

CRANFIELD UNIVERSITY

SHAMSUDDEEN ASHURAH ABUBAKAR

MONITORING OF STRESS CORROSION CRACKING UNDER
REPRESENTATIVE PIPELINE CONDITIONS

SCHOOL OF WATER, ENERGY AND ENVIRONMENT

PhD

Academic Year: 2019 - 2023

Supervisor: Dr Joy Sumner
Associate Supervisor: Dr Stefano Mori
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ABSTRACT

Pipelines are subjected to various stresses during operation, which are induced from factors including fluid flow, ocean currents, mechanical vibrations, or earth movements. These stresses, in combination with the corrosive environment can cause an increase in pipeline's corrosion rate and, subsequently, lead to stress corrosion cracking. The presence of trace gases (CO_2 , O_2 , H_2S), is expected to have an influence on this susceptibility. As such, the aim of the research is to access the impact of trace gases linked to CO_2 transportation, carbon capture and storage, enhanced oil recovery and other pipeline operations. This is key to understanding whether pipelines are at increased risk of failure.

In this research, the stress corrosion behaviour of API 5L X65, X70, X80 and X100 has been investigated. Tests were conducted in 3.5 % NaCl solution with either N_2 , CO_2 , or mixtures of O_2/N_2 and O_2/CO_2 bubbled through. Liquid temperatures were maintained at either at 5 °C, 15 °C or 25 °C. C-ring and 3-point bending specimens were stressed at 80 % or 95 % of yield strength. Linear polarization resistance monitored corrosion rates. Corrosion extent and morphology were examined by optical microscopy (to measure metal loss), followed by scanning electron microscopy analysis.

The results from baseline experiment (N_2) showed correlations between corrosion rates and both stress and temperature. All samples exposed with mixed O_2/N_2 presented higher corrosion rates by 1 order of magnitude. Their damage morphology consisted of metal loss and pits features. These pits had deeper, elliptical morphology in comparison with N_2 -only data. Results from the pure CO_2 gas showed more rapid corrosion rates than in pure N_2 and mixed O_2/N_2 . However, with change in trace gas mixture from pure CO_2 to O_2/CO_2 , a large increase in corrosion rates of about 70% was observed. Similar morphologies were observed on X65, X70 and X80 samples in solution with pure CO_2 and mixed O_2/CO_2 at all solution temperatures, with a deep undercutting morphology and discontinuous microcracks being observed. In contrast, X100 showed wide, deep ellipse-shaped pits.

Keywords: trace gases, corrosion rate, metal loss, pits, morphology, CO_2 .

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LIST OF ABBREVIATIONS

AE	Auxiliary electrode
Ag/AgCl	Silver-silver chloride
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
B	Stern-Geary constant
β_a	Anodic Tafel Constant
β_c	Cathodic Tafel Constant
CE	Counter electrode
CF	Corrosion fatigue
EAC	Environmental assisted cracking
EDX	Energy dispersive X-ray spectroscopy
E_{corr}	Corrosion potential
EIS	Electrochemical impedance spectroscopy
EL	Elongation
EN	Electrochemical noise
EW	Equivalent weight
FBE	Fusion bonded epoxy
HE	Hydrogen embrittlement
HF	Hydrogen fluoride
HIC	Hydrogen induced cracking
I_{corr}	Corrosion current
IPA	Isopropyl alcohol
LME	Liquid metal embrittlement
LPR	Linear polarization resistance
NACE	National Association of Corrosion Engineers
NaCl	Sodium chloride
NDE	Non-destructive evaluation
NS4	Near-neutral soil solution
OCP	Open circuit potential
OD	Outer diameter

OPS	Office of Pipeline Safety
PP	Potentiodynamic polarization
PIGS	Pipeline inspection gauges
Ppm	Parts per million
Ppt	Parts per thousand
PTFE	Polytetrafluoroethylene
RA	Area reduction
RE	Reference electrode
Rp	Polarisation resistance
RRA	Area reduction ratio
RSPA	Research and Special Programs Administration
SCE	Saturated calomel electrode
SCC	Stress corrosion cracking
SEM	Scanning electron microscope
SSCC	Sulphide stress corrosion cracking
SSRT	Slow strain rate test
T	Temperature
TFR	Time to failure ratio
UKOPA	United Kingdom Onshore Pipeline Operators' Association
WE	Working electrode
Wt.%	Weight percent
XRD	X-ray diffraction

1 INTRODUCTION

For decades carbon steel pipelines have been used to transport various types of fluids (gas or liquid), mixtures of fluids, solids, fluid–solid mixtures, or capsules (freight-laden vessels or vehicles moved by fluids through a pipe) [1]. They are considered to be an effective, economic and safe means of oil and gas transportation around the globe [2,3].

The most commonly installed pipeline materials, used in various locations, both offshore and onshore globally, include API 5L X46, X52, X65, X70 and X80 [4–11]. Table 1-1 shows examples of the currently installed pipelines, their construction materials, locations and the types of fluids transported.

Table 1-1 – Examples of currently installed pipelines, their locations and types of fluids transported [12,13].

Pipeline material	Fluid transported	Location of usage	Company of operation
X65	Sour fluids (fluids containing H ₂ S, HF)	UK North sea	Britannia
X70	Non-sour fluids (fluids containing CO ₂ , O ₂)	North sea, Gulf of Mexico	Statoil, British Petroleum
X80	Non-sour fluid	East Germany	Statoil

Grade X100 is actively being developed to be used as a pipeline material for transportation of crude oil and natural gas [12,13].

The fluids and conditions that pipelines operate in when transporting various types will affect their lifetime, and so must be understood. For example, fluids or gases are often moved at different temperatures, ranging from 5 °C to 90 °C, (both offshore and onshore) [4–11]. To ensure the pipeline operates safely, proper selection of their construction materials is essential, and appropriate material characteristics must be considered to ensure the intended service of the

pipeline [14]. Factors that are considered before material selection for pipeline applications include [2,14-16]

- Product to be conveyed (flow medium),
- Operating conditions (temperature and pressure),
- Location or area of usage (operating environment),
- Fabricability characteristics etc.

The selection of pipeline materials should be made after careful consideration of all conditions to ensure that the pipeline can remain fit-for-purpose throughout its service life [17]. This plays a vital role in setting up the most economical and effective transportation methods and hence will reduce material and corrosion related failures, which leads to savings in costs of production and installation.

1.1 Overview and History of Pipelines

As defined by Liu [1], the term 'pipe' is a closed conduit usually of circular cross section which can be made of any appropriate material such as steel or plastic. Liu [1] and Nayyar et al. [14]. defined pipeline as a long line of connected segments of pipe supported by hangers, with pumps (for liquid) or compressors (for gas), fittings (e.g., valves, couplings), auxiliary equipment (e.g., flow meters, pigs, transducers, cathodic protection systems) and automatic control systems including computers and programmable logic controllers needed for operating the system. Pipelines generally have a minimum diameter of 4 inches (102 mm) and a minimum length of 1.6 km. The largest and longest pipelines can have a diameter of more than 120 inches (3048 mm) and a length of over 1609 km [1].

The use of pipelines has a long history [1]. As early as 400 B.C., the Chinese used bamboo pipes wrapped in wax to transport natural gas to their capital, Beijing, for lighting [1,18,19]. In 500 B.C., the Romans used lead pipes in their aqueduct system to supply water to Rome and other developed cities [1,18,19]. According to Liu [1] clay pipes were used as early as 4000 B.C. for drainage purposes in Egypt. Milz [19] further discussed that Egyptians used copper pipe to transport water in 3000 B.C., while the Cretians used earthenware pipe to

transport water from 2000 B.C. to 1500 B.C. and the Greeks used earthenware, lead, bronze and stone pipes from 1600 B.C. to 300 B.C. During that era, blacksmiths connected the metal pipes together by simply hammering the red hot ends together [19].

The use of steel or iron pipelines started in the UK in 1820, when cast iron musket barrels left over from Napoleonic wars were used to transport gas made from coal and at the same time (early 1821), hollowed out logs were used in the USA to transport natural gas used for lighting [18,19]. The oil and gas industry first started to use steel pipelines in the USA in the mid-1800s. In those days, oil was transported in barrels on rivers by horse-drawn barges [18,19]. This was dangerous because weather and labour disputes often disrupted flow of the oil. In 1879, with the discovery of oil in Pennsylvania (USA), the first long-distance oil steel pipeline was built, with a length of 175 km with a 6 inches (152 mm) diameter [1,18,20]. This pipeline was used to transport crude oil to tank cars for the New York market. According to Liu [1] and Kennedy [20], nine years later, a 140 km, 8 inches (203 mm) diameter pipeline was built to transport natural gas from Pennsylvania to Buffalo (New York).

The 19th century was a time of scientific and technological advances in many pipeline industries; for example: lap-jointed wrought iron pipe, riveted or flanged together, became available [19]. One milestone achieved in the late 1920s was the development of electric arc welding to join pipes which made it possible to construct leak proof, high pressure, and large diameter pipelines [19]. The Introduction of large, seamless steel pipe was another milestone achieved in the 1920s [1,19]. These advances, made in the early 20th century paved the way for the pipeline industry to create more innovations in pipeline technology. Some of these major innovations made since 1950, include:

- The introduction of new pipeline materials such as ductile iron [18].
- Integrity monitoring of pipelines (e.g., use of PIGS (pipeline inspection gauges) through pipes to detect wall corrosion or cracks of pipelines) [19].
- Multiphase flow in pipelines (flow of different products in a single pipeline) [19].

- Development of cathodic protection systems (use of sacrificial anode or impressed current) and external coatings to reduce pipeline corrosion rate and extend its service life [1].
- The use of computers to control and operate pipelines [1].

The use of pipelines to transport oil and gas is presently evolving and is still considered the most economical and safe means of transportation. As such, pipelines are an important method of conveying materials needed for society. However, their performance needs to be reliable, as failure can have significant consequences. Corrosion of pipelines is one of the major life-limiting factors associated with their usage. As such, the following sections will raise both the materials from which pipelines are typically made, and then the mechanisms of corrosion which can contribute to their failures.

1.2 Chemical Compositions and Microstructures of Pipeline Carbon Steels

Due to their size, pipelines must be made from readily available, easily fabricated and relatively cheap materials. One such material class is carbon steel. Carbon steels are alloys in which iron serves as the principal element, with a carbon content typically not exceeding 2.5 wt.% [21]. It is the most commonly used alloy in the oil and gas industry due to its inexpensiveness, easily fabricability and readily availability [21,22], meaning that nearly 80 % of all pipeline components in the oil and gas industry are made from carbon steels [21].

In carbon steels, the addition of small amounts of carbon to iron produces an interstitial solid solution without changing the microstructure. However, the final properties can be tailored by the additions of other elements (such as nickel, copper, chromium etc.) as discussed in section 3.1 and application of various type of heat treatments as reported in section 2.3.2.1.1. Together, these produce carbon steels with various microstructures [21,22]. The chemical compositions of the most frequently used pipeline carbon steels are presented in Table 1-2.

Table 1-2 - Chemical compositions of commonly used pipeline carbon steels (w t.%) [4,6,7,9].

Material grade	C	Mn	Si	S	P	Mo	Cr	Cu	Ti	V	Ni	Fe
X46	0.25	1.28	0.34	0.009	0.014	0.030	0.020	-	-	-	0.010	98.047
X52	0.08	1.05	0.26	0.003	0.019	-	0.020	0.019	0.002	0.054	0.020	98.473
X65	0.10	1.43	0.19	0.001	0.007	0.160	0.120	0.070	-	0.070	-	97.832
X70	0.027	1.51	0.10	0.002	0.014	0.004	0.270	0.280	0.011	-	0.160	97.494
X80	0.06	1.91	0.35	0.001	0.013	0.157	0.201	0.023	0.017	0.001	0.036	97.231
X100	0.06	1.96	0.22	0.002	0.007	0.180	0.020	0.210	0.014	-	0.300	97.027

Carbon steels can form several types of phases or mixtures of phases (microstructures) depending on the composition, type of heat treatment and cooling rate carried out on the steels. Phases include, ferrite, martensite, cementite, austenite, etc, and microstructures include pearlite and bainite [21,23] etc. Figure 1-1 show micrographs of the common carbon steel microstructures.

Ferrite grains are a major component of most carbon steels, and can further be classified into acicular ferrite, polygonal ferrite, allotriomorphic ferrite, globular ferrite and idiomorphic ferrite depending on the grain morphology [21,23]. Figure 1-2 shows examples of these ferrite grain structures. The production mill's annealing temperature ($T < 1000\text{ }^{\circ}\text{C}$) determines the grain size of a metal or alloy, with grain size decreasing with decreasing mill annealing temperature [23], and the processing impacts the grain shape. As will be seen in section 2.3.2.1, microstructures that are more susceptible to stress corrosion cracking (SCC) are characterised by high yield strength, high residual stress, high hardness, small and fine grain shapes [22,24].

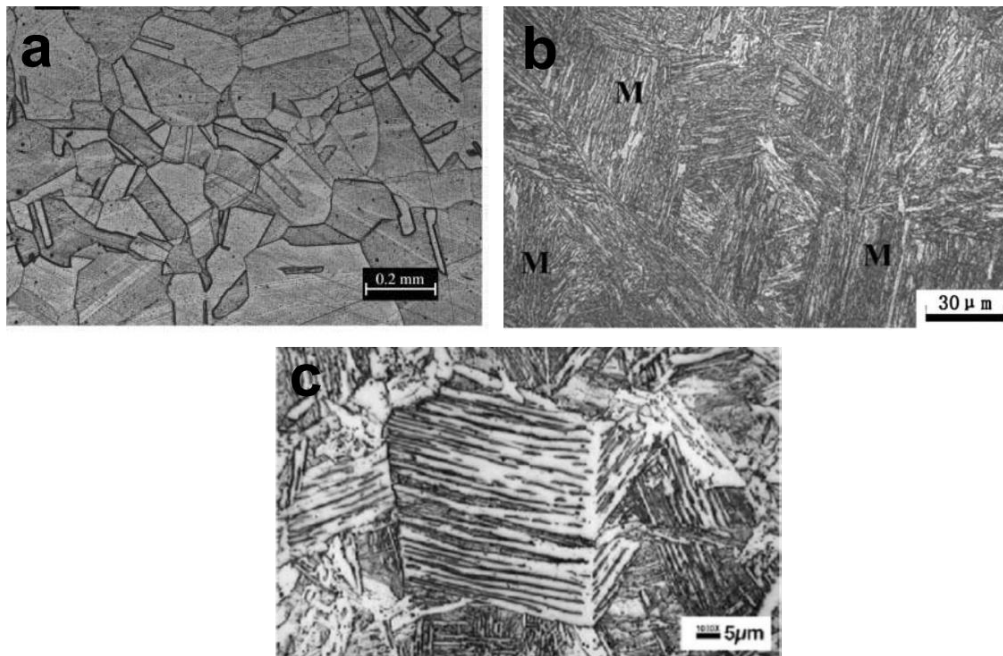


Figure 1-1 - Example micrographs of different types of microstructures; (a) austenite [25], (b) martensite [26], (c) bainite [27].

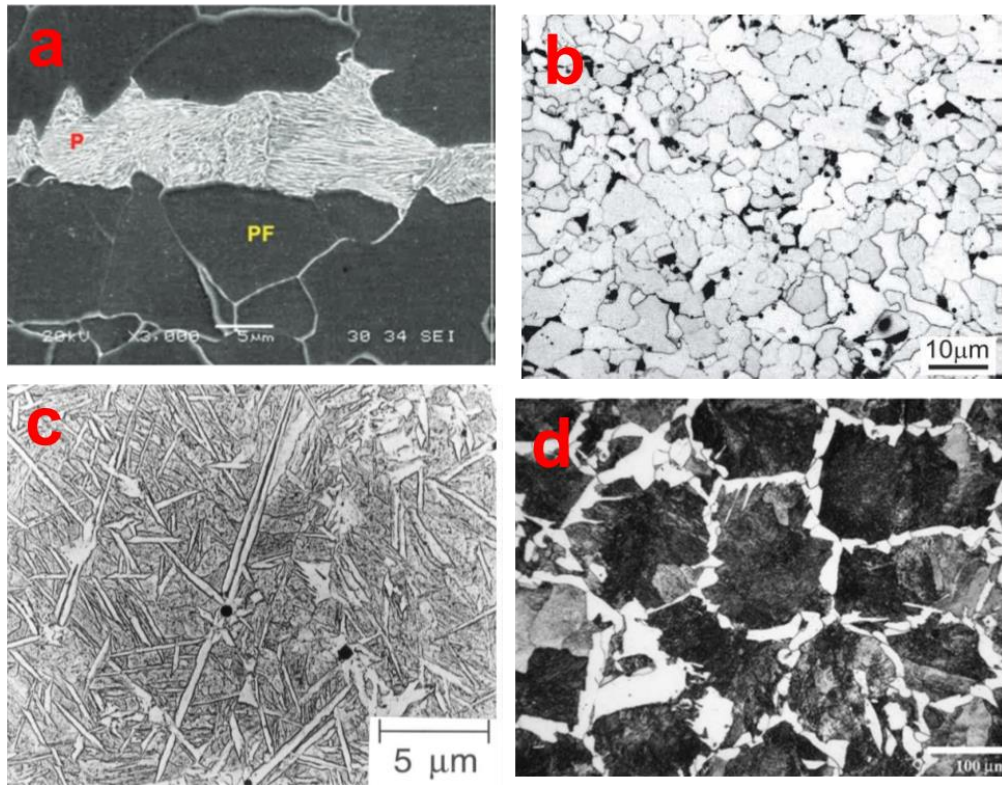


Figure 1-2 - Examples of ferrite grain structures; (a) PF: polygonal ferrite, P: pearlite [28], (b) globular ferrite (white); grain boundary pearlite (black) [29], (c) acicular ferrite [30], (d) allotriomorphic ferrite (white); pearlite (black) [31].

1.3 Corrosion of Pipeline Carbon Steels

Corrosion is defined as the destruction or deterioration of a metal that results from a reaction with its environment [22,32,33]. Corrosion in both onshore and offshore pipelines is a naturally occurring phenomenon and is regarded as one of the major causes of pipeline failures [2,3,32], with corrosion damage accounting for about 20–40% of recorded pipeline incidents and failures [34].

Corrosion of pipeline carbon steels is affected by several factors; namely [21,22, 35]:

- The chemical composition and microstructure of the steel.
- The temperature of the environment.
- The presence of oxidizers in the corrosive medium (O_2 , CO_2 , H_2S , etc.).
- The composition and concentration of the corrosive medium.

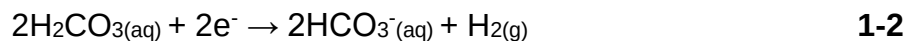
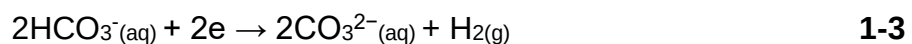
- The pH of the medium.
- The applied stress on the steel.

In terms of temperature dependence, corrosion is accelerated by increasing temperatures as for most chemical reactions. However, the type of corrosive environment also determines the corrosion behaviour of metals or alloys at a particular temperature [21,22].

The presence of oxidizers such as dissolved oxygen, carbon-dioxide or other oxidizing species (including ferric ions in corrosive environments) have a pronounced influence on the corrosion susceptibility of metals or alloys [22,36, 37]. When oxygen is present in high amounts in a corrosive medium, it increases its aggressiveness, by accelerating the oxidation reaction of the metals, leading to high anodic dissolution and subsequent may lead to SCC as will be discussed in section 2.3.2 [9,21,35]. Furthermore, carbon-dioxide is understood for its high impact on corrosion and when present in corrosive environment produces hydrogen ions that cause hydrogen embrittlement on pipeline steels [22]. This causes premature brittle fracture of normally ductile alloys under applied stresses less than the yield strength of the materials, and can also lead to premature failure [6,21,38]. Johnson et al. [39] stated that increasing CO₂ concentration from 0.5 wt.% to 25 wt.% in NS4 solution (near-neutral simulated soil) accelerates crack growth rate during cyclic loading.

The corrosion reactions encountered in aqueous CO₂ medium can be explained thus; CO₂ combines with H₂O to form H₂CO₃ (carbonic acid), H₂CO₃ then further dissociates into HCO₃⁻, H⁺ and CO₃²⁻ [40,41].

The main cathodic reactions are the reduction of H⁺, H₂CO₃ and HCO₃⁻ as presented in equation 1-1 to 1-4 [42,43]:



The reactions occurring at the anodic site are the dissolution of Fe (iron) then followed by formation of FeCO_3 (iron carbonate) as shown in equation 1-5 to 1-6 [42,43]:



More detailed discussion on electrochemical corrosion mechanism is covered in section 2.3.1.

Offshore pipelines are subjected to more corrosive environments in comparison with onshore pipelines due to the presence of chlorides and other halide ions, fluid flow in combination with solid particles and macro-organisms in seawater [44]. The presence of chlorides in seawater increases electrical conductivity. This produces conditions favourable to pitting as discussed in section 2.3.4 and other forms of localized and general corrosion. Fluid flow and/or in combination with solid particles can cause erosion attack on pipeline carbon steels. This can lead to reduction in pipeline wall thickness and subsequently may lead to failure [22,44,45]. At ambient seawater ($25^\circ\text{C} \pm 2^\circ\text{C}$) the corrosion rate of carbon steels is in the range of 0.13-0.41 mm/year [44,45].

Pipelines are subjected to various stresses during their operations. For example, stress from internal fluid movement or other external forces such as, mechanical vibration from near-by equipment, flood, heavy ocean currents, earth movement, etc. When pipelines are under these stresses and in the presence of a corrosive environment, they can be susceptible to stress corrosion, commonly known as stress corrosion cracking. Figure 1-3 show an example of a failed gas pipeline due to SCC.

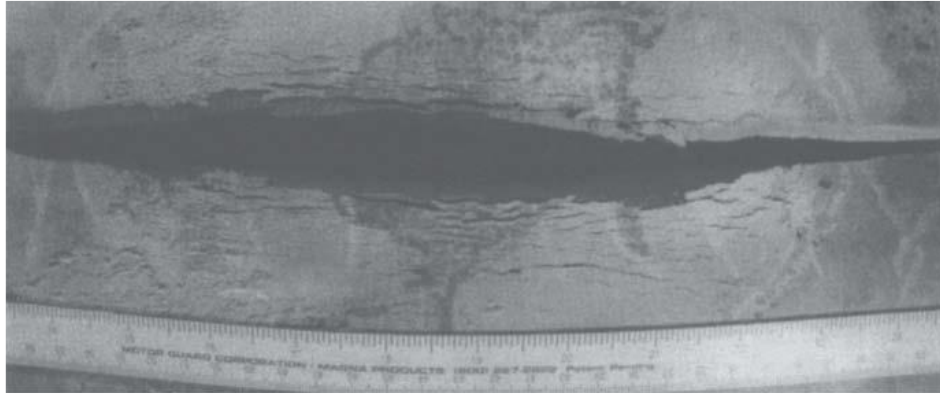


Figure 1-3 - Example of SCC on a gas pipeline [46].

Stress corrosion cracking is caused by the combined action of simultaneous mechanical stress and a specific corrosive environment that a metal or alloy is susceptible to [22,38,47]. For SCC to occur on a metal or alloy, the following conditions must be met simultaneously: specific conditions to promote crack initiation and propagation must be present; the metallurgy of the metal or alloy must be susceptible to SCC in the specific environment; and there must be an applied stress that exceeds a certain threshold value that the metal or alloy can withstand [21,38,46]. The applied stress can originate from external loads, temperature fluctuations, internal metal stress induced by heat treatment or residual stress from welding or fabrication [22,46,47].

SCC propagates trans-granularly and/or inter-granularly or may be branched depending on the type of metal/corrosive environment combination [21,38,46, 47]. Figures 1-4a and 1-4b, respectively show examples of trans-granular and inter-granular SCC morphology on pipeline carbon steels.

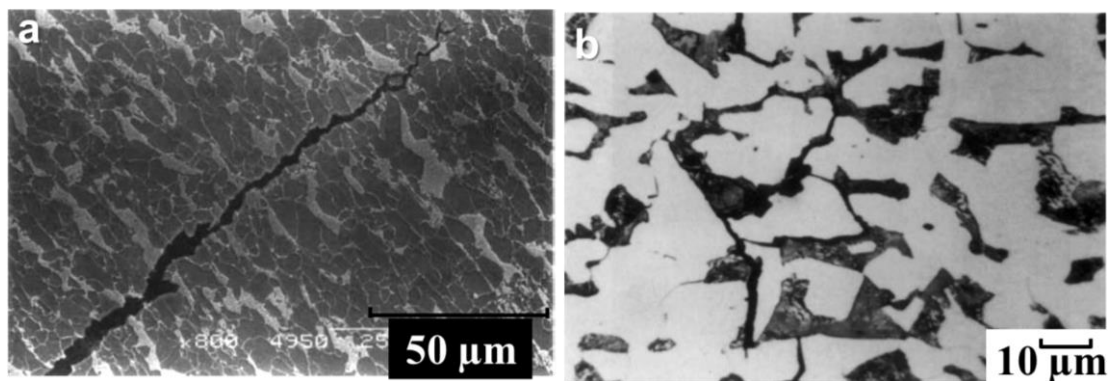


Figure 1-4 - Typical SCC morphology on pipeline carbon steel surfaces; (a) trans-granular mode of SCC (cracks on the steel surface propagate across the grain boundaries); (b) inter-granular mode of SCC (cracks on the metal surface propagate along the grain boundaries [48].

Generally, two types of SCC have been reported for pipeline carbon steels in the literature: high pH SCC and near-neutral pH SCC. High pH SCC is characterised by an intergranular mode of cracking and has been investigated in concentrated carbonate/bicarbonate environments with pH values higher than 9. On the other hand, near-neutral SCC (pH = 6–8) is characterised by a trans-granular cracking mode and is associated with dilute carbonate/bicarbonate medium or in seawater environment where the pH level is between 7-8 [4,5,9,49,50].

1.4 Research Gap

The risk of SCC occurrence on pipelines is continuously increasing due to its continuous usage in transportation of carbon-dioxide and in carbon capture and storage. Carbon capture and storage as the name implies is the capture of CO₂ emissions from power generation plants and industrial processes (such as burning fossil fuels, steel production, cement production etc.) and then transported from production area via pipelines or ship to storage facilities [40]. With pipelines being the major preferred means of CO₂ transportation to their storage location, the impact of CO₂ on stress corrosion of the pipelines is also a major concern in its usage [51]. The risk of hydrogen embrittlement of pipeline steels, associated with CO₂ transportation is a major concern in their operation

[6]. Hydrogen embrittlement results in loss of ductility of the steels and potential formation of cracks or blisters, especially when under high pressure [51,52].

Pipelines are also used in transportation of various oil and gas products. These products contain mixtures of different corrosive elements and trace gases (O_2 , CO_2 , H_2S etc.). Trace gases can also be present in the surrounding environment (onshore or offshore) in which the pipelines are installed and operated. SCC is considered a major form of deterioration of steel structures and has been reported to cause over 8 % of offshore pipeline damages [53]. As such, much research is now focused on environmental assisted cracking (EAC) due to the combined effect of corrosion and applied stress. However, detailed understanding of corrosion behaviour before failure of pipeline carbon steels in presence of trace gases and applied stress under marine environmental conditions has not yet been researched and reported.

The impact of CO_2 on SCC of pipeline carbon steels in water under applied stress have been studied by few researchers [5]. However, the impact of O_2 alone or with CO_2 on the SCC of offshore pipeline carbon steels under applied stress in seawater has not yet been reported and understanding the corrosion behaviours of the pipeline steels in the different operating conditions is the basis prior to their installations and usage. As such, this research focuses on investigating the impact of trace gases and their influence on SCC of representative offshore pipeline carbon steels in different simulated seawater operating conditions. The impact of CO_2 on pipeline carbon steels encountered during its transportation in seawater will be assessed. The impact of trace gas mixtures of O_2/CO_2 , O_2/N_2 encountered during CO_2 transportation and from the surrounding seawater environment during the service life of representative offshore pipeline carbon steels will also be assessed.

It is essential to understand the effect of these gases on SCC of pipeline carbon steels, as they play a vital role in setting up the most economical and effective corrosion mitigation strategies and hence will reduce corrosion related failures, leading to savings in costs of production. Failure of these pipelines can impose

serious risks to human life and can present economic and environmental problems.

1.5 Aim and Objectives

The aim of this research is to study the corrosion behaviour and cracking mechanisms of representative offshore pipeline carbon steels under varying simulated seawater environmental conditions and provide a comprehensive explanation of how trace gases and changing temperature affect their corrosion behaviour.

The following objectives have been set in order to achieve the stated aim:

1. To monitor and evaluate the effect of temperature and trace gases (N_2 , O_2 and CO_2) on the corrosion rate and cracking mechanism of representative offshore pipeline carbon steels.
2. To monitor and assess the impact of different experimental methods of applying stress, applied stress levels and specimen surface damage on corrosion rates, morphology, crack initiation and propagation mechanism.
3. To propose a corrosion mechanism for the initiation of SCC on these carbon steels in the various simulated seawater environmental conditions.

1.6 Thesis Structure

This report is structured into ten chapters as discussed below:

- Chapter 1 contains the overview, history and usage of pipelines. Corrosion, chemical composition and microstructure of pipeline carbon steels are discussed. Research gap, aim and objectives are also highlighted.
- Chapter 2 presents detailed discussion on major causes of pipeline failures. Seawater and its characteristics, such as composition, temperature variation, solubility of trace gases are discussed. Literature review on stress corrosion cracking and factors affecting it which is the main focus of this research are presented. Laboratory techniques for

evaluating the susceptibility of metals to SCC and for monitoring the change in corrosion rates with time are discussed.

- In chapter 3, the different methods and operating procedures carried out to monitor and access the stress corrosion cracking susceptibility of carbon steels are presented. Electrochemical corrosion monitoring and post-exposure analysis techniques are presented.
- Chapter 4 presents the results obtained from the exposed specimens in simulated 3.5 % NaCl solution with N₂ at 5 °C and 25 °C. This includes corrosion rates and potentials, metal loss, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis.
- Chapter 5 discusses the results obtained from the exposed specimens in simulated 3.5 % NaCl solution with CO₂ at 5 °C, 15 °C and 25 °C. This includes corrosion rates and potentials, metal loss exceedance, SEM and EDS analysis, tensile strength test, hardness analysis and metal surface roughness.
- Chapter 6 presents the results obtained from the exposed specimens in simulated 3.5 % NaCl solution with O₂/N₂ (20%/80%) at 5 °C and 25 °C. This includes corrosion rates and potentials, metal loss exceedance, SEM and EDS analysis, tensile strength test and hardness analysis.
- Chapter 7 presents the results obtained from the exposed specimens in simulated 3.5 % NaCl solution with O₂/CO₂ (20%/80%) at 5 °C, 15 °C and 25 °C. This includes corrosion rates and potentials, metal loss exceedance, SEM and EDS analysis, tensile strength test and hardness analysis.
- Chapter 8 contains general discussion on all obtained results, including corrosion rates and potentials of the exposed carbon steels in all the different test conditions, metal loss exceedance, SEM analysis results, tensile and hardness tests results. Evaluation of all obtained data and their impact in the real pipeline world is also presented in this chapter.
- Lastly, conclusions of results and recommendations for future work are presented in chapter 9.

2 LITERATURE REVIEW

In this chapter the various offshore pipeline carbon steels currently in use worldwide and major causes of pipeline failures are highlighted. This includes discussing the alloy properties important to pipeline performance, which must be considered in this research. The characteristics of seawater, which mainly affect the corrosion of pipeline carbon steels, have been outlined. Stress corrosion cracking and factors affecting it are discussed. In addition, brief reviews of the other corrosion mechanisms, such as hydrogen embrittlement, pitting and galvanic corrosion, are discussed briefly. Laboratory techniques for evaluating the susceptibility of metals to SCC and corrosion rate monitoring techniques are also presented. The various methods currently in use for controlling and monitoring corrosion of pipelines are also briefly covered.

2.1 Seawater and its Characteristics

The salt content of seawater mainly determines the corrosion susceptibility of metal or alloys. Other pertinent factors that determine corrosion behaviour of a material in seawater are; amount of dissolved oxygen, temperature and flow rate of the seawater. Furthermore, plants, microorganisms or other aquatic animals can directly or indirectly have an impact on the corrosion behaviour of a metal or alloy [54,36].

2.1.1 Salinity of Seawater

The salt content of seawater is defined as the total amount of salts in 1 kg of seawater (g/kg) [36], while its salinity is measured by the amount of chloride in the seawater. Highest salinity levels in seawater varies with location, higher salinities are encountered in regional areas, with high evaporation rates. The level of salinity decreases poleward and near equator as evaporation decreases and with high precipitation [55]. Furthermore, level of fresh water and other riverine discharges into the sea can also lower its salinity level. Table 2-1 shows the variations in salinity of seawater around the world. The salinity of seawater is calculated as [54- 56]:

Chlorinity is the total amount of halide in the seawater which is commonly expressed as chloride [54]. Salinity and chloride content are measured in parts per thousand (ppt) or grams per kilogram (g/kg).

Table 2-1 - Salinity of seawater around the world oceans [36,54,55].

Type of Sea	Total dissolved substances, g/kg
Baltic Sea	8
Black Sea	22
Irish Sea	32.5
North Sea	35
Open Sea	33 to 37
Atlantic Sea	37
Persian Gulf	39-42
Red Sea	40-41
Mediterranean Sea	41
Caspian Sea	130
Dead Sea	260

2.1.2 Composition of Seawater

The major constituent of seawater is generally 'table salt' (sodium chloride), and it is regarded as the main cause of seawater's corrosive nature [54]. However, seawater contains other dissolved gases and, certainly near to the surface, it well oxygenated. The bicarbonate concentration of seawater causes the pH to be buffered at a pH level of 8.2 ± 0.1 . pH of seawater is lowered due to influx of fresh water to a value of about 8. Lower pH values can also occur due to presence of acidic compounds such as H_2S , CO_2 in the seawater [54,55].

Furthermore, seawater's composition is significantly affected by seasonal changes. This include temperature cycles from summer to winter, 'red tide' with an absence of oxygen, and the presence of planktonic organisms which can increase the amounts of solids in seawater [57]. Table 2-2 shows seawater compositions and the concentrations of dissolved substances for some global locations.

Table 2-2 - Composition of seawater around the world oceans

Elements, g/kg	Na	Mg	Ca	K	Cl	SO ₄	HCO ₃	Br	Total
Sea type									
Open Sea [54]	10.556	1.272	0.400	0.380	18.98	2.649	0.14	0.065	34.442
Atlantic Ocean, USA [36]	10.59	1.292	0.404	0.403	19.20	2.664	-	-	34.550
Mediterranean Sea [58]	10.8	1.3	0.4	0.39	19.4	3.0	-	0.07	35.36
Dead Sea [58]	33	36	13	6	181	1	-	4.5	274.5
Gulf of Kuwait [59]	-	1.69	0.4	-	24.0	3.4	-	0.08	46.00
Annapolis Maryland, USA [36]	3.250	0.397	0.137	-	5.770	0.833	0.01	-	10.397

2.1.3 Solubility of Trace Gases in Seawater

The amount of dissolved oxygen in seawater has a major impact on its corrosion behaviour. Oxygen reduction is regarded as the most common cathodic corrosion reaction in seawater and it is involved in the passivation of most metals or alloys in seawater [54,56,60]. As such, the impact of oxygen can be varied. By allowing faster electrochemical reactions, corrosion can become more rapid. However, oxygen and other species can cause some scales to form to limit corrosion (while most noticeable in the formation of Cr_2O_3 over stainless steel, other oxides/carbonates/etc can form on carbon steels).

In general, the solubility of trace gases in seawater decreases with increasing temperature and salinity levels [56]. Table 2-3 show the concentration of dissolved oxygen in equilibrium with air at varying temperatures and salinity levels. As such, the oxygen concentration in surface seawater can be as high as 11-12 ppm in the Arctic region and as low as 6 ppm in tropic region [56]. Saturation of dissolved oxygen in seawater occurs only at its surface and can become supersaturated due to photosynthesis by marine plants, algae or by wave movement or action. However, in highly polluted harbours, ports and coastal waters, oxygen concentration level can fall to zero [36,56]. In addition, variation in oxygen concentration changes with influx of fresh water and depth. Table 2-4 show the average concentration of dissolved gases in seawater at atmospheric pressure. As oxygen concentration in seawater is dependent on many factors [36], the impact on corrosion must be considered.

Table 2-3 - Concentration of dissolved oxygen in equilibrium with air with change in temperature and salinity level [36,56].

Salinity, g/kg	0	8	16	24	31	36
Temperature, °C	Oxygen solubility, ppm					
0	14.6	13.9	13.1	12.4	11.8	11.4
5	12.5	11.9	11.3	10.7	10.2	9.9
10	10.9	10.4	9.8	9.4	8.9	8.7
15	9.5	9.1	8.7	8.2	7.9	7.7
20	8.5	8.1	7.7	7.3	7.0	6.8
25	7.6	7.2	6.9	6.6	6.3	6.2
30	6.8	6.5	6.2	6.0	5.7	5.6

Table 2-4 - Average concentration of dissolved gases in seawater at atmospheric pressure [36].

Gases	Concentration	
	ppm	mL/L
Oxygen	0-16	0-12
Carbon dioxide	64-107	33-56
Nitrogen	10-18	8-15
Argon	0.4-0.7	0.2-0.4
Helium and Neon	0.3×10^{-4}	1.7×10^{-4}

2.1.4 Sea Surface and Subsurface Temperatures

Surface seawater temperatures are highly variable and influenced by factors such as location and season. While deep waters have temperatures typically in the range of 2 °C and 4 °C, surface temperatures are more variable. Normal seawater temperature in the oceans varies between 4 °C and 25 °C, but in tropical regions it can reach about 30 °C. In Polar regions, when ice begins to form, the temperature can reach a freezing point of about -2 °C [36,55,60]. In

addition, seasonal variations at a particular locations, depending on the elevation of the sun and surface currents, means that temperature variations in the range of ± 5 °C, are observed, caused by the large thermal capacity of water. Table 2-5 shows the average annual sea surface temperatures across the world's sea.

Table 2-5 - Average annual sea surface temperatures across the world oceans in the range of years indicated.

Sea type	Average sea surface temperature, °C		
	Annual mean	Maximum	Minimum
Active Atlantic Mediterranean sea from 1982- 2012 [61]	19.2	22.00	18.51
Black Sea from 1982 to 2012 [61]	15.0	23.2	7.5
North Sea from 2014 to 2016 [62]	11.0	11.4	10.6
Dead Sea from 1992 to 2002 [63]	27.2	33.7	21.5
Red Sea from 1994 to 2015 [64,65]	28.2	31.1	25.0
UK coastal waters in 2014 [66]	12.3	15.9	8.8
Icelandic Sea from 1991 to 2004 [67]	5.7	8.3	4.2

2.2 Causes of Pipeline Failures

Pipeline incidents and failures due to corrosion have been documented by several bodies such as; regulatory agencies, trade journals, articles, internet, etc. [2,68,69,4]. Failures of pipelines can cause detrimental impact on the industry including loss of lives or injuries to employees, damage of properties and possible environment hazards such as pollution.

Offshore pipeline failures are usually caused by vibrations (flow-induced and/or mechanical-induced), fatigue, equipment defects and/or material, erosion, crack

of weld joints, corrosion, improper equipment installation and/or repairs and third-party damages [70]. According to Roberge [71], U.S. Department of the Interior compiled data on offshore pipeline failure analysis collected for over 30 years, which showed that of all the 4000 thousand pipeline failures and incidents in the Gulf of Mexico, 55 % where caused by corrosion damage, with 70 % and 30 %, respectively from external and internal corrosion damage [71]. Figure 2-1 show the offshore pipeline failure statistics in the Gulf of Mexico.

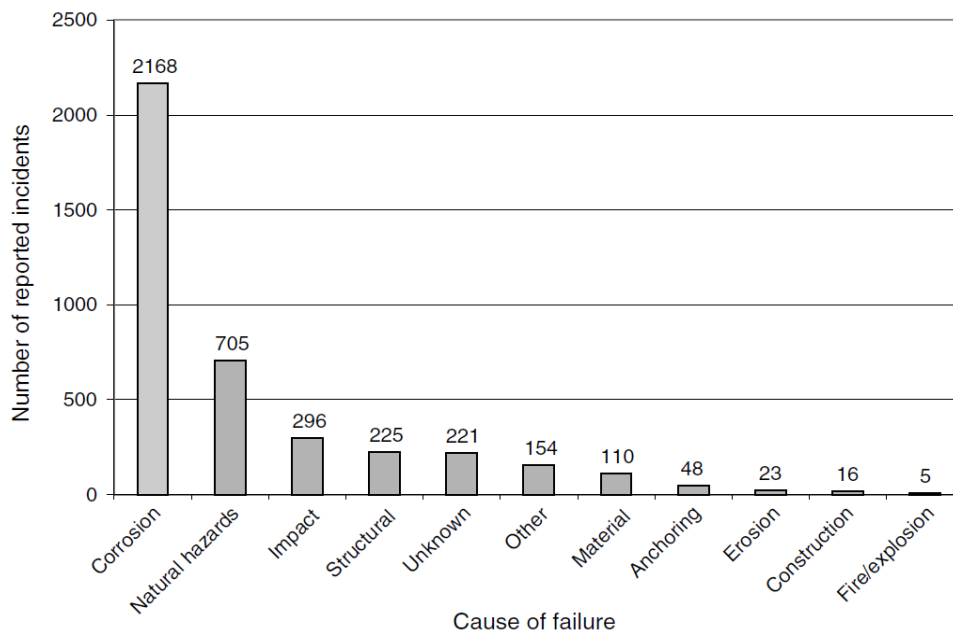


Figure 2-1 - Offshore pipeline failure statistics in the Gulf of Mexico. As shown corrosion damage is the major cause of pipeline failures, with 2168 reported incidents for the given period of analysis [71].

The US Department of Transportation’s Research and Special Programs Administration, Office of Pipeline Safety (RSPA/OPS) compiled data on pipeline accidents and failures with their causes. These compiled data show that “outside forces” damage contributed to a higher number of pipeline accidents and failures [2]. According to Menon [2], failure of onshore pipelines due to outside forces includes natural causes such as lightning, heavy flood and rains, earth movement, high winds, high temperature and other third-party damages. Figures 2-2 and 2-3, respectively, shows pipeline failure statistics in the USA over a 20 year period (1993–2012) on its 800, 000 km network of onshore liquid (petroleum

and petroleum products) and natural gas pipelines [32]. Figure 2-4 shows pipeline failure analysis in the UK from 1962-2013 on its network of onshore liquid and natural gas pipelines carried out by the United Kingdom onshore pipeline operators' association (UKOPA) [3].

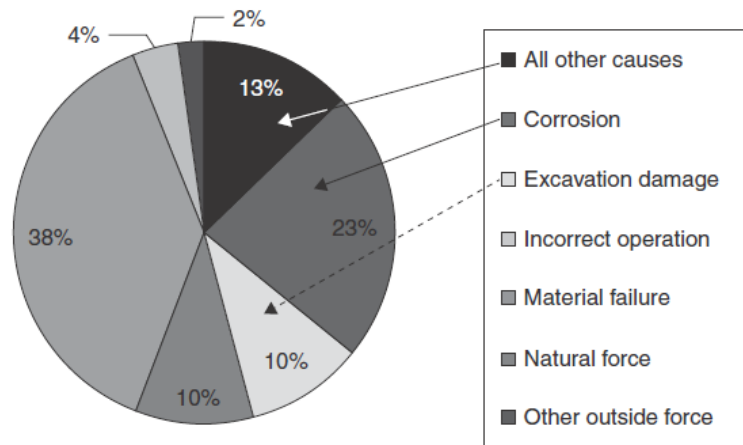


Figure 2-2 - Causes of pipeline failures in USA from 1993-2012 (liquid pipelines) [32].

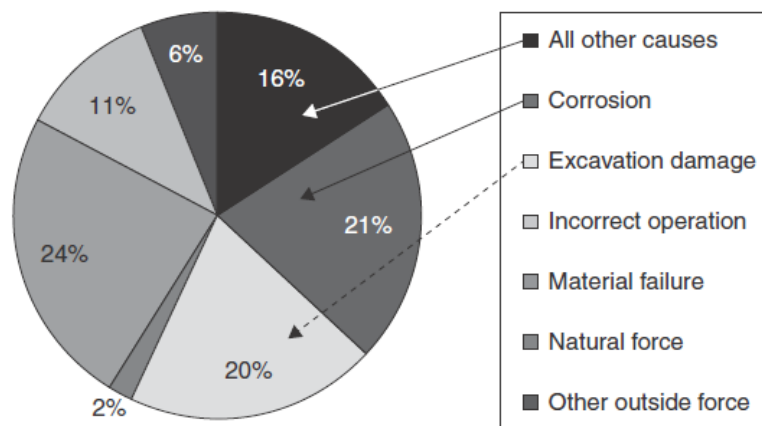


Figure 2-3 - Causes of pipeline failures in USA from 1993-2012 (natural gas pipelines) [32].

As shown in Figures 2-2 and 2-3, corrosion is one of the major causes of pipeline failures in these statistics, causing 23 % of failures for liquid pipelines (Figure 2-2) and 21 % for natural gas pipelines failure (Figure 2-3). Material failures, such as joining methods (riveting, welding) has the highest percentage of pipeline failure with 38 % for liquid pipelines and 24 % for natural gas pipelines.

Excavation damage (where pipelines are impacted by earth moving equipment, piling machines) is also a major cause of pipeline failures in both the liquid and natural pipelines.

Pipeline failures can have detrimental and deadly consequences when they occur. Table 2-6 show the consequences of the liquid and natural gas pipeline failures from 1993 to 2012 as shown in Figures 2-2 and 2-3, respectively.

Table 2-6 - Consequences of pipeline failures in the USA from 1993-2012 [32].

Cause of failures	Liquid pipelines		Natural gas pipelines	
	Fatalities	Casualties	Fatalities	Casualties
Excavation damages	12	38	15	51
Corrosion failures	1	18	13	4
Material failures	4	12	8	71
Incorrect operations	9	20	0	9
Natural forces	0	1	0	2
Outside forces (other)	3	5	0	13
All other causes	10	43	6	38

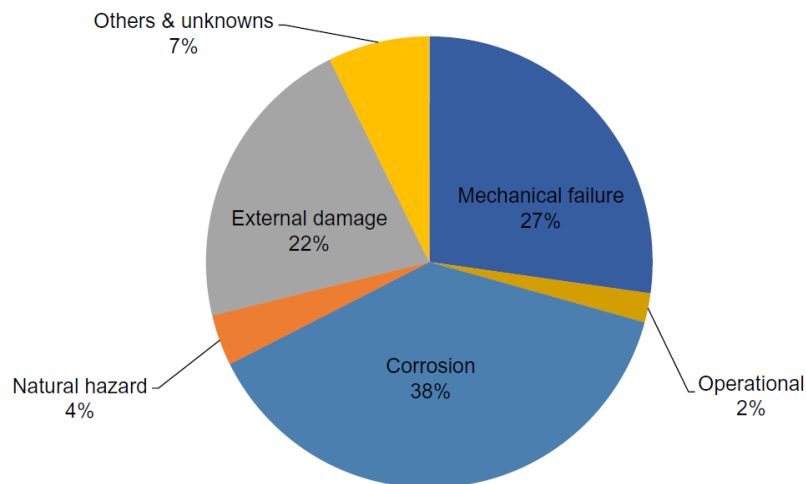


Figure 2-4 - Causes of pipeline failures in UK for onshore liquid and natural gas pipelines (1962-2013) [3]. Corrosion is the major cause of pipeline failures (38 %) in the UK from 1962-2013 according to the statistical analysis carried out by United Kingdom onshore pipeline operators' association (UKOPA).

2.3 Corrosion of Pipelines

A general definition of corrosion by Peabody [72], gives corrosion as the degradation of a material through environmental interaction. This includes all type of materials, both man-made and naturally occurring; metals, plastics, and ceramics. NACE International defines corrosion as the deterioration of a substance/material or its properties due to reaction with its environment [32]. Another definition of corrosion by Singh [33] and Fontana [22] is that it is the destruction or deterioration of a material that results due to reaction with its environment. Evaluating all three definitions of corrosion, it can be stated that a material will only corrode when it reacts with its environment.

Pipelines that are buried in the ground, situated above ground, or submerged in sea are subjected to their surrounding environment which over a period of time causes corrosion of the external pipe walls. Internal corrosion of pipelines also occurs as a result of various factors, namely; chemical composition of the conveyed liquids or gases that contain other corrosive substances such as H_2S , CO_2 , O_2 , etc, dissolved solids. Physical factors of the fluids can also cause internal corrosion of pipelines such as pressure, temperature, velocity. Furthermore, physical factors of the pipelines such as construction material, operating/residual stresses can also have effect on its corrosion susceptibility.

The factors to be considered in this research are effect of temperature and presence of trace gases in the corrosive environment. Generally, an increase in solution temperature will lead to an increase in corrosion rates. As reported by Sastri [46], the corrosion rates of carbon steel in acidic environment usually doubles for every 10 °C increase (between 15 °C and 70 °C). Furthermore, the diffusion of oxygen or other oxidizers through the formed oxide layer on a metal or alloy surfaces, increases with increasing temperature [44].

Several types or forms of corrosion have been outlined in the literature; namely: general or localized corrosion (pitting corrosion, crevice corrosion, filiform corrosion, etc.), galvanic corrosion, environment assisted cracking (EAC), hydrogen induced cracking (HIC), liquid metal embrittlement (LME) and corrosion

fatigue (CF)), flow assisted corrosion, microbiologically influenced corrosion, high-temperature degradation, intergranular corrosion, hydrogen embrittlement, sulphide stress corrosion cracking (SSCC), etc. [2,21,22,46–48]. Most pipeline corrosion failures occur due to a combination of one or more of the mentioned corrosion types [2].

In this research focus will be on environmental assisted cracking, specifically on stress corrosion cracking of pipeline carbon steels in different simulated 3.5 % NaCl conditions, as such discussion will focus on SCC. Hydrogen embrittlement and pitting corrosion of pipeline carbon steels will also be discussed. The possibility of galvanic corrosion between the exposed materials will also be considered.

2.3.1 Electrochemical Corrosion Mechanism (Aqueous Solution)

The corrosion of metals or alloys in contact with aqueous environment occurs by electrochemical corrosion mechanism. This involves the transfer of electrons (electrical component) across the metal-electrolyte interface and, oxidation and reduction reactions (chemical component) [32,33,21]. Aqueous corrosion, also known as wet corrosion consist of four important elements necessary for the corrosion to take place: an anode, cathode, an electrolyte solution or other conducting medium; and an electron conductor (metallic) [21,73].

The corrosion of a metal in aqueous environment involves oxidation (anodic reaction) which occurs at the anode and then reduction (cathodic reaction) which occurs at the cathode. At the anode, the oxidation process of the metal results in dissolution of the metal, which goes into the solution as M^{n+} ions (e.g., Fe^{2+}). During this process it leaves electrons on the metal surface and therefore the metal is said to be oxidized (it loses electrons at the anode). The reduction (cathodic reaction) involves dissolved oxygen or hydrogen ions depending on the pH of the medium. The electrons at the metal or alloy surface are then released by the anodic process and are conducted through the metallic path to the cathode where they are consumed (gain electrons) by the cathodic reaction [21,47,73].

Figure 2-5 shows an example of aqueous corrosion of carbon steel in seawater (water and sodium chloride) in the presence of dissolved oxygen.

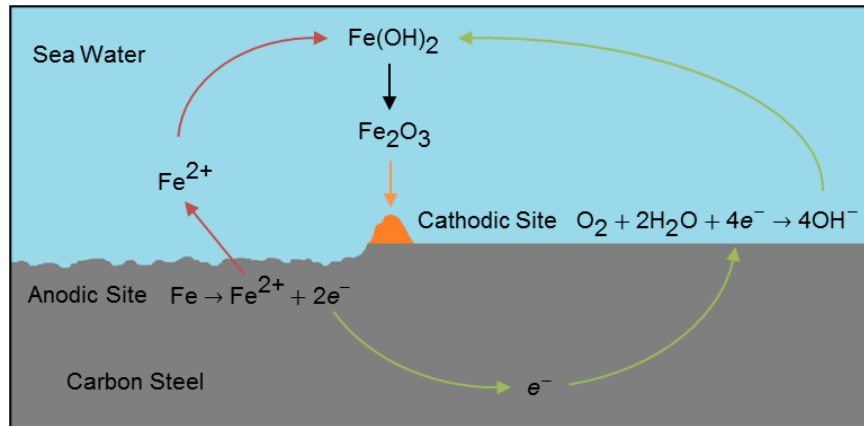


Figure 2-5 - Aqueous corrosion of carbon steel in seawater in the presence of dissolved oxygen [74].

As shown in Figure 2-5, the iron reacts with water and dissolved oxygen to form iron hydroxide, this iron hydroxide then further reacts with oxygen to form iron oxide which is deposited on the metal surface as rust or corrosion product.

The reactions taking place in Figure 2-5 are:

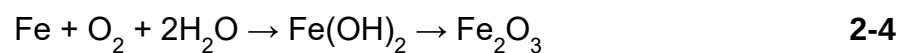
At the cathode, the cathodic half-cell reaction (reduction reaction) is:



At the anode, the anodic half-cell reaction (oxidation reaction) is:



The overall corrosion reaction process is:



2.3.2 Stress Corrosion Cracking

Stress corrosion cracking is caused by the combined action of simultaneous mechanical stress, such as applied tensile or static stress and a specific corrosive media [22,47,38]. Papavinasam [21] defined SCC as the brittle fracture of a ductile metal or alloy which is under applied stress in a corrosive environment.

Papavinasam [21], Sastri [46] and Davis [38], stated that for SCC to occur on a metal or alloy surface the following three conditions must be met simultaneously, a specific crack-propagating environment must be present; the metallurgy of the material must be susceptible to SCC; and there must be presence of applied tensile or static stress. This tensile stress can originate from centrifugal forces, external loads, temperature changes, internal stress from welding, cold working or heat treatment [22,46,47]. According to Fontana [22], the minimum stress required for cracking to occur on a metal or alloy depends on temperature, alloy composition and composition of corrosive environment. In some instances cracking can be observed to occur for as low as 10 % of the yield strength of the alloy or metal [22,46], while in other cases, cracking does not take place below about 70 % of the metal's or alloy's yield strength [22].

SCC failed specimens usually appear microscopically brittle. The cracks usually propagate trans-granularly (across grain boundaries) and/or inter-granularly (along the grain boundaries) or may be branched depending on the type of metal/corrosive media composition [21,22,46,47]. Figures 2-6 and 2-7, respectively shows an example of intergranular and trans-granular cracking morphology. According to Sastri [46] trans-granular cracks propagation is usually discontinuous on a microscopic scale and occurs by period jumps, while intergranular cracks proceed continuously or discontinuously depending on the type of corrosive environment. Furthermore, intergranular and trans-granular cracking often occur in the same alloy, depending on the corrosive environment and/or the alloy microstructure [22,46].

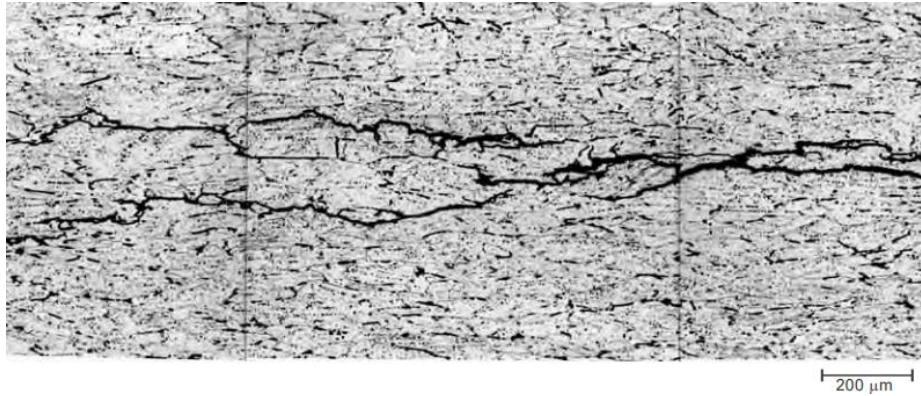


Figure 2-6 - Intergranular mode of SCC produced on carbon steel [38]. As shown the cracks on the metal surface propagate along the grain boundaries. This indicates an intergranular mode of SCC with a discontinuous cracking mode.

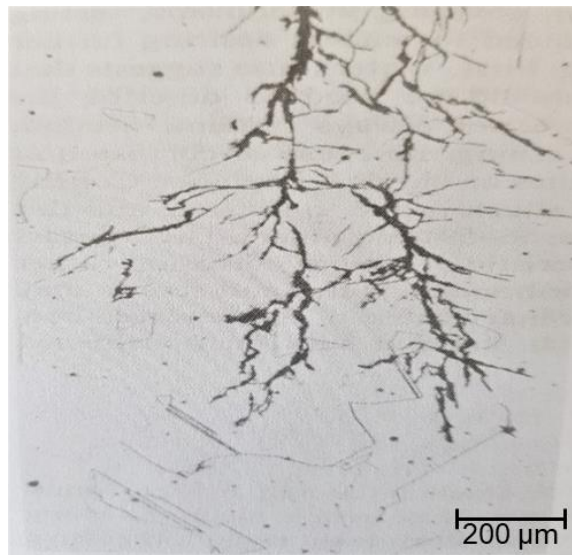


Figure 2-7 - Trans-granular mode of SCC on a steel surface [22]. As shown the cracks on the metal surface propagate across the grain boundaries. This indicates a trans-granular mode of SCC.

Generally, the carbon steels in pipeline applications are subjected to two forms of stress corrosion cracking (SCC) as reported in the literatures: a high-pH SCC and near-neutral pH SCC. High pH SCC is characterised by an intergranular cracking mode and is evaluated in concentrated carbonate/bicarbonate solutions with pH value higher than 9 [4,5,49,50]. However, near-neutral SCC (pH = 6-8) is characterised by a trans-granular mode of cracking and is associated with dilute carbonate/bicarbonate medium [4,5,49,50].

2.3.2.1 Factors Affecting Stress Corrosion Cracking

The susceptibility of a metal or alloy to SCC is affected by several metallurgical factors; namely: chemical composition and microstructure, the preferential orientation of grains, the composition and distribution of precipitates. Other factors that affect SCC of metals or alloy include, temperature of the environment; composition, concentration and presence of oxidizers in a corrosive medium; the pH of the medium; and applied stress level on the alloy or metal [21,22,38,46]. These factors are discussed in more detail in the subsequent sections.

2.3.2.1.1 Microstructure of the Metal/Alloy

Metals or alloys that are more susceptible to SCC are characterised by under-tempered martensitic or bainitic microstructures and/or metals or alloys without post weld heat treatment. Furthermore, microstructures that are more susceptible to SCC are also characterised by fine and small grain microstructures, high yield strength, high residual stress, high hardness and relatively low or no grain boundaries precipitates. This low grain boundary precipitates results from low mill annealing temperature ($< 1000\text{ }^{\circ}\text{C}$). Mill annealing temperature also determines the grain size of a metal or alloy, it decreases with decreasing mill annealing temperature. Susceptibility of metal or alloy to SCC is also can be determined by grain size, better resistance is observed on alloys or metals with larger grain sizes [75,76].

Furthermore, another pertinent factor determining SCC susceptibility of metal or alloy to SCC is the amount and distribution of carbon in a steel matrix. The amount of carbon in the steel matrix determines the threshold stress for crack occurrence. Regular steels tend to be less resistance to SCC as their carbon content gets lower than 0.1 wt.%, while ferritic steels with chromium percent of between 18 wt.% to 20 wt.% are less susceptible to SCC. Furthermore, the cracking resistance of ferritic steels decreases with increasing amounts of nickel and copper (wt.%) [47]. Increasing amounts of nickel decreases the toughness and strength of the steels by refining the grains sizes to a finer microstructure, hence leading to more susceptibility of the steel to SCC. Research studies have

shown that the use of more than 1 wt.% Ni lowers the low alloy steel's resistance to both sulphide and hydrogen stress cracking [77]. Furthermore, copper is more active and has higher electronegativity than iron, so it pulls electrons away from the iron, making it more likely to corrode, hence increased loss in metal thickness and subsequently SCC may occur [47]. The effect of microstructure on SCC of various pipeline carbon steels exposed in different environmental conditions have been reported by several researchers as discussed in subsequent paragraphs.

Gonzalez-Rodriguez et al. [78] tested the SCC susceptibility of X80 carbon steel with various heat treatments of quenched and tempered, water sprayed, water quenched, and as-received in various concentrations of NaHCO_3 solutions (0.01 M and 0.05 M) at $25^\circ\text{C} \pm 2^\circ\text{C}$. Table 2-7 shows the different microstructures of the exposed X80 pipeline carbon steel. Figure 2-8 shows images of the different microstructures of the exposed X80 pipeline carbon steel. The test results showed that the exposed specimens are less resistant to SCC in 0.01 M NaHCO_3 solution irrespective of alloy's microstructure. The quenched specimens were observed to show lower SCC resistivity. This is because the martensite was a highly stressed microstructure as a result of the excess carbon trapped interstitially, then followed by the quenched and tempered samples. The as-received samples were observed to show higher SCC resistivity.

Table 2-7 - Different microstructures of the exposed X80 pipeline carbon steel [78].

Heat treatment	Microstructure
As-received sample	Ferrite and pearlite bands with dispersion of precipitates.
Water-sprayed	Incomplete transformation of perlite grains with few precipitates.
Water quenched	Martensite with high segregation at martensitic lath boundaries and dispersion of precipitates.
Quenched and tempered	Partially recrystallized grains with incipient acicular ferrite and isolated pearlite grains

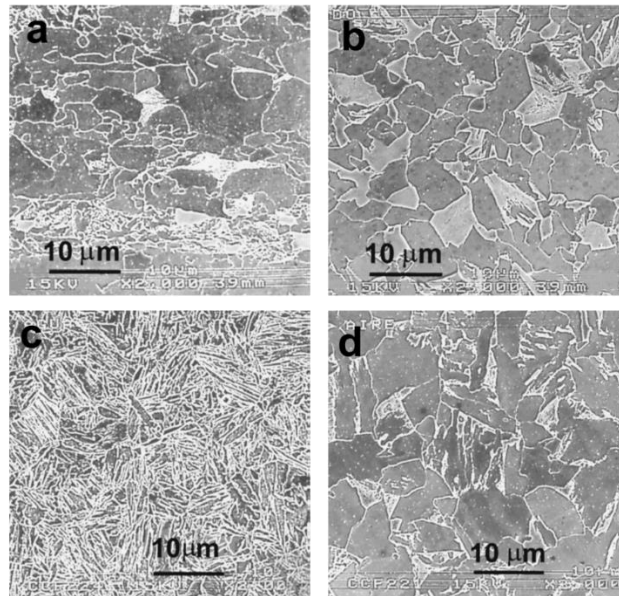


Figure 2-8 - Microstructures of the exposed X80 carbon steel in the different concentrations of NaHCO_3 solutions; (a) as-received, (b) water sprayed, (c) water quenched, (d) quenched and tempered [78].

Similar results were reported by Torres-Islas et al. [79] from X70 micro-alloyed pipeline steel with different microstructures exposed in various concentrations of NaHCO_3 solutions of 0.1, 0.05, 0.01 and 0.005 M with application of different cathodic potentials. Tests were conducted by use of slow strain rate tests at a strain rate of 1.36×10^{-6} in/s. at 50 °C. The different microstructures of the exposed X70 steel are presented in Table 2-8. Figure 2-9 shows images of the different microstructures of the exposed X70 micro-alloyed carbon steel.

Table 2-8 - Microstructures of the exposed X70 micro-alloyed carbon steel [79].

Heat treatment	Microstructure
As-received	Ferrite grains with pearlite alternation
Quenched and tempered	Incipient acicular ferrite with isolated perlite grains
Water-sprayed (Cooled)	Incomplete transformation of pearlite in a recrystallized ferrite matrix
Water-quenched	Martensite with segregation at martensitic lath boundaries

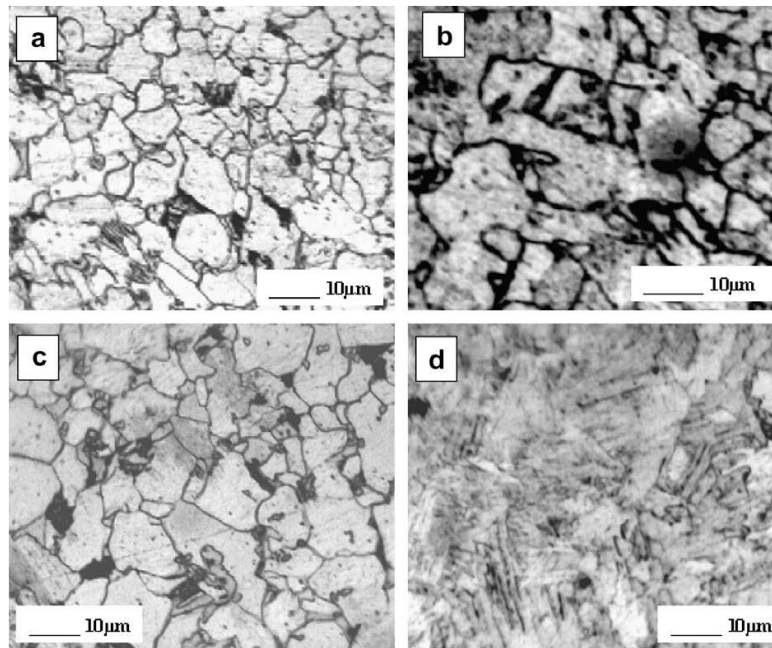


Figure 2-9 - Microstructures of the exposed X70 micro-alloyed carbon steel in the different concentrations of NaHCO_3 solutions; (a) as-received, (b) quenched and tempered, (c) water sprayed, (d) water quenched [79].

The tests results showed that the exposed samples has highest loss of ductility and was less resistant to SCC in the most diluted solution of NaHCO_3 , irrespective of alloy's microstructure. In the diluted NaHCO_3 solution, applied cathodic potentials close to their corrosion potential decreased the SCC susceptibility of the samples regardless of the alloy's microstructure, whereas higher applied cathodic potentials were observed to increase the SCC susceptibility in all the different sample microstructures. The obtained percentage reduction in area showed that hydrogen ingress into the alloy's crystalline structure affected the quenched and quenched-tempered samples both in air and most diluted solution of NaHCO_3 . This indicates that hydrogen ingress had higher impact on the reduction in ductility on the quenched and quenched-tempered samples. Trans-granular cracks were observed in the quenched-tempered specimen.

Liu et al. [80] investigated the SCC resistivity of an X70 carbon steel with various applied heat treatments and microstructures as shown in Table 2-9. Figure 2-10 shows images of the different microstructures of the exposed X70 carbon steel.

Table 2-9 - Microstructures of the exposed API 5L X70 carbon steel [80].

Heat treatment	Microstructure
As-received	Ferrite matrix grain with dark austenite/martensite grains
Air-cooled (normalised)	Coarse ferrite with granular bainite grains
Water quenched	Feather bainite grains

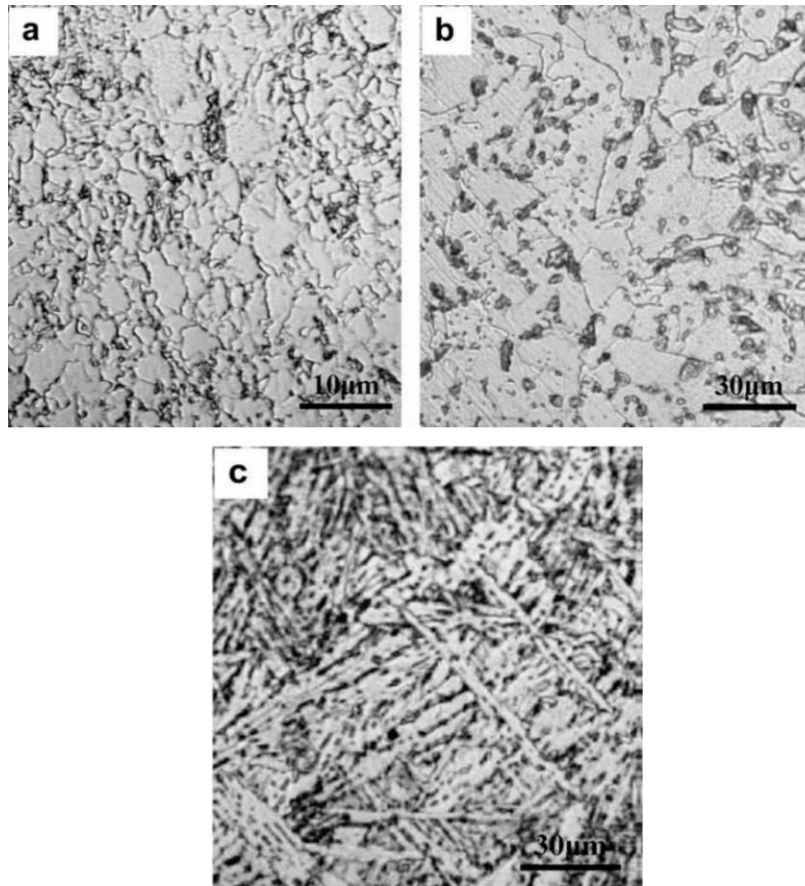


Figure 2-10 - Microstructures of the exposed X70 carbon steel in the acidic soil extracts; (a) as-received, (b) air cooled, (c) water quenched [80].

The experiments were conducted by use of SSRT technique at a strain rate of 5×10^{-7} in/s in an acidic soil extract with a pH of 4.41. Different cathodic potentials below the corrosion potential were applied on the samples. The results of the tests indicated a mixed-mode of SCC mechanism, which is by anodic dissolution and hydrogen embrittlement. The water quenched specimen was observed to

show higher SCC susceptibility, whereas the as-received sample showed lower susceptibility to SCC. It was observed that the SCC mechanism changed with varying applied cathodic potentials. At lower negative potential, the sample's cracking mechanism was based mainly on anodic dissolution. When the potential is applied more negatively, hydrogen was involved in the cracking process, and trans-granular cracks were observed. With further negative application of potential, the SCC mechanism was completely based on hydrogen-induced, with brittle feature of the fractured surface.

Similar results were reported by Fu et al. [81], when they conducted SCC susceptibility test on X70 carbon steel with application of varying cathodic potentials below their open circuit potential in a simulated soil solution. The tests results showed that at an applied cathodic potential of -450 mV, the mechanism of SCC was observed to be anodic dissolution, when the potential is increased to -850 mV, the anodic dissolution of the steel was reduced and when a potential of -1200 mV is applied, the specimens showed higher susceptibility to SCC, and the mechanism of SCC is solely by hydrogen embrittlement. Jeffrey et al. [82] reported similar results on X70 water quenched samples exposed in NS4 (Near-neutral solution) with a pH of 6.7, the quenched specimens with acicular and polygonal ferrite grains were observed to show higher SCC susceptibility. Similar results of higher SCC susceptibility were obtained by Bulger et al. [24] on quenched X70 carbon steel with bainitic microstructure relative to normalised and annealed samples with ferritic/pearlitic microstructures exposed in NS4 solution. It was noticed that the water-quenching treatment increased the tensile strength of the carbon steel [24].

Jeffrey et al. [82] conducted SCC susceptibility study on different microstructures of X70 carbon steel samples as shown in Table 2-10. The samples were exposed in a near neutral NS4 soil solution purged with 95%N₂/5%CO₂ with a pH value of 6.7.

Table 2-10 - Microstructures of the exposed X70 carbon steel samples [82].

Heat treatment	Microstructure
Mill annealed	Ferritic-pearlitic grains
Normalized	Ferritic-pearlitic grains
Water quenched	Acicular with polygonal ferrite grains
Quenched and tempered	Coarsened quenched microstructure with some degree of recrystallization

Figure 2-11 presents the variations in SCC susceptibility of the different exposed samples in relation to the calculated area reduction ratio. The obtained area reduction ratio as shown in Figure 2-11 indicated that the annealed samples had higher resistance to SCC, while the water quenched samples presented higher susceptibility to SCC. The annealed microstructure was observed to have larger grain sizes relative to the normalised samples and as such showed higher SCC resistance. On the other hand, the water quenched samples with smaller grain sizes were observed showed higher SCC susceptibility. As stated by Thomson et al. [75] and Park et al. [76], the susceptibility of metal or alloy to SCC is also determined by their grain size, better resistance is observed on alloys with larger grain sizes, as such higher SCC resistance observed on the annealed microstructure.

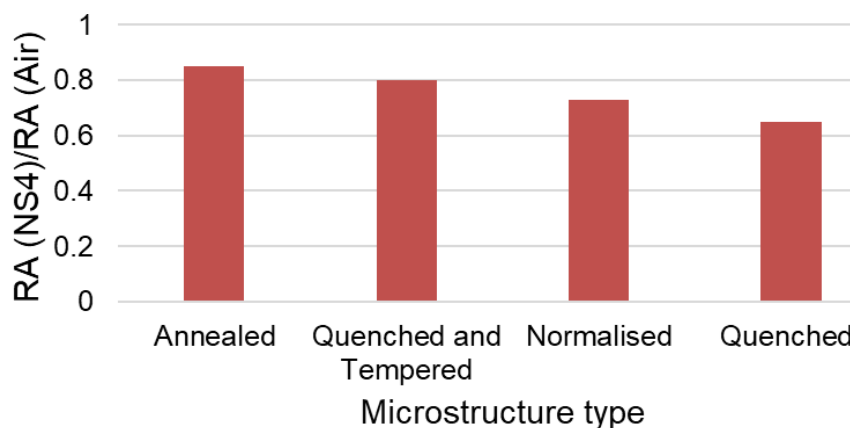


Figure 2-11 - Variations in susceptibility to SCC of the different exposed X70 samples in relation to area reduction ratio [82], data from Jeffrey et al. [82].

Lu and Luo [83] investigated the relationship between microstructure and yield strength on SCC susceptibility of different grades of carbon steels exposed in a near neutral soil solution. The steel grades consist of API 5L X52, X60, X65, X70, X80 and X100. The different microstructures of the carbon steels are presented in Table 2-11. Figure 2-12 shows the micrographs of the different microstructures.

Table 2-11 - Different microstructures of the carbon steels [83].

Material grade	Microstructure
X52, X60, X65	Typical ferritic pearlite grains
X70, X80, X100	Fine grained bainitic ferrite

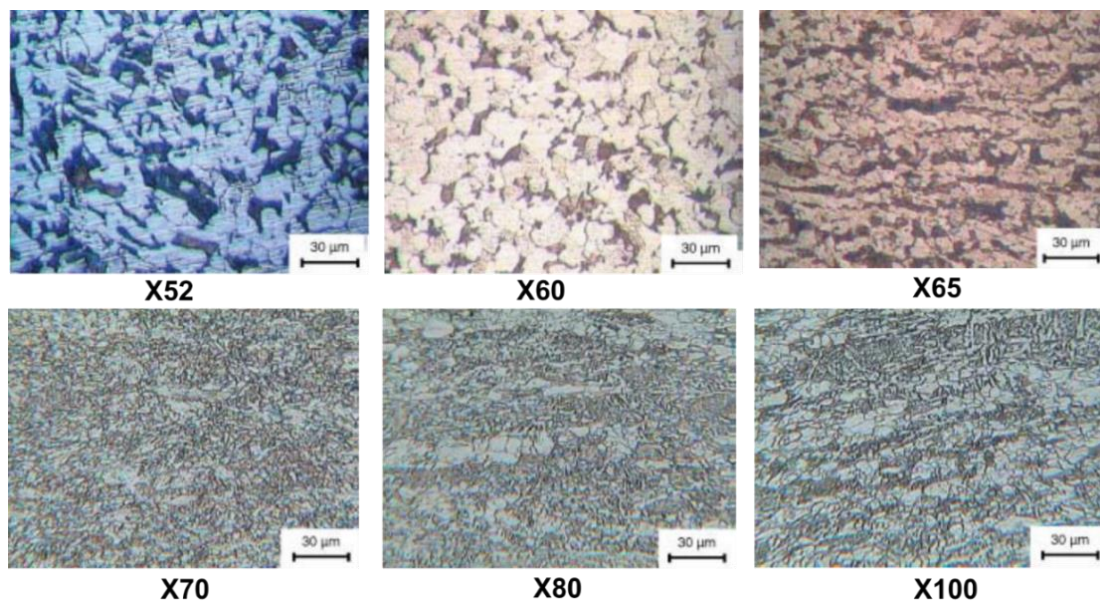


Figure 2-12 - Microstructures of the exposed carbon steel grades [83].

SSRT method was carried out on the samples to assess their SCC susceptibility at a strain rate of 10^{-7} in/s in the near neutral solution saturated with 95 % N_2 + 5 % CO_2 with a pH of 6.7. The results obtained from the tests indicated that near-neutral pH SCC susceptibility of the exposed carbon steel grades generally increases with an increasing yield strength level, but the yield strength dependence on SCC susceptibility was highly affected by the microstructures of

the carbon steels. SEM images of the fractured surfaces on the specimens showed trans-granular SCC appearance in some areas.

In general, it is observed that carbon steels with water quenched and, quenched and tempered heat treatment and made up of bainitic and/or acicular ferrite, or martensitic grains show higher SCC susceptibility irrespective of composition and type of solution. The quenched specimens made of up bainitic and/or acicular microstructures were observed to have fine grains with fine dispersion of precipitates, while the martensitic grains contain large amounts of carbon trapped interstitially, as such they have higher susceptibility to SCC.

The reviewed literature on effect of microstructure on SCC susceptibility of pipeline carbon steels was observed to be predominantly on X70 carbon steel, with few data reported on X65, X80 and X100. Majorly the samples are exposed in NS4 soil solution, NaHCO_3 and acidic soil extract without putting into account the effect of trace gases (O_2 , CO_2 , H_2S) on SCC susceptibility of the exposed carbon steels. No data reported on SCC susceptibility of carbon steels with varying microstructures in seawater simulated environment, with putting into account effect of traces gases and applied stress.

2.3.2.1.2 Composition, Concentration and Presence of Oxidizers in the Corrosive Medium

Most alloys are susceptible to SCC in specific corrosive medium, especially at moderate applied stress level. For example, carbon steels are more susceptible to SCC in concentrated alkaline medium with presence of nitrates in the solutions. Stainless steels are mainly susceptible to SCC in chloride containing environment but not in nitric or sulfuric acids [21,22,47]. SCC is well known to occur in various aqueous environment and it is also influenced by the presence of oxidizers (oxygen, carbon-dioxide etc.) or other ferric ions [22,21]. These oxidizers when in high amount increases the aggressiveness of corrosive environments, and hence accelerates the oxidation reactions of the metal, which can lead to high metal dissolution and subsequent SCC occurrence [22]. Several studies have been conducted to assess the impact of different compositions of corrosive

solutions with and without trace gases on the susceptibility of various pipeline carbon steels to SCC. These studies are discussed in more detail in subsequent paragraphs.

Omura et al. [50] investigated the SCC susceptibility of grade X65 and X80 carbon steels at a temperature of 25 °C in various solution compositions of 1 g/L NaHCO₃ with no trace gas, saturated with CO₂ and saturated with CO₂ and air. Tests were carried out at free corrosion potential at strain rate of 1×10^{-6} in/s. The tests results showed significant reduction in elongation (EL) and area reduction (RA) on the specimens exposed in the solutions as relative to the results obtained in air. No significant difference in RA and EL observed between the samples exposed in solution saturated with CO₂ and mixture of air and CO₂. Secondary cracks and loss in ductility were observed on all the specimens. The test results indicated that SCC could occur with or without application of cathodic potential when under the influence of severe applied stress.

Rebak et al. [84] investigated SCC susceptibility on X52 pipeline carbon steel exposed in NS4 solution by use of constant extension rate tests with application of various applied cathodic potentials. The tests results showed that SCC susceptibility was at minimal near their corrosion potential, and it increased with increasing applied cathodic potential. Bueno et al. [9] reported similar results on API 5L X46 carbon steel exposed in NS4 solution, aqueous extracts from soil samples and in air at 25 °C. Table 2-12 shows standard composition of NS4 simulated soil solution. Cathodic potentials of 100 mV and 300 mV below the sample's corrosion potential (E_{corr}) were applied at strain rates of 9×10^{-7} in/s and 9×10^{-6} in/s. Figure 2-13 shows the variations in time to failure of the specimens in the different solutions with and without the influence of applied cathodic potentials. As shown in Figure 2-13 lower time to failure was observed at potential of 300 mV in both NS4 solutions and soil extracts. The tests results indicated trans-granular cracks in the samples with decrease in ductility as higher cathodic potentials are applied. It is observed that cracking occurred by SCC, but hydrogen generated from applied cathodic potential contributed to the initiation and crack

propagation of the specimens. Contreras et al. [7] also reported similar results obtained from SCC susceptibility tests on X52 carbon steel exposed in NS4 solution by use of SSR method with application of different cathodic potentials. The tests results indicated that highest corrosion rates of the specimens was obtained at the highest applied potential. Brittle fracture with trans-granular mode were observed on the samples. This usually occurs on specimens due to the effect of hydrogen embrittlement.

Table 2-12 - Standard chemical composition of NS4 soil solution [7].

Substance	KCl	NaHCO ₃	CaCl ₂ .2H ₂ O	MgSO ₄ .7H ₂ O
Concentrations (g/l)	0.122	0.483	0.181	0.131

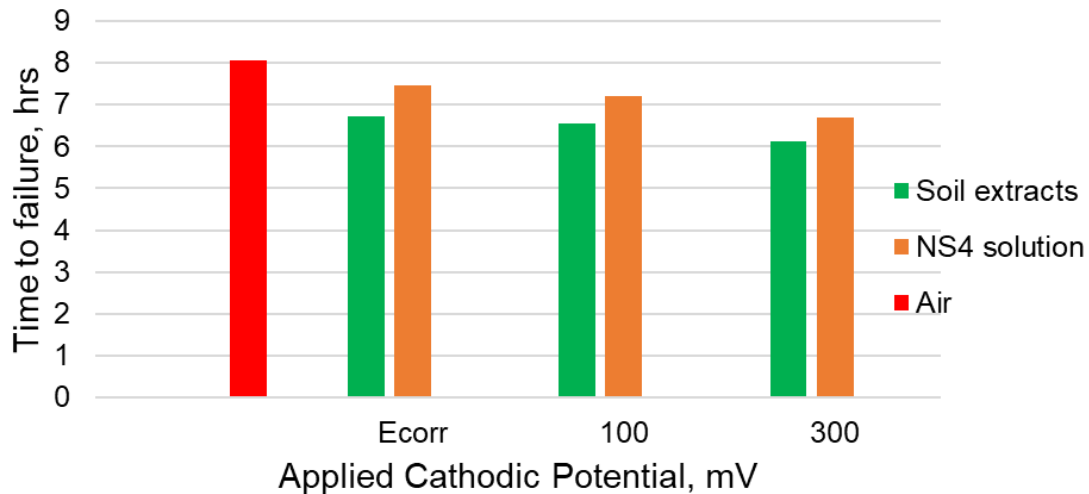


Figure 2-13 - Time to failure variations of the exposed X46 samples in aqueous soil extracts, NS4 solution and in air, at rest corrosion potential (E_{corr}), 100 mV and 300 mV below their potential [9], data from Bueno et al. [9].

Furthermore, Zhang et al. [85] studied the impact of hydrogen embrittlement on X70 in comparison with X80 and X90 carbon steels with application of cathodic protection in simulated soil solutions. The tests results obtained from the hydrogen permeation analysis and hydrogen content measurement showed an increased diffusion rate and concentration of hydrogen on the steel surfaces with increasing ultimate tensile strength of steels under the different applied cathodic protections levels. This shows that the rate of hydrogen accumulation and uptake

is higher in higher strength steels and can lead to higher susceptibility to hydrogen embrittlement and subsequently may lead to higher SCC susceptibility. Decreasing percentage in RA was also observed with increasing material's ultimate tensile strength.

Majchrowicz et al. [5] studied the susceptibility of P110 pipeline steel to SCC in CO₂-rich environments (pure CO₂ and wet CO₂ (CO₂+H₂O) where used as the solution samples), with a pH of 4-6. Table 2-13 presents the chemical composition of the P110 pipeline steel. SCC susceptibility was investigated by use of U-bended samples, tensile tests of miniaturized samples cut from the exposed U-bended specimens and SSRT at different strain rates of 2×10^{-6} in/s., 10^{-5} in/s and 10^{-4} in/s. The tests results showed no clear long visible SCC cracks on the specimens exposed in CO₂ and wet CO₂. According to area reduction ratio U-bended specimen is more susceptible to SCC in the wet CO₂ solution than SSRT tensile specimen. Overall results indicated that P110 steel is susceptibility to SCC in CO₂ rich solutions and is associated with anodic dissolution and hydrogen embrittlement.

Table 2-13 - Chemical composition of the exposed P110 steel (wt.%) [5].

Material grade	C	Mn	Si	S	P	Fe
P110	0.243	0.990	0.196	0.002	0.014	Bal.

Zhang et al. [86] evaluated the SCC susceptibility of X70 carbon steel in different CO₂ concentrations by use of SSRT technique at an applied strain rate of 1×10^{-6} in/s. Soil extracts solution with increasing CO₂ concentrations of 0, 5, 10, 15, 20 and 100 %, balanced with N₂ were used as tests conditions. Rapid fall in RA of specimens were observed with increasing CO₂ percentage. The SCC susceptibility of the samples were observed to increase with increasing CO₂ partial pressure. Similar results were observed by Johnson et al. [39] on X65 pipeline steel, which showed that increasing CO₂ concentration from 0.5 % to 25 % in simulated near-neutral solution facilitates its crack initiation and propagation rate during cyclic loading. Also, the brittleness of the fractured sites

increases with applied CO₂ partial pressure. This contributed to ingress of hydrogen atoms into the steels crystal lattices, hence further decreasing its ductility and thus facilitating crack propagation. It is observed that with increasing percentage of CO₂ polarization resistance (R_p) and pH of the solution decreases and corrosion current density (I_{corr}) increases. Jeffrey et al. [87] and, Asher and Singh [88] also reported a decrease in solution pH with increasing percentage of CO₂ in carbonate/bicarbonate solutions used in investigating SCC susceptibility of X65 carbon steel. However, it was observed that the application of cathodic protection increases the pH of the solution, shifting the medium away from near-neutral pH conditions [88].

Nevertheless, Johnson et al. [39] investigated the SCC susceptibility of X65 carbon steel by use of cyclic loading technique in NS4 soil solution with different percentages of CO₂ and O₂ at 35 °C. The tests results indicated that with increasing percentage of CO₂, hydrogen permeation and corrosion rate increased, and also accelerated crack propagation of the exposed samples. The measured crack length over time showed a well-defined increase in crack velocity with increasing CO₂ concentration from 0 to 5 %. The effects of increasing amount of O₂ on corrosion rates were observed to be very little relative to CO₂. It was observed that increasing the concentration of O₂ decreased the hydrogen permeation rate on the samples but increased crack propagation rate. Gu et al. [89] also reported that increasing CO₂ percentage facilitates SCC occurrence on carbon steels as observed in an SCC susceptibility test of X52 and X80 carbon steels exposed in a near neutral solution. This indicated that metal dissolution and hydrogen embrittlement are involved in the SCC occurrence [89].

In general, it is observed that SCC of pipeline carbon steels in a near neutral solution varies with solution composition, concentration of oxidizers and their applied partial pressure. It is also observed that with increasing CO₂ percentage corrosion rate increases, hence facilitating SCC occurrence on carbon steels. It is clear that with increasing applied cathodic potential, the severity of SCC occurrence increases. It can be concluded that, the mechanism for crack initiation

and propagation in concentrations of CO₂ and O₂ constitute metal dissolution and hydrogen embrittlement.

The reviewed literature on effect of corrosive medium composition and presence of trace gases on SCC susceptibility of pipeline carbon steels was observed to be majorly in simulated near neutral soil solution, carbonate/bicarbonate solutions with varying concentrations of CO₂, O₂ and N₂. No data reported on SCC susceptibility of pipeline carbon steels, specifically on X65, X70, X80 and X100 in simulated seawater environment with putting into account the effect of trace gases. Furthermore, the rate at which the exposed samples are corroding needs to be monitored to clearly understand their SCC behaviour.

2.3.2.1.3 Temperature of the Corrosive Medium

Generally, increasing environmental temperature accelerates SCC occurrence on metals or alloys like in most other chemical reactions. However, the type of corrosive environment also determines the cracking susceptibility of a metal or alloy at a particular temperature [22]. In some corrosive environments cracking occurs readily at room temperature, while in other environments higher temperatures close to boiling points are required. Majority of alloys that are susceptible to SCC will start cracking in an environment with temperature as low as 100 °C [22,21]. The impact of temperature on SCC susceptibility of pipeline carbon steels in different simulated environmental conditions has been investigated by several researchers as presented and discussed in the subsequent paragraphs.

Asher et al. [90] assessed the SCC behaviour of X65 carbon steel by use of SSR test method in different concentrations bicarbonates bubbled with 5 % CO₂ at 15 °C, 25 °C and 35 °C. The SCC behaviour of the exposed samples was assessed based on crack velocity. Highest crack velocity was obtained in the solution with 0.5 g/L NaHCO₃ at 15 °C and lowest at 25 °C with 0.5 g/L NaHCO₃.

Contreras et al. [91] investigated the SCC behaviour and cracking mechanisms of X60 carbon steel by use of SSRT technique at an applied strain rate of 1×10⁻⁶ in/s. The tests were conducted in simulated NS4 solution at different pH

level of 3 and 10 at 25 °C and 50 °C. The calculated time to failure and area reduction ratios show that the samples were more susceptible to SCC at pH level 3 irrespective of the exposure temperatures. At pH level 10 the susceptibility to SCC of the samples was observed to be higher at 50 °C. Brittle type of fracture with trans-granular cracking mechanism were observed on the failed samples. In general, the mechanism of failure on the exposed X60 samples can be said to occur due to combination of anodic dissolution and hydrogen embrittlement.

Ye et al. [92] evaluated the SCC susceptibility of X70 carbon steel by use of SSRT method. The tests were conducted in NACE solution (0.5% acetic acid + 5 % NaCl) at 25 °C and 60 °C. The tests results showed lower SCC susceptibility at 25 °C. At 60 °C, the SCC susceptibility increased, and indicated clear tendency to SCC. Faster movement of O₂ and Cl⁻ was observed at 60 °C. This obviously led to change in SCC susceptibility, as O₂ diffusion plays a vital role in facilitating SCC occurrence.

Fragiel et al. [93] assessed the SCC behaviour of two X65 micro-alloyed carbon steels with typical ferritic/pearlitic and martensitic grains. The samples were stressed by constant displacement and exposed in NACE solution (5 % NaCl plus 0.5 % acetic acid) at 25 °C and 55 °C. The test results showed that at 25 °C, the samples with ferritic/pearlitic grains were observed to have crack tip dissolution with cavitation at the crack tip. Trans-granular cracks and some degree of hydrogen embrittlement were also observed on the samples. The samples with martensitic grains exposed at 25 °C were observed to have a mixed trans-granular and intergranular cracks, with no cavitation at the crack tip. Trans-granular cracks were observed on both samples at 50 °C, with longer cracks in comparison with samples exposed at 25 °C. This clearly indicates some degree of involvement of hydrogen embrittlement in combination to the anodic dissolution.

Furthermore, Ramirez et al. [94] evaluated the SSC behaviour of a micro-alloyed carbon steel (C-Mn steel) with varying microstructures of ferritic grains, martensitic grains, and ferritic/bainitic grains. Specimens were exposed in a

NACE solution at a strain rate of 1×10^{-6} in/s at varying temperatures of 25 °C, 50 °C, 70 °C and 90 °C. The test results showed that percentage area reduction and concentration of hydrogen atoms at the surface of the exposed samples increased with increasing temperature until 90 °C. Figure 2-14 shows the effect of increasing temperature on the percentage reduction in area. As shown in Figure 2-14 the sample with martensitic grains (2F) showed the highest SSC susceptibility at all temperatures, whereas the samples with ferritic (2A) and ferritic/bainitic grains (1T) showed higher SCC susceptibility at 25 °C. Generally, the SCC susceptibility was observed to decrease with increasing temperature for all the different microstructural samples from 25 °C to 70 °C, which then increased with an increase of temperature to 90 °C.

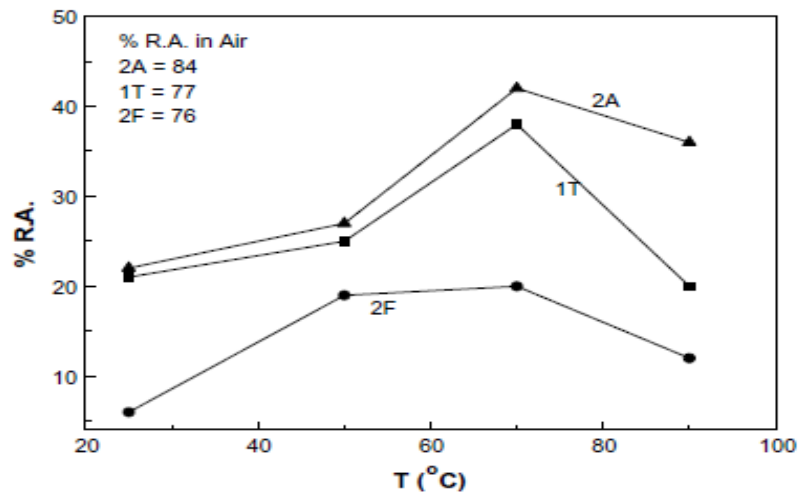


Figure 2-14 - Effect of increasing temperature on percentage area reduction on the different microstructures: 2A (Ferritic grains), 1T (Ferritic/bainitic grains), 2F (Martensitic grains) [94].

In general, the reviewed research articles showed that SCC susceptibility of carbon steels exposed at a particular temperature strongly depends on the microstructure of the steel, type and composition of the corrosive environment.

Similarly, as reported in section 2.3.2.1.1 and 2.3.2.1.2, in the reviewed literature, the effect of temperature on SCC susceptibility of pipeline carbon steels was also observed to be in NS4 soil solution, NaHCO_3 and majorly in NACE solution. The effect of trace gases with varying temperature on SCC susceptibility was not

considered in their investigation, also the change in corrosion rates with time of the exposed carbon steels was not monitored. Furthermore, no data reported on SCC behaviour of pipeline carbon steels (X65, X70, X80 and X100) in seawater environments with putting into account effect of trace gases and with changing temperature on their corrosion rates and surface morphology.

2.3.2.1.4 Applied Stress Level and Stress Application Method

Several factors such as metal or alloy composition, environmental temperature and corrosive media composition determines the minimum stress required for SCC to occur on the metal or alloy. In few instances cracking can occur on a metal or alloy stressed from as low as 10 % of its yield strength [22,46], whereas in some cases, cracking does not occur below about 70 % of the material's yield strength [22]. Furthermore, the minimum stress for crack initiation on metal or alloy is observed to depend on the percentage of carbon in a steel matrix [46,47]. Several research as discussed in subsequent paragraphs have been conducted to understand the effect of applied stress level and stressing technique on SCC behaviour of pipeline carbon steels.

Gui et al. [11] evaluated the SCC susceptibility of X46 carbon steel in three different laboratories to investigate the effect of fuel grade ethanol. Strain rates of 3.7×10^{-7} in/s, 4×10^{-7} in/s and 5×10^{-7} in/s, respectively, were applied on the samples in the three laboratories. The test results in the first two laboratories showed that the exposed samples are susceptible to SCC with presence of trans-granular cracks. However, in the third laboratory, no presence of SCC observed on the sample unless some certain amount of chloride was added into the solution. Lou et al. [95] stated that the presence of chloride and acetic acid in fuel grade ethanol accelerates the occurrence of SCC on carbon steels. Similarly, Samusawa et al. [96] also reported that presence of chloride ions facilitates SCC initiation under cyclic loading of steels. In summary, it can be stated that applied stress level on a material plays a significant role in its SCC behaviour and also amount of chloride ions in a solution accelerates SCC occurrence on carbon steels.

Omura et al. [50] investigated the SCC susceptibility of X65 carbon steel in comparison with X80 by use of cyclic loading test and constant load test. 85 % and 100 % of the material's Y.S. were applied on the samples in cyclic loading test, 90 % Y.S. in constant load test. The tests were conducted at 25 °C in NS4 soil solution with 10 % CO₂ and 90 % N₂. The test results showed that SCC occurred on the samples when stressed at 100 % Y.S. in the cyclic loading test, with no SCC occurrence at 85 % Y.S. No presence of SCC observed on the exposed samples in the constant load tests at applied stress level of 90 % Y.S. Samusawa et al. [96] reported similar results on SCC resistance of X52 carbon steel exposed at 23 °C (± 2 °C) in various simulated fuel grade ethanol (SFGE) with application of constant load and low frequency cyclic load. 110 % of the material's Y.S. was applied on the sample in constant load test, and 105 % and 110 % Y.S. were applied in the cyclic loading test. The test results indicated that SCC occurred on the specimens with mixture of inter-granular and trans-granular cracking mode in the low-frequency cyclic loading test, with no visible evidence of SCC observed in the constant load test. Furthermore, Lu and Luo [97] also reported similar SCC susceptibility outcome on X70 carbon steel exposed in NS4 solution under low-frequency cyclic loading test. The test results indicated that increasing applied stress level facilitates crack initiation on the exposed samples. However, the crack propagation rates were observed to be independent of stress level.

Nevertheless, Wang et al. [98] evaluated the SCC behaviour of X65 and X80 carbon steels by pre-cyclic loading of the samples prior to exposure in a near neutral soil solution. Tests were conducted at rest potential of -740 mV_{SCE} and at -790 mV_{SCE}. 80 % and 90 % of the material's Y.S. were applied on the samples during the pre-cyclic loading and constant loading tests. The test results indicated that pre-cyclic loading prior to exposure caused formation of micro-cracks on the specimens under constant load tests with mild applied cathodic potential. No visible microcracks observed on the specimen's exposed at rest potential irrespective of the samples loading conditions. Microcracks were observed on all

pre-cyclic loaded specimens when exposed to the solution with applied cathodic potential of $-790 \text{ mV}_{\text{SCE}}$ at constant load of 80 % Y.S. and 90 % Y.S.

