthermore, keeping the welding electrodes in dry conditions reduces the influence of moisture and water vapour, as main sources of hydrogen during the welding process. [33].

In order to get rid of the cold cracking, micro-cracks and residual stresses some cautionary actions such as baking the electrodes before welding, preheating and post weld heat treatment should be employed [5]. Weldability, as a significant factor in hydrogen embrittlement, is strongly depends on the chemical composition and the carbon equivalent value (CE) of steel. The weldability of steels with lower CE is much better than for steels with high CE. The maximum CE is defined by the equation 4:

\[
CE = C + \frac{Mn}{6} + \frac{Cr+Mo+V}{5} + \frac{Ni+Cu}{15}
\]
- **Temperature**

Temperature significantly affects susceptibility of ferrous alloys to hydrogen embrittlement. Higher temperature increases the diffusion of hydrogen atoms into steel but lowers the required stress for crack initiation and enhances the growth rate of propagation [16].

- **Metal hydride**

The fracture of the oxide layer of steels in contact with sodium chloride solutions causes transport of Cl\(^-\) from the solution to where the localized corrosion occurs through damaged oxide layer and an increased the chloride ion concentration. Hydrogen produced during cathodic protection or through the corrosion process is present near the cracks. Some amount of the hydrogen atoms are recombined and create hydrogen molecules and leave the site. Some hydrogen enter the bulk material and can form a brittle metal hydride at the crack tips or become entrapped in vacancies, along grain boundaries and produce hydrogen molecules which finally will cause HE [16].

- **H\(_2\)S**

The H\(_2\)S is introduced to the steels during their service by the environmental factors such as natural gas, sulphate-reducing bacteria (SRB) and hydrocarbon compounds in transportation containers. Nowadays, one of the most critical problems in using high strength low alloy steel in seawater with presence of the H\(_2\)S is its susceptibility to sulphide stress cracking (SSC). Studies show that if the materials were sensitive, very low concentration of hydrogen sulphide is enough to cause SSC failure. The reaction between wet H\(_2\)S and the high strength steels produces atomic hydrogen (i.e. H\(_2\)S → HS\(^-\) + H\(^+\)). Sulphide stress corrosion cracking (SSCC) may in addition occur by combination of applied stress, residual stress and diffused hydrogen atoms through hydrogen embrittlement [11].

It is clear that the X-52 and X-70 steels tested in a solution saturated with H\(_2\)S presents high susceptibility to SCC [24]. Fracture surface analysis of showed brittle failure for the sample tested in saturated solution with H\(_2\)S [24]. Corrosion effects were observed as important factors in crack initiation during the corrosive attack.
When carbon dioxide dissolves in water, carbonic acid forms:

\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \] (5)

Carbonic acid decomposes to \(\text{H}^+\) and \(\text{HCO}_3^-\). An increase in hydrogen concentration (i.e. proton concentration) in solution leads to a reduction of the pH value. This can subsequently increase the anodic dissolution process and enhance hydrogen permeation into the metal [25]. In addition, investigations show that the composition of the natural water solution and trapped water in the vicinity of the crack tips differs in \(\text{HCO}_3^-\) concentration. In turn, increasing the \(\text{CO}_2\) partial pressure in an aqueous solution with a resulting formation of \(\text{H}_2\text{CO}_3\) subsequently decreases the pH. The tendency to uptake hydrogen is increased due to dissociation of \(\text{H}_2\text{CO}_3\) to \(\text{H}^+\) and \(\text{HCO}_3^-\). Therefore the steel's susceptibility to anodic dissolution and stress corrosion cracking (i.e. controlled by hydrogen embrittlement) will increase [25, 34].

### 3.4 Hydrogen-assisted stress corrosion cracking in high strength steel

Based on the controlling experimental parameters several models such as enhanced localised plasticity, film-induced cleavage, hydrogen embrittlement and slip – dissolution (cyclic formation and rupture of films of corrosion product) for SCC mechanism are proposed. However none of them can be accepted as universal model and each of them should be considered in specific condition [12, 16].

The influence of atomic hydrogen on the SCC mechanism is a controversial issue. Hydrogen generated on the surface and at the advancing crack tips due to electrochemical reactions continuously diffuses into the steel. Hydrogen penetrating into steel increases its brittleness and intensely influences the plastic deformation of the steel [35]. The solubility and diffusion rate of hydrogen atoms in steel matrix determined by the suitable sites (i.e. tetrahedral and octahedral) to accommodate the hydrogen atoms and the distance between the ion atoms. It is well known that in ferritic steel, body centred cubic (b.c.c) structure, the diffusion rate of hydrogen atom is very high due to the relatively wide distance between the atoms and the solubility of hydrogen is very low because of lacking of the fitting sites. However, the austenitic steels with face centred cubic (f.c.c) structure have higher hydrogen solubility and a lower diffusion coefficient. Despite the shorter
distance between the holes in f.c.c structure there are more appropriate sites for hydrogen. In this competition, mobile hydrogen atoms can move much easier through the steel with ferritic structure. Thus, the ferritic steels are more susceptible to hydrogen assisted stress corrosion cracking than that of austenitic steel [35].

Hydrogen tends to be attracted to regions close to the tip of cracks where the metal structure is put under the highest triaxial tensile stress compared to the other parts of the structure [35]. By accumulation of hydrogen at the grain boundaries, the bonds between grain boundaries and other segregated particles like Sb band P are weakened. Consequently, hydrogen facilitates local intergranular fracture, cleavage or increased micro-plasticity in the affected region [12].

Research has shown that hydrogen uptake from a crack can be reduced by increasing the pH if the best range of current density in cathodic protection was applied [12]. However, in practice cathodic protection systems for the materials which are susceptible to SCC, high strength steels, locally reduce the potential to very low values that is critical for the structures [6, 12]. Additionally, adding some elements such as P, As, S, Se in aqueous solution (electrolyte) leads to inhibit the hydrogen recombination mechanism \( H_{\text{ads}}^+ + H_{\text{ads}} = H_2 \) [12, 16]. Furthermore, the stress favours both the interstitial solubility of hydrogen on the crack tip and the precipitation of the hydride phase such as Nb and Ti on the grain boundaries and increase the susceptibility of the steel to the hydrogen assisted stress corrosion cracking.