In summary, it can be stated that applied stress level, fluctuating stress and concentration or their combination has a significant role in SCC initiation and propagation of carbon steels.

Similarly, as reported from reviewed literature on effect of temperature, corrosive medium composition and microstructure variation on SCC susceptibility of carbon steels, no data reported on SCC susceptibility of pipeline steels in seawater operating conditions with change in applied stress level and stressing method. Investigations are majorly in NS4 soil solution and simulated fuel grade ethanol.

2.3.2.1.5 pH of the Corrosive Environment

The pH of corrosive medium has great influence on the corrosion rate and SCC susceptibility of a metal or alloy and can also depend on the type and composition of the material [46]. Acidic media with pH of less than 5 are observed to be highly aggressive and accelerates corrosion rates of most metals. For example, the corrosion rates of iron and zinc is accelerated in low pH medium (acidic medium) [46]. On the other hand, alkaline media are less aggressive and easily can form protective films on metal's or alloy's surfaces [37]. Several research have conducted to understand the impact of pH on SCC susceptibility of various carbon steels in different corrosive medium as discussed in subsequent paragraphs.

Contreras et al. [8] evaluated the SCC susceptibility of X52 carbon steel at a strain rate of $1 \times 10^{-6} \text{ in/s}$. The samples were exposed in simulated NS4 soil solution with pH value of 5, 8 and 10. The test results indicated lowest time to failure for sample exposed at pH level 8 relative to sample exposed at pH 5 and 10, and in air. Figure 2-15 show the variations in time to failure of the exposed samples with change in pH of the solutions. Ductile fractures were observed on the specimens exposed in solution with pH 8, 10, and in air, whereas the samples exposed in solution with pH 5 showed brittle fracture with trans-granular appearance. The observed brittle fracture on the samples exposed in solution with pH 5 can be explained to occur due to the acidic environment (pH 5) the

samples are exposed to. Exposure of the samples in the acidic environment produces hydrogen ions, which diffuse into the steel's crystalline structure, hence reducing its ductility and thus increasing its potential for hydrogen embrittlement. According to calculated area reduction ratio (RRA) and time to failure ratio (TFR), the samples exposed in solution with pH 5 showed higher SCC susceptibility.

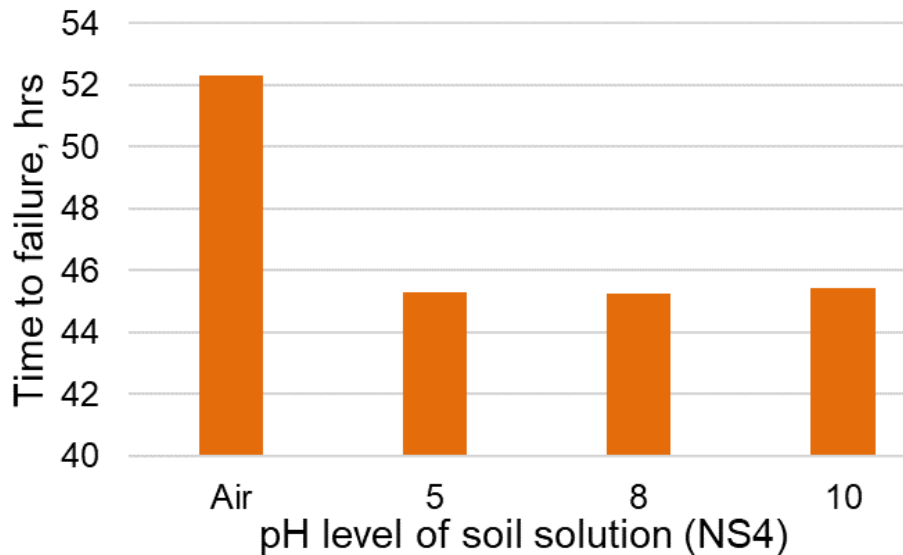


Figure 2-15 - Variations in time to failure of the exposed X52 carbon steel in the different pH level of NS4 soil solution [8], data from Contreras et al. [8].

Cui et al. [99] assessed the impact of changing pH level on SCC and electrochemical behaviour of X70 carbon steel. The samples were exposed in NS4 soil solution with pH value of 4.0, 4.5, 5.0, 5.5, 6.0 and 6.8 at a strain rate of 1×10^{-6} in/s. The NS4 test solutions were continuously bubbled with 5 % CO₂ and 95 % N₂. Generally, it was observed that the susceptibility of the samples to SCC changes with decreasing pH level of the NS4 solution. When the solution pH level was decreased from 6.8 to 6, both anodic dissolution and cathodic reduction reaction increased. Increase in cathodic reduction reactions was also observed with further decrease in pH level of the NS4 solution. When the solution pH was decreased from 6.8 to 5.5, susceptibility to SCC was observed to decrease because of the acceleration of the anodic dissolution process. On the other hand, when the solution pH was reduced from 5.5 to 4.0, susceptibility of the samples to SCC increased steadily. This is because of the acceleration of the cathodic

reduction reactions. Furthermore, it was observed that as the solution pH level was decreased, the observed secondary cracks on the samples presented no clear differences until the pH value was reduced to 4.0. The secondary cracks became wider and deeper in the solution with pH level of 4.0, and thus the susceptibility to SCC of the sample is higher. The test results showed clear change in open circuit potential (OCP) of the samples with change in solution pH level. Figure 2-16 show the variations in the obtained OCP values with change in solution pH level. The obtained OCP values were observed to move more negatively as the solution pH increases.

Liu et al. [100] reported similar results of change in OCP values to more positive with decreasing pH level of an acidic soil solutions while conducting SCC susceptibility tests on X70 pipeline carbon steel. Similarly, Alfantazi et al. [10,100] also reported the electrochemical behaviour of X100 carbon steel exposed in NS4 soil solution and chloride-containing solution saturated with CO₂ at pH level of 4.7 to 9. The test results also showed that the obtained OCP values move more negatively as the solution pH increases. Also, the corrosion rates of the samples were observed to increase with decreasing pH levels of the solutions [101].

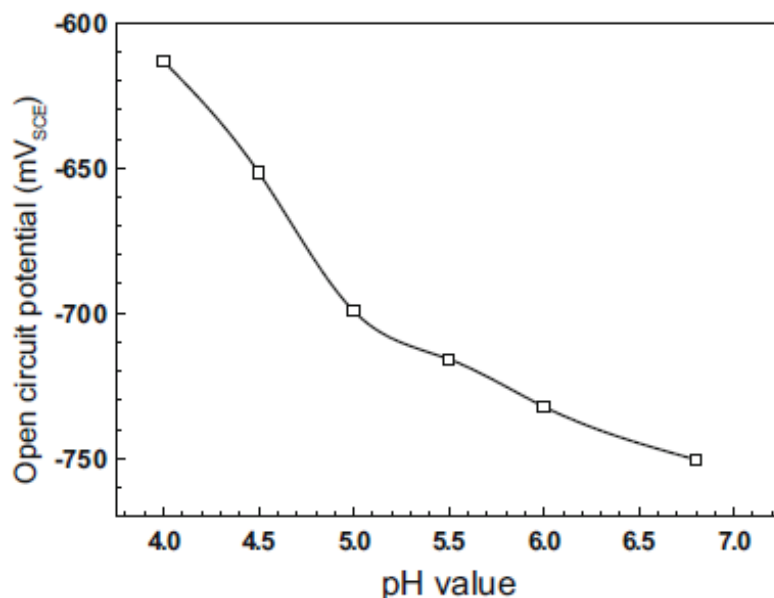


Figure 2-16 - Change in open circuit potential of the exposed X70 samples in the various pH level NS4 solutions [99].

Furthermore, Nesic et al. [42] investigated the electrochemical behaviour of mild carbon steel in CO₂ solutions (aqueous) with pH levels of 4-6. The tests results indicated that pH level had no clear effect on metal dissolution of the samples in the exposure conditions. Chen et al. [102] assessed the SCC susceptibility of X70 carbon steel in four various soil samples saturated with N₂/CO₂ mixture. The SCC susceptibility of the exposed samples was observed to increase with increasing solution pH level from 5.5 to 7.0. Liu et al. [100] also evaluated the impact of different acidic soil solution pH level from 3.5 to 6.5 on SCC behaviour of X70 carbon steel. The tests results show that the samples were more susceptibility to SCC under pH level of 4.5. This can be said to occur due to strong synergistic effect of hydrogen induced-embrittlement and metal dissolution. It was detected that when the solution pH was lower or greater than 4.5, susceptibility to SCC of the samples decreased [100].

Nevertheless, Parkins et al. [103] conducted an SCC susceptibility test on X52, X60 and X65 pipeline carbon steels in simulated NS4 soil solution with different pH level of 5.1, 6.3 and 8.3 exposed at 23 ± 1 °C. Hydrogen permeation analysis was conducted on the three different specimens exposed in the different solution pH levels. The test results showed an increase in hydrogen concentration on the sample's surfaces with decreasing pH level of the solution, regardless of the carbon steel grade. It was observed that hydrogen embrittlement is not fully involved in the SCC occurrence since there is evidence of metal dissolution on the fractured section. Similarly, Jeffrey et al. [87] reported an increasing hydrogen concentration on X65 sample's surfaces with decreasing pH level of a near neutral carbonate/bicarbonate solutions.

In summary, it can be stated that the impact of changing solution pH level on SCC susceptibility of pipeline carbon steels is still not clear. However, most carbon steels are more susceptible to SCC at solution pH value of between 4 and 5, irrespective of the solution type and composition. It is observed that increasing percentage of CO₂ in a solution leads to reduction in pH level of a solution. This increases the hydrogen concentration on carbon steel surfaces, hence

accelerating its susceptibility to hydrogen embrittlement and subsequent SCC occurrence.

As reported from the reviewed literature the effect of pH level on SCC susceptibility of pipeline carbon steels is still not clearly understood. Furthermore, during their investigation the effect of pH on corrosion rate of the exposed carbon steels was not monitored.

Several methods or measures are applied to reduce or prevent stress corrosion cracking of metal/alloys; namely:

1. Lowering the magnitude of the stress below the threshold value. This can be achieved by annealing out residual stresses on the section of the metal or alloy, reducing the applied load or thickening the stressed section of the material [21,22,47].
2. Changing the metal or alloy is another possible method of reducing SCC if neither the stress nor the corrosive environment can be changed. The selection of more resistant material to the applied stress and environment is a possible way of mitigating SCC [21,22,38].
3. Application of cathodic protection. The use of cathodic protection technique such as sacrificial anode and/or impressed current is another method of reducing SCC occurrence [21,22,48].
4. Use of inhibitors. Adding inhibitors to the corrosive environment reduces the rate of SCC occurrence of metallic structures. For example, phosphates, inorganic or organic inhibitors are used to reduce SCC effects in mildly corrosive medium. [22,38,47].
5. Changing the environment. The removal of aggressive environmental compositions by several processes such as degasification and/or demineralization is an effective method to reduce SCC occurrence on metals or alloys. Lowering the temperature of the corrosive environment can also be effective way of reducing SCC effects [22,38,48].

2.3.3 Hydrogen Embrittlement

Hydrogen embrittlement as defined by Papavinasam, Sastri and Cicek [21], [46] and [47] respectively, is the loss or reduction of tensile strength and ductility of a metal or alloy due to diffusion of hydrogen atoms into the metal or alloy crystal lattices during a corrosion process. Hydrogen atoms are generally produced during the cathodic reduction reaction in corrosion process of metals or alloys in acidic solution such as hydrogen sulphide (H_2S) and hydrogen fluoride (HF). Hydrogen atoms can also be produced when carbon dioxide reacts with water to produce carbonic acid (H_2CO_3).

Hydrogen embrittlement causes brittle fracture of normal ductile metal or alloy and the cracks are often intergranular [21,38]. It usually occurs during plastic deformation of quenched and tempered high strength steels and precipitation hardened steels [46,38]. The susceptibility of an alloy or metal to HE increases with its increasing ultimate tensile strength [22,47]. Furthermore, susceptibility of metals or alloys to HE varies with microstructure. For example, martensitic steels are more susceptible to HE, while ferritic, bainitic and austenitic steels are more resistant [47]. The high HE susceptibility of martensitic steels is considered to occur due to its atomic vacancies, grain boundaries, dislocations, inclusions and precipitates [21,47]. These factors provide nucleation sites for hydrogen traps, hence leading to accumulation of hydrogen atoms and subsequent reduction in material ductility. High interaction energy between hydrogen and lattice defects can consequently lead to various degrees of hydrogen invasion and result in different HE susceptibility [47]. Figure 2-17 show a typical example of hydrogen embrittlement on an X46 pipeline carbon steel surface.

In the context of this research the susceptibility of different offshore pipeline carbon steels with different microstructures to HE in simulated 3.5 % NaCl solutions specifically in the presence of carbon-dioxide, and combination of other trace gases will be assessed.

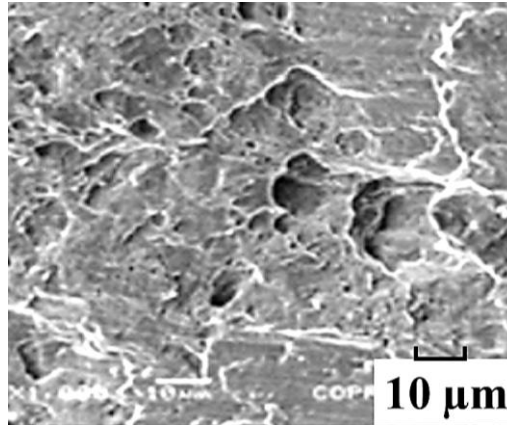


Figure 2-17 - Example of hydrogen embrittlement on an X46 pipeline carbon steel [9].

2.3.4 Pitting Corrosion

Pitting corrosion occurs on a metal or alloy surface when the percentage of anodic area on the material surface is smaller than that of cathodic area [22,47]. It is a form of localised corrosion on a metal or alloy surface that results in the formation of narrow hole or cavity with radius of lesser or equal magnitude than its depth [21,46,47]. Pits formed on metals surfaces are usually with irregular walls and in various sizes and shapes. Figure 2-18 shows some typical pit shapes on a metal surface.

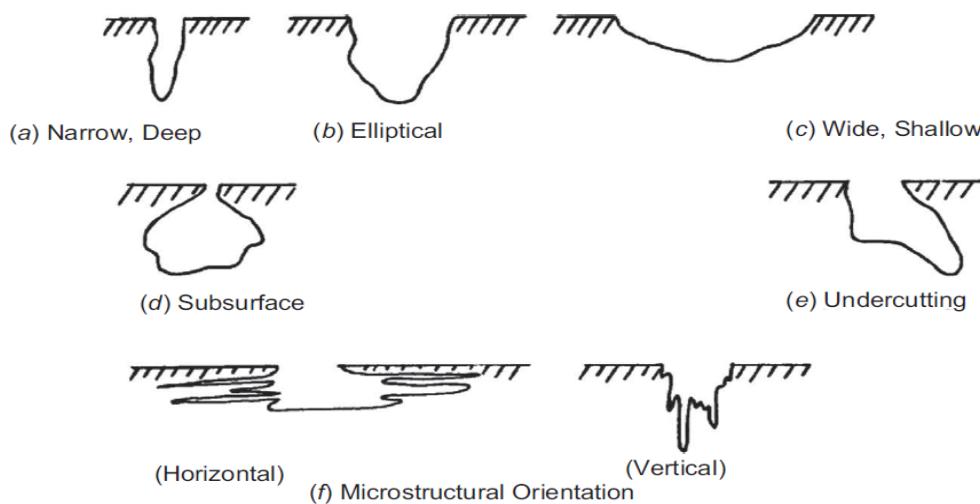


Figure 2-18 - Typical cross-sectional shapes of corrosion pits on a metal surface [21,71].

The initiation of pits depends on factors such as, composition of passive layer, concentration of extraneous ions, such as chloride ions. Mostly pit propagation or growth rate reduces with time as passive layer reforms at the tip of the initiated pit. Pitting is mostly observed in steels and aluminium and most aggressive in static near neutral pH solution with corrosive anions such as Cl^- , Br^- , SO_4^{2-} etc. [22,47,48].

2.3.5 Galvanic Corrosion

Galvanic corrosion also known as bimetallic or dissimilar metallic corrosion [46,103] is defined as a form of corrosion which occurs when dissimilar metals or alloys with different compositions and electrochemical potentials are electrically connected to each other in to a corrosive environment [21,47,48,103]. When two metals or alloys are electrically connected to each other in a conductive medium, it results in the generation and flow of electrons due to their potential differences [22,47,45]. The corrosion of the least corrosion resistant metal or high corrosion potential metal (active metal) is usually increased and the attack on the more corrosion resistant metal or low corrosion potential metal (noble metal) is decreased, as compared to the corrosion behaviour of these metals when they are not in contact with each other [22,46,103]. Figure 2-19 show galvanic series of some common metals and alloys in seawater.

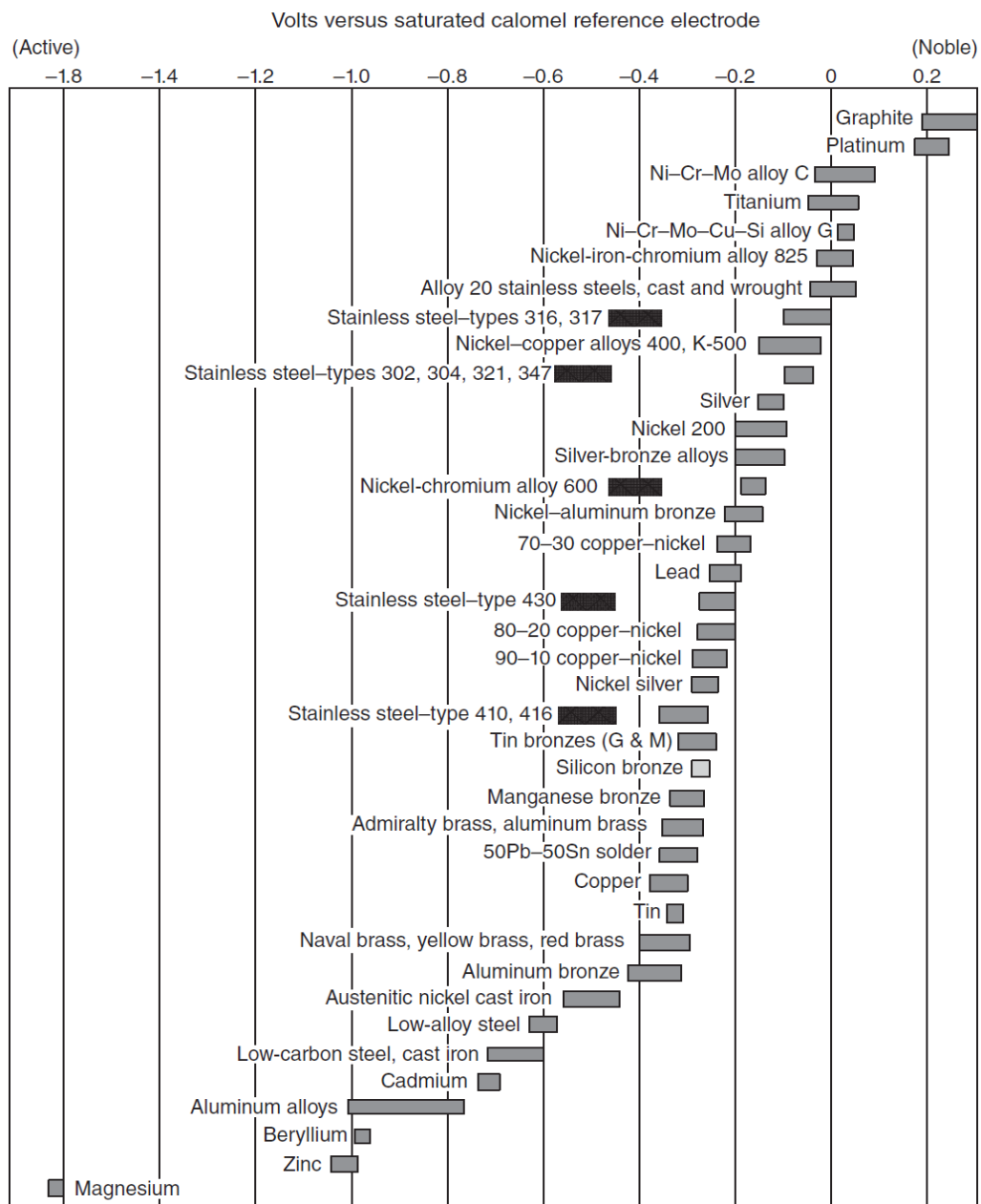


Figure 2-19 - Galvanic series of common metals and alloys in seawater [46,38].
Black boxes indicate the activity behaviour of the alloys (active-passive behaviour). The most noble metal is graphite and the least active is magnesium.

2.4 Laboratory Tests for Evaluating the Susceptibility of Metals to Stress Corrosion

The selection of materials for oil and gas industry applications starts with an evaluation and selection of materials in the laboratory. Several laboratory tests methods are used to evaluate the susceptibility of metals and/or alloys to various types of corrosion. In these research focus will be on evaluating SCC of pipeline carbon steels in simulated 3.5 % NaCl solution bubbled with different trace gases. Several stress or load application techniques are used to measure or determine the stress resistance of a metal or alloy in the laboratory, among these are [21,104]:

2.4.1 Constant Load Technique

This method is usually applied on a test piece when the load to be applied on the specimen is small, normally a hanging weight is suspended on the specimen [21]. Common test specimens in this method are notched beam and direct tension specimens [105]. In notched beam specimen, a single notch is made in the specimen in order to focus the influence of applied stress and corrosion. In this method once the crack initiates, the applied stress increases as cross-sectional area decreases [21].

2.4.2 Deflected Sample Technique

In this method, stress is applied on the specimen by deflecting it. In deflected test samples, the applied stress decreases as crack propagates. This test method is commonly identified by the geometry of the test piece; namely: C-ring, bent-beam, U-bend, rough ground and hairpin specimen tests [21,104]. In bent-beam test method, the test sample can be stressed by two, three or four-point loading method [21]. Figures 2-20 and 2-21, respectively shows schematic diagrams of different methods of loading C-ring and bent-beam test specimens.

In the context of this research C-ring constant strain, notched constant strain and 3-point bent-beam techniques will be used to assess the susceptibility of different

representative offshore pipeline carbon steels to SCC in simulated 3.5 % NaCl solution saturated with different trace gases.

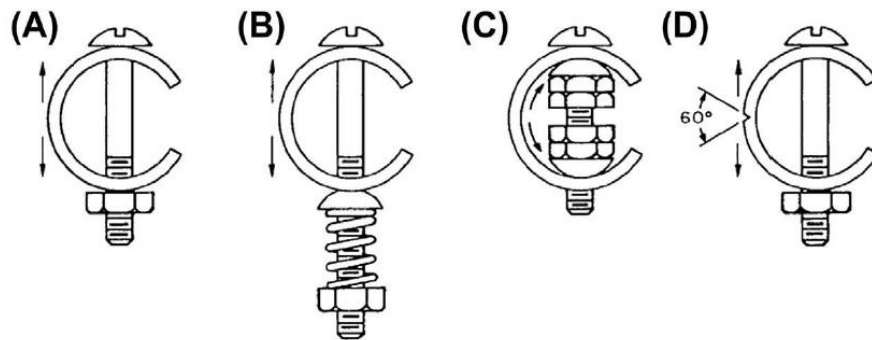


Figure 2-20 - Schematic diagrams of loading C-ring test specimens [21,105]. A and C: Constant strain method; B: Constant load method; D: Notched constant strain method.

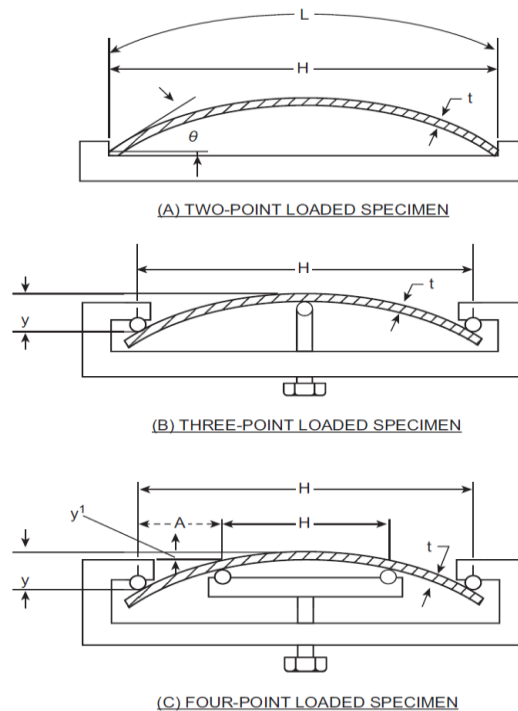


Figure 2-21 - Schematic diagrams of loading bent-beam samples [21,106]. A: Two point loaded samples; B: Three-point loaded sample; C: Four-point loaded sample.

2.4.3 Dynamic Load Technique

The dynamic load method is considered the most widely used test for assessing the susceptibility of a metal or alloy to SCC. The most common stress application method in dynamic load system is the slow strain rate test method (SSRT).

Commonly used test specimens in this method are in the form of round tensile and tube [105]. SSRT is conducted by continuously increasing the applied stress level at a constant strain rate while the specimen is exposed to the test corrosive solution [21,34]. This test method produces result within a short period of time, generally one to two days after exposure to the test solution. The susceptibility of a metal or alloy in SSRT is usually evaluated by conducting the test in inert environment (usually in air) and in a corrosive medium [21].

2.5 Corrosion Monitoring Techniques

Corrosion monitoring techniques determine corrosion rate simulated by laboratory methodologies. These techniques are classified into three distinct groups, namely [21,107]:

2.5.1 Online, Non-destructive Techniques

These techniques determine the corrosion rate of the specimens periodically while the experiment is in progress because they do not change the state of metal or alloy. They are electrochemical techniques which involve application of electrochemical signal to the test piece, known as working electrode (WE), and recording the response of the specimen to the applied signal. The test specimen is the main electrode, whose rate of corrosion is been measured. Other components in online, non-destructive techniques include, a counter or auxiliary electrode (CE; AE), reference electrode (RE), conducting medium (electrolyte), a potentiostat (potential measuring device), current measuring device, and a luggin capillary with a salt bridge connection to the reference electrode (in cases where the RE is placed in a separate container from the WE, to minimize contamination of the RE with corrosion products) [21,108].

During electrochemical monitoring technique, the potential of a single electrode cannot be measured; difference between two electrodes (RE and WE) can only be measured. The counter electrode is used to apply potential to the specimen. AEs are generally made from inert materials, such as high-density graphite or

platinum or can be made from the same material as the working electrode [21,108].

Most commonly used online non-destructive electrochemical monitoring techniques include linear polarization resistance (LPR), electrochemical noise (EN) and electrochemical impedance spectroscopy (EIS). Other electrochemical corrosion monitoring techniques include, tafel extrapolation, cyclic potentiodynamic polarization, cyclic galvanostatic polarization, potentiostatic polarization, and zero resistance ammeters [21,71,107,108,109].

In the context of this research linear polarization resistance technique will be used to monitor the corrosion rate of various offshore pipeline carbon steels in simulated 3.5 % NaCl solutions bubbled with different trace gases. To calculate the corrosion rate of the pipeline carbon steels, the Stern-Geary equation will be used.

LPR technique is a method in which the electrochemical response of a working electrode (corroding metal/alloy) is measured near its rest potential. It involves the polarization of ± 10 mV around the corrosion potential of the metal or alloy [21, 109,110]. A slow scan rate of 0.167 mV/s or 0.6 V/h is advisable to ensure that the test is carried out in a condition close to steady state [110]. This will ensure that the test is conducted in a less agitated condition. Hence, will provide a more stable and accurate electrochemical measurements.

Furthermore, Stern and Geary discovered that the slope of a current-potential plot around the rest potential of metal or alloy is practically linear, and referred to it as polarization resistance slope (R_p) [21,111]. Figure 2-22 show a hypothetical polarization resistance plot.

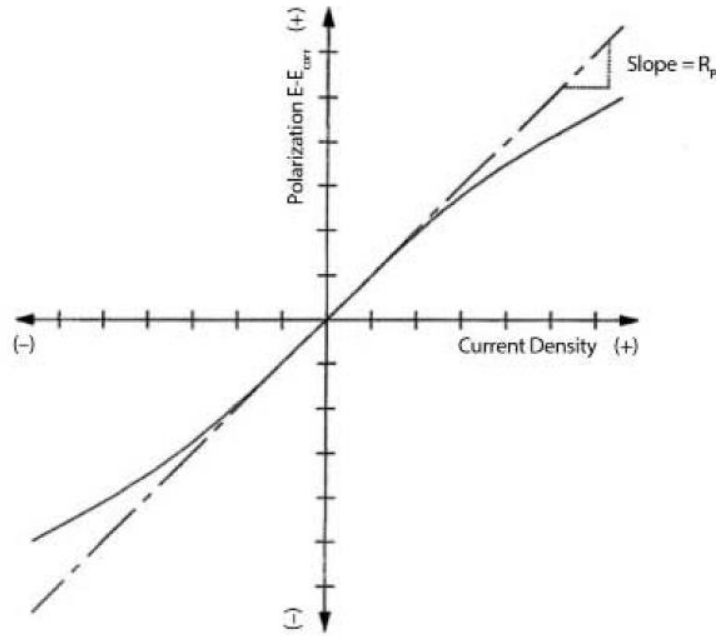


Figure 2-22 - Hypothetical polarization resistance plot [21,104,111].

As shown in Figure 2-22, during LPR measurements the polarization of the WE starts at negative potential towards upon circuit potential (corrosion potential) and proceeds in the positive direction through the upon circuit potential. The R_p is determined from the slope of the potential-current plot as shown in figure 2-22. Stern and Geary derived an equation known as Stern-Geary equation [21,110]. In this equation, the R_p is related to corrosion current (I_{corr}) as follows [21,104,111]:

$$I_{corr} = \frac{B}{R_p} \quad 2-5$$

B constant is calculated as:

$$B = \frac{\beta_a \beta_c}{2.303 (\beta_a + \beta_c)} \quad 2-6$$

Where; β_a and β_c are Tafel constants (anodic and cathodic constants). Combining equations 2-5 and 2-6:

$$I_{corr} = \frac{1}{R_p} \left(\frac{\beta_a \beta_c}{2.303 (\beta_a + \beta_c)} \right) \quad 2-7$$

The values of β_a and β_c are determined by Tafel extrapolation method or can be assumed in some cases. When these values are known the corrosion rate can be calculated from polarization resistance. In many cases the value of β (β_a and β_c) fall within the range of 60 and 120 mV, so in many cases a value of 120 mV is assumed for both [21]. By imputing the assumed values, equation 2-7 can be rewritten as [21]:

$$I_{corr} = \frac{25}{R_p} \quad 2-8$$

The value of B of carbon steels in seawater is calculated to be 25 mV [21,104].

Assuming that corrosion current distribution across the corroding specimen is uniform [21]:

$$i_{corr} = \frac{I_{corr}}{A} \quad 2-9$$

Where i_{corr} is current density ($\mu\text{A}/\text{cm}^2$) and A is sample's surface area (cm^2).

Based on Faraday's law, the corrosion rate (CR) can be calculated as in equation 2-10 [21,107,109]:

$$CR = K_{corr} \left(\frac{i_{corr}}{\rho_{metal}} \right) EW \quad 2-10$$

where CR is corrosion rate (mm/y); i_{corr} is corrosion current $\mu\text{A}/\text{cm}^2$; K_{corr} is corrosion constant with a value of $3.27 \times 10^{-3} \text{ mm g}/\mu\text{A cm y}$ [21,104,107]; EW is equivalent weight and defined as the mass in grams of corroding metal that will be oxidized by the passage of one Faraday (96,489 C (amp-sec)) of electric charge. The EW of pure metals is calculated as in equation 2-11 [21]:

$$EW = \frac{A_{wt}}{n} \quad 2-11$$

Where; A_{wt} is the atomic weight of the element; n is the valence of the element.

For alloys EW can be calculated as in equation 2-12 [21]:

$$EW = \frac{1}{\sum \frac{n_i f_i}{w_i}} \quad 2-12$$

Where; n_i is the valence of the i^{th} element of the alloy; A_{wti} is the atomic weight of the i^{th} element of the alloy, and f_i is the mass fraction of the i^{th} element of the alloy.

2.5.2 Online, Destructive Techniques

These are electrochemical techniques that determine the corrosion rate of the specimen while the experiment is in progress. An example of online destructive technique is potentiodynamic polarization (PP). In potentiodynamic polarization, large potential (typically more than ± 500 mV) is applied to the WE and in some cases the scan is reversed, which involves continuous changing or sweeping of the applied potential (known as cyclic potentiodynamic polarization) [21,109]. They are used to measure the corrosion rate once, because they change the state of the specimen during the measurement. According to Yang [112], cyclic PP technique is often used to determine the ability of a metal or alloy to undergo pitting corrosion.

2.5.3 Offline Monitoring Techniques

These are corrosion monitoring techniques that determine the corrosion rate of the specimen (known as coupons) after it has been taken out from the test solution. An example of this type of technique is the mass or weight loss technique. [21,107]. The corrosion rate of the coupon after the test is calculated as in equation 2-13 [21,107]:

$$CR = k \frac{W}{dAt} \quad 2-13$$

Where; W is metal weight loss (g); d is density of coupon (g/cm^3); A is coupon exposure area (cm^2); t is exposure time of specimen (hr), and k is corrosion constant of conversion depending on the corrosion rate unit. Value of k can be taken as 8.76×10^4 (mm/y) or 3.45×10^6 (mpy).

2.6 Control of External Corrosion of Pipelines

Various corrosion protection methods are presently in use to protect pipelines against corrosion. This includes the use of external pipe coatings, cathodic protection (use of either impressed current method or sacrificial anodes), use of

corrosion inhibitors, proper materials selection [2,46]. Proper use of today's modern technology can extend the service life of pipelines, but require proper application and maintenance [2]. Furthermore, employing trained personnel in corrosion control is vital to achieving a successful corrosion mitigation strategy [2].

2.7 Control of Internal Corrosion of Pipelines

Internal corrosion in pipelines occurs due to transportation of corrosive fluids or condensates through the pipelines [46]. Its control can be minimised by modifying the environment, by use of corrosion inhibitors, increase of corrosion allowances in the pipelines, and installation of various corrosion monitoring devices [71,33]. In addition, internal coatings such as fusion bonded epoxy (FBE), and lining are also used to effectively minimise internal corrosion [33,112].

2.8 Corrosion Monitoring of Pipelines

Corrosion monitoring as described by Roberge [71] are measurements performed under industrial or laboratory conditions to acquire data on the rate of metal or alloy corrosion or deterioration. However, the obtained data are of limited use until they are converted into useful information for use in corrosion management mitigation strategies [71].

The major objectives of corrosion monitoring of pipelines are: to select the most appropriate and corrosion resistant material for pipeline construction and corrosion mitigation program, and to ensure that the selected material and mitigation strategy continue to be effective for the designed service life of the system [21]. Pipeline corrosion monitoring methods ranges from simple visual inspection to very high-tech electronic devices that are used to monitor from online and remote locations. These devices can be grouped into:

- Use of visual inspection devices, such as pipeline inspection gauges (PIG) [21,71].

- Use of non-destructive evaluation (NDE) methods, such as magnetic flux leakage, magnetic particle testing, electromagnetic, ultrasonic and radiographic inspections [33,46].
- By monitoring the cathodic protection system [33].

2.9 Chapter Summary

The major areas around the world offshore pipelines are currently installed and operated, such as in Karsto (Norway) and Dornum (Germany) and also in the Gulf of Mexico have discussed. Major causes of pipeline failures have been identified to be corrosion, material and equipment defects, erosion, improper equipment installation and repairs, weld joints crack and excavation damages. Corrosion of pipelines can be controlled by use of coatings, corrosion inhibitors, cathodic protection (use of sacrificial anodes or impressed current), use of corrosion allowance in the pipeline walls, proper material selection and installation of effective corrosion monitoring devices (pipeline inspection gauges (PIG), magnetic flux leakage, radiographic, electromagnetic and ultrasonic inspection devices.

Major factors affecting SCC initiation and propagation of pipeline carbon steels have been researched to be temperature of the corrosive environment, compositions and concentrations of corrosive medium, microstructure of the materials, pH of the medium and applied stress level. Reliable laboratory techniques for accessing SCC susceptibility of metals or alloys have been researched and identified to deflected sample method (by use of C-rings, bent-beam, U-bend), constant load method (by use of notched beam, direct tension samples) and dynamic load method (by use slow strain rate test). The use of linear polarization resistance has been understood to be an effective and reliable technique for corrosion rate monitoring. Characteristics of seawater such as salinity, composition, solubility of trace gases and variations in sea surface and subsurface temperatures are briefly appraised.

3 METHODOLOGY

This chapter presents the different techniques and operating procedures carried out to understand the stress corrosion behaviour of different representative offshore pipeline carbon steels (X65, X70, X80 and X100) as introduced in chapter 1 and also discussed in chapter 2.1. Specimens are exposed in simulated 3.5 % NaCl solution and continuously bubbled with different trace gases of N₂, CO₂ and mixtures of O₂/N₂ and O₂/CO₂ at varying temperatures of 5 °C, 15 °C and 25 °C. These variables are selected to evaluate the impact of trace gases, temperature and stress application methods on SCC initiation and propagation mechanisms of the pipeline carbon steels. The change in corrosion rates and potentials of the samples were monitored by use linear polarization resistance technique, cumulative probability of metal loss exceedance was measured using dimensional metrology technique. Scanning electron microscopy, energy dispersive spectroscopy, X-ray diffraction, tensile strength and Vickers hardness analysis were conducted on the exposed samples.

3.1 Materials

The materials exposed in this research are API 5L X65, X70, X80 and X100 carbon steels. These carbon steel grades are currently the most established materials use in oil and gas transportation pipelines in many countries due to their proven reliability. Presently, grades X70, X80 and X100 carbon steels have being developed for use as subsea pipelines for non-sour fluid services and grade X65 and X70 for sour fluid services. The chemical compositions of the carbon steels from the ladle check analysis as-received from the manufacturers (Tata Steel UK Limited) are presented in Table 3-1. An increasing amount of manganese was observed from X65 (with a value of 1.61 wt.%) to X100 (with a value of 1.96 wt.%), with approximately equal amount of carbon for all steels (0.05 wt.% for X70 and 0.06 wt.% for X65, X80 and X100). Nickel content is observed to be highest for the X100 (0.30 wt.%), with lowest for X80 steel (0.036 wt.%). Increasing amount of Cr, Cu, Nb and Ti were observed from X65 to X80. The additions of these

elements, with application of different forms of heat treatments produces carbon steels with different ultimate tensile strengths and microstructures [21,22].

Table 3-1 - As-received chemical compositions (ladle check analysis) of the API 5L X65, X70, X80 and X100 carbon steels (wt.%).

Material Grade	C	Si	Mn	P	S	Cr	Mo	Ni	Al	Cu	Nb	Ti	Fe
X65	0.06	0.18	1.61	0.006	0.002	0.016	0.100	0.140	0.030	0.014	0.018	0.011	Bal.
X70	0.05	0.26	1.66	0.007	0.001	0.020	0.070	0.240	0.045	0.015	0.045	0.015	Bal.
X80	0.06	0.35	1.91	0.013	0.001	0.201	0.157	0.036	0.030	0.023	0.047	0.017	Bal.
X100	0.06	0.22	1.96	0.007	0.002	0.020	0.180	0.300	0.003	0.210	0.045	0.014	Bal.

As observed from scanning electron microscope analysis, the carbon steels are composed of different microstructures as shown in Figures 3-1a to 3-1d, respectively. The X65 is made up of typical ferritic-pearlite microstructure with polygonal ferrite grains and large distribution of pearlite grains, the X70 steel is composed of globular ferrite grains with grain boundary pearlite grains and coarse dispersion of precipitates, X80 is composed of ferrite grains with large distribution of pearlite bands and fine dispersion of precipitates, while the X100 steel is made up of bainitic ferrite grains with finely dispersed austenite grains. The observed micrographs of the carbon steels are consistent with the literature [21,23,113,114].

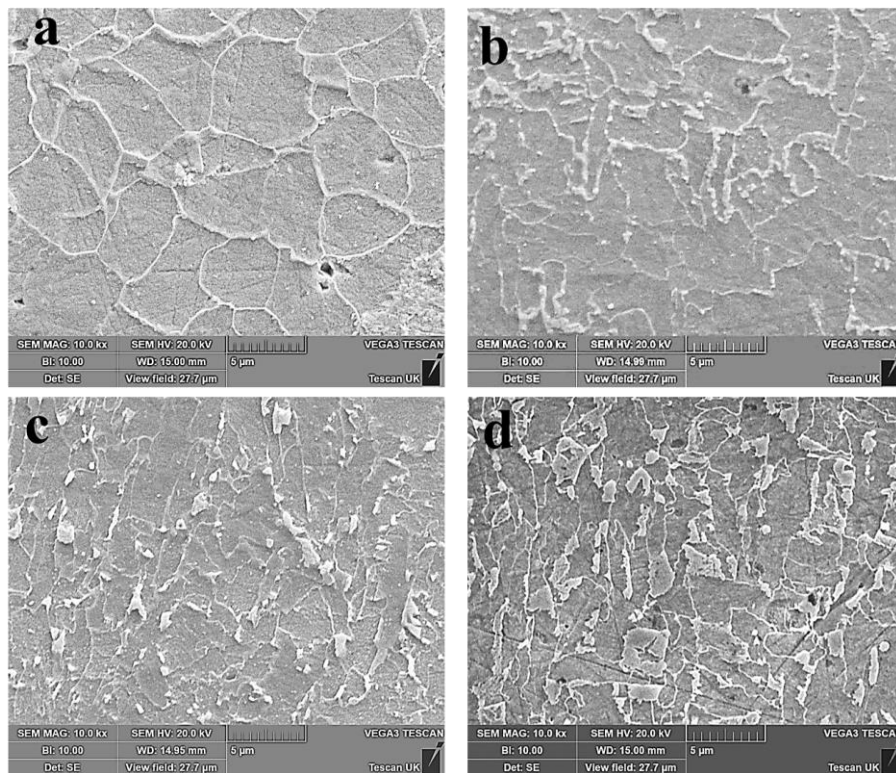


Figure 3-1 - Microstructures of the exposed carbon steels as observed from SEM: (a) API 5L X65; (b) API 5L X70; (c) API 5L X80; (d) API 5L X100.

3.2 Samples Geometry and Stress Application Techniques

C-rings and three-point bent-beam specimens were used to assess the impact of stress application methods on the corrosion resistance of the pipeline carbon steels. Dog-bone samples were also machined and exposed to assess the

change in tensile strength and hardness of the material with change in solution conditions. All samples were cut and machined from lengths of 1 m pipe with 762 mm outer diameter (OD) and wall thickness of 38.2 mm supplied by Tata Steel UK Limited.

3.2.1 C-ring Loading Method

C-rings specimens were designed and machined in accordance with ASTM G38-01 [106] and NACE TM0177-05 [116] standards, using ratios of between 10 and 100 outer diameter to wall thickness (d/t) and of between 2 and 10 width to wall thickness (w/t). This gives final dimensions of 18.5 mm outer diameter, 12 mm width and 1.3 mm wall thickness (with OD/t ratio of 14.23 and W/t ratio of 9.23). The samples were finished with a P1200 (600 grit) surface roughness. Figure 3-2 shows the C-ring design and dimensions.

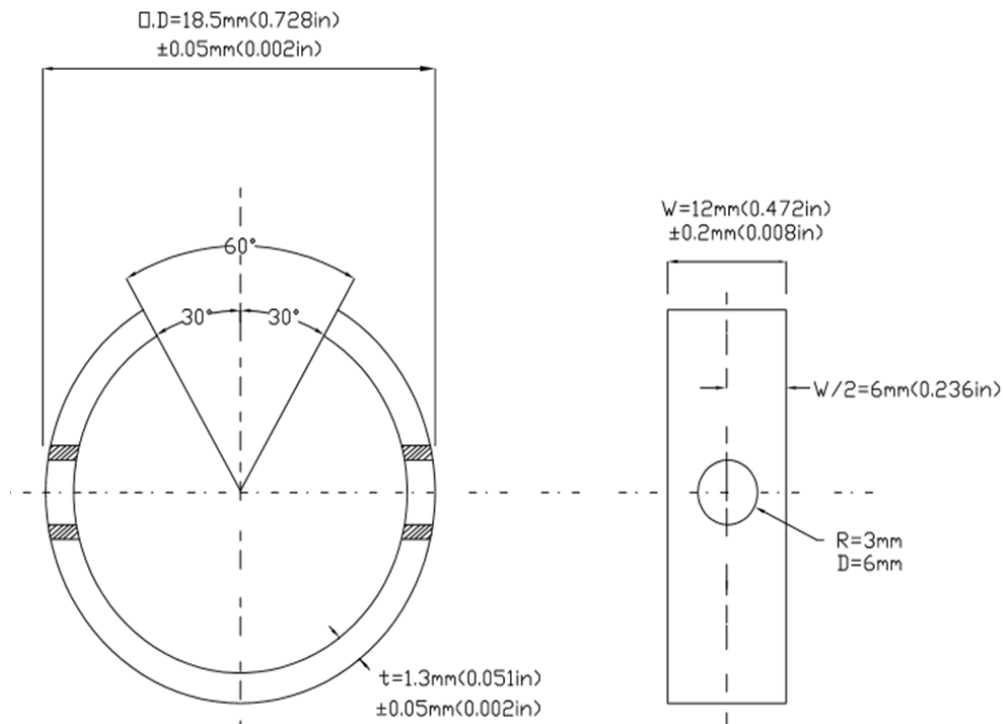


Figure 3-2 - C-ring design and dimensions [105,115].

A constant strain technique was used to stress the samples to the desired stress levels of 80 % and 95 % of the yield strength of the carbon steels for unnotched samples and notched samples stressed at 80 % yield strength. Mechanically pre-damaged samples stressed at 80 % and 95 % yield strength, and chemically pre-

damaged sample stressed at 80 % yield strength. The selection of applied stress level of 80 % Y.S. and 95 % Y.S. is based on understanding the effect of increased applied stress level beyond normal operating pressure (NOP) of pipelines during their service life. NOP of liquid and gas pipelines is reported to be 60 % Y.S. [68]. Table 3-2 shows the as-received yield strengths of the carbon steels and calculated applied yield strengths. The stress on the C-rings is exerted on the diameter of the C-ring by tightening a bolt a calculated distance based on the C-ring's outer diameter, its elastic modulus and wall thickness as outlined in ASTM G38-01 standard [106] and shown in equation 3-1:

$$OD_f = OD - \Delta; \quad \mathbf{3-1}$$

$$\text{where: } \Delta = \frac{f\pi D^2}{4EtZ}; \quad \mathbf{3-2}$$

$$D = (OD - t) \quad \mathbf{3-3}$$

Where: OD_f = outer diameter of stressed C-ring, mm; OD = outer diameter of C-ring before stressing, mm; Δ = change of OD giving desired stress, mm; f = desired stress, MPa; D = mean diameter, mm; E = modulus of elasticity, MPa; t = wall thickness, mm; Z = correction factor for curved beams.

Table 3-2 - As-received and applied yield strengths of the exposed samples.

Material grade	Yield strength, MPa (as received)	Desired applied stress, MPa	
		80 % Y.S.	95 % Y.S.
X65	511	408.80	485.45
X70	510	408.00	484.50
X80	633	506.40	601.35
X100	698	558.40	663.10

3.2.2 Three-point Bent-beam Method

The 3-point bent beam specimens and stressing jigs were designed and machined in accordance with ASTM G39 – 99 [107] standard. The machined specimens gave final dimensions of 102 mm length, 20 mm width and 1.1 mm thickness. Both the samples and stressing jigs were finished with a P1200 (600 grit) surface roughness. Figures 3-3a and 3-3b respectively, shows the 3-point bent-beam specimen and stressing jig design and dimensions.

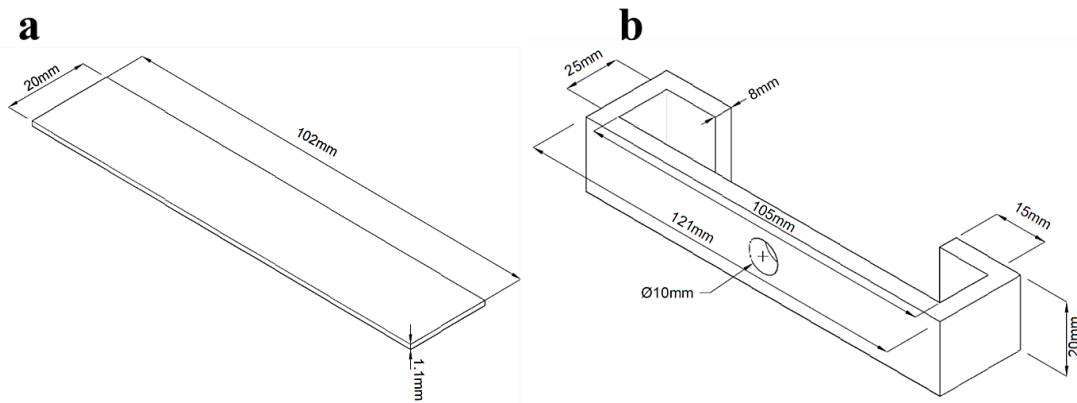


Figure 3-3 - Three-point bent-beam design and dimensions. (a) specimen design; (b) stressing jig design [107].

The specimens were stressed to the desired stress levels of 80 % and 95 % of the yield strength of the carbon steels as outlined in ASTM G39 – 99 [107] standard and shown in equation 3-4.

$$\sigma = \frac{6Ety}{H^2} \quad 3-4$$

where: σ = maximum tensile stress, MPa; E = modulus of elasticity, (210,000 MPa); t = wall thickness of sample, mm; y = maximum deflection of stressed specimen, mm; H = distance between outer supports of stressing jig, mm.

3.2.3 Dog-bone Specimen for Tensile Strength Tests

The dog-bone specimens used to assess the change in tensile strengths in the exposed conditions were designed and machined in accordance with ASTM E8/E8M–21 [117] and ASTM G129–21 [118] standards. Figure 3-4 shows the design and dimensions of the dog-bone.

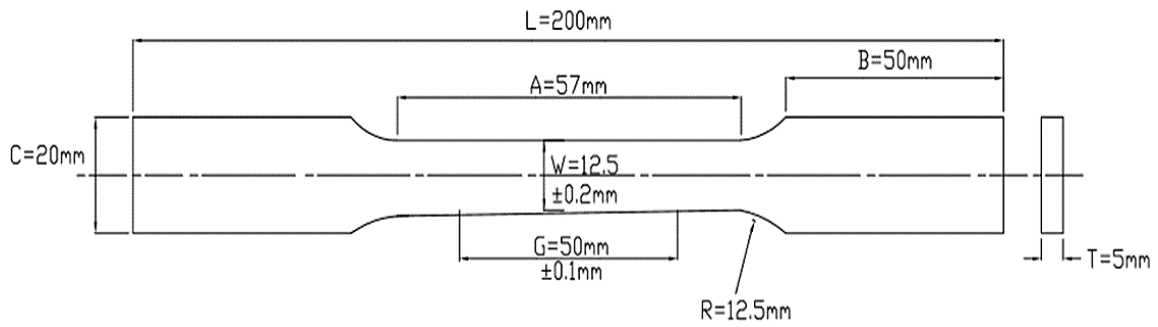


Figure 3-4 - Dog-bone specimen design and dimensions [116,117].

3.3 Sample Preparation

Before exposure, sample preparation was carried out on all samples'. Initially samples are immersed in a beaker containing acetone and placed in an ultrasonic bath for 15 mins, then dried and immersed in a beaker containing isopropyl alcohol (IPA) for another 15 mins and dried again. This process of cleaning is carried out on the samples to get rid of any left-over oil or grease from the machining process. This avoids contamination of the test's solutions. After cleaning of the samples, before exposure weight and dimensional measurements were taken. The widths, lengths and diameters of the samples were measured using Mitutoyo digital caliper with an accuracy of 0.03 mm, while thicknesses were measured using Mitutoyo digimatic micro-meter with an accuracy of 0.001 mm. Appendix B presents the dimensional measurements, pre and post-exposure weights of all samples exposed in the different simulated 3.5 % NaCl solution.

To understand the effect of pre-exposure surface damage on stress corrosion susceptibility of the samples, notched samples were prepared. In addition, mechanically and chemically pre-damage samples were also prepared. The notched samples were prepared by engraving or machining 200 μm V-notches across the top centre of the C-rings. This is carried out in order to create a triaxial stress condition adjacent to the root of the notch on the specimens' surfaces. Figure 3-5 shows an example of a notched sample and position of the engraved notch.



Figure 3-5 - Example of a notched sample showing the position of the notch.

To mechanically pre-damage the samples, a coarse sandpaper with a P120 grade was used to make scratches on the stress-oriented sections of the C-rings. For the chemically pre-damaged sample, a highly concentrated NaCl solution of 30g NaCl dissolved in 100ml of distilled water was sprayed on the sample and left in an open environment for 168 hrs. The salt spray was conducted in order to cause pitting corrosion on the sample's surface. Figures 3-6a and 3-6b, respectively, shows the before and after mechanical damage of the samples. Figures 3-7a and 3-7b, respectively, shows the image of the sample at the time of salt spray and after 168 hrs (1 week) of application. After preparation of the samples, the change in surface roughness relative to a reference sample was analysed.

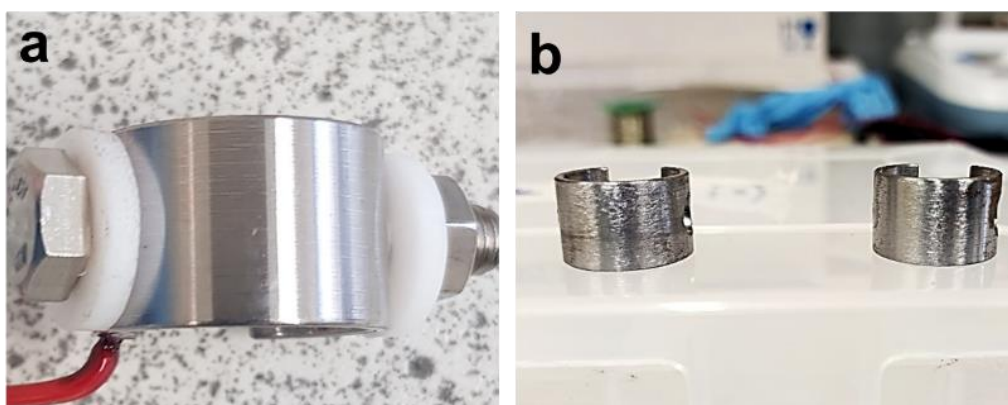


Figure 3-6 - C-ring samples: (a) before mechanical damage; (b) after mechanical damage.

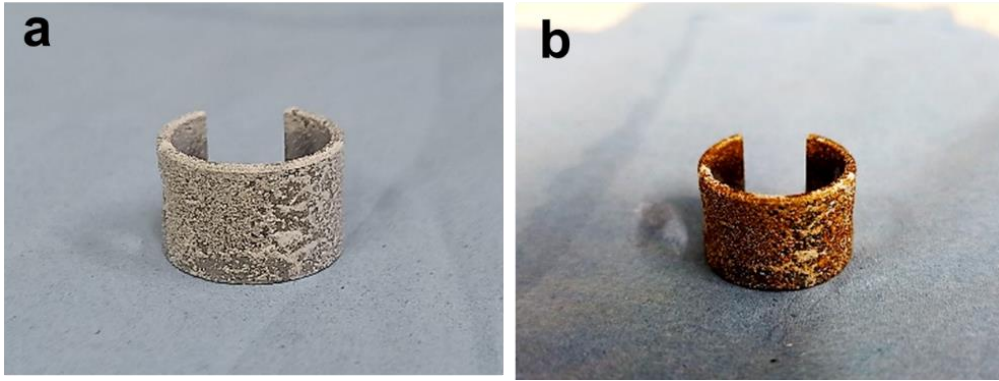


Figure 3-7 - C-ring samples: (a) at time of salt spray; (b) after 168 hrs of salt application.

After dimensional measurements and pre-damaging of the samples, wires are soldered at the edge of the samples to provide electrical connections for linear polarization resistance and open circuit potential measurements as discussed in section 2.5.1. Lacomit varnish is then applied on the soldered areas to reduce galvanic effect between the sample's surfaces and the soldered area. Polytetrafluoroethylene (PTFE) washers are placed between the C-rings and nuts and also PTFE tape wrapped around the bolts to avoid galvanic effect. Lacomit varnish was also applied on the stressing jig of the 3-point bending tests and PTFE tape wrapped on the outer support of the jig to reduce galvanic effects between the stressing jig and the sample. Figures 3-8a and 3-8b, respectively shows an example of C-ring and 3-point bending tests prepared samples.

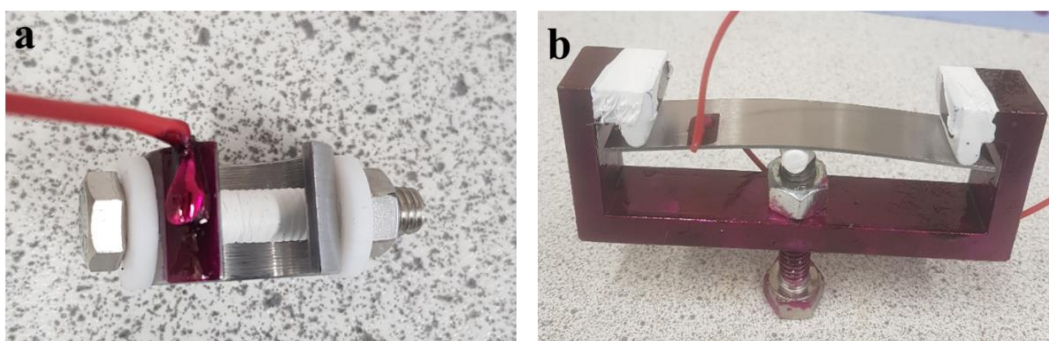


Figure 3-8 - Images of prepared samples before exposure: (a) C-ring sample; (b) 3-point bending test sample.

3.4 Experimental Set-up

Sodium chloride (NaCl) was mixed to give 3.5 % salinity (35 g of NaCl dissolved in every one litre of deionised water). The selection of 3.5 % NaCl salinity is to simulate an average salinity of open sea and North Sea (3.5 %) as presented in Table 2-1. The 3.5 % NaCl solution is then added into a three-electrode electrochemical cell, which consists of working electrode (test sample), reference electrode (Ag/AgCl electrode) and counter electrode (Pt electrode). Figure 3-9 shows the schematic diagram.

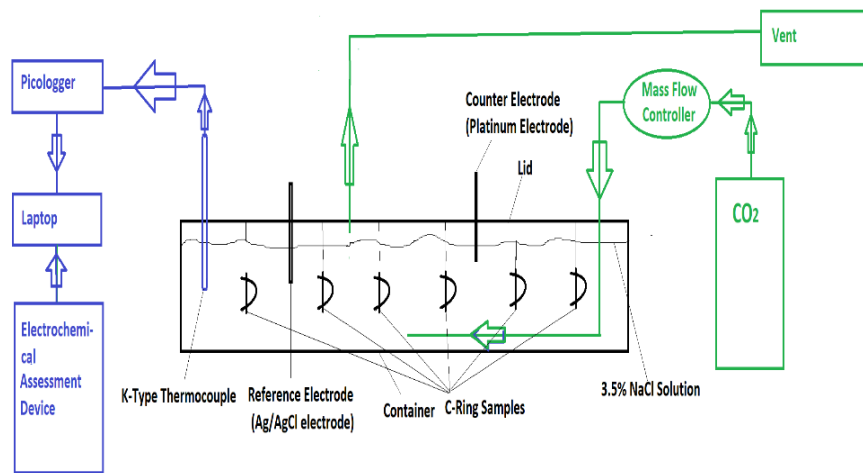


Figure 3-9 - Schematic diagram of experimental set up.

The test cell solution is then heated or cooled to the desired temperature of 5 °C, 15 °C or 25 °C. The selection of test solution temperature is based on the reviewed sea surface and subsurface temperatures in the oceans, as discussed in section 2.1.4. To cool the test solution to 5 °C, a flexible silicon tube was wrapped around the test cell and connected to a grant recirculating-chiller (LT-ecocool 150). The chiller reservoir was filled with 50 % water and 50 % antifreeze (ethylene glycol) to avoid freezing of the solution when lowered to below 0 °C. The chiller is then switched on and regulated accordingly to cool the test solution to the desired temperature of 5 °C.

To heat the test solution to 15 °C or 25 °C, a heating tape was wrapped around the test cell and regulated accordingly to heat the test solution to the desired temperature. A k-type thermocouple was inserted into the test cells via the lid to

measure and log the temperature change of the test solution with changing ambient temperature and recorded with a picologger connected to a laptop. Data from the temperature logs shows fluctuations in the set solution temperatures with an average value of about +1.5 °C and -1 °C. Appendix C shows the chiller and heating tape calibration tests conducted prior to actual experimental tests.

After cooling or heating of the test solution, the stressed specimens are then suspended in the test cell and sealed. Depending on the test condition, the desired gas or gas mixture (N₂, CO₂, O₂/N₂ or O₂/CO₂) is continuously bubbled in the test cell at 50 ml/min flowrate throughout the duration of the experiment. Low gas flowrate is selected in order to minimise agitation of the test solution, which can lead to increase in electron transfer across the test cell and subsequently can lead to increase in corrosion rates. Agitation of the test solution can cause an increased risk of pitting damage on the metal's surfaces. This can subsequently lead to increased loss in metal thickness and wall strength. Hence, increased SCC susceptibility. The gas flow pipe was inserted into the test cell through the lid and set to lie at the bottom centre of the test cell in order to achieve even distribution of the gas during flow. The tests conditions are maintained for a period of 5 weeks (840 hrs) for each experiment. This will enable better understanding of the corrosion behaviour of the exposed samples when surface oxide films are formed and possible rupture may also occur. Hence, fluctuations in corrosion rates can be observed with time as in real pipeline exposure environments. As presented from the reviewed literature in section 2.3.2.1, experiments were majorly conducted by use of slow strain rate test technique and cyclic loading test. These techniques gives results within 2 to 3 days (48 hrs to 72 hrs) of exposure [21]. As such not much exposure time to understand the corrosion behaviour of the specimens in the selected environment. Exposure of the samples for a longer period of time will aid to understand its corrosion resistance in a particular environment. Understanding the corrosion resistance of a particular material to be used for a specific pipeline operation will help in selecting the most effective corrosion mitigation strategy. Hence, reduced risk of SCC occurrence. Figure 3-10 shows the real-life experimental set up for the chiller and heating tape

set up. Table 3-3 show summary of all tests conducted and chapters where their obtained results are presented and discussed.

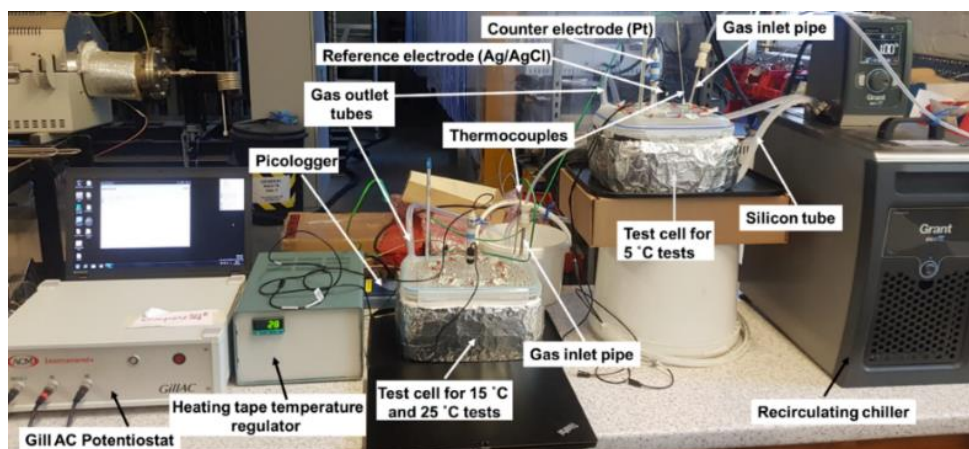


Figure 3-10 - Real life experimental set ups for 5 °C test (chiller set up), and 15 °C and 25 °C tests (heating tape set up).

Table 3-3 - List of all tests carried out.

Temperature, °C	Gas	Samples geometry	Chapters of results
5, 25	N ₂	C-rings	4
5, 15, 25	CO ₂	C-rings	5
5, 25	CO ₂	3 point bent-beam	5
5, 25	O ₂ /N ₂	C-rings	6
5, 15, 25	O ₂ /CO ₂	C-rings	7

3.5 In situ Electrochemical Analysis of Corrosion

During the exposure time corrosion rates of the carbon steels were monitored by use of linear polarization resistance technique and change in corrosion potentials were also measured over time.

3.5.1 Linear Polarization Resistance and Open Circuit Potential Measurements

Linear polarization resistance measurements were taken using an ACM Instruments GillAC with Sequencer V5 software. The GillAC is calibrated with measurement resolutions of 1 μ V. In each measurements a silver-silver chloride electrode (Ag/AgCl) and a platinum electrode, respectively, were used as reference and counter electrodes.

To measure the resistance, the working electrodes (specimens) were polarized at a potential of ± 10 mV around its open circuit potential. A slow scan rate of 0.167 mV/s was used during the LPR measurements in order to maintain the tests conditions close to steady state and lower agitation of the test solution as recommended by Papavinasam [21] and Baboian [105]. Periodic polarizations of the whole working electrode directly exposed in the solutions were conducted to monitor the change in corrosion rates and potentials after every 1 week (168 hrs).

The corrosion rates of each sample after polarization were calculated using the Stern- Geary equation as presented in equation 3-5 to 3-9 [21,104,118,119];

$$I_{corr} = \frac{B}{R_p}; \quad 3-5$$

$$\text{where: } B = \frac{\beta_a \cdot \beta_c}{2.303 (\beta_a + \beta_c)} \quad 3-6$$

where: I_{corr} = total anodic current, μ A; B = Stern-Geary constant with a value of 25 for carbon steels exposed under seawater conditions [21,104], V; R_p = polarization resistance of the working electrode (specimen), $\Omega \cdot \text{cm}^2$; β_a = slope of the anodic Tafel reaction, V/decade; β_c = slope of the cathodic Tafel reaction, V/decade.

Based on Faraday's law, the corrosion rates (CR) were calculated using equation 3-7 [21,104,119];

$$CR\left(\frac{\text{mm}}{\text{y}}\right) = K_{corr} \left(\frac{i_{corr}}{\rho_{metal}} \right) EW; \quad 3-7$$

$$\text{Where: } i_{corr} = \frac{I_{corr}}{A}; \quad 3-8$$

$$EW = \frac{A_{wt}}{n} \quad 3-9$$

where: CR = corrosion rate, mm/year; K_{corr} = corrosion constant with a value of 3.27×10^{-3} , mm g/ μ A (cm yr.) [21,104,119]; ρ = density of material, g/cm³; i_{corr} = corrosion current density, μ A/cm²; I_{corr} = total anodic current, μ A; A = exposed specimen area, cm²; EW = equivalent weight, Da; A_{wt} = atomic weight of the element, Dalton (Da); n = valence of the element.

Corrosion rates errors were calculated using propagation of error method as outlined by Taylor [121]. The calculated errors were observed to be negligible in the range of 10^{-5} to 10^{-7} mm/yr.

3.6 Post Exposure Analysis

Post exposure analysis such as scanning electron microscopy and energy dispersive spectroscopy analysis, X-ray diffraction (XRD) on exposed samples and dimensional metrology analysis to determine metal change on the exposed specimens were carried out. Tensile strength tests and Vickers hardness tests were also conducted on exposed dog-bone samples. Surface Roughness Analysis

3.6.1 Scanning Electron Microscopy and Energy Dispersive Spectroscopy Analysis

Scanning electron microscopy analysis of exposed samples' surfaces after testing is a requirement that gives a better understanding of the materials' corrosion behaviour in the tested conditions. Cross-sectional areas of the stress-oriented sections of the exposed specimens were ground and polished using 1 μ m diamond suspension in order to obtain a mirror surface finish and then examined to understand the type of corrosion morphology on the samples' surfaces. The scanning electron microscopy images and energy dispersive spectroscopy data were obtained by use of a Tescan Vega 3 Large SEM and Oxford Instruments AztecEnergy V2.2 with AztecHKL V2.2 software. An error of ± 5 % can be assumed for all EDS measurements [122].

3.6.2 X-ray Diffraction

X-ray diffraction analysis was carried out on the exposed specimens to understand the type of formed corrosion products and their diffraction pattern. The X-ray diffraction analysis was conducted using a Siemens D5005 X-Ray Diffractometer, and Bruker DIFFRAC plus XRD Commander V2.4.1 with EVA V4.1 software, with a Cu X-ray source. To carry out the XRD analysis, the XRD wizard was used to set up scan parameters of 40kV; 40mA; to scan over $10^{\circ}2\theta$ to $90^{\circ}2\theta$; 4000 data points; 0.02° per step with a time per step of 1 second and a scan time of 1 hour 6 minutes.

3.6.3 Tensile Strength Tests

Dog-bone samples were exposed in every test condition to evaluate the impact of the different trace gases and temperature on the tensile strength of the carbon steels. The tensile tests were conducted using an Instron 5500R (model 6025) mechanical machine with Instron Merlin software to record the data. The instrument was calibrated to ISO7500 at a class 0.5. To measure the tensile strength of the specimens, a load of 100 kN was applied on the samples at a speed of 3 mm/min as outlined in ASTM E8/E8M–21 standard [117]. This rate is selected for materials with expected elongations of more than 5 % as outlined in ASTM E8/E8M–21 standard [117].

3.6.4 Vickers Hardness Tests

Hardness tests were conducted on the exposed dog-bone samples to evaluate the change in hardness of the carbon steels due to the effect of the different test's conditions. The hardness tests were conducted using Zwick Roell ZHV indentec with INDENTEC C.A.M.S. software to record data. To measure the hardness of the specimens a load of 200 g was applied at a particular point on the specimens for 15 secs. The applied load and time were selected by use of HV 0.2 scale as outlined in ASTM E92-23 standard [123].

3.6.5 Surface Roughness Analysis

Before and after exposure surface roughness of chemically and mechanically damaged C-rings samples were measured. To measure the roughness, samples were scanned with a Taylor Hobson- Ultra software with 2.5 microns stylus profilometer placed at 5 mm length along the top centre section of the C-rings at a scan rate of 0.5 mm/s.

3.6.6 Dimensional Metrology Analysis

Dimensional metrology of the specimens after an exposed period of 840 hrs was conducted by optical microscopy as outlined by Sumner et al. [122,123]. The measured samples' coordinates were used to calculate the cumulative probability of metal loss exceedance. Figure 3-11 show the stages of the dimensional metrology technique.

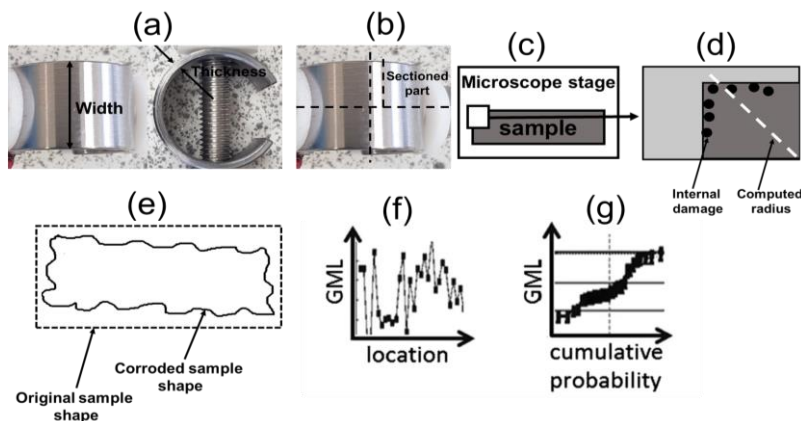


Figure 3-11 - Stages of dimensional metrology technique to determine metal loss [122,123]. (a) pre-exposure dimensions are taking from specimens; (b) specimens are then exposed and cross-sectioned after exposure; (c) specimens then placed on x–y calibrated Leitz Wetzlar AxioCam ICc 1 microscope stage with an image analyser subroutine to measure evenly spaced images of the sample; (d) key points such as internal damage and remaining metal on the image are selected; (e) comparison of pre- and post-exposure sample radii; (f) acquiring around the sample a range of different metal losses or internal damages, formed oxides or scale thicknesses; (g) data ordering from most to least damaged to give the cumulative probability of damage [122,123]. Collected data are plotted against cumulative normal distribution (in standard deviations) with a metal loss error of $\pm 5 \mu\text{m}$.

3.7 Chapter Summary

Standard operating procedures and techniques using published literature have been followed to design an experimental set-up that was used to investigate the stress corrosion behaviour of different representative offshore pipeline carbon steels. C-rings, 3-point bent-beam and dog-bone samples were designed by use of ASTM and NACE standards as referenced in section 3.2. Reliable corrosion monitoring and evaluation techniques were used to access the change in corrosion rate and extent with time, and also surface morphology of exposed samples with changing exposure conditions.

4 RESULTS AND DISCUSSION FOR EXPERIMENTS IN SOLUTION WITH NITROGEN

This chapter presents the baseline tests results obtained from the exposed X65, X70, X80 and X100 C-rings samples exposed in simulated 3.5 % NaCl solution with N₂. Tests involving N₂ bubbling acted to reduce dissolved O₂ [75,124]. As described in chapter 3.4, the solution was continuously bubbled with N₂ at 50 mL/min flow rate for a period of 5 weeks (840hrs). An average nitrogen gas concentration of 10-18 ppm can be reached in seawater at atmospheric pressure [36]. Corrosion rates, metal loss exceedance, SEM analysis and EDS analysis were conducted on the exposed samples.

4.1 Experiments in Solution with N₂ at 5 °C and 25 °C

The tests were conducted at different solution temperatures of 5 °C and 25 °C. This is carried out to understand the effect of temperature on the exposed carbon steel samples.

4.1.1 Corrosion Rates and Potentials

The change in corrosion rates and potentials with time of the exposed samples were monitored by use of linear polarization resistance technique. Specimens were polarized at a potential of ± 10 mV at a scan rate of 0.167 mV/s. Periodic polarization of the specimens was carried out after every 168 hrs to monitor the change in resistance and potential. The corrosion rates are then calculated by use of Stern-Geary equation. Two measurements were carried out on each data point in all conducted experiments at all exposure conditions and average corrosion rates were calculated and values plotted against time. Corrosion rate errors were calculated using propagation of error method as outlined by Taylor [120]. The calculated errors were observed to be negligible in the range of 10^{-5} to 10^{-7} mm/yr.

4.1.1.1 Corrosion Rates and Potentials of X65 C-rings Specimens

Figures 4-1a to 4-1d show the corrosion rates and potentials of the exposed X65 carbon steel samples in solution with N₂ at 5 °C and 25 °C. As shown in graph

4-1a, fluctuations in corrosion rates were observed for all samples at 5 °C (Figure 4-1a). A continuous increase in corrosion rates with time were observed with a maximum value of 0.013 mm/year for the sample stressed at 95 % Y.S. at 480 hrs, however a decrease was observed for all the samples at 649 hrs of exposure, with increasing corrosion rate at 816 hrs. At 25 °C, a continuous increase in corrosion rates was observed for all samples throughout the duration of the tests, with a maximum value of 0.026 mm/year observed on the notched sample stressed at 80 % Y.S. (Figure 4-1c). The observed fluctuations in corrosion rates can be explained to occur due to continuous formation and rupture of surface films on the samples surfaces. This causes variations in cathodic reaction rates place on the sample's surfaces, hence the change in corrosion rates. Similar trends in corrosion potentials as observed in the corrosion rates at both 5 °C and 25 °C were observed. A maximum value of -754 mV_{Ag/AgCl} was observed for the sample stressed at 80 % Y.S. at 5 °C and -722 mV_{Ag/AgCl} at 25 °C. The different corrosion potentials observed on the exposed samples, shows the change in their thermodynamic behaviour in the exposure solution with change in temperature.

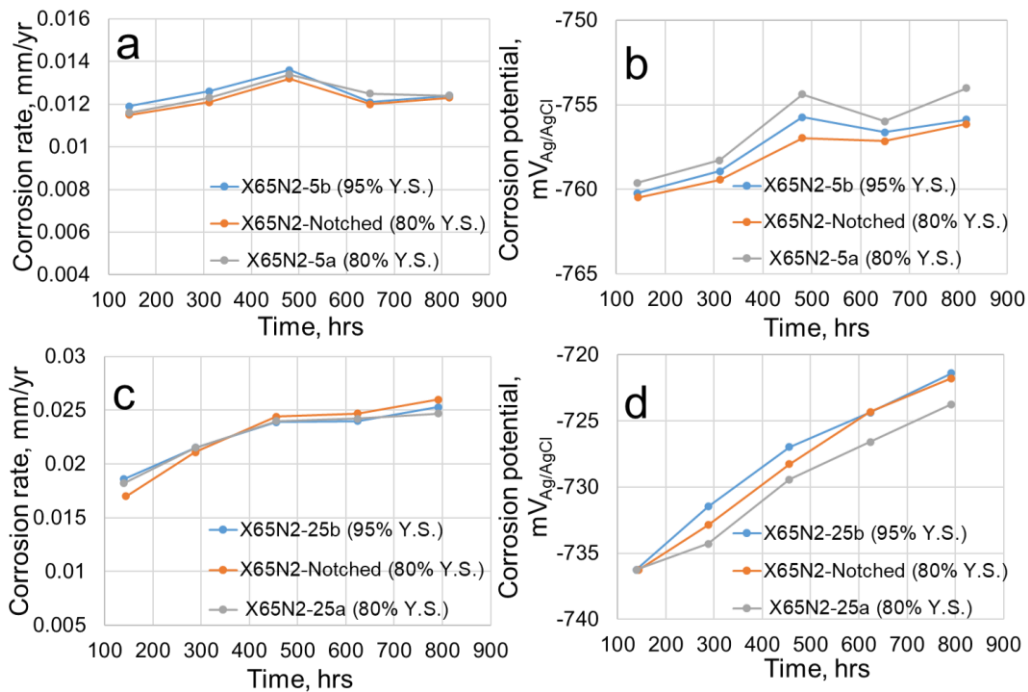


Figure 4-1 - Corrosion rates and potentials of the exposed X65 carbon steel C-rings in simulated saltwater solution with N₂: (a) corrosion rates at 5 °C; (b) potentials at 5 °C; (c) corrosion rates at 25 °C; (d) potentials at 25 °C.

In general, no significant change in corrosion rates observed with increasing applied stress level from 80 % Y.S. to 95 % Y.S. and change in surface state of the samples (notched state). With increasing temperature from 5 °C to 25 °C, the corrosion of the samples was observed to increase by about 100 %. In comparison with published literature corrosion rates of carbon steels in seawater as reported by Davies and Michael [44,45] with a value of 0.13-0.41 mm/year, 0.102-0.178 mm/year reported by Fontana [22], lower corrosion rates were observed on the exposed X65 samples at all solution temperatures. This is due to the continuous bubbling of nitrogen gas in the test solution, which eliminates any entrained air or oxygen [75,124]. From the observed low corrosion rates of the exposed X65 samples in the simulated 3.5 % NaCl in the presence of N₂, installation and usage of the carbon steel as a pipeline material in a seawater environment saturated with nitrogen does not impose risk of associated SCC occurrence on the material.

4.1.1.2 Corrosion Rates and Potentials of X70 C-rings Specimens

Figures 4-2a to 4-2d present the corrosion rates and potentials of the exposed X70 carbon steel samples in solution with N₂ at 5 °C and 25 °C. As shown in graph 4-2c, continuous increases in corrosion rates with time were observed with a maximum value of 0.031 mm/year for the sample stressed at 95 % Y.S. at 788 hrs at 25 °C, however a decrease was observed for the sample stressed at 80 % Y.S. and notched sample at 620 hrs of exposure. Corrosion rate fluctuations were observed for all samples at 5 °C (Figure 4-2a). A decrease in corrosion rates was observed for samples stressed at 80 % Y.S. and 95 % Y.S. at 644 hrs of exposure, however a decrease was observed for the notched sample at 477 hrs of exposure. Similarly, as reported from the obtained corrosion rates fluctuations of X65 samples, the observed fluctuations in corrosion rates of the X70 samples can be explained to occur due to continuous formation and rupture of surface films on the samples surfaces. A continuous increase in potential was observed for all samples throughout the duration of the experiment (Figure 4-2d) with a maximum value of -718 mV_{Ag/AgCl} obtained from the sample stressed at 95 % of Y.S. at 25 °C. At 5 °C, a decrease in potential was observed for all samples at

648 hrs of exposure, with a maximum value of $-754 \text{ mV}_{\text{Ag}/\text{AgCl}}$ observed for the sample stressed at 80 % Y.S. (Figure 4-2b). Figures 4-3a and 4-3b show the images of after exposure X70 samples in solution with N_2 at 25°C .

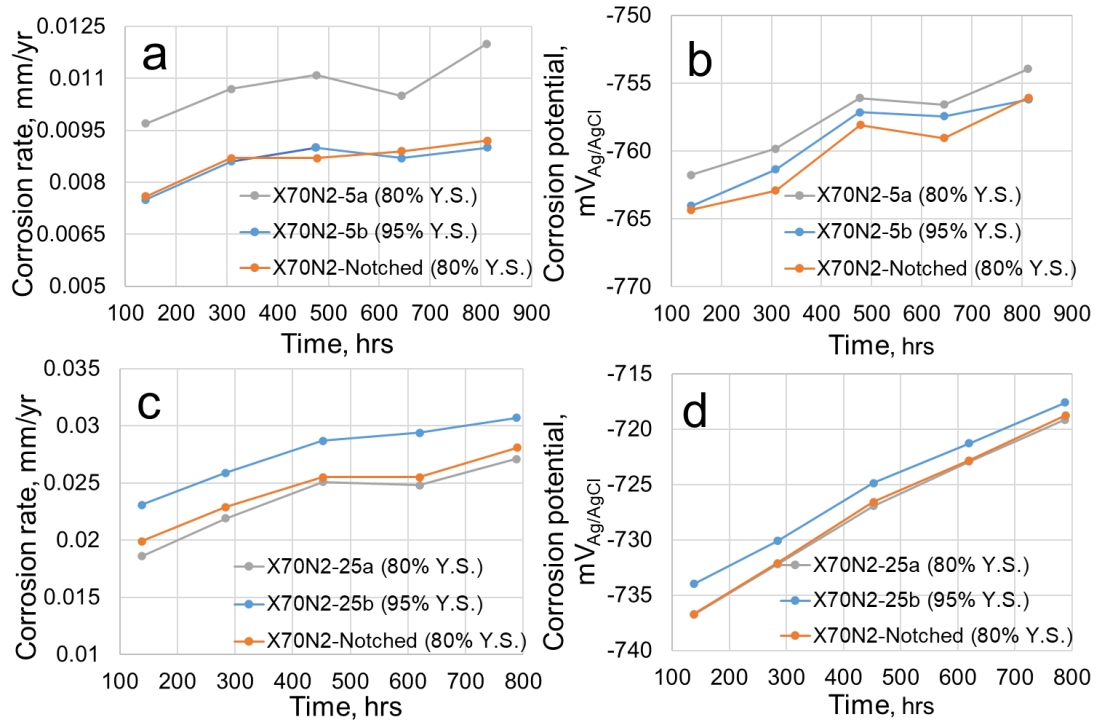


Figure 4-2 - Corrosion rates and potentials of the exposed X70 carbon steel C-rings in simulated saltwater solution with N_2 : (a) corrosion rates at 5°C ; (b) potentials at 5°C ; (c) corrosion rates at 25°C ; (d) potentials at 25°C .

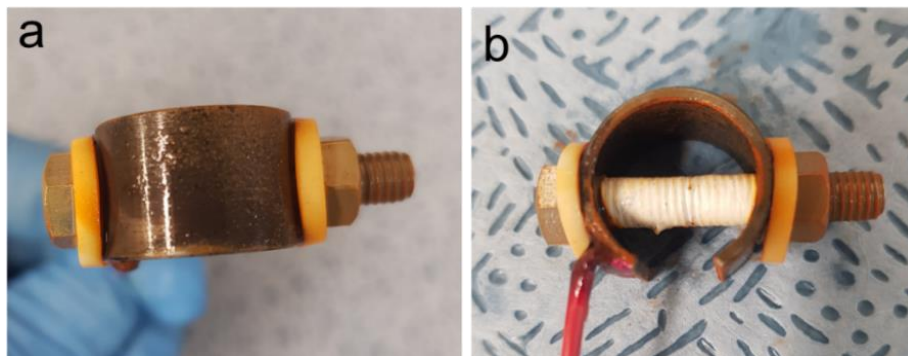


Figure 4-3 - Images of X70 C-rings sample after 840 hrs of exposure in simulated saltwater solution with N_2 at 25°C .

Relative to the exposed X65 samples, variations in corrosion rates were observed on the X70 samples with increasing applied stress level from 80 % Y.S. to 95 % Y.S. and change in surface state of the samples (notched state). The samples

stressed at 80 % Y.S. at 5 °C (Figure 4-2a) and 95 % Y.S. at 25 °C (Figure 4-2c) were observed to show higher corrosion rates. However, the differences are statistically insignificant. This can be explained to occur as a result of error in placements of the samples in the test cell, which leads to differential aeration on the exposed samples [125,126]. An increase in corrosion rates of about 100 % was also observed with increasing solution temperature from 5 °C to 25 °C. The X70 samples were observed to show higher corrosion rates (max. of 0.031 mm/year at 25 °C) in comparison with X65 samples (max. of 0.026 mm/year). This can be explained to occur due to the change in ultimate tensile strengths and microstructures of the material and its reaction to the exposure environment.

Lower corrosion rates were observed on the exposed X70 samples at all solution temperatures, relative to published literature corrosion rates of carbon steels in seawater as reported by Davies and Michael [44,45] with a value of 0.13-0.41 mm/year, 0.102-0.178 mm/year reported by Fontana [22]. This can also be explained to occur due to the continuous bubbling of nitrogen gas in the test solution, which eliminates any entrained air or oxygen [75,124]. Similarly, from the obtained low corrosion rates of the exposed X70 carbon steel samples in the simulated 3.5 % NaCl in the presence of N₂, installation and usage of the carbon steel as a pipeline material in a nitrogen saturated seawater environment does not impose risk of associated SCC occurrence on the material. However, as higher corrosion rates were observed on the X70 carbon steel in comparison with X65 within the exposure period (840 hrs), the carbon steels should be exposed for longer time to ascertain their SCC susceptibility before making a final selection.

4.1.1.3 Corrosion Rates and Potentials of X80 C-rings Specimens

Figures 4-4a to 4-4d present the corrosion rates and potentials of the exposed X80 carbon steel samples in solution with N₂ at 5 °C and 25 °C. As shown in Figure 4-4a, fluctuations in corrosion rates were also observed on all samples exposed at 5 °C, as observed from the exposed X65 and X70 samples. Continuous increase in corrosion rates with time were observed for the samples stressed at 95 % Y.S. and notched sample until 478 hrs of exposure, with a

decrease at 648 hrs. However, a decrease was observed for the sample stressed at 80 % Y.S. at 477 hrs of exposure until 645 hrs of exposure, with increasing corrosion rate at 814 hrs. Maximum corrosion rate value of 0.014 mm/year obtained from the notched sample. Similar trends in corrosion rates were observed at 25 °C (Figure 4-4c) in comparison with 5 °C. A decrease in corrosion rates was observed for all samples at 622 hrs of exposure, however an increase was observed at 790 hrs of exposure, with a maximum value of 0.031 mm/year observed for the sample stressed at 95 % Y.S. Similarly, as reported from the obtained corrosion rates of X65 and X70 samples, the observed fluctuations in corrosion rates of the X80 samples can also be explained to occur due to continuous formation and rupture of surface films on the sample's surfaces. Change in corrosion potentials were observed for all samples at 5 °C with a maximum value of -755 mV_{Ag/AgCl}. Continuous increase in potential was observed for all samples at 25 °C with a maximum value of -721 mV_{Ag/AgCl} obtained for notched sample. The variation in potential can also be explained to occur due to change in thermodynamic behaviour of the exposed samples with change in temperature.

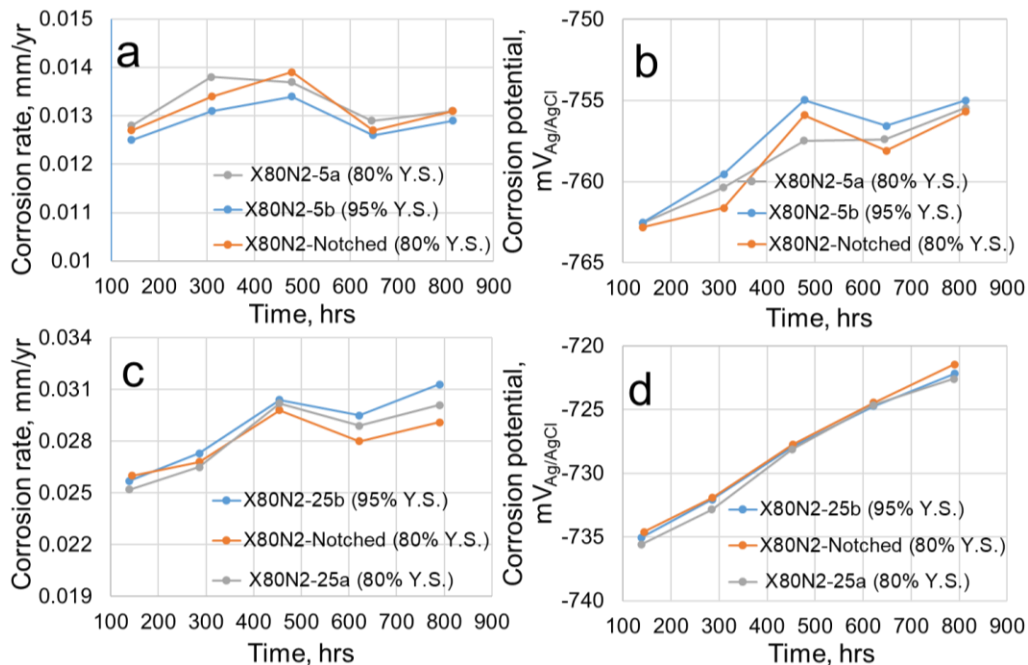


Figure 4-4 - Corrosion rates and potentials of the exposed X80 carbon steel C-rings in simulated saltwater solution with N₂: (a) corrosion rates at 5 °C; (b) potentials at 5 °C; (c) corrosion rates at 25 °C; (d) potentials at 25 °C.

Similarly, as reported from X65 and X70 exposed samples, no statistically significant change in corrosion rates observed with increasing applied stress level from 80 % Y.S. to 95 % Y.S. and change in surface state of the samples (notched state). An increase in corrosion rates of about 100 % was also observed with increasing solution temperature from 5 °C to 25 °C. Higher corrosion rates were observed on the X80 samples (max. of 0.032 mm/year at 25 °C), relative to the X70 (max. of 0.031 mm/year at 25 °C) and X65 (max. of 0.026 mm/year). It is clear that with increasing ultimate tensile strengths and microstructure change of the materials, their corrosion rates increases in the simulated saltwater solution.

Furthermore, the obtained corrosion rates on the exposed X80 samples at all solution temperatures were observed to be lower than published literature corrosion rates of carbon steels in seawater with a value of 0.102-0.178 mm/year reported by Fontana [22] and 0.13-0.41 mm/year reported by Davies and Michael [44,45]. As reported by Mu et al. and Kim et al. [75,124], respectively continuous bubbling of nitrogen gas in a test solution, eliminates any entrained air or oxygen, hence leading to lower corrosion rates. Similarly, from the obtained low corrosion rates of the exposed X80 carbon steel samples in the simulated 3.5 % NaCl in the presence of N₂, installation and usage of the carbon steel as a pipeline material in a nitrogen saturated seawater environment does not impose risk of associated SCC occurrence on the material. However, as higher corrosion rates were observed on the X80 carbon steel in comparison with X65 and X70 samples within the exposure period (840 hrs), the carbon steels should be exposed for longer time with putting into account all necessary environmental factors to ascertain their SCC susceptibility before making a final selection.

4.1.1.4 Corrosion Rates and Potentials of X100 C-rings Specimens

Similar trends in corrosion rates and potentials behaviour were observed on the X100 samples (Figures 4-5a to 4-5d) in comparison with the exposed X65 and X70 samples at both 5 °C and 25 °C. Fluctuations in corrosion rates were observed on all samples exposed at 5 °C, with a decrease at 648 hrs of exposure and an increase at 815 hrs observed from the samples stressed at 80 % Y.S. and notched sample. A continuous decrease was however observed on the samples

stressed at 95 % Y.S. after 648 hrs to end of exposure period. This fluctuations in corrosion rates can also be explained to occur due to rupture and formation of surface layers on the sample's surfaces. A maximum value of 0.013 mm/year was obtained from the samples stressed at 80 % Y.S. at 5 °C. A continuous increase in corrosion rates was observed on all samples throughout the duration of the test at 25 °C. A maximum value of 0.036 mm/year was obtained from the notched sample stressed at 80 % Y.S. Maximum potential of -742 mV_{Ag/AgCl} and -705 mV_{Ag/AgCl} (Figures 4-5b and 4-5d) respectively, were observed for the samples stressed at 80 % Y.S. at 5 °C and 25 °C.

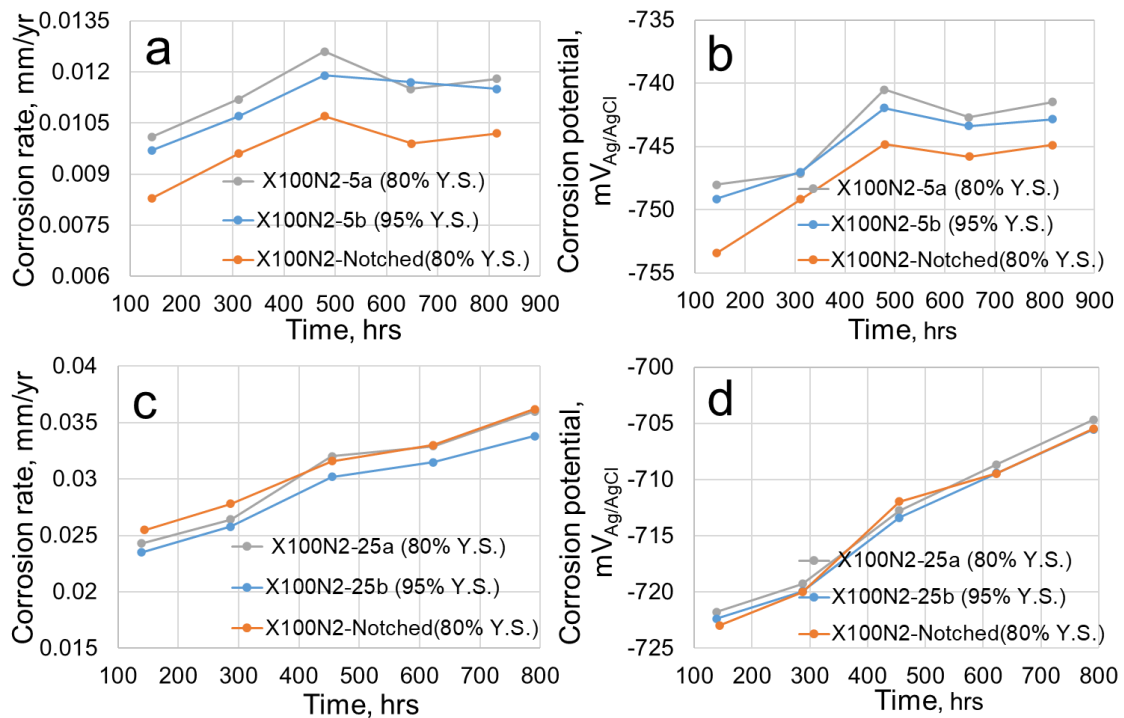


Figure 4-5 - Corrosion rates and potentials of the exposed X100 carbon steel C-rings in simulated saltwater solution with N₂: (a) corrosion rates at 5 °C; (b) potentials at 5 °C; (c) corrosion rates at 25 °C; (d) potentials at 25 °C.

In general, no significant change in corrosion rates observed with increasing applied stress level from 80 % Y.S. to 95 % Y.S. and change in surface state of the samples (notched state at 25 °C. However, at 5 °C, the notched sample was observed to show lower corrosion rates relative to samples stressed at 80 % Y.S. and 95 % Y.S. This could also be explained to occur as a result of differential aeration on the exposed samples due to error in placement of samples in the test

cell [125,127]. An increase in corrosion rates of more than 100 % was also observed with increasing temperature from 5 °C to 25 °C. Higher corrosion rates were observed on the X100 samples (max. of 0.036 mm/year at 25 °C), relative to the X80 (max. of 0.032 mm/year), X70 (max. of 0.031 mm/year) and X65 (max. of 0.026 mm/year). It is clear that with increasing ultimate tensile strengths and microstructure change of the materials, their corrosion rates increases in the simulated saltwater solution at 25 °C. However, the observed increase in the corrosion rates of the carbon steels from X65 to X100 shows that the presence of N₂ gas in the solution have not much impact on their corrosion rates.

Similarly, the obtained corrosion rates on the exposed X100 samples at all solution temperatures were observed to be lower than published literature corrosion rates of carbon steels in seawater. This is also achieved through continuous bubbling of nitrogen gas in a test solution, eliminates any entrained air or oxygen, hence leading to lower corrosion rates [75,124]. Similarly, from the obtained low corrosion rates of the exposed X100 carbon steel samples in the simulated 3.5 % NaCl solution in the presence of N₂, installation and usage of the carbon steel as a pipeline material in a nitrogen saturated seawater environment does not impose risk of associated SCC occurrence on the material. However, the X100 carbon steel can be said to be more susceptible to SCC in the simulated 3.5 % NaCl solution saturated with N₂ due to the obtained higher corrosion rates, in comparison with X65, X70 and X80. Therefore, material selection should be between X65, X70 or X80 if readily available.

4.1.2 Metal Loss Exceedance

Dimensional metrology after an exposed period of 840 hrs was conducted on the exposed samples by optical microscopy to measure the cumulative probability of metal loss exceedance of the samples. An error of ±5 µm is assumed for all metal loss measurements.

4.1.2.1 Cumulative Probability of Metal Loss Exceedance of X65 C-rings Specimens

Figures 4-6a and 4-6b, respectively, show the cumulative probability of metal loss exceedance, obtained from the datasets of the exposed X65 samples in solution with N₂ at 5 °C and 25 °C. Datasets for the samples stressed at 80 % Y.S and 95 % Y.S. at 5 °C show a relative metal change over most of the sample's surfaces, with an even distribution of metal change observed on the notched sample. An even distribution of metal change was observed on all samples at 25 °C, with low pits formation below about 15 % probability level or less. Maximum metal loss of -15.0 µm and -31 µm, respectively at 5 °C and 25 °C was observed on the samples stressed at 95 % Y.S.

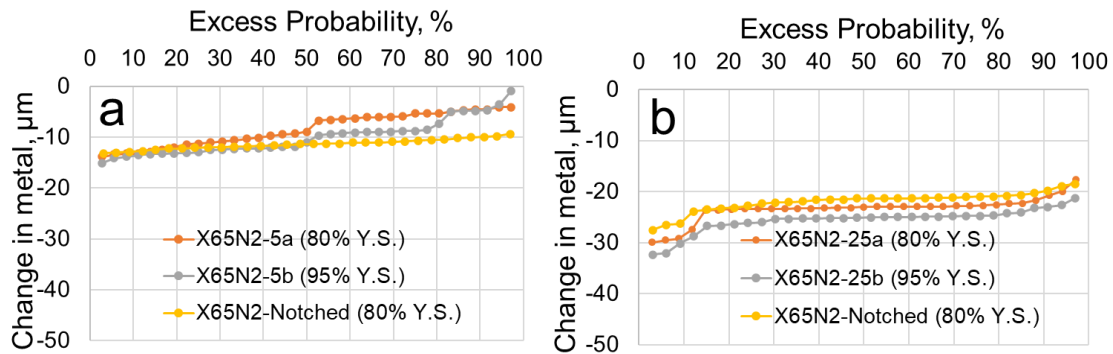


Figure 4-6 - Cumulative probability of metal loss exceedance graphs of X65 C-ring samples exposed in simulated saltwater solution with N₂: (a) at 5 °C; (b) at 25 °C.

In general, as shown in Figure 4-6, no significant change in metal loss value observed on the samples with change in applied stress level from 80 % Y.S. to 95 % Y.S. and notched sample, with putting into account an error in measurement of ± 5 µm in the measured metal loss of the samples. The measured metal loss exceedance on the samples which is another technique of measuring corrosion rates of samples tally with the obtained corrosion rates from LPR measurements. As observed from the calculated corrosion rates from LPR measurements Corrosion Rates and Potentials of X65 C-rings Specimens, an increase in metal loss of about 100 % was obtained on the X65 samples with increasing temperature from 5 °C to 25 °C.

4.1.2.2 Cumulative Probability of Metal Loss Exceedance of X70 C-rings Specimens

Figures 4-7a and 4-7b, respectively, show the cumulative probability of metal loss exceedance, obtained from the datasets of the exposed X70 samples in solution with N₂ at 5 °C and 25 °C. At 5 °C, an even distribution of metal change was observed on all samples at all stress levels, with low pits features below about 10 % or less probability level. The notched sample was observed to present a maximum metal loss of -13 μ m. At 25 °C, dataset for the sample stressed at 80 % Y.S. show a relatively low metal change over half of the sample surface. Relatively even distribution of metal change was observed over most of the sample that was stressed at 95 % Y.S., with significant pits formation below 6 % or less probability level. The notched sample presented higher metal change over the sample's surface. Maximum metal loss of -29 μ m was observed on the sample stressed at 95 % Y.S.

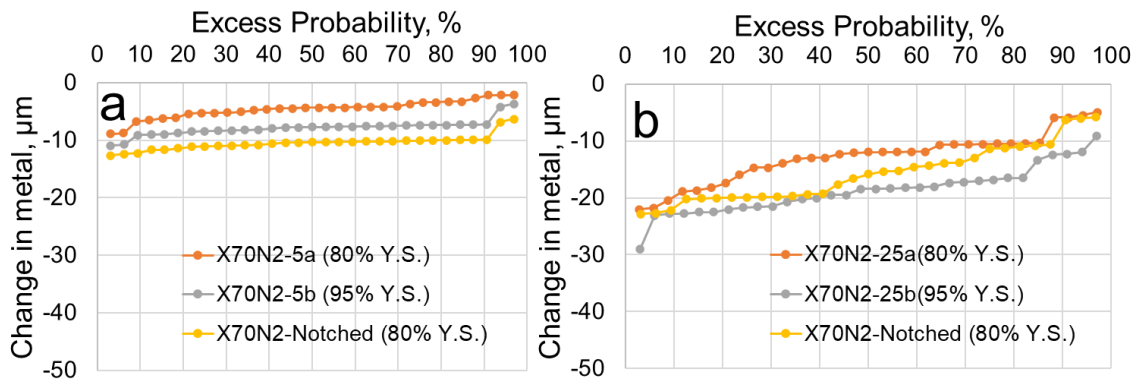


Figure 4-7 - Cumulative probability of metal loss exceedance graphs of X70 C-ring samples exposed in simulated saltwater solution with N₂: (a) at 5 °C; (b) at 25 °C.

Similarly, as observed from the calculated corrosion rates values on the X70 samples, no significant change in metal loss value observed on the samples as shown in Figure 4-7 with change in applied stress level from 80 % Y.S. to 95 % Y.S. and notched sample, with putting into account an error in measurement of $\pm 5 \mu$ m in the measured metal loss exceedance of the samples. No significant difference in measured metal loss between the exposed X65 samples (max. of -31 μ m) and X70 samples (max. of -29 μ m), as also observed from the calculated

corrosion rates from LPR measurements. An increase in metal loss of about 100 % was measured on the X70 samples with increasing temperature from 5 °C to 25 °C, as observed from the calculated corrosion rates from LPR measurements.

4.1.2.3 Cumulative Probability of Metal Loss Exceedance of X80 C-rings Specimens

Figures 4-8a and 4-8b, respectively, show the cumulative probability of metal loss exceedance, obtained from the datasets of the exposed X80 samples in solution with N₂ at 5 °C and 25 °C. Relatively low metal change was observed on the sample stressed at 95 % Y.S. and notched sample at 5 °C, with significant metal change observed over most of the sample stressed at 80 % Y.S. Higher metal change with even damage distribution was observed at 25 °C, with low pits features below about 6 % or less probability level. Significant pits features were observed on the notched sample below about 12 % or less probability level. Maximum metal loss of -15.0 µm and -32 µm, respectively at 5 °C and 25 °C was observed on the samples stressed at 80 % Y.S.

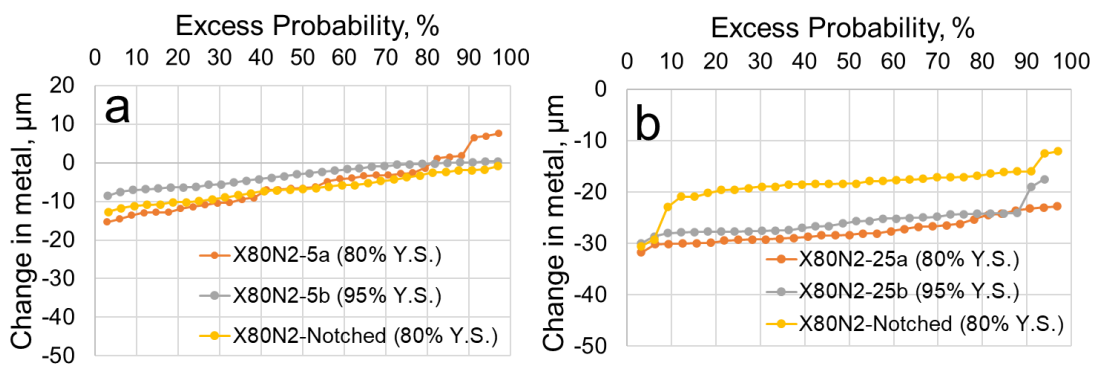


Figure 4-8 - Cumulative probability of metal loss exceedance graphs of X80 C-ring samples exposed in simulated saltwater solution with N₂: (a) at 5 °C; (b) at 25 °C.

As observed and reported from the calculated corrosion rate values and measured metal loss exceedance on the X65 and X70 samples, no significant change in metal loss value observed on the X80 samples (Figure 4-8) with change in applied stress level from 80 % Y.S. to 95 % Y.S. and surface state (notched state) of the samples, with putting into account an error of $\pm 5 \mu\text{m}$ in the

measurement of metal loss exceedance. Furthermore, no significant difference in measured metal loss between the X65 samples (max. of -31 μm), X70 samples (max. of -29 μm) and X80 samples (max. of -32 μm), as obtained from the calculated corrosion rates from LPR measurements. Similarly, as observed from the calculated corrosion rates of the exposed X65, X70 and X80 samples from LPR measurements, increasing metal loss of about 100 % was obtained on the X80 samples with change in solution temperature from 5 °C to 25 °C.

4.1.2.4 Cumulative Probability of Metal Loss Exceedance of X100 C-rings Specimens

Datasets for the X100 samples as presented in Figures 4-9a and 4-9b (at 5 °C and 25 °C, respectively), at all applied stress levels and solution temperatures show a relatively low metal change throughout majority of the samples surfaces with an even damage distribution. However, at 25 °C low pits features were observed on the notched sample below about 6 % probability level. Maximum metal loss of -34 μm and -63 μm , respectively at 5 °C and 25 °C was observed on the notched samples stressed at 80 % Y.S.

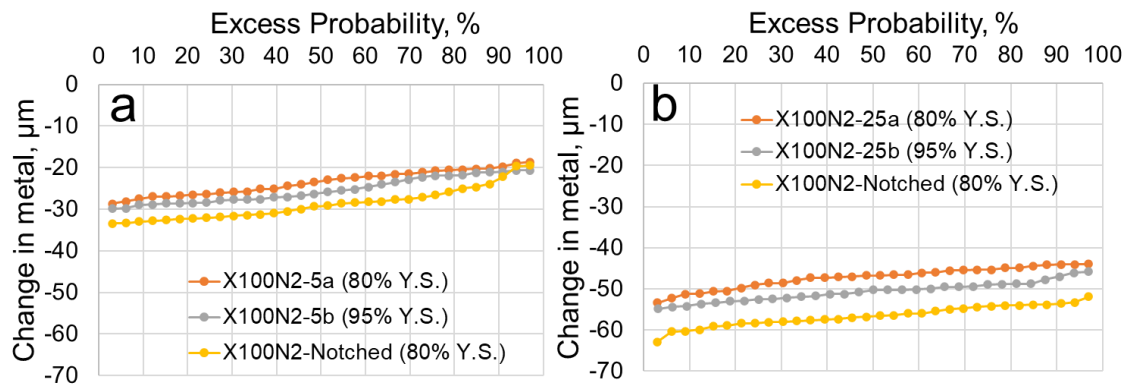


Figure 4-9 - Cumulative probability of metal loss exceedance graphs of X100 C-ring samples exposed in simulated saltwater solution with N₂: (a) at 5 °C; (b) at 25 °C.

In general, as observed from calculated corrosion rates from LPR measurements, the X100 samples at all exposure temperatures presented higher metal loss (max. of -63 μm at 25 °C) in comparison with X65, X70 and X80 samples. Similarly, as reported from the calculated corrosion rate values and measured

metal loss exceedance on the X65, X70 and X80 samples, no significant change in metal loss values observed on the X100 samples at both 5 °C and 25 °C with change in applied stress level from 80 % Y.S. to 95 % Y.S. and surface state (notched) of the samples, with accounting an error of $\pm 5 \mu\text{m}$ in the measured metal loss exceedance. An increase in metal loss of about 100 % was measured on the X100 samples with change in temperature from 5 °C to 25 °C, as observed from LPR measurements of corrosion rates.

The increased value in metal loss observed on the X100 samples relative to X65, X70 and X80 samples shows that the X100 carbon steel is more susceptible to SCC in the simulated saltwater solution with N_2 . As suggested from the calculated corrosion rates analysis between the X65, X70, X80 and X100 carbon steels, selection of carbon steel to be used as a pipeline material in nitrogen saturated seawater environment should be focused between X65, X70 or X80 if readily available.

4.1.3 Scanning Electron Microscopy Analysis

SEM analysis was conducted on the cross-sectional areas of the stress-oriented sections of the exposed C-rings samples to understand the type of corrosion morphology on the samples' surfaces with change in exposure conditions.

4.1.3.1 Scanning Electron Microscopy Images of X65 C-rings Specimens

Figures 4-10a to 4-10f, respectively, show the SEM images of the X65 samples stressed at 80 % Y.S, 95 % Y.S., and notched sample stressed at 80 % Y.S. exposed in solution with N_2 at 5 °C and 25 °C. All samples were observed to show little surface roughness at 5 °C, with different morphology from that formed at 25 °C. A considerable degree of anodic dissolution was observed on the samples at 5 °C which was greater at 25 °C.

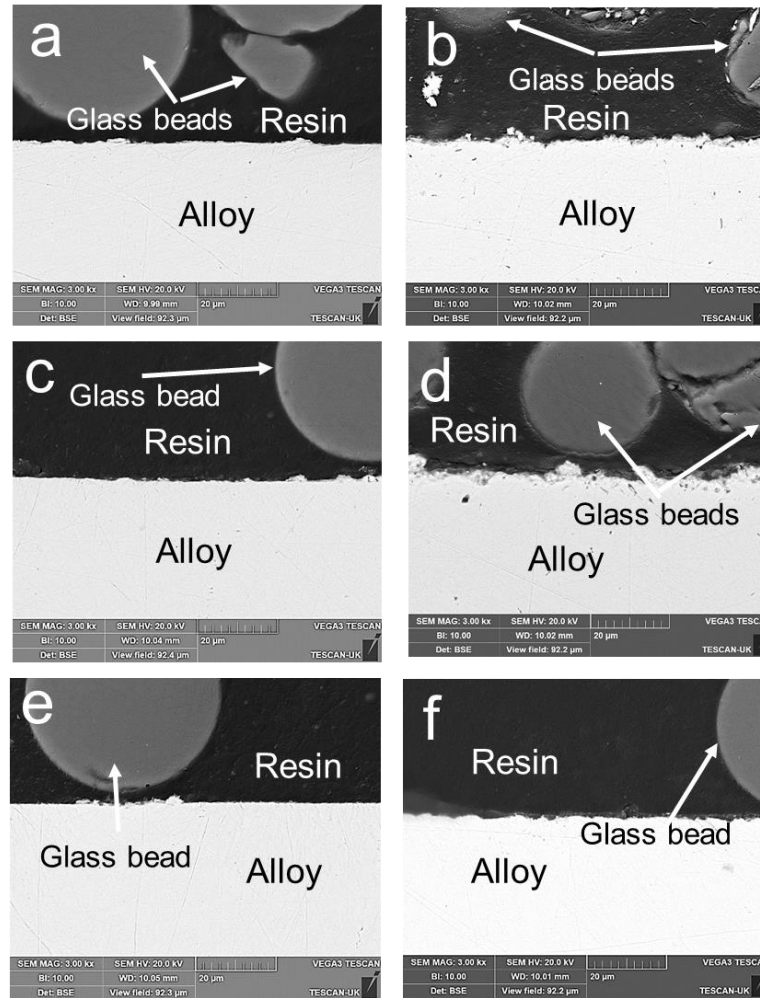


Figure 4-10 - SEM backscattered electron images of the exposed X65 C-ring samples in simulated saltwater solution with N₂ stressed at 80 % Y.S., 95 % Y.S. and notched sample stressed at 80 % Y.S.: (a) 80 % Y.S. at 5 °C; (b) 80 % Y.S. at 25 °C; (c) 95 % Y.S. at 5 °C; (d) 95 % Y.S. at 25 °C; (e) Notched sample at 5 °C; (f) Notched sample at 25 °C.

4.1.3.2 Scanning Electron Microscopy Images of X70 C-rings Specimens

Figures 4-11a to 4-11f, respectively, show the SEM images of the X70 samples stressed at 80 % Y.S, 95 % Y.S., and notched sample stressed at 80 % Y.S. exposed in solution with N₂ at 5 °C and 25 °C. Change in surface roughness was observed on all samples with increasing solution temperature from 5 °C to 25 °C. Greater anodic dissolution was observed on all samples at 25 °C.

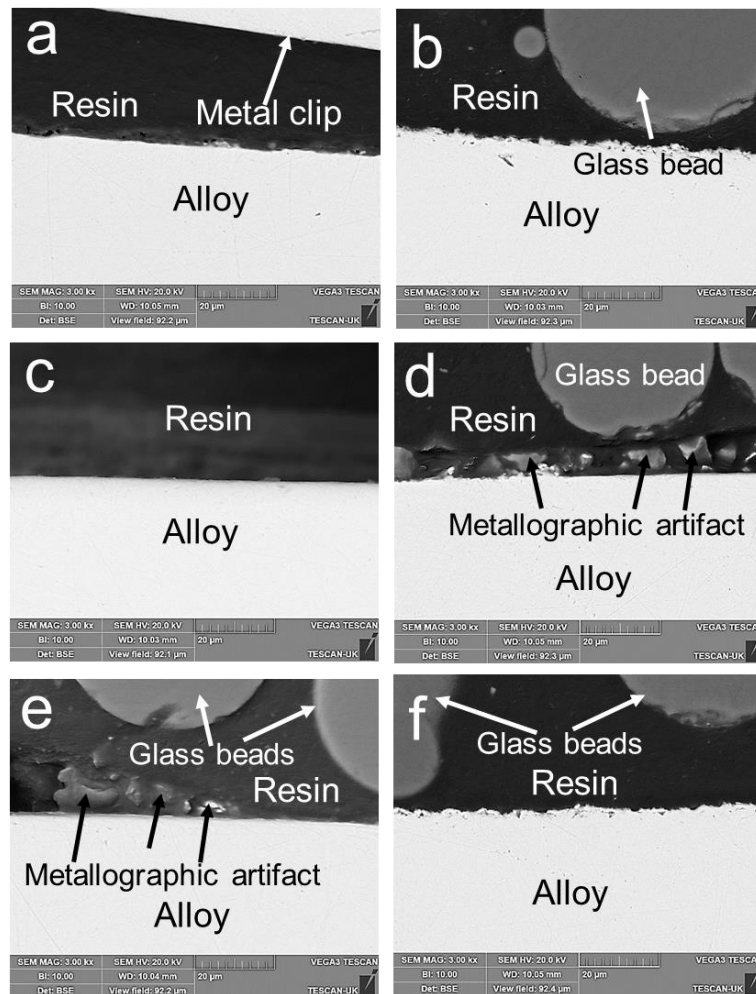


Figure 4-11 - SEM backscattered electron images of the exposed X70 C-ring samples in simulated saltwater solution with N₂ stressed at 80 % Y.S., 95 % Y.S. and notched sample stressed at 80 % Y.S.: (a) 80 % Y.S. at 5 °C; (b) 80 % Y.S. at 25 °C; (c) 95 % Y.S. at 5 °C; (d) 95 % Y.S. at 25 °C; (e) Notched sample at 5 °C; (f) Notched sample at 25 °C.

4.1.3.3 Scanning Electron Microscopy Images of X80 C-rings Specimens

Figures 4-12a to 4-12f, respectively, show the SEM images of the X80 samples stressed at 80 % Y.S, 95 % Y.S., and notched sample stressed at 80 % Y.S. exposed in solution with N₂ at 5 °C and 25 °C. Similarly, as observed on the exposed X65 and X70 samples, increasing surface roughness was observed on

the X80 samples with increasing solution temperature from 5 °C to 25 °C on all the different stressed samples.

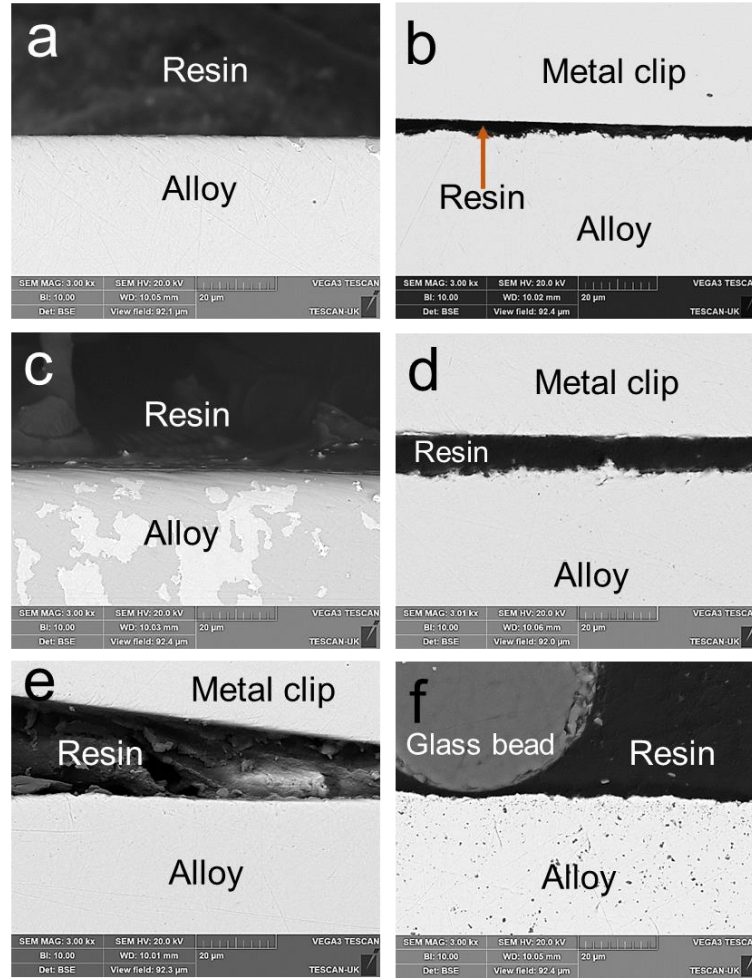


Figure 4-12 - SEM backscattered electron images of the exposed X80 C-ring samples in simulated saltwater solution with N₂ stressed at 80 % Y.S., 95 % Y.S. and notched sample stressed at 80 % Y.S.: (a) 80 % Y.S. at 5 °C; (b) 80 % Y.S. at 25 °C; (c) 95 % Y.S. at 5 °C; (d) 95 % Y.S. at 25 °C; (e) Notched sample at 5 °C; (f) Notched sample at 25 °C.

4.1.3.4 Scanning Electron Microscopy Images of X100 C-rings Specimens

Figures 4-13a to 4-13f, respectively, show the SEM images of the X100 samples stressed at 80 % Y.S, 95 % Y.S., and notched sample stressed at 80 % Y.S. exposed in solution with N₂ at 5 °C and 25 °C. The exposed X100 samples at all stress levels at 25 °C show an even surface roughness in comparison with the

X65, X70 and X80 samples. Little change in metal dissolution was observed with increasing solution temperature from 5 °C to 25 °C.

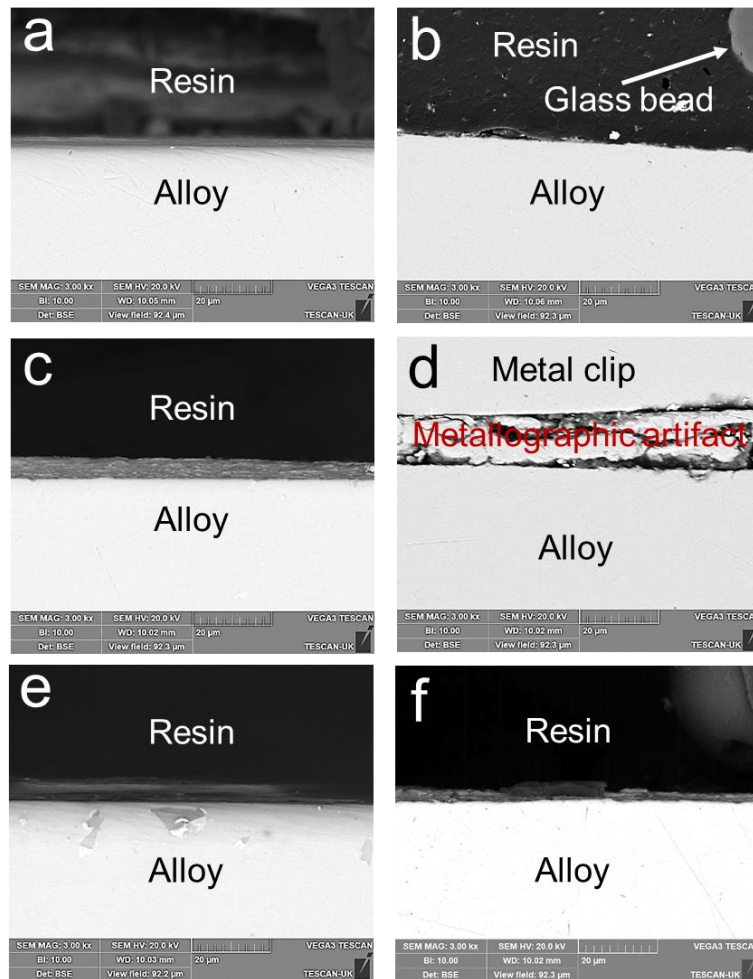


Figure 4-13 - SEM backscattered electron images of the exposed X100 C-ring samples in simulated saltwater solution with N₂ stressed at 80 % Y.S., 95 % Y.S. and notched sample stressed at 80 % Y.S.: (a) 80 % Y.S. at 5 °C; (b) 80 % Y.S. at 25 °C; (c) 95 % Y.S. at 5 °C; (d) 95 % Y.S. at 25 °C; (e) Notched sample at 5 °C; (f) Notched sample at 25 °C.

In general, images from SEM analysis show change in surface corrosion morphology on the exposed carbon steel C-rings samples with increasing solution temperature from 5 °C to 25 °C. An uneven surface morphology with shallow ellipses was observed on all exposed X65, X70 and X80 samples. However, the X100 samples show a more even surface morphology. This variation in surface morphology can be explained to occur due to differences in microstructures of the steels and their reaction to solution temperatures.

4.1.4 Energy Dispersive Spectroscopy

EDS analysis was conducted on the exposed samples to understand the variation in elemental compositions of the samples with change in exposure conditions. An error of $\pm 5\%$ is assumed for all EDS measurements.

4.1.4.1 Energy Dispersive Spectroscopy Analysis of X70 C-rings Specimens

The compositions of the EDS spectra (Figure 4-14) of the exposed X70 sample in solution with N_2 stressed at 80 % Y.S. at 5 °C, are presented in Figure 4-15 (in weight percentages). Figure 4-16 show the line scan analysis of the exposed sample. Spectrum 1 which is mainly resin will not be reported in the analysis. The carbon content from all spectra will also not be reported as EDS does not correctly quantify the percentage of carbon present in the analyzed samples. Variations in percentage of Mn was observed with change in spectrum location. Spectrum 3 which is close to the alloy-resin interface presented higher percentages of Fe and Mn with 92.65 wt.% and 1.95 wt.%, respectively, relative to spectrum 4 with 91.41 wt.% and 1.55 wt.%, respectively.

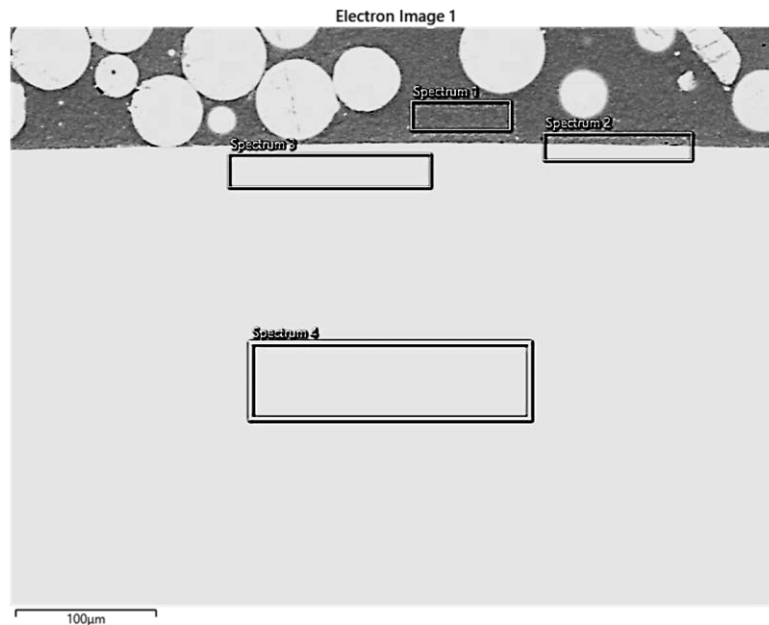


Figure 4-14 - SEM backscattered electron image of the exposed X70 C-ring sample in simulated saltwater solution with N_2 at 5 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 4-15.

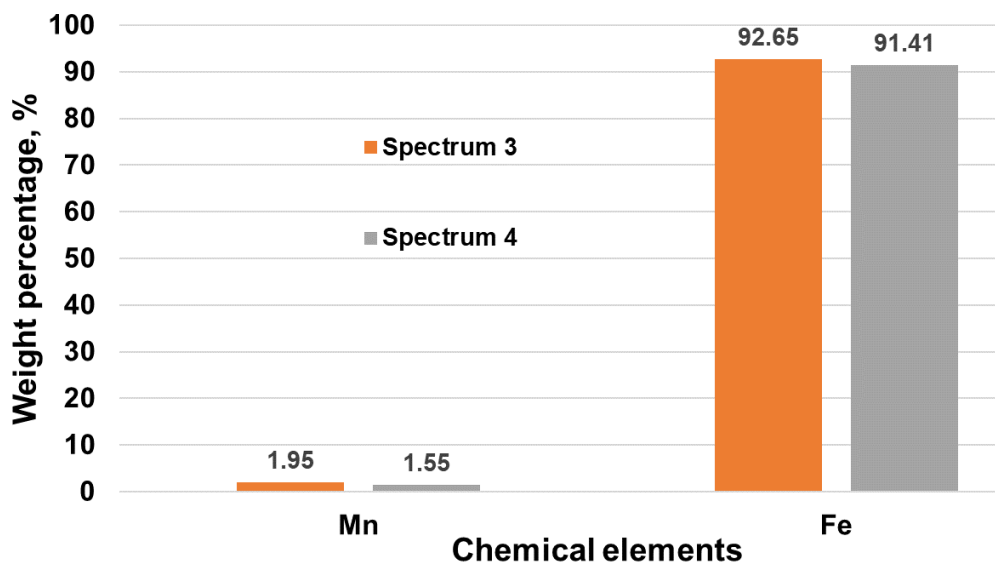


Figure 4-15 - EDS compositions of the exposed X70 sample elements in simulated saltwater solution with N₂ at 5 °C stressed at 80 % Y.S.

In Figure 4-16 as shown, at about 56 μm into the resin, a sharp increase of Fe concentration was clearly observed between the alloy-resin interface. Amount of C was clearly shown to be higher in the resin, with sharp increase below about 59 μm into the resin. Mn and Si were observed to have higher contents in the alloy, with highest concentration of Si observed between the alloy-resin interface.

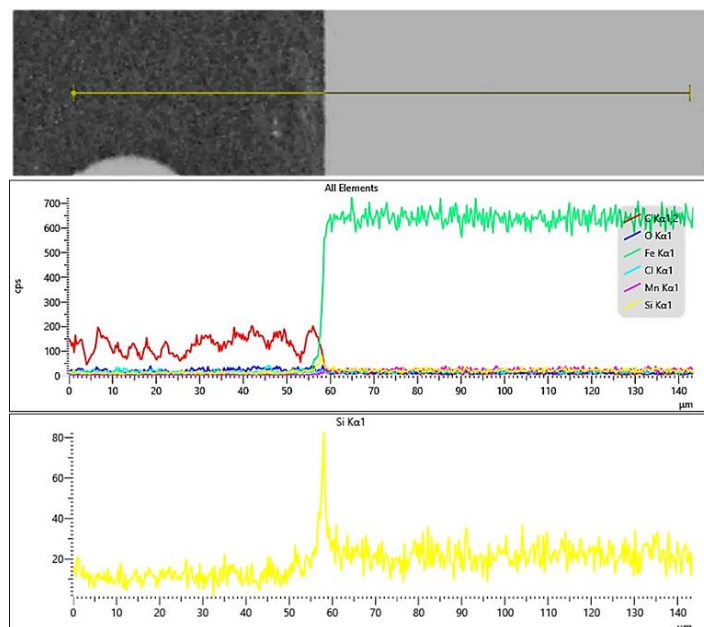


Figure 4-16 - EDS line scan analysis of the exposed X70 sample elements in simulated saltwater solution with N₂ at 5 °C stressed at 80 % Y.S.

Different compositions of the EDS spectra (Figure 4-17) of the exposed X70 sample in solution with N₂ at 25 °C stressed at 80 % Y.S., were observed as shown in Figure 4-18 (in weight percentages). Clear increase in percentage of Fe and Mn was observed with change in spectrum location from 3 to 4, with highest Fe percentage of 92.41 wt.% and Mn percentage of 1.96 wt.% observed in spectrum 4. Approximately equal percentages of Fe were observed in both X70 samples exposed at 5 °C and 25 °C, with highest values of 92.65 wt.% and 92.41 wt.% observed in spectrum 3 and 4 at 5 °C and 25 °C, respectively.

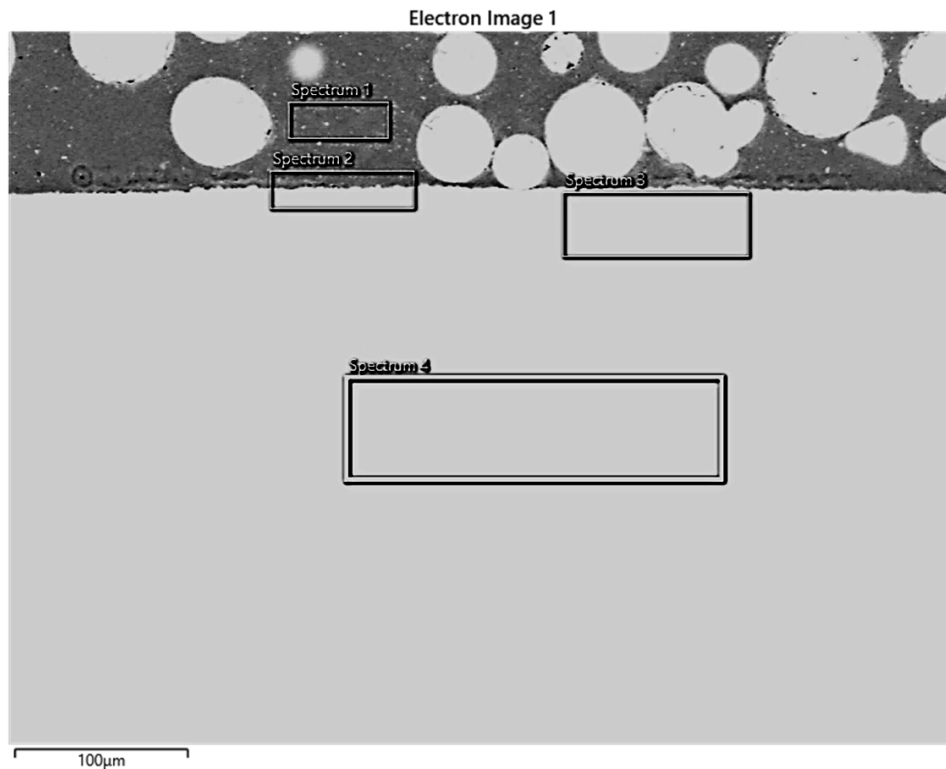


Figure 4-17 - SEM backscattered electron image of the exposed X70 C-ring sample in simulated saltwater solution with N₂ at 25 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 4-18.

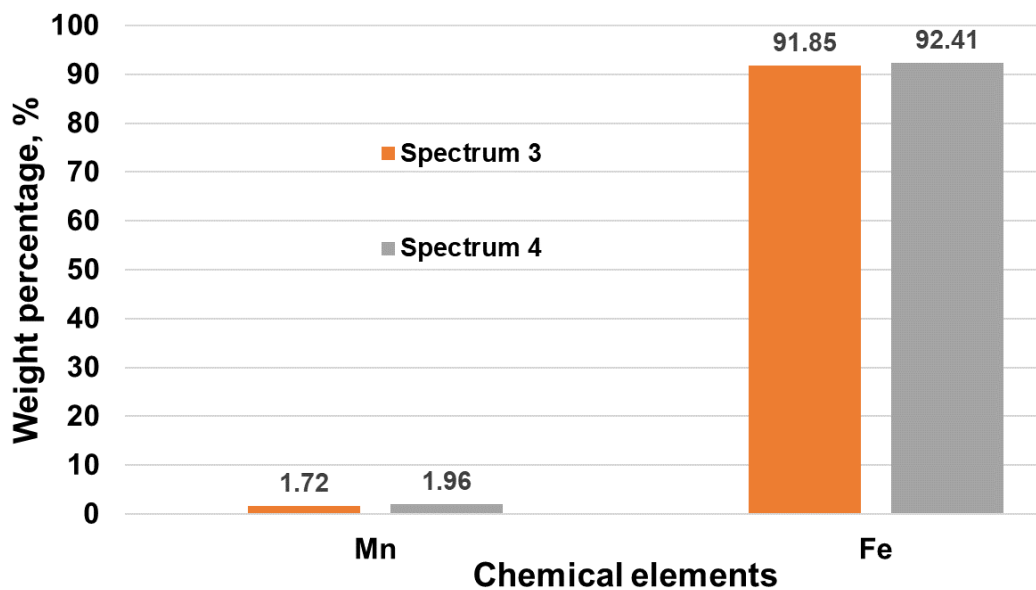


Figure 4-18 - EDS compositions of the exposed X70 sample elements in simulated saltwater solution with N₂ at 25 °C stressed at 80 % Y.S.

In comparison with X70 sample exposed at 5 °C, similar trend in line scan analysis was observed in the sample exposed at 25 °C as shown in Figure 4-19. Approximately equal concentration of Fe was observed in the alloy at both 5 °C and 25 °C. The concentration of Mn was generally observed to have higher contents in the alloy after about 57 µm into the resin. Si was observed to present highest concentration at about 35 µm and then followed by the interface (Figure 4-19). In general, not much significant differences observed in Mn and Fe percentages between the analyzed X70 samples exposed at 5 °C and 25 °C.

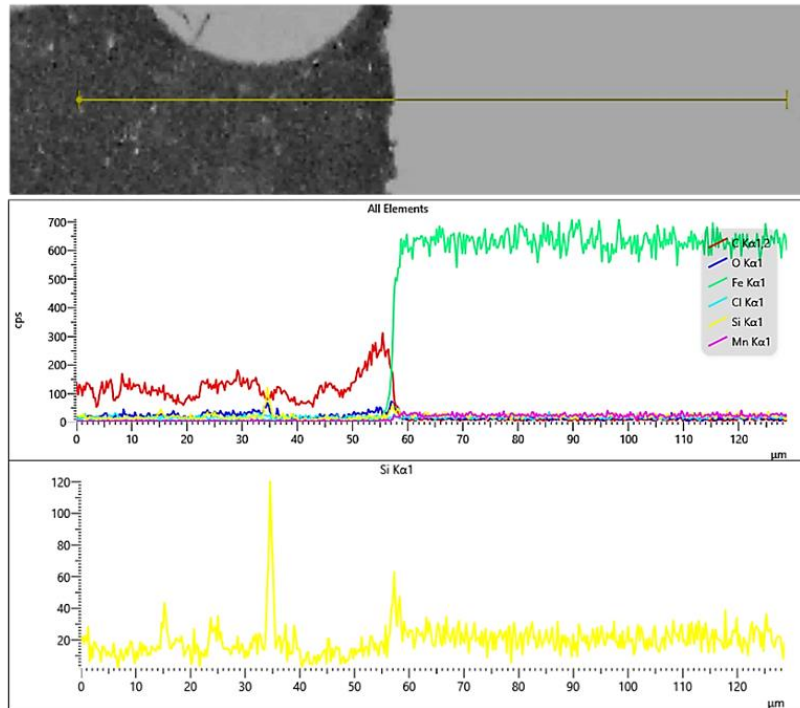


Figure 4-19 - EDS line scan analysis of the exposed X70 sample elements in simulated saltwater solution with N₂ at 25 °C stressed at 80 % Y.S.

4.1.4.2 Energy Dispersive Spectroscopy Analysis of X100 C-rings Specimens

The compositions of the EDS spectra (Figure 4-20) of the exposed X100 sample in solution with N₂ stressed at 80 % Y.S. at 5 °C, are presented in Figure 4-21 (in weight percentages). Similarly, as observed on the X70 samples at 5 °C, change in Mn concentration was observed with spectrum location. Spectrum 3 was also observed to contain higher percentage of Mn (1.93 wt.%). Similar values of Fe were observed in spectrum 3 and 4 with 93.28 wt.% and 93.36 wt.%, respectively.

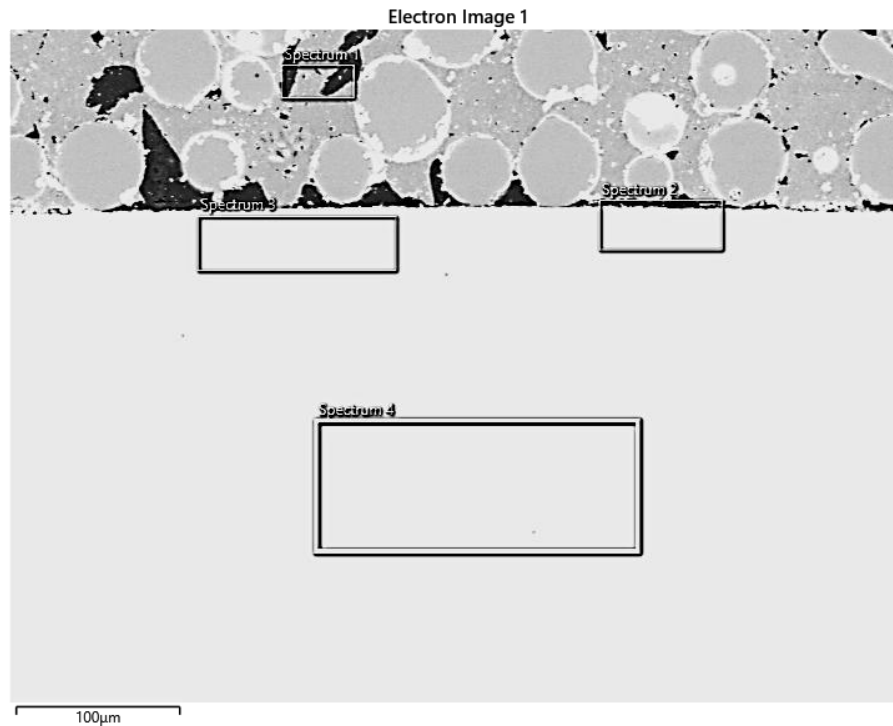


Figure 4-20 - SEM backscattered electron image of the exposed X100 C-ring sample in simulated saltwater solution with N₂ at 5 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 4-21.

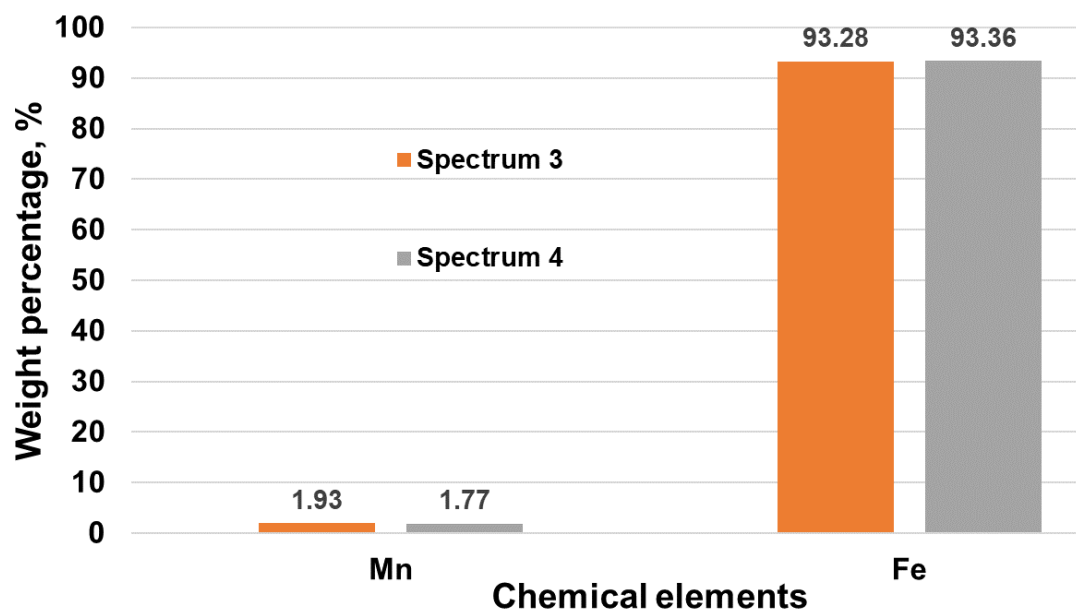


Figure 4-21 - EDS compositions of the exposed X100 sample elements in simulated saltwater solution with N₂ at 5 °C stressed at 80 % Y.S.

The line scan analysis as shown in Figure 4-22 show higher concentration of Fe, with sharp increase between alloy-resin interface at about 20 μm into the resin. Amount of Mn was clearly shown to be higher in the alloy after about 21 μm into the resin, with sharp increase in C content below about 23 μm into the resin. Highest concentration of Si was observed between the alloy-resin interface at about 22 μm into the resin (Figure 4-22).

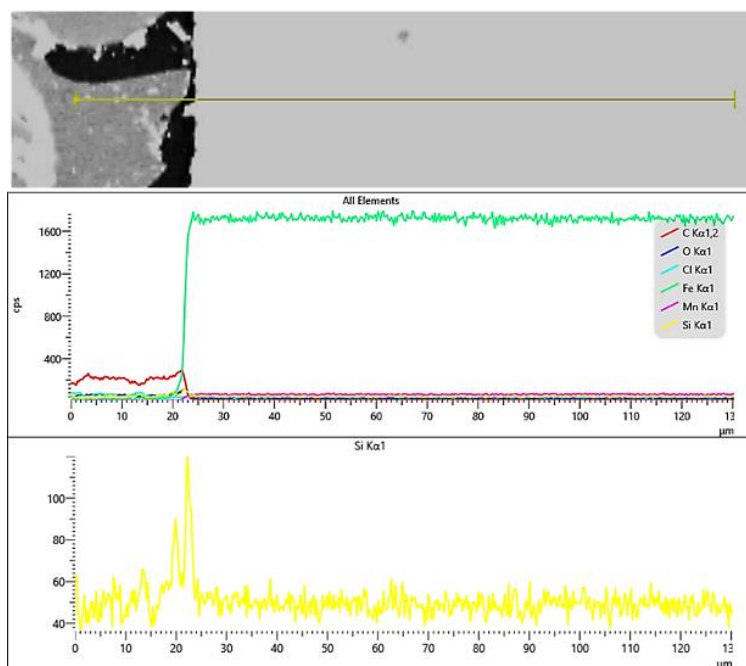


Figure 4-22 - EDS line scan analysis of the exposed X100 sample elements in simulated saltwater solution with N_2 at 5 °C stressed at 80 % Y.S.

The compositions of the EDS spectra (Figure 4-23) of the exposed X100 sample in solution with N_2 at 25 °C stressed at 80 % Y.S. are presented in Figure 4-24 (in weight percentages). Higher value of Mn with 2.16 wt.% was observed in spectrum 3 of the sample exposed at 25 °C in comparison with 5 °C (1.93 wt.%). Variations in Fe concentration was observed with change in spectrum location from 3 to 4. A value of 90.88 wt.% was detected in spectrum 3, with a value of 91.43 wt.% observed in spectrum 4.

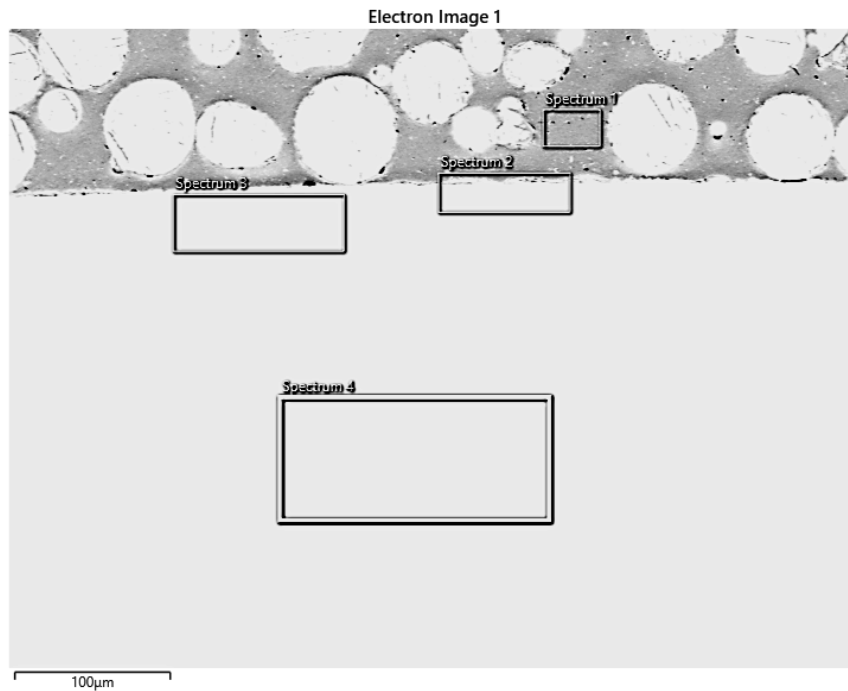


Figure 4-23 - SEM backscattered electron image of exposed X100 C-ring sample in simulated saltwater solution with N_2 at 25 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 4-24.

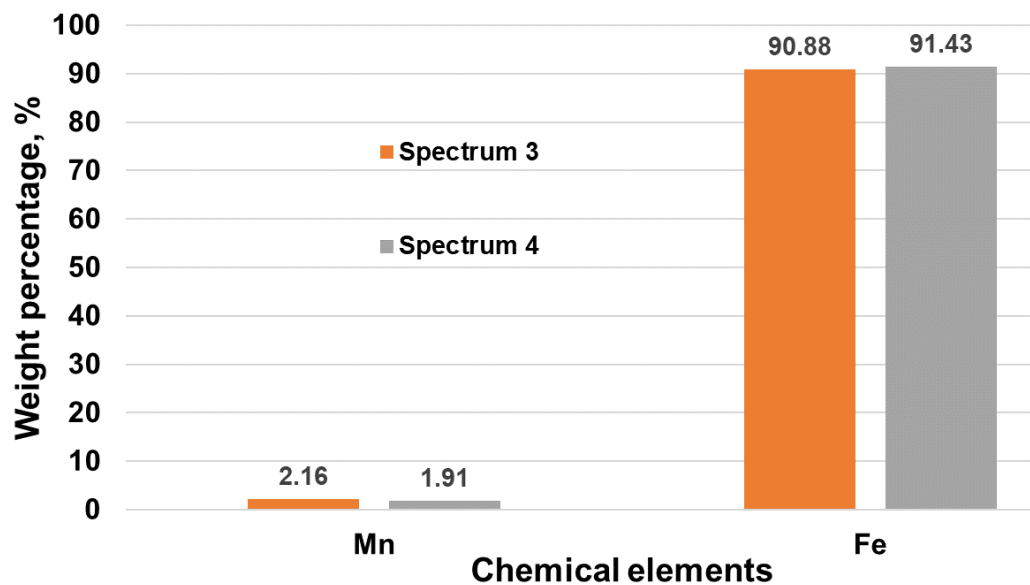


Figure 4-24 - EDS compositions of the exposed X100 sample elements in simulated saltwater solution with N_2 at 25 °C stressed at 80 % Y.S.

The line scan analysis (Figure 4-25) shows higher Fe concentration in the alloy from about 25 μm into the resin as obtained at 5 °C. Amount of Mn was also

observed to be higher in the alloy after about 27 μm . Highest concentration of Si was also observed between the alloy-resin interface (Figure 4-25).

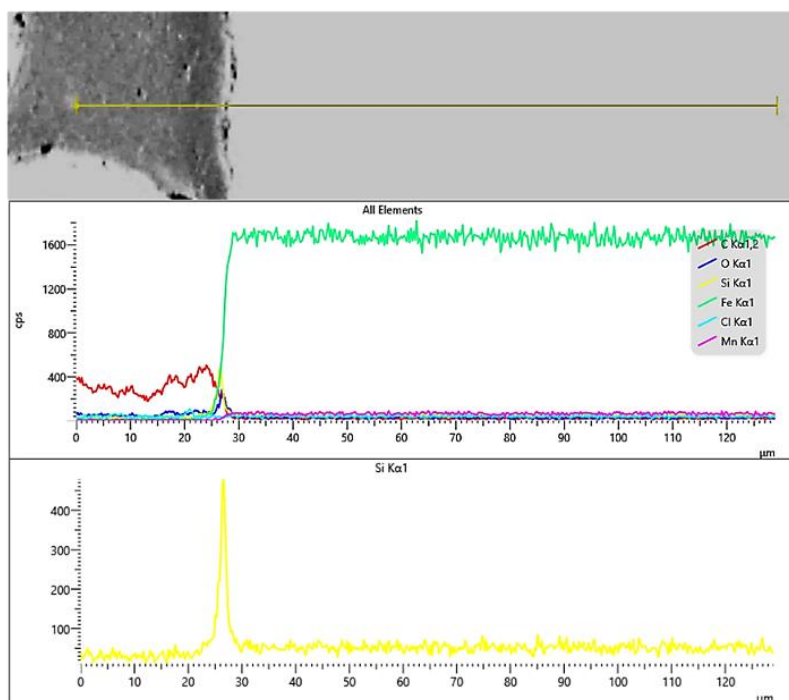


Figure 4-25 - EDS line scan analysis of the exposed X100 sample elements in simulated saltwater solution with N_2 at 25 °C stressed at 80 % Y.S.

In general, not much significant difference in Fe and Mn content observed on both X70 and X100 samples in the simulated saltwater saturated with N_2 at both 5 °C and 25 °C. Highest percentage of Fe (93.36 wt.% and 92.65 wt.%, respectively.) were observed in the X100 and X70 samples exposed at 5 °C. Maximum Mn percentage of 2.16 wt.% and 1.96 wt.%, respectively were observed in the X100 and X70 samples.

4.2 Chapter Summary

In general, an increase in corrosion rates of more than 100 % was observed with increased solution temperature from 5 °C to 25 °C. The fluctuations in corrosion rates as observed in Figures 4-1a, c to 4-5a, c) can be explained to occur due to continuous formation and rupture of the sample's surface films (iron oxide). This causes fluctuations in the cathodic reactions rates taking place on the samples' surfaces, leading to variations in corrosion rates with time. The different corrosion

potentials observed on the exposed carbon steels in the simulated 3.5 % NaCl solution, shows the change in the thermodynamic behaviour of the different carbon steels with change in the material's microstructure and exposure solution temperature. The obtained experimental corrosion rate values were observed to be lower than the corrosion rates of carbon steels in seawater published in the literature, with a value of 0.13-0.41 mm/year reported by Davies and Michael [44,45], 0.102-0.178 mm/year by Fontana [22] and a value of 0.1 mm/year in quiet seawater to 0.75 mm/year at 3 m/s seawater velocity reported by Kreysa and Schutze [36]. The lower corrosion rates were observed due to the continuous bubbling of nitrogen gas in the test solution, which eliminates any entrained air or oxygen [75,124]. A comparison of the obtained corrosion rates of the exposed carbon steels shows that at all exposure temperatures, the X65 carbon steel is more resistant to SCC in the simulated 3.5 % NaCl solution saturated with N₂, whereas X100 is more susceptible to SCC. Therefore, material selection to be used as a pipeline material in nitrogen saturated seawater environment should be between X65, X70 or X80 if readily available.

At all stress levels and solution temperatures, the X65, X70 and X80 samples presented an uneven distribution of metal change over most of the sample's surfaces. The X100 dataset was observed to show low metal change with an even damage distribution over most of the sample's surfaces. This variation in metal change can be explained to occur due to difference in microstructures of the exposed carbon steels. Higher pits features were observed on the X65, X70 and X80 samples, in comparison with the X100 sample. No significant difference in metal loss observed between the X65, X70 and X80 samples. However, higher metal loss was observed on the X100 relative to X65, X70 and X80 samples as observed from the obtained corrosion rates values from LPR measurements.

The images from SEM analysis show change in surface corrosion morphology on the exposed samples with increasing solution temperature from 5 °C to 25 °C. An uneven surface morphology with shallow ellipses was observed on all exposed X65, X70 and X80 samples. However, the X100 samples show a more even surface morphology.

In general, not much significant difference in Fe and Mn content observed on both X70 and X100 samples at both 5 °C and 25 °C. Highest percentage of Fe (93.36 wt.% and 92.65 wt.%, respectively) were observed in the X100 and X70 samples exposed at 5 °C. Maximum Mn percentage of 2.16 wt.% and 1.96 wt.%, respectively were observed in the X100 and X70 samples. The concentration of Si was observed to be highest mostly at the alloy-resin interface, as observed in X100 sample exposed at both 5 °C and 25 °C, and X70 sample exposed at 5 °C. This can be explained to occur due to accumulation of glass beads used in making the resin, which contains some certain amount of Si.

5 RESULTS AND DISCUSSION FOR EXPERIMENTS IN SOLUTION WITH CARBON-DIOXIDE

This chapter presents the results obtained from the exposed X65, X70, X80 and X100 C-rings and 3-point bent-beam samples exposed in simulated 3.5 % NaCl solution with CO₂. Similarly, solution was continuously bubbled with CO₂ at 50 mL/min flow rate for a period of 5 weeks (840hrs), with an average concentration of 64-107 ppm at atmospheric pressure [36]. Tests involving CO₂ bubbling acted to lower the pH of the solution from a near-neutral pH of about 7.3 to between 6.1 and 5.6. Corrosion rates, metal loss exceedance, SEM analysis, EDS analysis, tensile strength analysis, Vickers hardness analysis and surface roughness analysis were conducted on the exposed samples.

5.1 Experiments in Solution with CO₂ at 5 °C, 15 °C and 25 °C

The tests were conducted at different solution temperatures of 5 °C, 15 °C and 25 °C. This is carried out to understand the effect of temperature on the exposed carbon steel samples.

5.1.1 Corrosion Rates and Potentials

The change in corrosion rates and potentials with time of the exposed samples were monitored by use of linear polarization resistance technique. Specimens were polarized at a potential of ± 10 mV at a scan rate of 0.167 mV/s. Periodic polarization of the specimens was carried out after every 168 hrs to monitor the change in resistance and potential. The corrosion rates are then calculated by use of Stern-Geary equation. As expected, and reported in section 2.3.2.1.2 from the reviewed literature on effect of corrosive medium composition and presence of oxidizers on SCC susceptibility of pipeline carbon steels, a very high increase in corrosion rate was observed with change in solution trace gas from N₂ to CO₂.

5.1.1.1 Corrosion Rates and Potentials of X65 C-rings Specimens

Figures 5-1a to 5-1f show the corrosion rates and potentials of the exposed X65 samples in solution with CO₂ at 5 °C, 15 °C and 25 °C. As shown in graph 5-1a,

a continuous decrease in corrosion rates was observed for all samples at 5 °C, with an increase at 839 hrs. A maximum value of 0.483 mm/year was obtained on the notched sample stressed at 80 % Y.S. at 164 hrs of exposure. At 15 °C, a continuous decrease in corrosion rates was observed on all samples throughout the duration of the tests, with a maximum value of 0.709 mm/year observed on the sample stressed at 95 % Y.S. (Figure 5-1c). At 25 °C, a sharp continuous increase in corrosion rates was observed for all samples after 427 hrs of exposure, with a maximum value of 1.331 mm/year observed on the sample stressed at 95 % Y.S. (Figure 5-1e). Silva et al. [6] reported a corrosion rate value of 1 mm/year to 1.3 mm/year observed on X65 carbon steel exposed to 3.5 % NaCl solution saturated with CO₂ at ambient temperature. Variations in corrosion potentials were observed with change in solution temperature from 5 °C to 25 °C. A decrease in potential at 839 hrs was observed on all samples at 5 °C, with a continuous increase in potential observed throughout the tests at 15 °C. A maximum value of -648 mV_{Ag/AgCl} was observed for the sample stressed at 80 % Y.S. at 5 °C and -628 mV_{Ag/AgCl} for the sample stressed at 95 % Y.S. at 15 °C. Fluctuations in potential was observed on all samples at 25 °C, with a decrease at 596 hrs. A maximum value of -625 mV_{Ag/AgCl} was observed on the sample stressed at 95 % Y.S.

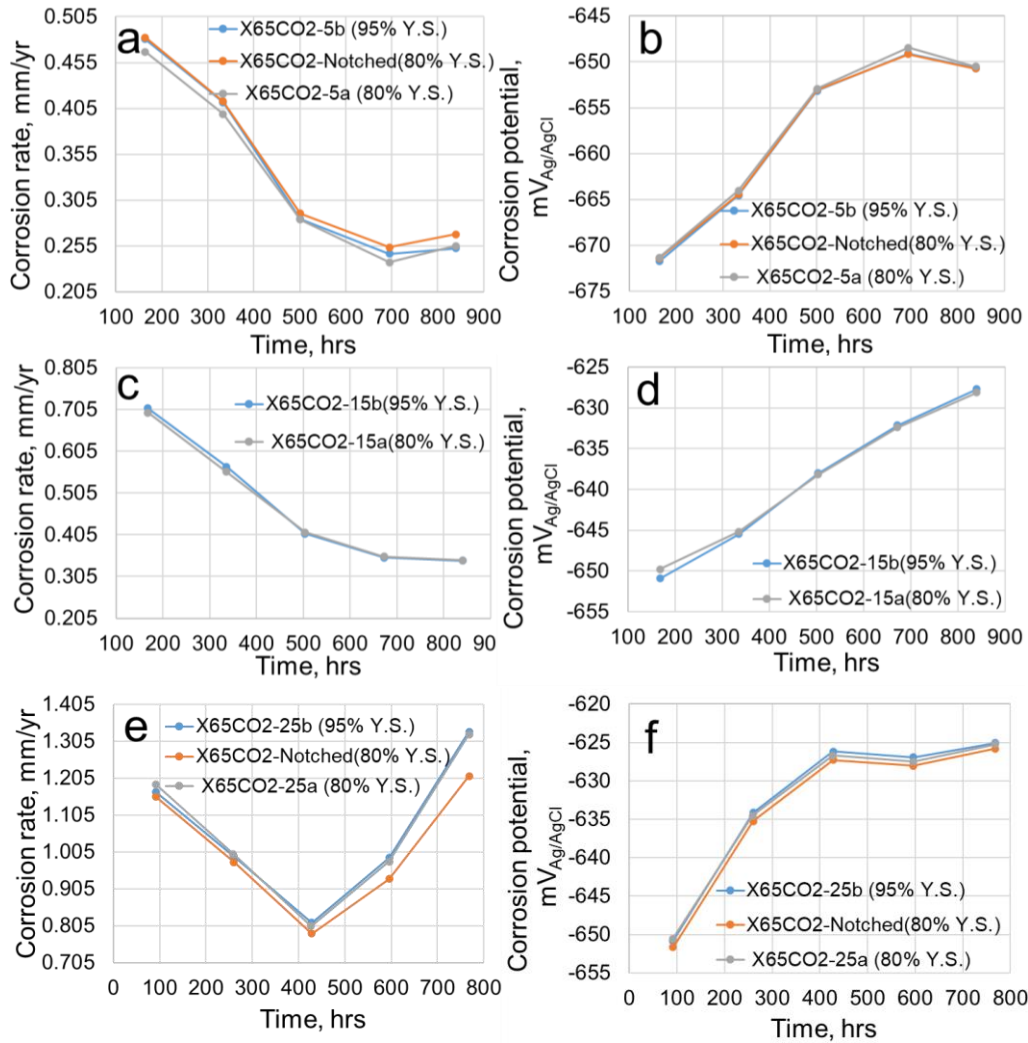


Figure 5-1 - Corrosion rates and potentials of the exposed X65 carbon steel C-rings in simulated saltwater solution with CO₂: (a) corrosion rates at 5 °C; (b) potentials at 5 °C; (c) corrosion rates at 15 °C; (d) potentials at 15 °C; (e) corrosion rates at 25 °C; (f) potentials at 25 °C.

In general, no significant statistical change in corrosion rates observed with increasing applied stress level from 80 % Y.S. to 95 % Y.S. and change in surface state of the samples (notched state) at 5 °C and 15 °C. However, at 25 °C, variations in corrosion rates was observed on the notched after 428 hrs of exposure with lower corrosion rates relative to samples stressed at 80 % Y.S. and 95 % Y.S. This could also be explained to occur as a result of differential aeration in the test cell [129]. An increase in corrosion rates of about 50 % was observed with increasing temperature from 5 °C to 15 °C, with an increase of

more than 100 % observed with increasing temperature from 5 °C to 25 °C. The obtained experimental corrosion rates (max. of 1.331 mm/year) are more or less similar to published corrosion rates observed on X65 carbon steel exposed in simulated 3.5 % NaCl saturated with CO₂ as reported by Silva et al. [6] with a value of 1 to a maximum of 1.3 mm/year. From the observed corrosion rates of the exposed X65 carbon steel in the simulated 3.5 % NaCl in the presence of CO₂, installation and usage of the carbon steel as a pipeline material in a seawater environment for transportation of CO₂ or in carbon capture and storage should not be operated at higher temperatures above 25 °C to avoid risk of increased corrosion rates, and subsequent SCC occurrence. Installation and usage of the carbon steel in tropical regions where sea surface temperatures can reach above 30 °C as reported in section 2.1.4 should be avoided. Installations and operations should rather be in deep waters or polar regions where the temperatures are below 5 °C. This will lead to reduction in corrosion rate of the carbon steel and hence reduced potential of SCC occurrence.

5.1.1.2 Corrosion Rates and Potentials of X70 C-rings Specimens

Figures 5-2a to 5-2f show the corrosion rates and potentials of the exposed X70 samples in solution with CO₂ at 5 °C, 15 °C and 25 °C. Relative to X65 samples, similar trends in corrosion rates and potentials were observed on all exposed X70 samples at all solution temperatures. It was observed that the higher the applied stress level, the higher the corrosion rates at 5 °C and 15°C, while at 25 °C, the higher the applied stress, the lower the corrosion rates. A maximum value of 0.518 mm/year and 0.780 mm/year, respectively were observed on the sample stressed at 80 % Y.S. at 5 °C (Figure 5-2a) and a repeat sample (X70CO₂-15a-R, Figure 5-2c) stressed at 80 % Y.S. at 15 °C. A maximum corrosion rate value of 1.4050 mm/year and a minimum of 0.852 mm/year was obtained for the sample stressed to 80% Y.S. at 25 °C (Figure 5-2e). Similarly, as observed on X65 samples, a decrease in potential was observed at 840 hrs and 596 hrs of exposure for the X70 samples at 5 °C and 25 °C, respectively. A maximum potential of -625 mV_{Ag/AgCl} was obtained for the X70 notched sample stressed to

80 % Y.S. at 25 °C. Figure 5-3a and b, respectively, show the after- exposure images of X70 and X100 C-rings samples in solution with CO₂ at 25 °C.

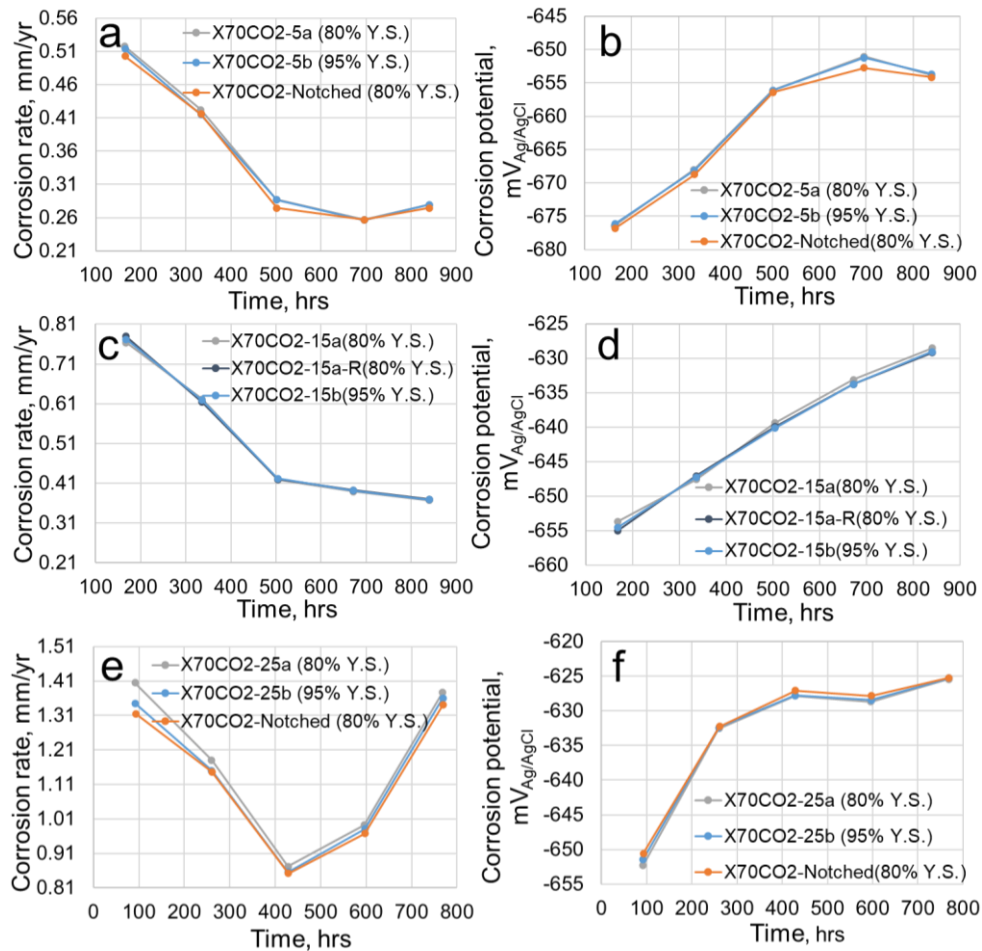


Figure 5-2 - Corrosion rates and potentials of the exposed X70 carbon steel C-rings in simulated saltwater solution with CO₂: (a) corrosion rates at 5 °C; (b) potentials at 5 °C; (c) corrosion rates at 15 °C; (d) potentials at 15 °C; (e) corrosion rates at 25 °C; (f) potentials at 25 °C.

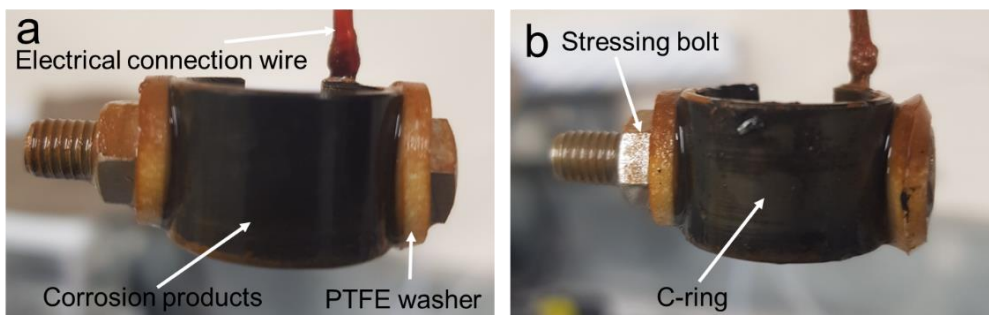


Figure 5-3 - Images of C-rings samples after 840 hrs of exposure in simulated saltwater solution with CO₂ at 25 °C: (a) X70; (b) X100.

Similarly, as observed from the exposed X65 samples, no statistical difference in corrosion rates observed on the X70 samples with increasing applied stress level from 80 % Y.S. to 95 % Y.S. and change in surface state of the samples (notched state). Also, an increase in corrosion rates of about 50 % was observed with increasing temperature from 5 °C to 15 °C, with an increase of more than 100 % observed with increasing solution temperature from 5 °C to 25 °C. The calculated experimental corrosion rates values at 25 °C, with maximum and minimum value of 1.405 mm/year and 0.852 mm/year, respectively are more or less similar to the values reported by Zhang et al. [86]. A value of 0.991 mm/year was observed on X70 steel exposed in a soil-extracted solution saturated with 100 % CO₂ at 25 °C. This indicates that presence of chloride in a solution increases its aggressiveness, which leads to higher corrosion rates as reported in section 2.3.2.1.4. From the observed corrosion rates of the exposed X70 carbon steel in the simulated 3.5 % NaCl in the presence of CO₂, installation and usage of the carbon steel as a pipeline material in a seawater environment for transportation of CO₂ or in carbon capture and storage should not be operated at higher temperatures above 25 °C to avoid risk of increased corrosion rates, and subsequent SCC occurrence. Installations and usage should be in deep waters or polar regions where the temperatures are below 5 °C and not in tropical regions where temperatures are above 30 °C. The use of X70 carbon steel as a pipeline material in the North Sea with an annual mean sea surface temperature of 11 °C will have a reduced risk of SCC occurrence due to lower expected corrosion rates. Furthermore, as not much significant difference in maximum corrosion rates were observed on the X70 carbon steel (max. of 1.405 mm/year) in comparison with X65 (max. of 1.331 mm/year) in the simulated saltwater solution with CO₂ within the exposure period of 840 hrs, the carbon steels should be exposed for longer time to ascertain their SCC susceptibility before making a final selection.

5.1.1.3 Corrosion Rates and Potentials of Mechanically and Chemically Pre-damaged X70 C-rings Specimens

Figures 5-4a and 5-4b show the corrosion rates and potentials of the exposed mechanically and chemically pre-damaged X70 carbon steel samples in solution

with CO₂ at 25 °C. The mechanically and chemically pre-damaged samples were taking out of exposure after 268 hrs, rinsed in deionized water and dried in an oven at 30 °C for 24 hrs. After cleaning and drying, the samples are then analysed for change in surface roughness with exposure time. Data for the change in surface roughness will be presented in subsequent headings. Fluctuations in corrosion rates and potentials as shown in Figures 5-4a and 5-4b, respectively, were observed on all samples. Relative to normal exposed X70 samples (Figure 5-2e) in solution with CO₂, the mechanically and chemically pre-damaged samples presented a different corrosion rate trend. Sharp increase in corrosion rates was observed for all samples after 268 hrs of exposure, then continuously with time till 771 hrs of exposure. This trend in sharp increase in corrosion rates (Figure 5-4) observed after 268 hrs can be explained to occur as a result of the taking out of the samples from the test solution after 268 hrs. They were then cleaned with IPA and dried in an oven for 24 hrs at 30 °C, and then analysed for change in surface roughness. The analysed samples were afterwards exposed back in the solution, as such the corrosion process will approximate that of the initial stage of exposure. A maximum of 1.529 mm/year was observed on the mechanically pre-damaged sample stressed at 95 % Y.S. at 96 hrs of exposure. Variations in corrosion potentials were also observed relative to normal exposed X70 samples (Figure 5-2f), a decrease in potential was observed at 435 hrs, with sharp increase afterwards throughout the duration of test. A maximum of -645 mV_{Ag/AgCl} was observed on the scratched sample stressed at 80 % Y.S.

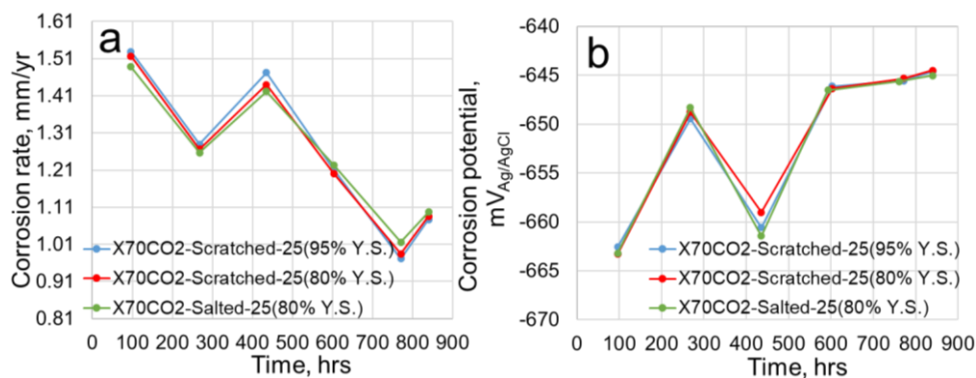


Figure 5-4 - Corrosion rates and potentials of the exposed mechanically and chemically pre-damaged X70 carbon steel C-rings samples in simulated saltwater solution with CO₂ at 25 °C: (a) corrosion rates at 25 °C; (b) potentials at 25 °C.

In general, no significant statistical difference in maximum corrosion rates observed between the chemically (max. of 1.488 mm/year) and mechanically (max. of 1.529 mm/year) pre-damaged samples. In comparison with normal exposed (undamaged) X70 samples (max of 1.405 mm/year at 25 °C), the mechanically and chemically pre-damaged samples presented a bit higher corrosion rates. This could be explained to occur as a result of tempering with the surface structure of the samples, thus making them more vulnerable to the fast release of electrons and subsequent increase in cathodic reaction rates. With the higher observed corrosion rates of the mechanically and chemically pre-damaged samples relative to normal exposed (undamaged) samples, machining of selected carbon steel as a pipeline material should be to an accepted and up to date standard surface finish.

5.1.1.4 Corrosion Rates and Potentials of X70 3-point Bent-beam Specimens

Figures 5-5a to 5-5d show the corrosion rates and potentials of the exposed X70 3-point bent-beam samples in solution with CO₂ at 5 °C and 25 °C. As shown in Figure 5-5a, variations in corrosion rate trend were observed on the X70 3-point bent-beam sample relative to the X70 C-ring sample stressed at 80 % Y.S. exposed at 5 °C (Figure 5-2a). An increase in corrosion rate was observed on all samples at 672 hrs, followed by decrease at 840 hrs. This trend could be said to occur due to formation and rupture of formed surfaces layers. This causes fluctuations in the cathodic reaction rates taking place on the samples surface, hence the change in corrosion rate with time. Maximum corrosion rate of 0.420 mm/year was observed on the sample stressed at 80 % Y.S., with a value of 0.425 mm/year on the repeat sample at 5 °C. At 25 °C, more or less similar trend is observed on the X70 3-point bent beam sample relative to X70 C-ring sample. A sharp continuous increase in corrosion rate was also observed after 336 hrs of exposure (Figure 5-5c). A maximum value of 1.174 mm/year was observed on the sample stressed at 80 % Y.S., with a value 1.178 mm/year observed on the repeat sample. Variations in potential trends were also observed on all samples at both 5 °C and 25 °C. At 5 °C, more positive potential values

were observed on the X70 3-point bent beam sample (Figure 5-5b) relative to X70 C-ring sample exposed at 5 °C, with a decrease at 672 hrs and a maximum of -636 mV_{Ag/AgCl}. More negative potential values were observed on the 3-point bent beam samples at 25 °C (Figure 5-5d), with a decrease observed at 840 hrs and a maximum of -646 mV_{Ag/AgCl}. Figures 5-6a and b, respectively, show the after-exposure images of X70 3-point bent-beam samples in solution with CO₂ at 5 °C and 25 °C.

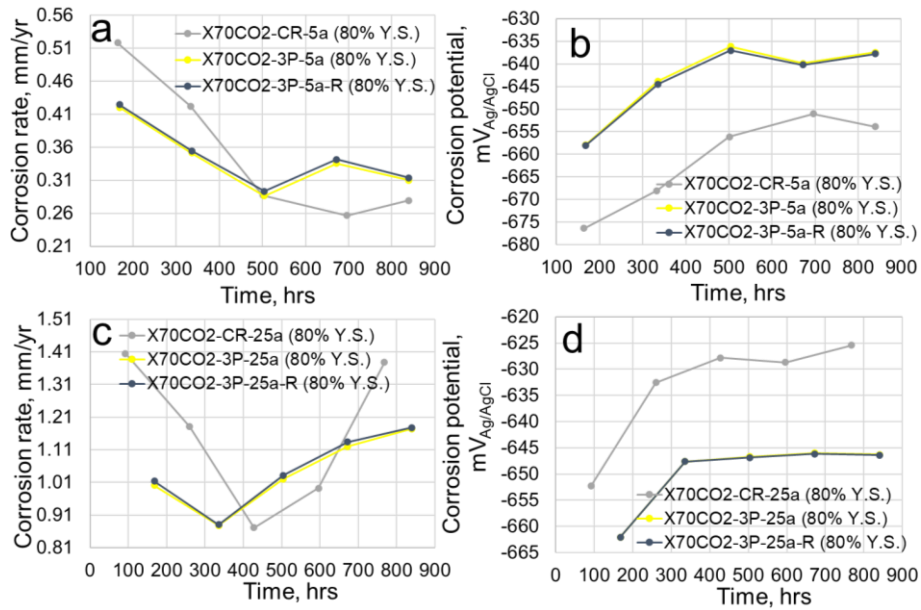


Figure 5-5 - Corrosion rates and potentials of the exposed X70 carbon steel 3-point bent-beam samples in simulated saltwater solution with CO₂: (a) corrosion rates at 5 °C; (b) potentials at 5 °C; (c) corrosion rates at 25 °C; (d) potentials at 25 °C.

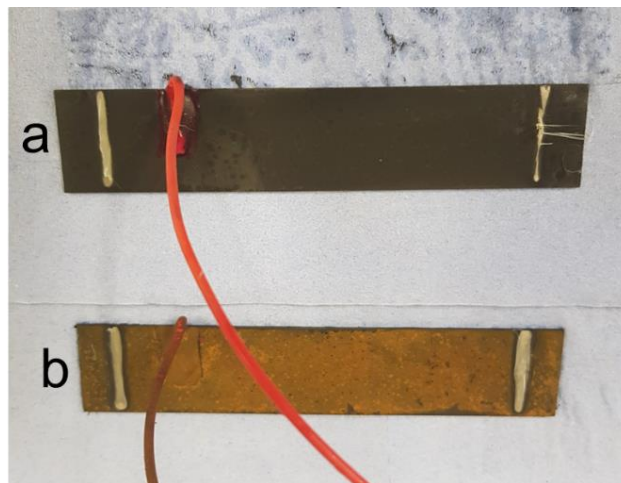


Figure 5-6 - Images of X70 3-point bent-beam samples after 840 hrs of exposure in simulated saltwater solution with CO₂: (a) at 5 °C; (b) at 25 °C.

In general, as observed on the X70 C-ring sample stressed at 80 % Y.S., an increase in corrosion rates of more than 100 % was observed on the 3-point bent-beam samples stressed at 80 % Y.S. with increasing temperature from 5 °C to 25 °C. No significant difference in corrosion rates observed between the samples stressed at 80 % Y.S. and repeat samples at both 5 °C and 25 °C. The X70 C-rings samples at all exposure conditions were observed to show higher corrosion rates (max. of 0.518 mm/year and 1.405 mm/year, respectively at 5 °C and 25 °C) relative to the 3-point bent-beam samples (max. of 0.425 mm/year and 1.178 mm/year, respectively at 5 °C and 25 °C) as shown in figure 5-5a and 5-5c. This indicates that stressing technique does have impact on corrosion behaviour of the exposed X70 samples in the simulated 3.5 % NaCl solution bubbled with CO₂. The variation in corrosion rate values can be explained to occur due to larger surface area of the 3-point bent-beam samples, with lower stress concentration across the samples in comparison with C-rings samples.

5.1.1.5 Corrosion Rates and Potentials of X80 C-rings Specimens

Figures 5-7a to 5-7f show the corrosion rates and potentials of the exposed X80 carbon steel samples in solution with CO₂ at 5 °C, 15 °C and 25 °C. As presented in Figures 5-7a to 5-7f, similar trends in corrosion rates and potentials were observed on the X80 samples relative to X65 and X70 samples. The corrosion rates of all samples at 5 °C were also observed to continuously decrease with time until after 696 hrs of exposure. A maximum of 0.506 mm/year was observed on the sample stressed at 80 % Y.S. Similarly, continuous decrease in corrosion rates was observed on all samples at 15 °C, with a maximum of 0.753 mm/year observed on the sample stressed at 80 % Y.S.

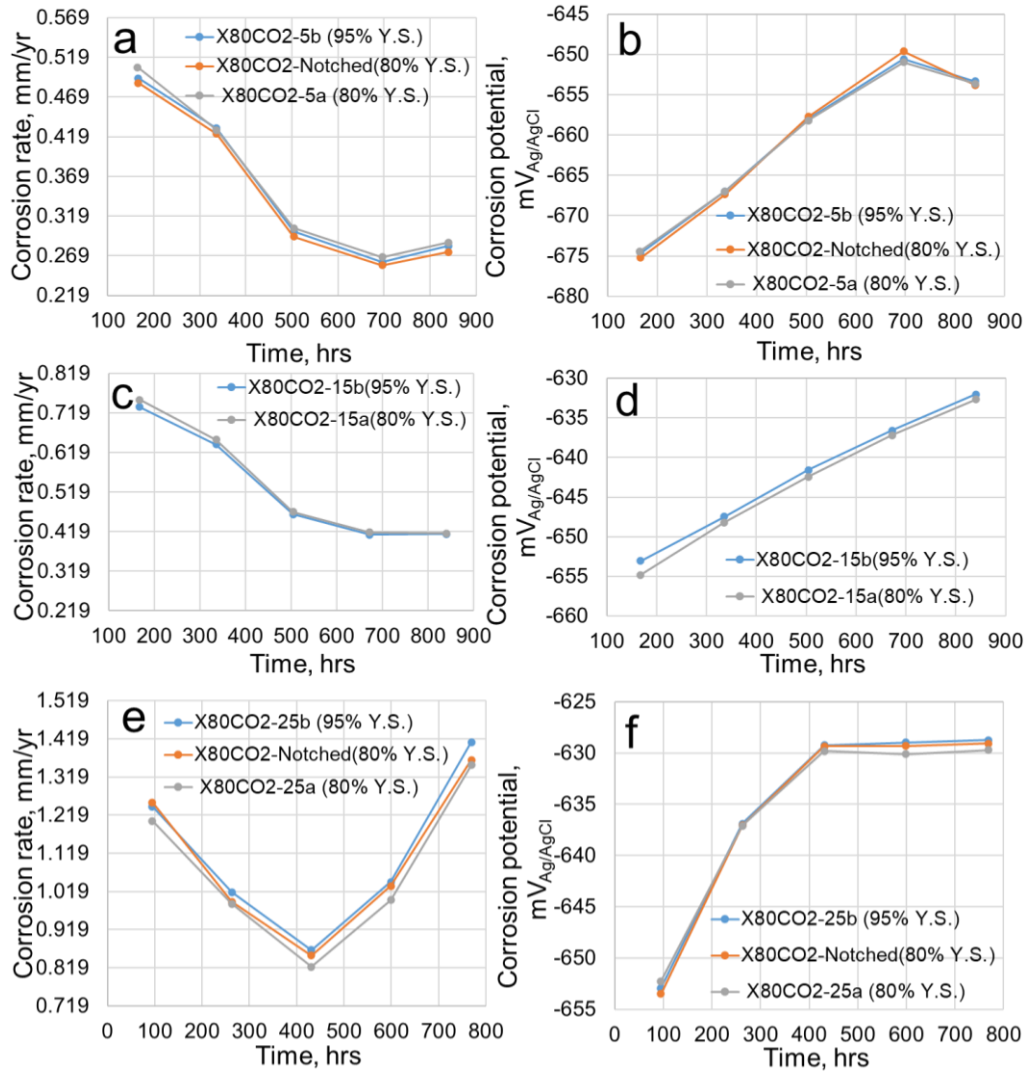


Figure 5-7 - Corrosion rates and potentials of the exposed X80 carbon steel C-rings in simulated saltwater solution with CO₂: (a) corrosion rates at 5 °C; (b) potentials at 5 °C; (c) corrosion rates at 15 °C; (d) potentials at 15 °C; (e) corrosion rates at 25 °C; (f) potentials at 25 °C.

As observed on the X65 (Figure 5-1e) and X70 (Figure 5-2e) samples at 25 °C, a sharp continuous increase in corrosion rates after 431 hrs of exposure was also observed on the X80 samples. A maximum value of 1.410 mm/year was obtained on the sample stressed at 95 % Y.S. at 769 hrs. Maximum corrosion potentials of -650 mV_{Ag/AgCl}, -633 mV_{Ag/AgCl} and -629 mV_{Ag/AgCl}, respectively, were obtained for the notched sample at 5 °C, samples stressed at 95 % Y.S. at 15 °C and 25 °C.

Similarly, as observed from the exposed X65 and X70 samples in solution with CO₂, no significant change in corrosion rates observed between the X80 samples stressed at 80 % Y.S., 95 % Y.S. and change in surface state of the samples (notched state). An increase in corrosion rates of about 50 % was also observed with increasing temperature from 5 °C to 15 °C, with an increase of about 100 % observed with increasing temperature from 5 °C to 25 °C. From the observed corrosion rates of the exposed X70 carbon steel in the simulated 3.5 % NaCl in the presence of CO₂, installation and usage of the carbon steel as a pipeline material in a seawater environment for transportation of CO₂ or in carbon capture and storage should not be operated at higher temperatures above 25 °C to avoid risk of increased corrosion rates, and potential of SCC occurrence in a long duration of usage. Similarly, as suggested for X65 and X70 carbon steels, installations and usage should be in deep waters or polar regions where the temperatures are below 5 °C and not in tropical regions with temperatures above 30 °C. As not much significant difference in maximum corrosion rates were observed between the X80 carbon steel (max. of 1.410 mm/year), X70 (max. of 1.405 mm/year) and X65 (max. of 1.331 mm/year) in the simulated 3.5 % NaCl solution bubbled with CO₂ within the exposure period of 840 hrs, the carbon steels should be exposed for longer time to ascertain their SCC susceptibility before making a final selection. However, with the higher corrosion rates observed on the X80 carbon steel, it can be concluded that the carbon steel is more susceptible to SCC in the exposed environment. This can be as a result of difference in microstructure and its reaction to the exposure conditions and higher ultimate tensile strength of the material as reported from reviewed literature in section 2.3.2.1.1.

5.1.1.6 Corrosion Rates and Potentials of X100 C-rings Specimens

Figures 5-8a to 5-8f show the corrosion rates and potentials of the exposed X100 carbon steel samples in solution with CO₂ at 5 °C, 15 °C and 25 °C. In general, the corrosion rates of the exposed X100 samples (Figures 5-8a, c and e) were observed to increase with increasing applied stress levels at all solution temperatures. However, fluctuations in corrosion rates from higher to lower with

change in applied stress level and surface state (notched) were observed between the samples. This trend in corrosion rate variations could be said to occur as a result of stressed-induced diffusion of the formed oxides into the steel's microstructure [128,129]. This phenomenon depends on change in solution temperature and the steel's microstructure. Completely different trends in corrosion rates were observed on the X100 samples in comparison with X65, X70 and X80 samples. A continuous increase in corrosion rates was observed on all samples at 5 °C and 15 °C, with a maximum of 1.112 mm/year observed on the notched sample at 5 °C and 1.666 mm/year observed on the sample stressed at 95 % Y.S. at 15 °C. At 25 °C, a sharp continuous decrease in corrosion rates was obtained on all samples after 264 hrs of exposure. Maximum and minimum corrosion rate values of 2.821 mm/year and 1.714 mm/year, respectively at 264 hrs and 770 hrs of exposure were observed on the notched sample. A continuous increase in corrosion potentials was observed on all samples at both 5 °C and 15 °C (Figures 5-8b and d). Maximum potentials of -630 mV_{Ag/AgCl} and -602 mV_{Ag/AgCl}, respectively, were obtained on notched sample at 5 °C and sample stressed at 95 % Y.S. at 15 °C. At 25 °C, a decrease in potential was only observed after 432 hrs of exposure, with a maximum value of -600 mV_{Ag/AgCl} (Figure 5-8f).

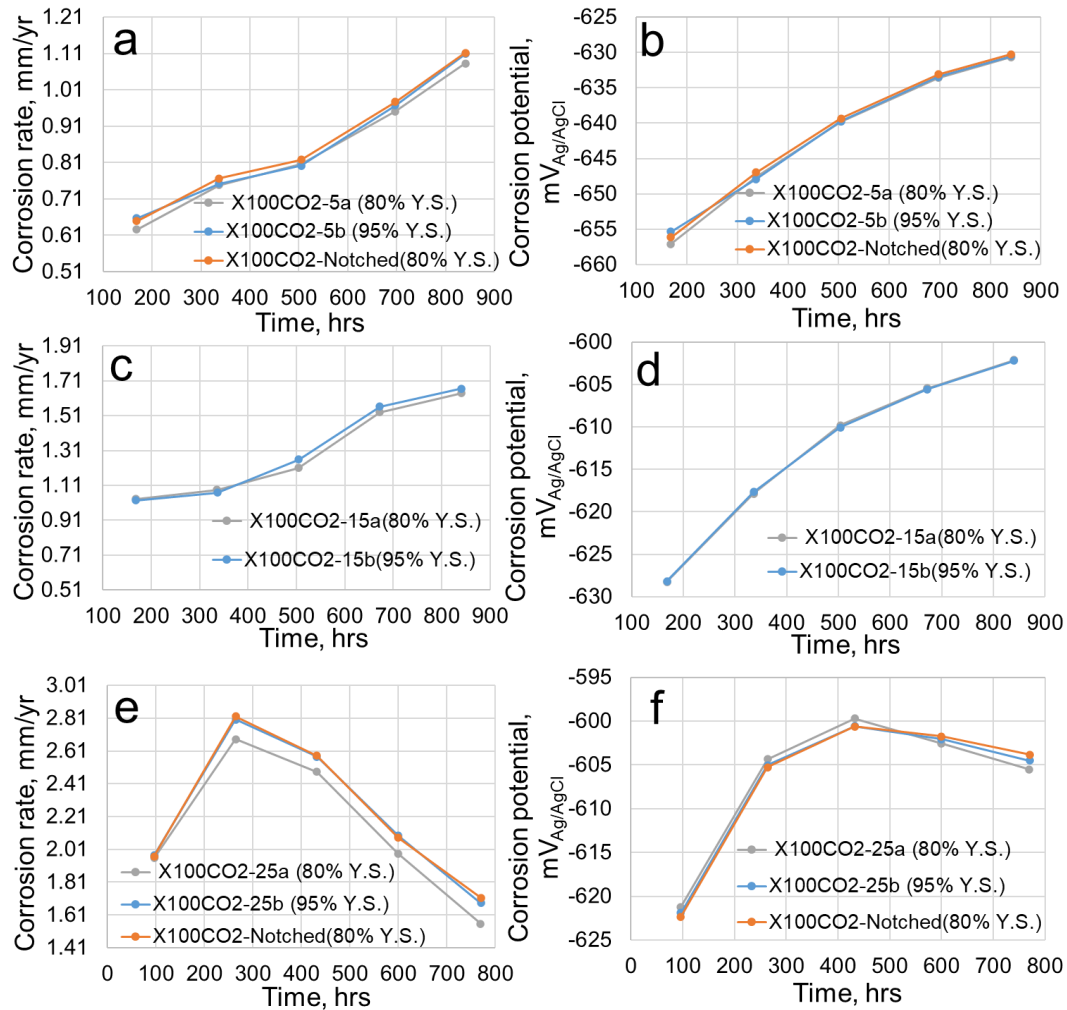


Figure 5-8 - Corrosion rates and potentials of the exposed X100 carbon steel C-rings in simulated saltwater solution with CO₂: (a) corrosion rates at 5 °C; (b) potentials at 5 °C; (c) corrosion rates at 15 °C; (d) potentials at 15 °C; (e) corrosion rates at 25 °C; (f) potentials at 25 °C.

As observed from the exposed X65, X70 and X80 samples in solution with CO₂, no statistically significant change in corrosion rates observed on the exposed X100 samples with increasing applied stress level from 80 % Y.S. to 95 % Y.S. and change in surface state of the samples (notched state) at 5 °C and 15 °C. However, at 25 °C the samples stressed at 80 % Y.S. was observed to have lower corrosion rates relative to samples stressed at 95 % Y.S. and notched sample. This can similarly be explained to occur as a result of differential aeration on the sample, which leads to lower cathodic reactions and subsequently lower corrosion rates [126,127]. Similarly, as observed on the exposed X65, X70 and

X80 samples, an increase in corrosion rates of about 50 % was also observed on the X100 samples with increasing temperature from 5 °C to 15 °C, with an increase of more than 100 % observed with increasing temperature from 5 °C to 25 °C. The calculated experimental corrosion rates values, with maximum of 2.821 mm/year obtained at 25 °C, was observed to be higher than values reported by Alfantazi and Gadala [10]. A value of 2.336 mm/year was obtained on X100 carbon steel sample exposed in a near-neutral simulated soil solution saturated with CO₂ at 25 °C. This also indicates that presence of chloride ions in a solution increases its aggressiveness, which leads to higher corrosion rates as reported in section 2.3.2.1.4.