Although it is proposed that in some cases crack propagation occurs under the influence of micro ruptures, the interaction between anodic dissolution and hydrogen diffusion close to the crack tips controls the process of SCC crack propagation [16]. On one hand, local attack encouraged the hydrogen adsorption that leads to bulk or local embrittlement. On the other hand, hydrogen permeation and anodic dissolution simultaneously affect the SCC mechanism. It is well observed that the aqueous solutions, the transport of water (e.g. sodium chloride solution) to crack tip, highly is involved in the SCC mechanism [16, 20]. The threshold stress intensity for cracking of high strength steel strongly decreases during exposure to environments saturated with hydrogen [16]. Increasing time and current density of hydrogen charging of the steels leads to higher hydrogen concentration in metal causing hydrogen-induced cracking [20]. Hydrogen-
induced crack growth has been proposed for ferritic steels and aluminium alloys as the major factor participating in the SCC process [20].

Generally, electrochemical polarisation (anodic and cathodic) can be employed to distinguish between SCC controlled by anodic dissolution or HE mechanisms. However, for high strength steel both cathodic and anodic polarisation increase the hydrogen evolution, resulting in higher crack growth rate and shorter failure time [16, 33]. HE cracks normally start from subsurface inclusions while SCC cracks initiate from the surface. SCC failure shows more cracks branching (depending on hydrogen concentration, stress intensity and the surrounding environment) than visible cracking by HE [36].

Presence of corrosive environments during the service, absence of pre-treatment before the operation and susceptibility to pitting corrosion of the materials can be addressed as some significant factors which favour SCC [15]. However, humid environment during the service, incorrect heat treatments during production and inadequate baking of coatings can also increase the sensitivity of the material to HE fracture [36].
4 Experimental

4.1 Materials specification

A high strength steel grade Type A with a minimum yield strength value of 590 (N/mm²) with a thickness ≤ 16mm was investigated in this project. The carbon equivalent (CE) of Type A is 0.54. These high strength steel pipes have been tempered (austenitic temperature at 950 °C) for 26 minutes followed by quenching in water and subsequent tempering at 665 °C for 45 minutes. The material is produced according to the new Eurocode 3 standard (sections 1-12). Figure 6 shows the heat treatment process of as-received base metal Type A Q&T high strength steel grade.

![Figure 6. Schematic diagram of heat treatment processing of Type A Q&T steel grade](image)

The Type B as an ordinary low-alloy steel grade with approximate yield strength of 350 MPa which is commonly utilized in marine engineering applications was used as reference material. The chemical compositions of the two tested steels are presented in Table 2. The steels contain low carbon and sulphur content.

| Chemical composition (wt %) of Type A and Type B steel grade [31] |
|-----------------|---|---|---|---|---|---|---|---|---|---|
| Steel grade     | Fe | C  | Mn | Si | P  | S  | Ni | V  | Cr | Mo |
| Type A          | Balance | ≤ 0.22 | ≤ 1.70 | ≤ 0.50 | ≤ 0.03 | ≤ 0.01 | ≤ 0.40 | ≤ 0.18 | ≤ 0.40 | ≤ 0.40 |
| Type B          | Balance | ≤ 0.23 | ≤ 1.60 | ≤ 0.50 | ≤ 0.03 | ≤ 0.03 | -  | -  | -  | -  |

Figure 7 illustrates the cut of samples from K-joint offshore welded tubes for SSRT testing. The dimensions of the K-joint high strength steel are given in Table 3.
Table 3. The parameters of the K-joint configuration

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Steel grade</th>
<th>Diameter (mm)</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chord</td>
<td>Type A</td>
<td>355</td>
<td>12</td>
</tr>
<tr>
<td>Brace</td>
<td>Type A</td>
<td>193</td>
<td>10</td>
</tr>
</tbody>
</table>

4.2 Analytical techniques

4.2.1 Polarisation resistance

Uniform corrosion rate of the base metal and weld metal was measured in two different solutions, 1 wt% and 3.5 wt% NaCl. Test solutions were made from analytical grade reagent NaCl and deionised water in order to simulate offshore and seawater environments, respectively. The tests were carried out at room temperature (~ 25 °C). The pH value of the solution was 6.5 at the beginning of the experiments. The effect of oxygen concentration on uniform corrosion resistance in sodium chloride solution was investigated in aerated and de-aerated (N₂-bubbleing) conditions. In de-aerated condition, the solution was purified before running the experiment with dry nitrogen gas for 10 minutes to remove dissolved oxygen. The nitrogen bubbling was kept during the test.

The specimens for the electrochemical measurement test were cut from the weld metal, base metal of the K-joint and the reference material. Prior to the tests, the specimens were wet ground with 600-grade SiC paper and rinsed with de-ionized water and ethanol, dried and exposed to air for approximately 24 hours. The exposed surface area of each specimen was approximately 100 mm².
The linear polarisation resistance technique, based on the change in potential and recording the polarisation resistance (Rp) (the slope of the linear polarisation curve dE/di is termed the Rp) was used to measure the corrosion rate. The polarisation resistance is a significant parameter to estimate the uniform corrosion rate of a metal. The variation of polarisation resistance over time is automatically recorded. Each point of Rp and potential vs. time is saved from one scan. The system rests between two successive measurements. The time needed for system rest at open circuit potential (OCP) is defined by the user. The polarisation resistance can be determined by means of second Stern method. Stern and Geary (1957) showed that there is a linear relationship between potential and applied current at potentials only slightly removed from the corrosion potential. The relationship between polarisation resistance Rp and corrosion current $i_{corr}$ is shown as:

$$i_{corr} = \frac{B_a B_c}{2.303 R_p (B_a + B_c)}$$

where $B_a$ and $B_c$ are constant and determined by anodic and cathodic Tafel slopes.

Moreover, it is also possible to measure the corrosion rate by Tafel calculation. In this technique Rp is determined as the slope of the tangent to this parabola at the zero current potential. The corrosion rate is calculated from the current by using Faraday’s law [14].

DC Potentiodynamic experiments were performed using a potentiostat model PGP201. A PC computer with the electrochemical software (VOLTA MASTER 4) controlled the potentiostat. The tests were carried out in an Avesta cell. The arrangement of a three-electrode Avesta cell is shown in Figure 8.

1. Working electrode (WE): Specimen
2. Counter electrode (CE): Platinum coil
3. Reference electrode: Silver Chloride electrode (Ag/AgCl)
4.2.2 SSRT- Slow Strain Rate Test

Samples from Type A and Type B were longitudinally cut from weld metal, base metal and HAZ region. The SSRT specimens, with 3.00 mm in gauge diameter and 31 mm in gauge length (± 0.05 mm) were machined from the two different kinds of weld configurations (i.e. K and X-joint). Figure 9 shows a photo of a SSRT tensile specimen. The length direction of the tensile sample was parallel to the longitudinal of the pipe. The samples’ surfaces were abraded with 600-grith SiC abrasive paper.

The equipment for SSRT testing, Figure 10, combines slow strain rate in corrosive environment and is used to evaluate the susceptibility of materials to stress corrosion cracking and hydrogen embrittlement.
The SSRT was performed in air, 1 wt% and 3.5 wt% NaCl solutions open in contact with air in ambient temperature (~ 25 °C). The solution pH was about 6.5 in the beginning of the experiments. A strain rate of 10^{-6} s^{-1} was applied throughout the experiments. Furthermore, in some cases cathodic polarisation with the magnitude of 40 mA (4 mA/cm^2) was employed throughout the test to enable diffusion of hydrogen into the specimens. During the tests, load-time curves were recorded on a PC. The SSRT test in distilled water as reference is recommended to compare the effect of sodium chloride concentration. However, in this project the tests performed in air are considered as reference. No measurement was performed for weld metal Type A X-joint in 1 wt% NaCl with 4 mA/cm^2 as well as Type B in 1 wt% NaCl with 4 mA/cm^2, base metal 1 wt% NaCl and weld metal 1 wt% NaCl with 4 mA/cm^2 due to the lack of raw materials.

In this project, the SSRT were performed with the following experimental conditions:

1. Air – To simulate an inert environment
2. E_{cor} – Open Circuit Potential
3. Cathodic polarisation by applying 4 mA/cm^2 current density – To simulate impressed cathodic protection in 1 wt% and 3.5 wt% NaCl solutions
The materials susceptibility to SCC is usually expressed in terms of reduction in area (RA%), time to failure (TTF) and the elongation (EL%). A lower RA% means more susceptibility to SCC. The equation 7 is used to calculate RA%:

\[
RA\% = \left( \frac{A_0 - A}{A_0} \right) \times 100
\]  

(7)

\(A_0=\) Initial area \hspace{1cm} \(A=\) Final area after failure

### 4.2.3 LOM- Light Optical Microscopy

The examined samples were cut from weld metal, base metal and HAZ (heat affected zone) of K-joints. The samples were ground from 80 to 1200-grade with SiC abrasive paper and polished with diamond pastes 3µm, 1µm and 0.25µm. The samples were etched with 4 % nital solution (4 ml concentrated nitric acid in 98 ml ethyl alcohol) during 18 seconds.

The LOM used was a LEICA DM-RME model with magnifications ranging between (50X) and (1000X). In this project, LOM was employed to study the effect of microstructure on corrosion and hydrogen embrittlement susceptibility of weld-simulated Type A Q&T steel and Ordinary Steel-Type B.

### 4.2.4 SEM- Scanning Electron Microscopy

The SEM with secondary electron (SE) detector used was a LEO 1520 Field Emission Gun Scanning Electron Microscope equipped with an Oxford EDS/EBSD system with magnifications up to 100 000X. The SEM was used to observe the morphology of the fracture surface of the SSRT samples tested in air, 1 wt% and 3.5 wt% NaCl solutions under OCP condition and cathodic protection. The loss of plasticity due to hydrogen charging was correlated by a change in fracture appearance.
5 Results

Figure 11 shows stress vs. strain curves achieved after SSRT tests carried out in air (as a reference), 1 wt% and 3.5 wt% NaCl solutions under open circuit potential and cathodic polarisation. Mechanical properties such as EL%, yield stress (YS) and ultimate tensile strength (UTS) were calculated from the stress vs. strain curves. The obtained results are illustrated in Appendix 1, Table 7-10.

![Figure 11. Typical plotted stress vs. strain curves after SSRT tests performed in air as reference, 1 wt% and 3.5 wt% NaCl solutions under OCP and cathodic polarisation](image)

### 5.1 Mechanical properties

Table 4 shows some measured mechanical properties of Type A and Type B steels grade after SSRT tests performed in air including YS, UTS, TTT, EL% and RA%.

No significant differences were observed in YS and UTS for the HAZ and weld metal in two welded joints configuration of type A base steel. The EL% as a measure of ductility confirmed that the base metal, HAZ and weld metal tested in air showed approximately the same sensitivity to applied stress in K-joint, whereas the X-joint revealed slightly more ductile behaviour in HAZ. The calculated EL% values for Type B demonstrate higher ductility in base metal, weld metal and HAZ compared to Type A.
Table 4. Mechanical properties of Type A, Type B and their welded joints tested in air

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>Test environment</th>
<th>YS (MPa)</th>
<th>UTS (MPa)</th>
<th>TTF(hr)</th>
<th>EL (%)</th>
<th>RA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type A K-joint</td>
<td>Base metal</td>
<td>782</td>
<td>818</td>
<td>34.13</td>
<td>9.86</td>
<td>75.67</td>
</tr>
<tr>
<td></td>
<td>HAZ</td>
<td>774</td>
<td>840</td>
<td>35.33</td>
<td>10.00</td>
<td>73.55</td>
</tr>
<tr>
<td></td>
<td>Weld metal</td>
<td>820</td>
<td>893</td>
<td>36.33</td>
<td>10.00</td>
<td>70.57</td>
</tr>
<tr>
<td>Type A X-joint</td>
<td>HAZ</td>
<td>740</td>
<td>806</td>
<td>38.92</td>
<td>11.60</td>
<td>78.38</td>
</tr>
<tr>
<td></td>
<td>Weld metal</td>
<td>730</td>
<td>820</td>
<td>27.77</td>
<td>11.30</td>
<td>42.66</td>
</tr>
<tr>
<td>Type B K-joint</td>
<td>Base metal</td>
<td>765</td>
<td>803</td>
<td>37.00</td>
<td>10.40</td>
<td>72.30</td>
</tr>
<tr>
<td></td>
<td>HAZ</td>
<td>470</td>
<td>564</td>
<td>50.58</td>
<td>15.30</td>
<td>78.78</td>
</tr>
<tr>
<td></td>
<td>Weld metal</td>
<td>485</td>
<td>600</td>
<td>53.75</td>
<td>16.80</td>
<td>70.49</td>
</tr>
</tbody>
</table>

5.2 Microstructure characterization

5.2.1 High strength steel Type A, K-joint

The iron-carbon equilibrium diagram, Figure 43, Time Temperature Transformation (TTT) diagram, Figure 44, and continuous cooling transformation (CCT) diagram, Figure 45, were used for identification of the microstructure after heat treatment. The used diagrams are shown in Appendix 2. The microstructure images of welded joint including base metal, weld metal and HAZ of Type A high strength steel grade analysed with LOM are shown in Figure 12-15. The microstructure produced after welding procedure clearly shows different regions on the welded sample including base metal, weld metal, fusion line and HAZ were observed in Figure 12. The zone near the weld pool consists of fine grains due to rapid cooling rate.
Figure 12. Light optical micrograph of Type A high strength steel, distinct difference in the microstructure of the welded joint after welding. The microstructure revealed using 4% nital solution.