In comparison with obtained maximum corrosion rates from X65 (max. of 1.331 mm/year), X70 (max. of 1.405 mm/year) and X80 (max. of 1.410 mm/year), the X100 carbon showed much higher corrosion rates with a maximum 2.821 mm/year. This indicates that susceptibility of the carbon steels to SCC in the simulated 3.5 % NaCl solution increases with increasing ultimate tensile strengths of the materials as reported in the reviewed literature in section 2.3.2.1.2. It can be stated that the X100 carbon steel is more susceptible to SCC under the exposed environmental conditions. As such its usage as pipeline material in a seawater environment for transportation of CO₂ or in carbon capture and storage should not be considered if there is availability of X80, X70 or X65.

5.1.1.7 Corrosion Rates and Potentials of X100 3-point Bent-beam Specimens

Figures 5-9a to 5-9d show the corrosion rates and potentials of the exposed X100 carbon steel 3-point bent-beam samples in solution with CO₂ at 5 °C and 25 °C stressed at 80 % Y.S. As presented in Figure 5-9a, similar trend in corrosion rates was observed on the X100 3-point bent beam sample relative to X100 C-ring sample at 5 °C. A continuous increase in corrosion rates was observed throughout the duration of the tests, with a maximum of 1.198 mm/year at 840 hrs. At 25 °C, a continuous decrease in corrosion rates was observed throughout the duration of the test, with a maximum of 2.304 mm/year observed at 168 hrs of exposure. Similar trends in corrosion potentials were observed on the 3-point

bent beam samples relative to C-rings samples. Continuous increase was observed at 5 °C throughout the duration of tests, with a continuous decrease after 672 hrs of exposure at 25 °C. The variation in potential observed on the samples can be said to occur as a result of change in thermodynamic behaviour of the samples with change in solution temperature and stressing technique. Maximum potential values of -605 mV_{Ag/AgCl} (Figure 5-9b) and -626 mV_{Ag/AgCl} (Figure 5-9d), respectively, were observed at 5 °C and 25 °C.

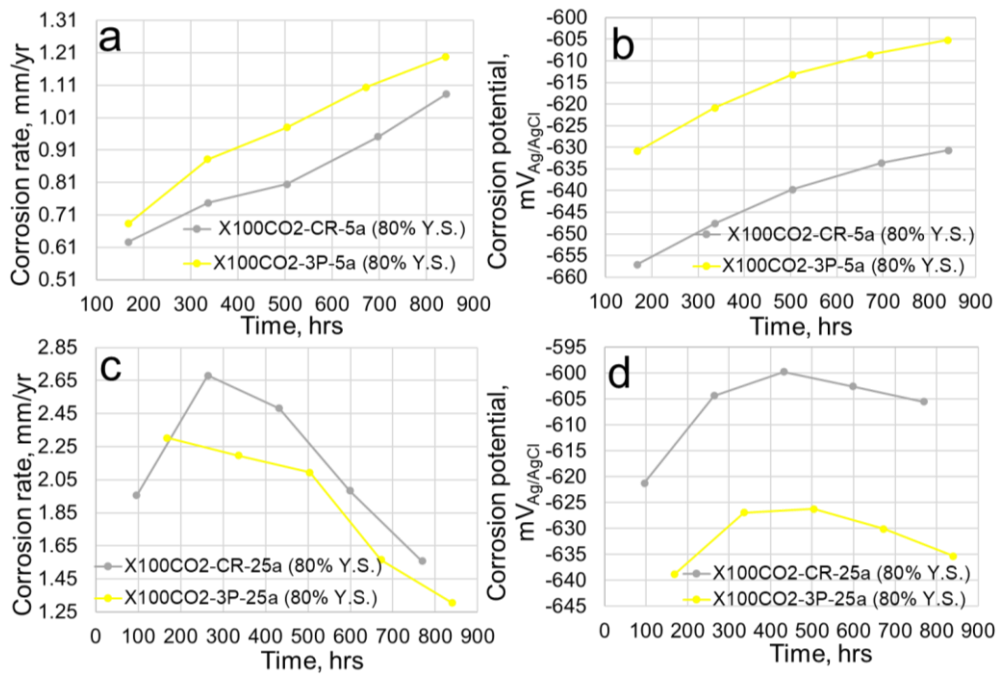


Figure 5-9 - Corrosion rates and potentials of the exposed X100 carbon steel 3-point bent-beam samples in simulated saltwater solution with CO₂: (a) corrosion rates at 5 °C; (b) potentials at 5 °C; (c) corrosion rates at 25 °C; (d) potentials at 25 °C.

As observed on the X100 C-rings samples stressed at 80 % Y.S., an increase in corrosion rates of more than 100 % was also observed on the 3-point bent-beam samples stressed at 80 % Y.S. with increasing solution temperature from 5 °C to 25 °C. The X100 3-point sample exposed at 5 °C was observed to show higher corrosion rates with 1.198 mm/year relative to X100 C-ring sample with a value of 1.082 mm/year as shown in Figure 5-9a. However, at 25 °C the X100 C-ring sample presented higher corrosion rates with a maximum value of 2.681 mm/year, with a maximum value of 2.304 mm/year obtained from the 3-point

bent-beam sample as shown in Figure 5-9c. This indicates that stressing technique does have impact on corrosion behaviour of the exposed X100 samples in the simulated 3.5 % NaCl solution saturated with CO₂. The variation in corrosion rate values can be explained to occur due to the effect of stress concentration across the samples, which also varies with sample geometry and solution temperature.

To understand the variations in corrosion rate trends observed on the X65, X70 and X80 samples relative to X100 samples exposed in solution with CO₂ at 25 °C. The observed sudden change in the corrosion rates with time, with a continuous increase observed in Figures 5-1e, 5-2e and 5-7e and a continuous decrease in Figure 5-8e. X-ray diffraction (XRD) analysis was conducted on the exposed samples and revealed the presence of an iron carbonate layer (FeCO₃). Figure 5-10 shows the XRD analysis of a X70 sample exposed at 25 °C. As shown in the XRD data (Figure 5-10; red peaks), diffraction peaks are recorded at 2 theta values expected from an iron carbonate phase. This implies that the steels were able to form a surface layer of iron carbonate in the saturated CO₂ solution, which could serve as a protective layer on the surfaces, thereby, decreasing the corrosion rate [6,10,130]. Its effect decreases the cathodic reaction rates by surface blocking from FeCO₃ crystals. This hinders the movement of electro-chemically active species to take part in the charge-transfer process [6,131]. The formation of the iron carbonate layer was observed to strongly depend on the microstructure of the steel and solution's temperature [134].

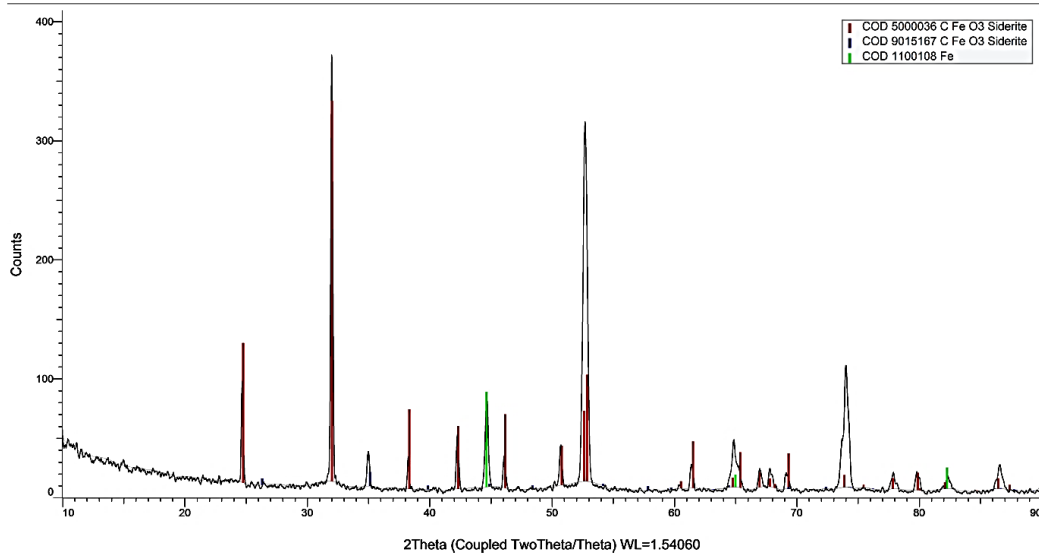


Figure 5-10 - XRD analysis of the exposed X70 C-ring specimen in simulated saltwater solution with CO₂ at 25 °C after 840 hours of exposure.

5.1.2 Metal Loss Exceedance

Dimensional metrology after an exposed period of 840 hrs was conducted on the exposed samples by optical microscopy to measure the cumulative probability of metal loss exceedance of the samples. An error of $\pm 5 \mu\text{m}$ is assumed for all metal loss measurements.

5.1.2.1 Cumulative Probability of Metal Loss Exceedance of X65 C-rings Specimens

Figures 5-11a, 5-11b and 5-11c, respectively, show the cumulative probability of metal loss exceedance, obtained from the datasets of the exposed X65 samples in solution with CO₂ at 5 °C, 15 °C and 25 °C. Datasets for all samples exposed at 5 °C show an even distribution of metal change over most of the sample's surfaces, with higher pits features observed on the sample stressed at 80 % Y.S. below about 9 % probability level or less. A maximum metal loss of $-49 \mu\text{m}$ was observed on the notched sample stressed at 80 % Y.S. Significant metal change was observed on all samples at 15 °C, with pits features below about 6 % probability level or less. An even distribution of metal change was observed on all samples at 25 °C, with low pits formation below about 9 % probability level or

less. Maximum metal loss of -71 μm and -122 μm , respectively at 15 °C and 25 °C were observed on the samples stressed at 80 % Y.S. and 95 % Y.S. An increase in metal loss of more than 100 % was observed with increasing solution temperature from 5 °C to 25 °C.

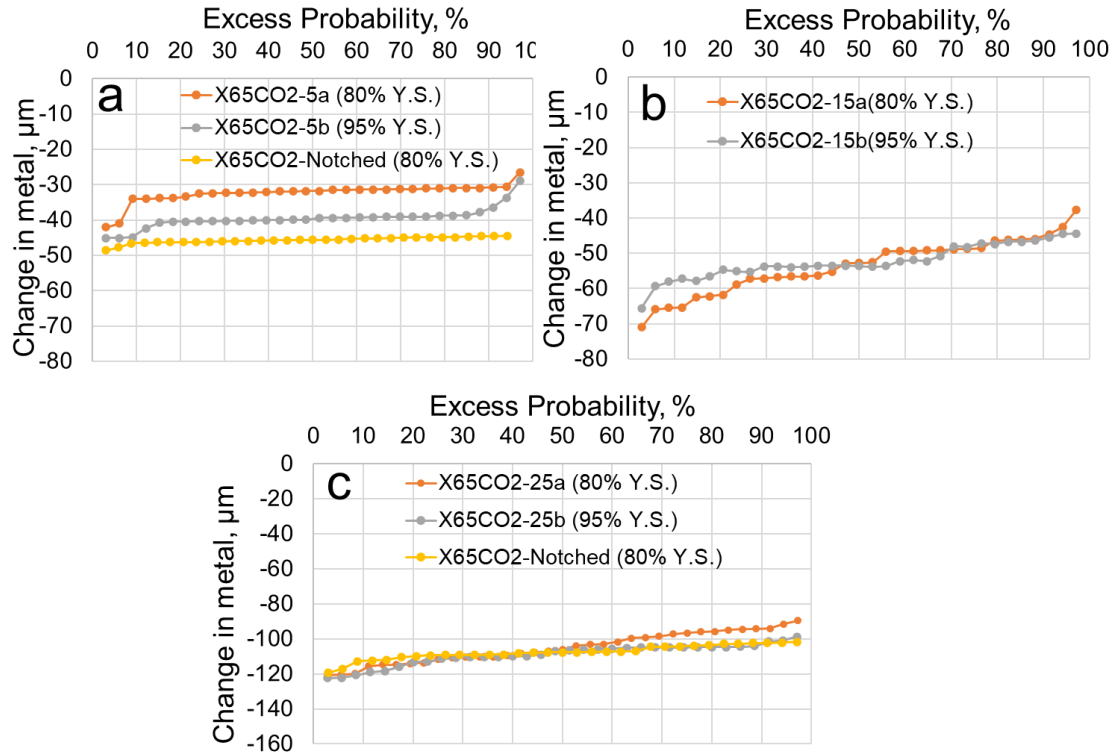


Figure 5-11 - Cumulative probability of metal loss exceedance graphs of X65 C-rings samples exposed in simulated saltwater solution with CO₂: (a) at 5 °C; (b) at 15 °C; (c) at 25 °C.

In general, as observed from the calculated corrosion rates of the exposed X65 samples, no significant difference in metal loss observed on the samples with change in applied stress level from 80 % Y.S. to 95 % Y.S. and notched sample stressed at 80 % Y.S., with putting into account an error in measurement of $\pm 5 \mu\text{m}$ in the measured metal loss of the samples. The measured metal loss exceedance values on the samples which is also a technique of measuring corrosion rates of samples tally with the calculated corrosion rates from LPR measurements when converted to 840 hrs (5 weeks) exposure time. A maximum value of 1.331 mm/year was calculated for the X65 sample stressed at 95 % Y.S. as shown in Figure 5-1e, converting the calculated corrosion rate value to a metal loss of 840 hrs gives a value of -128 μm (with error of $\pm 5 \mu\text{m}$). As observed from

the calculated corrosion rates from LPR measurements, an increase in metal loss of about 50 % was observed with increasing temperature from 5 °C to 15 °C, with more than 100 % obtained with increasing temperature from 5 °C to 25 °C.

5.1.2.2 Cumulative Probability of Metal Loss Exceedance of X70 C-rings Specimens

Figures 5-12a, 5-12b and 5-12c, respectively, show the cumulative probability of metal loss exceedance, obtained from the datasets of the exposed X70 samples in solution with CO₂ at 5 °C, 15 °C and 25 °C. At 5 °C, low metal change was observed on all samples at all stress levels, with low pits features below about 12 % or less probability level. The sample stressed at 80 % Y.S. presented higher metal loss relative to sample stressed at 95 % Y.S. and notched sample, with a maximum of -52 µm. At 15 °C, dataset for all the samples show a significant metal change over half of the sample's surfaces. Higher pits features were observed on the repeat sample stressed at 80 % Y.S. (X70CO₂-15a-R, Figure 5-12b), below 9 % or less probability level and on the sample stressed at 95 % Y.S. below 6 % or less probability level. Maximum metal loss of -72 µm was observed on the sample stressed at 95 % Y.S. Significant metal change was observed on all samples exposed at 25 °C, with higher pits features below 12 % probability level observed on the sample stressed at 80 % Y.S. Highest metal loss of -128 µm was observed on the sample stressed at 80 % Y.S. Similarly, relative to the X65 exposed samples, an increase of more than 100 % metal loss was observed with increasing temperature from 5 °C to 25 °C.

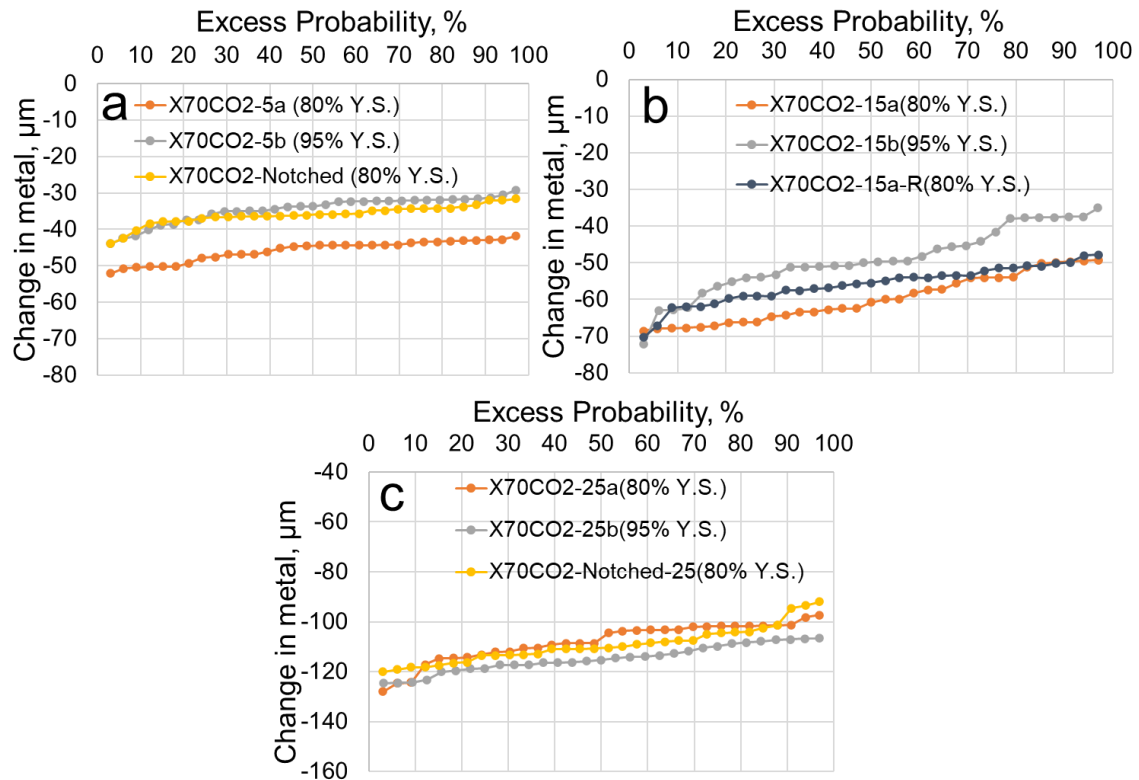


Figure 5-12 - Cumulative probability of metal loss exceedance graphs of X70 C-rings samples exposed in simulated saltwater solution with CO₂: (a) at 5 °C; (b) at 15 °C; (c) at 25 °C.

As observed from the calculated corrosion rate values on the X70 samples exposed in the simulated 3.5 % NaCl solution bubbled with CO₂, no significant change in metal loss value observed on the samples with change in applied stress level from 80 % Y.S. to 95 % Y.S. and surface state of the samples (notched state), with an error in measurement of $\pm 5 \mu\text{m}$ in the measured metal loss values. Similarly, as observed from the calculated corrosion rates of the X70 samples, highest metal loss was also observed on the sample stressed at 80 % Y.S. with a value of -128 μm . The calculated corrosion rates from LPR measurements tally with the measured metal loss value when converted to 840 hrs of exposure. A maximum value of 1.405 mm/year was calculated for the X70 sample stressed at 80 % Y.S. as shown in Figure 5-2e, converting the calculated corrosion rate value to a metal loss of 840 hrs gives a value of -135 μm ($\pm 5 \mu\text{m}$).

No significant difference in measured metal loss exceedance values between the exposed X65 samples (max. of -122 μm) and X70 samples (max. of -128 μm), as also observed from the calculated corrosion rates from LPR measurements. As observed from the calculated corrosion rates of the exposed X70 samples from LPR measurements, an increase in metal loss of more than 100 % was measured on the samples with increasing temperature from 5 °C to 25 °C, with about 50 % from 5 °C to 15 °C.

5.1.2.3 Cumulative Probability of Metal Loss Exceedance of Mechanically and Chemically Pre-damaged X70 C-rings Specimens

Figure 5-13 show the cumulative probability of metal loss exceedance, obtained from the datasets of the Mechanically and Chemically Pre-damaged X70 C-rings samples exposed in solution with CO_2 at 25 °C. The datasets for all samples (Figure 5-13) present relatively significant metal change over most of the sample's surfaces. The chemically pre-damaged sample (salted) show higher pits features below about 12 % probability or less, with low pits features observed on the scratched sample stressed at 80 % Y.S below 21 % probability level or less. Higher pits features observed on the chemically pre-damaged sample can be said to occur as a result of the pre-exposure salt spraying carried out on the sample, which causes pits formation on the surface of the sample. Relative to normal exposed X70 sample (X70CO₂-25a, Figure 5-12c), the mechanically and chemically pre-damaged X70 samples presented more or less higher metal change and pits features on the sample's surfaces. The scratched sample stressed at 95 % Y.S. presented maximum metal loss of -144 μm .

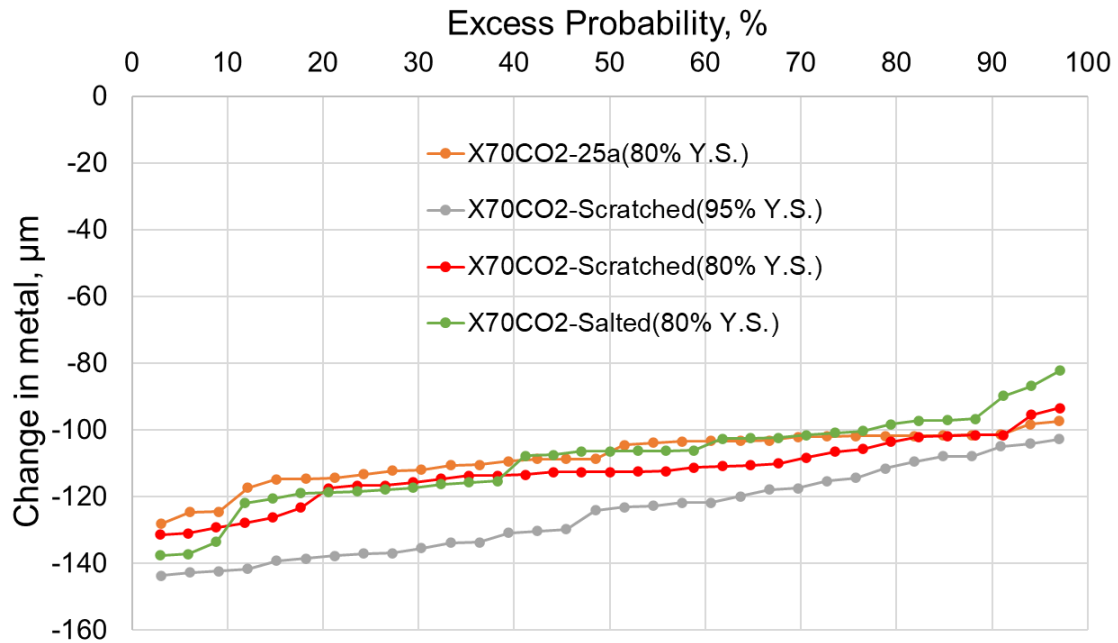


Figure 5-13 - Cumulative probability of metal loss exceedance graphs of mechanically and chemically pre-damaged X70 C-rings samples exposed in simulated saltwater solution with CO₂ at 25 °C.

In general, as observed from the calculated corrosion rates as presented in Figure 5-4, no significant difference in maximum metal loss exceedance values observed between the chemically (max. of -138 μm) and mechanically pre-damaged samples (max. of -144 μm, sample stressed at 95 % Y.S.), with putting into account an error in measurement of ±5 μm. In comparison with normal exposed X70 samples (max of -128 μm at 25 °C), the mechanically and chemically pre-damaged samples presented higher metal loss values as also observed from the calculated corrosion rates from LPR measurements. Similarly, as observed from normal exposed X70 samples, the maximum calculated corrosion rates of the pre-damaged samples (max. of 1.529 mm/year) tally with the measured metal loss value when converted to 840 hrs (5 weeks) of exposure with a value of -147 μm (±5 μm).

5.1.2.4 Cumulative Probability of Metal Loss Exceedance of X70 3-point Bent-beam Specimens

Figures 5-14a and 5-14b show the cumulative probability of metal loss exceedance, obtained from the datasets of X70 3-point bent-beam samples exposed in solution with CO₂ at 5 °C and 25 °C. At 5 °C, similar trend in metal change (Figure 5-14a) was observed on all samples relative to X70 C-ring sample (X70CO2-CR-5a). Low metal change and pits features were observed on all samples. The 3-point bent-beam repeat sample (X70CO2-3P-5-R) was observed to show higher metal loss of -44 µm relative to normal X70 3-point sample (X70CO2-3P-5) with a value of -39 µm. Datasets at 25 °C (Figure 5-14b) show significant metal change on all samples, with low pits features. Relative to the 3-point bent-beam samples, the X70 C-ring sample (X70CO2-CR-25a) presented higher pits features below about 12 % probability or less. Approximately equal metal loss was observed on both X70 3-point sample and the repeat sample with maximum values of -107 µm and -108 µm, respectively at 25 °C.

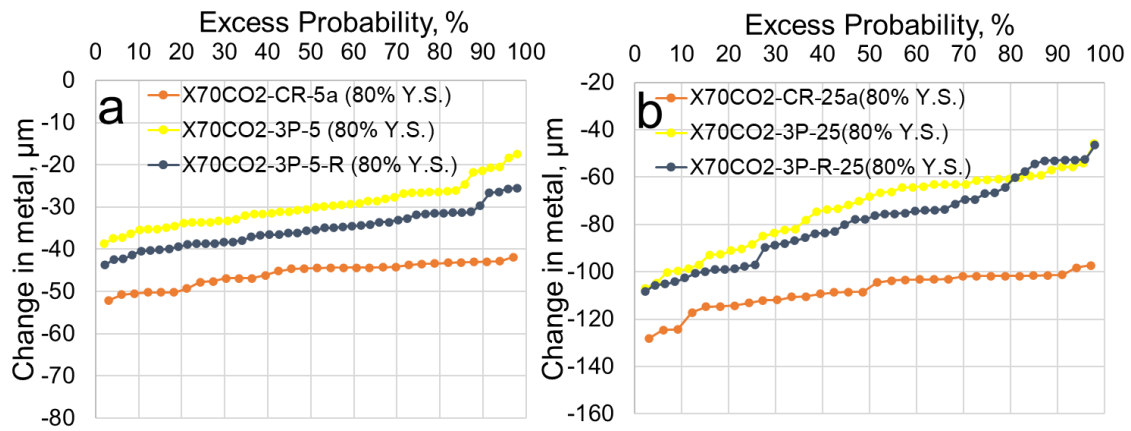


Figure 5-14 - Cumulative probability of metal loss exceedance graphs of X70 3-point bent-beam samples exposed in simulated saltwater solution with CO₂: (a) at 5 °C; (b) at 25 °C.

Similarly, as obtained from the calculated corrosion rates of the 3-point bent-beam samples as presented in Figure 5-5, an increase in metal loss of more than 100 % was observed with increasing temperature from 5 °C to 25 °C as shown in Figure 5-14. No significant difference in metal loss observed between the samples stressed at 80 % Y.S. and repeat samples at both 5 °C and 25 °C.

Similarly, as observed from the calculated corrosion rates, the X70 C-ring sample stressed at 80 % Y.S. at all solution temperatures presented higher metal loss value (max. of -52 μm and -128 μm , respectively at 5 °C and 25 °C) relative to the 3-point bent-beam samples (max. of -44 μm and -108 μm , respectively at 5 °C and 25 °C). The calculated maximum corrosion rate (max. of 1.178 mm/year) of the 3-point bent-beam sample also tally with the measured metal loss exceedance value, with a value of -113 μm ($\pm 5 \mu\text{m}$).

5.1.2.5 Cumulative Probability of Metal Loss Exceedance of X80 C-rings Specimens

Figures 5-15a, 5-15b and 5-15c, respectively, show the cumulative probability of metal loss exceedance, obtained from the datasets of the exposed X80 samples in solution with CO₂ at 5 °C, 15 °C and 25 °C. Datasets for all samples at 5 °C show relatively high metal change over half of the sample's surfaces, with low pits features below about 28 % probability for the sample stressed at 80 % Y.S. and below about 34 % probability or less for sample stressed at 95 % Y.S. and notched sample stressed at 80 % Y.S. Maximum metal loss of -53 μm was obtained on the sample stressed at 95 % Y.S. Low metal change was observed on all samples, with low pits features observed on the sample stressed at 80 % Y.S. below about 21 % probability or less, and a maximum metal loss value of -76 μm . At 25 °C, high pits features were observed for all samples, with higher pits formation on the sample stressed at 80 % Y.S. below 24 % probability or less. Maximum metal loss of -145 μm was observed on the sample stressed at 95 % Y.S. Similarly, as observed on the X65 and X70 samples, an increase in metal loss of more than 100 % was observed on the X80 samples with increasing solution temperature from 5 °C to 25 °C. Higher pits features were observed on the X80 samples relative to X65 and X70 samples.

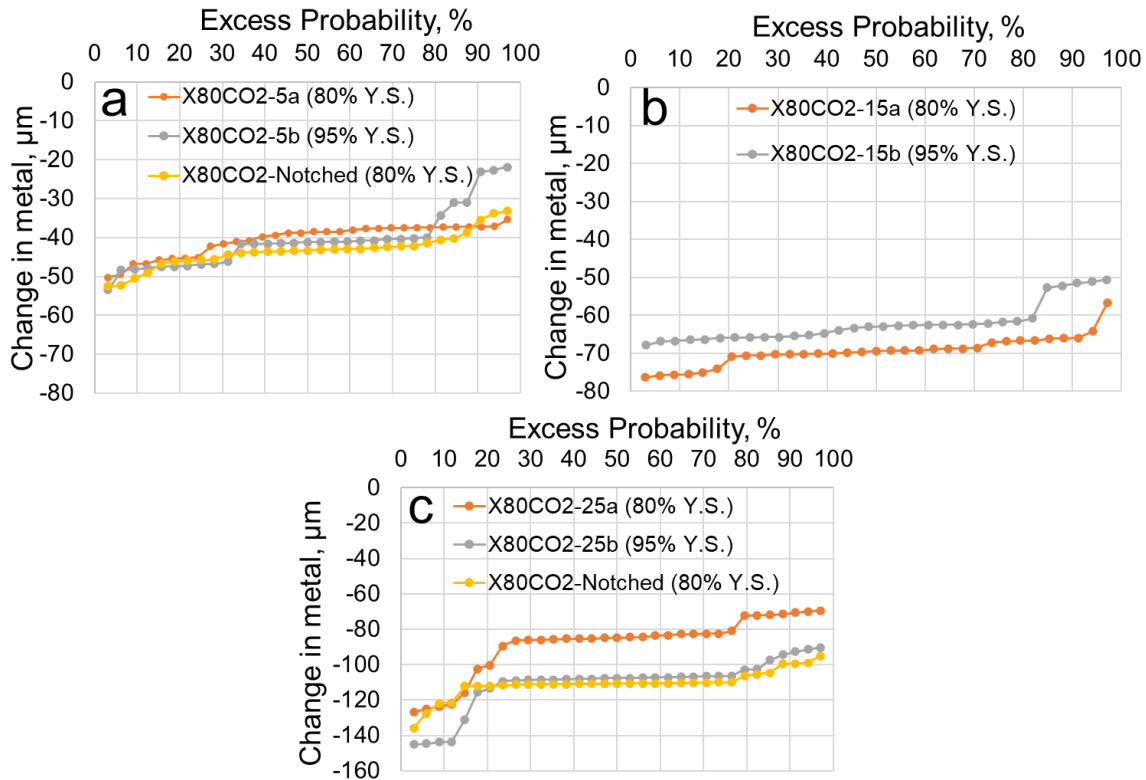


Figure 5-15 - Cumulative probability of metal loss exceedance graphs of X80 C-rings samples exposed in simulated saltwater solution with CO₂: (a) at 5 °C; (b) at 15 °C; (c) at 25 °C.

As reported from the calculated corrosion rates and metal loss exceedance values on the X65 and X70 samples, no significant change in metal loss value observed on the X80 samples with change in applied stress level from 80 % Y.S. to 95 % Y.S. and surface state (notched state) of the samples, with accounting an error of $\pm 5 \mu\text{m}$ in the measurement of the metal loss. Similarly, as observed from the corrosion rates from LPR measurements, no significant difference in metal loss between the X70 samples (max. of $-128 \mu\text{m}$) and X80 samples (max. of $-145 \mu\text{m}$). The calculated corrosion rates of the X80 samples (max. of 1.410 mm/year) also tallies with measured metal loss exceedance values when converted to 840 hrs of exposure, with a value of $-135 \mu\text{m} (\pm 5 \mu\text{m})$. Similarly, as observed from the calculated corrosion rates of the exposed X65 and X70 samples from LPR measurements, an increase in metal loss of about 50 % was observed with increasing solution temperature from 5 °C to 15 °C, with more than 100 % from 5 °C to 25 °C as shown in Figure 5-15.

5.1.2.6 Cumulative Probability of Metal Loss Exceedance of X100 C-rings Specimens

Figures 5-16a, 5-16b and 5-16c, respectively, show the cumulative probability of metal loss exceedance, obtained from the datasets of the exposed X100 samples in solution with CO₂ at 5 °C, 15 °C and 25 °C. The obtained datasets for all samples at 5 °C and 15 °C presented low metal change over most of the sample's surfaces. Maximum metal loss of -112 µm was obtained from the notched sample at 5 °C and -165 µm obtained from the sample stressed at 95 % Y.S at 15 °C. At 25 °C the samples were observed to show relatively higher metal change in comparison with 15 °C. Maximum metal loss value of -264 µm was obtained from the notched sample at 25 °C.

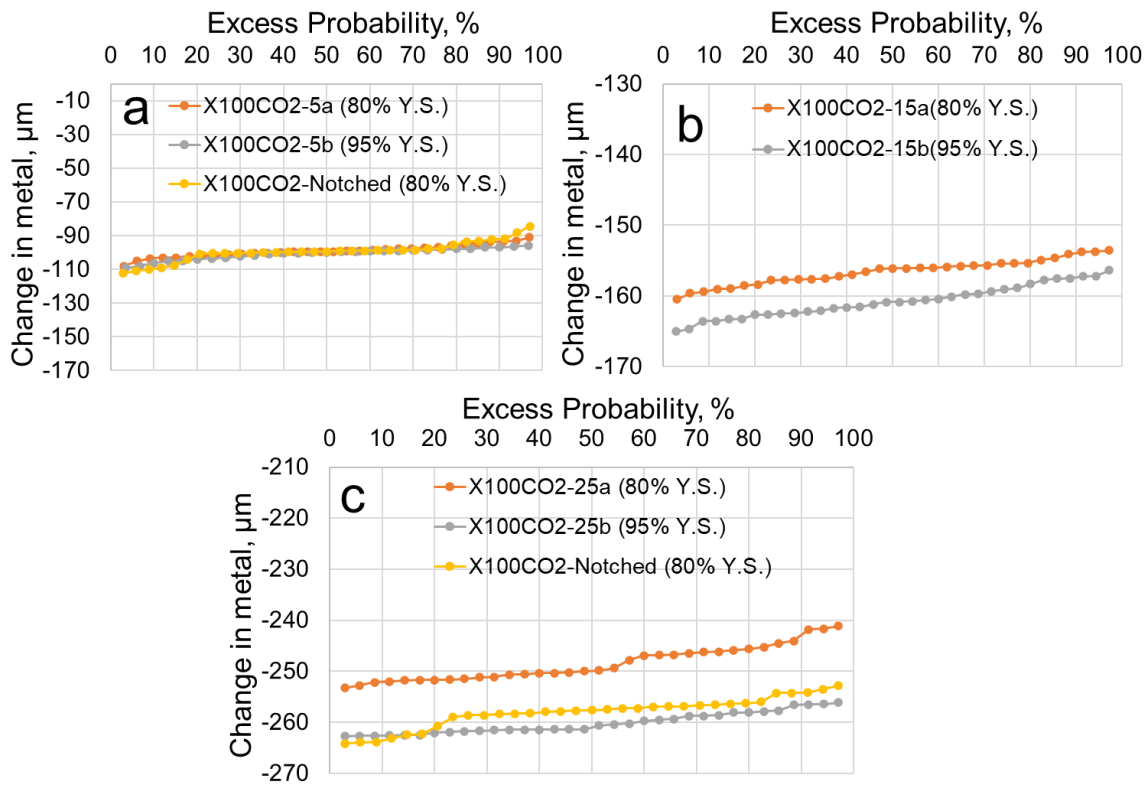


Figure 5-16 - Cumulative probability of metal loss exceedance graphs of X100 C-rings samples exposed in simulated saltwater solution with CO₂: (a) at 5 °C; (b) at 15 °C; (c) at 25 °C.

In general, as observed from the calculated corrosion rates from LPR measurements, the X100 samples at all exposure temperatures presented higher metal loss (max. of -264 µm at 25 °C) in comparison with X65 (max. of -122 µm),

X70 (max. of -128 μm) and X80 (max. of -145 μm) samples. No significant difference in metal loss values observed on the X100 samples at all solution temperatures with change in applied stress level from 80 % Y.S. to 95 % Y.S. and surface state (notched state) of the samples, with accounting an error of ± 5 μm in the measurement of the metal loss exceedance. The calculated corrosion rates of the X100 samples (max. of 2.821 mm/year) also tallies with measured metal loss exceedance values when converted to 840 hrs of exposure, with a value of -270 μm (± 5 μm). Similarly, as observed from the calculated corrosion rates of the exposed X65, X70 and X80 samples from LPR measurements and measured metal loss values, an increase in metal loss of more than 100 % was measured on the X100 samples with increasing temperature from 5 °C to 25 °C. The increased value in metal loss observed on the X100 samples relative to X65, X70 and X80 samples shows that the X100 carbon steel is more susceptible to SCC in the simulated saltwater solution saturated with CO₂. As suggested from the calculated corrosion rates analysis between the X65, X70, X80 and X100 carbon steels exposed in solution with CO₂, selection of X100 carbon steel as pipeline material in a seawater environment for transportation of CO₂ or in carbon capture and storage should not be considered if X80, X70 or X65 is readily available.

5.1.2.7 Cumulative Probability of Metal Loss Exceedance of X100 3-point Bent-beam Specimens

Figures 5-17a and 5-17b, respectively, show the cumulative probability of metal loss exceedance, obtained from the datasets of the X100 3-point bent-beam samples exposed in solution with CO₂ at 5 °C and 25 °C. Similar trend in low metal change was observed on the X100 3-point samples at all solution temperatures relative to the X100 C-ring samples (X100CO₂-CR-5a and 25a). Maximum metal loss of -109 μm was observed on the 3-point sample stressed at 80 % Y.S. at 5 °C and -215 μm at 25 °C.

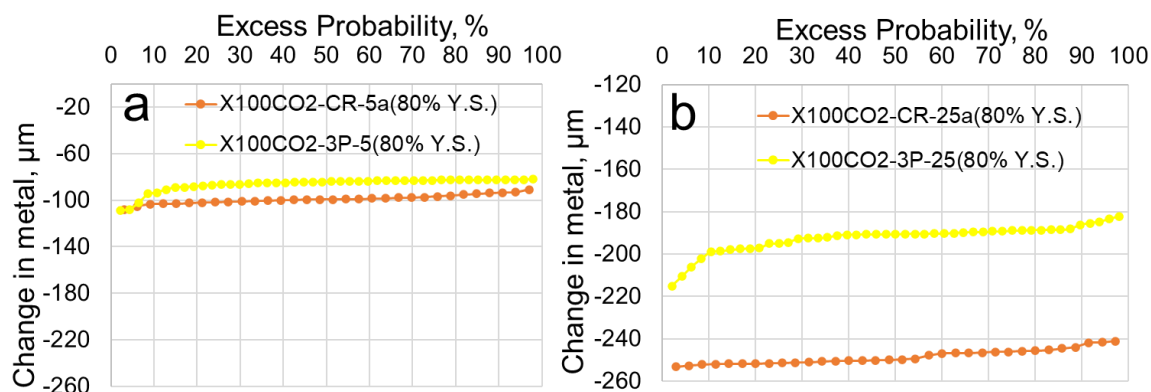


Figure 5-17 - Cumulative probability of metal loss exceedance graphs of X100 3-point Bent-beam samples exposed in simulated saltwater solution with CO₂: (a) at 5 °C; (b) at 25 °C.

Similarly, as observed on the X100 C-rings samples stressed at 80 % Y.S., an increase in metal loss of about 100 % was also observed on the 3-point bent-beam samples with increasing temperature from 5 °C to 25 °C. No significant difference in metal loss observed between the X100 3-point sample (max. of -109 μm) and X100 C-ring sample (max. of -108 μm) exposed at 5 °C as also observed in the calculated corrosion rates from LPR measurements as presented in Figure 5-9. However, at 25 °C the X100 C-ring sample (X100CO2-CR-25a) presented higher metal loss with a maximum value of -253 μm, and a maximum value of -215 μm obtained from the 3-point bent-beam sample as shown in figure 5-17b. The calculated corrosion rate (max. of 2.304 mm/year at 25 °C) on the X100 3-point bent-beam sample from LPR measurements tallies with measured metal loss exceedance when converted to 840 hrs of exposure, with a value of -221 μm (±5 μm).

5.1.3 Scanning Electron Microscopy Analysis

SEM analysis was conducted on the cross-sectional areas of the stress-oriented sections of the exposed C-rings and 3-point bent beam samples to understand the type of corrosion morphology on the samples' surfaces with change in exposure conditions.

5.1.3.1 Scanning Electron Microscopy Images of X65 C-ring Specimens

Figures 5-18a to 5-18h, respectively, show the SEM images of the X65 samples stressed at 80 % Y.S, 95 % Y.S., and notched sample stressed at 80 % Y.S. exposed in solution with CO₂ at 5 °C, 15 °C and 25 °C. A clear change in surface roughness and metal dissolution was observed on the sample's surfaces with increasing temperature from at 5 °C to 25 °C. At 5 °C, the corrosion morphologies on the samples were observed to have elliptical but wide and deep pits (Figures 5-18a, d and g). The sample stressed at 80 % Y.S. exposed at 5 °C to show a bit higher dissolution relative to sample stressed at 95 % Y.S. and notched sample. This can be explained to occur as a result of differential aeration. The samples exposed at 15 °C (Figures 5-18b and e) were observed to show a deep undercutting metal dissolution, which was observed to be deeper at 25 °C (Figures 5-18c, f and h). No clear increase in metal dissolution observed on the samples with increasing applied stress level from 80 % Y.S. to 95 % Y.S. and surface state of the samples. Discontinuous micro-cracks were observed on all samples exposed at 15 °C and 25 °C.

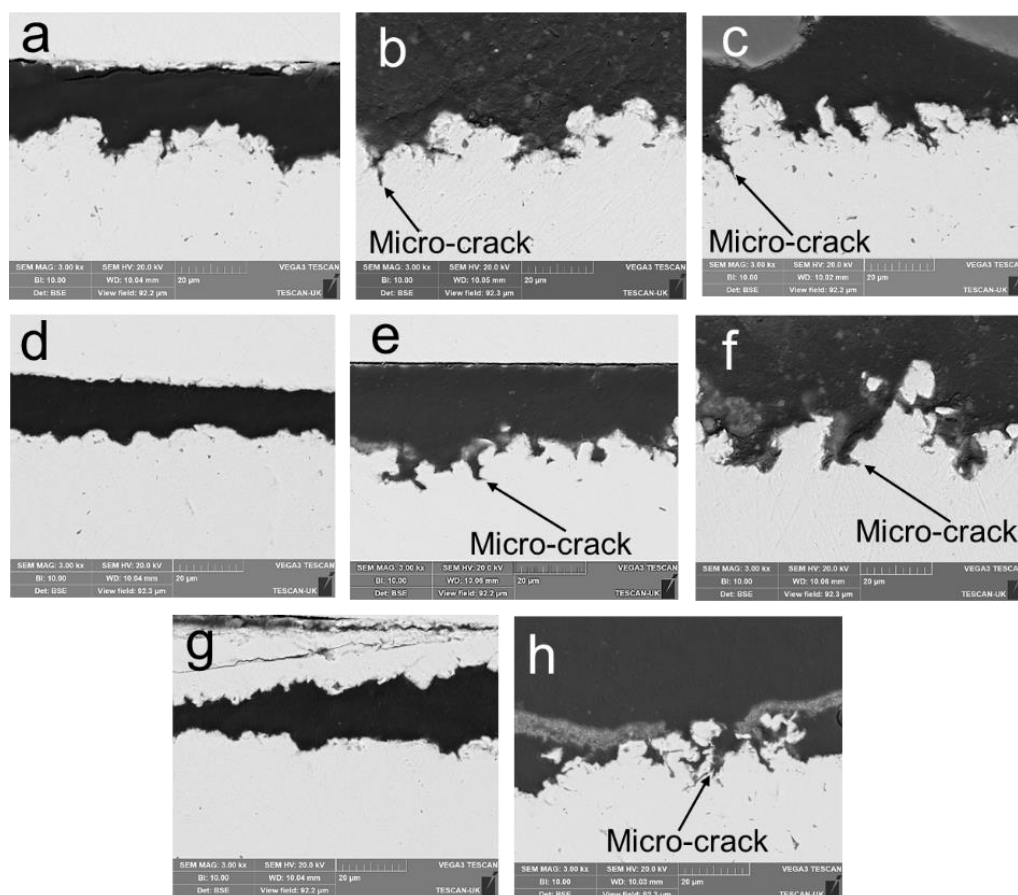


Figure 5-18 - SEM backscattered electron images of the exposed X65 C-rings samples in simulated saltwater solution with CO₂ stressed at 80 % Y.S., 95 % Y.S. and notched sample stressed at 80 % Y.S.: (a) 80 % Y.S. at 5 °C; (b) 80 % Y.S. at 15 °C; (c) 80 % Y.S. at 25 °C; (d) 95 % Y.S. at 5 °C; (e) 95 % Y.S. at 15 °C; (f) 95 % Y.S. at 25 °C; (g) Notched sample at 5 °C; (h) Notched sample at 25 °C.

5.1.3.2 Scanning Electron Microscopy Images of X70 C-ring Specimens

Figures 5-19a to 5-19h, respectively, show the SEM images of the X70 C-ring samples stressed at 80 % Y.S, 95 % Y.S., and notched sample stressed at 80 % Y.S. exposed in solution with CO₂ at 5 °C, 15 °C and 25 °C. Similarly, as observed on the X65 samples (Figure 5-18), a clear increase in metal dissolution was observed on the X70 samples with increasing temperature from 5 °C to 25 °C. Relative to the X65 samples, the surface morphologies on the X70 samples exposed at 5 °C (Figures 5-19a, d and g) were observed to have shallow pits with wide elliptical morphologies. More or less similar type of corrosion

morphologies were observed on the X70 samples at 15 °C (Figures 5-19b and e) and 25 °C (Figures 5-19c, f and h), relative to X65 samples (Figure 5-18), with a deep undercutting metal dissolution. Discontinuous micro-cracks were also observed on the samples exposed at 15 °C and 25 °C. No clear increase in surface deterioration was observed with change in applied stress level and surface state of the samples at all exposure temperatures.

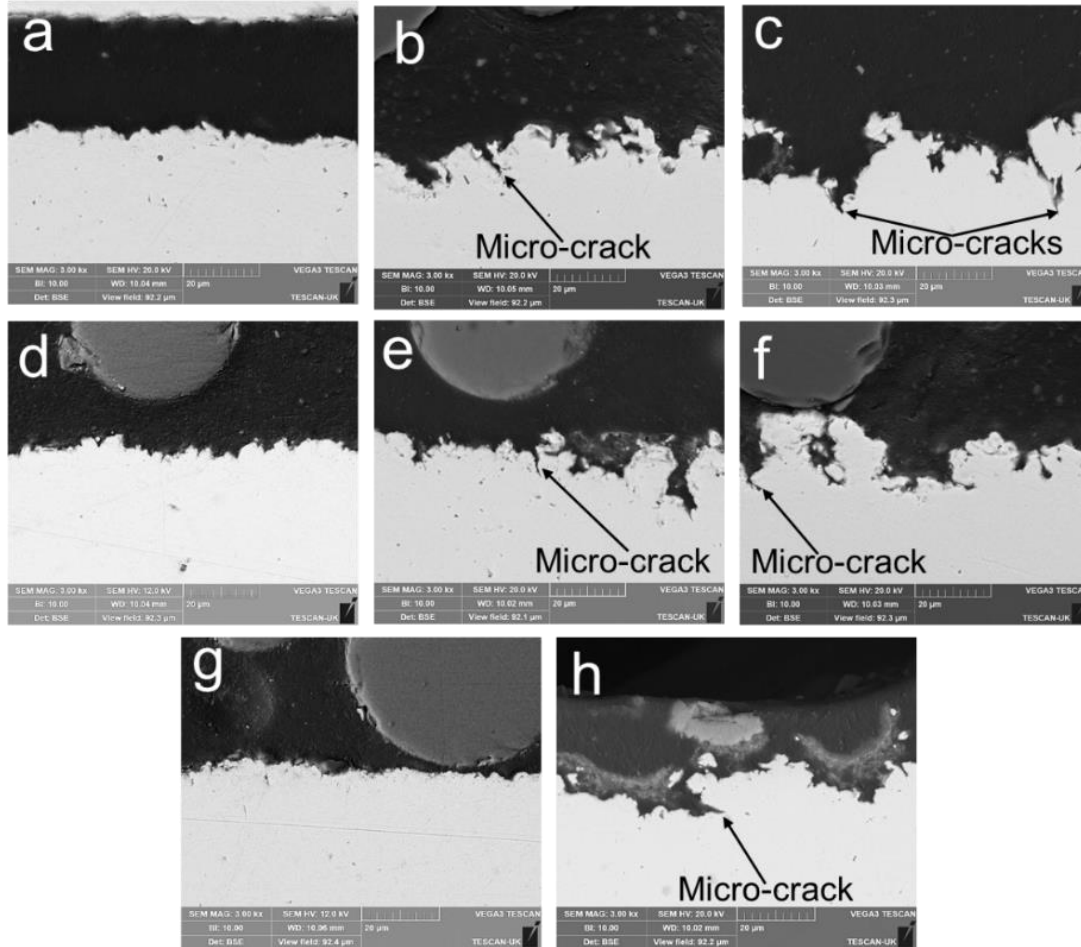


Figure 5-19 - SEM backscattered electron images of the exposed X70 C-ring samples in simulated saltwater solution with CO₂ stressed at 80 % Y.S., 95 % Y.S. and notched sample stressed at 80 % Y.S.: (a) 80 % Y.S. at 5 °C; (b) 80 % Y.S. at 15 °C; (c) 80 % Y.S. at 25 °C; (d) 95 % Y.S. at 5 °C; (e) 95 % Y.S. at 15 °C; (f) 95 % Y.S. at 25 °C; (g) Notched sample at 5 °C; (h) Notched sample at 25 °C.

5.1.3.3 Scanning Electron Microscopy Images of the Mechanically and Chemically Pre-damaged X70 C-ring Specimens

The SEM images of the mechanically and chemically pre-damaged X70 C-rings samples stressed at 80 % Y.S and 95 % Y.S. exposed in solution with CO₂ at 25 °C are shown in Figures 5-20a to 5-20c. Similar type of surface corrosion morphology was observed on all samples relative to normal exposed X70 C-rings samples (Figure 5-19). Deep undercutting surface metal dissolution was observed on both mechanically and chemically pre-damaged samples, with presence of micro-cracks. No clear change in surface roughness was observed between the mechanically (Figures 5-20a and b) and chemically pre-damaged samples (Figure 5-20c).

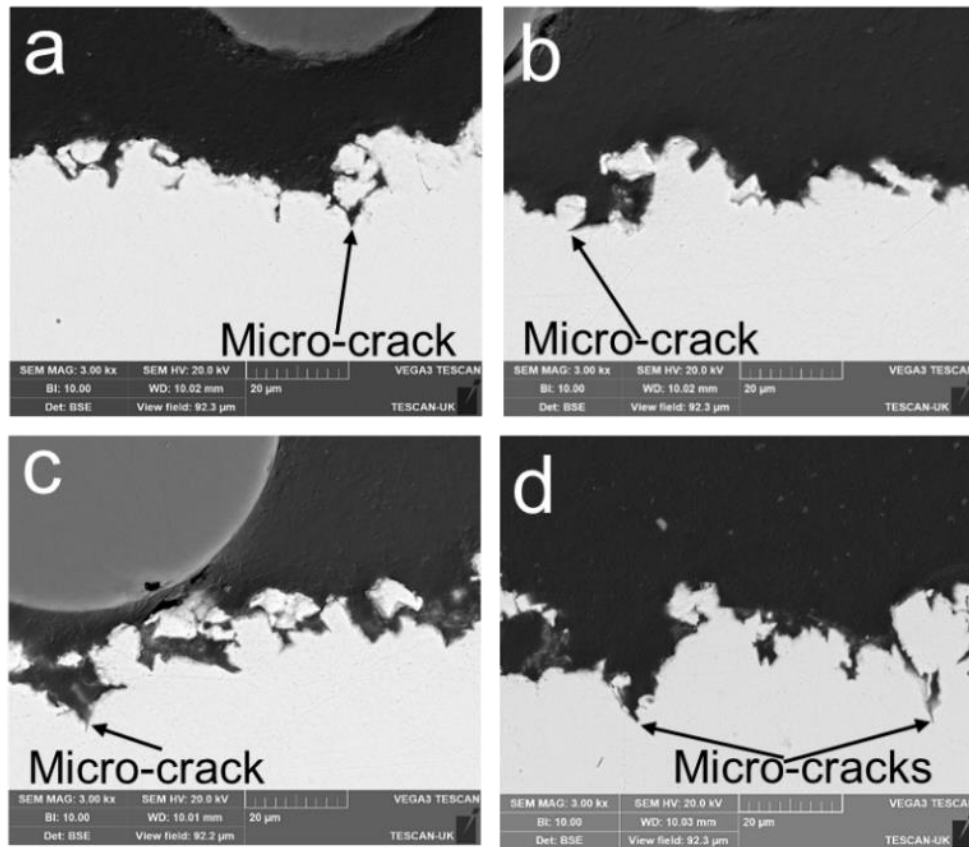


Figure 5-20 - SEM backscattered electron images of mechanically and chemically pre-damaged X70 C-rings samples stressed at 80 % Y.S. and 95 % Y.S. exposed in solution with CO₂ at 25 °C.: (a) scratched (80 % Y.S.); (b) scratched (95 % Y.S.); (c) salted (80 % Y.S.); (d) normal exposed X70 (80 % Y.S.).

5.1.3.4 Scanning Electron Microscopy Images of X70 3-point Bent-beam Specimens

Figures 5-21a to 5-21d, respectively, show the SEM images of the X70 3-point bent-beam samples stressed at 80 % Y.S. exposed in solution with CO₂ at 5 °C and 25 °C. A combination of shallow elliptical and narrow undercutting type of corrosion morphology was observed on the sample exposed at 5 °C (Figure 5-21a), including the repeat sample (Figure 5-21b). At 25 °C, deep and wide elliptical type of corrosion morphology was observed on the sample's surfaces as shown in Figures 5-21d and e (repeat sample stressed at 80 % Y.S.). All samples at both 5 °C and 25 °C were observed to show higher dissolution and deterioration relative to the X70 C-rings samples (Figures 5-19a and c at 5 °C and 25 °C, respectively). It can be stated that stressing technique does have an impact on the corrosion morphology, crack initiation and propagation of the exposed carbon steel samples.

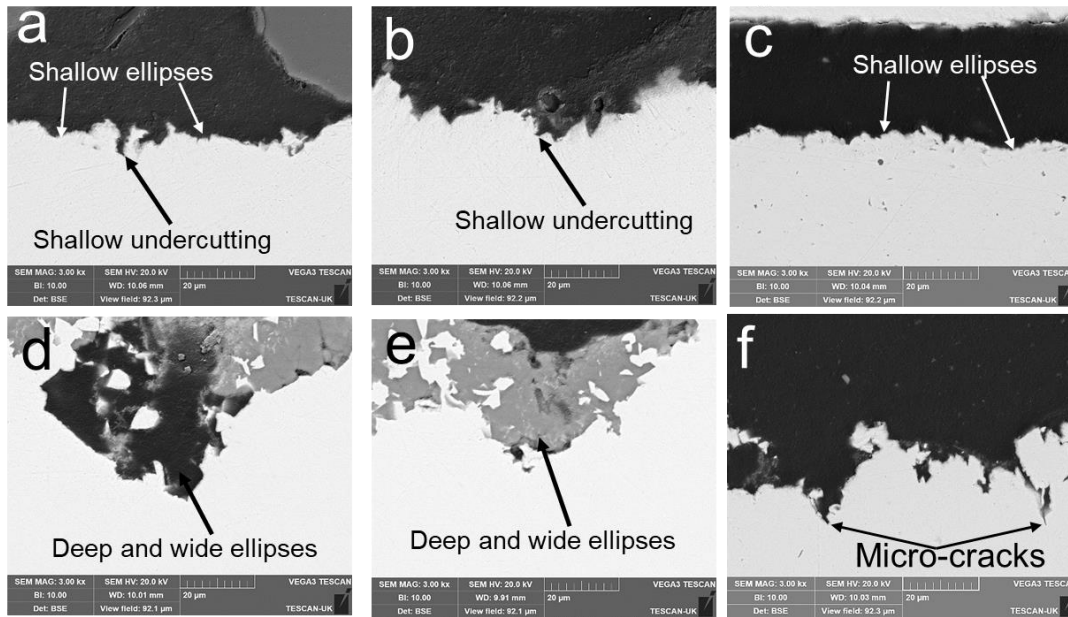


Figure 5-21 - SEM backscattered electron images of the X70 3-point bent-beam samples stressed at 80 % Y.S. exposed in solution with CO₂ at 5 °C and 25 °C.: (a) 80 % Y.S. at 5 °C; (b) repeat sample - 80 % Y.S. at 5 °C; (c) X70 C-ring sample - 80 % Y.S. at 5 °C; (d) 80 % Y.S. at 25 °C; (e) repeat sample - 80 % Y.S. at 25 °C; (f) X70 C-ring sample - 80 % Y.S. at 25 °C.

5.1.3.5 Scanning Electron Microscopy Images of X80 C-ring Specimens

Figures 5-22a to 5-22h, respectively, show the SEM images of the X80 samples stressed at 80 % Y.S, 95 % Y.S., and notched sample stressed at 80 % Y.S. exposed in solution with CO₂ at 5 °C, 15 °C and 25 °C. The X80 samples exposed at 5 °C at all stress levels (Figures 5-22a, d and g) were observed to have a deep and narrow elliptical surface morphology, with a combination of vertical dissolution. Clear increase in metal dissolution was observed with increasing solution temperature from 5 °C to 15 °C. At 15 °C, the samples at all stress levels (Figures 5-22b and e) presented similar surface morphology relative to samples exposed at 5 °C, but with wider elliptical morphology and a combination of horizontal dissolution. Much wider and deeper elliptical corrosion morphology was observed on the samples exposed at 25 °C (Figure 5-22c, f and h). Similarly, as observed on the X65 and X70 samples, no clear change in surface morphology was observed on all samples with increasing applied stress level from 80 % Y.S. to 95 % Y.S. and change in surface state of the samples. No presence of micro-cracks was observed on the samples at all stress levels and solution temperatures.

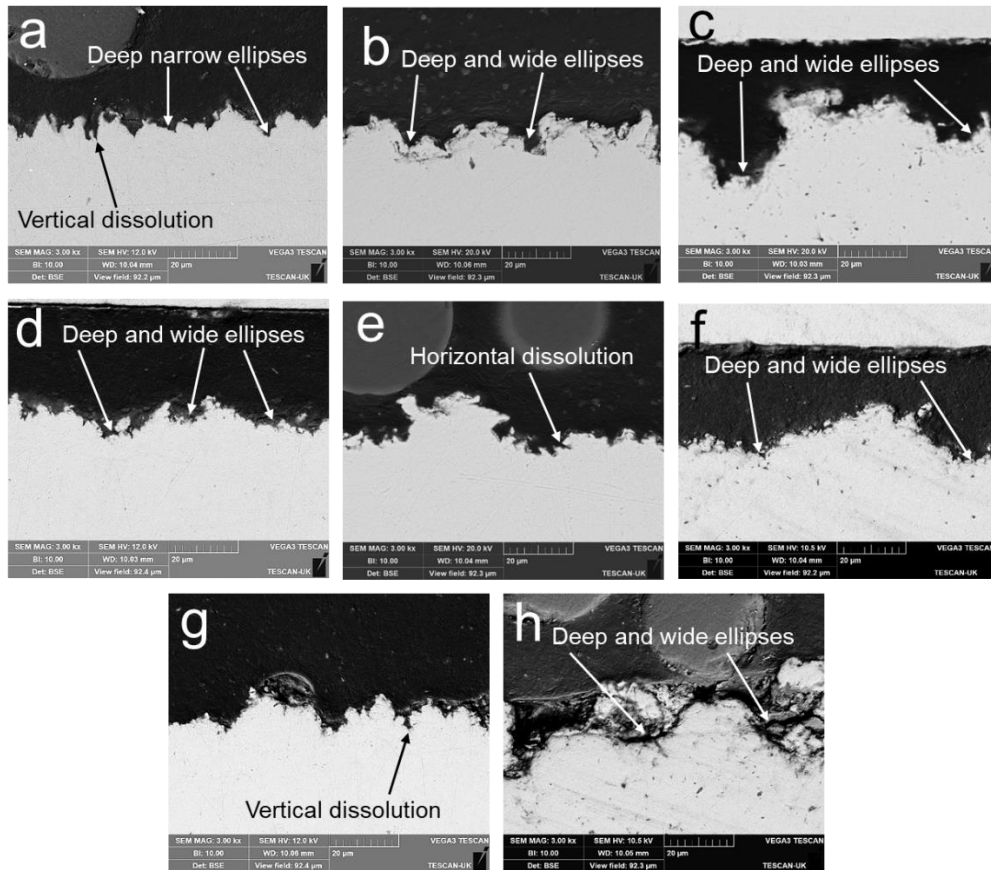


Figure 5-22 - SEM backscattered electron images of the exposed X80 C-ring samples in simulated saltwater solution with CO₂ stressed at 80 % Y.S., 95 % Y.S. and notched sample stressed at 80 % Y.S.: (a) 80 % Y.S. at 5 °C; (b) 80 % Y.S. at 15 °C; (c) 80 % Y.S. at 25 °C; (d) 95 % Y.S. at 5 °C; (e) 95 % Y.S. at 15 °C; (f) 95 % Y.S. at 25 °C; (g) Notched sample at 5 °C; (h) Notched sample at 25 °C.

5.1.3.6 Scanning Electron Microscopy Images of X100 C-ring Specimens

Figures 5-23a to 5-23h, respectively, show the SEM images of the X100 samples stressed at 80 % Y.S, 95 % Y.S., and notched sample stressed at 80 % Y.S. exposed in solution with CO₂ at 5 °C, 15 °C and 25 °C. Different corrosion morphologies were observed on all X100 samples relative to X65, X70 and X80 samples. The corrosion morphologies of the X100 samples at all stress levels presented wide and shallow elliptical surface corrosion morphologies, which increased in size with increasing temperature from 5 °C to 25 °C. More or less an even metal dissolution was observed on the samples. Similarly, as observed

on the X65, X70 and X80 samples no clear change in surface roughness was observed with increasing applied stress level from 80 % Y.S. to 95 % Y.S. and change in surface state of the samples. No presence of micro-cracks was observed on the samples at all solution temperatures.

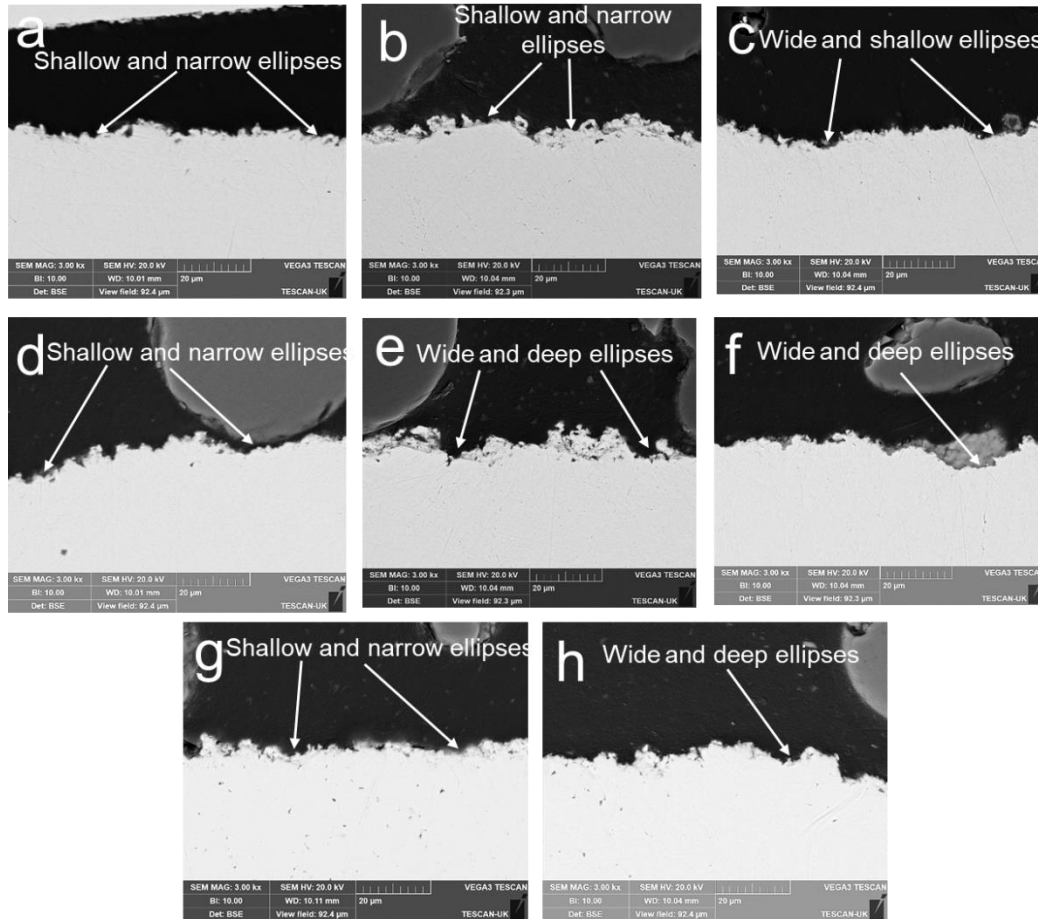


Figure 5-23 - SEM backscattered electron images of the exposed X100 C-ring samples in simulated saltwater solution with CO₂ stressed at 80 % Y.S., 95 % Y.S. and notched sample stressed at 80 % Y.S.: (a) 80 % Y.S. at 5 °C; (b) 80 % Y.S. at 15 °C; (c) 80 % Y.S. at 25 °C; (d) 95 % Y.S. at 5 °C; (e) 95 % Y.S. at 15 °C; (f) 95 % Y.S. at 25 °C; (g) Notched sample at 5 °C; (h) Notched sample at 25 °C.

5.1.3.7 Scanning Electron Microscopy Images of X100 3-point Bent-beam Specimens

Figures 5-24a and 5-24c, respectively, show the SEM images of the X100 3-point bent-beam samples stressed at 80 % Y.S. exposed in solution with CO₂ at 5 °C

and 25 °C. Relative to the X100 C-rings samples (Figures 5-23a and 5-23c at 5 °C and 25 °C, respectively), the X100 3-point bent-beam samples showed similar type of corrosion morphology with wide and shallow elliptical morphology at all solution temperatures. Low increase in metal dissolution depth was observed on the samples with increasing temperature from 5 °C to 25 °C. No clear change in surface roughness observed between the exposed C-rings samples and 3-point bent-beam samples at all exposure conditions.

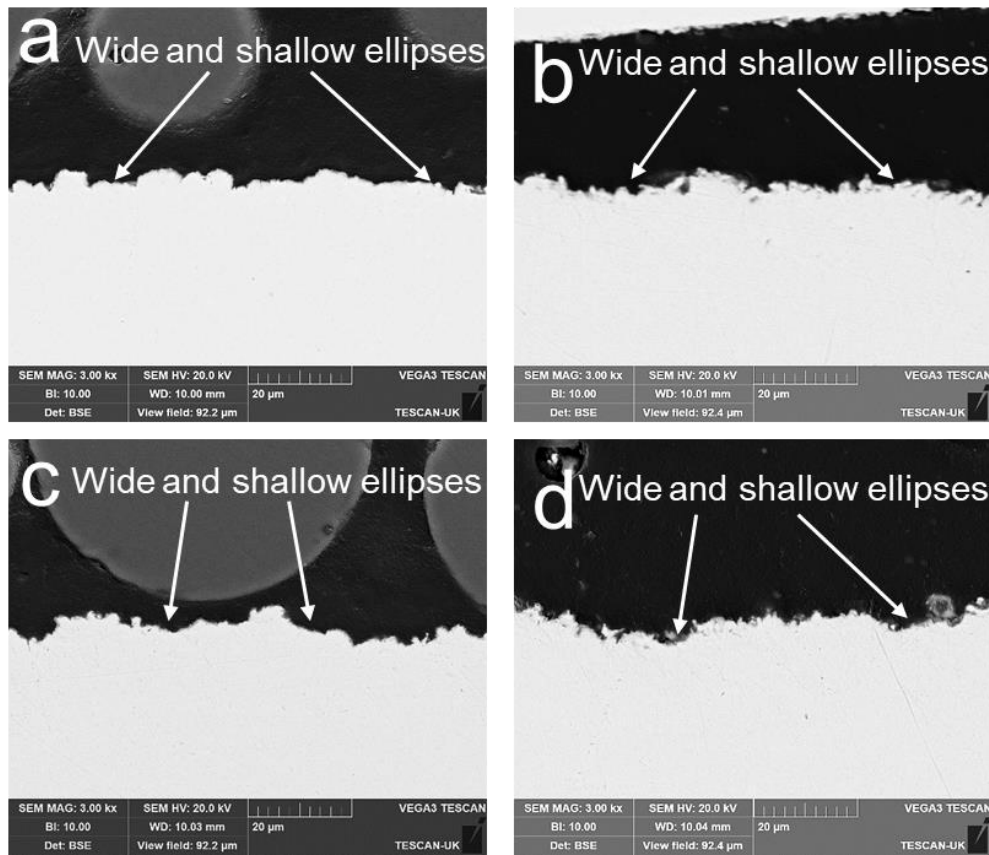


Figure 5-24 - SEM backscattered electron images of the X100 3-point bent-beam samples stressed at 80 % Y.S. exposed in solution with CO₂ at 5 °C and 25 °C.: (a) 80 % Y.S. at 5 °C; (b) X100 C-ring sample - 80 % Y.S. at 5 °C; (c) 80 % Y.S. at 25 °C; (d) X100 C-ring sample - 80 % Y.S. at 25 °C.

In general, change in corrosion morphology was observed on all exposed samples with increasing solution temperature from 5 °C to 25 °C. The X65 and X70 samples at all applied stress levels and solution temperatures presented similar type of corrosion morphology with wide and shallow elliptical (at 5 °C) and

deep undercutting metal dissolution (at 15 °C and 25 °C). The X80 samples presented different morphology relative to X65 and X70 samples with deep and narrow elliptical pits and a combination of vertical and horizontal metal dissolution (at 5 °C and 15 °C, respectively). Much wider and deeper elliptical metal dissolution was observed on the samples exposed at 25 °C. X100 samples presented wide and shallow elliptical morphology at all solution temperatures. More or less an uneven surface metal dissolution was observed on all X65, X70 and X80 samples, with a more even dissolution observed on the X100 samples. The variation in corrosion morphologies observed on the exposed carbon steels can be said to occur as a result of differences in the microstructure of the carbon steels and the presence of precipitates in their microstructures. As reported by Wang et al. [135], the presence of precipitate in a microstructure provides nucleation sites for crack initiation and hydrogen traps, which leads to hydrogen embrittlement. This causes reduction in ductility of the carbon steels and increases potentiality of SCC occurrence.

5.1.4 Energy Dispersive Spectroscopy

EDS analysis was conducted on the exposed samples to understand the variation in elemental compositions of the samples with change in exposure conditions. An error of $\pm 5\%$ is assumed for all EDS measurements.

5.1.4.1 Energy Dispersive Spectroscopy Analysis of X70 C-rings Specimens

The compositions of the EDS spectra (Figure 5-25) of the exposed X70 sample in solution with CO₂ at 5 °C stressed at 80 % Y.S., are presented in Figure 5-26 (in weight percentages). As reported in the N₂ solution (chapter 4), the carbon content from all spectra will not be reported as EDS does not correctly quantify the percentage of carbon present in the analyzed samples. Spectrum 1 which is mainly composed of resin will not also be reported in the analysis. Different concentrations of Mn were observed with change in spectrum location. Spectrum 3 which is close to the alloy-resin interface was observed to have highest percentage of Mn with a value of 2.01 wt.%. relative to spectrum 4 with a value

of 1.98 wt.%. Approximately equal percentages of Fe were observed in spectrum 3 and 4 with a value of 91.21 wt.% and 91.20 wt.%, respectively.

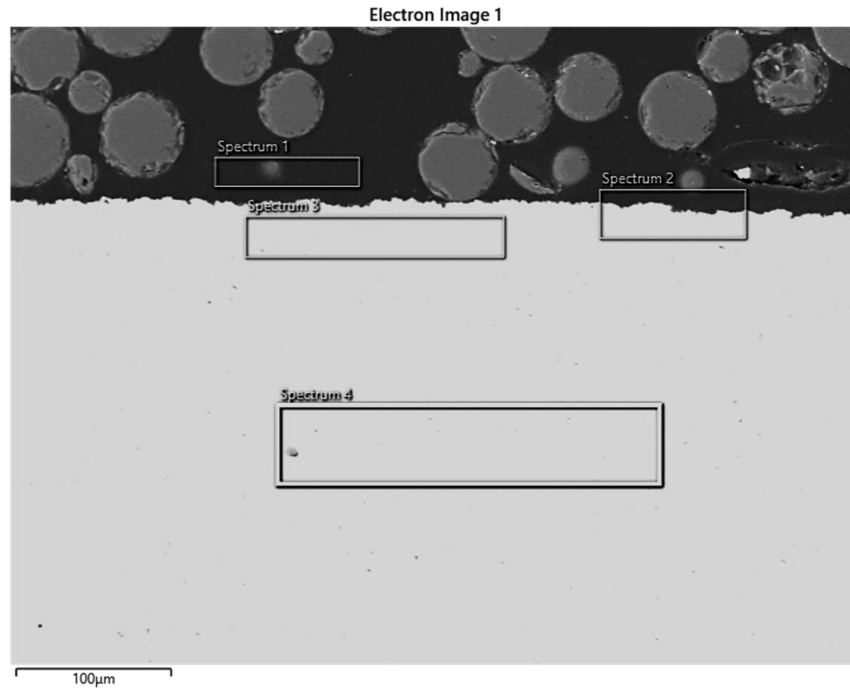


Figure 5-25 - SEM backscattered electron image of the exposed X70 C-ring sample in simulated saltwater solution with CO₂ at 5 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 5-26.

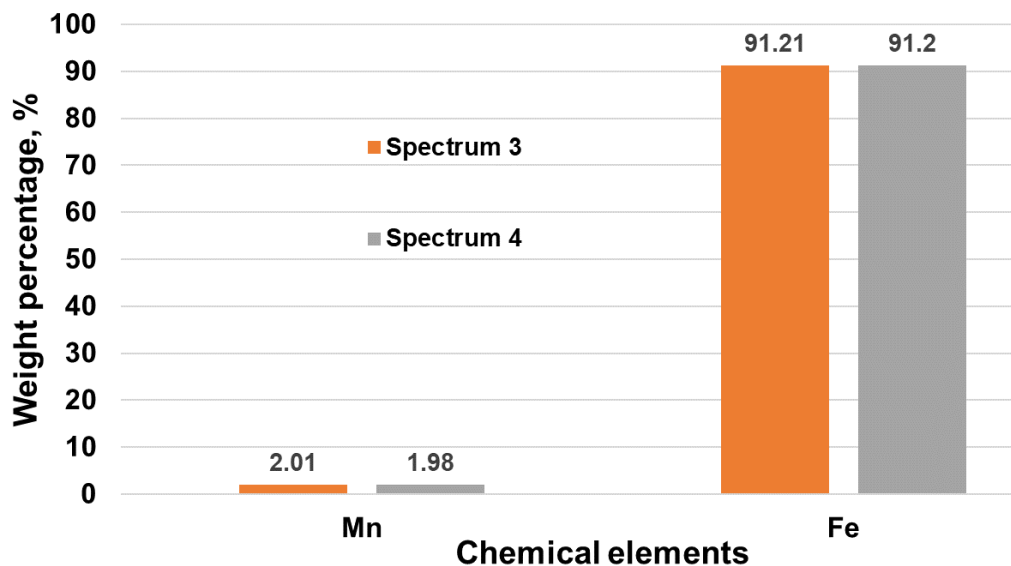


Figure 5-26 - EDS compositions of the exposed X70 C-ring sample elements in simulated saltwater solution with CO₂ at 5 °C stressed at 80 % Y.S.

As shown in the line scan analysis (Figure 5-27), a sharp increase in Fe concentration was clearly observed between the alloy-resin interface. Amount of C was clearly shown to be higher in the resin, with sharp increase below about 58 μm into the resin. Amount of Si was observed to have higher contents in the alloy, with highest concentration observed at about 105 μm along the line.

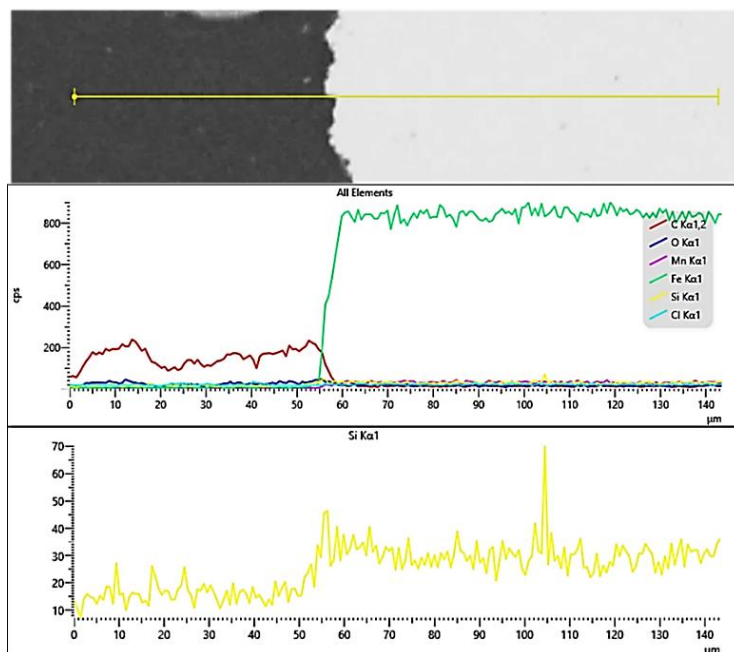


Figure 5-27 - EDS line scan analysis of the exposed X70 C-ring sample elements in simulated saltwater solution with CO_2 at 5 °C stressed at 80 % Y.S.

Variations in compositions of the EDS spectra (Figure 5-28) of the exposed X70 C-ring sample in solution with CO_2 at 15 °C stressed at 80 % Y.S., were observed as presented in Figure 5-29 (in weight percentages). Similarly, concentration of Fe and Mn was observed to change with spectrum location. Highest percentage of Mn was observed in spectrum 4 with a value of 1.94 wt.%. In comparison with spectrum 3 (1.91 wt.%). Spectrum 3 which is close to the interface was observed to have higher percentage of Fe with a value of 91.97 wt.% in comparison with spectrum 4 (91.61 wt.%).

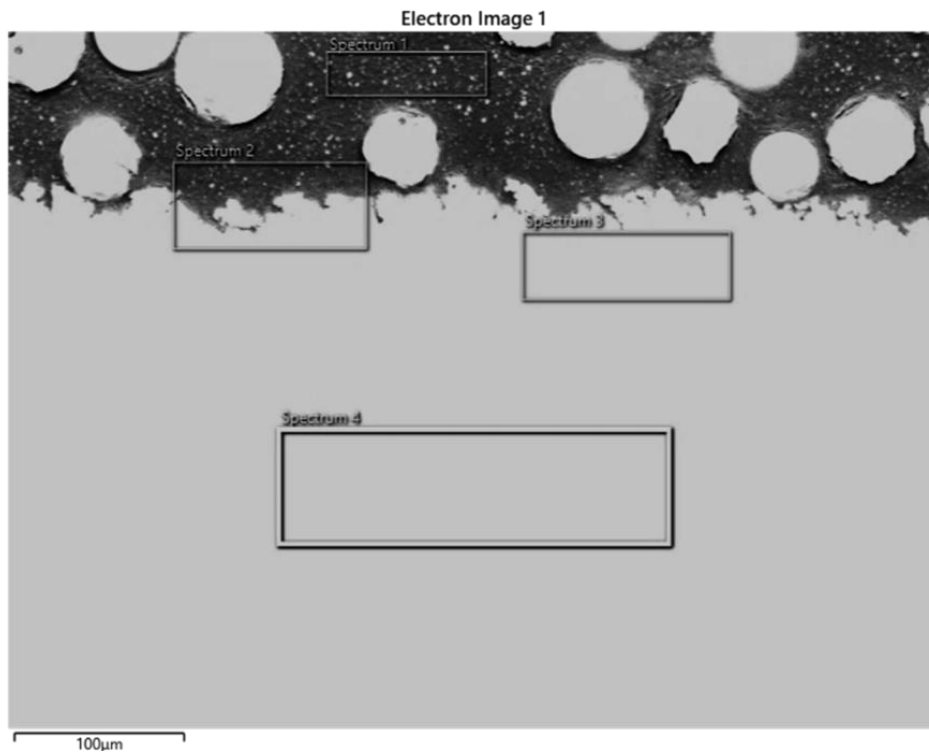


Figure 5-28 - SEM backscattered electron image of the exposed X70 C-ring sample in simulated saltwater solution with CO₂ at 15 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 5-29.

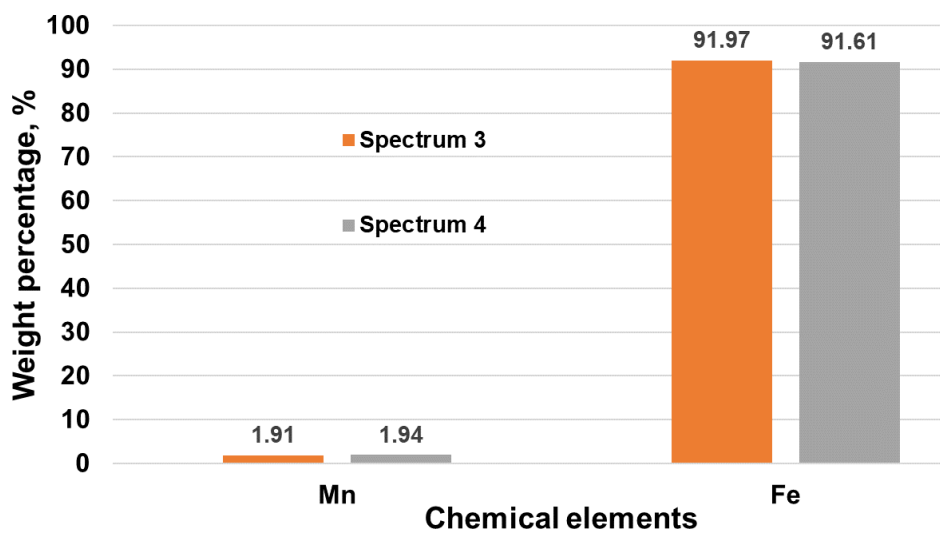


Figure 5-29 - EDS compositions of the exposed X70 C-ring sample elements in simulated saltwater solution with CO₂ at 15 °C stressed at 80 % Y.S.

The line scan analysis of the exposed X70 C-ring sample at 15 °C is presented in Figure 5-30. Similarly, as observed at 5 °C, the analysis showed a sharp

increase of Fe concentration at the interface. C content was also observed to be higher in the resin with sharp increase below about 43 μm into the resin. Variations in Si concentrations were observed along the line, with higher content observed at 2 μm and 43 μm into the resin.

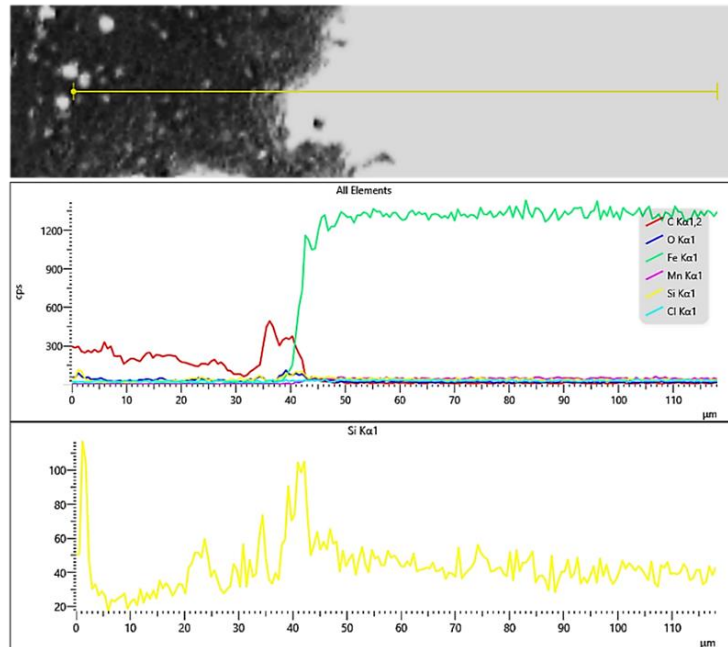


Figure 5-30 - EDS line scan analysis of the exposed X70 C-ring sample elements in simulated saltwater solution with CO₂ at 15 °C stressed at 80 % Y.S.

Different compositions of the EDS spectra (Figure 5-31) were observed in the X70 C-ring sample stressed at 80 % Y.S. exposed at 25 °C as shown in Figure 5-32. Relative to samples exposed at 5 °C and 15 °C, higher percentage of Fe was observed on the sample exposed at 25 °C in spectrum 4 with 93.72 wt.% and a value of 93.64 wt.% observed in spectrum 3 which is close to the interface. Concentration of Mn was observed to change with spectrum location, with highest percentage observed in spectrum 4 (1.89 wt.%). Presence of Si was observed on all spectra, with higher value of 0.33 wt.% observed in spectrum 4.

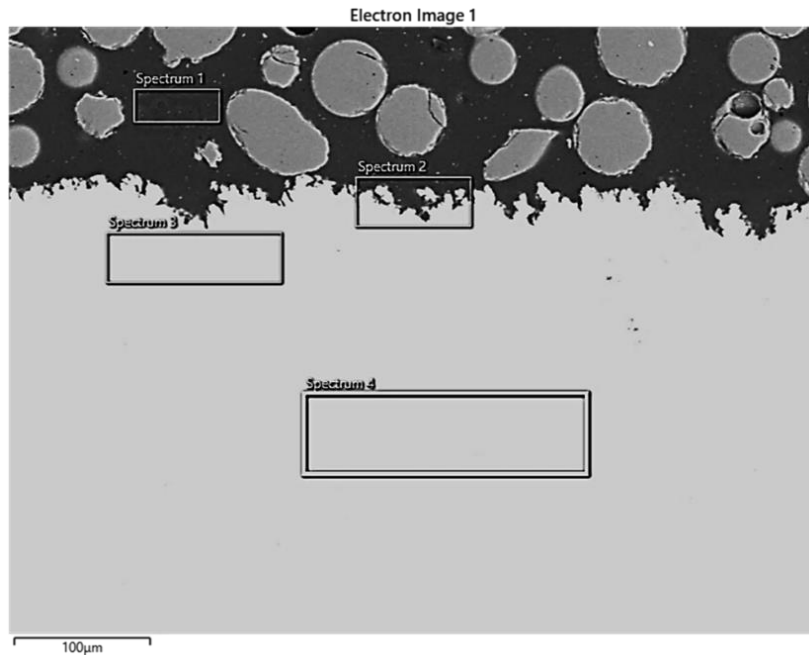


Figure 5-31 - SEM backscattered electron image of the exposed X70 C-ring sample in simulated saltwater solution with CO₂ at 25 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 5-32.

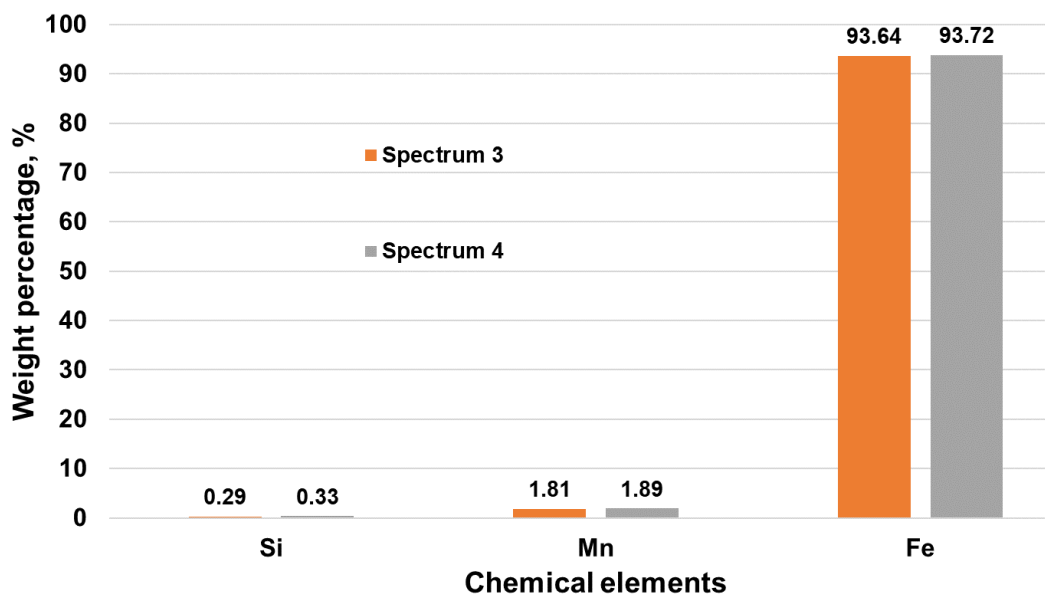


Figure 5-32 - EDS compositions of the exposed X70 C-ring sample elements in simulated saltwater solution with CO₂ at 25 °C stressed at 80 % Y.S.

Similarly, as observed at 5 °C and 15 °C, the line scan analysis of the X70 C-ring sample exposed at 25 °C (Figure 5-33) showed a sharp increase of Fe concentration at the interface. Amount of Si was observed to be higher at the

interface at about 65 μm into the resin. C content is also clearly observed to be higher in the resin with sharp increase below about 66 μm .

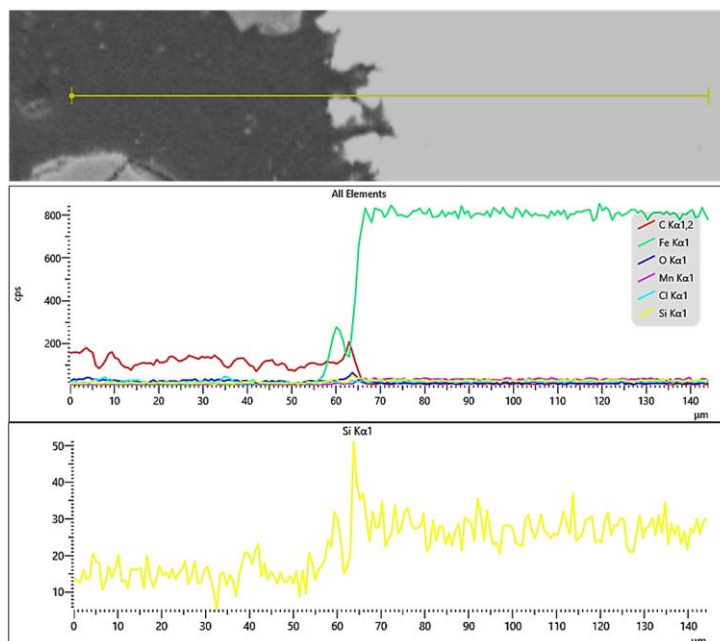


Figure 5-33 - EDS line scan analysis of the exposed X70 C-ring sample elements in simulated saltwater solution with CO_2 at 25 °C stressed at 80 % Y.S.

5.1.4.2 Energy Dispersive Spectroscopy Analysis of Mechanically and Chemically Pre-damaged X70 C-rings Specimens

The compositions of the EDS spectra (Figure 5-34) of the mechanically pre-damaged X70 -ring sample stressed at 80 % Y.S. exposed at 25 °C are presented in Figure 5-35. Approximately equal percentages of Fe were observed in spectrum 3 and 4 relative to normal exposed (undamaged) X70 C-ring sample exposed at 25 °C (Figure 5-32), with a maximum value of 93.77 wt.% observed in spectrum 4. Variations in Mn concentration were observed with change in spectrum location. The percentages of Mn obtained for the mechanically pre-damaged samples were observed to be lower than those of normal exposed (undamaged) X70 C-ring sample, with a maximum value of 1.76 wt.% obtained in spectrum 3. Variations in Si content was observed in all spectra of the mechanically pre-damaged sample as detected in normal exposed (undamaged) X70 C-ring sample. Maximum values of 0.33 wt.% and 0.35 wt.%, respectively,

were obtained in spectrum 4 for the normal exposed X70 C-ring and mechanically pre-damaged C-ring samples.

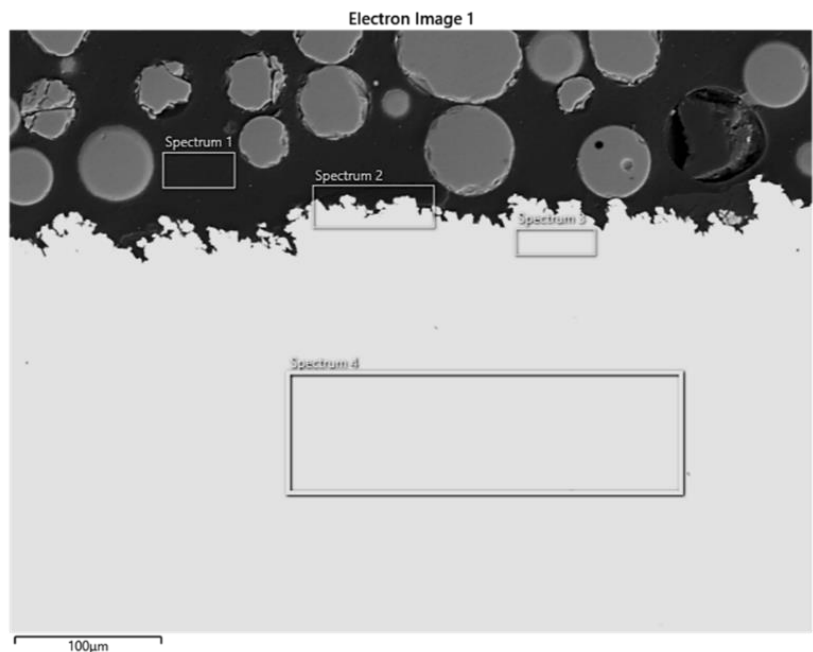


Figure 5-34 - SEM backscattered electron image of mechanically (scratched) pre-damaged X70 C-ring sample exposed in simulated saltwater solution with CO₂ at 25 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 5-35.

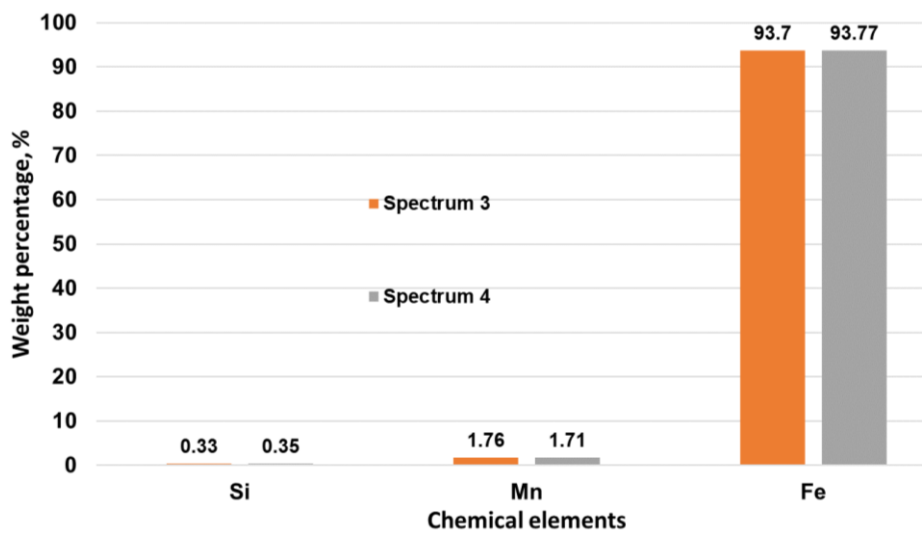


Figure 5-35 - EDS compositions of mechanically pre-damaged X70 C-ring sample exposed in simulated saltwater solution with CO₂ at 25 °C stressed at 80 % Y.S.

The line scan analysis of the mechanically pre-damaged sample (Figure 5-36) showed similar trend in concentration of the elements relative to normal exposed

X70 C-ring sample exposed at 25 °C (Figure 5-33). A sharp increase in Fe content was observed at the interface after about 34 μm into the resin. Si content was also observed to be higher at the interface at about 38 μm into the resin. C content was also observed to be higher in the resin.

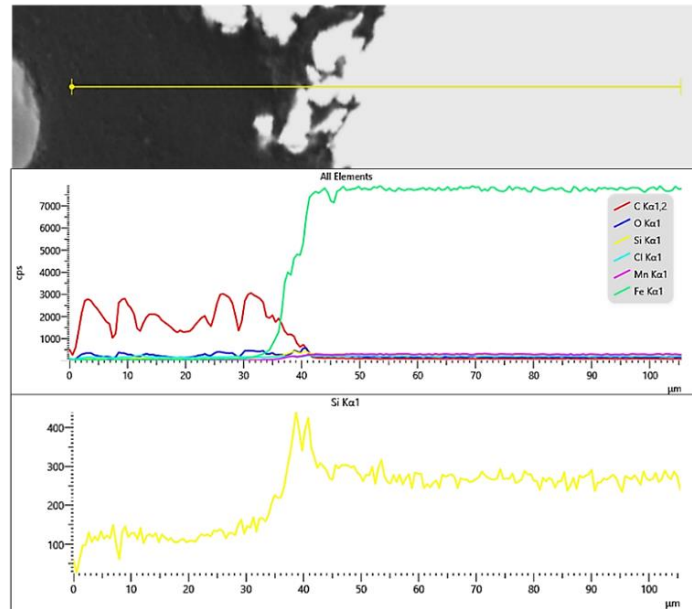


Figure 5-36 - EDS line scan analysis of mechanically pre-damaged X70 C-ring sample exposed in simulated saltwater solution with CO_2 at 25 °C stressed at 80 % Y.S.