Figure 13. Light optical micrograph of Type A high strength steel sample base metal. The microstructure revealed using 4% nital solution.

Figure 13 shows the microstructures of the as-received base metal Type A steel grade. The microstructure of the base material after tempering consists of tempered martensite and
retained austenite. The microstructure of weld metal of the K-joint, Figure 14, comprises of interpenetrating acicular ferrite (AF), a spot of pro-eutectoid ferrite (PF) and bainite.

*Figure 14. Light optical micrograph of Type A high strength steel, weld metal. The microstructure revealed using 4 % nital solution*

*Figure 15. Light optical micrograph of Type A high strength steel, HAZ. The microstructure revealed using 4 % nital solution*
The microstructure of the HAZ of Type A consists of low carbon lath martensite and prior austenite with different grain size as demonstrated in Figure 15. The HAZ is typically composed of coarse grained region, fine grained region and inter-critical region.

5.2.2 High strength steel Type A X-joint

The weld metal of Type A X-joint consisted of a bainite, AF and PF microstructure as is revealed in Figure 16. It was visible that the PF content slightly decreased with bainite fraction of ~ 30% compared with base metal of Type A.

![Figure 16. Light optical micrograph of Type A high strength steel, weld metal. The microstructure revealed using 4 % nital solution](image)

Figure 17 shows the microstructure of HAZ of the X-joint of Type A which consists of coarse grains of prior austenite (light areas) and bainite (dark region).
5.2.3 The Type B steel grade

The optical images of base material, weld metal and HAZ of the Type B ordinary steel grade (normalized steel) are shown in Figures 18-21.

Figure 18 clearly illustrates two separate microstructures formed HAZ (left side) and weld metal (right side) after welding process. According to the microstructure of base metal shown in Figure 19, it is easy to distinguish the typical microstructure of normalized steel, which is dominated by equiaxed bands of ferrite (light) and pearlite (dark) structure. The weld metal has a completely different appearance. The microstructure of weld metal mainly consists of acicular ferrite in interior of grain and grain boundary ferrite, polygonal ferrite, pro-eutectoid ferrite and ferrite side plate from boundaries to interior as shown in Figure 20. According to Figure 21, the microstructure examinations of the HAZ under the optical microscope revealed lath martensite with retained austenite islands.
Figure 18. Light optical micrograph of Type B ordinary steel HAZ (left side) and weld metal (right side). The microstructure revealed using 4 % nital solution

Figure 19. Light optical micrograph of Type B ordinary steel, base metal. The microstructure revealed using 4 % nital solution
Figure 20. Light optical micrograph of Type B ordinary steel, weld metal. The microstructure revealed using 4% nital solution

Figure 21. Light optical micrograph of Type B ordinary steel, HAZ. The microstructure revealed using 4% nital solution

A summary of observed microstructures of base metal, weld metal and HAZ for Type A and Type B steels after welding process is presented in Table 5.
Table 5. Observed microstructure of Type A and Type B steel, base metal, weld metal and HAZ after welding process

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>Samples</th>
<th>Observed phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type A K-joint</td>
<td>Base metal</td>
<td>Tempered martensite + retained austenite</td>
</tr>
<tr>
<td></td>
<td>Weld metal</td>
<td>Acicular ferrite + pro-eutectoid ferrite + bainite</td>
</tr>
<tr>
<td></td>
<td>HAZ</td>
<td>Lath martensite + prior austenite</td>
</tr>
<tr>
<td>Type A X-joint</td>
<td>Weld metal</td>
<td>Acicular ferrite + pro-eutectoid ferrite + bainite</td>
</tr>
<tr>
<td></td>
<td>HAZ</td>
<td>Bainite + prior austenite</td>
</tr>
<tr>
<td>Type B K-joint</td>
<td>Base metal</td>
<td>Ferrite + pearlite</td>
</tr>
<tr>
<td></td>
<td>Weld metal</td>
<td>Acicular ferrite + pro-eutectoid ferrite + polygonal</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ferrite + ferrite side plate</td>
</tr>
<tr>
<td></td>
<td>HAZ</td>
<td>Lath martensite + retained austenite</td>
</tr>
</tbody>
</table>

5.3 Corrosion rate measurement

The corrosion rates of steel, Type A and Type B, for base metal and weld metal in aerated and de-aerated sodium chloride solutions with different NaCl concentrations at room temperature (~ 25 °C) are shown in Figure 22-23. After the experiments, no apparent crevice or pitting corrosion was observed on the corroded surface. The corrosion rate of the two steel grades, except for the weld, decreased when de-aerated solution was used. The obtained results show that the corrosion rates for Type A and Type B for both base and weld metal in aerated 3.5 wt% NaCl solution were higher than those obtained from tested specimens in de-aerated 3.5 wt% NaCl solutions.
Analysing the corrosion rates of Type A high strength steel and ordinary steels, it is apparent that the corrosion rate of Type A for base and weld metal is less than that of the Type B ordinary steel grade, particularly in presence of high concentration (3.5 wt%) of
the NaCl and de-oxygenated conditions. Furthermore, maximum corrosion rates for both materials were obtained in the presence of oxygen. In 1 wt% NaCl solution, in the absence of oxygen, the corrosion rate of the weld metal of Type A steel grade was higher than that of Type B weld, whereas the opposite was achieved for the base metal.

5.4 Stress Corrosion Cracking

After the slow strain rate test, the side view images, reduction of area and time to failure were investigated for Type A steel with K and X-joint in order to characterise different modes of fracture.

5.4.1 Type A

Photos of the fractures of the cracked specimens of base metal, HAZ and weld metal of Type A steel tested in different environments are shown in Figure 24-26. It is clear that the materials tested in air, 1 wt% and 3.5 wt% solution under open circuit potential almost showed the same behaviour. In other words, the fracture surface of samples consisted of a typical ductile behaviour with a cup-and-cone configuration. Considerable necking was seen for the samples tested in air, 1 wt% and 3.5 wt% NaCl solutions under OCP condition accompanied with high reduction in area (RA%). The samples tested under cathodic polarisation with 4 mA/cm² of current density did not show any non-uniform plastic deformation after the necking point. Accordingly, the brittle fractures appeared after the SSRT tests.
Figure 24. Fractography corresponding to Type A base metal tested in Air; 3.5 wt% NaCl (OCP); 1 wt% NaCl (OCP) and 1 wt% NaCl under cathodic protection.

Figure 25. Fractography corresponding to Type A HAZ tested in Air; 3.5 wt% NaCl (OCP); 1 wt% NaCl (OCP) and 1 wt% NaCl under cathodic protection.
5.4.1.1 Reduction in area

K-joint

Figure 26. Fractography corresponding to Type A weld metal tested in Air; 3.5 wt% NaCl (OCP); 1 wt% NaCl (OCP) and 1 wt% NaCl under cathodic protection

Figure 27. RA% of base steel, welded metal and HAZ of Type A K-joint pipeline steel after SSRT test

Figure 27 shows the RA% of base steel, welded metal and HAZ after SSRT testing under open circuit potential condition. The RA% of the base metal for fractured samples in air, 1 wt% and 3.5 wt% NaCl were measured to be 75.7%, 78.9% and 76.3% respectively,
which was larger than all RA% achieved with HAZ and weld metal. No significant effect of test environments, 1 wt% and 3.5 wt% NaCl solutions, on RA% was observed at OCP condition for Type A k-joint.

Figure 28. RA% of tested samples in air and polarised base steel, welded metal and HAZ Type A K-joint pipeline steel tested in 1 wt% NaCl and 3.5 wt% NaCl using 4 mA/cm² current density during SSRT testing

Figure 28 shows the RA% of tested Type A steel grade in air and cathodically polarised samples in 1 wt% and 3.5 wt% NaCl solutions using 4 mA/cm². The RA% were decreased when the cathodic polarisation was applied regardless the solution concentration. The loss of RA% was as high as 38% for base metal, 23% for HAZ and 15% for weld metal in the 1 wt% solution. Further increase of NaCl increases the RA% for weld metal and HAZ, to some extent decreases for base metal.

**X-joint**

After SSRT a large reduction in cross-sectional of area was observed for the weld specimens tested in air, as shown in Figure 29. As it is shown, no significant effect on RA% of base metal, HAZ and weld metal was observed for tested samples in 1 wt% and 3.5 wt% NaCl solutions at OCP condition. However, it seems that the obtained result from weld metal tested in air is not logical.
Figure 29. RA% of base steel, welded metal and HAZ of Type A X-joint pipeline steel after SSRT test

The measured RA% in air and different sodium chloride concentration solution under cathodic polarisation with applied 4 mA/cm² current density are shown in Figure 30. It is obvious that the cathodic polarisation drastically decreases the reduction in area of all tested samples prepared from base metal and HAZ. The loss of plasticity for weld metal in the corrosive 3.5 wt% NaCl solution is higher in comparison with base metal tested in 1 wt% NaCl and HAZ sample tested in 3.5 wt% NaCl solution. Based on the obtained results, the RA% of base metal is higher than the HAZ in 1 wt% NaCl but the opposite trend was observed in 3.5 wt% NaCl solution.
5.4.1.2 Time to failure

K-joint

The time to failure can also be taken into account as a measure of susceptibility to SCC. Figure 31 clarifies the relative time to failure vs. test environment of Type A K-joint of base metal, HAZ and weld metal tested specimens, in two different types of sodium chloride solution under OCP condition and applied cathodic polarisation. The tests performed under cathodic polarisation with applied 4 mA/cm², revealed that the time to failure of base metal and weld metal severely decreased in 1 wt% NaCl and 3.5 wt% NaCl solutions compared to OCP condition. The HAZ showed a high reduction in relative time to failure in 3.5 wt% NaCl solutions under cathodic polarisation comparing to the same solution at OCP.
The relative time to failure bar charts for tested samples in four different environments is shown in Figure 32. There were three types of samples in each test environment; base metal, HAZ and weld metal. It is seen that all base metal and HAZ had almost the same relative time to failure in 1 wt% and 3.5 wt% NaCl solutions at OCP condition. However, a considerable reduction in relative time to failure was observed for HAZ tested sample in 3.5 wt% NaCl solutions under cathodic polarisation condition. The relative time to failure of weld metal was higher than base metal and HAZ at OCP condition in 1 wt% and 3.5 wt% NaCl solutions and 3.5 wt% NaCl solutions under cathodic polarisation.

Figure 32. Relative time to failure vs. test solution of Type A X-joint under OCP and cathodic polarisation condition
5.4.1.3 Fractography

Examples of characteristic fracture surfaces of the base metal and its welded joint of Type A K-joint tested in air, 1 wt% and 3.5 wt% NaCl solutions after SSRT test are presented in Figures 33–35.

Air

When a ductile fracture occurs, a typical cup-and-cone surface is observed with three different textures: fibrous zone (central region), radial marks and shear lips. The slant shear region of failed surface is clearly observed in Figure 33 a, b, c. The fibrous region and radial marks are clearly distinguished from each other with a clear boundary as shown in Figure 33 a, b. The presence of the radial marks implies that cracks were initiated in the periphery and propagated in radial direction towards the centre of the tensile specimen as shown in Figure 33 a, b.