The elemental compositions of the chemically (salted) pre-damaged X70 C-ring sample stressed at 80 % Y.S. exposed at 25 °C as obtained from the EDS spectra (Figure 5-37) are presented in Figure 5-38. Lower concentrations of Fe were observed on the chemically pre-damaged sample (salted sample) in comparison with the normal exposed (undamaged) X70 sample (Figure 5-32) and the mechanically pre-damaged (Figure 5-35) X70 sample. A maximum value of 92.95 wt.% was observed in spectrum 4. Lower Mn concentration was also observed with a maximum value of 1.69 wt.% obtained in spectrum 4. No significant difference in maximum Si concentration was observed on the salted sample (0.34 wt.%) relative to the mechanically pre-damaged (0.35 wt.%). Traces of O were detected in all spectra with a value of 0.62 wt.% and 0.68 wt.% detected in spectrum 3 and 4, respectively.

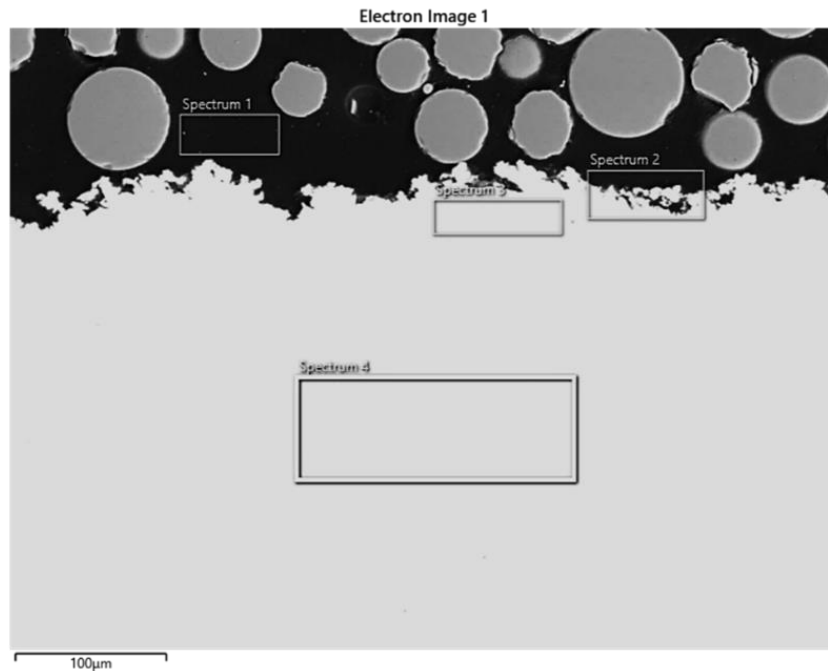


Figure 5-37 - SEM backscattered electron image of chemically (salted) pre-damaged X70 C-ring sample exposed in simulated saltwater solution with CO₂ at 25 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 5-38.

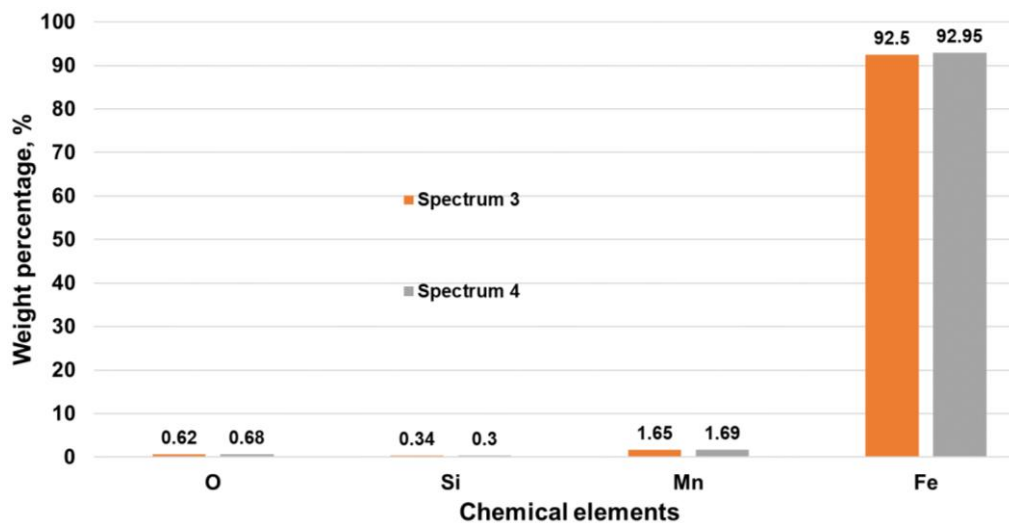


Figure 5-38 - EDS compositions of chemically pre-damaged X70 C-ring sample exposed in simulated saltwater solution with CO₂ at 25 °C stressed at 80 % Y.S.

The line scan analysis of the chemically pre-damaged sample (Figure 5-39) also showed similar trend in elemental concentration of Fe and C as observed in the normal exposed X70 C-ring and mechanically pre-damaged samples. However,

concentration of Si was observed to be higher not at the interface, but after about 2 μm into the resin and then on the alloy at about 61 μm .

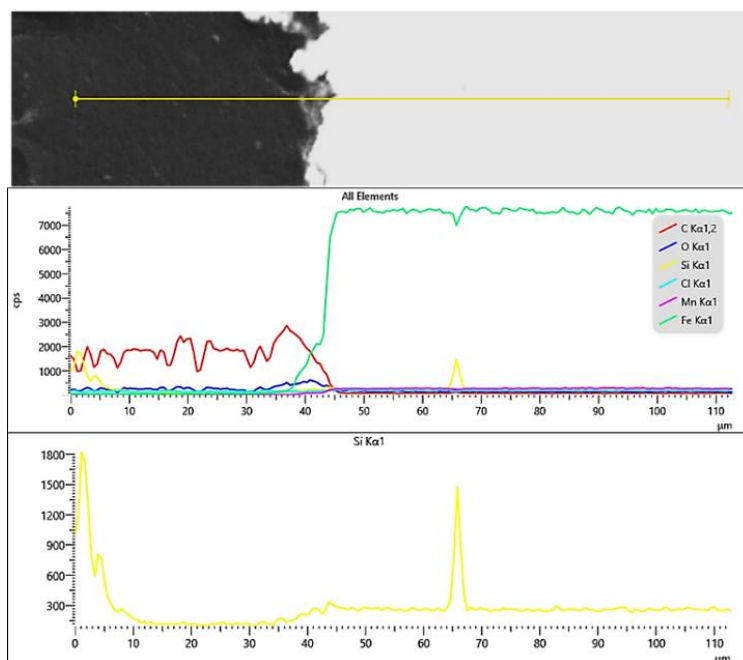


Figure 5-39 - EDS line scan analysis of chemically pre-damaged X70 C-ring sample exposed in simulated saltwater solution with CO_2 at 25 $^\circ\text{C}$ stressed at 80 % Y.S.

5.1.4.3 Energy Dispersive Spectroscopy Analysis of X70 3-point Bent-beam Specimens

The elemental compositions of the EDS spectra (Figure 5-40) of the X70 3-point bent-beam sample stressed at 80 % Y.S. exposed at 5 $^\circ\text{C}$ are presented in Figure 5-41. Relative to X70 C-ring sample exposed at 5 $^\circ\text{C}$ (Figure 5-26), higher percentages of Fe were observed with a value of 92.2 wt.% and 92.79 wt.% obtained in spectrum 3 and 4, respectively. Increasing Mn concentration was observed with change in spectrum location. Lower values of Mn were observed in the X70 3-point sample in all spectra relative to X70 C-ring sample (2.01 wt.%) with a maximum of 1.93 wt.% obtained in spectrum 4. Presence of Si and O was observed in all spectra in the X70 3-point sample unlike in the X70 C-ring sample with maximum values of 0.45 wt.% and 0.79 wt.%, respectively obtained in spectrum 3 and 4. Traces of Cl was observed in spectrum 4 with a value of 0.06 wt.%.

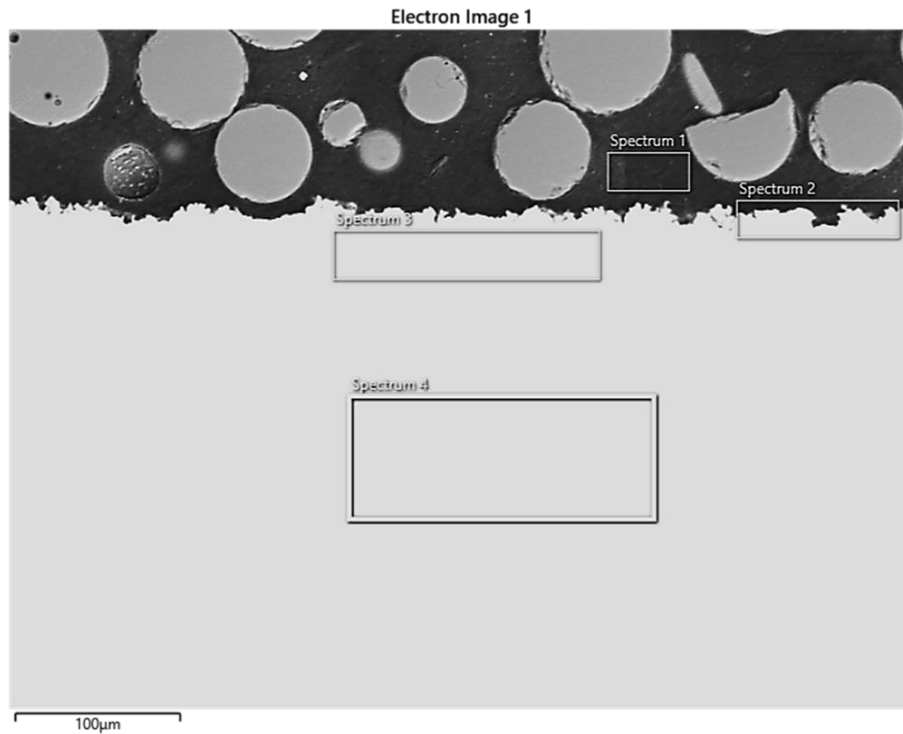


Figure 5-40 - SEM backscattered electron image of the exposed X70 3-point bent-beam sample in simulated saltwater solution with CO₂ at 5 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 5-41.

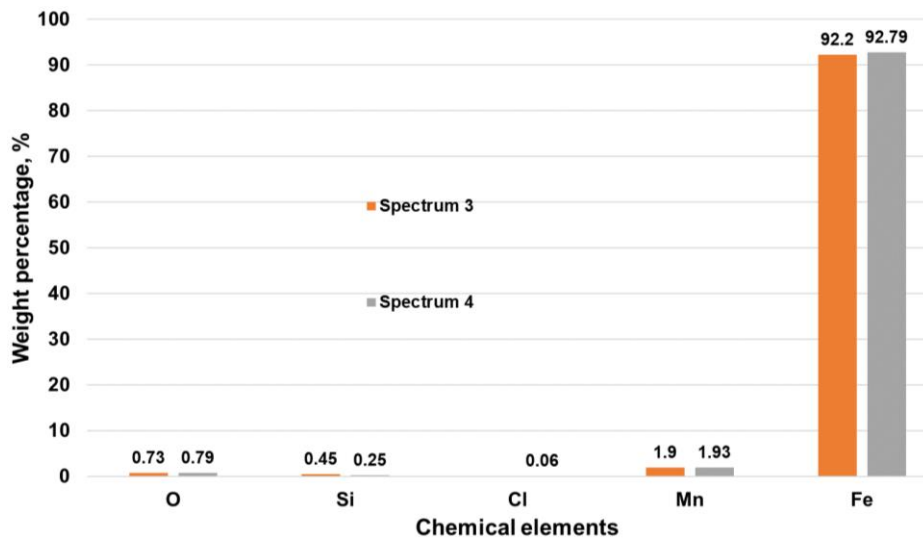


Figure 5-41 - EDS compositions of the exposed X70 3-point bent-beam sample in simulated saltwater solution with CO₂ at 5 °C stressed at 80 % Y.S.

The line scan analysis of the X70 3-point bent-beam sample exposed at 5 °C stressed at 80 % Y.S. is presented in Figure 5-42. A sharp increase in Fe concentration was observed at the alloy-resin interface as obtained in the X70

C-ring sample exposed at 5 °C (Figure 5-27). Variation in Si concentration was observed in the X70 3-point sample relative to X70 C-ring sample. Maximum Si concentration was observed at the interface at about 31 μm into the resin. Similarly, as observed in the X70 C-ring sample, the amount of C was observed to be higher in resin.

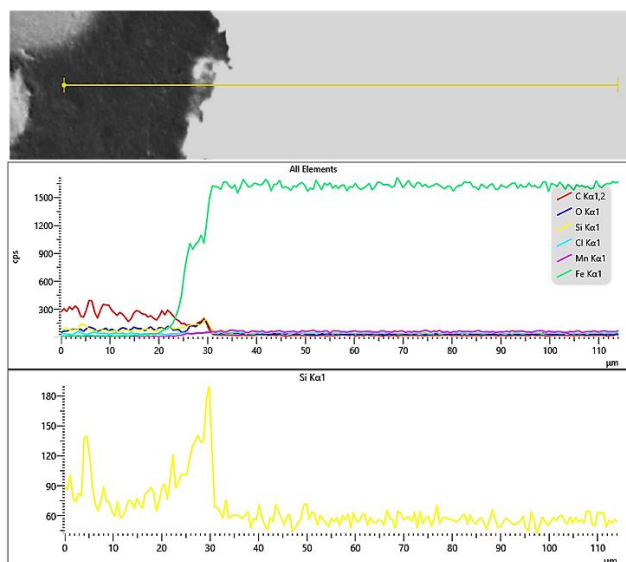


Figure 5-42 - EDS line scan analysis of the exposed X70 3-point bent-beam sample in simulated saltwater solution with CO_2 at 5 °C stressed at 80 % Y.S.

The compositions of the EDS spectra as shown in Figure 5-43 for the X70 3-point bent-beam sample stressed at 80 % Y.S. exposed at 25 °C are presented in Figure 5-44. Approximately equal percentages of Fe were observed in spectrum 4 with a value 93.6 wt.%, relative to X70 C-ring sample exposed at 25 °C with 93.64 wt.%, in spectrum 3 (Figure 5-32). Maximum value of 93.97 wt.% was observed in spectrum 5. Increasing amount of Mn was observed with change in spectrum location. Lower percentage of Mn was observed on the X70 3-point bent-beam sample in spectrum 4 with a value of 1.73 wt.%, relative to X70 C-ring sample with a value of 1.89 wt.% (Figure 5-32). Presence of O and Si was detected in all spectra with a maximum value of 0.52 wt.% and 0.37 wt.% obtained in spectrum 4. Unlike in the X70 C-ring sample, presence of Cl was observed on the 3-point bent-beam sample in spectrum 5 with 0.06 wt.%. The presence of Cl in the analyzed sample could result from exposure of the samples in the simulated 3.5 % NaCl solution.

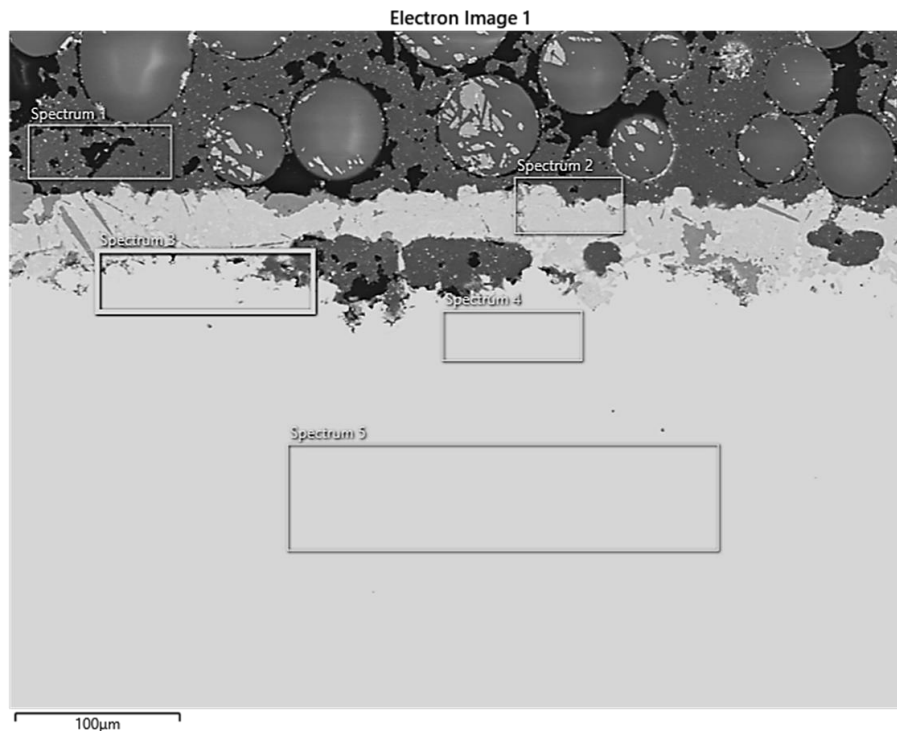


Figure 5-43 - SEM backscattered electron image of the exposed X70 3-point bent-beam sample in simulated saltwater solution with CO₂ at 25 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 5-44.

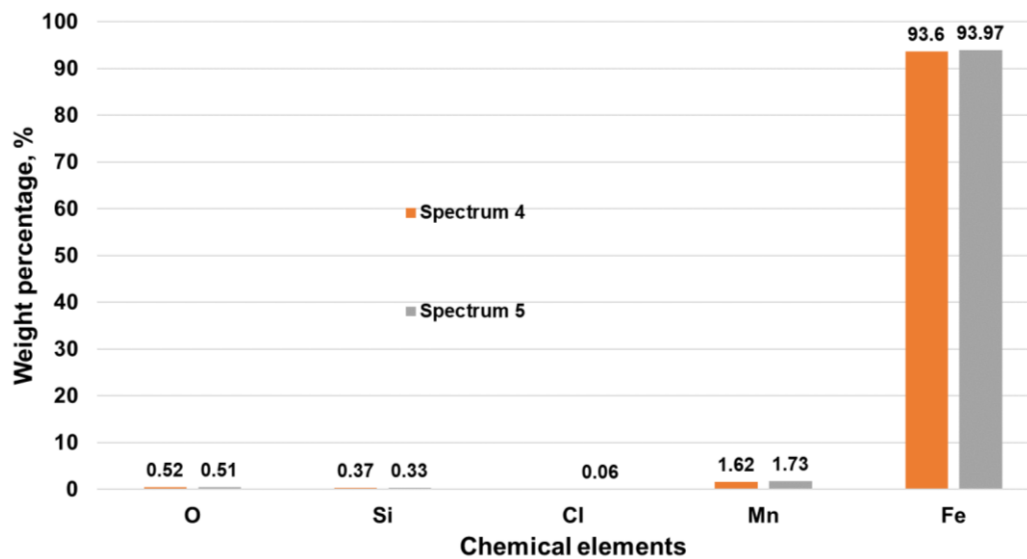


Figure 5-44 - EDS compositions of the exposed X70 3-point bent-beam sample in simulated saltwater solution with CO₂ at 25 °C stressed at 80 % Y.S.

The line scan analysis of the X70 3-point bent-beam sample stressed at 80 % Y.S. exposed at 25 °C is shown in Figure 5-45. different trend in Fe

concentration was observed in the X70 3-point sample, in comparison with X70 C-ring sample (Figure 5-33). Fluctuations in Fe concentration was observed across the line, with sharp increase observed at the alloy-resin interface. The amount of Fe detected in the resin between 20 μm and 82 μm into the resin was observed to be higher than those obtained in X70 C-ring sample at all temperatures. This can be explained to occur due to accumulation of corrosion products which contain high content of Fe. Similar trend in Si concentration was detected in the X70 3-point sample as observed in the X70 C-ring sample (Figure 5-33), with higher concentration observed at the alloy-resin interface.

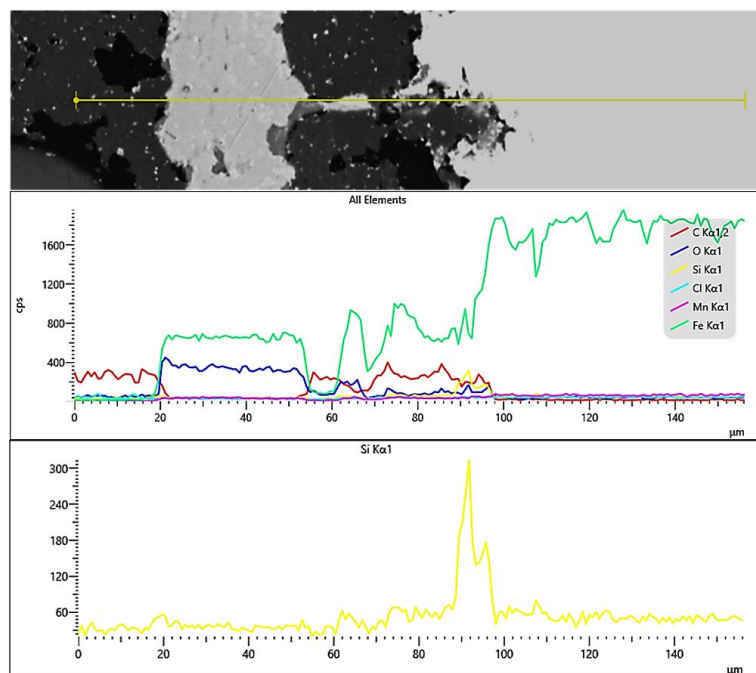


Figure 5-45 - EDS line scan analysis of the exposed X70 3-point bent-beam sample in simulated saltwater solution with CO_2 at 25 °C stressed at 80 % Y.S.

5.1.4.4 Energy Dispersive Spectroscopy Analysis of X100 C-rings Specimens

The elemental composition of the EDS spectra as shown in Figure 5-46 for the X100 C-ring sample stressed at 80 % Y.S. exposed at 5 °C is presented in Figure 5-47. Increasing percentage of Fe was observed with change in spectrum location. Spectrum 4 which is on the alloy presented highest value of 91.65 wt.%. Concentration of Mn was also observed to change with spectrum

location with maximum value of 2.01 wt.% observed in spectrum 4. No presence of O, Si or Cl detected in all spectra.

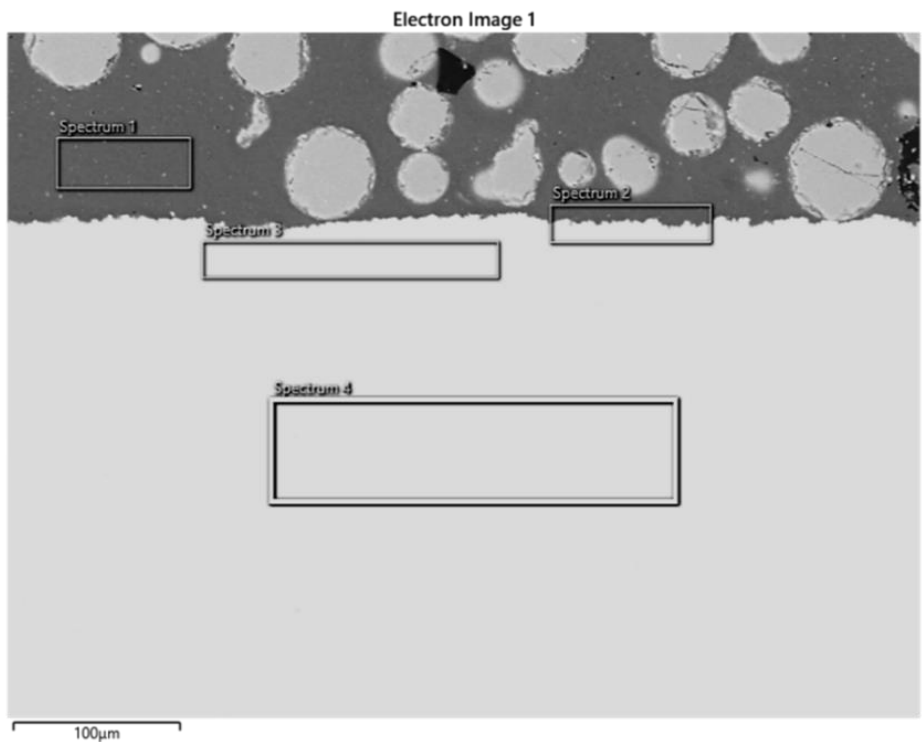


Figure 5-46 - SEM backscattered electron image of the exposed X100 C-ring sample in simulated saltwater solution with CO₂ at 5 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 5-47.

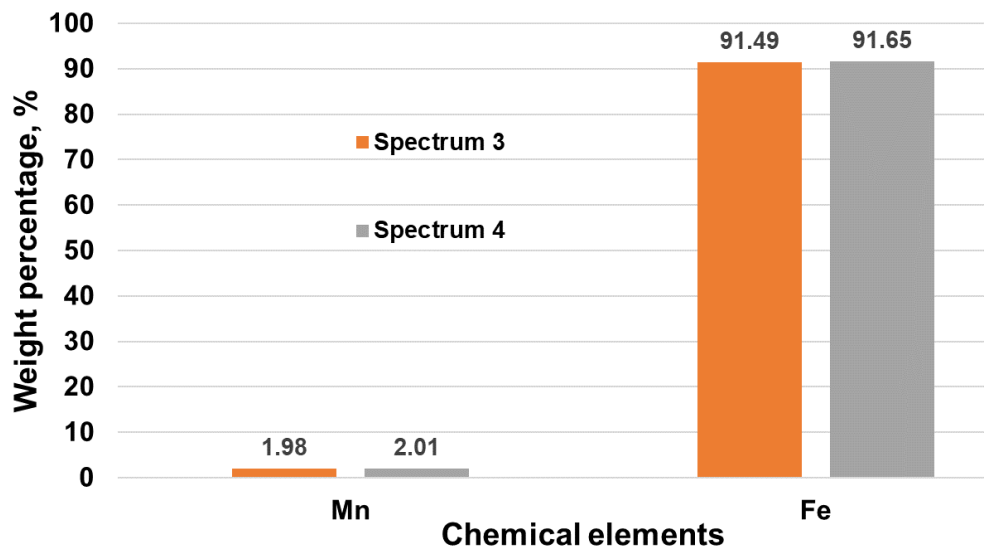


Figure 5-47 - EDS compositions of the exposed X100 C-ring sample elements in simulated saltwater solution with CO₂ at 5 °C stressed at 80 % Y.S.

The line scan analysis of the X100 C-ring sample exposed at 5 °C is presented in Figure 5-48. As shown in the line scan, concentration of Fe is observed to be higher in the alloy section, with sharp increase at the interface from about 60 µm into the resin. Concentration of Mn is also observed to be higher on the alloy section from about 60 µm. Si content is detected to be higher at about 50 µm into the resin. Similarly, as observed in other X70 samples, the concentration of C is clearly observed to be higher in the resin.

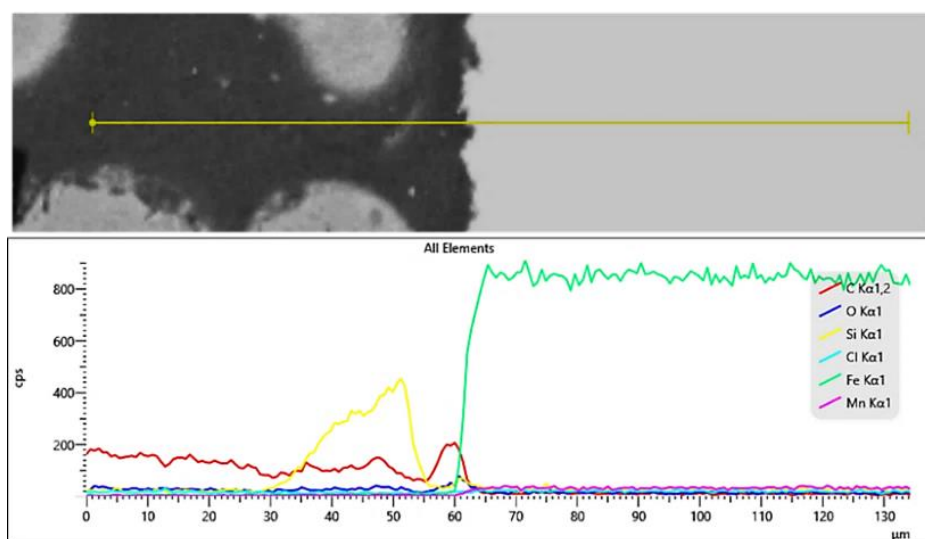


Figure 5-48 - EDS line scan analysis of the exposed X100 C-ring sample elements in simulated saltwater solution with CO₂ at 5 °C stressed at 80 % Y.S.

Variations in elemental compositions of the EDS spectra (Figure 5-49) of the X100 C-ring sample stressed at 80 % Y.S. exposed at 15 °C were observed, relative to X100 C-ring sample exposed at 5 °C (Figure 5-47). The percentage of Fe and Mn as shown in Figure 5-50 were detected to be higher than those observed at 5 °C. Maximum values of 92.1 wt.% and 2.03 wt.%, respectively were detected for Fe and Mn concentration in spectrum 3, which is close to the alloy-resin interface. Similarly, as reported from sample exposed at 5 °C, no presence of O, Si or Cl detected on the X100 sample exposed at 15 °C.

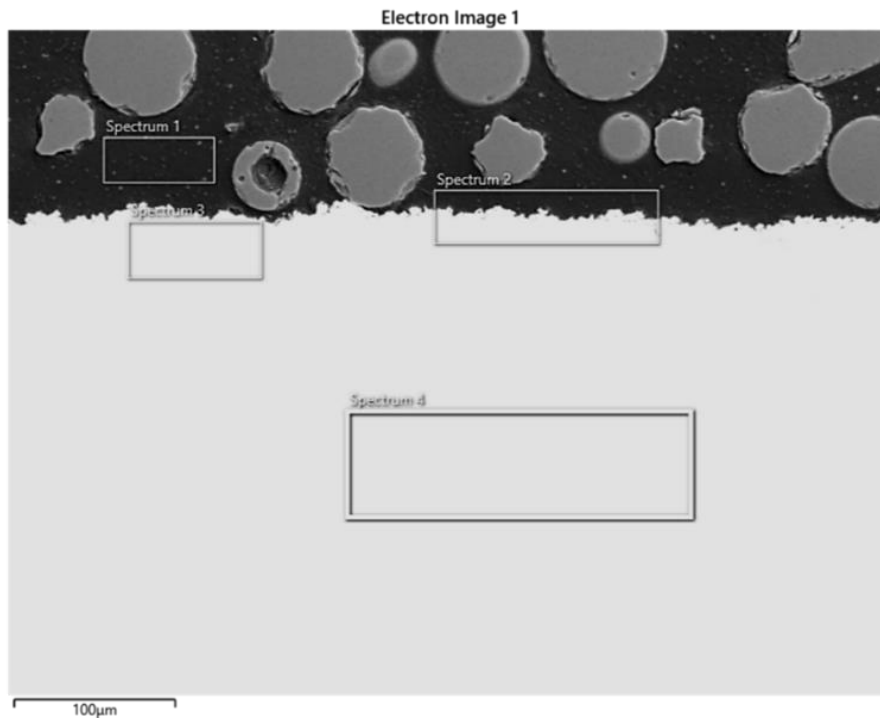


Figure 5-49 - SEM backscattered electron image of the exposed X100 C-ring sample in simulated saltwater solution with CO₂ at 15 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 5-50.

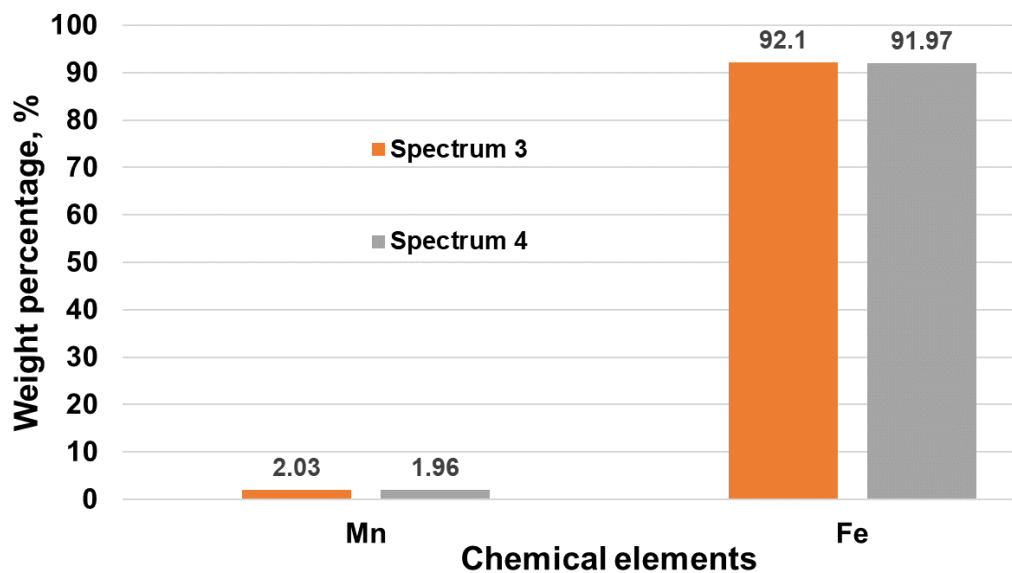


Figure 5-50 - EDS compositions of the exposed X100 sample elements in simulated saltwater solution with CO₂ at 15 °C stressed at 80 % Y.S.

The line scan analysis of the X100 C-ring sample exposed at 15 °C is presented in Figure 5-51. As presented in the line scan, similar trend in Fe and Mn

concentration as observed at 5 °C was detected. A sharp increase in Fe and Mn concentration was observed at the interface from about 50 μm into the resin. However, Si content is detected to be higher at the alloy-resin interface, relative to 5 °C (Figure 5-48). Similarly, as observed in the X100 sample at 5 °C, the concentration of C is clearly observed to be higher in the resin.

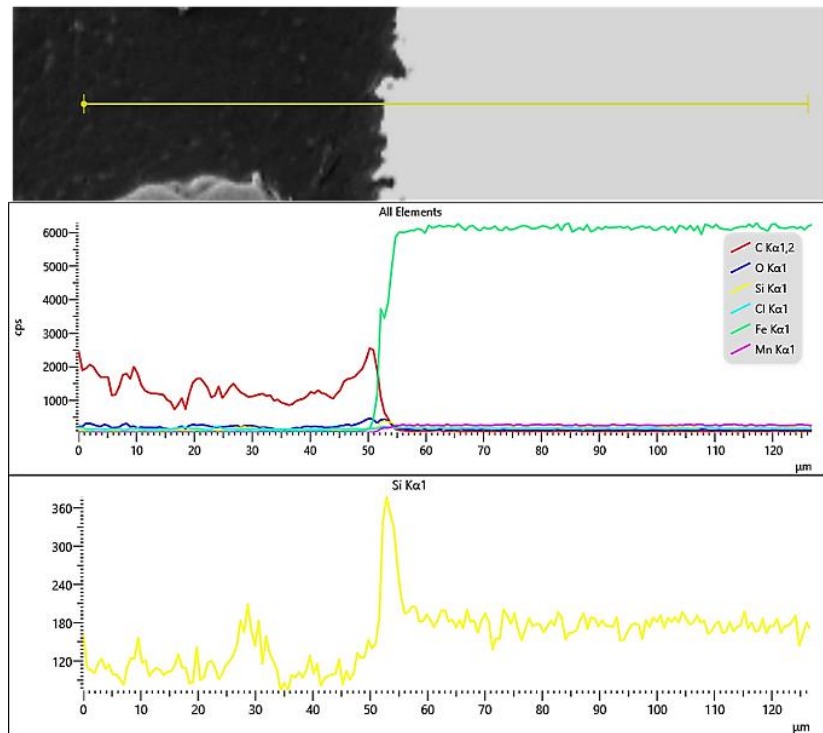


Figure 5-51 - EDS line scan analysis of the exposed X100 sample elements in simulated saltwater solution with CO_2 at 15 °C stressed at 80 % Y.S.

The elemental composition of the EDS spectra (Figure 5-52) of the X100 C-ring sample stressed at 80 % Y.S. exposed at 25 °C is presented in Figure 5-53. Increasing percentage of Fe was observed with change in spectrum location. Approximately equal concentration of Fe was observed in spectrum 3 at both 15 °C and 25 °C with values of 92.1 wt.% and 92.2 wt.%, respectively. Equal highest percentage of Mn was observed in spectrum 3 with a value of 2.03 wt.%, at both 15 °C and 25 °C. Unlike in the X100 samples exposed at 5 °C and 15 °C, presence of Si was detected in all spectra with a maximum of 0.98 wt.% observed in spectrum 3 which is close to the alloy-resin interface.

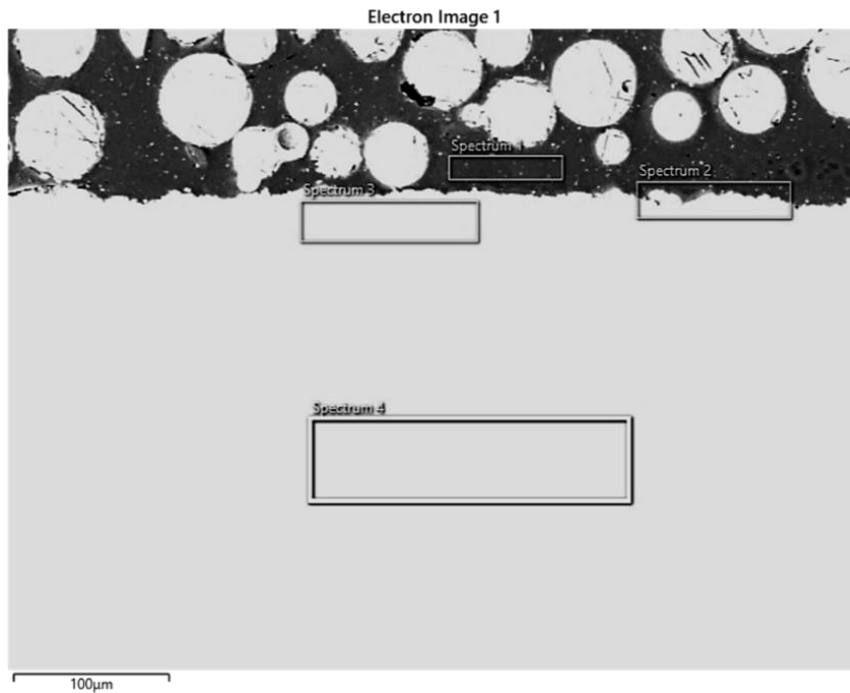


Figure 5-52 - SEM backscattered electron image of the exposed X100 C-ring sample in simulated saltwater solution with CO₂ at 25 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 5-53.

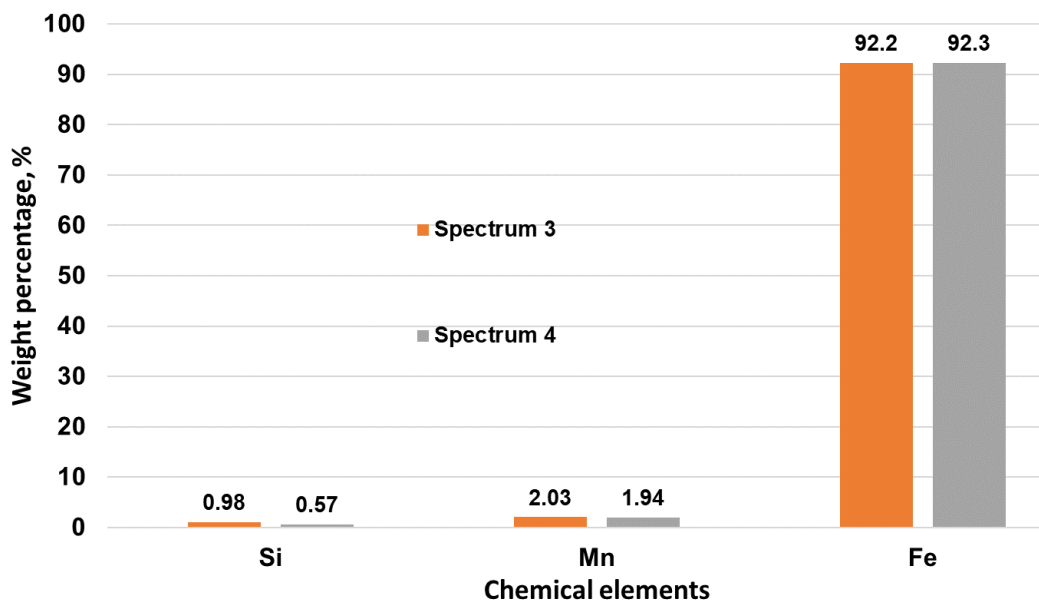


Figure 5-53 - EDS compositions of the exposed X100 sample elements in simulated saltwater solution with CO₂ at 25 °C stressed at 80 % Y.S.

The line scan analysis of the X100 C-ring sample exposed at 25 °C (Figure 5-54) showed similar trend in Fe and Mn concentration as observed at 5 °C and 15 °C.

Higher concentration of Fe and Mn was observed on the alloy, with sharp increase of Fe content observed at the interface. More or less similar trend in Si concentration was observed at both 5 °C (Figure 5-48) and 25 °C (Figure 5-54), with higher percentage observed in the resin and not at the alloy-resin interface as observed at 15 °C (Figure 5-51). Similarly, as observed at 5 °C and 15 °C, the concentration of O and C were detected to be higher in the resin.

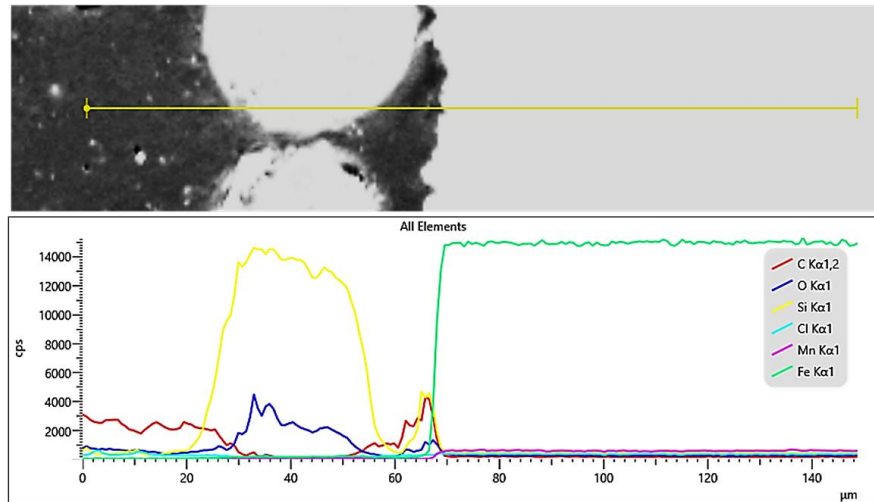


Figure 5-54 - EDS line scan analysis of the exposed X100 sample elements in simulated saltwater solution with CO₂ at 25 °C stressed at 80 % Y.S.

5.1.4.5 Energy Dispersive Spectroscopy Analysis of X100 3-point Bent-beam Specimens

The composition of the EDS spectra (Figure 5-55) of the X100 3-point bent-beam sample stressed at 80 % Y.S. exposed at 5 °C is shown in Figure 5-56. Equal percentage of Fe was observed in spectrum 3 and 4 with a value of 93.17 wt.%. In comparison with the X100 C-ring sample exposed at 5 °C (Figure 5-47), the percentage of Fe was observed to be higher in the exposed X100 3-point sample. Increasing concentration of Mn was observed with change in spectrum location from 3 to 4 with approximately equal percentages as observed in X100 C-ring sample exposed at 5 °C. Maximum Mn concentration values of 2.12 wt.% and 2.01 wt.%, respectively, were observed in spectrum 4 of the X100 3-point bent-beam and C-ring samples. The presence of O and Si was observed in all spectra in the 3-point bent-beam sample, unlike in the X100 C-ring sample. Maximum

values of 0.57 wt.% and 0.23 wt.% were observed as the concentration of O and Si in spectrum 3 and 4, respectively.

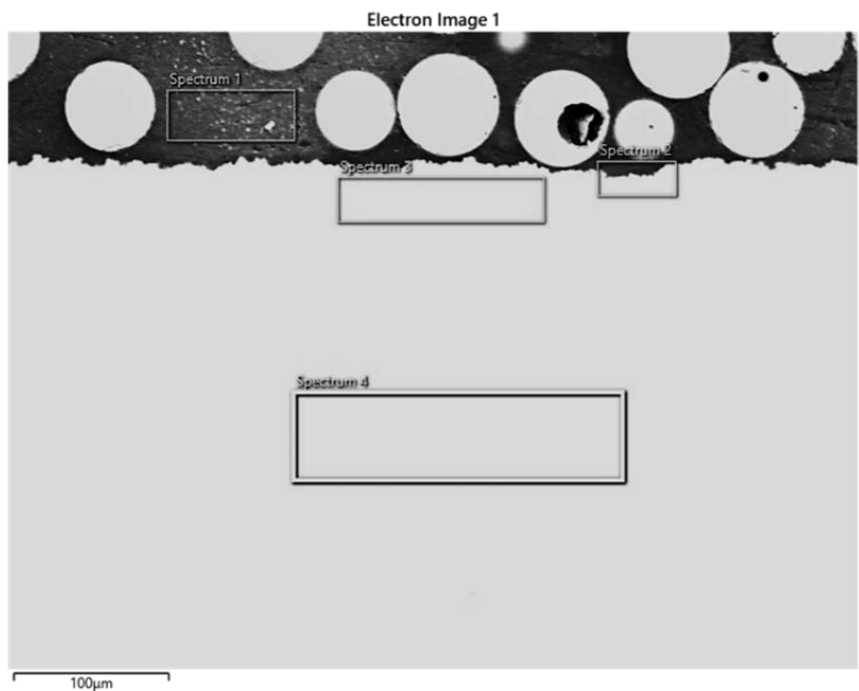


Figure 5-55 - SEM backscattered electron image of the exposed X100 3-point bent-beam sample in simulated saltwater solution with CO₂ at 5 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 5-56.

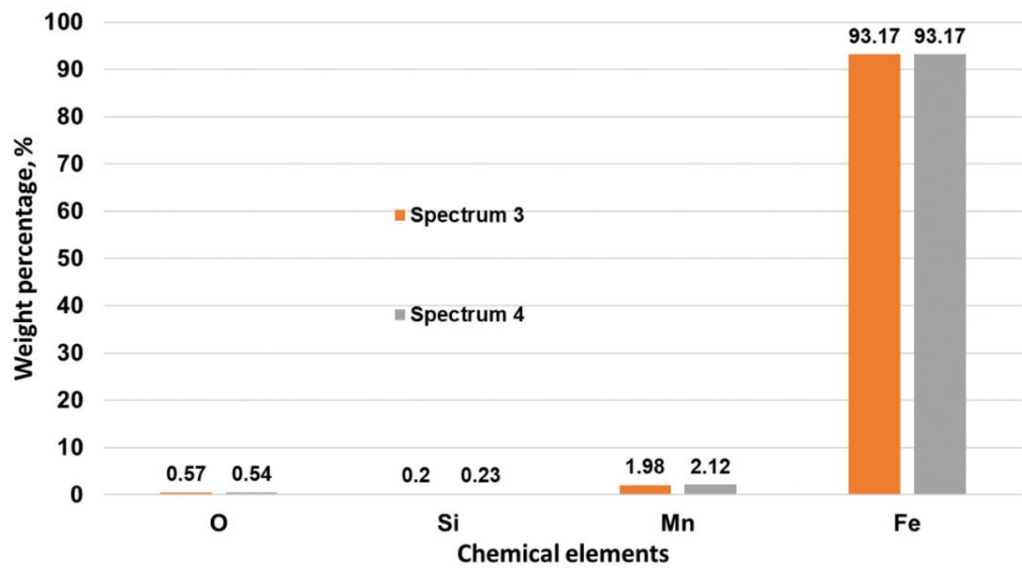


Figure 5-56 - EDS compositions of the exposed X100 3-point bent-beam sample in simulated saltwater solution with CO₂ at 5 °C stressed at 80 % Y.S.

The line scan of the X100 3-point beam sample exposed at 5 °C (Figure 5-57) showed similar trend in Fe and Mn concentration, relative to X100 C-ring sample exposed at 5 °C (Figure 5-48). Sharp increase in Fe and Mn concentration was observed at the alloy-resin interface at about 18 μm into the resin. Variations in maximum Si concentration was observed in the 3-point bent-beam sample, relative to X100 C-ring sample. Maximum concentration was observed at about 1 μm into the resin, unlike in the X100 C-ring sample, with maximum concentration at 53 μm into the resin. Highest concentration of C was also observed to be higher in the resin in both X100 3-point and C-ring samples.

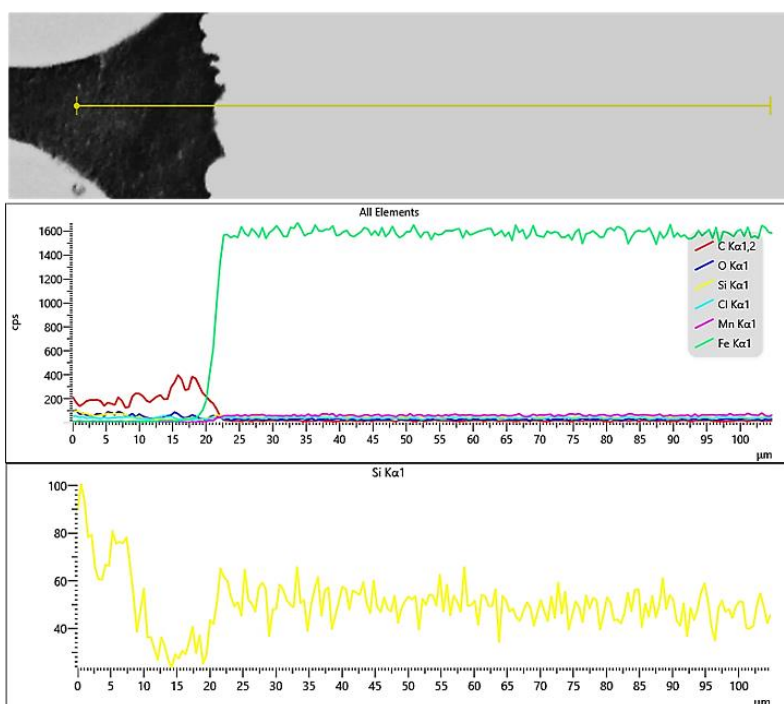


Figure 5-57 - EDS line scan analysis of the exposed X100 3-point bent-beam sample in simulated saltwater solution with CO_2 at 5 °C stressed at 80 % Y.S.

Different elemental compositions (Figure 5-59) were detected from the EDS spectra (Figure 5-58) of the X100 3-point bent-beam sample stressed at 80 % Y.S. exposed at 25 °C, relative to the X100 3-point bent beam sample exposed at 5 °C (Figure 5-56). The percentages of Fe and Mn detected in the EDS spectra of the X100 3-point bent-beam sample exposed at 25 °C are lower, with maximum values of 92.68 wt.% and 1.93 wt.%, respectively, relative to X100 3-point sample exposed at 5 °C (Figure 5-56). Presence of O and Si was also observed in all

spectra in the X100 3-point bent-beam samples exposed at 25 °C, with values of 0.76 wt.% and 0.25 wt.%, respectively observed in spectrum 4 and 3. Traces of Cl was observed in spectrum 4 of the X100 3-point bent-beam sample exposed at 25 °C with a value of 0.03 wt.%. relative to sample exposed at 5 °C.

In comparison with the X100 C-ring sample exposed at 25 °C (Figure 5-53), percentage of Fe was observed to be higher in the X100 3-point sample exposed at 25 °C. Maximum Fe concentration values of 92.68 wt.% and 92.3 wt.%, respectively, were observed in spectrum 3 of the X100 3-point bent-beam and spectrum 4 of the X100 C-ring samples. The percentage of Mn and Si were observed to be lower in the X100 3-point sample, relative to X100 C-ring sample. Maximum Mn concentration of 2.03 wt.% and 1.93 wt.% at 25 °C, respectively, were detected in spectrum 3 of the X100 C-ring and spectrum 4 of the X100 3-point samples. Highest concentration of Si with a value of 0.25 wt.% was detected in spectrum 3 of the X100 3-point sample, with a maximum value of 0.98 wt.% observed in spectrum 3 of the X100 C-ring sample. Presence of O was detected in all spectra in the X100 3-point sample, relative to X100 C-ring sample.



Figure 5-58 - SEM backscattered electron image of the exposed X100 3-point bent-beam sample in simulated saltwater solution with CO₂ at 25 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 5-59.

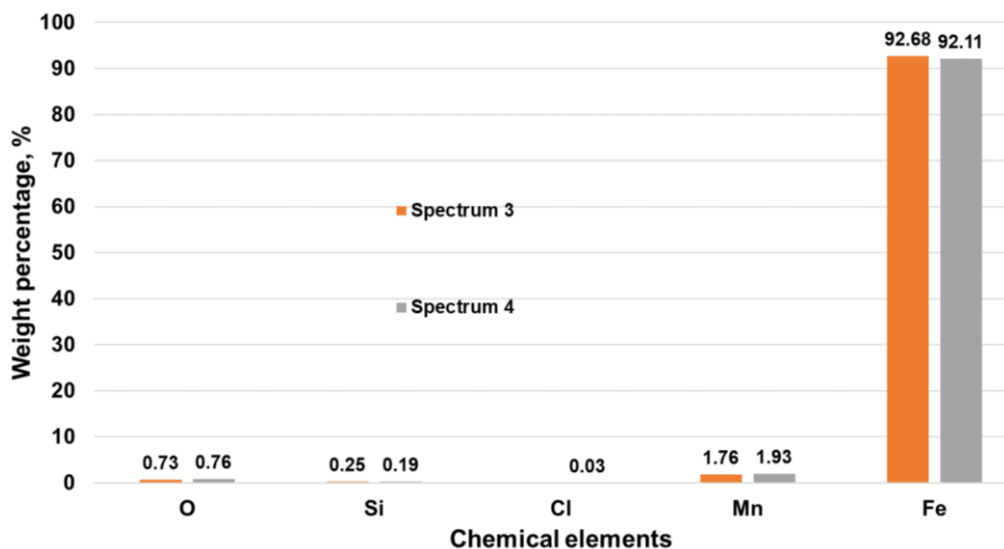


Figure 5-59 - EDS compositions of the exposed X100 3-point bent-beam sample in simulated saltwater solution with CO₂ at 25 °C stressed at 80 % Y.S.

The line scan of the X100 3-point sample exposed at 25 °C as presented in Figure 5-60 showed similar trend in Fe and Mn concentration as observed on the X100 3-point sample exposed at 5 °C (Figure 5-57) and X100 C-ring sample exposed at 25 °C (Figure 5-54). Sharp increase on Fe and Mn concentrations were also observed at the interface. The concentration of Si was also observed to be higher in the resin at about 10 µm into the resin and not at the interface. C content as observed in all samples is higher in the resin.

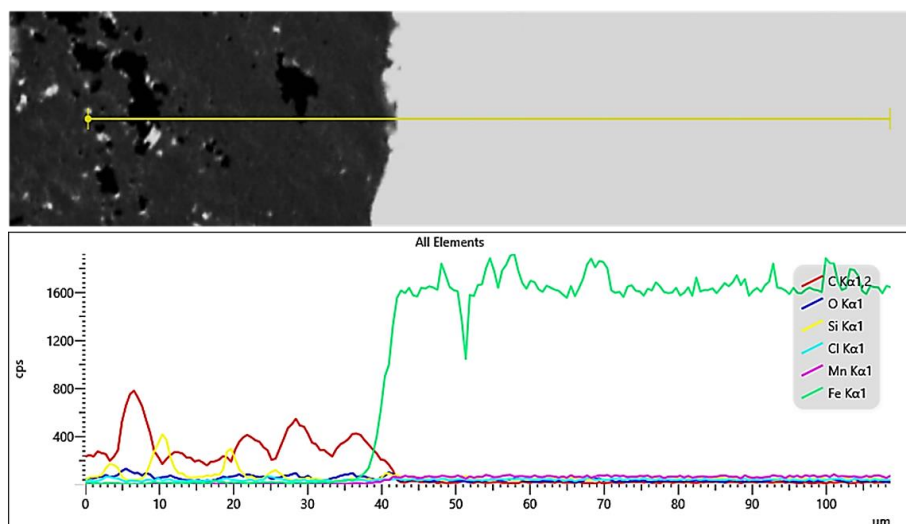


Figure 5-60 - EDS line scan analysis of the exposed X100 3-point bent-beam sample in simulated saltwater solution with CO₂ at 25 °C stressed at 80 % Y.S.

In general, as observed in the EDS analysis of X70 and X100 C-ring sample in solution with N₂ (chapter 4), no significant difference in Fe and Mn content was observed on all X70 and X100 C-rings and 3-point bent-beam samples in solution with CO₂ at all solution temperatures. The concentrations of Fe and Mn were observed to change with spectrum location. Highest percentage of Fe (93.97 wt.%) was observed in spectrum 4 of the X70 3-point sample exposed at 25 °C, with lowest of 91.2 wt.% observed in spectrum 4 of the X70 C-ring sample exposed at 5 °C. Highest percentage of Mn (2.12 wt.%) was detected in spectrum 4 of the X100 3-point sample exposed at 5 °C. Similarly, as analysed in the N₂ solution, the concentration of Si was observed to be highest mostly at the alloy-resin interface. However, in Figure 5-48 (X100 C-ring sample exposed at 5 °C) and Figure 5-54 (X100 C-ring sample exposed at 25 °C), for example, the highest concentration was observed to be in the resin, where the line passed through the glass beads used in making the resin. As such, the detection of varying amount of Si with change in spectrum location, could be explained to occur due to accumulation of glass beads in the resin, which contains some certain amount of Si. The presence of Cl in the analysed samples can be explained to occur as a result of exposure of the samples in the simulated 3.5 % NaCl.

5.1.5 Tensile Strength Analysis

Tensile strength tests were conducted on X70 dog-bone samples exposed in every test condition to assess the impact of CO₂ and temperature on the tensile strength of the carbon steel.

5.1.5.1 Tensile Strength Tests of X70 Dog-bone Specimens

The stress-strain curves of the X70 dog-bone samples exposed in solution with CO₂ at 5 °C, 15 °C and 25 °C are presented in Figure 5-61. It is observed that with increasing solution temperature, elongation before failure decreases. A comparison of the tested samples at 5 °C, 15 °C and 25 °C showed decrease in ductility of the samples. Highest decrease in ductility was observed at 25 °C with an elongation of about 26.7 % and, 27.6 % and 28.2 % elongation, respectively observed at 15 °C and 5 °C. The reference sample was observed to show highest

elongation of about 28.42 % on the sample before failure. In general, no significant elongation changes before failure observed on the tested X70 dog-bone samples with change in solution temperatures.

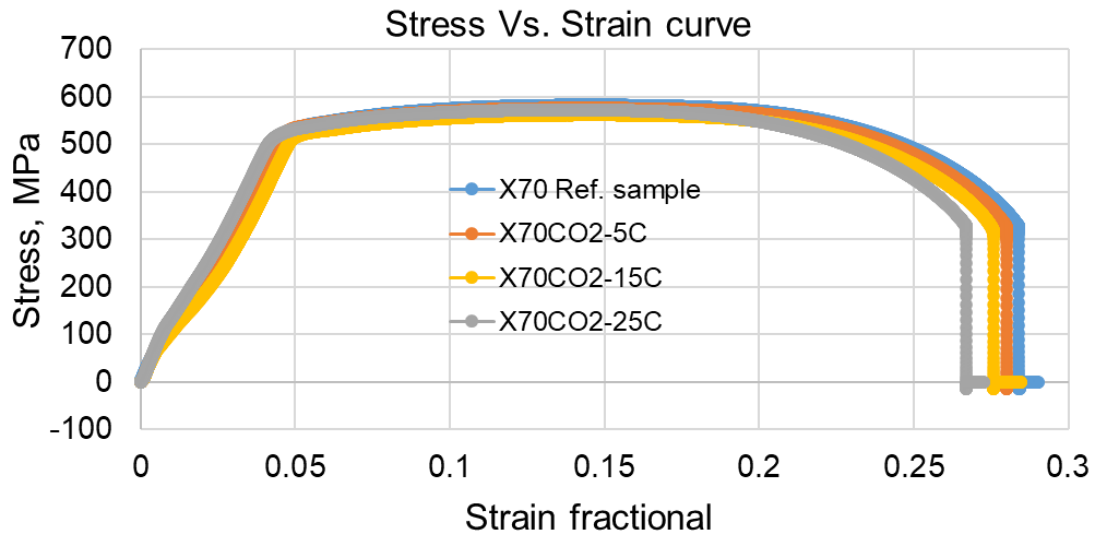


Figure 5-61 - Tensile tests stress-strain curves of the X70 dog-bone samples exposed in simulated saltwater solution with CO₂ at 5 °C, 15 °C and 25 °C.

5.1.6 Vickers Hardness Analysis

Vickers hardness tests were carried out on the exposed X70 dog-bone samples to assess the impact of CO₂ and temperature on the hardness of the carbon steel.

5.1.6.1 Hardness Tests of X70 Dog-bone Specimens

The Vickers hardness results obtained from the exposed X70 dog-bone samples in solution with CO₂ at 5 °C, 15 °C and 25 °C are presented in Figure 5-62. Tests on samples were conducted from the start of the reduced parallel section of the dog-bone towards the fracture point. (x-axis indicates test locations from 1 to 8, 1- indicates start of reduced parallel section and, 8- end of fracture point). Three measurements were conducted on each test location and its average calculated. Hardness variations were observed with change in test location at all solution temperatures. Highest average hardness was observed on the reference sample towards the fracture point with a value of 257.33 HVC. Highest and lowest average values of 247.70 HVC and 212.30 HVC, respectively were observed on

the samples at 25 °C and 5 °C. In general, no significant difference in hardness observed on the samples with change in solution temperatures as shown in Figure 5-62. In general, the reference sample was observed to have higher average hardness, relative to all exposed samples. However, the trend appears to lie within the same scatter (Figure 5-62). This indicates no change in hardness in the simulated CO₂ solution, which implies no change in hardness and wear resistance of the samples within the exposure time (840hrs) and change in temperature.

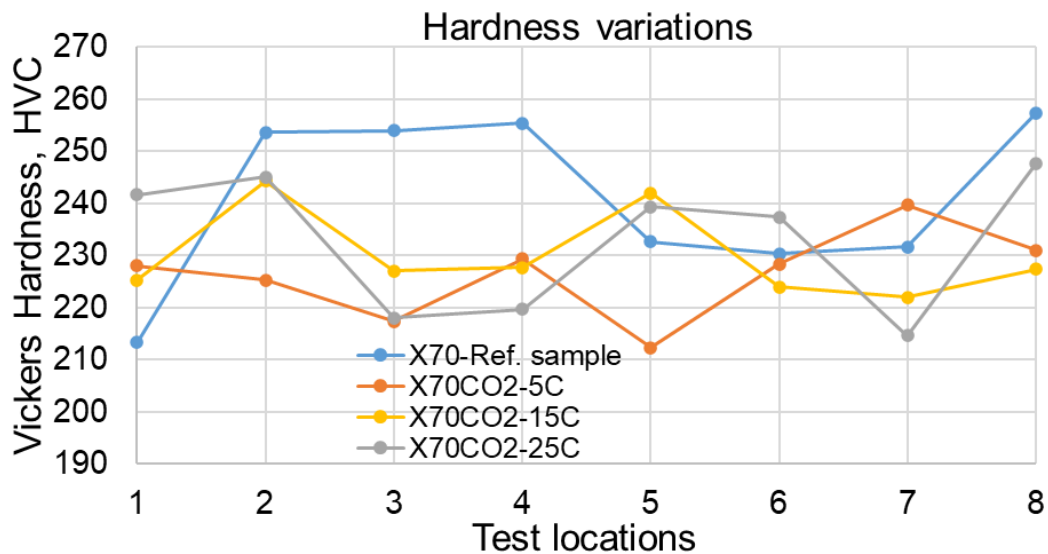


Figure 5-62 - Vickers hardness of the X70 dog-bone samples exposed in simulated saltwater solution with CO₂ at 5 °C, 15 °C and 25 °C.

5.1.7 Surface Roughness Analysis

Before and after exposure surface roughness analysis were conducted on chemically and mechanically pre-damaged X70 C-rings samples. This is conducted to assess the impact of surface damage on the corrosion behaviour of the carbon steel in the different exposure conditions.

5.1.7.1 Surface Roughness Assessment of Mechanically Pre-damaged X70 C-ring Specimens

The surface roughness assessment of the mechanically pre-damaged X70 C-ring sample stressed at 80 % Y.S. exposed at 25 °C is shown in Figures 5-63a and b.

Change in surface roughness was observed on the post-exposed sample (Figure 5-63b), relative to pre-exposed sample as shown in Figure 5-63a. Increasing surface roughness ($0.410\text{ }\mu\text{m}$) was observed on the pre-exposed mechanically pre-damaged sample, relative to uncorroded reference sample with an average value of $0.2158\text{ }\mu\text{m}$ (Figure 5-64). An average surface roughness of $0.410\text{ }\mu\text{m}$ was observed on the pre-exposed sample, which increased to $1.9782\text{ }\mu\text{m}$ after exposure.

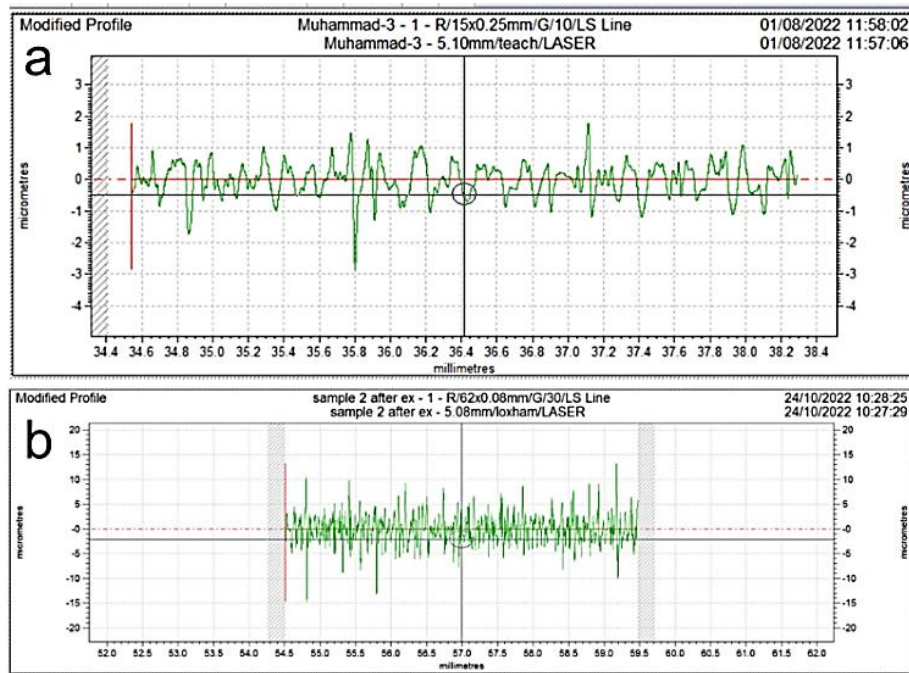


Figure 5-63 - Pre-exposure (a) and post-exposure (b) surface roughness of the mechanically pre-damaged X70 C-ring sample stressed at 80 % Y.S. exposed in solution with CO_2 at $25\text{ }^\circ\text{C}$.

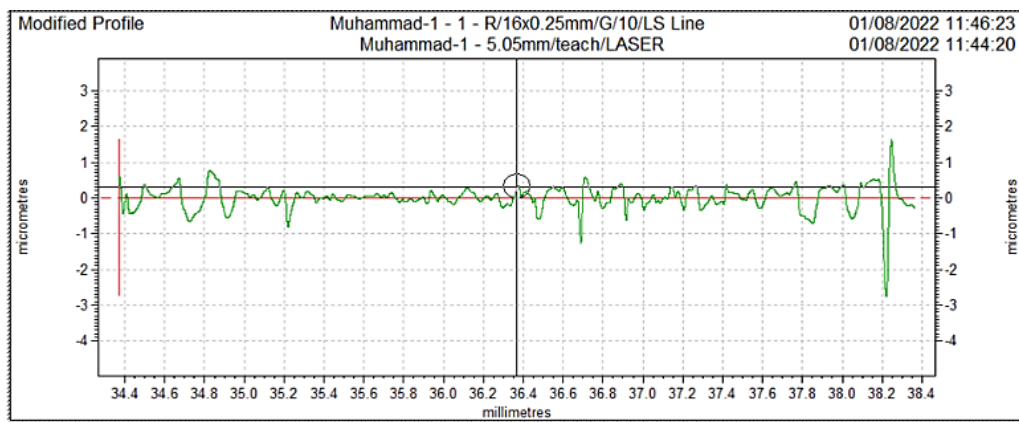


Figure 5-64 - Surface roughness of the X70 C-ring reference sample.

Similarly, as observed on the mechanically pre-damaged X70 C-ring sample stressed at 80 % Y.S., increasing surface roughness was also observed on the mechanically pre-damaged X70 sample stressed at 95 % Y.S. Increasing average roughness from 0.335 μm to 2.2603 μm was observed on the pre-exposed and post-exposed samples (Figures 5-65a and b, respectively).

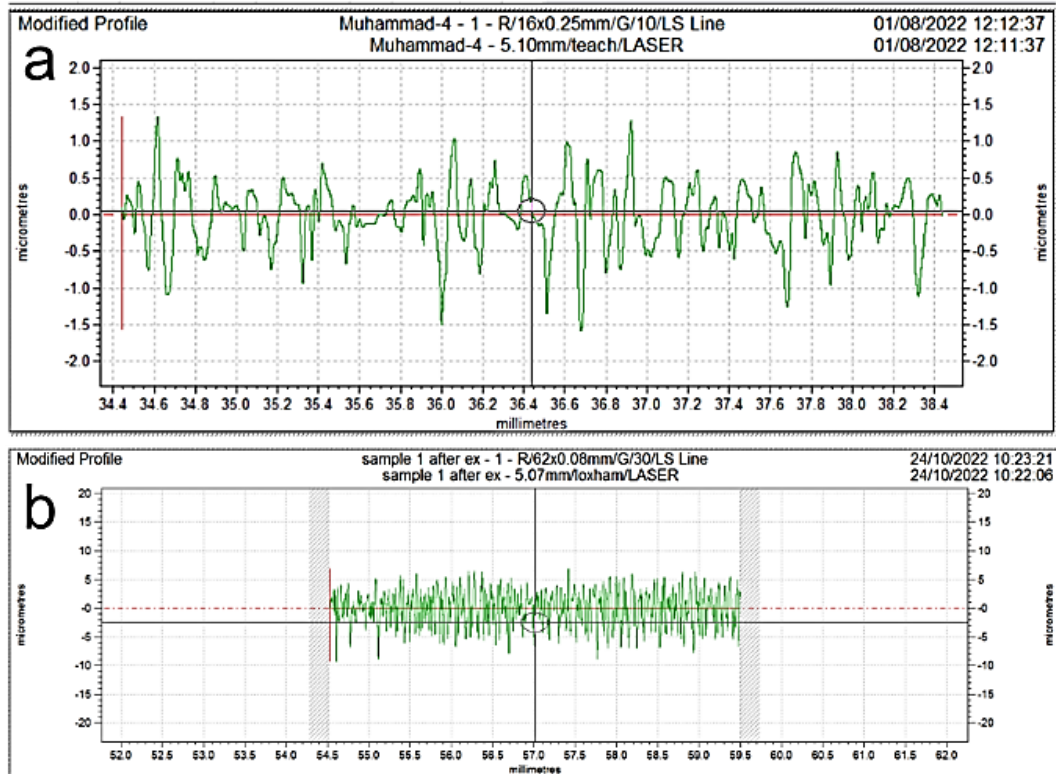


Figure 5-65 - Pre-exposure (a) and post-exposure (b) surface roughness of the mechanically pre-damaged X70 C-ring sample stressed at 95 % Y.S. exposed in solution with CO₂ at 25 °C.

5.1.7.2 Surface Roughness Assessment of Chemically Pre-damaged X70 C-ring Specimens

The surface roughness assessment of the chemically pre-damaged X70 C-ring sample stressed at 80 % Y.S. exposed at 25 °C is shown in Figures 5-66a and b. Change in surface roughness was also observed on the chemically pre-damaged sample, as observed on the mechanically pre-damaged samples. The chemically pre-damaged (salted) sample presented higher post-exposure average roughness of 2.2988 μm , relative to mechanically pre-damaged (scratched samples), with average roughness of 1.9782 μm for sample stressed at 80 %

Y.S. and 2.2603 μm for sample at 95 % Y.S. Increasing average roughness was observed on the mechanically pre-damaged samples with increasing applied stress level. Table 5-1 presents the average roughness of both pre-exposed and post-exposed mechanically and chemically pre-damaged X70 C-ring samples.

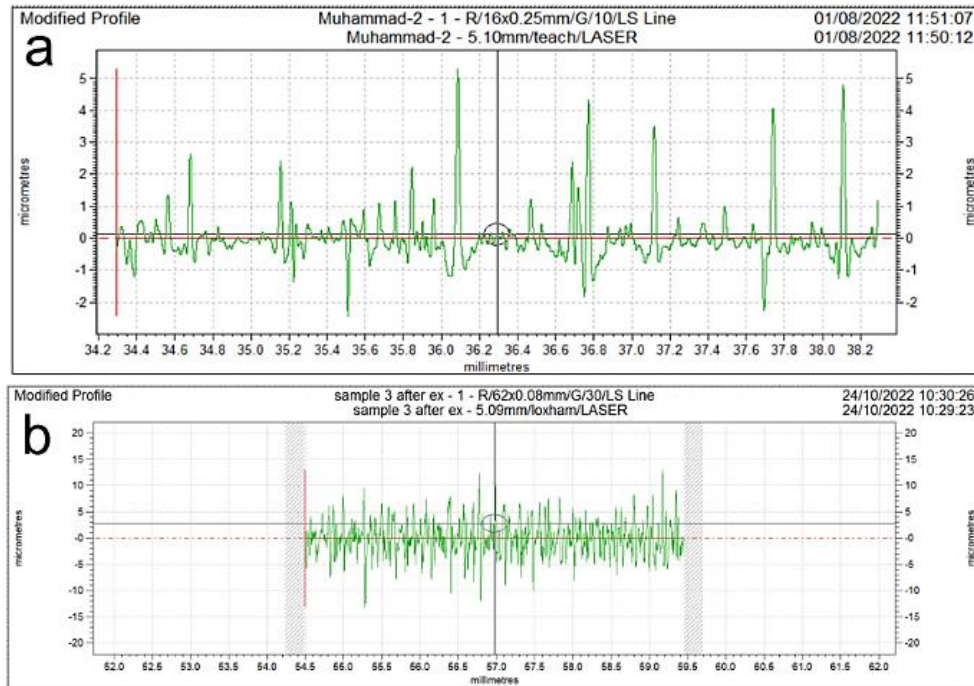


Figure 5-66 - Pre-exposure (a) and post-exposure (b) surface roughness of the chemically pre-damaged X70 C-ring sample stressed at 80 % Y.S. exposed in solution with CO₂ at 25 °C.

Table 5-1 - Average surface roughness of the exposed X70 C-ring samples in solution with CO₂ at 25 °C.

Sample	Ra (pre-exposure), μm	Ra (post-exposure), μm
Reference sample	0.2158	-
Mechanically pre-damaged (80 % Y.S.)	0.410	1.9782
Mechanically pre-damaged (95 % Y.S.)	0.335	2.2603
Chemically pre-damaged (80 % Y.S.)	0.429	2.2988

5.2 Chapter Summary

Similarly, as observed on the samples exposed in solution with N_2 (chapter 4), an increase in corrosion rates of more than 100 % was observed with increasing solution temperature from 5 °C to 25 °C, with an increase of about 40 % observed with increasing temperature from 5 °C to 15 °C. In general, the X100 samples at all exposure conditions were observed to show higher corrosion rates relative to the X65, X70 and X80 samples. This indicates that the X100 samples have higher corrosion current density, which leads to higher corrosion rates. The obtained corrosion rates were observed to increase with increasing ultimate tensile strength of the material grades. The obtained corrosion rate values of the exposed samples (X65, X70 and X80) indicated lower values in comparison with the reviewed literature corrosion rates of carbon steels in CO_2 environments [6]. This can be explained as a result of low applied flow rate pressure (atmospheric pressure) of the CO_2 in the solution [136]. From the analysis of the obtained corrosion rates, It can be stated that the X100 carbon steel is more susceptible to SCC under the exposed environmental conditions. As such its usage as pipeline material in a seawater environment for transportation of CO_2 or in carbon capture and storage should be the least to consider if there is availability of X80, X70 or X65.

Similarly, as observed on the samples in solution with N_2 , variations in potentials were also observed on all exposed material grades exposed in solution with CO_2 with change in solution temperature and sample geometry. More negative potential values were observed on all samples exposed at 5 °C. This also indicates variation in the thermodynamic behavior of the different material grades with change in microstructure, sample geometry and solution temperature. The change in thermodynamic behavior of the exposed carbon steels can occur as a result of several factors, such as differential aeration, temperature changes, agitation of the exposure solutions, thickness, formation, or rupture of surface films, etc.

Similar trends in metal change were observed on all X65, X70 and X80 samples relative to the X100 samples at all exposure temperatures. Higher pits features

were observed on X80 samples at 25 °C relative to X65 and X70 samples. All X100 samples as shown in Figures 5-16 and 5-17 were observed to show low metal change at all solution temperatures. This variation in metal change trend observed on the exposed samples can be said to occur due to differences in microstructures their reactions to the solution conditions. The calculated corrosion rates from LPR measurements were observed to tally with measured metal loss values from the dimensional metrology analysis at solution temperatures when converted to 840 hrs of exposure.

Change in corrosion morphology was observed on all exposed samples with increasing solution temperature from 5 °C to 25 °C. The X65 and X70 samples at all applied stress levels and solution temperatures presented similar type of corrosion morphology with wide and a combination of shallow and deep ellipses (at 5 °C) and deep undercutting metal dissolution (at 15 °C and 25 °C). The X80 samples presented different morphology relative to X65 and X70 samples with deep and narrow elliptical pits and a combination of vertical and horizontal metal dissolution (at 5 °C and 15 °C, respectively). Much wider and deeper elliptical metal dissolution was observed on the samples exposed at 25 °C. X100 samples presented wide and shallow elliptical morphology at all solution temperatures. More or less an uneven surface metal dissolution was observed on all X65, X70 and X80 samples, with a more even dissolution observed on the X100 samples. The variation in corrosion morphologies observed on the exposed carbon steels can be said to occur as a result of differences in the microstructure of the carbon steels and the presence of precipitates in their microstructures. As reported by Wang et al. [135], the presence of precipitate in a microstructure provides nucleation sites for crack initiation and hydrogen traps, which can potentially lead to hydrogen embrittlement. This causes reduction in ductility of the carbon steels and subsequently can lead to SCC occurrence.

Similarly, as observed in the EDS analysis of X70 and X100 C-ring sample in solution with N₂ (chapter 4), no significant difference in Fe and Mn percentage was detected on all X70 and X100 C-rings and 3-point bent-beam samples in solution with CO₂ at all solution temperatures. The concentrations of Fe and Mn

were also observed to change with spectrum location. Highest percentage of Fe (93.97 wt.%) was observed on the X70 3-point bent-beam sample exposed at 25 °C, with lowest of 91.2 wt.% observed on the X70 C-ring sample exposed at 5 °C. Highest percentage of Mn (2.12 wt.%) was detected on the X100 3-point bent-beam sample exposed at 5 °C. Similarly, as analysed in the N₂ solution, the concentration of Si was observed to be highest mostly at the alloy-resin interface. However, in Figure 5-48 (X100 C-ring sample exposed at 5 °C) and Figure 5-54 (X100 C-ring sample exposed at 25 °C), for example, the highest concentration was observed to be in the resin, where the line passed through the glass beads used in making the resin. As such, the detection of varying amount of Si with change in spectrum location, could be explained to occur due to accumulation of glass beads in the resin, which contains some certain amount of Si. The presence of Cl in the analysed samples can be explained to occur due to the simulated 3.5 % NaCl solution the samples are exposed to.

A comparison of the tensile strength analysis results show highest decrease in ductility on the dog-bone specimens exposed at 25 °C with an elongation of about 26.7 % before failure. This shows that highest diffusion and accumulation of hydrogen atoms into the steel's crystalline structure is higher on the sample's surfaces at 25 °C, hence the high decrease in ductility. Hardness analysis results show no significant changes in hardness observed across the tested sample area with change in solution temperatures. However, the uncorroded sample (reference) generally was observed to show higher hardness, in comparison to all exposed samples.

The obtained results from change in surface roughness show highest increase in both pre-exposure and post-exposure roughness on the chemically pre-damaged (salted) sample. This shows that sprayed salt which contains chloride ions was able to form pits on the sample's surfaces, hence the increased roughness.

6 RESULTS AND DISCUSSION FOR EXPERIMENTS IN SOLUTION WITH 20 % OXYGEN AND 80 % NITROGEN

This chapter presents the results obtained from the exposed X65, X70, X80 and X100 C-rings samples exposed in simulated 3.5 % NaCl solution with 20%O₂/80%N₂. As described in chapter 4 and 5, solution was continuously bubbled with 20%O₂/80%N₂ at 50 mL/min flow rate for a period of 5 weeks (840hrs). An average oxygen concentration of 0-16 ppm can be reached at atmospheric pressure [36]. At 5 °C and 25 °C, respectively an oxygen concentration values of 9.9 ppm and 6.2 ppm can be reached [36,56]. Tests involving O₂/N₂ bubbling acted to increase the percentage of O₂ in the solution. Corrosion rates, metal loss exceedance, SEM analysis, EDS analysis, tensile strength analysis and Vickers hardness analysis were conducted on the exposed samples.

6.1 Experiments in Solution with O₂/N₂ (20%/80%) at 5 °C and 25 °C

The tests were conducted at different solution temperatures of 5 °C, 15 °C and 25 °C. This is carried out to understand the effect of temperature on the exposed carbon steel samples in the simulated environment.

6.1.1 Corrosion Rates and Potentials

The change in corrosion rates and potentials with time of the exposed samples were monitored by use of linear polarization resistance technique. Specimens were polarized at a potential of ± 10 mV at a scan rate of 0.167 mV/s. Periodic polarization of the specimens was conducted after every 168 hrs to monitor the change in resistance and potential. The corrosion rates are then calculated by use of Stern-Geary equation. Two measurements were carried out on each data point in all conducted experiments at all exposure conditions and average corrosion rates were calculated and values plotted against time. Corrosion rate errors were calculated using propagation of error method as outlined by Taylor

[120]. The calculated errors were observed to be negligible in the range of 10^{-5} to 10^{-7} mm/yr.

Similarly, as observed in the increased corrosion rates of the exposed carbon steels with change in trace gas from N_2 (chapter 4) to CO_2 (chapter 5), also as expected with increasing percentage of oxygen in a solution, corrosion rates of carbon steels should increase as reported in section 2.3.2.1.2 from the reviewed literature on effect of corrosive medium composition and presence of oxidizers on SCC susceptibility of carbon steels. A high increase in corrosion rate was observed with change in solution trace gas composition from N_2 (100%) to 20% O_2 /80% N_2 as discussed in subsequent headings.

6.1.1.1 Corrosion Rates and Potentials of X65 C-rings Specimens

Figures 6-1a to 6-1d show the corrosion rates and potentials of the exposed X65 samples in solution with O_2/N_2 (20%/80%) at 5 °C and 25 °C. As presented in graph 6-1a, change in corrosion rates with time were observed for all samples at 5 °C. A continuous increase in corrosion rates with time was obtained with a maximum value of 0.192 mm/year for the notched sample stressed at 80 % Y.S. at 825 hrs. However, a decrease was observed for the samples stressed at 80 % and 95 % Y.S. at 495 hrs of exposure, with continuous increase throughout the duration of the test. At 25 °C, continuous increase in corrosion rates was observed for all samples throughout the duration of the tests, with the highest value of 0.386 mm/year obtained from the notched sample stressed to 80 % Y.S.

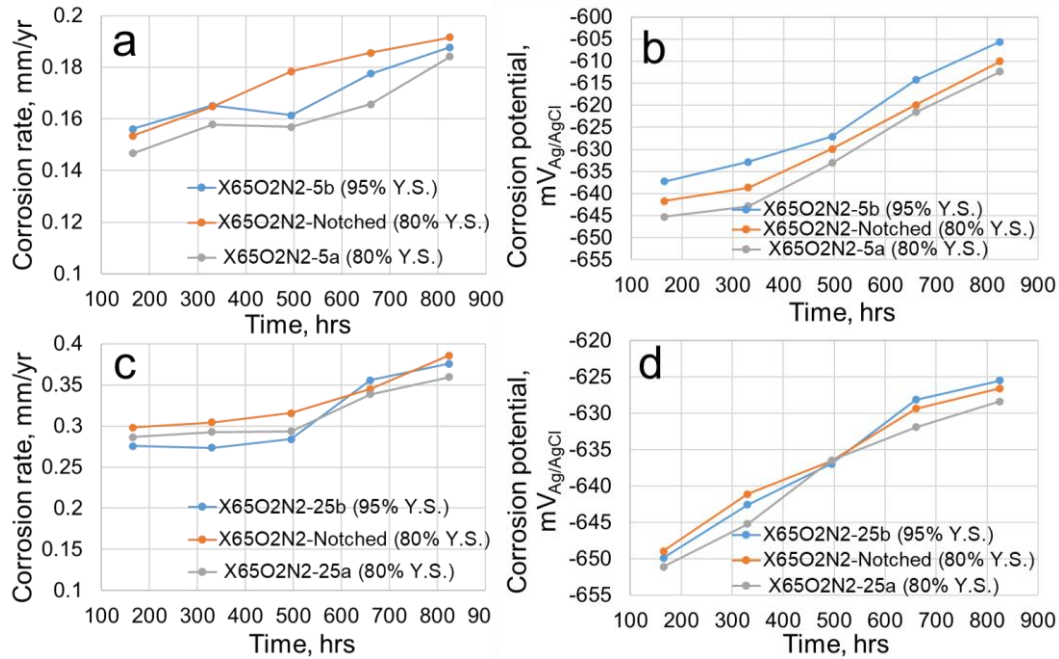


Figure 6-1 - Corrosion rates and potentials of the exposed X65 carbon steel C-rings in simulated saltwater solution with O₂/N₂: (a) corrosion rates at 5 °C; (b) potentials at 5 °C; (c) corrosion rates at 25 °C; (d) potentials at 25 °C.

Similar trends in corrosion potentials were observed on all samples at both 5 °C and 25 °C (Figures 6-1b and d), with continuous increase throughout the duration of the tests. Maximum potentials of -606 mV_{Ag/AgCl} and -627 mV_{Ag/AgCl}, respectively were obtained from the samples stressed at 95 % Y.S. at 5 °C and at 25 °C.

Similarly, as obtained from the X65 samples exposed in solution with N₂ (chapter 4), an increase in corrosion rates of about 100 % was observed with increasing temperature from 5 °C to 25 °C. Variations in change in corrosion rates with time with no significant statistical difference were observed on the samples with change in applied stress level from 80 % Y.S. to 95 % Y.S. and notched sample stressed at 80 % Y.S. This could also be attributed to differential aeration in the test cell, leading to variations in corrosion rates [127]. Approximately equal corrosion rates (max. of 0.386 mm/year at 25 °C) were observed on the exposed X65 carbon steels in the simulated 3.5 % NaCl bubbled with O₂/N₂ in comparison with published literature corrosion rates of carbon steels in seawater (seawater contains about 21 % O₂) as reported by Davies and Michael [44,45] with a value of 0.13-0.41 mm/year, 0.102-0.178 mm/year reported by Fontana [22], and a

value of 0.1 mm/year in quiet seawater to a maximum of 0.75 mm/year at 3 m/s seawater velocity reported by Kreysa and Schutze [36]. From the observed corrosion rates of the exposed X65 samples in the simulated 3.5 % NaCl saturated with 20%O₂/80%N₂, installation and usage of the carbon steel as a pipeline material in a seawater environment saturated with oxygen will lead to high increase in corrosion rates especially at higher temperatures above 30 °C as observed in tropical regions. This will increase reduction in pipeline wall thickness and strength, which can potentially lead to SCC occurrence on the material when higher pressures are applied. Installations and usage of pipelines in seawater environments should be in deep waters where oxygen saturation level is low and not at the surface with high saturation level as reported in section 2.1.3.

6.1.1.2 Corrosion Rates and Potentials of X70 C-rings Specimens

Figures 6-2a to 6-2d present the corrosion rates and potentials of the exposed X70 samples in solution with O₂/N₂ (20%/80%) at 5 °C and 25 °C. As shown in Figure 6-2a, continuous increases in corrosion rates with time were observed on the samples stressed at 80 % Y.S. and notched sample. Highest corrosion rate of 0.184 mm/year was obtained from the sample stressed at 80 % Y.S. at 830 hrs of exposure. The sample stressed at 95 % Y.S. was observed to slightly decrease in corrosion rate with time at 332 hrs, with continuous increase throughout the duration of the tests. At 25 °C, fluctuations in corrosion rates with time were observed for the samples stressed at 80 % and 95 % Y.S., with a decrease at 332 hrs of exposure. The notched sample, however, was observed to show continuous increase in corrosion rate throughout the tests. Highest corrosion rate of 0.361 mm/year was observed from the sample stressed at 95 % Y.S. At 5 °C, continuous fluctuations in potentials were observed for all samples throughout the duration of the tests, with a maximum potential of -637 mV_{Ag/AgCl} observed from the sample stressed at 80 % Y.S. (Figure 6-2b). A continuous increase in potential was observed for all samples exposed at 25 °C throughout the duration of the experiment (Figure 6-2d), with a maximum value of -638 mV_{Ag/AgCl} obtained from the notched sample stressed at 80 % of Y.S. The

variation in potential trends and values obtained from the exposed X70 samples at both 5 °C and 25 °C, shows the change in the thermodynamic behaviour of the steel with change in solution temperature.

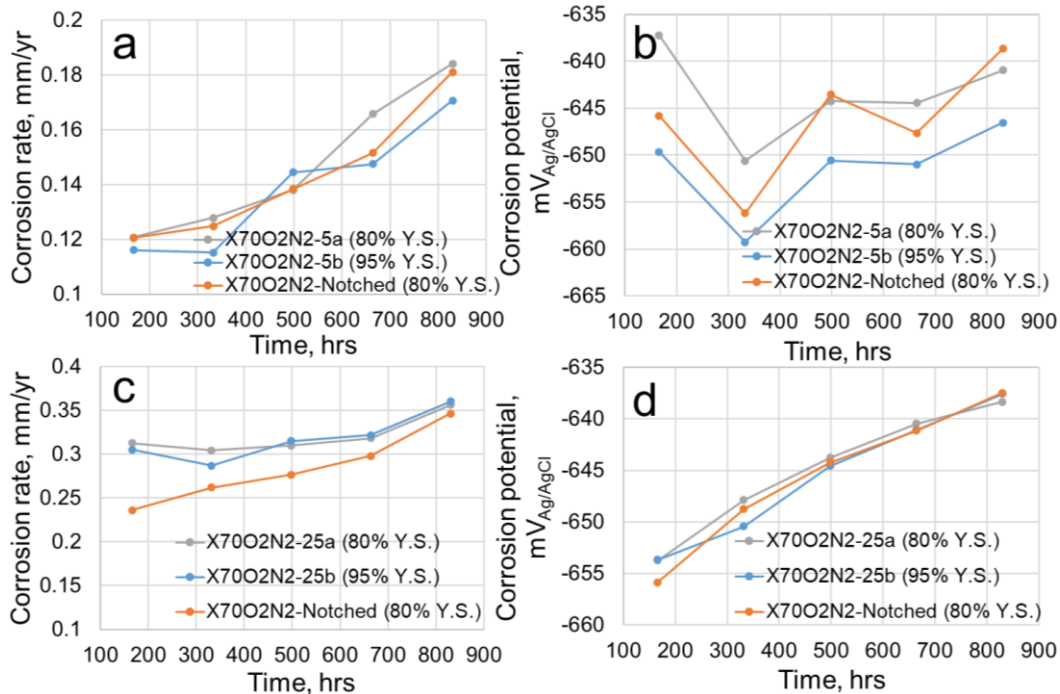


Figure 6-2 - Corrosion rates and potentials of the exposed X70 carbon steel C-rings in simulated saltwater solution with O₂/N₂: (a) corrosion rates at 5 °C; (b) potentials at 5 °C; (c) corrosion rates at 25 °C; (d) potentials at 25 °C.

Similarly, as reported from X65 samples, no significant statistical change in corrosion rates observed with increasing applied stress level from 80 % Y.S. to 95 % Y.S. and change in surface state of the samples (notched state) at 5 °C. Relative to the samples stressed at 80 % and 95 % Y.S. at 25 °C, the notched sample showed lower corrosion rates (Figure 6-2c). This can also be explained to occur as a result of error in placements of the sample in the test cell, which leads to differential aeration on the exposed sample, hence leading to variations in cathodic reactions rates and subsequently lower corrosion rates [125,127]. Relative to X65 samples, an increase in corrosion rates of about 100 % was also observed on the X70 samples with increasing solution temperature from 5 °C to 25 °C. The X70 samples were observed to show lower corrosion rates (max. of 0.361 mm/year at 25 °C) in comparison with X65 samples (max. of 0.386 mm/year), however the difference is insignificant with a value of 0.025 mm/year.

This can be explained to occur due to the change in ultimate tensile strengths and microstructures of the material and its reaction to the exposure environment. Similarly, the obtained experimental corrosion rates on the exposed X70 samples are more or less similar to published literature corrosion rates of carbon steels in seawater as reported by Davies and Michael [44,45] with a value of 0.13-0.41 mm/year, 0.102-0.178 mm/year reported by Fontana [22], and a value of 0.1 mm/year in quiet seawater to a maximum of 0.75 mm/year at 3 m/s seawater velocity reported by Kreysa and Schutze [36].

From the observed corrosion rates of the exposed X70 samples, installation and usage of the carbon steel in seawater environment should be in deep waters where oxygen saturation level is low and not at the surface with high saturation level as reported in section 2.1.3. This will reduce the increase in corrosion rates and lost in pipeline wall thickness and strength, which will reduce its susceptibility to SCC. However, as higher corrosion rates were observed on the X65 carbon steel in comparison with X70 within the exposure period (840 hrs), the carbon steels should be exposed for longer time to ascertain their SCC susceptibility before making a final selection.

6.1.1.3 Corrosion Rates and Potentials of X80 C-rings Specimens

Figures 6-3a to 6-3d present the corrosion rates and potentials of the exposed X80 samples in solution with O₂/N₂ (20%/80%) at 5 °C and 25 °C. The X80 samples at all stress levels exposed at 5 °C (Figure 6-3a) presented entirely different corrosion rates trend, relative to X65 (Figure 6-1a) and X70 (Figure 6-2a) samples exposed at 5 °C. As shown in Figure 6-3a, fluctuations in corrosion rates were observed on the samples stressed at 80 % and 95 % Y.S. An increase in corrosion rate with time was observed from the samples at 501 hrs. Continuous decrease in corrosion rates with time was observed from the sample stressed at 80 % Y.S. Variations in corrosion rate trends were observed at 25 °C (Figure 6-3c) in comparison with 5 °C. A continuous increase in corrosion rates with time was observed for the samples stressed at 80 % and 95 % Y.S. (Figure 6-3c) throughout the duration of the tests. However, a decrease was observed on the notched at 334 hrs of exposure, with continuous increase throughout the duration

of the tests. Highest corrosion rate of 0.511 mm/year at 835 hrs was obtained from the sample stressed at 95 % Y.S. at 25 °C, with highest value of 0.154 mm/year obtained from the sample stressed at 80 % Y.S. exposed at 5 °C. The fluctuations in corrosion rates on the samples can be explained to occur as a result of continuous formation and rupture of formed oxides (iron oxide) on the samples surfaces.