All the examined steels presented a mixture of ductile and brittle fracture. The SEM micrographs indicated a similar type of fracture mode for base metal and HAZ. The fracture surface consisted of a mixture of microvoids coalescence (MVC), typically observed in a ductile fracture and cleavage which is a common mechanism of brittle transgranular fracture. Transgranular fracture takes place through tear of the crystals along crystallographic planes in radial marks region. Large voids nucleated from metallic inclusions were also detected, as shown in Figure 33 a', b'. The weld metal suffered from a mixture of brittle-ductile fracture i.e. initially brittle, then ductile, Figure 33 c. The MVC was observed and no cleavage was detected, Figure 33 c'.
Figure 33. SEM images showing the fracture surfaces of the base metal, HAZ and weld of Type A after SSRT testing in air
NaCl 1 wt%

The micrographs fracture surface of the base Type A steel and its welded joint after SSRT testing in 1 wt% NaCl solution are illustrated in Figure 34. Corrosion products appeared on the fracture faces for steel Type A tested in 1 wt% NaCl solution, Figure 34 a, a'. The surface fractures of base metal and HAZ samples investigated in 1 wt% NaCl consisted of quasi-cleavage (i.e. various amounts of transgranular cleavage but with evidence of plastic deformation) and MVC. It can be seen that both base metal and HAZ had the same sensitivity to sodium chloride solution resulting in crack formation and propagation occurring in the same region. The area of fibrous zone for both cases has been slightly increased in 1 wt% NaCl solution. On the other hand, both for base and HAZ the shallower radial marks confirm this claim.
Figure 34. SEM images showing the fracture surfaces of the base metal, HAZ and weld of Type A after SSRT in 1 wt% NaCl solution under OCP condition.
NaCl 1 wt% solution with cathodic polarisation

After SSRT testing in 1 wt% NaCl with cathodic polarisation the failure fracture of Type A base material, HAZ and weld were investigated. The entire surface ruptures showed brittle failure when cathodic polarisation was applied. In other words, in hydrogen charged steels, brittle rupture occurred under the influence of hydrogen. The fracture surface under cathodic polarisation in sodium chloride solution consists of intergranular as well as transgranular crack propagation so that tested samples did not show any plastic deformation after necking and immediately started to break Figure 35 a, b, c. The base metal specimen showed a great number of cleavages on the fractured surface which formed in different crystallographic directions and planes as shown in Figure 35 a. No consequential RA% was observed for the weld metal tested specimen under cathodic polarisation as revealed in Figure 35 c. The fracture surface indicates cleavage face, Figure 35 c', which is a typical feature of brittle fracture.
Figure 35. SEM images showing the fracture surfaces of the base metal, HAZ and weld of Type A after SSRT testing in 1 wt% NaCl solution applying 4 mA/cm² current density for cathodic polarisation
5.4.1.4 Cracks morphology

As it is shown in Figure 36 and Figure 37, it can be clearly seen that the near fracture surface the cracks are big while their number reduced and their size decrease inward. In all tested samples under cathodic protection, it was observed that the cracks were initiated from the surface and propagated into the sample. This observation makes obvious that the most of the cracks are individual or isolated. The cracks were appeared in different directions as clearly as seen on the surface sample regardless of the applied stress direction. The sub-cracks which formed on the surface of the samples under the impact of cathodic polarisation are indicated by arrows.

![Fracture surface and sub-cracks](image1.png)

*Figure 36. SEM image clarifies the presence of sub cracks in 1 wt% NaCl solution with cathodic protection*

![LOM image clarifies the presence of sub cracks due to applied current density in order to cathodic protection in 1 wt% NaCl solution](image2.png)

*Figure 37. LOM image clarifies the presence of sub cracks due to applied current density in order to cathodic protection in 1 wt% NaCl solution*
Figure 38 demonstrates a typical propagated crack on the surface of the failed SSRT specimen.

![Image of a typical crack](image)

**Figure 38. A typical cracks feature appeared on the lateral surface under cathodic protection in 1 wt% NaCl solution**

The spectrum and the chemical composition of the steel in the crack vicinity was analysed and demonstrated in Figure 39 and Table 6, respectively. The presence of the aluminium in the crack vicinity could be evidence of the influence of aluminium particles on the HE mechanism.

![Image of a spectrum](image)

**Figure 39. Spectrum of the chemical composition of the crack vicinity**
Table 6. Chemical composition of the crack vicinity (wt%)

<table>
<thead>
<tr>
<th>Element</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium</td>
<td>2.0</td>
</tr>
<tr>
<td>Aluminium</td>
<td>6.6</td>
</tr>
<tr>
<td>Silicon</td>
<td>1.6</td>
</tr>
<tr>
<td>Chlorine</td>
<td>2.2</td>
</tr>
<tr>
<td>Iron</td>
<td>87.6</td>
</tr>
</tbody>
</table>

5.4.2 Type B

5.4.2.1 Reduction of area

Figure 40 illustrates the RA% of the Type B ordinary steel grade tested in air, 1 wt% and 3.5 wt% NaCl solutions under open circuit potential condition. The weld metal had lower RA% than the base and HAZ in all tested environments except in 1 wt% NaCl solution. HAZ had higher RA% compared with base metal under applied tensile stress in air while the opposite trend was observed in 3.5 wt% NaCl solution. The results show a lower RA% for weld metal in 3.5 wt% NaCl than in 1 wt% NaCl solution.

![Figure 40. RA% of base steel, welded metal and HAZ of Type B K-joint pipeline ordinary steel](image)

Results from measurements in air and 1 wt % NaCl solution with cathodic polarisation are shown in Figure 41. The results show a considerable lower RA% for both base and HAZ under cathodic polarisation in 1 wt% NaCl solution compare to air. The base metal showed a higher RA% than the HAZ with cathodic polarisation.
5.4.2.2 Time to failure

Analysing the load vs. time curves after slow strain rate test, it is presented that applied 4 mA/cm² of current density dramatically resulted in decrease of time to failure, shown in Figure 42. However, only slight decrease was observed in time to failure at open circuit potential comparing to the value obtained from performed test in air.
6 Discussion

6.1 Effect of environment

6.1.1 NaCl concentration on uniform corrosion and SCC

Based on the electrochemistry principle the corrosion rate of the metal in contact with electrolyte strongly depends on conductivity of the electrolyte and the accessibility to oxygen [37]. Dissolved salts, such as NaCl (Na\(^+\) and Cl\(^-\) ions), increase the solution conductivity and thus, enhance the corrosion rate of both base and weld metal of Type A and Type B steel grade, Figure 22 and Figure 23. Due to the lack of an effective passive layer, high strength low-alloyed steels are highly susceptible to uniform corrosion. It is found that the anodic dissolution of the HSLA occurs in the active potential region [39]. The corrosion products (i.e. Fe (OH)\(_2\)) formed on the metal surface are porous, and thus, Cl\(^-\) ions can easily penetrate it and reach the bare surface of the sample [13]. The chloride ions affect the metal surface uniformly and thus the metal uniformly corrodes.

Oxygen content dissolved in the solution also increases the corrosion rate of the steels. Higher corrosion rates (lowest R\(_p\)) were observed for the specimens tested in aerated condition compared with those tested in purged solutions with N\(_2\)-bubbling. Both for base and weld metal of Type B and Type A steel the corrosion rates in aerated 3.5 wt\% NaCl solution were higher than obtained for samples tested in de-aerated 3.5 wt\% NaCl solution.

Although chloride concentration significantly affected uniform corrosion of Type A and Type B steels, it did not have the same influence on SSRT testing. The materials did not show an increased susceptibility to SCC in presence of Cl\(^-\), when 1 wt\% and 3.5 wt\% NaCl solutions were used. According to the obtained SSRT results shown in Figure 24-26, both steels had a ductile fracture mode when tested in air, 1 wt\% and 3.5 wt\% NaCl solutions at OCP condition. The fractured surfaces consisted of a great number of microvoids, Figure 33-34 and Appendix 3, which suggest a typical ductile failure. No evidence of branched cracks, transgranular or intergranular, was found to confirm the SCC occurrence in Type A grade, Appendix 4 b. The failure occurred only under mechanical load and no effect of Cl\(^-\) was observed. In conclusion, NaCl increased the uniform corrosion rate of both steels including weld and base metal however this parameter did not influence the materials susceptibility to stress corrosion cracking.
6.1.2 Cathodic polarisation on hydrogen assisted stress corrosion cracking

The results show that applying cathodic polarisation during slow strain rate testing, prevented uniform corrosion of the steels but increased the risk of hydrogen-assisted stress corrosion cracking.

Hydrogen assisted stress corrosion cracking accompanied by transgranular fracture was found on fracture surfaces of Type A, Figure 35 a, a'. The intergranular cracking reduced the effective load-bearing area and consequently caused overloading with rapid failure. Ductile materials normally experience relatively large non-uniform plastic deformation before fracture point. The absence of non-uniform plastic deformation is a quantitative measure of materials susceptibility to brittle failure. This claim is confirmed by no significant reduction in area.

A drastic decrease in RA% and TTF obtained for Type A and Type B steel under cathodic polarisation confirmed the effect of hydrogen on materials susceptibility to hydrogen- assisted stress corrosion cracking as illustrated in Figure 28, Figure 30-32 and Appendix 1. For the samples tested in air as well as 1 wt% and 3.5 wt% NaCl solutions under cathodic polarisation condition the obtained data from SEM are in good agreement with the calculated relative time to failure, RA% and EL% after SSRT test. The fractured sample in air indicates shear at about 45° around the periphery of the tensile specimen, which underwent biaxial constraint, while the inner zone experienced triaxial condition fractured by planar quick fracture [37].

The fracture surface of tested samples in NaCl solution under cathodic protection consists of regions with intergranular cracking and transgranular cracking as well as the region with microvoids coalescence. In all tested samples under cathodic protection, it is observed that the cracks initiated on the surface and propagated into the materials, Figure 36-38. This is probably due to the diffusion of hydrogen into the material. Cracks rapidly connect to each other leading to a catastrophic fracture i.e. brittle failure, Appendix 4. To conclude, cathodic polarisation drastically increased the susceptibility of both Type A and Type B steel to hydrogen-assisted stress corrosion cracking.
6.2 Material comparison

6.2.1 Mechanical properties

Both steels became less ductile with applying cathodic polarization. The EL% of Type A and Type B steels for base metal, weld metal and HAZ was reduced when cathodic polarisation was applied as shown in Appendix 1 and Table 7-10. The yield strength of most of the samples tested under cathodic polarisation increased. This can be attributed to the influence of solution hardening of hydrogen atoms in the steel lattice [25]. Mechanical tests and microscopy inspections confirm the effect of hydrogen penetration into the specimens. Therefore, hydrogen-assisted stress corrosion cracking can be considered as one of the most dangerous phenomena influencing mechanical properties of the tested steels, able to produce either a loss of ductility or time-delayed fractures.

6.2.2 Effect of microstructure on SCC

The influence of microstructure on near-neutral pH SCC was investigated in this project. The microstructure of the steels depended on the previous heat treatments applied. The microstructure of the high strength low alloy steel after quenching in water is normally composed of lath martensite with body centred tetragonal structure (BCT) and a little retained austenite structure. The martensitic phase appeared like needle-shaped grains and the white regions are austenite that did not have enough time to transform during the rapid quench rate. Reheating the martensite at 665 ºC for 1500 seconds (45 minutes) caused formation of tempered martensite structure. Basically, tempering leads to decomposition of martensite into ferrite and cementite [38]:

\[
\text{Martensite (BCT, single phase) } \rightarrow \text{Tempered martensite (} \alpha \text{ (ferrite) } + \text{Fe}_3\text{C (cementite))}
\]

In other words, the martensite changed to ferrite and cementite plus small amount of austenite retained from the quenching. Type A base metal (quenched and tempered) had a tempered martensitic microstructure and Type B (normalized) a pearlitic and ferritic microstructure. The size of the HAZ depends on the heat input value and the cooling rate [3]. It is well accepted that the microstructure of the fusion region close to HAZ is similar to the quenched steel in water [25]. As shown in Figure 13, Figure 15 and Figure 18, the HAZ microstructure of the Type A with a coarse-grained martensite and retained austenite had higher sensitivity to hydrogen-assisted stress corrosion cracking compared to base metal with fine-grained tempered martensite. According to the Hall-Petch relationship,
steel with larger grain size tends to have smaller yield stress to fracture i.e. less resistance to SCC [29, 31, 39]. The weld metal Type A, with interpenetrating acicular ferrite, a spot of pro-eutectoid ferrite and bainite had the highest susceptibility to SCC, Figure 14 and Figure 18 [3, 40]. Generally, ferritic steels are more susceptible to HE compared to the austenitic and martensitic steel. Furthermore, there was less amount of pre-eutectoid ferrite in the Type A X-joint compared to Type A K-joint probably due to different heat input and cooling rate during welding. This fact explains higher resistance to HE found in X-joint compared to K-joint. Type B steel and its HAZ tested in 1 % NaCl solution showed higher resistance to HE compared to Type A. It is useful to mention that not only the microstructure but also the distribution, shape and size of the ferrite grains also have a considerable effect on the materials susceptibility to hydrogen-assisted stress corrosion cracking. To conclude, obtained results from slow strain rate testing and fractographic observations showed that the untempered martensite in Type A weld metal had higher susceptibility to hydrogen-assisted stress corrosion cracking compared with ordinary steel-Type B.