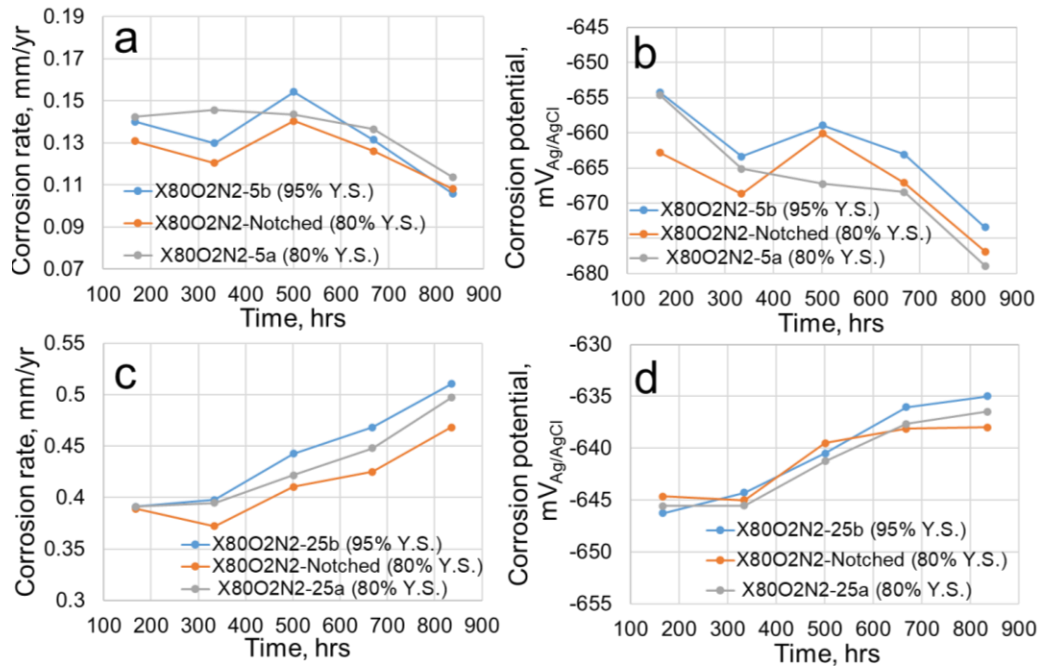


Figure 6-3 - Corrosion rates and potentials of the exposed X80 carbon steel C-rings in simulated saltwater solution with O₂/N₂: (a) corrosion rates at 5 °C; (b) potentials at 5 °C; (c) corrosion rates at 25 °C; (d) potentials at 25 °C.

Similar trends in corrosion potentials as observed in the corrosion rates at both 5 °C and 25 °C were obtained. Maximum potential of -654 mV_{Ag/AgCl} at 167 hrs was obtained from the sample stressed at 95 % Y.S. at 5 °C and -635 mV_{Ag/AgCl} at 835 hrs of exposure at 25 °C.

In general, variations in corrosion rates were observed on the samples at all solution temperature with change in applied stress level from 80 % Y.S. to 95 % Y.S. and notched sample. The notched sample at all temperatures presented lowest corrosion rates relative to samples stressed at 80 % Y.S. and 95 % Y.S. An increase in corrosion rates of more than 100 % was observed with increasing temperature from 5 °C to 25 °C. Higher corrosion rates were observed on the X80

samples at 25 °C (max. of 0.511 mm/year at 25 °C), relative to the X70 (max. of 0.361 mm/year at 25 °C) and X65 (max. of 0.386 mm/year). However, at 5 °C, the obtained maximum corrosion rate on the X80 samples (0.152 mm/year) was observed to be lower than that of X65 (max. of 0.192 mm/year) and X70 (max. of 0.184 mm/year). This variation in corrosion rates can be explained to occur due to differences in microstructures of the steels their reaction to the simulated saltwater solution with change in temperature.

Furthermore, the obtained corrosion rates on the exposed X80 samples at all solution temperatures were observed to be a bit higher than published literature corrosion rates of carbon steels in seawater (seawater contains about 21% O₂) with a value of 0.102-0.178 mm/year reported by Fontana [22], 0.13-0.41 mm/year reported by Davies and Michael [44,45] and a value of 0.1 mm/year in quiet seawater to a maximum of 0.75 mm/year at 3 m/s seawater velocity reported by Kreysa and Schutze [36]. This can be explained to occur due to higher ultimate tensile strength of the X80 carbon steel and in combination with continuous bubbling of O₂ in the test solution which keeps the O₂ saturation level high and thus increases the cathodic reactions rates and subsequent increase in corrosion rates of the carbon steels. As higher corrosion rates were observed on the X80 carbon steel at 25 °C, in comparison with X65 and X70 samples within the exposure period (840 hrs), it can be concluded that the X80 is more susceptible to SCC in the simulated saltwater environment saturated with O₂/N₂ mixture at 25 °C. As such the selection of carbon steel as a pipeline material in seawater environment should be focused between X65 or X70. However, the carbon steels can be exposed for longer time with putting into account all necessary environmental factors to ascertain their SCC susceptibility before making a final selection.

6.1.1.4 Corrosion Rates and Potentials of X100 C-rings Specimens

The X100 samples exposed in solution with O₂/N₂ (20%/80%) at 5 °C and 25 °C (Figures 6-4a and 6-4c) were observed to show higher corrosion rates with a maximum of 0.5671 mm/year obtained from the notched sample, in comparison with the X65, X70 and X80 samples exposed in solution with O₂/N₂ at 25 °C. This

shows that the presence of the O₂/N₂ gas mixture in the solutions have impact on the corrosion rates of the different exposed carbon steels with change in microstructures. Variations in corrosion rates and potentials trends were observed on the X100 samples relative to the exposed X65, X70 and X80 samples exposed in solution with O₂/N₂ at both 5 °C and 25 °C. As shown in Figure 6-a, decrease in corrosion rates were observed for all samples at 336 hrs of exposure, with continuous increase throughout the tests. The sample stressed at 95 % Y.S., presented higher corrosion rate of 0.334 mm/year relative to samples stressed at 80 % Y.S. and notched sample. At 25 °C, continuous increase in corrosion rates were observed for all samples throughout the duration of the tests (Figure 6-4c). Maximum corrosion rate of 0.567 mm/year was obtained from the notched sample at 25 °C. Similar trends in potentials as obtained in the corrosion rates were observed on all samples at both 5 °C and 25 °C. A decrease in potentials was observed at 336 hrs at 5 °C (Figure 6-4b), with continuous increase at 25 °C throughout the duration of the tests (Figure 6-4d). Maximum potentials of -622 mV_{Ag/AgCl} and -611 mV_{Ag/AgCl}, respectively, were observed for the samples stressed at 95 % Y.S. at 5 °C and 25 °C.

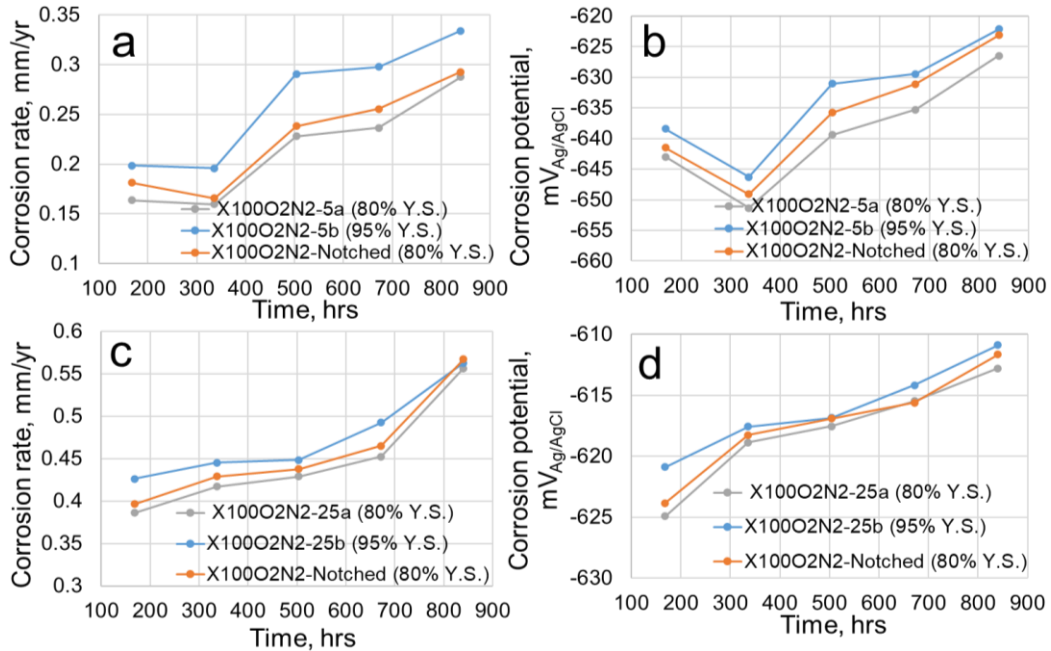


Figure 6-4 - Corrosion rates and potentials of the exposed X100 carbon steel C-rings in simulated saltwater solution with O₂/N₂: (a) corrosion rates at 5 °C; (b) potentials at 5 °C; (c) corrosion rates at 25 °C; (d) potentials at 25 °C.

In general, the corrosion rates of the exposed X100 samples at all solution temperatures were observed to increase with increasing applied stress level from 80 % Y.S. to 95 % Y.S. and change in surface state of the samples (notched state). Highest difference was observed on the sample stressed at 95 % Y.S. at 5 °C, which could result from higher aeration on the sample in the test cell. An increase in corrosion rates of about 60 % was observed with increasing temperature from 5 °C to 25 °C, relative to X65, 70 and X80 which presented about 100 % increase. At all solution temperature the X100 samples was observed to have higher corrosion rates (max. of 0.333 mm/year and 0.567 mm/year, respectively at 5 °C and 25 °C) relative to the X80 samples (max. of 0.152 mm/year and 0.511 mm/year, respectively at 5 °C and 25 °C), X70 (max. of 0.184 mm/year and 0.361 mm/year, respectively at 5 °C and 25 °C) and X65 (max. of 0.192 mm/year and 0.386 mm/year, respectively at 5 °C and 25 °C). This indicates that the X100 carbon steel at all solution temperatures has higher corrosion current density which leads to faster cathodic reactions rates and hence increased corrosion rates.

Similarly, as observed from the obtained corrosion rates on the exposed X80 samples, the X100 samples were also observed to present a bit higher corrosion rates than published literature corrosion rates of carbon steels in seawater (seawater contains about 21% O₂) with a value of 0.102-0.178 mm/year reported by Fontana [22], 0.13-0.41 mm/year reported by Davies and Michael [44,45] and a value of 0.1 mm/year in quiet seawater to a maximum of 0.75 mm/year at 3 m/s seawater velocity reported by Kreysa and Schutze [36]. This can also be explained to occur due to higher ultimate tensile strength of the X100 carbon steel, with effect of continuous bubbling of O₂ in the test solution which keeps the O₂ saturation level high and thus increases the cathodic reactions rates and subsequent increase in corrosion rates of the carbon steels. As higher corrosion rates were observed on the X100 carbon steel, in comparison with X65, X70 and X80 samples within the exposure period of 840 hrs (5 weeks), it can be concluded that the X100 carbon steel has higher SCC susceptible in the simulated saltwater environment saturated with O₂/N₂ mixture at all solution temperatures. As such the selection of carbon steel as a pipeline material in seawater environment

should be focused between X65 or X70 which presented lower corrosion rates. However, in the absence of X65 or X70, the X80 can be considered.

6.1.2 Metal Loss Exceedance

Dimensional metrology after an exposed period of 840 hrs was conducted on the exposed samples by optical microscopy to measure the cumulative probability of metal loss exceedance of the samples. An error of $\pm 5 \mu\text{m}$ is assumed for all metal loss measurements.

6.1.2.1 Cumulative Probability of Metal Loss Exceedance of X65 C-rings Specimens

Figures 6-5a and 6-5b, respectively, show the cumulative probability of metal loss exceedance, obtained from the datasets of the exposed X65 C-ring samples in solution with O_2/N_2 at 5 °C and 25 °C. At 5 °C, the datasets for all samples show significant metal change over most of the sample's surfaces, with higher pits features observed on the notched sample below about 9 % or less probability level. Higher metal change was observed on all samples at 25 °C relative to 5 °C, with low pits formation below about 6 % or less probability level observed on the sample stressed at 95 % Y.S. Maximum metal loss of $-23 \mu\text{m}$ and $-44 \mu\text{m}$, respectively at 5 °C and 25 °C was observed on the samples stressed at 95 % Y.S and notched sample stressed at 80 % Y.S.

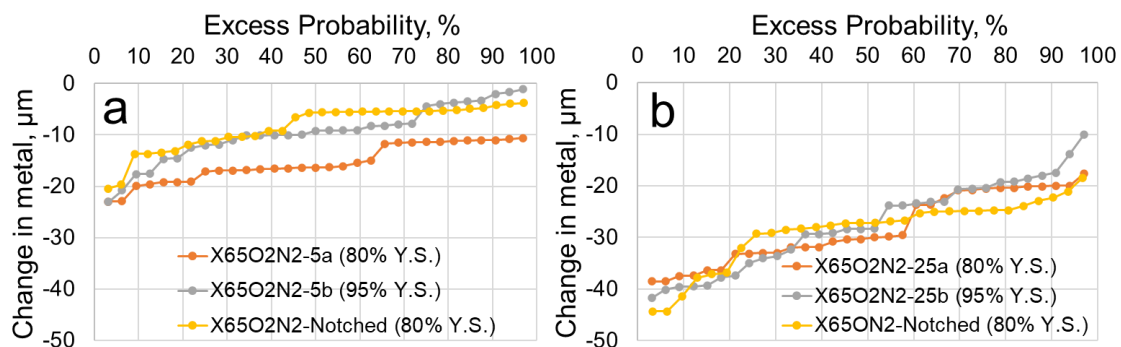


Figure 6-5 - Cumulative probability of metal loss exceedance graphs of X65 C-ring samples exposed in simulated saltwater solution with O_2/N_2 : (a) at 5 °C; (b) at 25 °C.

Similarly, as observed on the X65 samples exposed in solution with N₂ (chapter 4), an increase in metal loss of about 100 % was observed on the samples with increasing temperature from 5 °C to 25 °C. As also observed from the calculated corrosion rates of the exposed X65 samples in solution with O₂/N₂, no significant difference in metal loss observed on the samples (Figure 6-5) with change in applied stress level from 80 % Y.S. to 95 % Y.S. and notched sample stressed at 80 % Y.S., with accounting an error of $\pm 5 \mu\text{m}$ in the measurement of the metal loss. The measured metal loss exceedance values on the samples which is also a technique of measuring corrosion rates of samples tally with the calculated corrosion rates from LPR measurements when converted to 840 hrs (5 weeks) exposure time. A maximum value of 0.386 mm/year obtained from the notched sample stressed at 80 % Y.S. as presented in Figure 6-1c, converting the calculated corrosion rate value to a metal loss of 5 weeks results in a value of $-37 \mu\text{m}$ ($\pm 5 \mu\text{m}$). As observed from the calculated corrosion rates from LPR measurements, an increase in metal loss of about 100 % was measured with increasing temperature from 5 °C to 25 °C.

6.1.2.2 Cumulative Probability of Metal Loss Exceedance of X70 C-rings Specimens

Figures 6-6a and 6-6b, respectively, show the cumulative probability of metal loss exceedance, obtained from the datasets of the X70 C-ring samples exposed in solution with O₂/N₂ at 5 °C and 25 °C. Relatively, high distribution of metal change was observed on the samples stressed at 80 % and 95 % Y.S. at 5 °C, with low pits features below about 9 % or less probability level. In comparison with samples stressed at 80 % and 95 % Y.S., the notched sample stressed at 80 % Y.S. was observed to present higher metal change over most of the sample's surface and higher pits features below about 12 % or less probability level. Maximum metal loss of $-24 \mu\text{m}$ was obtained from the sample stressed at 80 % Y.S. At 25 °C, dataset for all samples show higher metal change over half of the sample's surfaces, relative to 5 °C. The sample stressed at 80 % Y.S. was observed to present higher pits features below about 9 % or less probability level, followed by notched sample stressed at 80 % Y.S. below about 6 % probability

level. Maximum metal loss of $-41\text{ }\mu\text{m}$ was observed on the sample stressed at 80 % Y.S. Similarly, as obtained from the X65 samples exposed in solution with O_2/N_2 (Figure 6-5), an increase in metal loss of about 100 % was measured with increasing solution temperature from $5\text{ }^\circ\text{C}$ to $25\text{ }^\circ\text{C}$.

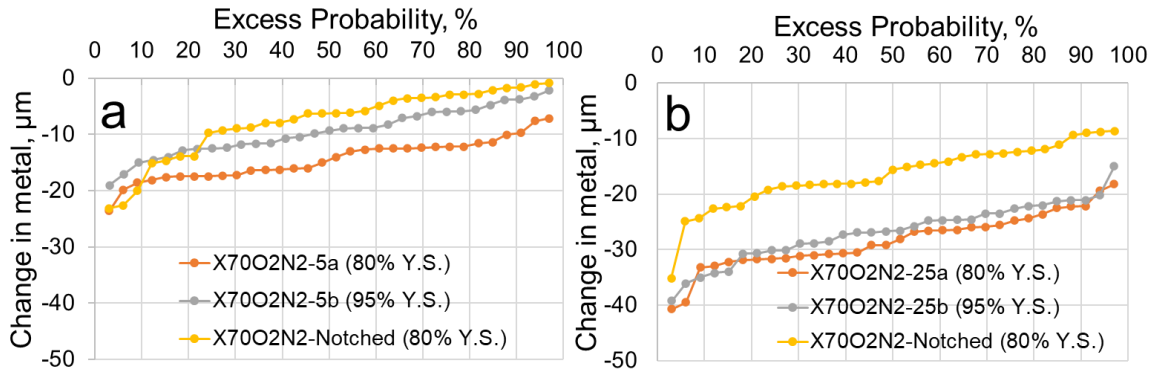


Figure 6-6 - Cumulative probability of metal loss exceedance graphs of X70 C-ring samples exposed in simulated saltwater solution with O_2/N_2 : (a) at $5\text{ }^\circ\text{C}$; (b) at $25\text{ }^\circ\text{C}$.

As observed from the calculated corrosion rate values on the X70 samples exposed in the simulated 3.5 % NaCl solution bubbled with O_2/N_2 , no significant change in metal loss value observed on the samples with change in applied stress level from 80 % Y.S. to 95 % Y.S. However, the notched sample presented lower metal loss relative to samples stressed at 80 % and 95 % Y.S., as also observed from the calculated corrosion rates (Figure 6-2c). The calculated corrosion rates from LPR measurements tally with the measured metal loss value when converted to 840 hrs (5 weeks) of exposure. Highest corrosion rate value of 0.361 mm/year was calculated from the sample stressed at 95 % Y.S. as shown in Figure 6-2c, converting the value to a metal loss of 840 hrs results in a value of $-35\text{ }\mu\text{m}$ ($\pm 5\text{ }\mu\text{m}$) as shown in Figure 6-6b.

Furthermore, no significant difference in measured metal loss values between the exposed X65 samples (max. of $-44\text{ }\mu\text{m}$) and X70 samples (max. of $-41\text{ }\mu\text{m}$), as also observed from the calculated corrosion rates from LPR measurements. As obtained from the calculated corrosion rates of the exposed X70 samples from LPR measurements, an increase in metal loss of about 100 % was measured on the samples with increasing temperature from $5\text{ }^\circ\text{C}$ to $25\text{ }^\circ\text{C}$.

6.1.2.3 Cumulative Probability of Metal Loss Exceedance of X80 C-rings Specimens

Figures 6-7a and 6-7b, respectively, show the cumulative probability of metal loss exceedance, obtained from the datasets of the exposed X80 C-ring samples in solution with O_2/N_2 at 5 °C and 25 °C. Low metal change was observed on all samples at 5 °C, with higher pits formation features below about 9 % or less probability level observed on the sample stressed at 95 % Y.S. Higher metal change with uneven damage distribution was observed on all samples at 25 °C. Significant pits features below about 6 % or less probability level were obtained from the sample stressed at 95 % Y.S. Maximum metal loss of -22 μm and -56 μm , respectively, at 5 °C and 25 °C was observed on the samples stressed at 95 % Y.S.

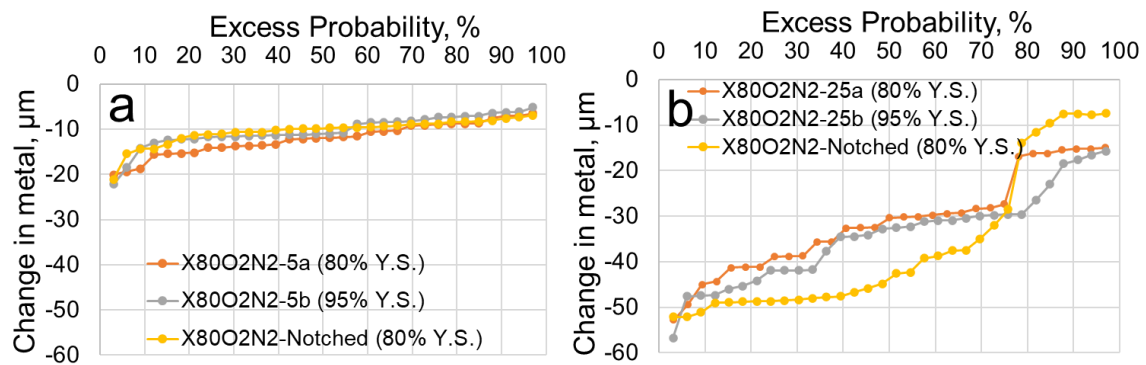


Figure 6-7 - Cumulative probability of metal loss exceedance graphs of X80 C-ring samples exposed in simulated saltwater solution with O_2/N_2 : (a) at 5 °C; (b) at 25 °C.

As reported from the calculated corrosion rates and metal loss exceedance values on the X65 and X70 samples, no significant change in metal loss value observed on the X80 samples with change in applied stress level from 80 % Y.S. to 95 % Y.S. and surface state (notched state) of the samples at all solution temperatures, with accounting an error of $\pm 5 \mu m$ in the measurement of the metal loss exceedance. As observed from the corrosion rates from LPR measurements, higher metal loss was measured on the X80 samples (max. of -56 μm) relative to X70 samples (max. of -41 μm) and X65 (max. of -44 μm). The calculated corrosion rates from the X80 samples (max. of 0.511 mm/year) as presented in

Figure 6-3c, also tallies with measured metal loss exceedance values when converted to 840 hrs of exposure, with a value of $-50 \mu\text{m}$ ($\pm 5 \mu\text{m}$). Relative to the X65 and X70 samples exposed in solution with O_2/N_2 , a metal loss increase of more than 100 % was also observed on the X80 samples with increasing solution temperature from 5°C to 25°C as shown in Figure 6-7.

6.1.2.4 Cumulative Probability of Metal Loss Exceedance of X100 C-rings Specimens

Similarly, as observed on the X65 and X70 samples at 5°C , the X100 samples at 5°C as presented in Figure 6-8a, at all applied stress levels show significant metal damage over majority of the sample's surfaces, with low pits features. However, at 25°C (Figure 6-8b), low metal change was observed over most of the samples surfaces at all stress levels. The notched sample showed higher pits features below about 6 % or less probability level. Maximum metal loss of $-38 \mu\text{m}$ and $-60 \mu\text{m}$, respectively at 5°C and 25°C was observed on the samples stressed at 95 % Y.S.

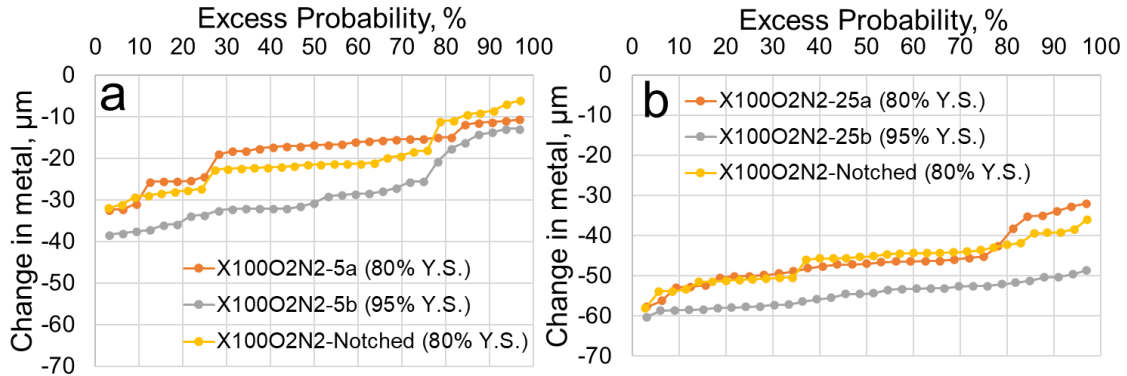


Figure 6-8 - Cumulative probability of metal loss exceedance graphs of X100 C-ring samples exposed in simulated saltwater solution with O_2/N_2 : (a) at 5°C ; (b) at 25°C .

In general, the X100 samples at all exposure temperatures as also observed in the measured metal loss exceedance in solution with N_2 (chapter 4) and CO_2 (chapter 5), presented higher metal loss in solution with O_2/N_2 with max of $-60 \mu\text{m}$ at 25°C , relative to X65 (max. of $-44 \mu\text{m}$), X70 (max. of $-41 \mu\text{m}$) and X80 (max. of $-56 \mu\text{m}$) samples. No significant difference in metal loss values observed on

the X100 samples at all solution temperatures with change in applied stress level from 80 % Y.S. to 95 % Y.S. and surface state (notched state) of the samples, with putting into account an error of $\pm 5 \mu\text{m}$ in the measurement of the metal loss exceedance. The calculated corrosion rates of the X100 samples (max. of 0.567 mm/year) as presented in Figure 6-4c, also tallies with the measured metal loss exceedance values when converted to 840 hrs of exposure, with a value of $-55 \mu\text{m}$ ($\pm 5 \mu\text{m}$). Similarly, as observed from the calculated corrosion rates from LPR measurements, a metal loss increase of about 65 % was measured on the X100 samples with increasing temperature from 5 °C to 25 °C. The increased value in metal loss observed on the X100 samples relative to X65, X70 and X80 samples shows that the X100 carbon steel has higher susceptibility to SCC in the simulated saltwater solution saturated with O_2/N_2 . As suggested from the calculated corrosion rates analysis between the X65, X70, X80 and X100 carbon steels exposed in solution with O_2/N_2 , selection of X100 carbon steel as pipeline material to be installed and operated in a seawater environment for transportation of various oil and gas products should be the least to consider if X80, X70 or X65 is readily available.

6.1.3 Scanning Electron Microscopy Analysis

SEM analysis was conducted on the cross-sectional areas of the stress-oriented sections of the exposed C-rings samples to understand the type of corrosion morphology on the samples' surfaces with change in exposure conditions.

6.1.3.1 Scanning Electron Microscopy Images of X65 C-rings Specimens

Figures 6-9a to 6-9f, respectively, show the SEM images of the X65 samples stressed at 80 % Y.S, 95 % Y.S., and notched sample stressed at 80 % Y.S. exposed in solution with O_2/N_2 at 5 °C and 25 °C. Clear change in surface roughness were observed on all samples at all stress level with change in solution temperature from 5 °C to 25 °C. Shallow and wide elliptical morphologies were observed on all samples exposed at 5 °C (Figures 6-9a, c, and e). Lower metal dissolution was observed on the sample exposed at 5 °C stressed at 80 % Y.S.

relative to samples stressed at 95 % Y.S. and notched sample. This can be said to occur as a result of the lower corrosion rate obtained from the sample as shown in Figure 6-1a. At 25 °C, deeper and wider elliptical morphologies were observed on the samples stressed at 80 % and 95 % Y.S. (Figures 6-9b and d). The notched sample (Figure 6-9f), however showed a combination of deep elliptical and shallow undercutting metal dissolution.

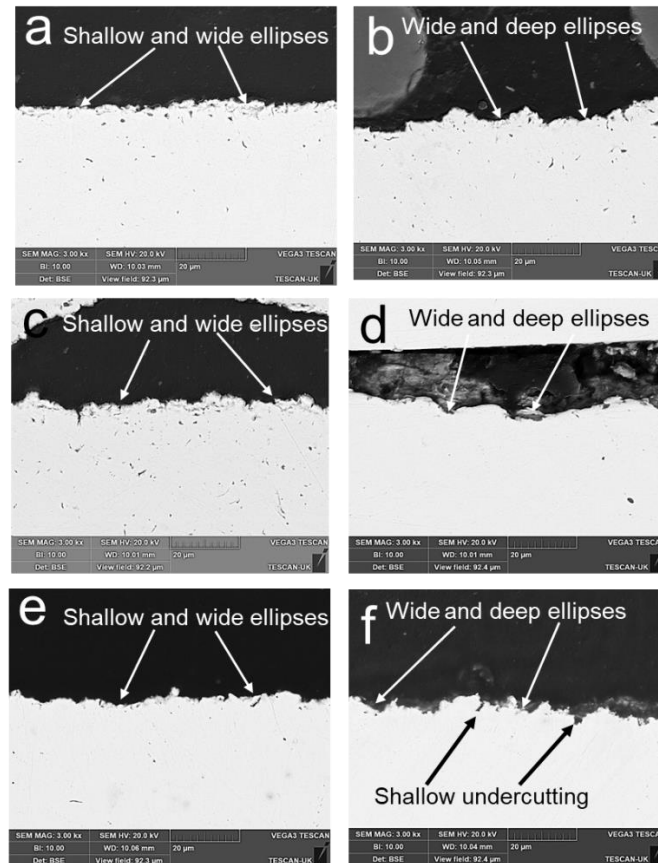


Figure 6-9 - SEM backscattered electron images of the exposed X65 C-ring samples in simulated saltwater solution with O₂/N₂ stressed at 80 % Y.S., 95 % Y.S. and notched sample stressed at 80 % Y.S.: (a) 80 % Y.S. at 5 °C; (b) 80 % Y.S. at 25 °C; (c) 95 % Y.S. at 5 °C; (d) 95 % Y.S. at 25 °C; (e) Notched sample at 5 °C; (f) Notched sample at 25 °C.

6.1.3.2 Scanning Electron Microscopy Images of X70 C-rings Specimens

Figures 6-10a to 6-10f, respectively, show the SEM images of the X70 samples stressed at 80 % Y.S, 95 % Y.S., and notched sample stressed at 80 % Y.S.

exposed in solution with O₂/N₂ at 5 °C and 25 °C. Similarly, as observed on the X65 samples, change in surface metal dissolution was observed on all samples with increasing solution temperature from 5 °C to 25 °C. The samples exposed at 5 °C (Figures 6-10a, c and e) presented similar surface morphology in comparison with X65 samples exposed at 5 °C. The samples stressed at 80 % Y.S. and 95 % Y.S. (Figures 6-10b and d) were observed to have wider and deeper elliptical surface morphology relative to the notched sample (Figure 6-10f). This can also be explained to occur due to increased corrosion rate observed on the samples (Figure 6-2c).

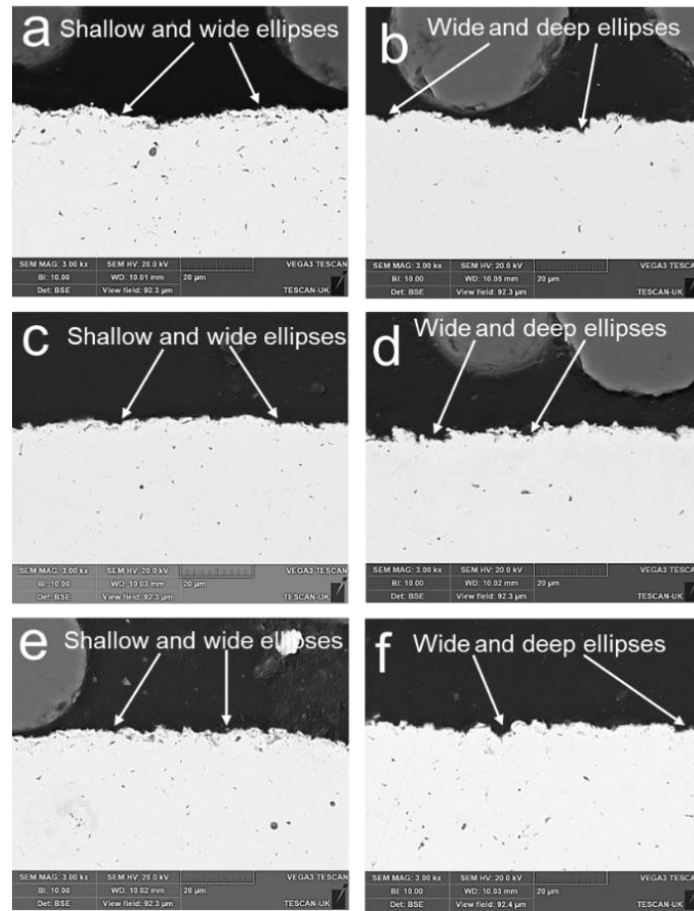


Figure 6-10 - SEM backscattered electron images of the exposed X70 C-ring samples in simulated saltwater solution with O₂/N₂ stressed at 80 % Y.S., 95 % Y.S. and notched sample stressed at 80 % Y.S.: (a) 80 % Y.S. at 5 °C; (b) 80 % Y.S. at 25 °C; (c) 95 % Y.S. at 5 °C; (d) 95 % Y.S. at 25 °C; (e) Notched sample at 5 °C; (f) Notched sample at 25 °C.

6.1.3.3 Scanning Electron Microscopy Images of X80 C-rings Specimens

Figures 6-11a to 6-11f, respectively, show the SEM images of the X80 samples stressed at 80 % Y.S, 95 % Y.S., and notched sample stressed at 80 % Y.S. exposed in solution with O₂/N₂ at 5 °C and 25 °C. Similarly, as observed on the exposed X65 and X70 samples, increasing surface metal dissolution was observed on the X80 samples with increasing solution temperature from 5 °C to 25 °C on all the different applied stressed samples. At all solution temperatures, deeper and wider elliptical, with combination of shallow undercutting metal dissolution were observed on the X80 samples relative to the X65 and X70 samples.

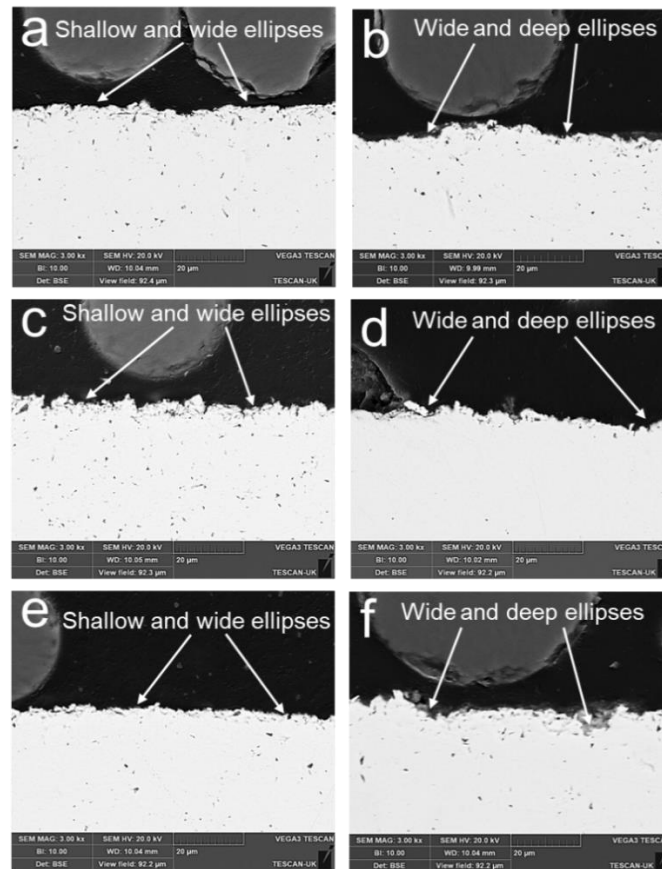


Figure 6-11 - SEM backscattered electron images of the exposed X80 C-ring samples in simulated saltwater solution with O₂/N₂ stressed at 80 % Y.S., 95 % Y.S. and notched sample stressed at 80 % Y.S.: (a) 80 % Y.S. at 5 °C; (b) 80 % Y.S. at 25 °C; (c) 95 % Y.S. at 5 °C; (d) 95 % Y.S. at 25 °C; (e) Notched sample at 5 °C; (f) Notched sample at 25 °C.

6.1.3.4 Scanning Electron Microscopy Images of X100 C-rings Specimens

Figures 6-12a to 6-12f, respectively, show the SEM images of the X100 samples stressed at 80 % Y.S, 95 % Y.S., and notched sample stressed at 80 % Y.S. exposed in solution with O₂/N₂ at 5 °C and 25 °C. The X100 samples at all stress levels and solution temperatures presented higher metal surface deterioration relative to X80 samples. A combination of deep and wide elliptical morphology with shallow vertical dissolution were observed on the samples stressed at 80 % Y.S. and 95 % Y.S. exposed at 5 °C (Figures 6-12a and c), which is greater at 25 °C. The notched samples at all solution temperatures (Figures 6-12e and f) showed deeper vertical dissolution relative to the samples stressed at 80 % Y.S. and 95 % Y.S.

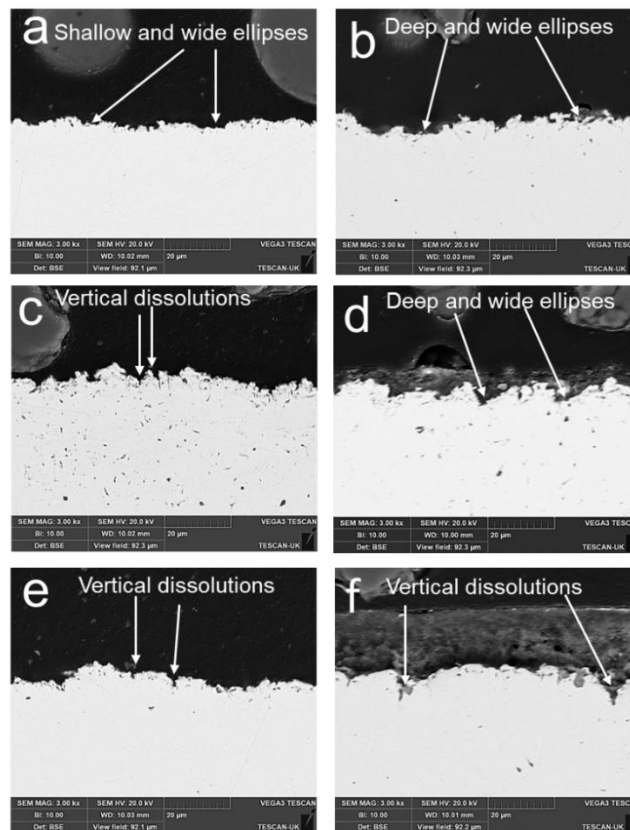


Figure 6-12 - SEM backscattered electron images of the exposed X100 C-ring samples in simulated saltwater solution with O₂/N₂ stressed at 80 % Y.S., 95 % Y.S. and notched sample stressed at 80 % Y.S.: (a) 80 % Y.S. at 5 °C; (b) 80 % Y.S. at 25 °C; (c) 95 % Y.S. at 5 °C; (d) 95 % Y.S. at 25 °C; (e) Notched sample at 5 °C; (f) Notched sample at 25 °C.

In general, increasing surface corrosion morphology was observed on all exposed samples with increasing solution temperature from 5 °C to 25 °C. All samples were observed to have an uneven surface morphology at all solution temperatures. Higher metal dissolution and deterioration were observed on the X100 samples relative to the X65, X70 and X80 samples. This can be said to occur due to higher ultimate tensile strength of the X100 carbon steel samples and variations in microstructures of the carbon steels and their reactions to the solution temperatures.

6.1.4 Energy Dispersive Spectroscopy

EDS analysis was conducted on the exposed samples to understand the variation in elemental compositions of the samples with change in exposure conditions. An error of $\pm 5\%$ is assumed for all EDS measurements.

6.1.4.1 Energy Dispersive Spectroscopy Analysis of X70 C-rings Specimens

The compositions of the EDS spectra (Figure 6-13) of the exposed X70 sample in solution with O₂/N₂ stressed at 80 % Y.S. at 5 °C, are presented in Figure 6-14 (in weight percentages). Figure 6-15 show the line scan analysis of the exposed sample. As reported in chapter four and five, spectrum 1 which is mainly resin will not be reported in the analysis. The carbon content from all spectra will also not be reported as EDS does not correctly quantify the percentage of carbon present in the analyzed samples. Variations in percentage of Mn was detected with change in spectrum location. Spectrum 3 which is close to the alloy-resin interface presented higher percentage of Mn (1.73 wt.%) in comparison with spectrum 4 (1.64 wt.%). The concentration of Fe was also observed to change with spectrum location, with values of 92.3 wt.% and 91.84 wt.%, respectively, in spectrum 3 and 4.

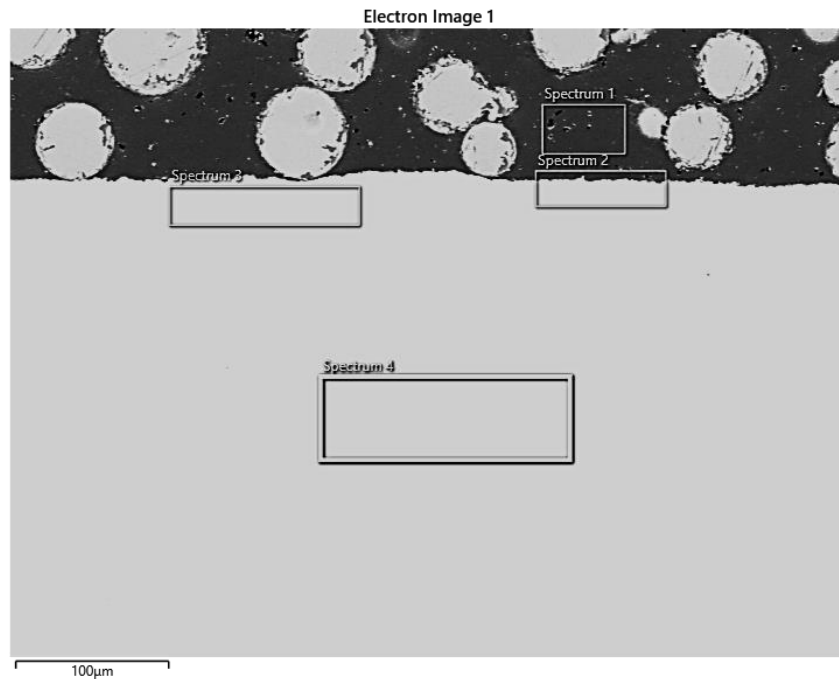


Figure 6-13 - SEM backscattered electron image of exposed X70 C-ring sample in simulated saltwater solution with O₂/N₂ at 5 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 6-14.

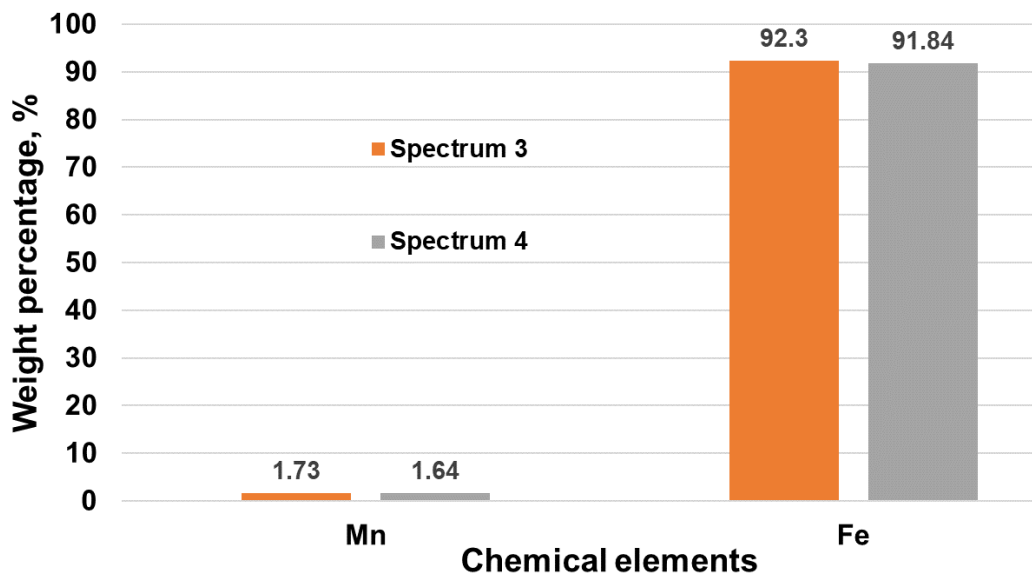


Figure 6-14 - EDS compositions of the exposed X70 sample elements in simulated saltwater solution with O₂/N₂ at 5 °C stressed at 80 % Y.S.

As shown in Figure 6-15, a sharp increase in Fe concentration is clearly observed between the alloy-resin interface at about 47 µm into the resin. Concentration of Mn and Si were clearly detected to have higher percentage in the alloy, with

highest concentration of Si observed detected at about 123 μm . The amount of C and O are clearly shown to be higher in the resin, with sharp increase below about 48 μm into the resin.

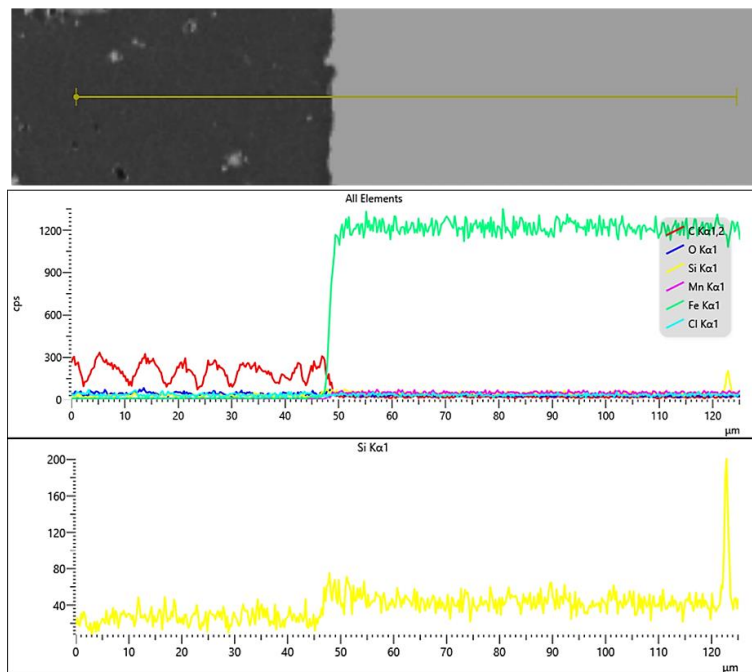


Figure 6-15 - EDS line scan analysis of the exposed X70 sample elements in simulated saltwater solution with O_2/N_2 at 5 °C stressed at 80 % Y.S.

Relative to X70 sample exposed at 5 °C, variations in elemental compositions of the exposed X70 sample in solution with O_2/N_2 at 25 °C were observed. The composition of the EDS spectra (Figure 6-16) of the X70 sample stressed at 80 % Y.S. exposed at 25 °C are presented in Figure 6-17 (in weight percentages). The percentage of Mn was observed to change with spectrum location as observed on the X70 sample exposed at 5 °C (Figure 6-14). Spectrum 3 which is close to the alloy resin interface showed higher percentage of Mn with a value of 1.81 wt.%. relative to spectrum 4 with 1.62 wt.%. Increasing percentage of Fe was observed with change in spectrum location from 3 to 4. Highest percentage of Fe (93.19 wt.%) was detected in spectrum 4. No presence of O or Si detected in the samples exposed at both 5 °C and 25 °C. Approximately equal percentages of Fe were detected in spectrum 3 of both samples exposed at 5 °C and 25 °C, respectively, with values of 92.3 wt.% and 92.11 wt.%. In general, no significant differences observed in Fe and Mn percentages between the analyzed X70

samples exposed at 5 °C (highest value of 92.3 wt.% in spectrum 3) and 25 °C (highest value of 93.19 wt.% in spectrum 4).

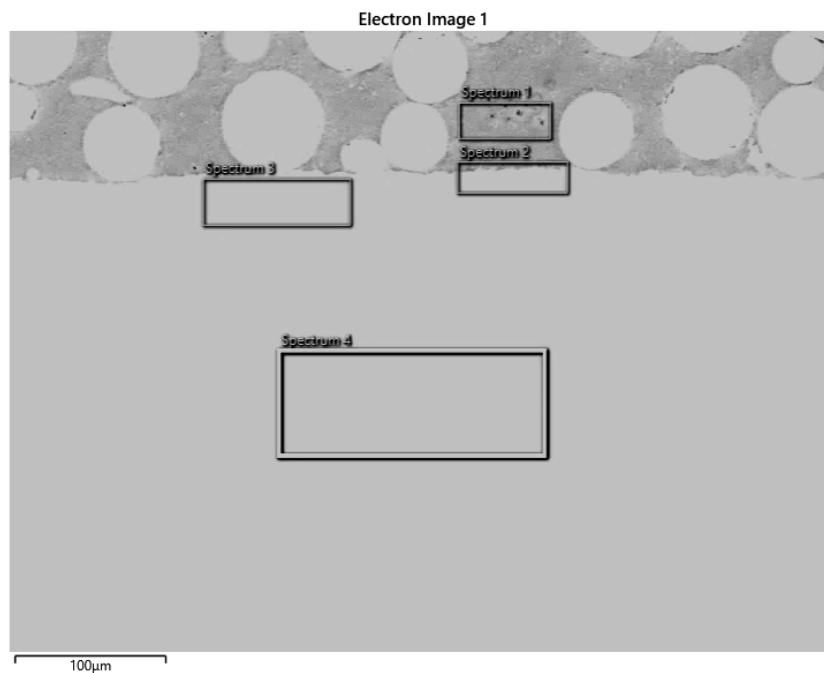


Figure 6-16 - SEM backscattered electron image of exposed X70 C-ring sample in simulated saltwater solution with O₂/N₂ at 25 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 6-17.

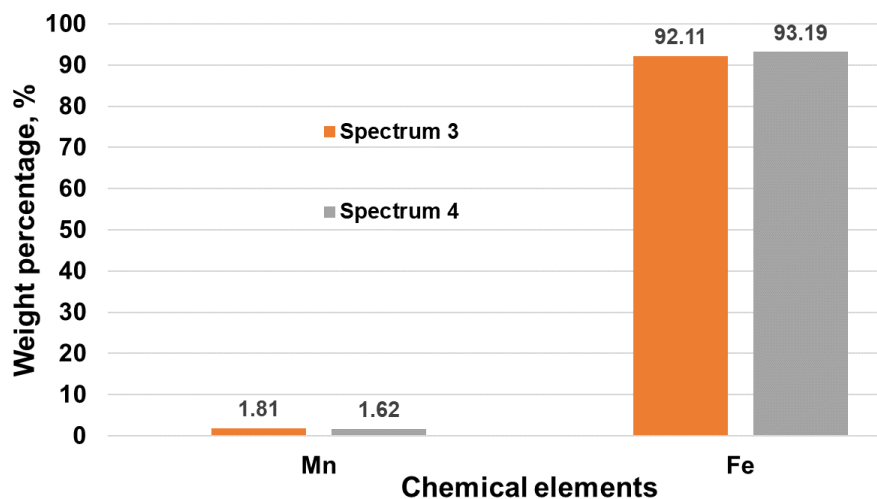


Figure 6-17 - EDS compositions of the exposed X70 sample elements in simulated saltwater solution with O₂/N₂ at 25 °C stressed at 80 % Y.S.

Relative to the X70 sample exposed at 5 °C, similar trend in line scan analysis was observed in the sample exposed at 25 °C as shown in Figure 6-18. Sharp

increase in Fe concentration at the interface was also observed at 25 °C. The percentage of Mn is also clearly observed to be higher in the alloy after about 40 μm into the resin. Amount of Si was observed to show highest concentration at about 6 μm into the resin and at the interface as shown in Figure 6-18.

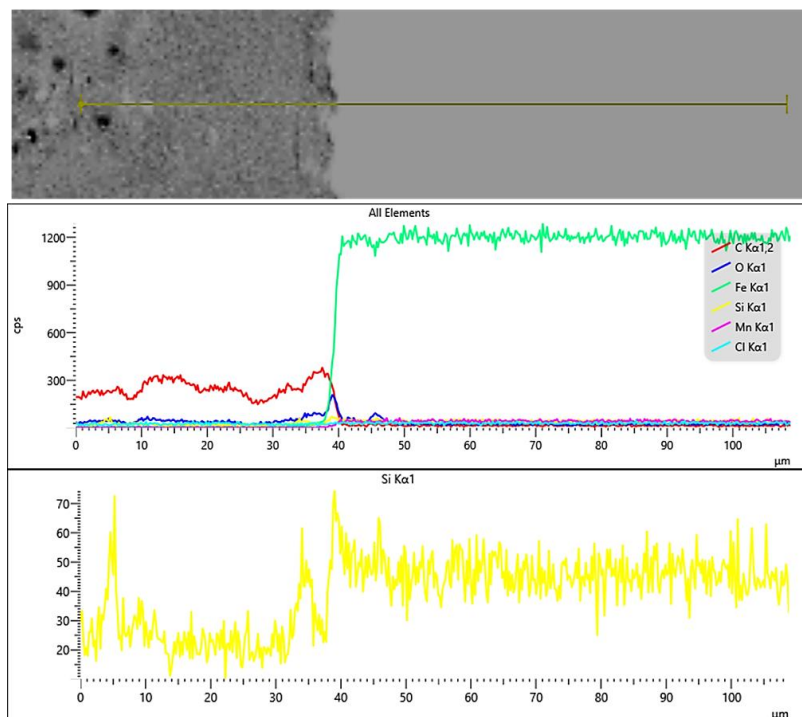


Figure 6-18 - EDS line scan analysis of the exposed X70 sample elements in simulated saltwater solution with O_2/N_2 at 25 °C stressed at 80 % Y.S.

6.1.4.2 Energy Dispersive Spectroscopy Analysis of X100 C-rings Specimens

The compositions of the EDS spectra (Figure 6-19) of the exposed X100 sample in solution with O_2/N_2 stressed at 80 % Y.S. exposed at 5 °C, are presented in Figure 6-20 (in weight percentages). As observed on the X70 samples at 5 °C, change in Mn concentration was also observed with change in spectrum location on the X100 sample exposed at 5 °C. Relative to X70 sample exposed at 5 °C, the percentage of Mn was observed to be higher in the X100 sample exposed at 5 °C with a value of 2.02 wt.% in spectrum 4. Spectrum 4 as shown in Figure 6-20 was observed to contain higher concentration of Fe in comparison with spectrum 3, with a value of 90.45 wt.% and 91.15 wt.%, respectively detected in spectrum 3 and 4. In general, higher percentage of Fe was observed on the X70

sample exposed at 5 °C (92.3 wt.%, spectrum 3) relative to X100 sample exposed at 5 °C (91.45 wt.%, spectrum 4), with higher percentage of Mn observed on X100 sample (2.02 wt.%).

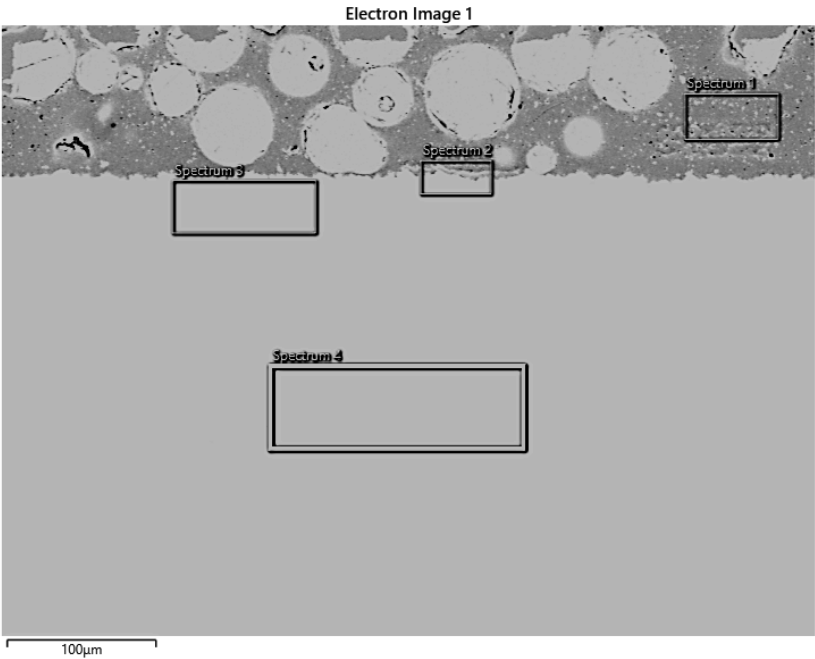


Figure 6-19 - SEM backscattered electron image of the exposed X100 C-ring sample in simulated saltwater solution with O₂/N₂ at 5 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 6-20.

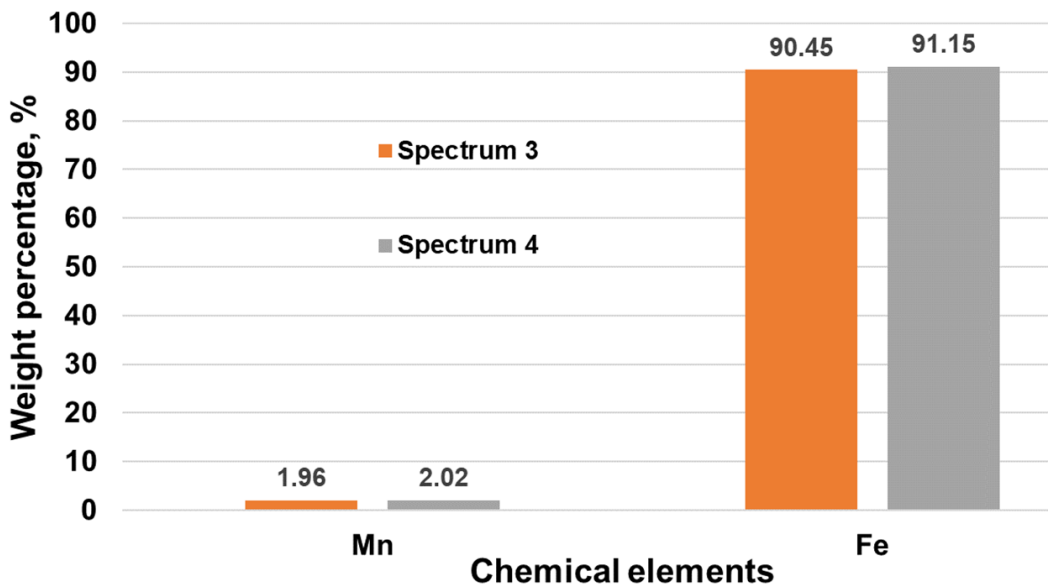


Figure 6-20 - EDS compositions of the exposed X100 sample elements in simulated saltwater solution with O₂/N₂ at 5 °C stressed at 80 % Y.S.

The line scan analysis as shown in Figure 6-21 show higher concentration of Fe, with sharp increase at the interface after about 23 μm into the resin. Amount of Mn was detected to be higher in the alloy after about 25 μm into the resin, with sharp increase in C content from below about 25 μm into the resin. Variation in Si concentration trend was observed on the X100 sample exposed at 5 $^{\circ}\text{C}$ relative to X70 sample exposed at 5 $^{\circ}\text{C}$ (Figure 6-15). Highest concentration of Si was detected to be higher between about 8 μm to 22 μm in the resin as shown in Figure 6-21.

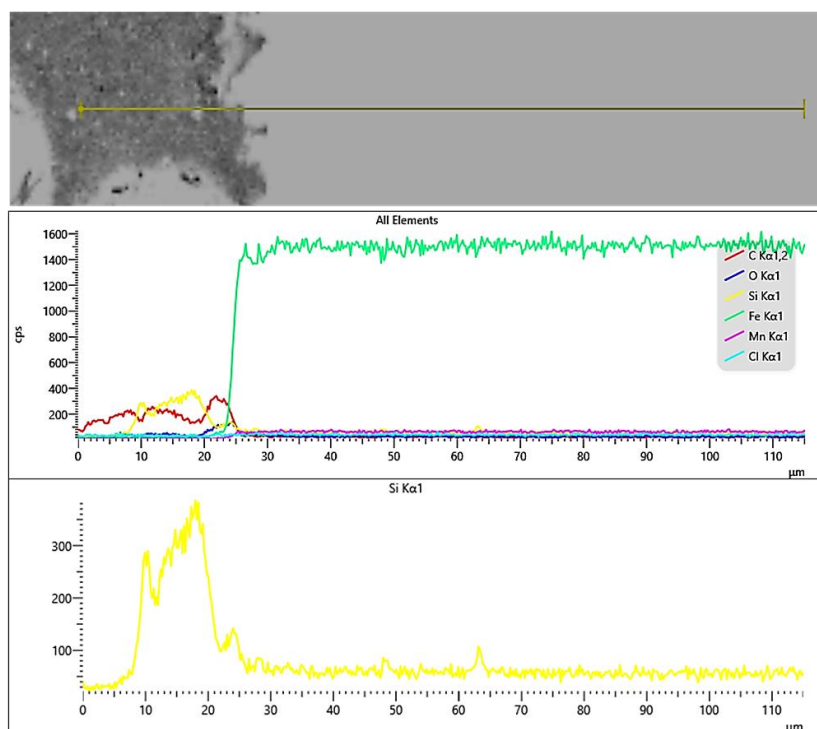


Figure 6-21 - EDS line scan analysis of the exposed X100 sample elements in simulated saltwater solution with O_2/N_2 at 5 $^{\circ}\text{C}$ stressed at 80 % Y.S.

The compositions of the EDS spectra (Figure 6-22) of the exposed X100 sample in solution with O_2/N_2 at 25 $^{\circ}\text{C}$ stressed at 80 % Y.S. are presented in Figure 6-23 (in weight percentages). Increasing percentage of Mn was observed with change in spectrum location from 3 to 4. The highest concentration of Mn detected on the X100 sample exposed at 25 $^{\circ}\text{C}$ (1.92 wt.%, spectrum 4) was observed to be lower than at 5 $^{\circ}\text{C}$ (2.02 wt.%, spectrum 4). Approximately equal maximum values of Fe were detected in the X100 sample exposed at 25 $^{\circ}\text{C}$ (91.23 wt.%, spectrum 3) in comparison with 5 $^{\circ}\text{C}$ (91.15 wt.%, spectrum 4).

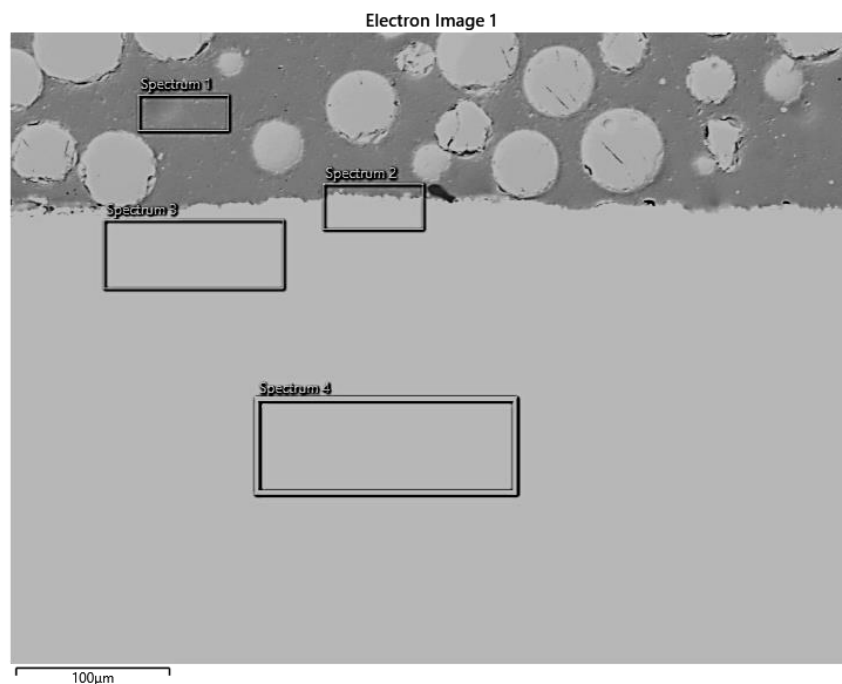


Figure 6-22 - SEM backscattered electron image of the exposed X100 C-ring sample in simulated saltwater solution with O_2/N_2 at 25 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 6-23.

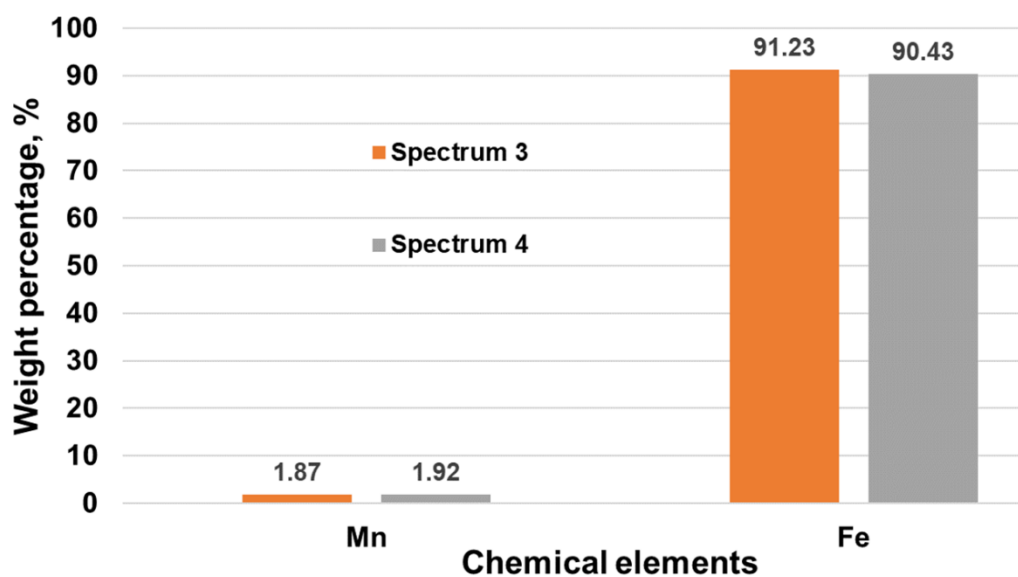


Figure 6-23 - EDS compositions of the exposed X100 sample elements in simulated saltwater solution with O_2/N_2 at 25 °C stressed at 80 % Y.S.

The line scan analysis of the X100 sample exposed at 25 °C (Figure 6-24), similarly, showed higher Fe concentration in the alloy from about 52 µm into the resin as obtained at 5 °C. Amount of Mn was also observed to be higher in the

alloy after about 54 μm . More or less similar trend in Si concentration was observed on the X100 sample exposed at 25 $^{\circ}\text{C}$ in comparison with 5 $^{\circ}\text{C}$. Highest concentration of Si was detected between 24 μm and 42 μm in the resin (Figure 6-24).

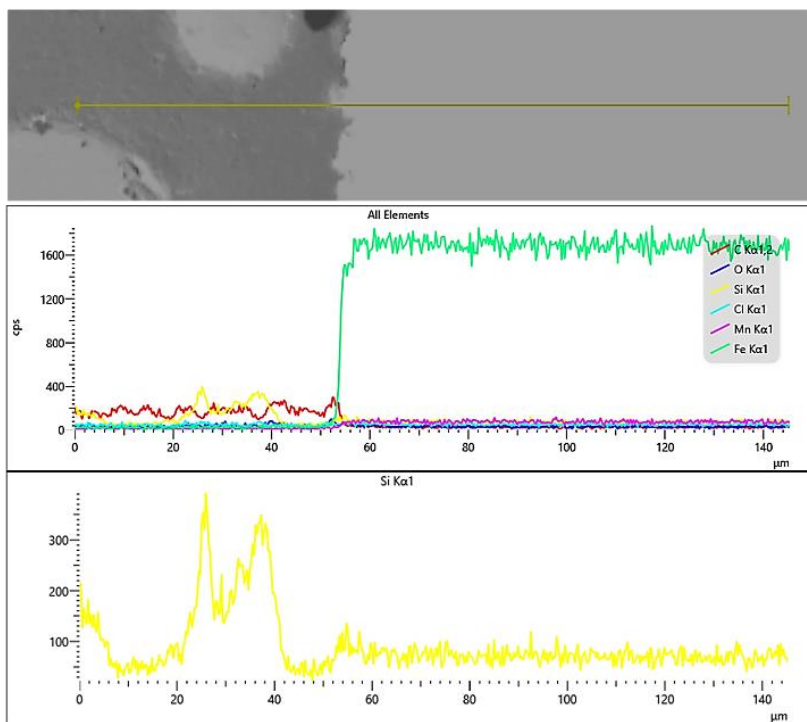


Figure 6-24 - EDS line scan analysis of the exposed X100 sample elements in simulated saltwater solution with O_2/N_2 at 25 $^{\circ}\text{C}$ stressed at 80 % Y.S.

In general, not much significant variation in Fe and Mn concentration observed between the X70 and X100 samples at both 5 $^{\circ}\text{C}$ and 25 $^{\circ}\text{C}$. Highest percentage of Fe (93.19 wt.%) was observed in the X70 sample exposed at 25 $^{\circ}\text{C}$, with highest in Mn (2.02 wt.%) observed in the X100 exposed at 5 $^{\circ}\text{C}$. The concentration of Si was observed to be highest mostly in the resin, as observed in X100 samples exposed at both 5 $^{\circ}\text{C}$ and 25 $^{\circ}\text{C}$. This can occur due to accumulation of glass beads used in preparing the resin, which contains some certain amount of Si.

6.1.5 Tensile Strength Analysis

Tensile strength tests were conducted on X70 dog-bone samples exposed in the different test conditions to assess the impact of O₂/N₂ mixture and temperature on the ductility of the carbon steel.

6.1.5.1 Tensile Strength Tests of X70 Dog-bone Specimens

The stress-strain curves of the X70 dog-bone samples exposed in solution with O₂/N₂ at 5 °C and 25 °C are presented in Figure 6-25. It is observed that with increasing solution temperature, elongation before failure increases. As shown in Figure 6-25, comparison of the analysed X70 dog-bone samples at 5 °C and 25 °C showed increase in ductility with increasing solution temperature. Highest decrease in ductility was observed at 5 °C with an elongation of about 28.62 % and, 28.74 % observed at 25 °C. However, the reference sample was observed to show lower percent elongation before failure of about 28.42 % relative to samples exposed at 5 °C and 25 °C. Similarly, as observed in solution with CO₂ (chapter 5), no significant change in elongation before failure observed on the analysed X70 samples with change in solution temperature.

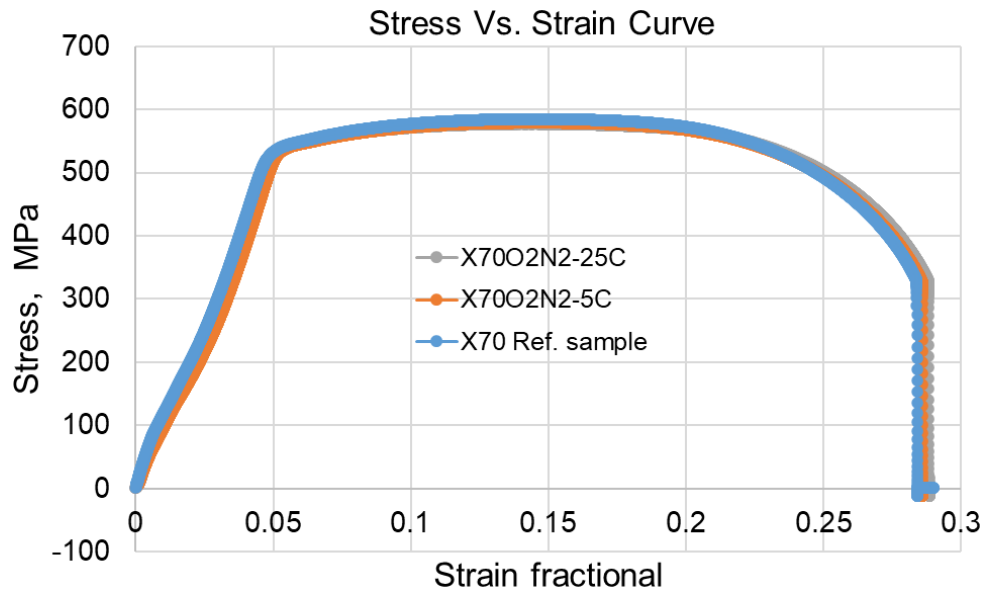


Figure 6-25 - Tensile tests stress-strain curves of the X70 dog-bone samples exposed in simulated saltwater solution with O₂/N₂ at 5 °C and 25 °C.

6.1.6 Vickers Hardness Analysis

Vickers hardness tests were conducted on the exposed X70 dog-bone samples to assess the impact of O₂/N₂ mixture and temperature on the hardness of the carbon steel.

6.1.6.1 Hardness Tests of X70 Dog-bone Specimens

The Vickers hardness results obtained from the exposed X70 dog-bone samples in solution with O₂/N₂ at 5 °C and 25 °C are presented in Figure 6-26. Similarly, as reported in chapter five, the hardness tests on samples were conducted from the start of the reduced parallel section of the dog-bone towards the fracture point. (x-axis in the graph indicates test locations from 1 to 8; 1- indicates start of reduced parallel section and, 8- end of fracture point). Three measurements were conducted on each test location and its average calculated. The analysis shows fluctuations in hardness with change in test location at all solution temperatures. Highest average hardness was observed on the sample exposed at 5 °C towards the fracture point with a value of 255.0 HVC, with lowest average observed on the sample exposed at 25 °C with a value of 186.0 HVC at the start of reduced parallel section. Generally, the reference sample as shown in Figure 6-26 was observed to show higher average hardness of 257.3 HVC towards the fracture point, relative to samples exposed at 5 °C and 25 °C. In general, no significant change in hardness value observed between the samples exposed at 5 °C and 25 °C. Similarly, as observed in solution with CO₂ as discussed in section 5.1.6.1, the reference sample was observed to have higher average hardness, relative to all exposed samples at all temperatures. This also indicates no change in hardness in the simulated O₂/N₂ solution, which implies no change in hardness and wear resistance of the samples within the exposure time (840hrs) and change in solution temperature.

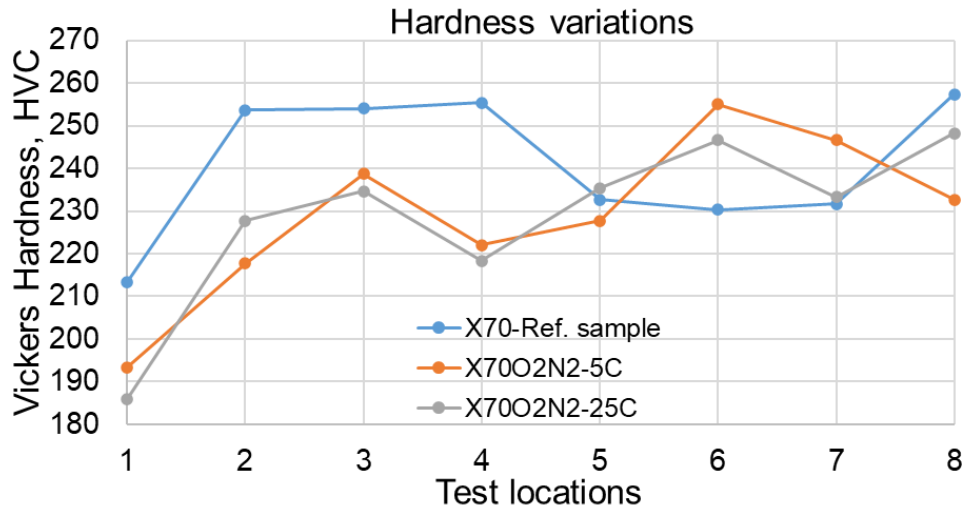


Figure 6-26 - Vickers hardness of the X70 dog-bone samples exposed in simulated saltwater solution with O₂/N₂ at 5 °C and 25 °C.

6.2 Chapter Summary

Similarly, as observed on the samples exposed in solution with N₂ (chapter 4), fluctuations in corrosion rates with time were also observed on all samples exposed in solution with O₂/N₂ mixture as shown in Figures 6-1a, c to 6-4a, c. This can be also be explained to occur due to continuous formation and rupture of surface layers on the samples (iron oxide). The X100 samples at all exposure conditions were also observed to present higher corrosion rates relative to the X65, X70 and X80 samples. This shows that the X100 carbon steel samples have higher anodic current and corrosion current density, thus leading to higher corrosion rates. As higher corrosion rates were observed on the X100 carbon steel, in comparison with X65, X70 and X80 samples within the exposure period of 840 hrs (5 weeks), it can be concluded that the X100 carbon steel is more susceptible to SCC in the simulated saltwater environment saturated with O₂/N₂ mixture.

It is observed that the obtained experimental corrosion rates of the exposed samples in solution with O₂/N₂ (20%/80%) are more or less similar to published corrosion rates of carbon steels in seawater (seawater contains about 21 % O₂). A value of 0.13-0.41 mm/year was reported by Michael and Davies [44,45], 0.102-0.178 mm/year reported by Fontana [22] and a value of 0.1 mm/year in quiet

seawater to a maximum of 0.75 mm/year at 3 m/s seawater velocity reported by Kreysa and Schutze [36]. Variations in corrosion potentials with time were also observed on the exposed carbon steels in the simulated 3.5 % NaCl solution saturated with O₂/N₂, which shows the change in thermodynamic behaviour of the carbon steels with change in microstructure and exposure conditions.

In general, higher metal loss and pits features were observed at 25 °C for all exposed carbon steel samples. Increasing metal loss of about 100 % with change in solution temperature from 5 °C to 25 °C was observed on the X65, X70 and X80 samples. However, the X100 showed an increased metal loss of about 60 % with change in solution temperature from 5 °C to 25 °C. At all applied stress levels and solution temperatures, the samples presented an uneven distribution of metal damage over half of the sample's surfaces. Higher pits features were observed on all samples at both 5 °C and 25 °C, in comparison with samples exposed in solution with N₂. This can be said to occur due to increasing percentage of O₂ in the simulated test solution. Hence, the presence of O₂ in a solution causes formation of pits on metal's surfaces.

Increased surface corrosion morphology was observed on all exposed samples with increasing solution temperature from 5 °C to 25 °C. All samples were observed to present an uneven surface morphology at all solution temperatures. No significant change in surface observed on all samples with increasing applied stress level from 80 % Y.S. to 95 % Y.S. and surface state of the samples (notched sample). Higher metal dissolution and deterioration were observed on the X100 samples, relative to the X65, X70 and X80 samples, with deeper and wider ellipses and combination of vertical metal dissolution at 25 °C. This shows that the X100 samples with bainitic ferrite and disperse austenite grains is more susceptible to stress corrosion in the presence of dissolved oxygen.

Similarly, as observed on the samples exposed in solution with N₂ (chapter 4) and CO₂ (chapter 5), no significant difference in Fe and Mn concentration observed between the X70 and X100 samples at both 5 °C and 25 °C. Highest percentage of Fe (93.19 wt.%) was observed in the X70 sample exposed at 25 °C, with highest in Mn (2.02 wt.%) observed in the X100 exposed at 5 °C. The

concentration of Si was observed to be highest mostly in the resin, as observed in the X100 samples exposed at both 5 °C (Figure 6-21) and 25 °C (Figure 6-24). This occurred due to accumulation of glass beads used in preparing the resin, which contains some certain amount of Si. Concentration of O was observed to decrease with increasing solution temperature on both X70 and X100 samples. This indicates that solubility of O decreases with increasing temperature of the exposure solution.

The obtained tensile strength analysis results of the exposed X70 dog bone samples show no significant change in elongation before failure with change in solution temperature from 5 °C to 25 °C as observed on the samples exposed in solution with CO₂ (chapter 5). Lowest elongation before failure of 28.62 % was observed on the sample at 5 °C, with an elongation of about 28.74 % observed at 25 °C. Results from hardness analysis shows fluctuations in hardness with change in test location at all solution temperatures. Highest average hardness was observed on the sample exposed at 5 °C towards the fracture point with a value of 255.0 HVC, and a value of 248.17 HVC obtained at the fracture point at 25 °C. In general, no significant difference in hardness observed on the samples with change in solution temperature.

7 RESULTS AND DISCUSSION FOR EXPERIMENTS IN SOLUTION WITH 20% OXYGEN AND 80% CARBON-DIOXIDE

This chapter presents the results obtained from the exposed X65, X70, X80 and X100 C-rings samples exposed in simulated 3.5 % NaCl solution with 20%O₂/80%CO₂. Solution was continuously bubbled with 20%O₂/80%CO₂ at 50 mL/min flow rate for a period of 5 weeks (840hrs). Corrosion rates, metal loss exceedance, SEM analysis, EDS analysis, tensile strength analysis and Vickers hardness analysis were conducted on the exposed samples.

7.1 Experiments in Solution with 20%O₂/80%CO₂ at 5 °C, 15 °C and 25 °C

The tests were conducted at different solution temperatures of 5 °C, 15 °C and 25 °C. This is carried out to understand the effect of temperature on the exposed carbon steel samples in the simulated environment.

7.1.1 Corrosion Rates and Potentials

The change in corrosion rates and potentials with time of the exposed samples were monitored by use of linear polarization resistance technique. Specimens were polarized at a potential of ± 10 mV at a scan rate of 0.167 mV/s. Periodic polarization of the specimens was conducted after every 168 hrs to monitor the change in resistance and potential. The corrosion rates are then calculated by use of Stern-Geary equation. Two measurements were carried out on each data point in all conducted experiments at all exposure conditions and average corrosion rates were calculated and values plotted against time. Corrosion rate errors were calculated using propagation of error method as outlined by Taylor [120]. The calculated errors were observed to be negligible in the range of 10^{-5} to 10^{-7} mm/yr. As observed in the increased corrosion rates of the exposed carbon steels with change in trace gas mixture from N₂ (chapter 4) to O₂/N₂ (chapter 6), a high increase as expected was also observed with change in trace

gas mixture from 100 % CO₂ (chapter 5) to 20%O₂/80%CO₂ as presented in subsequent headings.

7.1.1.1 Corrosion Rates and Potentials of X65 C-rings Specimens

Figures 7-1a to 7-1f show the corrosion rates and potentials of the exposed X65 samples in solution with O₂/CO₂ at 5 °C, 15 °C and 25 °C. As shown in graph 7-1a, a decrease in corrosion rates was observed for the samples stressed at 80 % Y.S. and notched sample stressed at 80 % Y.S. at 503 hrs of exposure, with low continuous increase for the duration of the tests. However, the sample stressed at 80 % Y.S. showed continuous decrease in corrosion rates with time till 671 hrs of exposure, with an increase at 839 hrs. Relative to sample stressed at 80 % Y.S. and notched sample, the sample stressed at 95 % Y.S. was observed to show higher corrosion rates with a maximum value of 0.772 mm/year obtained at 359 hrs. This could also be explained to occur due error in placement of the sample in the test cell, which leads to differential aeration. Maximum values of 0.687 mm/year and 0.661 mm/year, respectively were obtained for the notched sample and sample stressed at 80 % Y.S. at 359 hrs of exposure (Figure 7-1a). Similar trend in corrosion rates with time was observed at 15 °C (Figure 7-1c), in comparison with samples exposed at 5 °C. A decrease in corrosion rates was also observed on all samples at 504 hrs, with continuous increase for the duration of the tests. Maximum values of 1.561 mm/year and 1.537 mm/year, respectively were observed for the samples stressed at 80 % Y.S. and 95 % Y.S. (Figure 7-1c). Similarly, as obtained from samples exposed at 5 °C and 15 °C, a decrease in corrosion rates with time was also observed for all samples at 502 hrs of exposure at 25 °C, with continuous increase throughout the duration of the test. A maximum value of 2.525 mm/year was observed for the sample stressed at 80 % Y.S. (Figure 7-1e). As reported in chapter 4, 5 and 6, the observed fluctuations in corrosion rates with time can be explained to occur due to formation and rupture of surface layers on the samples.

Variations in corrosion potentials trend were observed for the samples exposed at 5 °C (Figure 7-1b), relative to samples exposed at 5 °C and 25 °C. An increase in potential was observed on all samples at 5 °C at 503 hrs of exposure, with a

continuous decrease throughout the test's duration. A maximum value of $-626 \text{ mV}_{\text{Ag}/\text{AgCl}}$ was observed for the sample stressed at 95 % Y.S. at 167 hrs (Figure 7-1b). A continuous increase in potential was observed on all samples at both 15°C (Figure 7-1d) and 25°C (Figure 7-1f). A maximum potential value of $-640 \text{ mV}_{\text{Ag}/\text{AgCl}}$ and $-655 \text{ mV}_{\text{Ag}/\text{AgCl}}$, respectively, were observed on the samples stressed at 80 % Y.S. at 15°C and 25°C . The obtained corrosion potentials were observed to decrease with increasing solution temperature from 5°C to 25°C . As discussed in chapter 4 and 5 and 6, variations in potentials can be said to occur due to change in thermodynamic behaviour of the stressed samples with change in solution temperature.

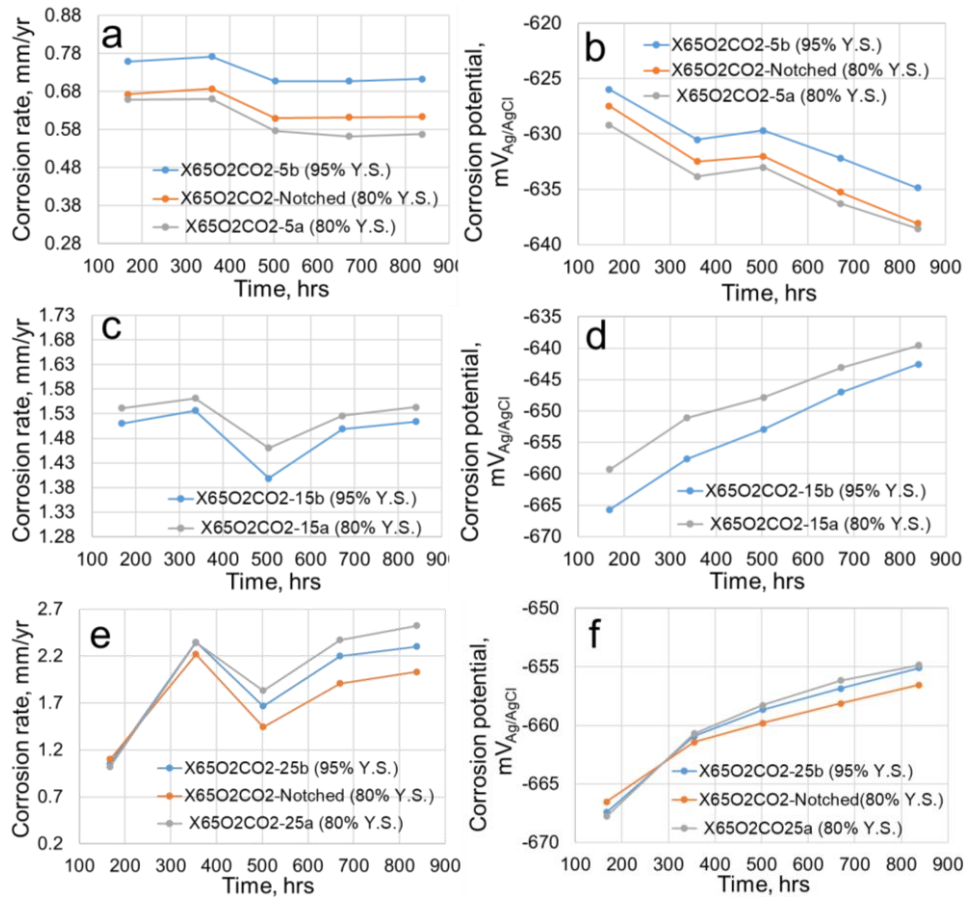


Figure 7-1 - Corrosion rates and potentials of the exposed X65 carbon steel C-rings in simulated saltwater solution with O_2/CO_2 : (a) corrosion rates at 5°C ; (b) potentials at 5°C ; (c) corrosion rates at 15°C ; (d) potentials at 15°C ; (e) corrosion rates at 25°C ; (f) potentials at 25°C .

In general, variations in corrosion rates were observed on the samples at all exposure conditions with increasing applied stress level from 80 % Y.S. to 95 % Y.S. and change in surface state of the samples (notched state). Increasing corrosion rates were observed at 5 °C with an increase in stress level from 80 % Y.S. to 95 % Y.S. At 15 °C and 25 °C, the observed change in corrosion rates were independent of applied stress level. The observed variations in corrosion rates are not statistically different and could be attributed to differential aeration. An increase in corrosion rates of more than 100 % was observed with increasing temperature from 5 °C to 15 °C, with an increase of about 60 % from 15 °C to 25 °C. An increase in corrosion rate of about 100 % was observed on the X65 samples with change in trace gas mixture from 100 % CO₂ (max. of 1.331 mm/year at 25 °C) to 20%O₂/80%CO₂ (max. of 2.525 mm/year at 25 °C). No comparison can be made between the obtained experimental corrosion rates of the exposed X65 carbon steel samples in solution with O₂/CO₂ and published literature as there is no data available on corrosion rates of carbon steels in 3.5 % NaCl solution or related environment saturated with O₂/CO₂. However, same standard operating procedures as outlined in section 3.5 were followed in the monitoring and calculation of corrosion rates.

From the observed high corrosion rates of the exposed X65 carbon steel in the simulated 3.5 % NaCl in the presence of O₂/CO₂, installation and usage of the carbon steel as a pipeline material in a seawater environment for transportation of CO₂ or other oil and gas products which contains traces of CO₂ should be operated at in deep waters or polar regions where the temperatures are below 5 °C as reported in section 2.1.4. This will help to reduce the rate of corrosion and hence lower the potential of hydrogen embrittlement and subsequent SCC occurrence in a long duration of usage.

7.1.1.2 Corrosion Rates and Potentials of X70 C-rings Specimens

Figures 7-2a to 7-2f show the corrosion rates and potentials of the exposed X70 samples in solution with O₂/CO₂ at 5 °C, 15 °C and 25 °C. In comparison with the exposed X65 samples, similar trends in corrosion rates and potentials were observed on all exposed X70 samples at all temperatures. Decrease in corrosion

rates at 503 hrs, 504 hrs and 502 hrs of exposure, respectively were observed on all samples at 5 °C, 15 °C and 25 °C, with continuous increase for the duration of the tests. A maximum corrosion rate value of 0.674 mm/year and 1.531 mm/year, respectively were observed on the sample stressed at 80 % Y.S. at 5 °C (Figure 7-2a) and sample stressed at 95 % Y.S. at 15 °C (Figure 7-2c). A maximum corrosion rate value of 3.465 mm/year and minimum of 1.534 mm/year was obtained for the sample stressed at 95 % Y.S. at 25 °C (Figure 7-2e). Similarly, as observed on the X65 samples, an increase in potential was observed at 503 hrs of exposure for all X70 samples at 5 °C, with continuous decrease throughout the test's duration.

A maximum potential value of -635 mV_{Ag/AgCl} was obtained for the repeat sample (X70O2CO2-5a-R, Figure 7-2b) stressed at 80 % Y.S. at 503 hrs. Similar trend of continuous increase in potential was also observed on all X80 samples at both 15 °C (Figure 7-2d) and 25 °C (Figure 7-2f), in comparison with X65 and X70 samples. Maximum potentials of -638 mV_{Ag/AgCl} and -648 mV_{Ag/AgCl}, respectively were observed on the samples stressed at 80 % Y.S. at 15 °C and notched sample at 25 °C. Figure 7-3a, b and c respectively, show the after-exposure images of X70 C-rings samples in solution with O₂/CO₂ at the different solution temperatures.

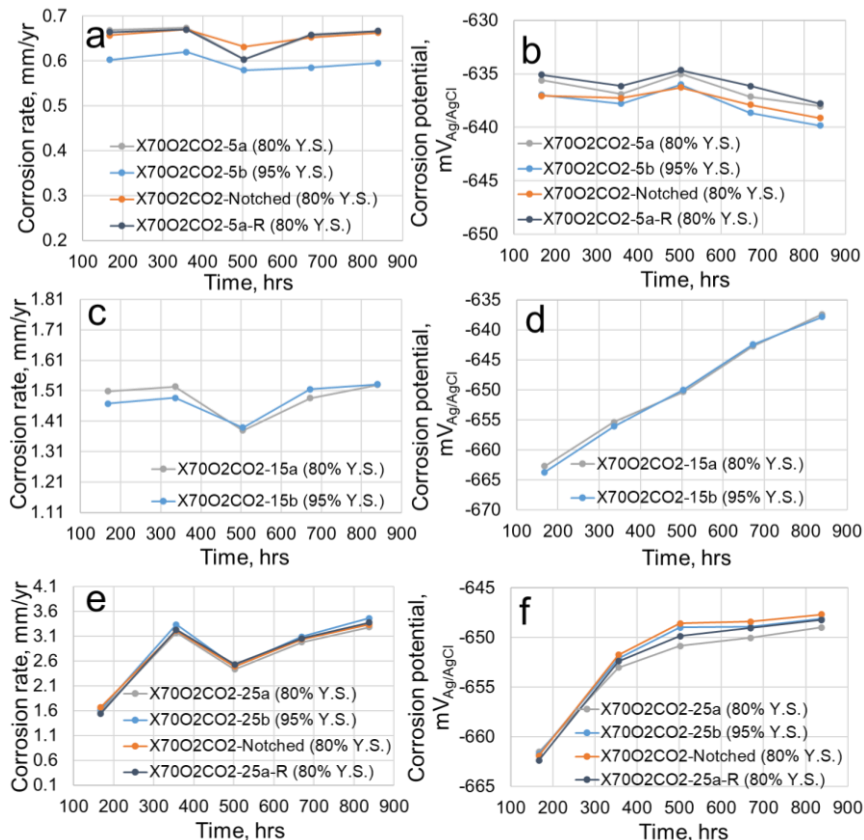


Figure 7-2 - Corrosion rates and potentials of the exposed X70 carbon steel C-rings in simulated saltwater solution with O_2/CO_2 : (a) corrosion rates at 5 °C; (b) potentials at 5 °C; (c) corrosion rates at 15 °C; (d) potentials at 15 °C; (e) corrosion rates at 25 °C; (f) potentials at 25 °C.

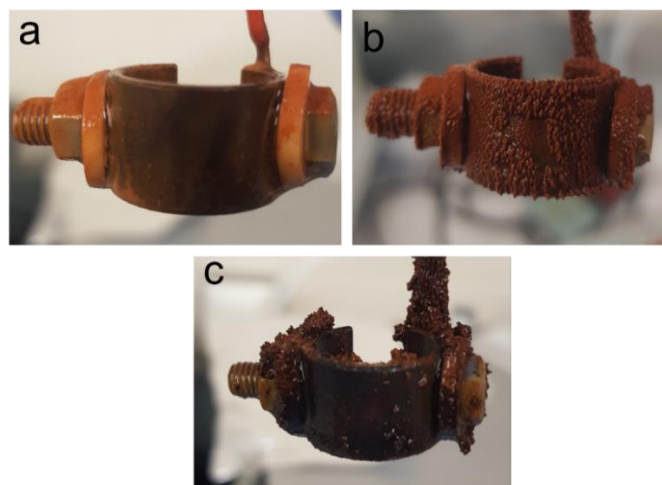


Figure 7-3 - Images of X70 C-rings samples after 840 hrs of exposure in simulated saltwater solution with O_2/CO_2 : (a) at 5 °C; (b) at 15 °C; (c) at 25 °C. As shown in the image increasing accumulation of corrosion products on the sample's surfaces is observed with increasing solution temperature.

In general, no significant statistical change in corrosion rates observed on the X70 samples with increasing applied stress level from 80 % Y.S. to 95 % Y.S. and change in surface state of the samples (notched state) at 15 °C and 25 °C. However, lower corrosion rates were observed on the sample stressed at 95 % Y.S. at 5 °C relative to samples stressed at 80 % Y.S. and notched sample. This can be also be attributed to differential aeration on the sample in the test cell, thus leading to lower cathodic reactions rates and hence lower corrosion rates [125,126]. Similarly, as observed on the X65 samples, an increase in corrosion rates of more than 100 % was observed on the X70 samples with increasing solution temperature from 5 °C to 15 °C. However, an increase of more than 100 % was observed on the X70 samples with increasing solution temperature from 15 °C to 25 °C, relative to X65 with an increase of about 60 %. Similarly, an increase in corrosion rate of more than 100 % was observed on the X70 samples with change in trace gas composition from 100 % CO₂ (max. of 1.405 mm/year at 25 °C) to 20%O₂/80%CO₂ (max. of 3.465 mm/year at 25 °C). No comparison can be made to evaluate the difference in calculated experimental corrosion rates of the exposed X70 samples in solution with O₂/CO₂ with published literature values as there is no data available on corrosion rates of carbon steels in simulated NaCl solution or similar environment saturated with O₂/CO₂.

From the observed higher corrosion rate of the exposed X70 carbon steel (max. of 3.465 mm/year) in comparison with X65 (max. of 2.525 mm/year). This indicates that the X70 carbon steel is more susceptible to SCC relative to the X65 in the simulated saltwater solution saturated with 20%O₂/80%/CO₂. As such its installation and operation as a pipeline material in a seawater environment for transportation of CO₂ or other oil and gas products which contains traces of CO₂ should be the least to consider if there is availability of X65. The operation of X70 carbon steel as a pipeline material in the North Sea as reported in section 2.1.4, with an annual mean sea surface temperature of 11 °C will have a reduced risk of SCC occurrence due to lower expected corrosion rates. Furthermore, as suggested in chapter 5, installations and usage of the carbon steel should be in deep waters or polar regions where the temperatures are below 5 °C and not in

tropical regions with temperatures above 30 °C to reduce risk of SCC occurrence induced by high corrosion rates.

7.1.1.3 Corrosion Rates and Potentials of X80 C-rings Specimens

Figures 7-4a to 7-4f show the corrosion rates and potentials of the exposed X80 carbon steel samples in solution with O_2/CO_2 at 5 °C, 15 °C and 25 °C. As presented in Figures 7-4a and 7-4c, variation in corrosion rates trends with time were observed on the X80 samples exposed at 5 °C and 15 °C relative to the X65 and X70 samples. The corrosion rates of all samples at 5 °C and 15 °C were also observed to continuously decrease with time until after 504 hrs of exposure. Maximum values of 0.706 mm/year and 1.571 mm/year, respectively were observed on the notched sample at 5 °C and sample stressed at 95 % Y.S. at 15 °C. The X80 samples exposed at 25 °C showed similar trend in corrosion rates with time as observed on the X65 (Figure 7-1e) and X70 (Figure 7-2e) samples at 25 °C. A decrease in corrosion rate was also observed on the X80 samples (Figure 7-4e) at 504 hrs of exposure, with continuous increase throughout the duration of the test. A maximum value of 2.830 mm/year and minimum of 1.041 mm/year, respectively were obtained from the sample stressed at 80 % Y.S. at 840 hrs and 168 hrs of exposure.