6.2.3 Base metal, HAZ and weld metal

The results obtained in this study show that base metal, weld metal and HAZ of both Type A and Type B tested steels were not significantly susceptible to SCC in 1 wt% and 3.5 wt% NaCl solutions under OCP condition, Figure 27, Figure 29 and Figure 40. From the measured RA%, it is obvious that Type A base steel showed higher resistance to hydrogen-assisted stress corrosion cracking compared to its weld metal and HAZ, Figure 28 and Figure 30. However, the results also confirm that the Type A weld metal experienced higher loss of plasticity compared to the base metal and HAZ under cathodic protection condition. This means that the materials showed brittle fracture. The results were in good agreement with stress vs. strain and time to failure plots from the SSRT tests. In addition, the base metal of Type B with ferrite and pearlite microstructure tested in 1 wt% NaCl solution under cathodic protection implied better resistance to hydrogen-assisted stress corrosion cracking compared to Type A with martensite and retained austenite structure as shown in Figure 13, Figure 19, Figure 28 and Figure 41. From these results, it can be summarised that susceptibility to hydrogen-assisted stress corrosion cracking was increased using cathodic polarisation for all tested materials.
7 Conclusions

From the study, the following main conclusions can be drawn regarding the susceptibility of Type A and Type B steels grade to general corrosion, stress corrosion cracking and hydrogen-assisted stress corrosion cracking:

1. Higher chloride concentration and dissolved oxygen content in the solution accelerated the uniform corrosion rate of the Type A steel and ordinary steel-Type B.

2. Samples of Type A and Type B were not susceptible to stress corrosion cracking in 1 wt% and 3.5 wt% NaCl solutions under open circuit potential condition. They showed a typical ductile fracture mode.

3. Type A steel grade was presented a susceptibility to hydrogen-assisted stress corrosion cracking when cathodic polarisation was applied.

4. The weld metal and HAZ of Type A had higher susceptibility to hydrogen-assisted stress corrosion cracking compare to base metal, confirmed by small reduction in area (RA%) and time to failure. The loss of plasticity was greater for welded joints than for the base metal.

5. Cathodic polarisation with using 4 mA/cm² increased the susceptibility to hydrogen-assisted stress corrosion cracking for base metal and HAZ of Type B steel.

6. A mixture of intergranular and transgranular cracks were observed for base metal of Type A Q&T due to hydrogen charging both in 1 wt% and 3.5 wt% NaCl solutions.
8 Acknowledgment

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My special thanks to the supervisor and examiner of this project at division of Surface Chemistry and Corrosion at KTH, Inger Odnevall Wallinder, who I would like to thank for providing me with useful guidelines and kind supervision.

Stockholm, August 2011

ROHOLLAH GHASEMI
9 References

13. Electrochemical corrosion behavior of 300M ultra high strength steel in chloride containing environment.


### Appendix 1.

**Table 7. Mechanical properties of Type A, Type B and their welded joints**

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>Test environment</th>
<th>1 wt% NaCl</th>
<th>4 mA/cm²</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Samples</td>
<td>YS (MPa)</td>
<td>UTS (MPa)</td>
</tr>
<tr>
<td>Type A K-joint</td>
<td>Base metal</td>
<td>770</td>
<td>812</td>
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<tr>
<td></td>
<td>HAZ</td>
<td>740</td>
<td>804</td>
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<td></td>
<td>Weld metal</td>
<td>745</td>
<td>796</td>
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<tr>
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<td>688</td>
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</tr>
<tr>
<td></td>
<td>Weld metal</td>
<td>700</td>
<td>765</td>
</tr>
<tr>
<td>Type B K-joint</td>
<td>Base metal</td>
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<td>-</td>
</tr>
<tr>
<td></td>
<td>HAZ</td>
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<td>593</td>
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<tr>
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<td>Weld metal</td>
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<td>653</td>
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**Table 8. Mechanical properties of Type A, Type B and their welded joints**

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>Test environment</th>
<th>1 wt% NaCl</th>
<th>4 mA/cm²</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Samples</td>
<td>YS (MPa)</td>
<td>UTS (MPa)</td>
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<tr>
<td>Type A K-joint</td>
<td>Base metal</td>
<td>755</td>
<td>804</td>
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<td></td>
<td>HAZ</td>
<td>760</td>
<td>834</td>
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<tr>
<td></td>
<td>Weld metal</td>
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<tr>
<td>Type A X-joint</td>
<td>HAZ</td>
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<td></td>
<td>Weld metal</td>
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<td>-</td>
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<td>Type B K-joint</td>
<td>Base metal</td>
<td>765</td>
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<tr>
<td></td>
<td>HAZ</td>
<td>430</td>
<td>558</td>
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</table>
Table 9. Mechanical properties of Type A, Type B and their welded joints

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>Test environment</th>
<th>YS (MPa)</th>
<th>UT S (MPa)</th>
<th>TTF (hr)</th>
<th>EL (%)</th>
<th>RA (%)</th>
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<td>Type A K-joint</td>
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<td>Type B K-joint</td>
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<td>Weld metal</td>
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Table 10. Mechanical properties of Type A, Type B and their welded joints

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<th>Test environment</th>
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<td>UT S (MPa)</td>
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<tr>
<td>Type A K-joint</td>
<td>Base metal</td>
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<td>HAZ</td>
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<td>Weld metal</td>
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<td>HAZ</td>
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<td>Weld metal</td>
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<td>849</td>
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<tr>
<td>Type B K-joint</td>
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<tr>
<td></td>
<td>HAZ</td>
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<tr>
<td></td>
<td>Weld metal</td>
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</table>
Appendix 2.

Figure 43. Schematic representations of the microstructures for an iron–carbon alloy of hypo-eutectoid composition $C_0$ (containing less than 0.76 wt% C) as it is cooled from within the austenite phase region to below the eutectoid temperature [38]

Figure 44. Time Temperature Transformation (TTT) diagram [38]
Figure 45. Continuous Cooling Transformation (CCT) diagram for carbon steel [38]
Appendix 3.

Environment 3.5 wt% NaCl

Sample

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<tr>
<th>Base metal</th>
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<table>
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<table>
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Figure 46. SEM images showing the fracture surfaces of the base metal, weld metal and HAZ of Type A steel grade after a SSRT test performed in 3.5 wt% NaCl solution under OCP
Appendix 4.

Figure 47. LOM images of cracks morphology cause to failure the sample in 1 wt% NaCl solution under: a) cathodic polarisation using 4 mA/cm²; b) OCP