Similarly, as observed on the X65 and X70 samples, an increase in potential was observed at 504 hrs of exposure for all X80 samples at 5 °C, with continuous decrease throughout the test's duration. A maximum potential of -631 mV_{Ag/AgCl} was obtained from the notched sample at 504 hrs of exposure as shown in Figure 7-4b. Similarly, as observed on the X65 and X70 samples, continuous increase in potential was also observed on all X80 samples at both 15 °C (Figure 7-4d) and 25 °C (Figure 7-4f). Maximum potentials of -641 mV_{Ag/AgCl} and -654 mV_{Ag/AgCl}, respectively were observed on the samples stressed at 95 % Y.S. at 15 °C and sample stressed at 80 % Y.S. at 25 °C. Relative to the exposed X65 and X70 samples, the obtained corrosion potentials values from X80 samples were also observed to decrease with increasing solution temperature from 5 °C to 25 °C.

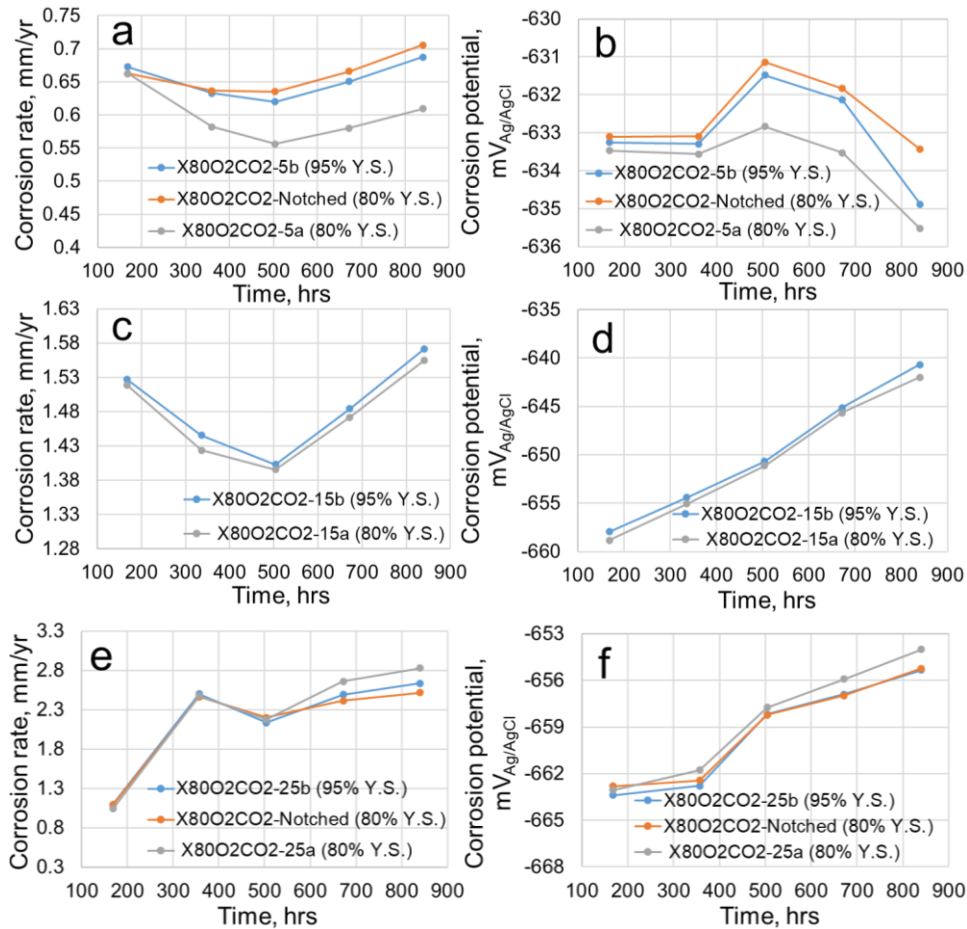


Figure 7-4 - Corrosion rates and potentials of the exposed X80 carbon steel C-rings in simulated saltwater solution with O₂/CO₂: (a) corrosion rates at 5 °C; (b) potentials at 5 °C; (c) corrosion rates at 15 °C; (d) potentials at 15 °C; (e) corrosion rates at 25 °C; (f) potentials at 25 °C.

Similarly, as observed and reported on the exposed X70 samples, no statistically significant change in corrosion rates observed on the X80 samples with increasing applied stress level from 80 % Y.S. to 95 % Y.S. and change in surface state of the samples (notched state) at 15 °C and 25 °C. However, lower corrosion rates were observed on the sample stressed at 80 % Y.S. at 5 °C relative to samples stressed at 95 % Y.S. and notched sample. This can also be explained to occur as a result of error in placement of the sample in the tests, which leads to differential aeration on the sample and subsequent decrease in corrosion rates with time [129]. Similarly, as observed on the X65 and X70 samples, an increase in corrosion rates of more than 100 % was observed with increasing solution temperature from 5 °C to 15 °C. As also observed from the exposed X65 an

increase of about 60 % was obtained on the X80 with change in temperature from 15 °C to 25 °C, relative to X70 with an increase of more than 100 %. This indicates that the X70 carbon steels has higher corrosion current density at 25 °C, which leads to higher corrosion rates. This can be said to occur due to variation in their microstructures and their reaction to the solution temperature at 25 °C. Similarly, as observed on the X65 and X70 samples, an increase in corrosion rate of more than 100 % was observed on the X80 samples with change in trace gas mixture from 100 % CO₂ (max. of 1.410 mm/year at 25 °C) to 20%O₂/80%CO₂ (max. of 2.830 mm/year at 25 °C). Similarly, as reported from calculated corrosion rates on X65 and X70 samples in solution O₂/CO₂, no published literature corrosion rate data on X80 carbon steel in solution with O₂/CO₂ to compare and validate the calculated experimental corrosion rates values of the exposed X80 samples.

From the analysed maximum corrosion rates of the exposed X80 carbon steel (max. of 0.706 mm/year, 1.571 mm/year and 2.830 mm/year, respectively at 5 °C, 15 °C and 25 °C) in comparison with X70 (max. of 0.674 mm/year, 1.531 mm/year and 3.465 mm/year, respectively at 5 °C, 15 °C and 25 °C) and X65 (max. of 0.687 mm/year, 1.561 mm/year and 2.525 mm/year, respectively at 5 °C, 15 °C and 25 °C), no significant difference in corrosion rates between the samples at lower temperatures of 5 °C and 15 °C. However, at 25 °C, the X70 carbon steel presented higher corrosion rates relative to the X80 and X65. This indicates that the X70 carbon steel is more susceptible to SCC in the simulated 3.5 % solution saturated with 20%O₂/80%/CO₂ at 25 °C. As such selection of carbon steels as a pipeline material for operation in a seawater environment for transportation of CO₂ or other oil and gas products which contains traces of CO₂ or O₂ should be between X65 and X80 if its operation will be at 25 °C or above, as in the case of tropical regions with temperatures above 30 °C.

7.1.1.4 Corrosion Rates and Potentials of X100 C-rings Specimens

Figures 7-5a to 7-5f show the corrosion rates and potentials of the exposed X100 carbon steel samples in solution with O₂/CO₂ at 5 °C, 15 °C and 25 °C. Different corrosion rates trends were observed for the exposed X100 samples as 5 °C and 15 °C, (Figures 7-5a, and c, respectively), relative to the X65, X70 and X80

samples (Figures 7-1a, c; 7-2a, c and 7-4a, c, respectively). Continuous increase in corrosion rates with time throughout the test's duration was observed on the X100 samples at both 5 °C and 15 °C. Maximum values of 1.157 mm/year were obtained from the notched sample at 5 °C and 2.285 mm/year from the sample stressed at 80 % Y.S. at 15 °C. The change in corrosion rates with time obtained from the X100 samples exposed at 25 °C, were observed to be similar to the exposed X65, X70 and X80 samples exposed at 25 °C (Figures 7-1e, 7-2e and 7-4e, respectively). A decrease in corrosion rates was observed on all the X100 samples at 500 hrs of exposure, with continuous increase throughout the test's duration (Figure 7-5e). Maximum and minimum corrosion rate values of 4.057 mm/year and 2.398 mm/year, respectively at 840 hrs and 168 hrs of exposure were observed on the sample stressed at 80 % Y.S. and 95 % Y.S. as shown in Figure 7-5e. Similarly, as obtained from the X65, X70 and X80 samples, an increase in corrosion rates of more than 100 % was observed on the X100 samples with increasing temperature from 5 °C to 25 °C. At all solution temperatures, continuous increase in corrosion potentials were observed on all X100 samples (Figures 7-5b, d and f). Maximum potentials of -608 mV_{Ag/AgCl} and -624 mV_{Ag/AgCl}, respectively, were obtained from the sample stressed at 95 % at 15 °C (Figure 7-5d) and sample stressed at 80 % Y.S. at 25 °C (Figure 7-5f). Figures 7-6a, b and c respectively, show the after exposure images of X100 C-rings samples in solution with O₂/CO₂ exposed at the different solution temperatures.

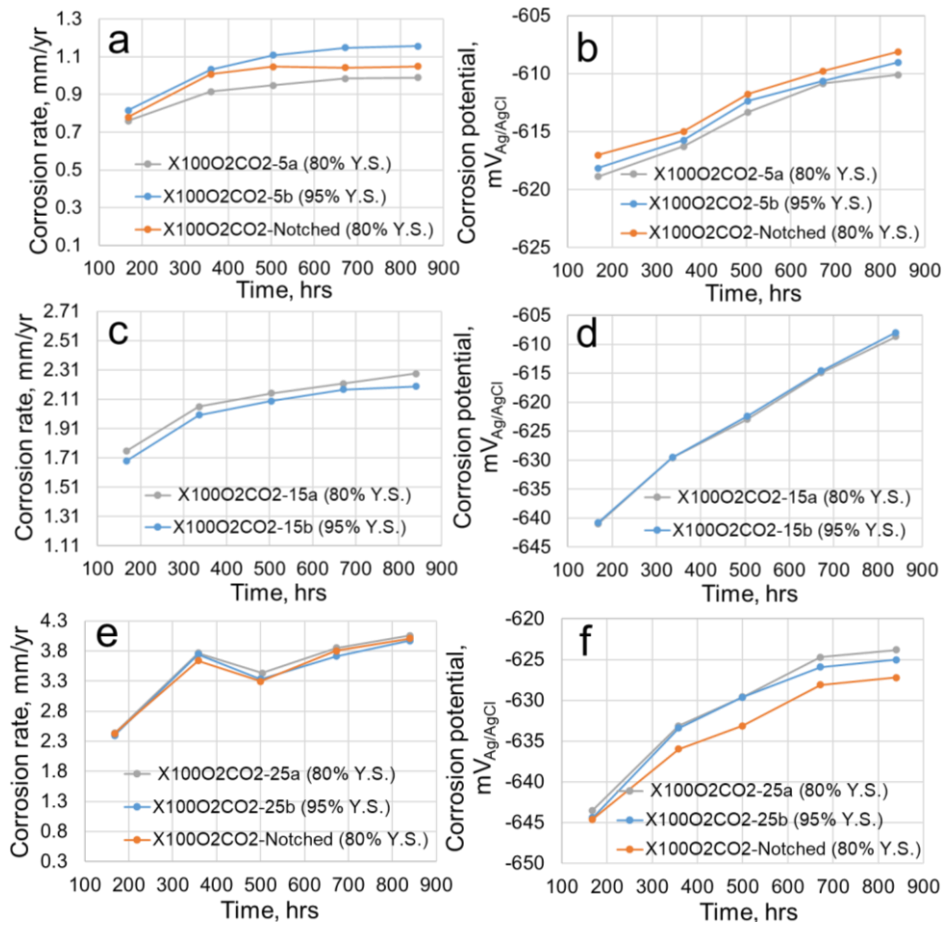


Figure 7-5 - Corrosion rates and potentials of the exposed X100 carbon steel C-rings in simulated saltwater solution with O₂/CO₂: (a) corrosion rates at 5 °C; (b) potentials at 5 °C; (c) corrosion rates at 15 °C; (d) potentials at 15 °C; (e) corrosion rates at 25 °C; (f) potentials at 25 °C.

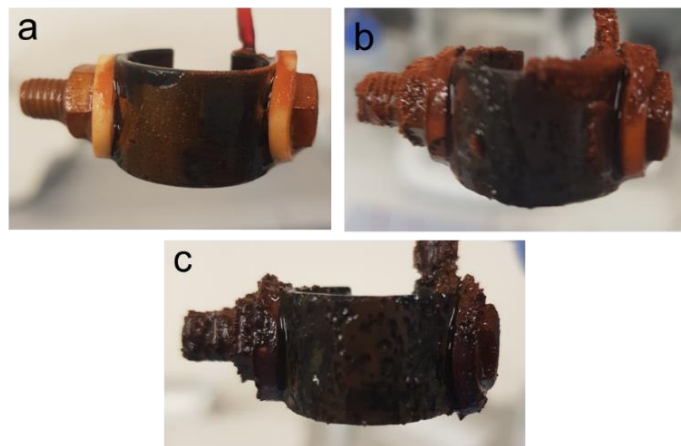


Figure 7-6 - Images of X100 C-rings samples after 840 hrs of exposure in simulated saltwater solution with O₂/CO₂: (a) at 5 °C; (b) at 15 °C; (c) at 25 °C. As shown in the image increasing accumulation of corrosion products on the sample's surfaces is observed with increasing solution temperature.

As observed from the calculated corrosion rates on the exposed X70 and X80 samples at 15 °C and 25 °C, no significant statistical variations in corrosion rates observed on the X100 samples with change in applied stress level from 80 % Y.S. to 95 % Y.S. at both 15 °C and 25 °C. However, increasing corrosion rates were observed at 5 °C with increasing stress level from 80 % Y.S. to 95 % Y.S. at 5 °C, with a decrease in corrosion rates with increasing applied stress level from 80 % to 95 % as also observed on the exposed X65 samples at 5 °C and 15 °C. As observed on the X70 carbon steel samples, an increase in corrosion rates of about 100 % was observed on the X100 samples with increasing temperature from 5 °C to 15 °C and 15 °C to 25 °C, relative to X65 and X80 with about 60 % increase from 15 °C to 25 °C. An increase in corrosion rates of about 70 % was observed on the X100 samples at 15 °C and 25 °C with change in trace gas mixture from 100 % CO₂ (max. of 1.666 mm/year and 2.821 mm/year, respectively at 15 °C and 25 °C) to 20%O₂/80%CO₂ (max. of 2.285 mm/year and 4.057 mm/year, respectively at 15 °C and 25 °C), relative to X65, X70 and X80 samples with an increase of more than 100 %. No significant change in corrosion rates on the X100 samples at 5 °C with change in trace gas from 100% CO₂ (max. of 1.112 mm/year) to 20%O₂/80%CO₂ (max. of 1.157 mm/year). No published literature data on corrosion rates of X100 carbon steel in saturated O₂/CO₂ environment to compare and validate the obtained experimental corrosion rates of the exposed X100 carbon steel samples.

The X100 samples in all exposure conditions, in solution with N₂ (chapter 4), CO₂ (chapter 5) and O₂/N₂ (chapter 6) were observed to present higher corrosion rates at all solution temperatures, in comparison with X65, X70 and X80 samples. Similarly, higher corrosion rates were observed on the X100 samples in solution with O₂/CO₂ at all solution temperatures (max. of 1.157 mm/year, 2.285 mm/year and 4.057 mm/year, respectively at 5 °C, 15 °C and 25 °C) in comparison with X80 (max. of 0.706 mm/year, 1.571 mm/year and 2.830 mm/year, respectively at 5 °C, 15 °C and 25 °C), X70 (max. of 0.674 mm/year, 1.531 mm/year and 3.465 mm/year, respectively at 5 °C, 15 °C and 25 °C) and X65 (max of 0.687 mm/year, 1.561 mm/year and 2.525 mm/year, respectively at 5 °C, 15 °C and 25 °C). This shows that the X100 carbon steels in all exposure conditions has higher corrosion

current density, which leads to fast release of electrons and cathodic reactions rates, and subsequent increase in corrosion rates.

From the analysed calculated corrosion rate values, the X100 carbon steel presented higher susceptibility to SCC in all exposure conditions. As such selection of carbon steels as a pipeline material for operation in a seawater environment for transportation of CO₂ or other oil and gas products which contains traces of CO₂ or O₂ should be between X65, 70 or X80, which showed lower susceptibility to SCC, relative to X100 in all the simulated representative pipeline operating conditions.

7.1.2 Metal Loss Exceedance

Dimensional metrology after an exposed period of 840 hrs was conducted on the exposed samples by optical microscopy to measure the cumulative probability of metal loss exceedance of the samples. An error of $\pm 5 \mu\text{m}$ is assumed for all metal loss measurements.

7.1.2.1 Cumulative Probability of Metal Loss Exceedance of X65 C-rings Specimens

Figures 7-7a, 7-7b and 7-7c, respectively, show the cumulative probability of metal loss exceedance, obtained from the datasets of the exposed X65 samples in solution with O₂/CO₂ at 5 °C, 15 °C and 25 °C. Datasets for all samples exposed at 5 °C as shown in Figure 7-7a presents significant metal change over whole sample's surfaces, with higher pits features observed on the sample stressed at 80 % Y.S. below about 15 % or less probability level. Maximum metal loss of -73 μm was observed on the sample stressed at 95 % Y.S. Low metal change was observed on all samples exposed at 15 °C (Figure 7-7b), with pits features below about 6 % probability level or less observed on the sample stressed at 80 % Y.S. The sample stressed at 80 % Y.S. and notched samples exposed at 25 °C (Figure 7-7c), show an even distribution of metal change over most of the sample's surfaces. However, the sample stressed at 95 % was observed to present significant metal change over half of the samples surface. Higher pits features were detected on the sample stressed at 80 % Y.S. below

about 9 % or less probability level. Maximum metal loss of -156 μm and -245 μm , respectively at 15 $^{\circ}\text{C}$ and 25 $^{\circ}\text{C}$ were observed on the sample stressed at 80 % Y.S.

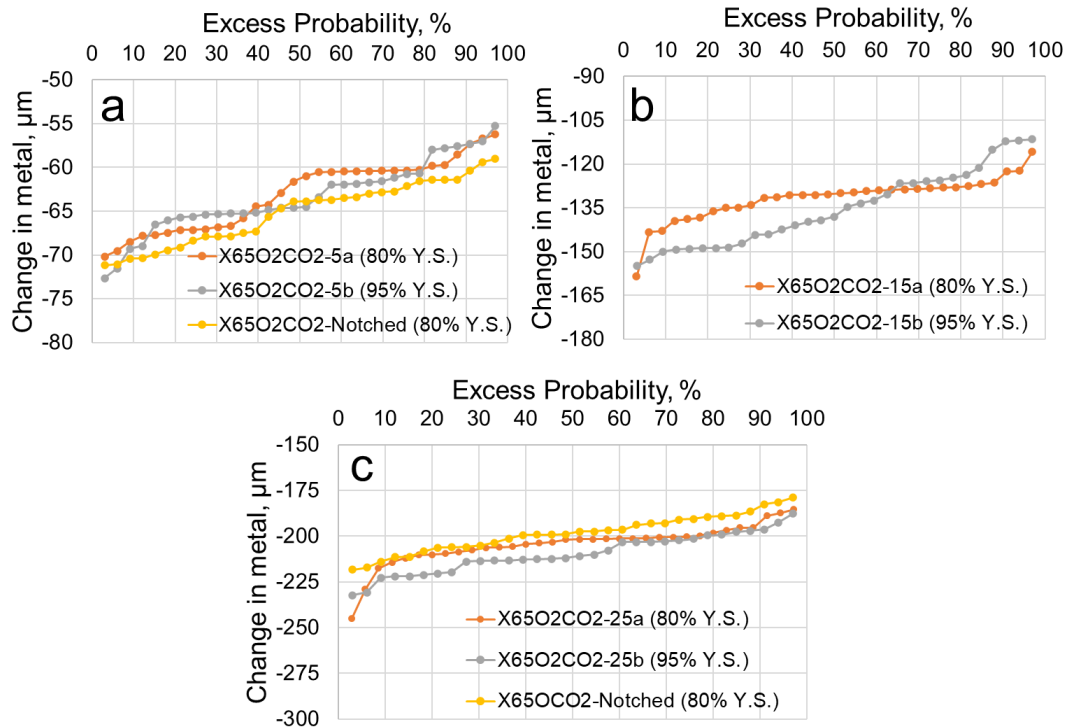


Figure 7-7 - Cumulative probability of metal loss exceedance graphs of X65 C-rings samples exposed in simulated saltwater solution with O_2/CO_2 : (a) at 5 $^{\circ}\text{C}$; (b) at 15 $^{\circ}\text{C}$; (c) at 25 $^{\circ}\text{C}$.

In general, as observed from the calculated corrosion rates of the exposed X65 samples from LPR measurements, no significant change in metal loss observed on the samples with change in applied stress level from 80 % Y.S. to 95 % Y.S. and surface state of the samples (notched state), with accounting an error of $\pm 5 \mu\text{m}$ in the measurement of the metal loss exceedance. The measured metal loss exceedance values tallies with the calculated corrosion rates from LPR measurements when converted to 840 hrs (5 weeks) exposure time. A maximum of 2.525 mm/year was observed for the sample stressed at 80 % Y.S at 25 $^{\circ}\text{C}$ as shown in Figure 7-1e, converting the calculated corrosion rate value to a metal loss of 840 hrs gives a value of -243 μm ($\pm 5 \mu\text{m}$). As observed from the calculated corrosion rates from LPR measurements, an increase in metal loss of more than

100 % was measured on the X65 samples with increasing temperature from 5 °C to 15 °C, with about 60 % from 15 °C to 25 °C.

7.1.2.2 Cumulative Probability of Metal Loss Exceedance of X70 C-rings Specimens

Figures 7-8a, 7-8b and 7-8c, respectively, show the cumulative probability of metal loss exceedance, obtained from the datasets of the exposed X70 samples in solution with O₂/CO₂ at 5 °C, 15 °C and 25 °C. Relatively low metal change was observed on all the X70 samples exposed at 5 °C at all stress levels in comparison with X65 samples exposed at 5 °C. Higher pits features were observed on the notched sample below about 24 % or less probability level, with higher metal loss of -70 µm. In comparison with samples exposed at 5 °C, dataset for the samples exposed at 15 °C show higher metal change over half of the sample's surfaces with an uneven damage distribution (Figure 7-8b). Low pits features were observed on all the samples at 15 °C below about 6 % or less probability level, with highest metal loss of -154 µm observed on the sample stressed at 80 % Y.S. An even distribution of metal damage was observed on all samples exposed at 25 °C (Figure 7-8c), with low pits features. Highest metal loss of -337 µm was observed on the sample stressed at 95 % Y.S. The exposed X65 samples at all solution temperatures were observed to show significant metal change in comparison with the exposed X70 samples.

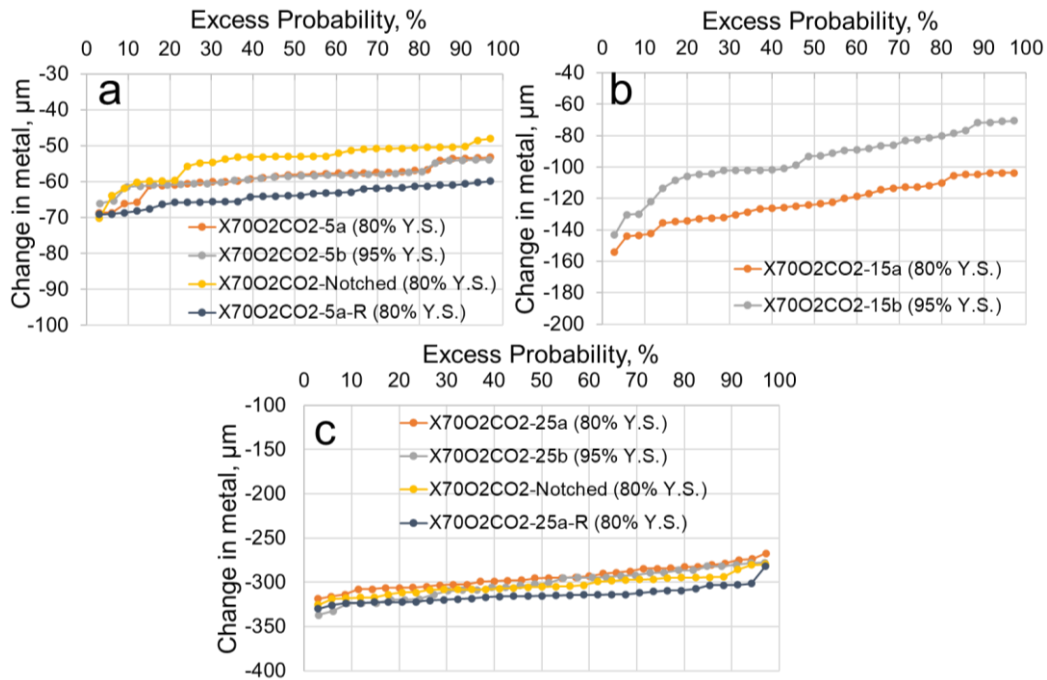


Figure 7-8 - Cumulative probability of metal loss exceedance graphs of X70 C-rings samples exposed in simulated saltwater solution with O₂/CO₂: (a) at 5 °C; (b) at 15 °C; (c) at 25 °C.

As observed from the calculated corrosion rate values on the exposed X70 samples in solution with O₂/CO₂, no significant change in metal loss value observed on the samples with change in applied stress level from 80 % Y.S. to 95 % Y.S. and surface state of the samples (notched state), with accounting an error $\pm 5 \mu\text{m}$ in the measured metal loss values. Similarly, as observed from the calculated corrosion rates of the X70 samples, highest metal loss was also observed on the sample stressed at 95 % Y.S. with a value of $-337 \mu\text{m}$ at 25 °C. The calculated maximum corrosion rates from LPR measurements with a value of 3.465 mm/year as shown in Figure 7-2e, tallies with the measured metal loss value when converted to 840 hrs (5 weeks) of exposure, with a value of $-333 \mu\text{m}$ ($\pm 5 \mu\text{m}$).

As observed from the calculated corrosion rates, significant difference in measured metal loss exceedance values at 25 °C were observed between the exposed X65 samples (max. of $-245 \mu\text{m}$) and X70 samples (max. of $-337 \mu\text{m}$). An increase in metal loss of more than 100 % was measured on the X70 samples

with increasing temperature from 5 °C to 15 °C, and also from 15 °C to 25 °C, as also observed from the calculated corrosion rates from LPR measurements.

7.1.2.3 Cumulative Probability of Metal Loss Exceedance of X80 C-rings Specimens

Figures 7-9a, 7-9b and 7-9c, respectively, show the cumulative probability of metal loss exceedance, obtained from the datasets of the exposed X80 samples in solution with O₂/CO₂ at 5 °C, 15 °C and 25 °C. The datasets for all samples at all stress levels exposed at 5 °C as shown in Figure 7-9a present an even distribution of metal change over most of the sample's surfaces. Low pits features were observed on the samples stressed at 95 % Y.S. and notched sample below about 6 % probability level or less. Maximum metal loss of -70 µm was obtained on the sample stressed at 95 % Y.S. Increasing metal loss of more than 100 % was observed with increasing solution temperature from 5 °C to 15 °C as shown in Figure 7-9b. Relative to samples exposed at 5 °C, the samples exposed at 15 °C (Figure 7-9b) showed higher metal change with an uneven damage distribution over half of the samples surfaces. Low pits features were observed on the sample stressed at 80 % Y.S. below about 18 % probability or less, with a maximum metal loss of -159 µm. Similarly, as observed on the samples exposed at 15 °C, an uneven of metal change was also observed on all samples at 25 °C, with low pits features. Maximum metal loss of -276 µm was observed on the sample stressed at 80 % Y.S. In comparison with exposed X65, X70 and X80 samples, higher metal change and pits features were observed on the X65 samples at all exposure temperatures. This can occur as a result of variation in microstructures of the steels and their reaction to the solution temperatures.

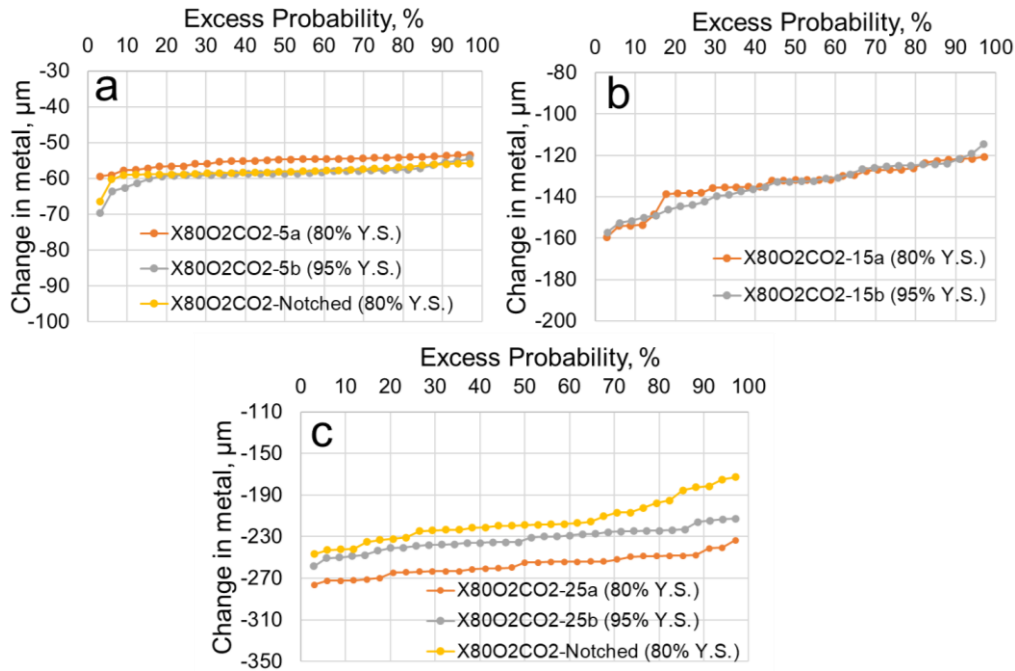


Figure 7-9 - Cumulative probability of metal loss exceedance graphs of X80 C-rings samples exposed in simulated saltwater solution with O_2/CO_2 : (a) at 5 °C; (b) at 15 °C; (c) at 25 °C.

Similarly, as reported from the calculated corrosion rates and metal loss values on the X65 and X70 samples, no significant difference in metal loss measured on the X80 samples with change in applied stress level from 80 % Y.S. to 95 % Y.S. and surface state (notched state) of the samples at all solution temperatures, with accounting an error of $\pm 5 \mu\text{m}$ in the measurement of the metal loss exceedance. However, the sample stressed at 80 % Y.S. as calculated from LPR measurements presented relatively higher metal loss in comparison with samples stressed at 95 % Y.S. and notched sample stressed at 80 % Y.S. As observed from the corrosion rates from LPR measurements, higher metal loss was measured on the X80 samples (max. of -276 μm at 25 °C), relative to X65 samples (max. of -245 μm at 25 °C). No significant difference in the measured metal loss at 5 °C and 15 °C, between the X65 (max. of -73 μm and -156 μm , respectively at 5 °C and 15 °C), X70 (max. of -70 μm and -154 μm , respectively at 5 °C and 15 °C) and X80 (max. of -70 μm and -159 μm , respectively at 5 °C and 15 °C) samples, as also observed from the calculated corrosion rates from LPR measurements.

The calculated corrosion rates from the X80 samples (max. of 2.830 mm/year) as presented in Figure 7-4e also tallies with measured metal loss exceedance values when converted to 840 hrs (5 weeks) of exposure, with a value of -272 μm ($\pm 5 \mu\text{m}$). As measured from the X65 samples, an increase in metal loss of more than 100 % was measured on the X80 samples with increasing temperature from 5 °C to 15 °C, and about 60 % from 15 °C to 25 °C.

7.1.2.4 Cumulative Probability of Metal Loss Exceedance of X100 C-rings Specimens

Figures 7-10a, 7-10b and 7-10c, respectively, show the cumulative probability of metal loss exceedance, obtained from the datasets of the exposed X100 samples in solution with O_2/CO_2 at 5 °C, 15 °C and 25 °C. The datasets for all exposed samples at 5 °C and 15 °C showed relatively even distribution of metal change over the sample's surfaces. No presence of pits features observed on the samples as shown in Figures 7-10a and b. Maximum metal loss of -116 μm was obtained from the sample stressed at 95 % Y.S. at 5 °C and -229 μm obtained from the sample stressed at 80 % Y.S at 15 °C. The samples exposed at 25 °C (Figure 7-10c) at all stress levels were observed to show relatively higher metal change over half of the sample's surfaces in comparison with samples exposed at 5 °C and 15 °C. High pits features were observed on the samples stressed at 80 % Y.S. and notched sample. Maximum metal loss of -396 μm was obtained from the sample at 25 °C.

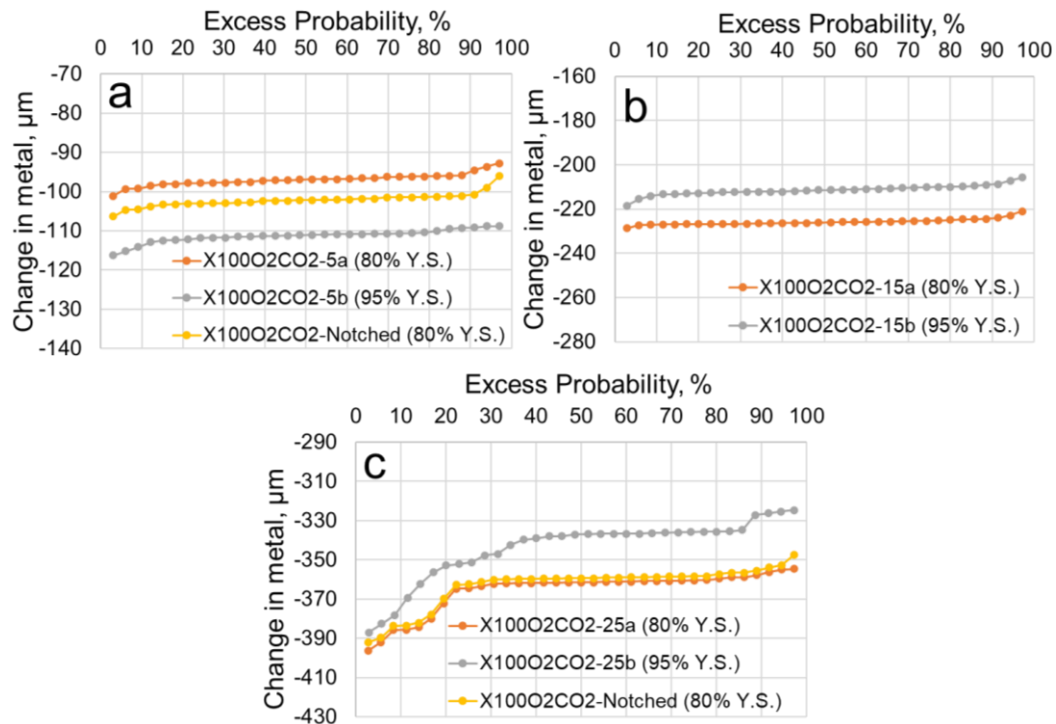


Figure 7-10 - Cumulative probability of metal loss exceedance graphs of X100 C-rings samples exposed in simulated saltwater solution with O₂/CO₂: (a) at 5 °C; (b) at 15 °C; (c) at 25 °C.

In general, the X100 samples at all exposure temperatures as also observed in the measured metal loss exceedance in solution with N₂ (chapter 4), CO₂ (chapter 5) and O₂/N₂ (chapter 6), presented higher metal loss in solution with O₂/CO₂ with max of -396 μm at 25 °C, in comparison with X65 (max. of -246 μm), X70 (max. of -337 μm) and X80 (max. of -276 μm) samples. Similarly, as observed from the calculated corrosion rates from LPR measurements, increasing metal loss was observed with increasing applied stress level at 5 °C, with a decrease in metal loss at 15 °C with increasing applied stress from 80 % Y.S. to 95 % Y.S.

The calculated corrosion rate of the X100 samples (max. of 4.057 mm/year) as presented in Figure 7-5e also tallies with the measured metal loss values when converted to 840 hrs of exposure, with a value of -390 μm (± 5 μm). Similarly, as observed and reported from the calculated corrosion from LPR measurements, a metal loss increase of more than 100 % was measured on the X100 samples with increasing temperature from 5 °C to 15 °C, with an increase of about 60 % from 15 °C to 25 °C. The increased metal loss observed on the X100 samples in

comparison with X65, X70 and X80 samples, indicated that the X100 carbon steel is more susceptible to SCC in the simulated 3.5 % NaCl solution saturated with O₂/CO₂ at all exposure temperatures. As such its selection as a pipeline material to be installed and operated in a seawater environment for transportation of various oil and gas products should be the least to consider if there is availability of X65, X70 or X80.

7.1.3 Scanning Electron Microscopy Analysis

SEM analysis was conducted on the cross-sectional areas of the stress-oriented sections of the exposed C-rings samples to understand the type of corrosion morphology on the samples' surfaces with change in exposure conditions.

7.1.3.1 Scanning Electron Microscopy Images of X65 C-ring Specimens

Figures 7-11a to 7-11h, respectively, show the SEM images of the X65 samples stressed at 80 % Y.S, 95 % Y.S., and notched sample stressed at 80 % Y.S. exposed in solution with O₂/CO₂ at 5 °C, 15 °C and 25 °C. Increasing metal surface dissolution was observed on the samples at all stress levels with increasing solution temperature from at 5 °C (Figures 7-11a, d and g) to 15 °C (Figures 7-11b, e). No significant change in metal surface roughness was observed on the samples with increasing solution temperature from 15 °C to 25 °C (Figures 7-11c, f and h). At 5 °C, the samples at all stress levels were observed to have a combination of wide elliptical and undercutting type of morphology. Presence of discontinuous micro-cracks were observed on the samples stressed at 80 % Y.S. and 95 % Y.S. (Figures 7-11a, d). In comparison with samples exposed at 5 °C, the samples exposed at 15 °C (Figures 7-11b and e) were observed to have wider and deeper elliptical and undercutting metal dissolution. No clear increase in metal dissolution observed on the samples with increasing applied stress level from 80 % Y.S. to 95 % Y.S. and surface state of the samples. At 25 °C (Figures 7-11c, f and h), the samples were observed to have higher surface deterioration relative to samples exposed at 15 °C, but with similar surface morphology. Similarly, as observed on samples in solution with

CO₂ (chapter 5), discontinuous micro-cracks were observed on all samples exposed in solution with O₂/CO₂ at 15 °C and 25 °C.

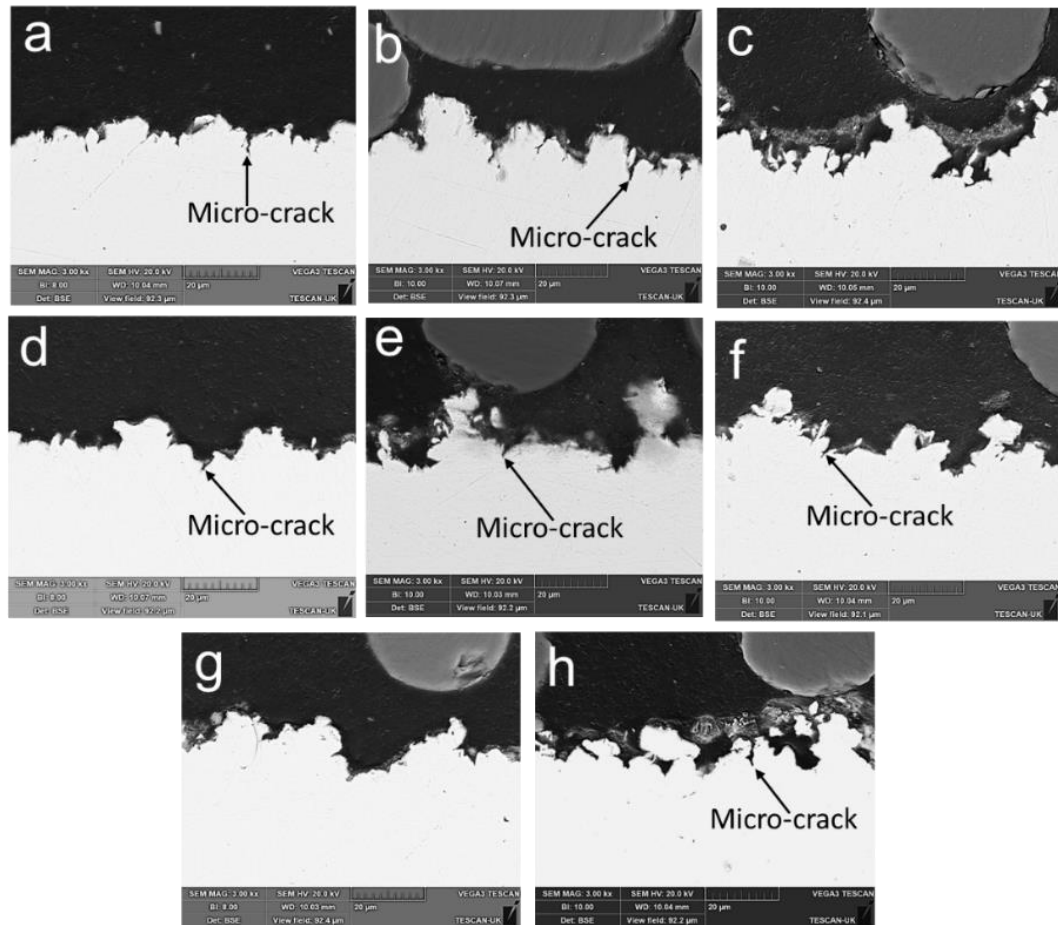


Figure 7-11 - SEM backscattered electron images of the exposed X65 C-ring samples in simulated saltwater solution with O₂/CO₂ stressed at 80 % Y.S., 95 % Y.S. and notched sample stressed at 80 % Y.S.: (a) 80 % Y.S. at 5 °C; (b) 80 % Y.S. at 15 °C; (c) 80 % Y.S. at 25 °C; (d) 95 % Y.S. at 5 °C; (e) 95 % Y.S. at 15 °C; (f) 95 % Y.S. at 25 °C; (g) Notched sample at 5 °C; (h) Notched sample at 25 °C.

7.1.3.2 Scanning Electron Microscopy Images of X70 C-ring Specimens

Figures 7-12a to 7-12h, respectively, show the SEM images of the X70 C-ring samples stressed at 80 % Y.S, 95 % Y.S., and notched sample stressed at 80 % Y.S. exposed in solution with O₂/CO₂ at 5 °C, 15 °C and 25 °C. As observed on the X65 samples (Figure 7-11), an increase in metal surface dissolution was

observed on the X70 samples with increasing solution temperature from 5 °C to 25 °C. The X70 samples (with globular ferrite grains with grain boundary pearlite) exposed at 5 °C, in comparison with the X65 samples (with ferritic-pearlite grains), presented similar type of surface morphologies at all solution temperatures. The samples exposed at 5 °C (Figures 7-12a, b, f and i) were also observed to have a combination of wide elliptical and undercutting type of surface morphology, which are greater at 15 °C (Figures 7-12c, g) and 25 °C (Figures 7-12d, e, h and j). Discontinuous micro-cracks were observed on the samples stressed at 95 % Y.S. (Figures 7-12f, g and h) at all solution temperatures. Similarly, as observed on X70 samples exposed in solution with CO₂ (chapter 5), no clear increase in surface deterioration was observed with change in applied stress level and surface state of the samples at the different solution temperatures.

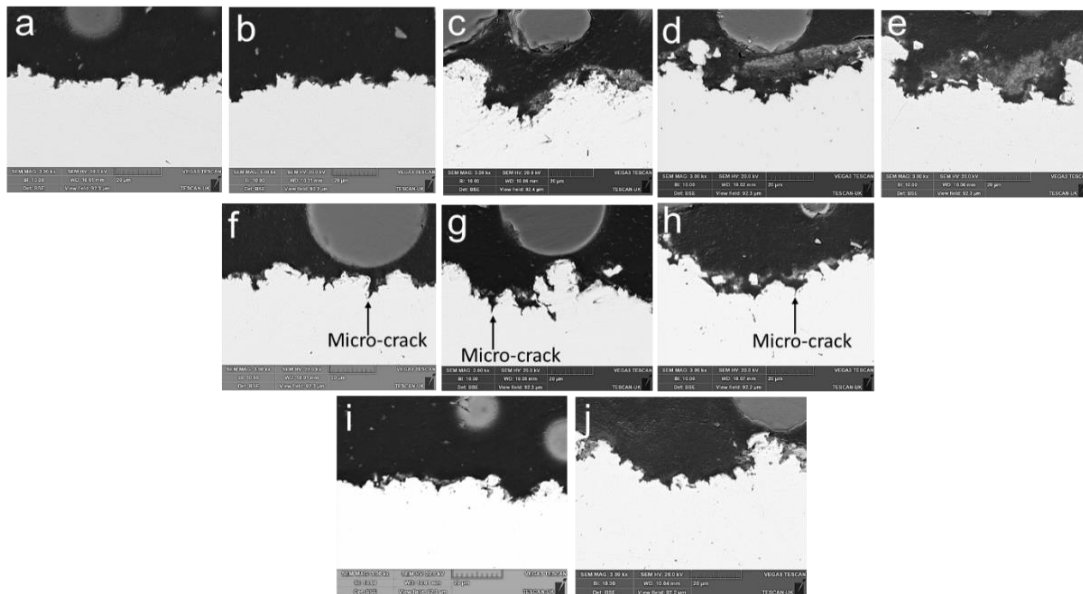


Figure 7-12 - SEM backscattered electron images of the exposed X70 C-ring samples in simulated saltwater solution with O₂/CO₂ stressed at 80 % Y.S., 95 % Y.S. and notched sample stressed at 80 % Y.S.: (a) 80 % Y.S. at 5 °C; (b) Repeat sample- 80 % Y.S. at 5 °C; (c) 80 % Y.S. at 15 °C; (d) 80 % Y.S. at 25 °C; (e) Repeat sample- 80 % Y.S. at 25 °C; (f) 95 % Y.S. at 5 °C; (g) 95 % Y.S. at 15 °C; (h) 95 % Y.S. at 25 °C; (i) Notched sample at 5 °C; (j) Notched sample at 25 °C.

7.1.3.3 Scanning Electron Microscopy Images of X80 C-ring Specimens

Figures 7-13a to 7-13h, respectively, show the SEM images of the X80 samples stressed at 80 % Y.S, 95 % Y.S., and notched sample stressed at 80 % Y.S. exposed in solution with O₂/CO₂ at 5 °C, 15 °C and 25 °C. As observed on the exposed X65 and X70 samples, increasing surface roughness was also observed on the X80 samples with increasing temperature from 5 °C to 25 °C. The samples exposed at 5 °C (Figures 7-13a, d and g) at all stress levels were observed to have a combination of shallow and wide elliptical surface morphology, with a combination of low undercutting morphology observed on the notched sample. The samples exposed at 15 °C at all stress levels (Figures 7-13b and e) were observed to show similar morphology relative to samples exposed at 5 °C, but with deeper and wider elliptical morphology. Higher metal surface deterioration with much wider and deeper elliptical corrosion morphology was observed on the samples exposed at 25 °C (Figures 7-13c, f and h) in comparison with samples exposed at 15 °C. The sample stressed at 95 % Y.S. and notched sample were also observed to have low undercutting metal dissolution. Presence on micro-crack was observed on the notched sample as shown in Figure 7-13h. As observed on the X65 and X70 samples, no clear difference in metal surface morphology observed on the samples with increasing applied stress level from 80 % Y.S. to 95 % Y.S.

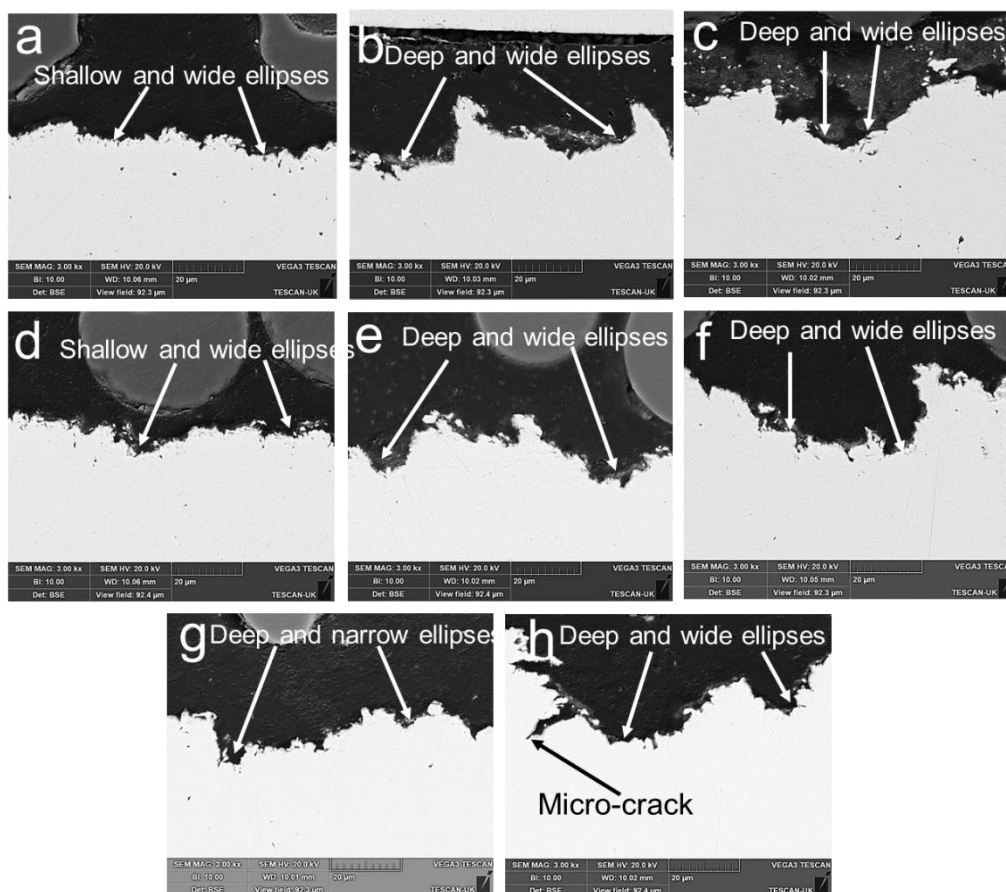


Figure 7-13 - SEM backscattered electron images of the exposed X80 C-ring samples in simulated saltwater solution with O_2/CO_2 stressed at 80 % Y.S., 95 % Y.S. and notched sample stressed at 80 % Y.S.: (a) 80 % Y.S. at 5 °C; (b) 80 % Y.S. at 15 °C; (c) 80 % Y.S. at 25 °C; (d) 95 % Y.S. at 5 °C; (e) 95 % Y.S. at 15 °C; (f) 95 % Y.S. at 25 °C; (g) Notched sample at 5 °C; (h) Notched sample at 25 °C.

7.1.3.4 Scanning Electron Microscopy Images of X100 C-ring Specimens

Figures 7-14a to 7-14h, respectively, show the SEM images of the X100 samples stressed at 80 % Y.S, 95 % Y.S., and notched sample stressed at 80 % Y.S. exposed in solution with O_2/CO_2 at 5 °C, 15 °C and 25 °C. Similar corrosion morphologies were observed on all X100 samples exposed in solution with O_2/CO_2 in comparison with X100 samples exposed in solution with CO_2 (chapter 5). The morphologies of the X100 samples (Figures 7-14a to h) at all stress levels were observed to have an even metal dissolution with shallow and wide elliptical

morphologies. Increasing surface roughness was observed on the samples with increasing temperature from 5 °C to 25 °C. Similarly, as observed on the X65, X70 and X80 samples no clear difference in metal surface roughness observed on the X100 with increasing applied stress level from 80 % Y.S. to 95 % Y.S. Similarly, as observed on the X100 samples exposed in solution with N₂ (chapter 4), CO₂ (chapter 5) and O₂/N₂ (chapter 6), no presence of micro-cracks observed on the X100 samples exposed in solution with O₂/CO₂ at all solution temperatures.

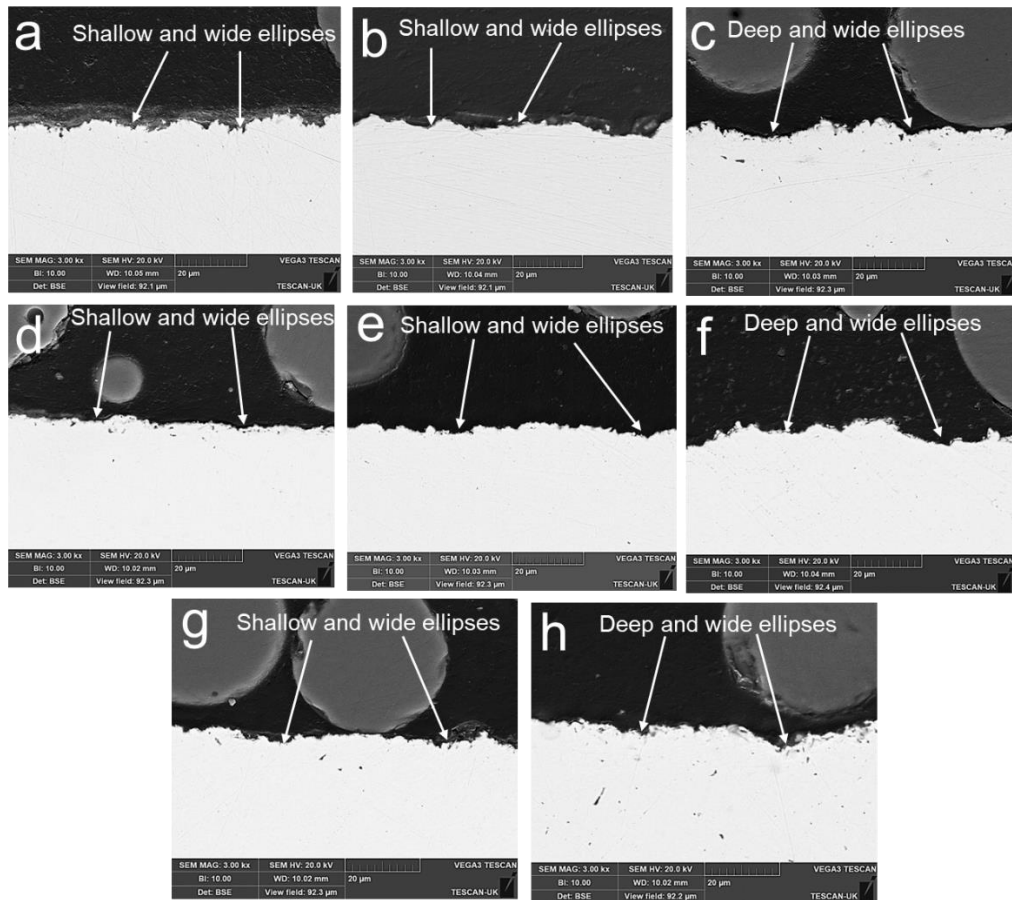


Figure 7-14 - SEM backscattered electron images of the exposed X100 C-ring samples in simulated saltwater solution with O₂/CO₂ stressed at 80 % Y.S., 95 % Y.S. and notched sample stressed at 80 % Y.S: (a) 80 % Y.S. at 5 °C; (b) 80 % Y.S. at 15 °C; (c) 80 % Y.S. at 25 °C; (d) 95 % Y.S. at 5 °C; (e) 95 % Y.S. at 15 °C; (f) 95 % Y.S. at 25 °C; (g) Notched sample at 5 °C; (h) Notched sample at 25 °C.

In general, change in surface corrosion morphology was observed on all exposed samples with increasing temperature from 5 °C to 25 °C. The X65 (with ferritic-pearlite grains) and X70 (with globular ferrite grains with grain boundary pearlite) exposed samples at all applied stress levels and solution temperatures presented similar type of surface corrosion morphology with a combination of wide elliptical and undercutting type of morphology, which are wider and deeper at 15 °C and 25 °C. In comparison with X65 and X70 samples, the X80 (with ferrite grains and pearlite bands) samples were observed to have deeper and wider elliptical, with shallow undercutting morphology at 15°C and 25 °C. Similarly, as observed on the X100 samples (with bainitic ferrite and austenite grains) exposed in solution with CO₂, the X100 samples exposed in solution with O₂/CO₂ also were observed to have a wide and shallow elliptical morphology, which increased in size with change in temperature from 5 °C to 25 °C. The X100 samples at all solution temperatures showed an even surface metal dissolution relative to X65, X70 and X80 samples. Similarly, as reported in chapter 5, the observed differences in surface corrosion morphologies of the carbon steels can be explained to occur as a result of differences in the microstructure of the carbon steels and the presence of precipitates in their microstructures. The presence of precipitate in a microstructure provides nucleation sites for crack initiation and hydrogen traps, which can lead to hydrogen embrittlement.

7.1.4 Energy Dispersive Spectroscopy

EDS analysis was conducted on the exposed samples to understand the variation in elemental compositions of the samples with change in exposure conditions. An error of ±5 % is assumed for all EDS measurements.

7.1.4.1 Energy Dispersive Spectroscopy Analysis of X70 C-rings Specimens

The compositions of the EDS spectra (Figure 7-15) of the exposed X70 sample in solution with O₂/CO₂ at 5 °C stressed at 80 % Y.S., are presented in Figure 7-16 (in weight percentages). As reported in previous chapters, the carbon content from all spectra will not be reported as EDS does not correctly quantify the

percentage of carbon present in the analyzed samples. Similarly, spectrum 1 which is mainly composed of resin will not also be reported in the analysis. As observed and reported on the X70 samples exposed in solution with N₂ (chapter 4), CO₂ (chapter 5) and O₂/N₂ (chapter 6), the percentage of Mn and Fe was also detected to change with change in spectrum location in exposed X70 sample in solution with O₂/CO₂ at 5 °C. Spectrum 4 which is fully on the alloy was observed to have higher percentage of Mn with a value 1.88 wt.%. Highest concentration of Fe was observed in spectrum 3 which is close to the interface with a value of 92.84 wt.%. and a value of 91.98 wt.% detected in spectrum 4.

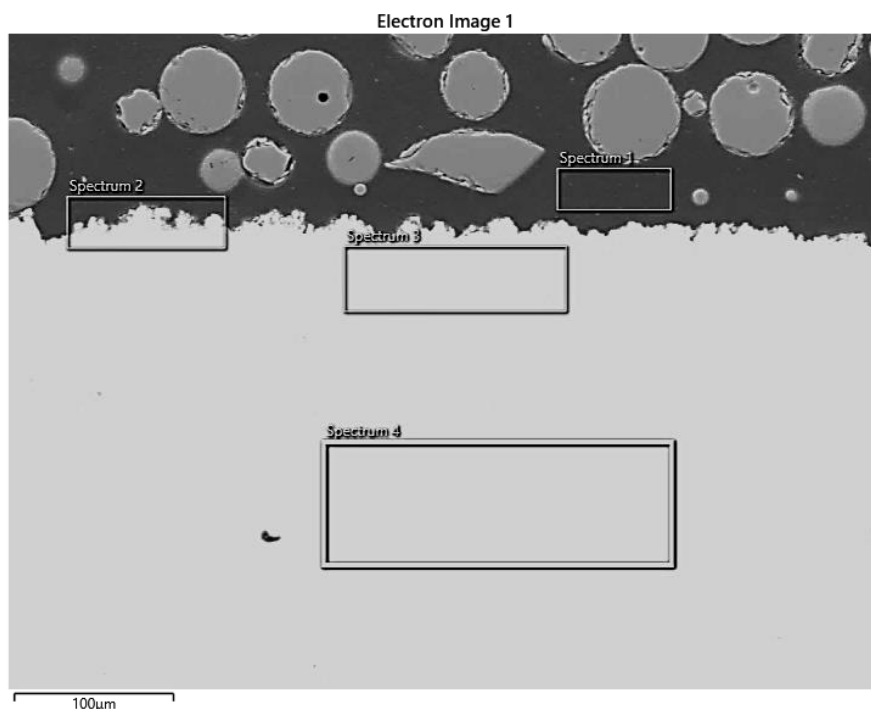


Figure 7-15 - SEM backscattered electron image of the exposed X70 C-ring sample in simulated saltwater solution with O₂/CO₂ at 5 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 7-16.

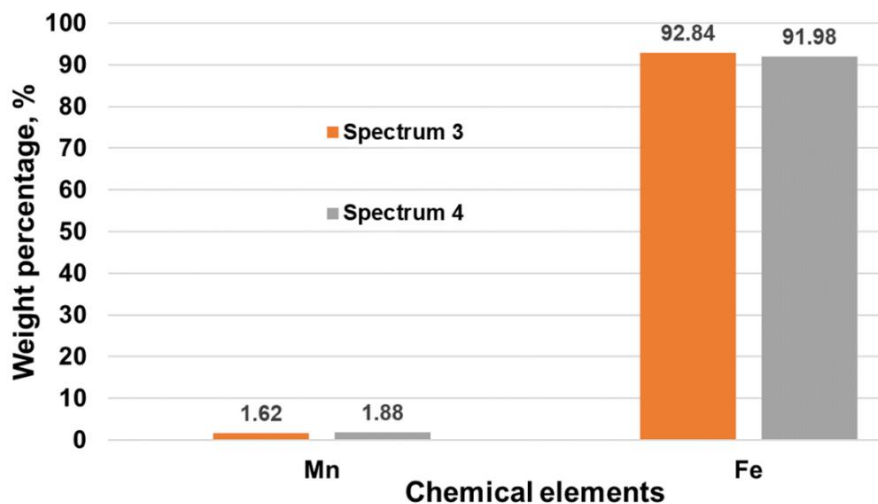


Figure 7-16 - EDS compositions of the exposed X70 C-ring sample elements in simulated saltwater solution with O₂/CO₂ at 5 °C stressed at 80 % Y.S.

Similarly, as observed on the X70 sample exposed in solution with CO₂ at 5 °C, a sharp increase of Fe content between the alloy-resin interface was also detected on the X70 samples exposed in solution with O₂/CO₂. Amount of O and C were also observed to be higher in the resin, with sharp increase below about 47 µm into the resin. Percentage of Si was detected to be higher in the alloy after about 45 µm.

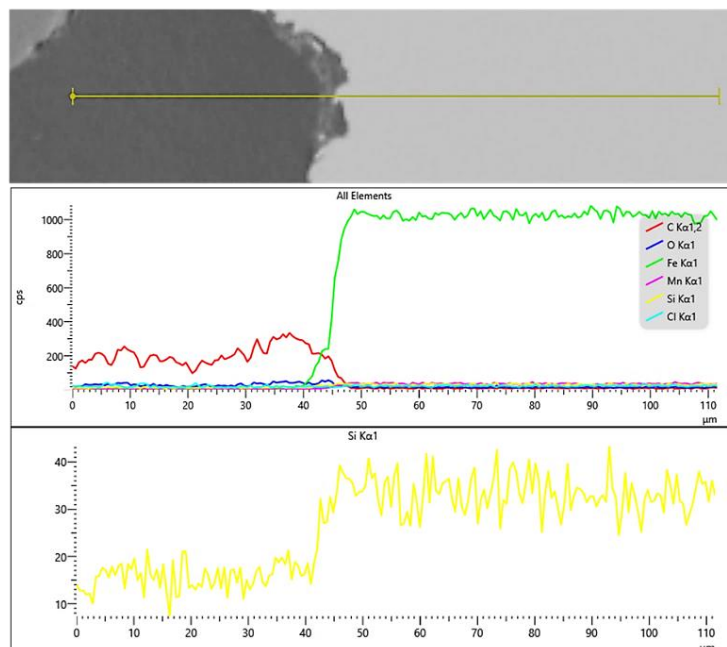


Figure 7-17 - EDS line scan analysis of the exposed X70 C-ring sample elements in simulated saltwater solution with O₂/CO₂ at 5 °C stressed at 80 % Y.S.

Differences in elemental compositions of the EDS spectra (Figure 7-18) of the exposed X70 C-ring sample in solution with O₂/CO₂ at 15 °C stressed at 80 % Y.S., were detected as shown in Figure 7-19 (in weight percentages). Similarly, as observed on the X70 samples exposed in solution with CO₂ at 15 °C (chapter 5), highest percentage of Mn was observed in spectrum 4 of the sample exposed in solution with O₂/CO₂ at 15 °C, with a value of 1.72 wt.%. Approximately, equal percentages of Fe were observed in spectrum 3 and 4, respectively, with values of 93.75 wt.% and 93.41 wt.%. No traces of O, Si or Cl detected in both samples exposed at both 5 °C and 15 °C.

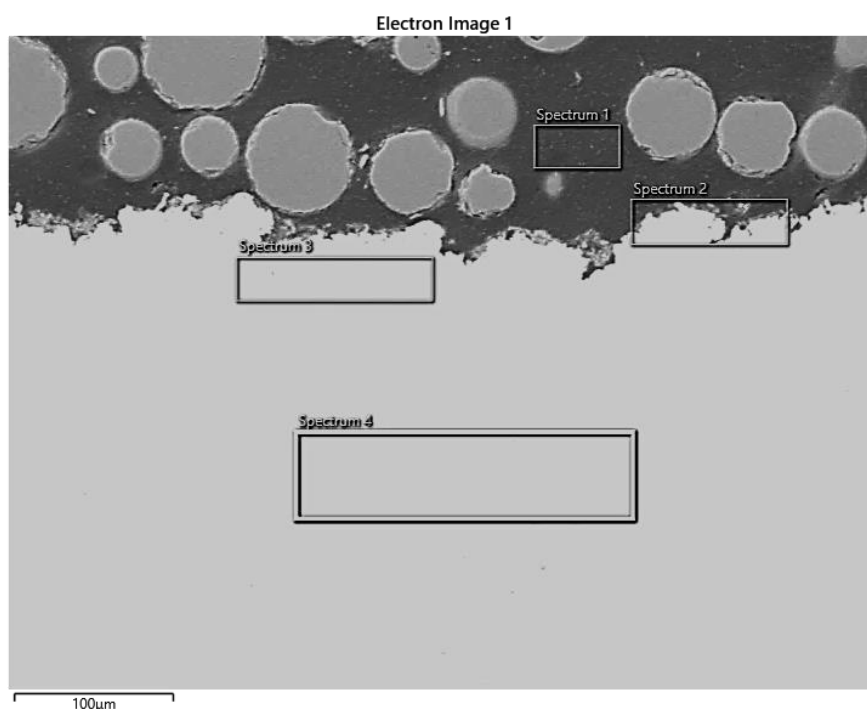


Figure 7-18 - SEM backscattered electron image of the exposed X70 C-ring sample in simulated saltwater solution with O₂/CO₂ at 15 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 7-19.

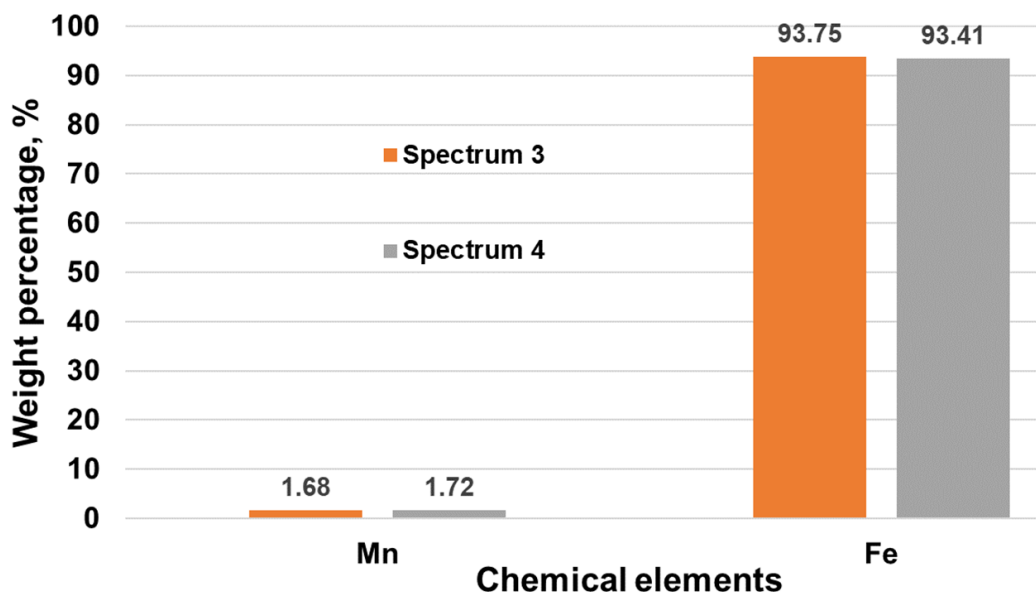


Figure 7-19 - EDS compositions of the exposed X70 C-ring sample elements in simulated saltwater solution with O₂/CO₂ at 15 °C stressed at 80 % Y.S.

The line scan analysis of the exposed X70 C-ring sample at 15 °C is shown in Figure 7-20. Similarly, as observed on the X70 sample exposed at 5 °C (Figure 7-17), the X70 sample exposed at 15 °C also showed a sharp increase of Fe concentration at the alloy-resin interface. The C concentration was similarly observed to be higher in the resin with sharp increase below about 60 µm into the resin. Similarly, as observed on the X70 samples exposed in solution with CO₂, differences in Si concentrations were observed along the line scan, with highest concentration detected at about 6 µm into the resin.

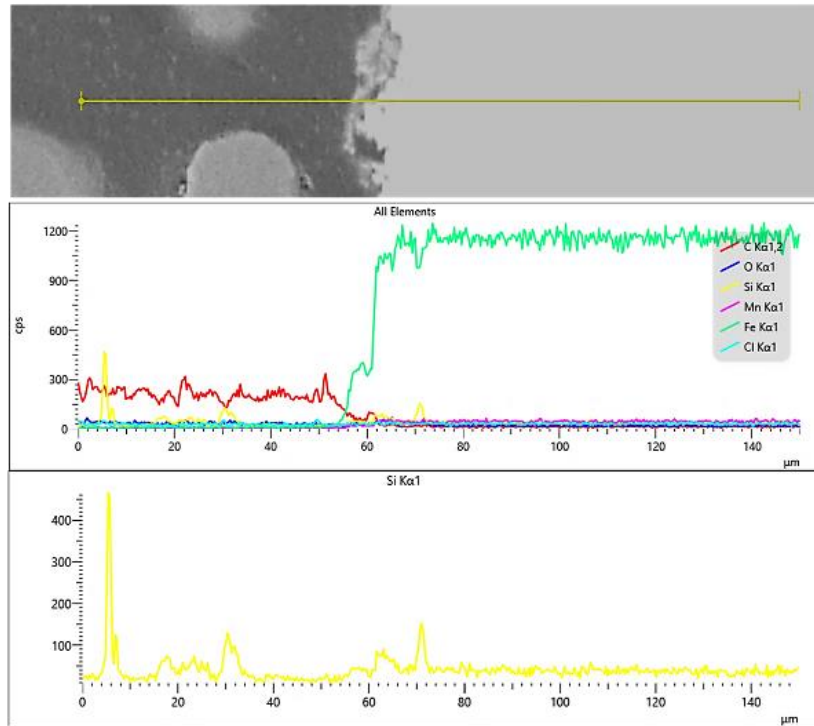


Figure 7-20 - EDS line scan analysis of the exposed X70 C-ring sample elements in simulated saltwater solution with O₂/CO₂ at 15 °C stressed at 80 % Y.S.

As presented in Figure 7-22, different compositions of the EDS spectra (Figure 7-21) were observed in the X70 C-ring sample stressed at 80 % Y.S. exposed in solution with O₂/CO₂ at 25 °C. Relative to sample exposed at 15 °C (with Fe concentration of 93.41 wt.%, spectrum 4), lower percentage of Fe was observed on the sample exposed at 25 °C in spectrum 4 which is fully on the alloy with a value of 92.64 wt.%. Concentration of Mn was also observed to be lower at 25 °C, with a value of 1.67 wt.%. in comparison with samples exposed at 15 °C with a value of 1.72 wt.% detected in spectrum 4.

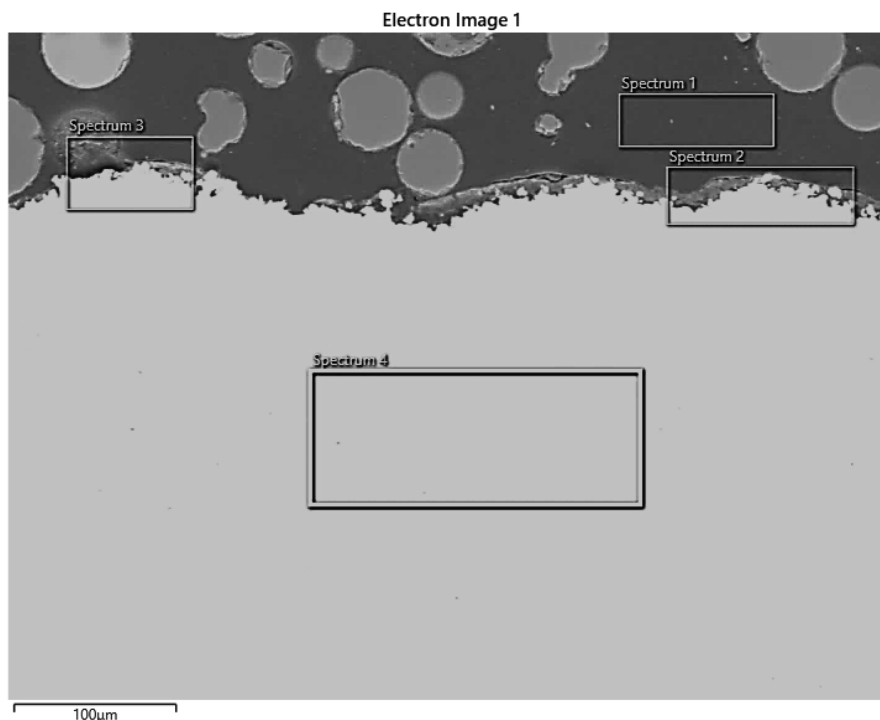


Figure 7-21 - SEM backscattered electron image of the exposed X70 C-ring sample in simulated saltwater solution with O_2/CO_2 at 25 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 7-22.

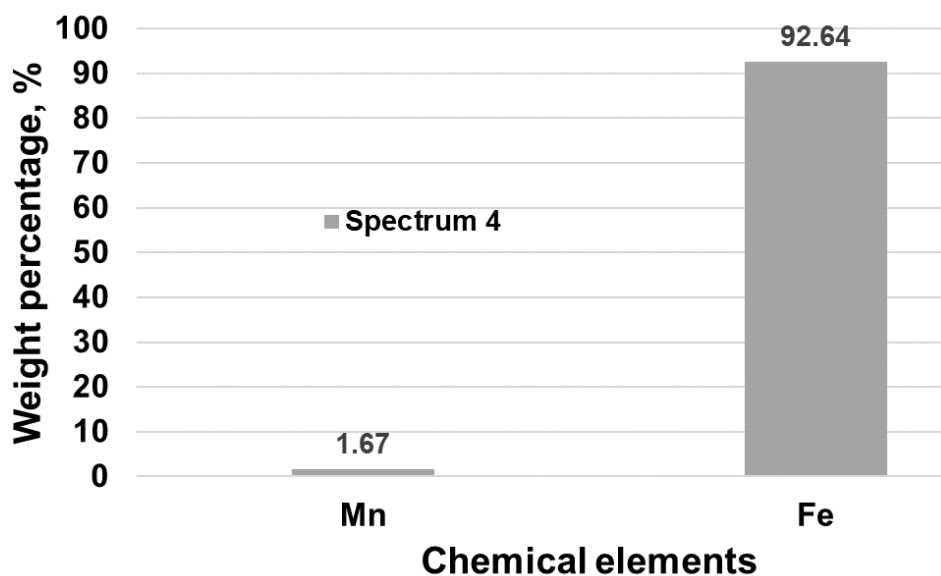


Figure 7-22 - EDS compositions of the exposed X70 C-ring sample elements in simulated saltwater solution with O_2/CO_2 at 25 °C stressed at 80 % Y.S.

Similarly, as presented from the analysis of the samples exposed at 5 °C and 15 °C, the line scan analysis of the X70 sample exposed at 25 °C (Figure 7-23)

also showed a sharp increase of Fe concentration at the alloy-resin interface. In comparison with samples exposed at 5 °C and 15 °C, the concentration of Si at 25 °C was observed to be higher at the alloy-resin interface at about 45 µm into the resin. Mn content is also clearly observed to be higher on the alloy from about 58 µm into the resin.

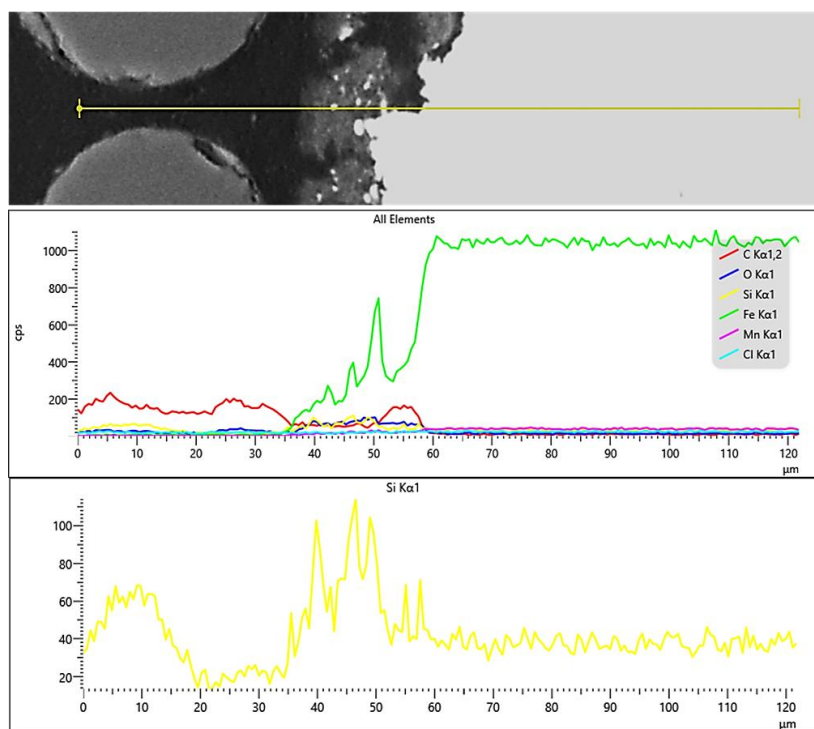


Figure 7-23 - EDS line scan analysis of the exposed X70 C-ring sample elements in simulated saltwater solution with O₂/CO₂ at 25 °C stressed at 80 % Y.S.

7.1.4.2 Energy Dispersive Spectroscopy Analysis of X100 C-rings Specimens

The composition of the EDS spectra as shown in Figure 7-24 for the X100 C-ring sample stressed at 80 % Y.S. exposed in solution with O₂/CO₂ at 5 °C is presented in Figure 7-25. As shown in Figure 7-25, spectrum 4 which is fully on the alloy material was detected to have Fe percentage of 91.87 wt.%, with Mn concentration of 1.95 wt.%. No traces of O, Si or Cl detected on the sample as also observed on the exposed X70 samples exposed in solution with O₂/CO₂ at all temperatures.

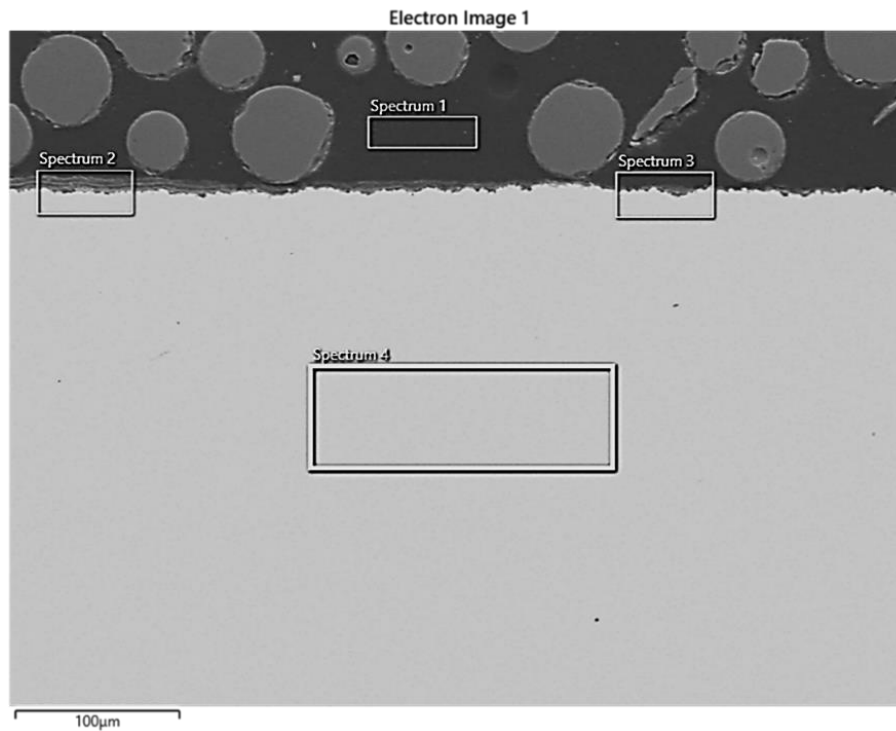


Figure 7-24 - SEM backscattered electron image of the exposed X100 C-ring sample in simulated saltwater solution with O_2/CO_2 at 5 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 7-25.

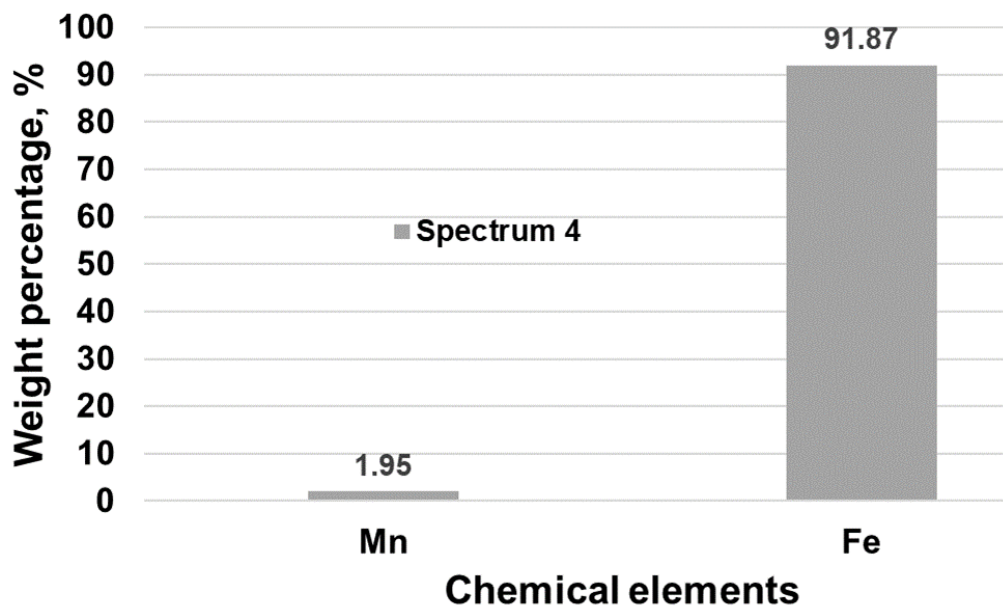


Figure 7-25 - EDS compositions of the exposed X100 C-ring sample elements in simulated saltwater solution with O_2/CO_2 at 5 °C stressed at 80 % Y.S.

The line scan analysis of the X100 C-ring sample exposed in solution with O₂/CO₂ at 5 °C is shown in Figure 7-26. Similarly, as observed on the sample exposed in solution with CO₂, concentration of Fe is also observed to be higher on the alloy section for the sample exposed in solution with O₂/CO₂, with sharp increase at the alloy-resin interface. The concentration of Mn is also detected to be higher on the alloy from about 51 μm into the resin. Si concentration is observed to be higher at about 3 μm into the resin. Similarly, as observed on other exposed X100 samples, the concentration of C is also detected to be higher in the resin.

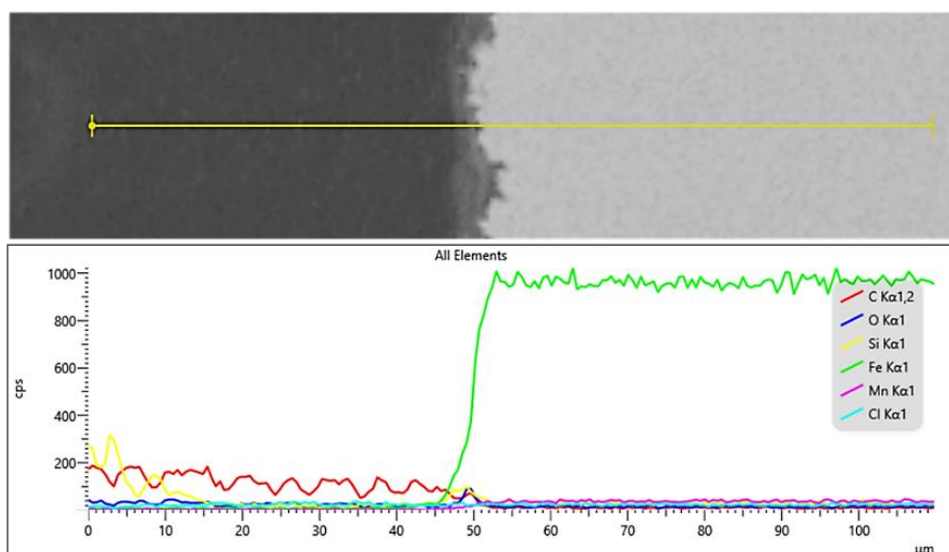


Figure 7-26 - EDS line scan analysis of the exposed X100 C-ring sample elements in simulated saltwater solution with O₂/CO₂ at 5 °C stressed at 80 % Y.S.

In comparison with X100 samples exposed at 5 °C (Figure 7-25), variations in elemental compositions of the EDS spectra (Figure 7-27) of the X100 C-ring sample exposed at 15 °C were observed. Generally, the percentage Mn and Fe detected on the sample as shown in Figure 7-28 were observed to be higher than those observed at 5 °C with values of 91.87 wt.% and 1.95 wt.%, respectively for Fe and Mn concentration. Maximum values of 2.04 wt.% and 93.79 wt.%, respectively were detected for Mn and Fe concentration in spectrum 3 and 4. No traces of O or Si detected on the samples at both 5 °C and 15 °C.

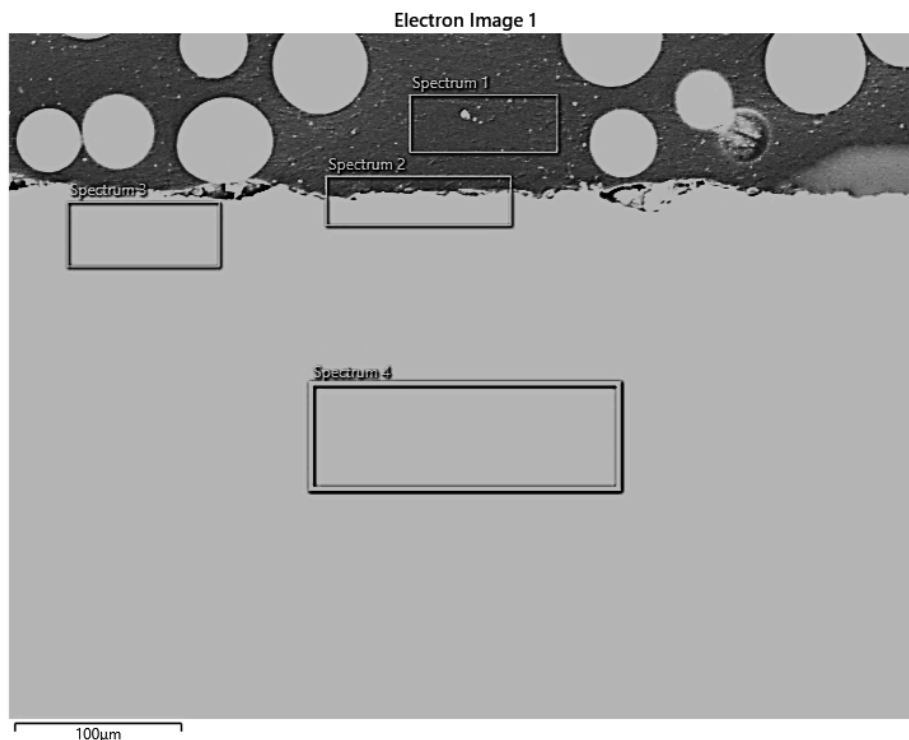


Figure 7-27 - SEM backscattered electron image of the exposed X100 C-ring sample in simulated saltwater solution with O₂/CO₂ at 15 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 7-28.

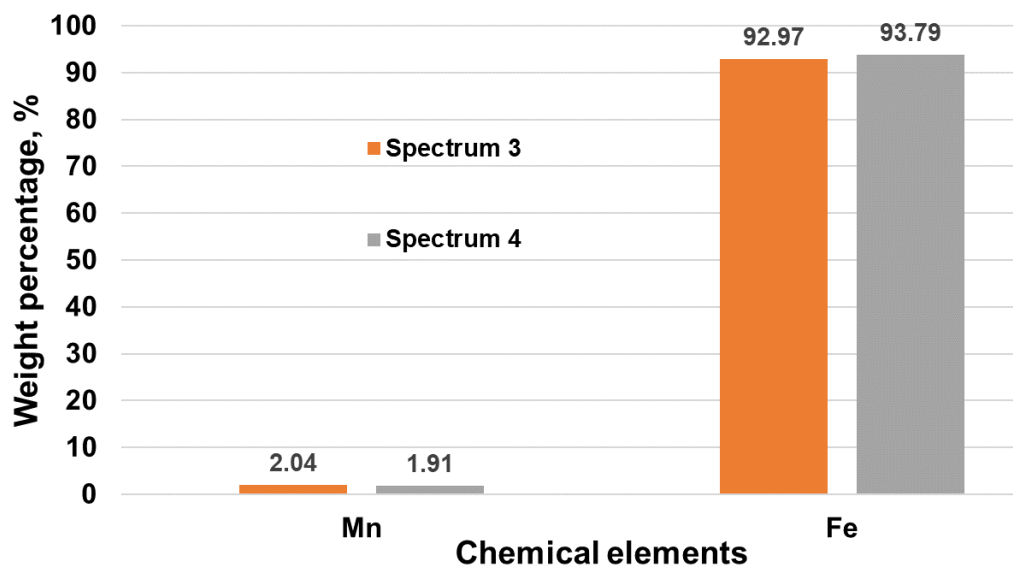


Figure 7-28 - EDS compositions of the exposed X100 sample elements in simulated saltwater solution with O₂/CO₂ at 15 °C stressed at 80 % Y.S.

The line scan analysis of the X100 C-ring sample exposed in solution with O₂/CO₂ at 15 °C is shown in Figure 7-29. In comparison with sample exposed at 5 °C,

similar trend in Mn and Fe concentration was observed at 15 °C. A sharp increase in Fe concentration was detected at the interface from about 49 μm into the resin. Mn content was also observed to be higher in the alloy. Relative to 5 °C (Figure 7-26), the Si content at 15 °C is detected to be higher at the alloy-resin interface.

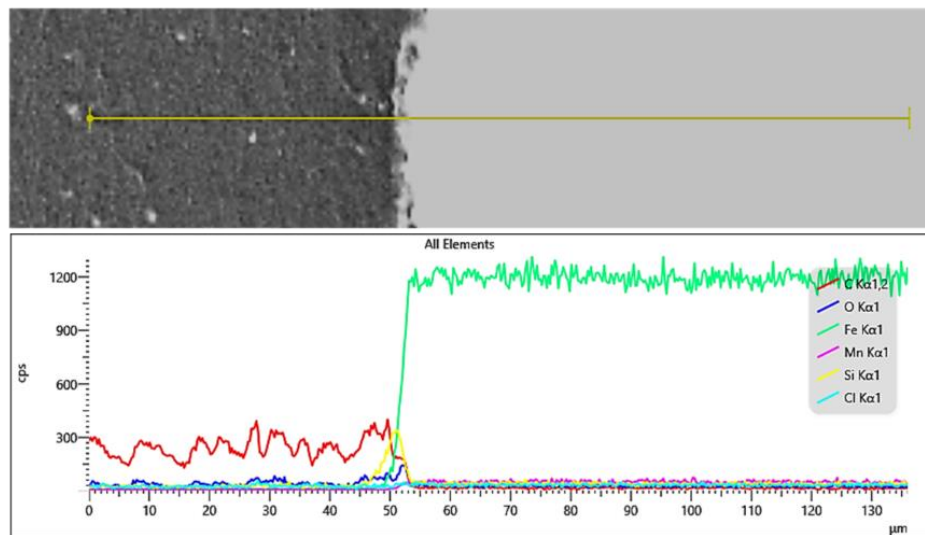


Figure 7-29 - EDS line scan analysis of the exposed X100 sample elements in simulated saltwater solution with O₂/CO₂ at 15 °C stressed at 80 % Y.S.

The elemental compositions of the EDS spectra (Figure 7-30) of the X100 C-ring sample stressed at 80 % Y.S. exposed at 25 °C are presented in Figure 7-31. Similarly, as observed on the exposed X70 and X100 samples exposed at 5 °C and 15 °C, change in percentage of Fe and Mn was observed with change in spectrum location. In comparison with the X100 sample exposed at 15 °C, lower percentages of Fe and Mn were detected on the sample exposed at 25 °C in spectrum 3, with values of 93.47 wt.% and 1.98 wt.%, respectively. Similarly, no presence of O, Si or Cl observed on the sample exposed at 25 °C.

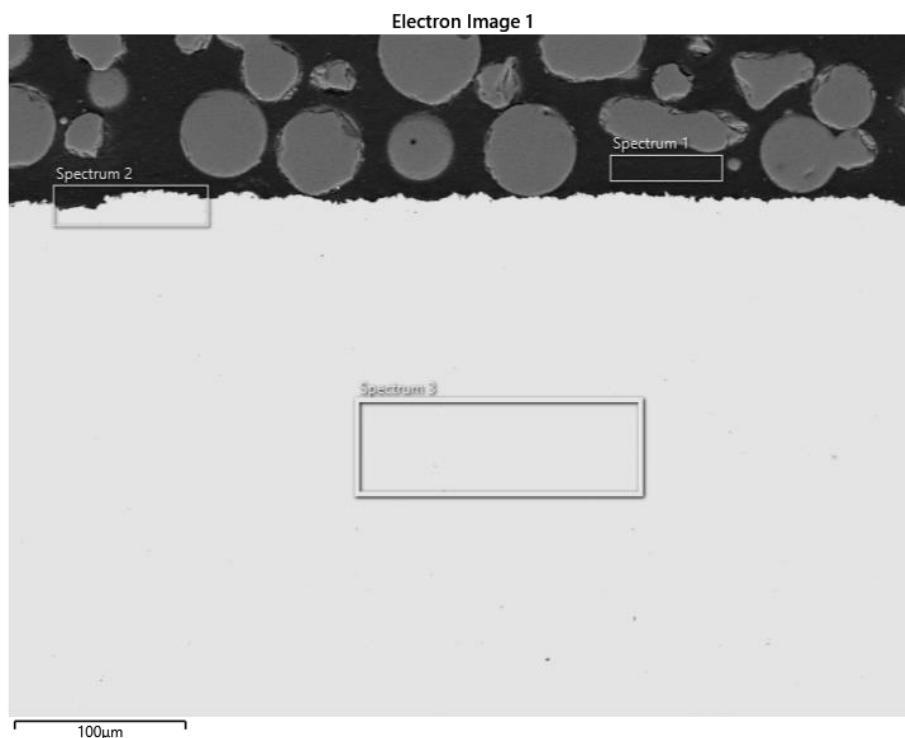


Figure 7-30 - SEM backscattered electron image of the exposed X100 C-ring sample in simulated saltwater solution with O_2/CO_2 at 25 °C stressed at 80 % Y.S. Data from the EDS spectra are reported in Figure 7-31.

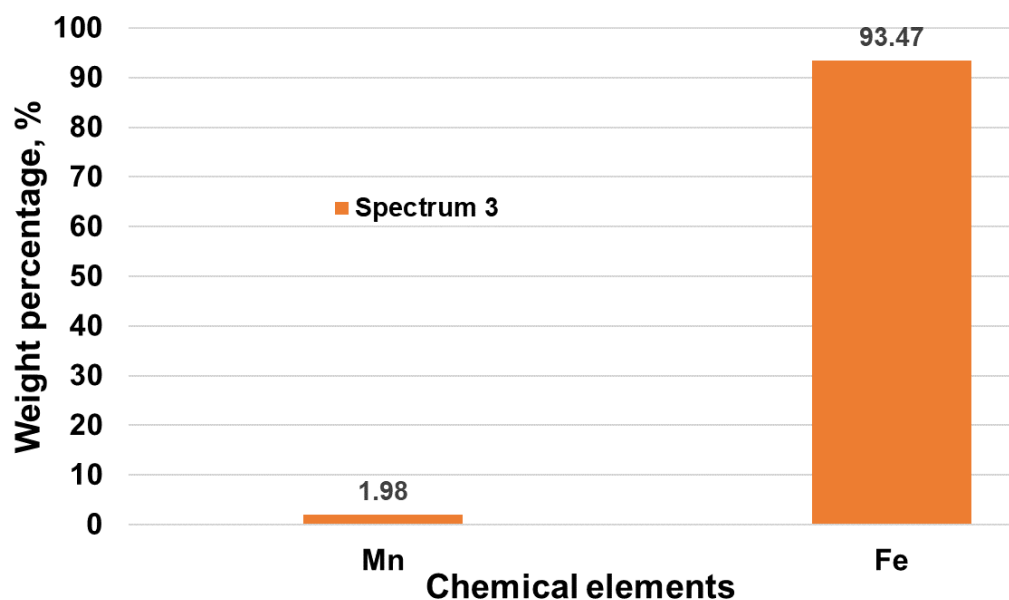


Figure 7-31 - EDS compositions of the exposed X100 sample elements in simulated saltwater solution with O_2/CO_2 at 25 °C stressed at 80 % Y.S.

The line scan analysis of the X100 sample exposed in solution with O₂/CO₂ at 25 °C (Figure 7-32) showed similar trend in Mn and Fe concentration in comparison with 5 °C and 15 °C. Highest concentration of Mn and Fe was detected on the alloy, with a sharp increase of Fe observed at the alloy-resin interface. Variation in Si concentration trend was observed at 25 °C, in comparison with 5 °C (Figure 7-26) and 15 °C (Figure 7-29). Highest concentration as shown in Figure 7-32 was detected on the alloy at about 109 μm into the line. As observed at 5 °C and 15 °C, the concentration of C and O were detected to be higher in the resin.

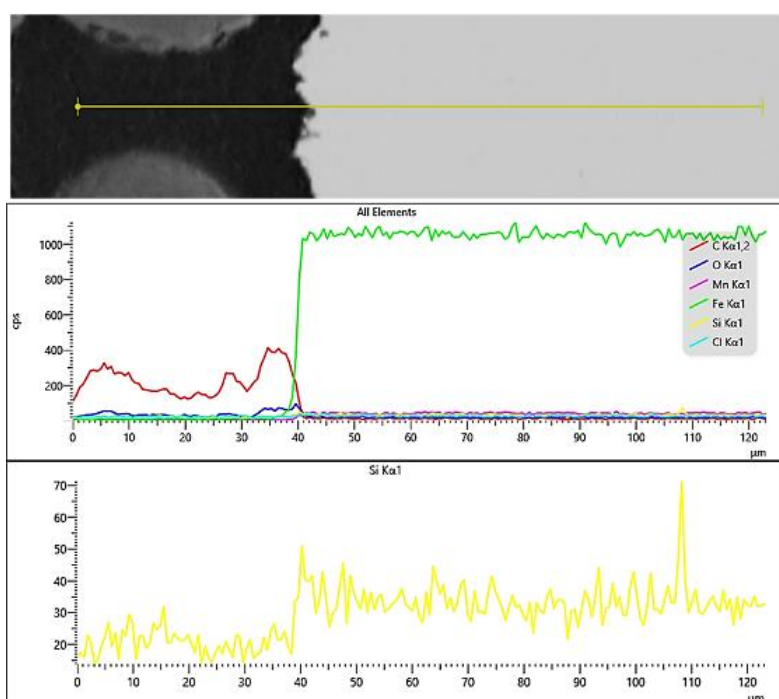


Figure 7-32 - EDS line scan analysis of the exposed X100 sample elements in simulated saltwater solution with O₂/CO₂ at 25 °C stressed at 80 % Y.S.

Similarly, as reported in the EDS analysis of the exposed X70 and X100 C-rings samples in solution with N₂ (chapter 4), CO₂ (chapter 5) and O₂/N₂ (chapter 6), no significant difference in Fe and Mn concentration observed between the X70 and X100 exposed in solution with O₂/CO₂. Generally, the concentrations of Fe and Mn were observed to change with spectrum location. Highest percentage of Fe (93.79 wt.%) was detected in spectrum 4 of the X100 C-ring sample exposed at 15 °C, with lowest of 91.87 wt.% detected in spectrum 4 of the X100 C-ring sample exposed at 5 °C. Highest percentage of Mn (2.04 wt.%) was detected in

spectrum 3 of the X100 C-ring sample exposed at 15 °C. Similarly, the concentration of Si as presented in the line scan was observed to be highest mostly at the alloy-resin interface.

7.1.5 Tensile Strength Analysis

Tensile strength tests were conducted on X70 dog-bone samples exposed in the different test conditions to assess the impact of O₂/CO₂ mixture and temperature on the ductility of the carbon steel.

7.1.5.1 Tensile Strength Tests of X70 Dog-bone Specimens

The stress-strain curves of the X70 dog-bone samples exposed in solution with O₂/CO₂ at 5 °C, 15 °C and 25 °C are presented in Figure 7-33. Similarly, as observed on the analysed X70 dog-bone samples in solution with CO₂ (chapter 5), elongation before failure decreases with increasing solution temperature. Lowest decrease in ductility was observed on the sample exposed at 5 °C, with an elongation before failure of 28.1 %. An elongation before failure of 26.5 % and 25.1 %, respectively were observed at 15 °C and 25 °C. The reference sample was observed to show higher ductility relative to the exposed samples with an elongation of 28.42 % on the sample before failure. In comparison with sample exposed in solution with CO₂ (chapter 5), higher decrease in ductility was observed on the sample exposed in solution with O₂/CO₂ at all solution temperatures. In general, elongation changes before failure were observed on the exposed X70 dog-bone samples with change in solution temperature.

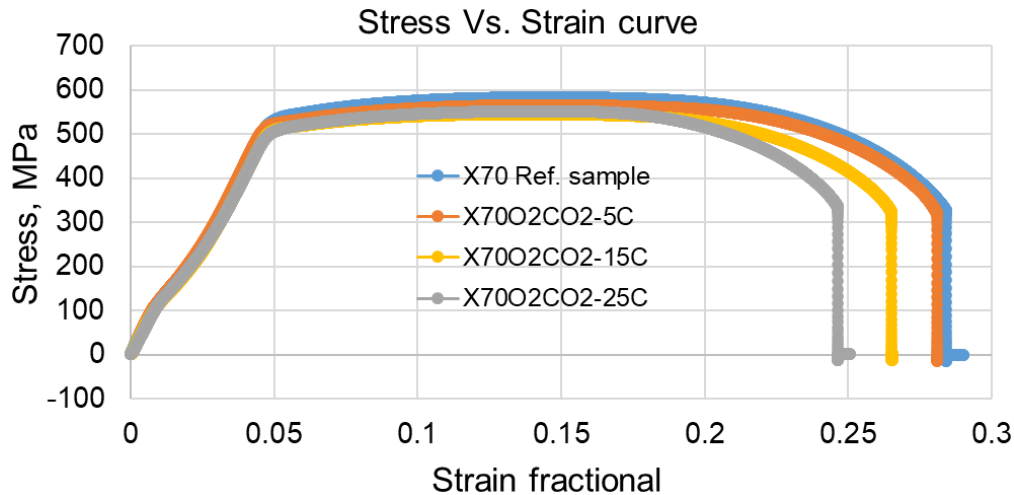


Figure 7-33 - Tensile tests stress-strain curves of the X70 dog-bone samples exposed in simulated saltwater solution with O₂/CO₂ at 5 °C, 15 °C and 25 °C.

7.1.6 Vickers Hardness Analysis

Vickers hardness tests were conducted on the exposed X70 dog-bone samples to assess the impact of O₂/CO₂ mixture and temperature on the hardness of the carbon steel.

7.1.6.1 Hardness Tests of X70 Dog-bone Specimens

The Vickers hardness results obtained from the exposed X70 dog-bone samples in solution with O₂/CO₂ at 5 °C, 15 °C and 25 °C are presented in Figure 7-34. Similarly, as reported in chapter 5 (in solution with CO₂) and 6 (in solution with O₂/N₂), the tests on samples were conducted from the start of the reduced parallel section of the dog-bone towards the fracture point. (x-axis indicates test locations from 1 to 8, 1- indicates start of reduced parallel section and, 8- end of fracture point). Three measurements were conducted on each test location and its average calculated. Hardness variations were observed with change in test locations at all exposure temperatures. Highest average hardness was observed on the reference sample towards the fracture point with a value of 257.33 HVC. Highest reduction in hardness was observed on the sample exposed at 25 °C with a value of 119.33 HVC, with highest average of 218.0 HVC observed at 5 °C. In general, no significant difference in average hardness observed on the samples with increasing solution temperatures. The sample exposed at 25 °C

generally was observed to show highest reduction in average hardness, relative to samples exposed at 5 °C and 15 °C. However, at 15 °C and 25 °C, the trend lies within the same scatter as shown in Figure 7-34. In comparison with samples exposed in solution with CO₂ (chapter 5), highest reduction in hardness was observed on the samples exposed in solution with O₂/CO₂ at all exposure temperatures. It can be concluded that the usage of carbon steels as a pipeline material for CO₂ transportation in seawater environment saturated with O₂ can lead to reduction in wear resistance of the material, and subsequently can decrease its wall thickness and hence increase its potential to SCC occurrence, especially if operated at temperatures above 25 °C.

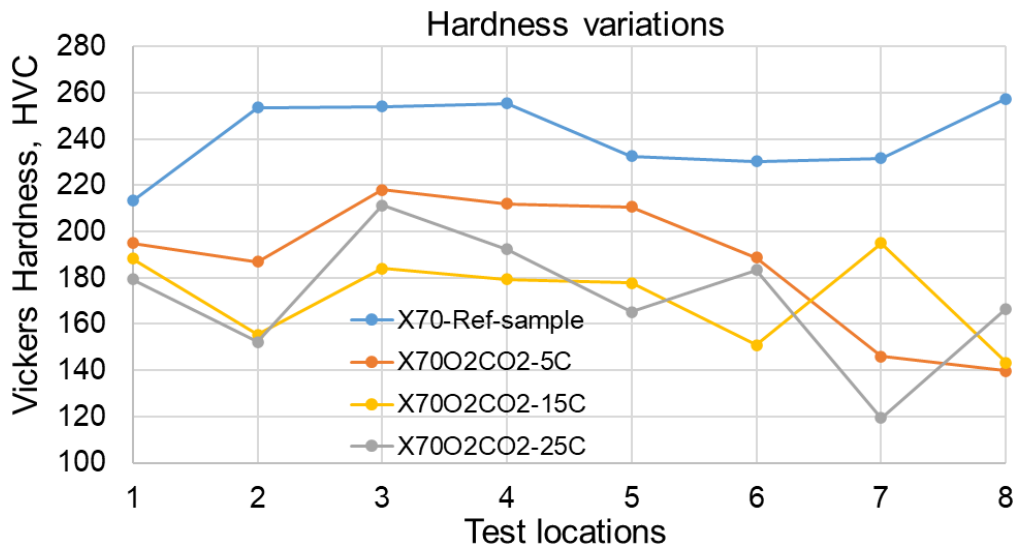


Figure 7-34 - Vickers hardness of the X70 dog-bone samples exposed in simulated saltwater solution with O₂/CO₂ at 5 °C, 15 °C and 25 °C.

7.2 Chapter Summary

Similarly, as reported in chapter 4, 5 and 6, the X100 samples exposed in solution with O₂/CO₂ at all solution temperatures were observed to show higher corrosion rates in comparison with the exposed X65, X70 and X80 samples. This also indicates that the X100 samples with bainitic ferrite and austenite microstructure have higher corrosion current density, which leads to higher corrosion rates. From the analysed calculated corrosion rate values, the X100 carbon steel was observed to show higher susceptibility to SCC in all exposure conditions. As such

selection of carbon steels as a pipeline material for operation in a seawater environment for transportation of CO₂ or other oil and gas products which contains traces of CO₂ or O₂ should be between X65, 70 or X80, which showed lower susceptibility to SCC, relative to X100 in all the simulated representative pipeline operating conditions.

Variations in corrosion potential values were also observed on the exposed material grades with change in solution temperature. Relative to samples exposed in solution with CO₂ (chapter 5), which showed more negative potential values on all samples exposed at 5 °C, the samples exposed in solution with O₂/CO₂, on the other hand were observed to have more negative potential values at 25 °C. This also can be explained to occur due to variations in the thermodynamic behavior of the exposed material grades with change in microstructures and solution temperature.

In general, variations in metal change over the sample's surfaces were observed on the different exposed carbon steel grades, ranging from uneven and even distribution of metal damage. As reported in chapter 4, 5 and 6, the variation in metal change observed on the exposed samples can be said to occur due to differences in microstructures and their reactions to the solution conditions. The X65 samples with ferritic-pearlite microstructure in comparison with X70 (globular ferrite grains with grain boundary pearlite), X80 (ferrite grains with pearlite bands) and X100 (bainitic ferrite and austenite microstructure) samples at all solution temperatures were observed to have higher pits features. Similarly, as observed on all X100 samples exposed in solution with CO₂ as reported in chapter 5, lowest metal change over the sample's surfaces at all exposure temperatures were observed on X100 samples exposed in solution with O₂CO₂.

Change in surface corrosion morphology was observed on all exposed samples with increasing temperature from 5 °C to 25 °C. The X65 (with ferritic-pearlite grains) and X70 (with globular ferrite grains with grain boundary pearlite) exposed samples at all applied stress levels and solution temperatures presented similar type of surface corrosion morphology with a combination of wide elliptical and undercutting type of morphology, which are wider and deeper at 15 °C and

25 °C. In comparison with X65 and X70 samples, the X80 (with ferrite grains and pearlite bands) samples were observed to have deeper and wider elliptical, with shallow undercutting morphology at 15 °C and 25 °C. Similarly, as observed on the X100 samples (with bainitic ferrite and austenite grains) exposed in solution with CO₂, the X100 samples exposed in solution with O₂/CO₂ were also observed to have a wide and shallow elliptical morphology, which increased in size with change in temperatures from 5 °C to 25 °C. The X100 samples at all solution temperatures showed an even surface metal change relative to X65, X70 and X80 samples. Similarly, as reported in chapter 5, the observed differences in surface corrosion morphologies of the carbon steels can be explained to occur as a result of differences in the microstructure of the carbon steels.

Similarly, as reported in the EDS analysis of the exposed X70 and X100 C-rings samples in solution with N₂ (chapter 4), CO₂ (chapter 5) and O₂/N₂ (chapter 6), no significant difference in Fe and Mn concentration observed between the X70 and X100. Generally, the concentrations of Fe and Mn were observed to change with spectrum location. Highest percentage of Fe (93.79 wt.%) was detected on the X100 sample exposed at 15 °C, with lowest of 91.87 wt.% detected on the X100 sample exposed at 5 °C. Highest percentage of Mn (2.04 wt.%) was detected on the X100 sample exposed at 15 °C. Similarly, as detected on the samples exposed in solution with O₂/N₂ (chapter 6), the O concentration on both X70 and X100 samples was observed to decrease with increasing solution temperature. Also, the concentration of Si was observed to be highest mostly at the alloy-resin interface.

The results from tensile strength analysis show similar trend in elongation before failure, as observed on the analysed X70 dog-bone samples in solution with CO₂ (chapter 5). Elongation before failure was also observed to decrease with increasing solution temperature. Highest loss in ductility was observed on the sample exposed at 25 °C, with a value of 25.1 %. Highest decrease in ductility was observed on the samples exposed in solution with O₂/CO₂ at all solution temperatures, in comparison with samples exposed in solution with CO₂ (chapter 5) and with O₂/N₂ (chapter 6). Similarly, as observed on samples in solution with

CO₂ (chapter 5) and with O₂/N₂ (chapter 6) fluctuations in hardness were also observed on the samples exposed in solution with O₂/CO₂ with change in test location. In general, decrease in metal hardness was observed with increasing solution temperature from 5 °C to 25 °C. Highest average of 218.0 HVC was observed at 5 °C, with highest of 211.33 HVC observed at 25 °C. In comparison with samples exposed in solution with CO₂ (chapter 5) and O₂/N₂ (chapter 6), highest reduction in hardness was observed on samples exposed in solution with O₂/CO₂ at all exposure temperatures.

8 GENERAL DISCUSSION

This chapter presents general discussion of the obtained experimental results in all exposure conditions. The results discussed include corrosion rates and potentials of the exposed carbon steels, cumulative probability of metal loss exceedance, SEM and EDS analysis, tensile strength and hardness analysis, and metal surface roughness.

8.1 Corrosion Rates and Potentials of Exposed Carbon Steels

In general, increasing corrosion rates were observed on all exposed samples with change in solution trace gases and temperature. The samples exposed in solution with N_2 were observed to have lower corrosion rates relative to samples exposed in solution with O_2/N_2 . A high increase as expected was also observed with change in trace gas mixture from 100 % CO_2 to 20% O_2 /80% CO_2 . Figure 8-1 shows the average corrosion rates values obtained from the exposed carbon steels with change in temperature and trace gases from N_2 to O_2/N_2 . As shown in Figure 8-1, the corrosion rates at all exposure conditions were observed to increase with increasing solution temperature with an increase of about 100 % from 5 °C to 25 °C.

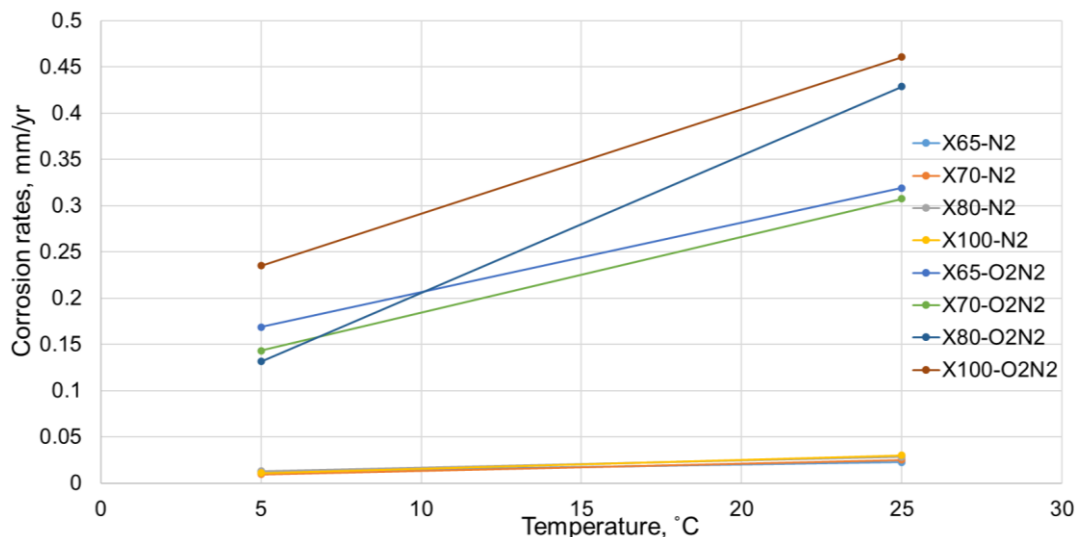


Figure 8-1 - Average corrosion rates values (mm/year) obtained from the exposed carbon steels with change in solution temperature and trace gases from N_2 (100%) to O_2/N_2 (20%/80%).

As shown in Figure 8-1, the obtained average corrosion rate values of the exposed carbon steels in solution with N_2 were observed to have lower values relative to published corrosion rates of carbon steels in seawater (seawater contains about 21 % O_2). This is achieved by the continuous bubbling of nitrogen gas in the test solution, which eliminates any entrained oxygen or air, thus lowering the corrosion rate. The low corrosion rates observed on the exposed carbon steels in solution with N_2 can be explained to occur due to NH_4^+ formation, i.e. the pH increase by H^+ consumption [75]. Additionally, for ferritic steels or Fe-Cr alloys, many authors assume a protective layer formation of Cr-N or Mo-N corrosion resistant nitrides in the pit bottom which stops the pitting attack [137]. Hence, lowering the corrosion rates.

Furthermore, with change in solution trace gas composition from N_2 (100 %) to O_2/N_2 (20%/80%), the obtained corrosion rates values were observed to be more or less similar to the published values. An average corrosion rate value of 0.13-0.41 mm/year was reported by Davies and Micheal [44,45], average of 0.102-0.178 mm/year reported by Fontana [22] and an average value of 0.1 mm/year in quiet seawater to 0.75 mm/year at 3 m/s seawater velocity reported by Kreysa and Schutze [36]. As the obtained experimental corrosion rates tallies with published literature corrosion rates, it can be stated that standard operating procedures as outlined in ASTM G96-90 [119], ASTM G102-89 [120] and NACE corrosion engineer's reference book [105] have been strictly adhered to.

From the obtained low corrosion rates of the exposed carbon steel samples in the simulated 3.5 % NaCl solution in the presence of N_2 , installation and usage of the carbon steel as a pipeline material in a nitrogen saturated seawater environment does not impose risk of associated SCC occurrence on the material. However, with the increased corrosion rate observed with increasing percentage of oxygen in the solution, pipelines installed in an oxygen saturated seawater environment are more prone to SCC occurrence due to the increased anodic dissolution and subsequent decrease in pipeline wall thickness, especially when operated at higher temperatures above 25 °C. Installations of pipelines should be in deep waters and polar regions where the temperatures are below 5 °C. This

will lower the corrosion rates of the pipelines and hence reduce risk of SCC occurrence. The X100 carbon steel in all exposure conditions in comparison with X65, X70 and X80 showed higher susceptibility to SCC due to the obtained higher corrosion rates as presented in Figure 8-1. Therefore, material selection should be between X65, X70 or X80 if readily available.

Similarly, as observed on the samples exposed in solution with N_2 and O_2/N_2 , an increase in corrosion rate of more than 100 % was observed on all exposed carbon steels in solution with CO_2 in all exposure conditions with increasing solution temperature from 5 °C to 25 °C as presented in Figure 8-2. Variations in average corrosion rates as shown in Figure 8-2 were obtained from the exposed carbon steels in solution with CO_2 , with change in sample geometry and surface state (mechanically and chemically pre-damaged). The mechanically and chemically pre-damaged X70 samples exposed at 25 °C as shown in Figure 8-2 were observed to have higher average corrosion rates values (1.253 mm/year), in comparison with the normal exposed (undamaged) X70 samples (1.143 mm/year) exposed at 25 °C. It can be stated that change in surface state or roughness of the samples does have an impact on the corrosion rates of the exposed X70 carbon steel. This could be explained to occur as a result of tempering with the surface structure of the samples, thus making them more vulnerable to the fast release of electrons and subsequent increase in cathodic reaction rates, hence leading to higher corrosion rates. With the higher observed corrosion rates of the mechanically and chemically pre-damaged samples relative to normal exposed samples, machining of selected carbon steel as a pipeline material should be to an accepted and up to date standard surface finish.

However, with change in sample geometry from C-rings to 3-point bent-beam specimens, lower average corrosion rates were observed on the X70 3-point bent-beam samples exposed at both 5 °C and 25 °C in comparison with X70 C-rings samples. The X100 3-point bent-beam sample exposed at 5 °C were observed to have higher values (0.969 mm/year) relative to the X100 C-ring sample at 5 °C (0.855 mm/year). However, at 25 °C the X100 C-rings samples presented higher values (2.197 mm/year), with a value of 1.893 mm/year

obtained from the X100 3-point sample. The change in corrosion rates of the exposed carbon steels with change in sample geometry can be attributed to possible differential aeration and fluctuations in solution temperatures at the exposure time. No significant change in corrosion rates observed on the exposed carbon steels with change in sample geometry.

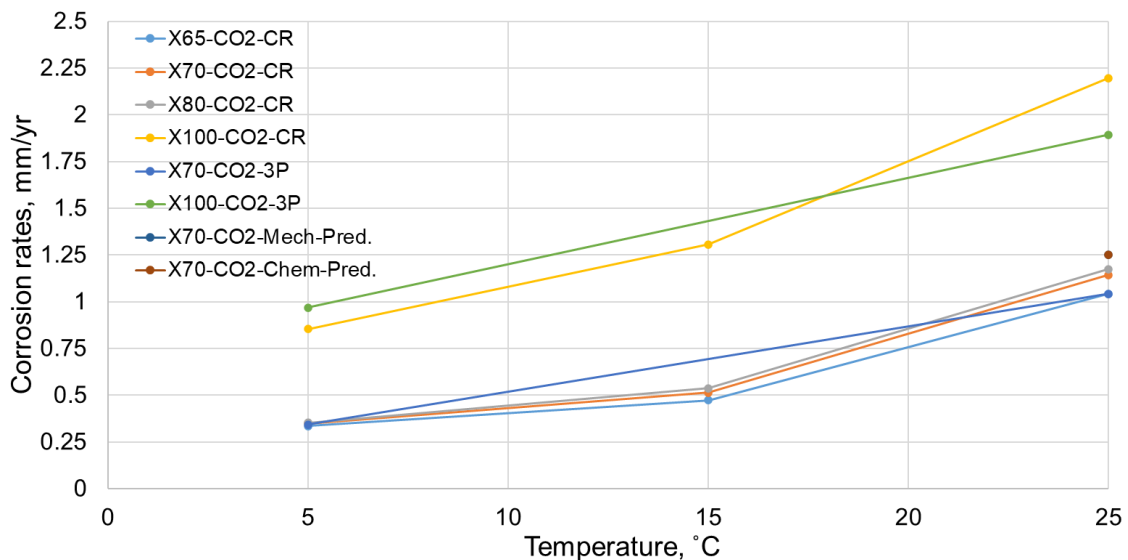


Figure 8-2 - Average corrosion rates values (mm/year) obtained from the exposed carbon steels in solution with CO₂ with change in solution temperature, sample geometry and surface damage.

The calculated corrosion rates values in solution with CO₂ are more or less similar to the published literature corrosion rates of carbon steels exposed in similar solutions saturated with 100 % CO₂. Silva et al. [6] reported a corrosion rate value of between 1 -1.3 mm/year obtained on X65 carbon steel exposed in 3.5 % NaCl solution with CO₂ at 25 °C. Similarly, Zhang et al. [86] reported a value of 0.9911 mm/year observed on X70 carbon steel exposed in a soil solution saturated with CO₂ 25 °C. Gadala and Alfantazi [10] also reported a corrosion rate value of 2.336 mm/year obtained from X100 carbon steel exposed in NS4 simulated soil solution with CO₂ at 25 °C.

From the observed average corrosion rates of the exposed carbon steels in the simulated 3.5 % NaCl saturated with CO₂, installation and usage of the carbon steel as a pipeline material in a seawater environment for transportation of CO₂ or in carbon capture and storage should not be operated at higher temperatures

above 25 °C to avoid risk of increased corrosion rates, and subsequent SCC occurrence. Installations and usage should be in polar regions and deep waters where the seawater temperatures are below 5 °C and not in tropical regions with temperatures above 30 °C as reported in section 2.1.4. The operation of X70 carbon steel as a pipeline material in the North Sea with an annual mean sea surface temperature of 11 °C as also reported in section 2.1.4, will have a reduced risk of SCC occurrence due to lower expected corrosion rates. In addition, as not much significant difference in average corrosion rates were observed on the X65 carbon steel (1.043 mm/year at 25 °C) in comparison with X70 (1.143 mm/year at 25 °C) and X80 (1.155 mm/year at 25 °C) in the simulated saltwater solution saturated with CO₂ within the exposure period of 840 hrs (5 weeks), the carbon steels should be exposed for longer time to ascertain their SCC susceptibility before making a final selection. Furthermore, with the observed higher average corrosion rate of the X100 carbon steel (2.197 mm/year at 25 °C), it can be stated that the carbon steel is more susceptible to SCC in the exposure environment at all solution temperatures. As such the selection of carbon steel to be used as an offshore pipeline material should be between X65, X70 or X80.

As expected, a high increase in average corrosion rates of about 65 % was observed with change in trace gas mixture from CO₂ (100%) to O₂/CO₂ (20%/80%) at 15 °C and 25 °C, with an increase of about 15 % at 5 °C as shown in Figure 8-3. An increase in average corrosion rate of more than 100 % was also observed on the carbon steels exposed in solution with O₂/CO₂ with change in temperature from 5 °C to 25 °C.

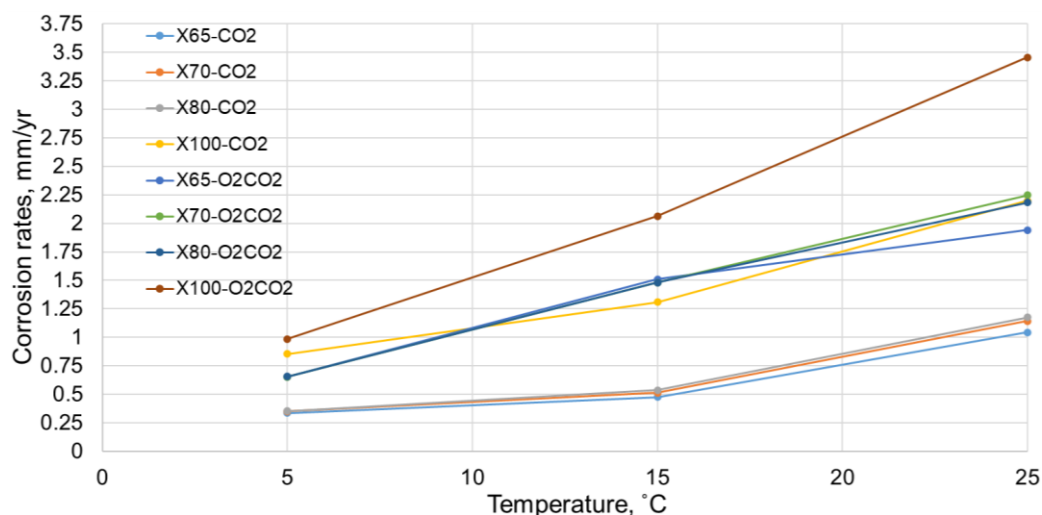


Figure 8-3 - Average corrosion rates values (mm/year) obtained from the exposed carbon steels with change in solution temperature and trace gases from CO₂ (100%) to O₂/CO₂ (20%/80%).

As presented in Figure 8-3, at all exposure temperatures, the X100 carbon steel observed to show higher corrosion rates in comparison with the X65, X70 and X80 samples. This shows that the X100 samples with bainitic ferrite and austenite grains have higher corrosion current density, which leads to higher corrosion rates. The obtained corrosion rates were observed to change with change in microstructure and increasing ultimate tensile strength of the alloy grades. The formation and rupture of surface films causes fluctuations in the cathodic reactions rates taking place on the samples' surfaces. This leads to variations in corrosion rates with time as observed on the exposed carbon steels.

Analysis of the observed corrosion rates of the carbon steels exposed in solution with O₂/CO₂, shows that installation and usage of pipelines in oxygen saturated seawater environments for CO₂ transportation is at increased risk of SCC occurrence due to the high values of obtained corrosion rates, especially if operation is at temperatures above 25 °C. In addition, the X100 carbon steel was observed to be more susceptible to SCC in the simulated saltwater solution saturated with O₂/CO₂ as compared to X65, X70 and X80, as also observed from the calculated corrosion rates of the exposed carbon steels in the simulated saltwater solution with N₂ (chapter 4), CO₂ (chapter 5) and O₂/N₂ (chapter 6).

Variations in corrosion potential values were observed on the exposed material grades with change in microstructures, exposure conditions, sample geometries and solution temperatures. In general, more negative potential values were obtained on all samples exposed in solution with N_2 , O_2/N_2 and CO_2 at 5 °C. The samples exposed in solution with O_2/CO_2 on the other hand were observed to present more negative potential values at 25 °C. This can be explained to occur because of variation in the thermodynamic behavior of the different exposed material grades with changes in microstructure, solution composition, sample geometry and solution temperature. The change in thermodynamic behavior can also occur due to several factors, which include differential aeration, agitation of the exposure solutions, thickness, formation, or rupture of surface films, etc.

8.2 Cumulative Probability of Metal Loss Exceedance of the Exposed Carbon Steels

In general, the X65, X70 and X80 samples exposed in solution with N_2 at all stress levels and solution temperatures showed higher and uneven distribution of metal change over most of the sample's surfaces. The X100 however, was observed to show low metal change with an even distribution over most of the sample's surfaces. All samples exposed in solution with O_2/N_2 at all applied stress levels and solution temperatures showed an uneven distribution of metal damage. Higher pits features were observed on all samples exposed in solution with O_2/N_2 at all temperatures, relative to samples exposed in solution with N_2 . This can be explained to occur due to increased percentage of O_2 in the simulated 3.5 % NaCl solution. Thus, the presence of O_2 in a medium causes formation of pits on the exposed carbon steel's surfaces.

The samples exposed in solution with CO_2 were observed to have similar trend in metal change as observed on the samples exposed in solution with N_2 . The X100 (bainitic ferrite and austenite grains) samples showed low metal change with an even metal dissolution across the sample's surfaces at all solution temperatures, with an uneven metal dissolution observed on the X65 (ferritic-pearlite grains), X70 (globular ferrite grains with grain boundary pearlite) and X80 (ferrite grains with pearlite bands) samples at all applied stress levels and

temperatures. No change in metal change trend observed on the exposed carbon steels with change in gas mixture from CO_2 to O_2/CO_2 at all solution temperatures. The variations in metal change trend observed on the different exposed carbon steels, which range from uneven and even distribution of metal damage, high and low pits features observed with change in trace gas mixture and temperature can be explained to occur due to the differences in microstructures of the carbon steels and their reaction to the exposure conditions.

Furthermore, Figures 8-4a to 8-4p show the medium cumulative probability of metal loss exceedance of the exposed carbon steels grades in all exposure conditions and applied stress levels. The X100 samples exposed in solution with N_2 , CO_2 and O_2CO_2 (Figures 8-4d, l and p, respectively.) at all solution temperatures were observed to show relatively equal medium metal loss values and obtained errors with change in applied stress levels and surface state (notched state) of the samples in comparison with the X100 samples exposed in solution with O_2/N_2 (Figure 8-4h). This shows that the X100 carbon steel (with bainitic and austenite grains) corroded in a more general and even metal dissolution in solution with N_2 , CO_2 and O_2/CO_2 , while in solution with O_2/N_2 corrosion of the carbon steel was more of in a localised form with pits features due to presence of O_2 in the solution. Fluctuations in medium metal loss values were observed on the X65, X70 and X80 samples in all exposure conditions. The X65 (Figures 8-4a and e), X70 (Figures 8-4b and f) and X80 (Figures 8-4c and g) exposed in solution with N_2 and O_2/N_2 at both 5 °C and 25 °C were observed to show highest variations in medium values and obtained errors with change in applied stress levels and surface state (notched) of the samples. This shows that the samples corroded in a localised form with possible pits features. The X65 (Figures 8-4i and m), X70 (Figures 8-4j and n) and X80 (Figures 8-4k and O) exposed in solution with CO_2 and O_2/CO_2 at all exposure temperatures were also observed to present approximately equal medium metal loss values and obtained errors with change in applied stress levels. In general, significant change in medium metal loss values were observed on the samples exposed in solution with O_2/N_2 at all exposure temperatures. This can be explained to occur due to presence of oxygen in the simulated 3.5 % NaCl solution which presented higher

pits features on the samples surfaces, hence the variations in medium metal loss values. A high standard deviation was observed on X80 Notched sample (80 % Y.S.) exposed in solution with O₂/N₂ at 25 °C, with a negative error value of -36 µm, relative to samples stressed at 80 % Y.S. and 95 % Y.S. with obtained negative error values of -15 µm and -17 µm, respectively (Figure 8-4g). This could be explained to occur due to the observed high mass change on the exposed notched sample (80 % Y.S.) with a metal gain value of -7 µm relative to -15 µm and -16 µm, respectively obtained on samples stress at 80 % Y.S. and 95 % Y.S. as shown in Figure 6-7. Hence, the increased metal thickness during post-exposure dimensional metrology measurement as compared to pre-exposure thickness.

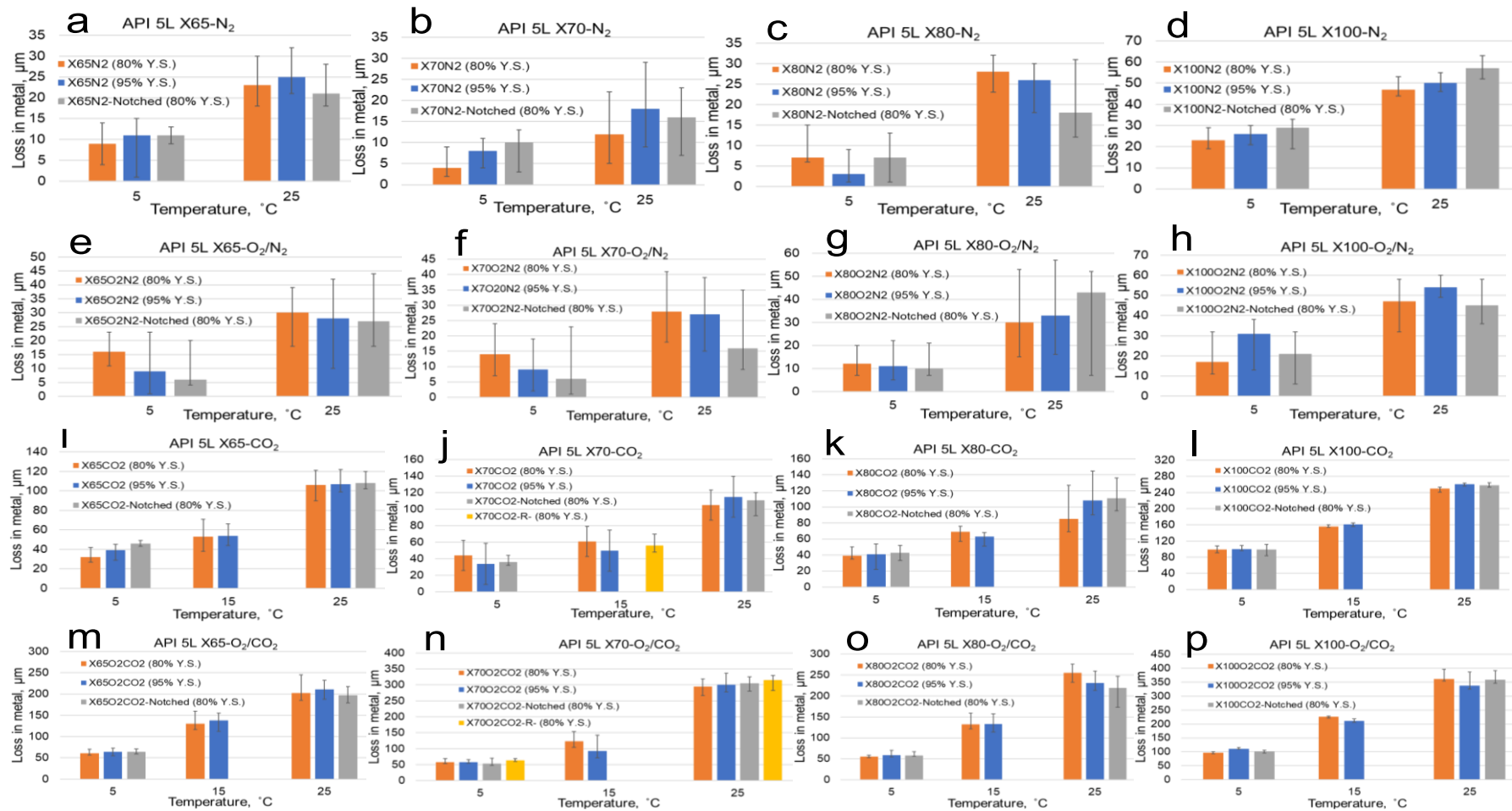


Figure 8-4 - Medium cumulative probability of metal loss exceedance values of the exposed carbon steel grades in the different 3.5 % NaCl simulated conditions: (a) to (d) in solution with N₂; (e) to (h) in solution with O₂/N₂ (20%/80%); (i) to (l) in solution with CO₂; (m) to (p) in solution with O₂/CO₂ (20%/80%).

Similarly, as observed from the calculated corrosion rates of the exposed carbon steels from LPR measurements, increasing metal loss of more than 100 % was observed with change in solution temperature from 5 °C to 25 °C at all exposure conditions. As expected, an increased metal loss was observed with change in solution trace gas mixture from N₂ to O₂/N₂, as also observed from the calculated corrosion rates from LPR measurements. An increasing in metal loss of about 100 % (on X65 and X80), more than 100 % (on X70) and about 70 % (on X100) was observed with change in trace gas mixture from CO₂ to O₂/CO₂ as also observed from calculated corrosion rates from LPR measurements. The calculated corrosion rates from LPR measurements at all exposure conditions and temperatures tallies with the measured metal loss values when converted to 840 hrs (5 weeks) of exposure time as presented in the previous sections. In addition, as observed from calculated corrosion rates from LPR measurements, the X100 carbon steel at all exposure conditions was measured to have higher metal loss relative to X65, X70 and X80. This shows that the X100 carbon steel is more susceptible to SCC in all the various simulated offshore pipeline operating conditions.

8.3 Scanning Electron Microscopy and Energy Dispersive Spectroscopy Analysis of the Exposed Carbon Steels

As observed and reported from the calculated corrosion rates from LPR measurements and measured metal loss exceedance values in all exposure conditions, increasing surface roughness and deterioration was also observed on all analysed carbon steel samples with change in solution temperature from 5 °C to 25 °C. Similarly, no significant change in surface corrosion morphology observed on all samples with change in applied stress level and surface state (notched) at all exposure conditions, as also presented in the calculated corrosion rates and measured metal loss exceedance values.

In general, variations in surface corrosion morphology were observed on all exposed carbon steels with change in trace gas mixture. Increase in metal surface roughness was observed on all exposed carbon steel samples with

change in gas mixture from N_2 to O_2/N_2 at all stress levels and temperatures, as reported from the calculated corrosion rates and metal loss values. The X65 (with ferritic-pearlite grains), X70 (with globular ferrite grains and grain boundary pearlite) and X80 (with ferrite grains and pearlite bands) samples at all stress levels exposed in solution with N_2 showed an uneven surface roughness, with shallow elliptical morphology. The X100 (with bainitic ferrite and austenite grains) samples however presented shallower and even elliptical surface morphology.

At all solution temperatures, the X65, X70 and X80 samples exposed in solution with O_2/N_2 showed deeper and wider ellipses, with combination of shallow undercutting metal dissolution in comparison with N_2 . Figures 8-5a to 8-5d shows SEM images of exposed X70 C-rings samples stressed at 80 % Y.S. in the simulated 3.5 % NaCl solution with change in trace gas mixture from N_2 (100%) to O_2/N_2 (20%/80%) at 5 °C and 25 °C. As shown in Figures 8-5a to 8-5d increasing surface roughness was observed on the X70 samples with change in solution trace gas composition and temperature.

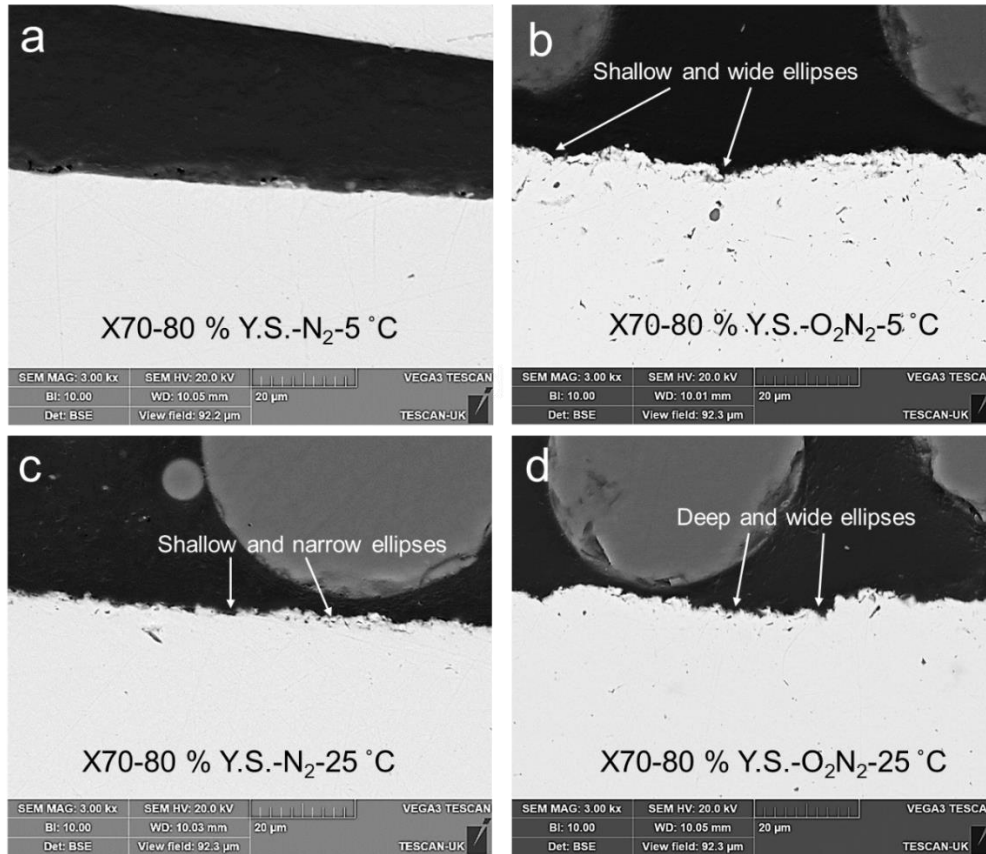


Figure 8-5 - SEM backscattered electron images of the exposed X70 C-rings samples stressed at 80 % Y.S. in the simulated 3.5 % NaCl solution with change in trace gas mixture from N₂ (100%) to O₂/N₂ (20%/80%); (a) in solution with N₂ at 5 °C; (b) in solution with O₂/N₂ at 5 °C; (c) in solution with N₂ at 25 °C; (d) in solution with O₂/N₂ at 25 °C.

However, the X100 samples exposed in solution with O₂/N₂ at all stress levels and temperatures presented higher metal dissolution and deterioration with a combination of shallow vertical dissolution relative to the X65, X70 and X80 samples. This can be explained to occur due to higher ultimate tensile strength of the X100 carbon steel samples and effect of O₂ on the microstructure (bainitic ferrite and austenite grains) of the carbon steel. This shows that the X100 samples are more susceptible to SCC in the presence of O₂. Figures 8-6a to 8-6d shows SEM images of exposed X100 C-rings samples stressed at 80 % Y.S. in the simulated 3.5 % NaCl solution with change in trace gas mixture from N₂ (100%) to O₂/N₂ (20%/80%) at 5 °C and 25 °C. As shown in Figures 8-6a to 8-6d increasing surface roughness was observed on the X100 samples with change

in solution trace gas mixture and temperature. The corrosion mechanism of all exposed carbon steels in the simulated 3.5 % NaCl solution saturated with N_2 and O_2/N_2 was observed to be solely based on anodic dissolution of the metal surfaces. As observed from the tensile strength analysis of the exposed X70 dog-bone bone samples exposed in solution with O_2/N_2 , no significant change in elongation before failure observed between the exposed samples and reference sample. As such no effect of hydrogen embrittlement observed on samples due to the non-reduction in ductility between the exposed and reference samples.

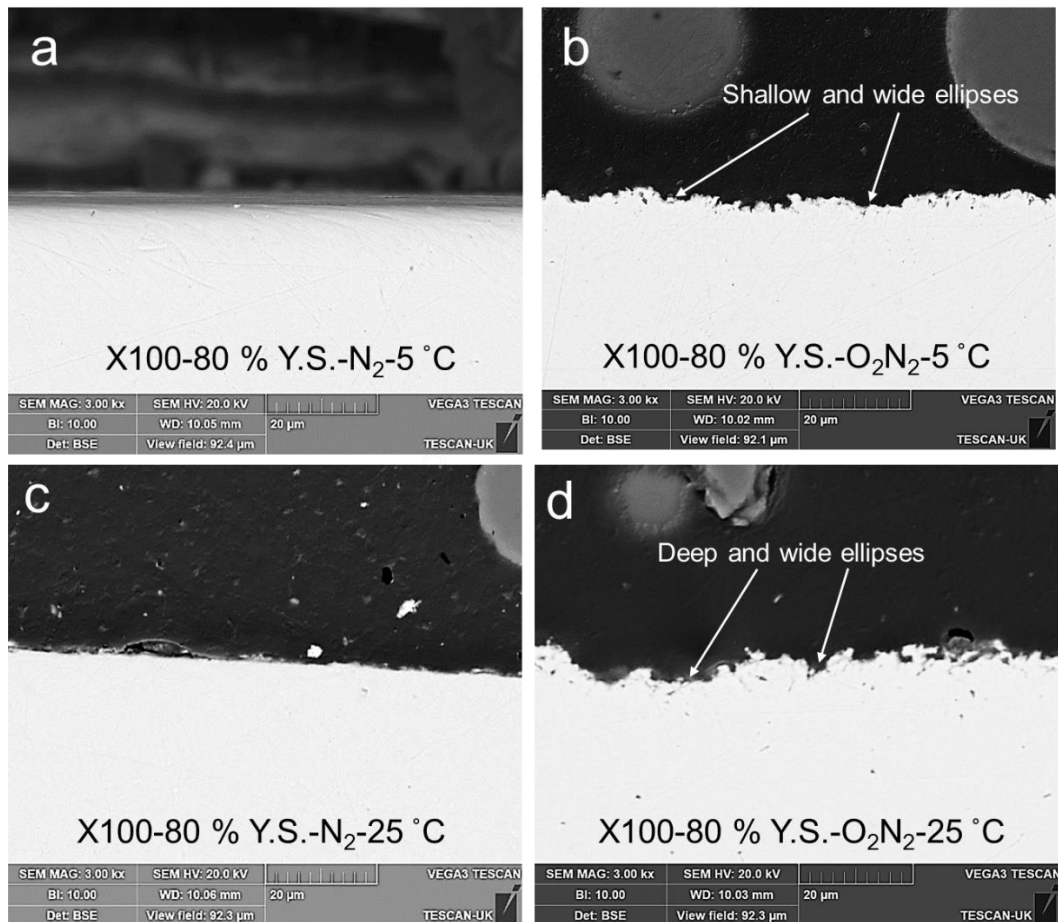


Figure 8-6 - SEM backscattered electron images of the exposed X100 C-rings samples stressed at 80 % Y.S. in the simulated 3.5 % NaCl solution with change in trace gas mixture from N_2 (100%) to O_2/N_2 (20%/80%); (a) in solution with N_2 at 5 °C; (b) in solution with O_2/N_2 at 5 °C; (c) in solution with N_2 at 25 °C; (d) in solution with O_2/N_2 at 25 °C.

Variations in surface morphologies and deteriorations were observed with change in stressing technique from C-rings to 3-point bent- beam and change in

surface state of the X70 C-rings samples (mechanically and chemically pre-damaged), as also observed in the calculated corrosion rates from LPR measurements and measured metal loss exceedance. All the X70 and X100 3-point bent-beam samples at both 5 °C and 25 °C were observed to show higher metal dissolution and deterioration in comparison with the C-rings samples exposed in solution with CO₂. It can be stated that stressing technique have an impact on the corrosion morphology and crack initiation of the exposed carbon steel samples. Figures 8-7a to 8-7d shows SEM images of exposed X70 C-rings and 3-point-bent beam samples in solution with CO₂ stressed at 80 % Y.S. at 5 °C and 25 °C.

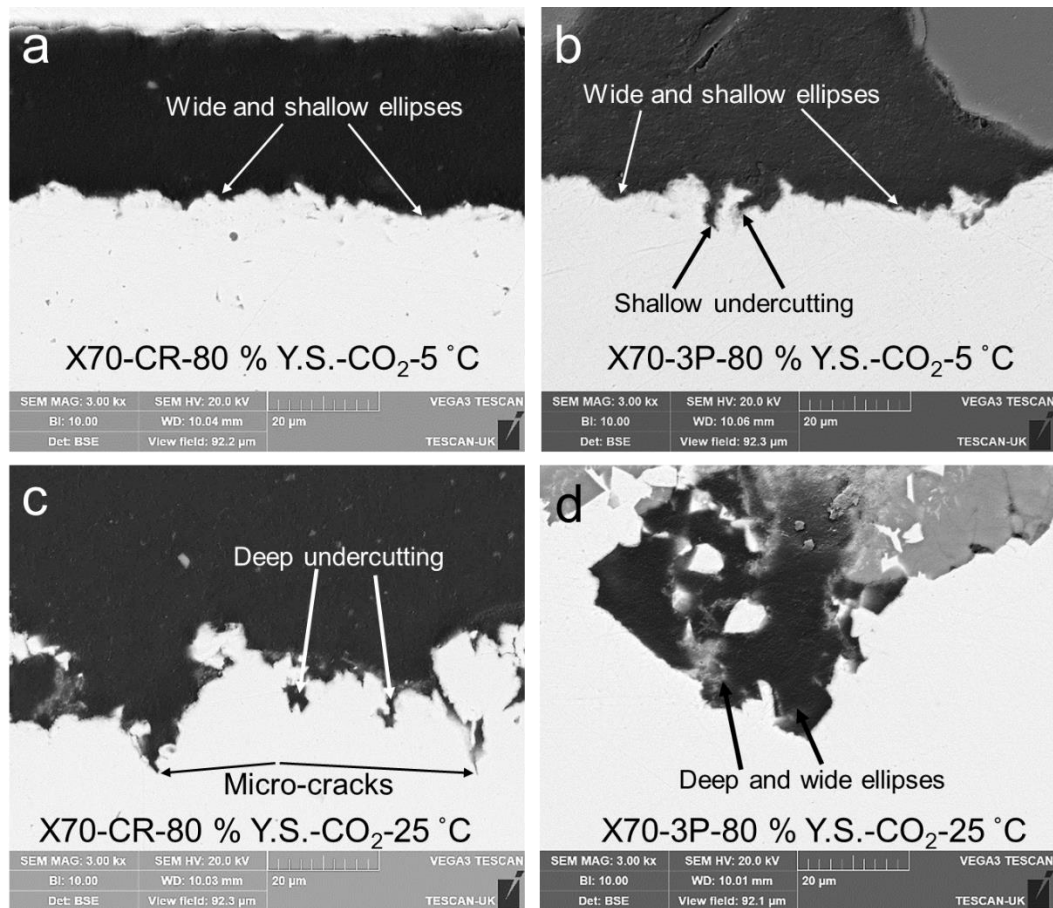


Figure 8-7 - SEM backscattered electron images of the exposed X70 C-rings and 3-point-bent beam samples in solution with CO₂ stressed at 80 % Y.S.; (a) X70 C-ring at 5 °C; (b) X70 3-point at 5 °C; (c) X70 C-ring at 25 °C; (d) X70 3-point at 25 °C.

Similar type of surface corrosion morphology was observed on both mechanically and chemically pre-damaged samples relative to normal exposed (undamaged)

X70 C-rings. The pre-damaged samples were also observed to have deep undercutting type of surface metal dissolution with micro-cracks. No visible significant change in surface metal dissolution observed between the chemically, mechanically pre-damaged and normal exposed (undamaged) samples as presented in section 5.1.3.3 as also observed from the calculated corrosion rates from LPR measurements.

With change in gas composition from CO_2 to O_2/CO_2 , more or less similar type of surface corrosion morphology was observed on the exposed samples at all solution temperatures, but with higher deterioration on the samples exposed in solution with O_2/CO_2 , as also observed from measured metal loss exceedance and calculated corrosion rates from LPR measurements. All the exposed X65 and X70 samples in both gas mixtures (CO_2 and O_2/CO_2) at all applied stress levels and solution temperatures presented a wide and shallow elliptical (at 5 °C) and deep undercutting metal dissolution (at 15 °C and 25 °C), which increased in depth in solution with O_2/CO_2 . Presence of micro-cracks were observed on the X65 and X70 samples in both CO_2 and O_2/CO_2 conditions, as presented in section 5.1.3 and section 7.1.3, respectively. The X80 samples at all stress levels exposed in solution with CO_2 were observed to have deep and narrow elliptical pits and a combination of vertical (at 5 °C) with deep and wide ellipses in solution with O_2/CO_2 (at 5 °C). At 15 °C and 25 °C, the samples in both solution with CO_2 and O_2/CO_2 were observed to have deep and wide elliptical pits, with shallow undercutting surface morphology. The X100 samples exposed in solution with CO_2 and O_2/CO_2 at all solution temperatures as observed in solution with N_2 presented wide and shallow elliptical morphology, which increased in size with change in temperature from 5 °C to 25 °C. This also shows the X100 samples (with bainitic and austenite grains) corroded in a more general and even form as observed in solution with N_2 , while the X65, X70 and X80 carbon steels corroded in a localized form, as also observed from the measured surface metal change from dimensional metrology analysis. Figures 8-8a to 8-8d shows SEM images of exposed X70 C-rings samples stressed at 80 % Y.S. in the simulated 3.5 %

NaCl solution with change in trace gas mixture from CO₂ (100%) to O₂/CO₂ (20%/80%) at 5 °C and 25 °C.

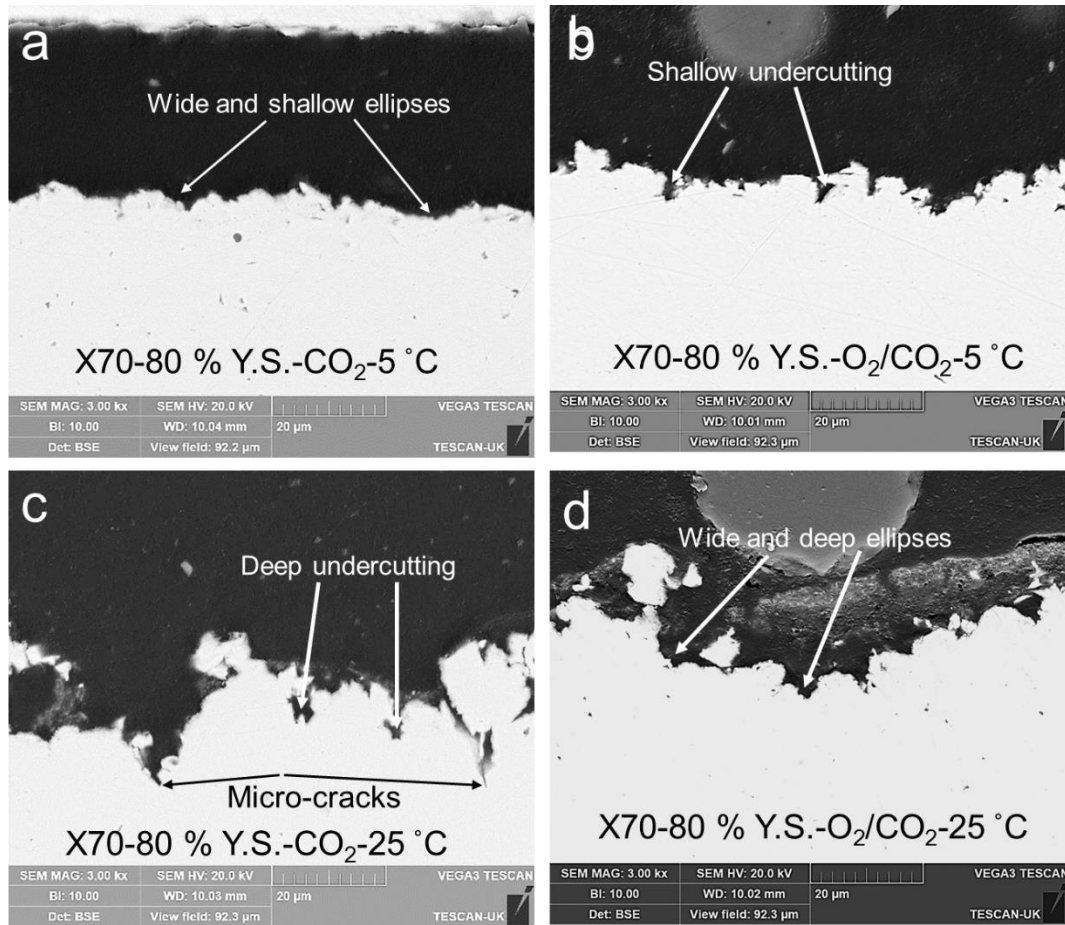


Figure 8-8 - SEM backscattered electron images of the exposed X70 C-rings samples stressed at 80 % Y.S. in the simulated 3.5 % NaCl solution with change in trace gas mixture from CO₂ (100%) to O₂/CO₂ (20%/80%); (a) in solution with CO₂ at 5 °C; (b) in solution with O₂/CO₂ at 5 °C; (c) in solution with CO₂ at 25 °C; (d) in solution with O₂/CO₂ at 25 °C.

The variation in corrosion morphologies observed on the exposed carbon steels in the different simulated 3.5 % NaCl solution, can be said to occur due to the differences in microstructures of the carbon steels and their reactions to temperature and solution trace gas mixtures. The presence of precipitates in the microstructures also contributes to the metal dissolution mechanism. Wang et al. [135] and Dugstad et. al [134] reported that the presence of precipitates in a steel's crystalline structure provides nucleation sites for hydrogen traps and crack initiation. This can lead to hydrogen embrittlement and subsequently may lead to

SCC occurrence [84,135]. From the analysis of the exposed samples in solution both solution with CO_2 and O_2/CO_2 , it can be stated that the predominant corrosion mechanism is by anodic dissolution. However, with the lowest percent elongation before failure observed on the X70 dog-bone samples exposed in solution with O_2/CO_2 as reported from the tensile strength analysis in section 7.1.5 and in solution with CO_2 as reported in section 5.1.5 in comparison with in solution with O_2/N_2 as discussed in section 6.1.5. It can be stated that highest reduction in ductility which is caused due to effect of hydrogen embrittlement should be expected on the samples exposed in solution with O_2/CO_2 and CO_2 , as such some degree of hydrogen embrittlement is involved in the corrosion mechanism of the exposed carbon steels.

Furthermore, as discussed in section 1.3, two types of SCC have been identified in pipeline carbon steels. Near neutral SCC (pH range of 6 to 8), which is characterized by a trans-granular cracking mode and high pH SCC (pH above 9), which is characterized by an intergranular cracking mode. During exposure, a pH range of 7.3 to 7.5 was measured in solution with N_2 and O_2/N_2 . No significant change in pH level was observed with increasing percentage of O_2 in the simulated 3.5 % NaCl solution, even with the observed increase in formed iron oxides (Fe_2O_3) in the test solution. As such, it is expected that near neutral SCC is most likely to occur on the exposed carbon steel samples. Nevertheless, with a change in trace mixture from CO_2 to O_2/CO_2 in the saltwater solution, a pH range of 6.1 to 5.6 was attained due to formation of carbonic acid (H_2CO_3) by the presence of CO_2 in the solution, which lowers the pH of the solution. Due to lack of failure of the test samples, analysis of the mode of SCC could not be conducted. As reported by Zhang et al. [86], it is expected that the exposed samples in solution with CO_2 which is considered acidic, will experience a different mode of SCC from those exposed in near neutral solution. To date limited research has been conducted on SCC behavior of pipeline carbon steels in CO_2 saturated environment [86].

Variations in elemental compositions were observed on all the exposed X70 and X100 samples with change in solution compositions, temperature, stressing

technique, and spectrum locations on the analyzed samples. Table 8-1 presents the different maximum concentration values of Fe and Mn (in wt.%) detected on the analyzed samples with change in solution trace gas mixture and temperature. As shown in Table 8-1 maximum Fe concentration of 93.97 wt.% was observed in the X70 3-point bent-beam sample exposed in solution with CO₂ at 25 °C. The X100 sample was observed to have highest Fe concentration (93.79 wt.%) in solution with O₂/CO₂ at 15 °C. Maximum Mn concentration was observed on the X100 C-ring sample exposed in solution with N₂ at 25 °C with a value of 2.12 wt.%. A maximum value of 2.01 wt.% was observed on the X70 C-ring sample exposed in solution with CO₂ at 5 °C. In general, no significant difference in maximum Fe and Mn concentrations observed between the analyzed X70 and X100 samples.

Table 8-1 - Variations in percent elongation (%) before failure of the exposed X70 dog-bone samples in the 3.5 % NaCl simulated solution with change in trace gas mixture and solution temperature.

Trace gases	N ₂				O ₂ /N ₂				CO ₂				O ₂ /CO ₂			
Carbon steel grade	X70		X100		X70		X100		X70-C-ring		X100-C-ring		X70		X100	
Chemical element	Fe	Mn	Fe	Mn	Fe	Mn	Fe	Mn	Fe	Mn	Fe	Mn	Fe	Mn	Fe	Mn
5 °C	92.65	1.95	93.36	1.93	92.30	1.73	91.15	2.02	91.21	2.01	91.65	2.01	92.84	1.88	91.87	1.95
15 °C	-	-	-	-	-	-	-	-	91.97	1.94	92.10	2.03	93.75	1.72	93.79	2.04
25 °C	92.41	1.96	91.43	2.16	93.19	1.81	91.23	1.92	93.72	1.89	92.30	2.03	92.64	1.67	93.47	1.98
Carbon steel									X70 3-point		X100 3-point					
Chemical element									Fe	Mn	Fe	Mn				
5 °C									92.79	1.93	93.17	2.12				
25 °C									93.97	1.73	92.68	1.93				

8.4 Tensile Strength Analysis

Variations in percent elongations before failure were observed on the exposed X70 dog-bone samples with change in solution trace gas mixture and temperature. As presented in Figure 8-9, no significant difference in percent elongation before failure observed on the samples exposed in solution with O₂/N₂ at all solution temperatures in comparison with the reference sample. The samples exposed in solution with O₂/CO₂ were observed to have lowest percent elongation before failure relative to samples exposed in solution with CO₂ at 15 °C and 25 °C. No significant difference in percent elongation observed between the samples exposed in solution with CO₂ and O₂/CO₂ at 5 °C. In general, the samples exposed in solution with O₂/CO₂ were observed to present highest lost in ductility with a value of 25.1 % at 25 °C. Analysis from the change in tensile strength values of the exposed X70 dog-bone samples in the different exposure conditions, indicates that installation and usage of pipelines in a seawater environment above 5 °C for transportation of CO₂ and in an oxygen saturated environment will have an increased risk of lost in ductility of the pipeline due to the effect of hydrogen embrittlement. This can lead to reduction in pipeline wall strength and potential of SCC occurrence. As such installations of pipelines should be in deep waters and polar regions where temperatures are below 5 °C.

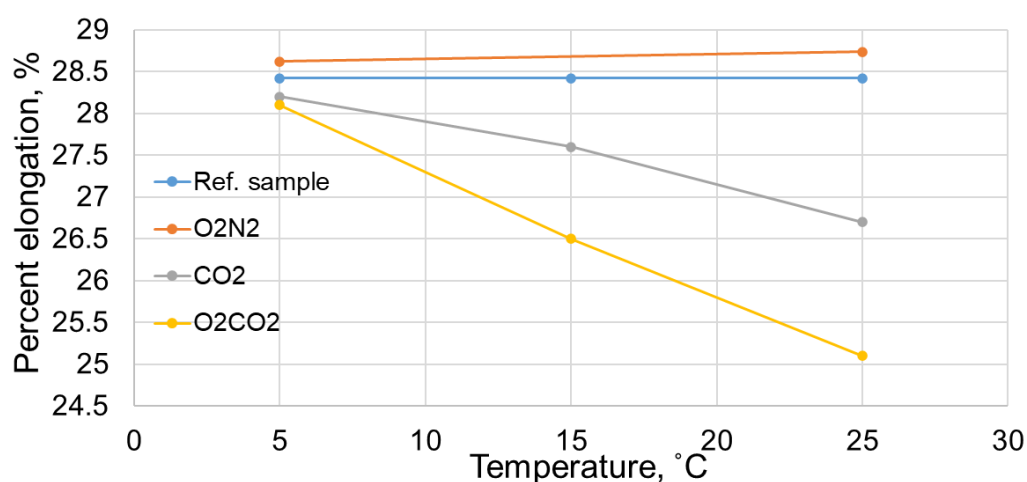


Figure 8-9 - Variations in percent elongation (%) before failure of the exposed X70 dog-bone samples in the 3.5 % NaCl simulated solution with change in trace gas mixture and solution temperature.

8.5 Vickers Hardness Analysis

Fluctuations in metal hardness were observed on the analysed X70 dog-bone samples with change in test location, trace gas mixture and solution temperatures. Figure 8-10 shows the lowest average metal hardness values obtained from the exposed X70 dog-bone samples in the different 3.5 % NaCl simulated conditions. Similarly, as obtained from the tensile strength percent elongation before failure, the samples exposed in solution with O₂/CO₂ at all exposure temperatures showed highest lost in hardness with a value of 119.3 HVC at 25 °C as presented in Figure 8-10. From the analysis of the obtained hardness values of the exposed X70 dog-bone samples in the different exposure conditions, it can be stated that the usage of carbon steels as a pipeline material for CO₂ transportation in seawater environment saturated with O₂ can lead to reduction in wear resistance of the material, and subsequently increase its potential to SCC occurrence, especially if operated at higher temperatures above 25 °C.

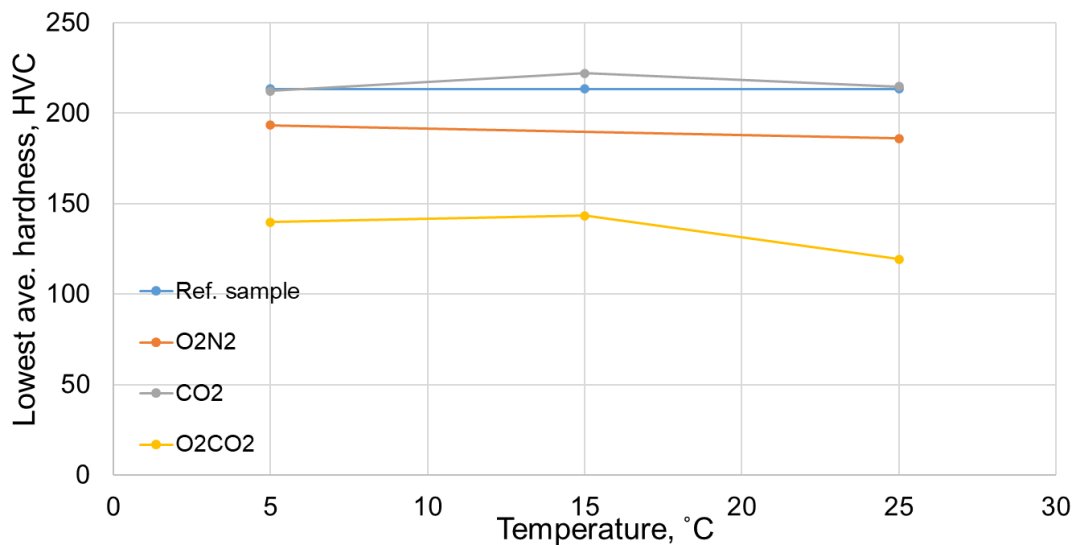


Figure 8-10 - Lowest average hardness values (HVC) of the exposed X70 dog-bone samples in the different 3.5 % NaCl simulated solution with change in trace gas mixture and solution temperatures.

8.6 Chapter Summary

The effect of temperature, traces gas mixture, applied stress levels and stress application techniques on stress corrosion susceptibility of the representative pipeline carbon steels exposed in the simulated 3.5 % NaCl solution has been clearly researched and understood.

In general, increasing temperature of the exposure environment was observed to increase corrosion rates of carbon steels. An increase in corrosion rates of more than 100 % was observed with increasing temperature from 5 °C to 25 °C. The X100 samples with bainitic ferrite and austenite grains were observed to present highest corrosion rates at all exposure temperatures relative to X65, X70 and X80 samples. This indicates that the X100 carbon is more susceptible to SCC in all the simulated offshore pipeline operating conditions. As such the selection of carbon steel to be used as a pipeline material in transportation of CO₂ in a seawater environment, in carbon capture and storage, or in transportation of various oil and gas products which contain trace gases should be between X65, X70 or X80 due to their observed lower corrosion rates in comparison with X100.

Increase in average corrosion rates were observed with change in trace gas mixtures in the simulated saltwater solution. Increasing the percentage of oxygen in the solution from 100 % N₂ to 20%O₂/80%N₂ greatly increased the corrosion rates of the exposed carbon steels as presented in Figure 8-1. Similarly, an increase in average corrosion rates of about 100 % was observed on the exposed carbon steels with change in solution trace gas from 100 % CO₂ to 20%O₂/80%CO₂ as shown in Figure 8-3. As presented in Figure 8-2, it can be stated that surface damage of a material does have effect on its corrosion susceptibility due to the observed increase in average corrosion rates from normal exposed X70 samples to mechanically/chemically pre-damaged. No significant difference in average corrosion rates observed on the exposed X70 and X100 samples with change in sample geometry from C-rings to 3-point bent-beam as also presented in Figure 8-2.

Similarly, an increase in metal loss of more than 100 % was observed on the exposed carbon steels with change in temperature from 5 °C to 25 °C as also observed from calculated corrosion rates from LPR measurements. Increased metal loss was also observed on all exposed samples with change in solution trace gas mixture and solution temperatures as observed from the calculated average corrosion rates from LPR measurements. Variations in surface metal change were observed on the exposed carbon steel grades with change in solution temperature, trace gas mixture and with effect of microstructure of the steels. The surface damages ranged from even distribution with low pits features (on X100) to uneven distribution with high pits features observed on X65, X70 and X80 steels.

Higher metal loss and pits features were observed on samples exposed in solution with O₂/N₂ relative to samples exposed in solution with N₂. Increasing metal loss with no significant change in metal change was also observed with change in trace gas mixture from CO₂ to O₂/CO₂ at all solution temperatures. With change in surface damage, the chemically pre-damaged samples (salted) presented higher surface metal change and pits features in comparison with mechanically pre-damaged and normal exposed samples. This indicates that presence of chloride ions contained in a salt causes formation of pits on carbon steel surfaces. No significant difference in metal change observed on the exposed samples with change in sample geometry from C-rings to 3-point bent-beam.

Different surface morphologies were observed with change in microstructure of the steels, increasing temperature, change in trace gas mixture and stressing technique. In general, the X100 samples (with bainitic ferrite and austenite grains) at all exposure conditions were observed to have wide and shallow elliptical morphology. The X65, X70 and X80 samples showed a type of deep undercutting metal dissolution with presence of micro-cracks on the X65 and X70 samples. Higher metal dissolution and deterioration were observed on samples exposed in solution with O₂/CO₂ in comparison with N₂, O₂/N₂ and CO₂. Higher metal dissolution and deterioration were observed on 3-point beat-beam samples in

comparison with C-rings samples. This indicates that stressing method has an effect on the stress corrosion susceptibility, crack initiation and propagation of the exposed carbon steel grades. No visible significant difference in surface morphology observed between the mechanically and chemically pre-damaged samples and also normal exposed samples. All analyzed surface morphologies were observed to increase in size with change in solution temperature from 5 °C to 25 °C. Results from EDS analysis shows no significant difference in Fe and Mn concentration between the exposed X70 and X100 samples in all exposure conditions.

Results from tensile strength analysis show variations in percent elongation before failure with change in trace gas mixtures and temperature. In general, lowest percent elongation before failure and lost in ductility were observed on the X70 dog bone sample exposed in solution with O₂/CO₂ at 25 °C with an elongation value of 25.1 % as presented in Figure 8-9. Similarly, highest lost in hardness was also observed on the X70 dog bone sample exposed in solution with O₂/CO₂ at 25 °C with a value of 119.3 HVC as presented in Figure 8-10.

9 CONCLUSIONS AND RECOMMENDATIONS

This chapter presents the major findings and contributions made during the course of this research. The impact of traces gases with change in temperature and applied stress on the stress corrosion behaviour of the selected offshore pipeline carbon steels has been clearly researched and understood, as such the aim of the research has been achieved. Furthermore, it is essential to understand the stress corrosion resistance of a particular carbon steel with careful consideration of its metallurgical properties prior to its installation and usage in an intended operating environment. This plays a vital role in selecting the most cost effective and economical corrosion mitigation techniques that will last throughout the service life of the selected material and hence will reduce corrosion associated failures.

9.1 Conclusions

It is vital that conclusions are made on major findings on the impact of trace gases on the exposed carbon steels with consideration of metallurgical differences and exposure conditions. Among the conclusions made from this research based on the research objectives are:

Objective one: To evaluate the effect of temperature and trace gases on corrosion rates (N_2 , CO_2 , O_2/N_2 and O_2/CO_2).

- ❖ The increase in solution temperature increases the corrosion rates and metal loss exceedance of the representative carbon steels samples exposed in the simulated pipeline operating conditions. As temperature increases from 5 °C to 25 °C, the corrosion rate of the samples increased by more than 100 %. It is observed that the X100 samples with bainitic ferrite and dispersed austenite grains at all exposure temperatures presented highest corrosion rates with an average value of 3.4570 mm/year in solution with O_2/CO_2 mixture at 25 °C. This shows that the X100 samples have higher corrosion current density, leading to higher corrosion rates. It can be concluded that increasing temperature of

simulated saltwater solution increases the transfer of electrons in a corrosion process, thus leading to increase in corrosion rate of pipeline carbon steels. Furthermore, the corrosion rate also depends on the microstructure and ultimate tensile strength of the exposed carbon steel.

- ❖ A clear increase in corrosion rates were observed on all exposed carbon steel grades with change in trace gas composition from N_2 to O_2/N_2 (an increase by 1 order of magnitude), and from CO_2 to O_2/CO_2 (an increase of about 70 % at 15 °C and 25 °C, with about 15 % at 5 °C). It can be concluded that increasing percentage of O_2 in the simulated saltwater solution enhances the anodic reaction rates, hence accelerating the corrosion rates of carbon steels with increasing temperature.

Objective two: To evaluate the effect of stress application techniques, applied stress levels and metal surface damage on corrosion rates and morphology.

- ❖ No significant change in corrosion rates observed on the exposed carbon steels with change in sample geometry from C-rings to 3-point bent beam samples. However, variations on surface corrosion morphology were observed with change in sample geometry. This shows that stress application methods have impact on corrosion morphology and crack initiation of carbon steels in the simulated 3.5 % NaCl solution.
- ❖ The Increase in applied stress levels from 80 % Y.S. to 95 % Y.S. and change in surface state of the carbon steels (notched state) presented no significant difference on corrosion rates and metal loss exceedance on the exposed carbon steels at all exposure conditions. However, the presence of higher change in surface state at a particular area (wear, bend, large scratch etc.) of an installed pipeline with application of higher pressure of about 100% Y.S. or more might have impact on its corrosion behaviour. In addition, the mechanically and chemical pre-damaged samples were observed to show higher corrosion rates relative to normal exposed (undamaged) samples. It can be concluded that, increasing surface roughness on carbon steel's surfaces have impact on its corrosion behaviour in the simulated 3.5 % NaCl solution saturated with CO_2 . As

such machining of selected carbon steel as a pipeline material should be to a widely accepted and up to date standard surface finish.

Objective three: To propose corrosion mechanisms on the exposed carbon steels in the various simulated seawater conditions.

- ❖ Variations in surface corrosion mechanisms were observed with change in trace gas mixtures and microstructures of the steels. In solution with N_2 (baseline tests) all samples presented shallow ellipses, which become wider and deeper with change in trace gas mixture from N_2 to O_2/N_2 . However, presence of vertical dissolution was also observed on the X100 samples in solution with O_2/N_2 . In solution with CO_2 and O_2/CO_2 mixture, the X65 samples (with polygonal ferritic-pearlitic grains) and X70 (with globular ferrite grains with grain boundary pearlite grains and coarse dispersion of precipitates) presented a type of undercutting morphology with presence of microcracks. The X80 samples (with ferrite grains and distribution of pearlite bands) showed a very deep and wide elliptical morphology with combination of vertical and horizontal dissolution. The X100 samples with bainitic ferrite and dispersed austenite grains showed similar morphology at all exposure conditions, with wide and shallow ellipses. It can be stated that surface corrosion morphology and cracking susceptibility of carbon steels strongly depends on steels' microstructures and their reaction to the solution composition and trace gas mixture.
- ❖ Furthermore, the obtained data sets from dimensional metrology analysis showed that the X100 (with bainitic ferrite and dispersed austenite grains) samples at all exposure conditions presented an even damage distribution with low pits features across the samples surface's, while the X65, X70 and X80 with mixture of ferritic and pearlitic grains showed an uneven damage distribution and higher pits features. This indicates that the X100 samples corroded in a form of general metal dissolution, while the X65, X70 and X80 samples corroded in a more localised form. It can be concluded that the form of corrosion and surface damage of carbon steels

in the different simulated seawater conditions depends on the microstructure of the carbon steel.

- ❖ Predominant corrosion mechanism of the exposed carbon steels in the different simulated environment conditions is by metal dissolution (anodic dissolution). However, reduction in ductility was observed of on exposed X70 carbon steels samples in solution with CO₂ and O₂/CO₂ with formation of microcracks. This indicates involvement of hydrogen embrittlement in the mechanism. This shows that presence of CO₂ in a corrosive medium have direct contribution to hydrogen charging mechanism on the steel's surfaces, hence resulting in ductility loss of the metals and potential formation of cracks.
- ❖ In general, the X100 samples were observed to be more susceptible to SCC due to higher corrosion rates in the different simulated 3.5 % NaCl solution. However, the X65 and X70 samples which presented microcracks in solution with CO₂ and mixture of O₂/CO₂ can potentially lead to SCC in a prolonged duration of usage and subsequently lead to premature failure.

9.2 Recommendations for Industry and Future Work

- ❖ The selection of carbon steels that are made up of bainitic and/or austenite grains should be avoided as pipeline materials, due to their observed higher corrosion rates in all simulated 3.5 % NaCl solutions, rather selection should be tailored on carbon steels with ferritic-pearlitic grains, which presented lower corrosion rates.
- ❖ Carbon steels with small and fine grain microstructures are reported to be more susceptible to SCC, as such, the selection of carbon steels as pipeline materials should be tailored on carbon steels with larger and coarse grain structures.
- ❖ Pipelines should be installed and operated in lower oxygen environment and at temperatures below 25 °C. This will help to reduce acceleration of

the cathodic reaction rates taking place on the material's surface, hence reducing its potential to corrosion and subsequent SCC occurrence.

- ❖ Lower ultimate tensile strength materials should be considered in carbon steels selection to be used as pipeline materials, as susceptibility to SCC is observed to increase with increasing ultimate tensile strength of carbon steels as reported in section 5.2.
- ❖ Experiments should be conducted for longer time (6 to 12 months), with application of cyclic loading or fluctuating stresses to simulate real time pipeline operating conditions. This will enable better understanding of stress corrosion resistance of the intended for service pipeline carbon steels.
- ❖ Experiments should be conducted on welded joints of pipeline carbon steels. This will enable better understanding of stress corrosion behaviour of heat affected zones in comparison with unwelded sections.

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APPENDICES

Appendix A : List of Publications and Posters

A.1 Appendix: Conference Paper

1. Abubakar, S. A., Mori, S. and Sumner, J. "The Effect of Dissolved CO₂ on SCC of Pipeline Steel in Simulated Marine Environments" EUROCORR 2022, paper No 36516, Berlin, Germany, 28 August - 01 September 2022.

A.2 Appendix: Articles

1. Shamsuddeen Ashurah Abubakar, Stefano Mori and Joy Sumner. "A Review of Factors Affecting SCC Initiation and Propagation in Pipeline Carbon Steels" Metals Journal, 2022, 12, 1-24.
2. Shamsuddeen Ashurah Abubakar, Stefano Mori and Joy Sumner. "Effect of Dissolved CO₂ on the Interaction of Stress and Corrosion for Pipeline Carbon Steels in Simulated Marine Environments" Metals Journal, 2023, 13, 1-20.

A.3 Appendix: Posters

1. Abubakar, S. A., Mori, S. and Sumner, J. "The Effect of Dissolved CO₂ on SCC of Pipeline Steel in Simulated Marine Environments" EUROCORR 2022, poster No 36516, Berlin, Germany, 28 August - 01 September 2022.
2. Shamsuddeen Abubakar, Stefano Mori and Joy Sumner. "The Effects of Dissolved O₂ on SCC of API 5L X70 Carbon Steel in Simulated Marine Environments" Microscopy of Oxidation 11, poster No 5539484, Cranfield University, England, 12-14 September 2022.
3. Abubakar, S. A., Mori, S. and Sumner, J. "Effect of Dissolved O₂/CO₂ Mixture on SCC of API 5L X70 Pipeline Steel in Simulated Environments " EUROCORR 2023, poster No 41825, Brussels, Belgium, 27-31 August 2023.

Appendix B : Dimensional measurements, pre and post-exposure weights of all samples exposed in the different simulated 3.5 % NaCl solution.

B.1 Appendix: Dimensional, pre- and post-exposure weight measurements of C-rings samples exposed in solution with N₂ at 5 °C and 25 °C.

Table B-1 - C-rings specimen's dimensions exposed in solution with N₂ at 5 °C solution temperature.

Material grade	Specimen #	Y.S., %	Weight of specimens, g		O.D (middle section), mm	O.D (edge sections), mm		Wall thickness (middle section), mm	Wall thickness (edge sections), mm		Width (middle section), mm	Mouth opening, mm	
			Pre-exposure	Post-exposure		1	2		1	2		Before stressing	After stressing
X65	X65N ₂ -5a	80	4.847	4.839	18.52	18.53	18.53	1.31	1.32	1.31	12.02	8.07	6.80
	X65N ₂ -5b	95	4.816	4.809	18.51	18.52	18.52	1.31	1.31	1.31	12.02	8.08	6.76
	X65N ₂ -Notched	80	4.845	4.839	18.52	18.51	18.51	1.31	1.32	1.31	12.03	8.03	6.71
X70	X70N ₂ -5a	80	4.881	4.872	18.50	18.48	18.49	1.30	1.31	1.31	12.02	8.15	6.87
	X70N ₂ -5b	95	4.892	4.885	18.51	18.51	18.50	1.31	1.32	1.32	12.02	7.96	6.65
	X70N ₂ -Notched	80	4.862	4.856	18.50	18.51	18.51	1.31	1.32	1.32	12.02	8.03	6.72
X80	X80N ₂ -5a	80	4.826	4.818	18.50	18.50	18.50	1.32	1.32	1.32	12.03	8.01	6.70
	X80N ₂ -5b	95	4.847	4.841	18.52	18.53	18.52	1.31	1.30	1.31	12.03	7.96	6.43
	X80N ₂ -Notched	80	4.834	4.829	18.50	18.50	18.49	1.31	1.31	1.30	12.02	7.88	6.82
X100	X100N ₂ -5a	80	4.834	4.828	18.51	18.52	18.51	1.32	1.32	1.32	12.02	8.16	6.86
	X100N ₂ -5b	95	4.853	4.844	18.50	18.51	18.51	1.31	1.32	1.32	12.03	8.04	6.48
	X100N ₂ -Notched	80	4.864	4.856	18.51	18.51	18.52	1.32	1.32	1.32	12.03	8.10	6.81

Table B-2 – C-rings specimen’s dimensions exposed in solution with N₂ at 25 °C solution temperature.

Material grade	Specimen #	Y.S ., %	Weight of specimens, g		O.D (middle section), mm	O.D (edge sections), mm		Wall thickness (middle section), mm	Wall thickness (Edge sections), mm		Width (middle section), mm	Mouth opening, mm	
			Pre-exposure	Post-exposure		1	2		1	2		Before stressing	After stressing
X65	X65N ₂ -25a	80	4.833	4.820	18.51	18.50	18.51	1.31	1.30	1.30	12.02	8.03	6.70
	X65N ₂ -25b	95	4.849	4.837	18.50	18.51	18.51	1.32	1.31	1.32	12.02	8.00	6.69
	X65N ₂ -Notched	80	4.825	4.812	18.52	18.53	18.52	1.32	1.32	1.32	12.03	8.08	6.76
	X70N ₂ -25a	80	4.842	4.830	18.51	18.51	18.51	1.32	1.32	1.32	12.03	8.03	6.70
	X70N ₂ -25b	95	4.864	4.851	18.50	18.51	18.51	1.32	1.32	1.31	12.02	8.04	6.71
	X70N ₂ -Notched	80	4.844	4.831	18.51	18.52	18.52	1.30	1.29	1.30	12.02	7.97	6.66
X80	X80N ₂ -25a	80	4.792	4.778	18.49	18.50	18.49	1.30	1.30	1.29	12.00	7.97	6.67
	X80N ₂ -25b	95	4.806	4.792	18.50	18.51	18.51	1.29	1.30	1.29	12.00	7.98	6.46
	X80N ₂ -Notched	80	4.800	4.786	18.50	18.50	18.50	1.30	1.29	1.29	12.02	8.02	6.72
X100	X100N ₂ -25a	80	4.883	4.868	18.52	18.53	18.53	1.31	1.31	1.32	12.02	8.06	6.78
	X100N ₂ -25b	95	4.824	4.807	18.51	18.49	18.50	1.30	1.31	1.31	12.02	8.07	6.52
	X100N ₂ -Notched	80	4.873	4.857	18.52	18.52	18.52	1.32	1.32	1.32	12.03	7.98	6.69

B.2 Appendix: Dimensional, pre- and post-exposure weight measurements of C-rings and 3-point bent-beam samples exposed in solution with CO₂ at 5 °C, 15 °C and 25 °C.

Table B-3 - C-rings specimen's dimensions exposed in solution with CO₂ at 5 °C solution temperature.

Material grade	Specimen #	Y.S., %	Weight of specimens, g		O.D (middle section), mm	O.D (edge sections), mm		Wall thick. (middle section), mm	Wall thick. (edge sections), mm		Width (middle section), mm	Width (edge sections), mm		Mouth opening/O.D., mm	
			Pre-exp.	Post-exp.		1	2		1	2		1	2	Bef. str.	M.O aft. str./O.D.
X65	X65CO ₂ -5a	80	4.818	4.655	18.52	18.50	18.50	1.296 1.301 1.306	1.297 1.293 1.298	1.304 1.296 1.307	12.00	12.00	12.00	8.15	7.04 18.15
	X65CO ₂ -5b	95	4.861	4.703	18.53	18.53	18.52	1.311 1.314 1.313	1.312 1.316 1.309	1.317 1.320 1.310	12.04	12.02	12.02	8.04	6.81 18.07
	X65CO ₂ -Notched	80	4.825	4.665	18.50	18.50	18.52	1.310 1.307 1.305	1.310 1.316 1.296	1.318 1.306 1.309	12.02	12.02	12.02	8.01	6.92 18.13
X70	X70CO ₂ -5a	80	4.885	4.723	18.49	18.46	18.48	1.296 1.314 1.311	1.332 1.344 1.329	1.318 1.334 1.308	12.03	12.02	12.01	8.14	7.02 18.13
	X70CO ₂ -5b	95	4.944	4.782	18.52	18.52	18.53	1.326 1.324 1.319	1.339 1.335 1.377	1.325 1.332 1.328	12.03	12.02	12.03	8.06	6.86 18.08
	X70CO ₂ -Notched	80	4.896	4.741	18.48	18.51	18.50	1.300 1.297 1.299	1.333 1.372 1.336	1.310 1.306 1.346	12.04	12.03	12.03	7.96	6.88 18.13
X80	X80CO ₂ -5a	80	4.838	4.674	18.51	18.49	18.52	1.297 1.295	1.290 1.311	1.302 1.312	12.07	12.08	12.06	7.92	6.76

								1.297	1.295	1.299					18.06
	X80CO ₂ -5b	95	4.825	4.668	18.53	18.50	18.53	1.308	1.305	1.311	12.04	12.02	12.03	8.02	6.80
								1.295	1.317	1.320					17.95
								1.294	1.309	1.305					
	X80CO ₂ -Notched	80	4.854	4.699	18.51	18.50	18.50	1.325	1.296	1.321	12.04	12.02	12.04	7.98	6.80
								1.315	1.319	1.308					
								1.318	1.303	1.299					18.04
X100	X100CO ₂ -5a	80	4.917	4.521	18.50	18.49	18.52	1.332	1.348	1.336	12.02	12.02	12.03	8.02	6.83
								1.338	1.367	1.356					18.02
								1.342	1.330	1.328					
	X100CO ₂ -5b	95	4.961	4.540	18.52	18.50	18.51	1.331	1.358	1.348	12.03	12.02	12.02	8.10	6.86
								1.333	1.400	1.420					17.93
								1.337	1.382	1.368					
	X100CO ₂ -Notched	80	4.847	4.438	18.47	18.49	18.50	1.311	1.336	1.323	12.02	12.03	12.02	8.03	6.67
								1.301	1.357	1.310					
								1.307	1.395	1.365					8.00

Table B-4 - C-rings specimen's dimensions exposed in solution with CO₂ at 15 °C solution temperature.

Material grade	Specimen #	Y.S., %	Weight of specimens, g		O.D (middle section), mm	O.D (edge sections), mm		Wall thick. (middle section), mm	Wall thick. (edge sections), mm		Width (middle section), mm	Width (edge sections), mm		Mouth opening/O.D., mm	
			Pre-exp.	Post-exp.		1	2		1	2		1	2	Bef. str.	M.O aft. str./O.D.
X65	X65CO ₂ -15a	80	4.831	4.535	18.47	18.47	18.49	1.304	1.311	1.302	11.98	11.98	11.99	8.05	6.81
								1.298	1.338	1.338					18.15
								1.291	1.312	1.302					
	X65CO ₂ -15b	95	4.808	4.517	18.49	18.49	18.50	1.298	1.321	1.333	12.02	12.00	12.02	8.04	6.62
								1.308	1.345	1.377					
								1.304	1.313	1.330					18.08

X70	X70CO ₂ -15a	80	4.864	4.578	18.47	18.46	18.48	1.315 1.325 1.323	1.332 1.348 1.323	1.330 1.339 1.331	12.00	12.01	12.02	8.06	6.81 18.13
	X70CO ₂ -15a-R	80	4.847	4.563	18.48	18.50	18.49	1.300 1.323 1.346	1.308 1.344 1.307	1.346 1.356 1.341	12.01	12.00	12.02	8.01	6.77 18.13
	X70CO ₂ -15b	95	4.897	4.616	18.50	18.48	18.50	1.322 1.320 1.308	1.327 1.350 1.330	1.303 1.345 1.307	12.02	12.03	12.02	8.12	6.95 18.06
X80	X80CO ₂ -15a	80	4.807	4.534	18.52	18.50	18.53	1.319 1.324 1.301	1.309 1.337 1.303	1.295 1.315 1.300	12.03	12.02	12.02	8.02	6.58 18.04
	X80CO ₂ -15b	95	4.804	4.526	18.49	18.49	18.50	1.298 1.301 1.313	1.323 1.351 1.331	1.291 1.326 1.299	12.02	12.00	12.01	8.04	6.50 17.96
X100	X100CO ₂ -15a	80	4.850	3.724	18.50	18.50	18.51	1.323 1.308 1.315	1.320 1.310 1.305	1.316 1.314 1.315	12.02	12.00	12.01	8.01	6.55 18.02
	X100CO ₂ -15b	95	4.865	3.779	18.52	18.50	18.51	1.340 1.324 1.304	1.338 1.335 1.326	1.331 1.329 1.331	12.01	12.00	12.03	8.10	6.52 17.91

Table B-5 - C-rings specimen's dimensions exposed in solution with CO₂ at 25 °C solution temperature.

Material grade	Specimen #	Y.S., %	Weight of specimens, g		O.D (middle section), mm	O.D (edge sections), mm		Wall thick. (middle section), mm	Wall thick. (edge sections), mm		Width (middle section), mm	Width (edge sections), mm		Mouth opening/O.D., mm	
			Pre-exp.	Post-exp.		1	2		1	2		1	2	Bef. Str.	M.O aft. str./O.D.
X65	X65CO ₂ -	80	4.826	4.416	18.53	18.52	18.52	1.308	1.299	1.305	12.02	12.01	12.01	8.01	6.98

	25a							1.296 1.300	1.330 1.312	1.324 1.315					18.15
	X65CO ₂ - 25b	95	4.832	4.428	18.50	18.51	18.50	1.299 1.293 1.296	1.304 1.309 1.324	1.298 1.311 1.330	12.03	12.01	12.02	8.01	6.91 18.07
	X65CO ₂ - Notched	80	4.854	4.479	18.50	18.49	18.50	1.312 1.319 1.323	1.291 1.313 1.292	1.315 1.326 1.299	12.02	12.03	12.02	8.09	7.07 18.14
X70	X70CO ₂ - 25a	80	4.874	4.491	18.49	18.47	18.47	1.311 1.316 1.315	1.310 1.329 1.336	1.308 1.334 1.325	12.03	12.02	12.02	8.01	7.01 18.14
	X70CO ₂ - 25b	95	4.846	4.461	18.46	18.50	18.49	1.304 1.301 1.299	1.318 1.344 1.313	1.312 1.334 1.307	12.02	12.02	12.04	8.00	6.92 18.06
	X70CO ₂ - Notched	80	4.906	4.497	18.47	18.48	18.48	1.326 1.321 1.320	1.303 1.334 1.308	1.305 1.324 1.331	12.03	12.04	12.03	7.94	6.93 18.13
	X70CO ₂ - Mech.pre- damaged	80	4.894	4.196	18.49	18.50	18.51	1.299 1.301 1.302	1.304 1.318 1.314	1.319 1.341 1.312	11.98	11.95	11.97	8.02	6.89 18.15
	X70CO ₂ - Mech.pre- damaged	95	4.889	4.185	18.47	18.47	18.48	1.316 1.323 1.335	1.320 1.321 1.325	1.327 1.318 1.319	12.01	11.99	11.98	8.04	6.95 18.06
	X70CO ₂ - Chem.pre- damaged	80	4.902	4.247	18.49	18.50	18.52	1.312 1.305 1.310	1.322 1.354 1.349	1.352 1.356 1.358	11.97	11.98	12.02	7.95	6.91 18.13
	X80CO ₂ - 25a	80	4.840	4.462	18.50	18.50	18.51	1.321 1.326 1.316	1.328 1.355 1.337	1.323 1.360 1.326	12.03	12.03	12.03	8.01	18.05 6.56
	X80CO ₂ - 25b	95	4.860	4.445	18.51	18.52	18.50	1.305 1.312	1.305 1.336	1.309 1.322	12.03	12.04	12.02	8.02	17.95

								1.303	1.309	1.307					6.51
	X80CO ₂ -Notched	80	4.865	4.459	18.53	18.52	18.52	1.308 1.304 1.310	1.292 1.318 1.306	1.304 1.322 1.310	12.02	12.03	12.04	8.00	18.05 6.54
X100	X100CO ₂ -25a	80	4.947	3.714	18.52	18.51	18.51	1.340 1.342 1.339	1.340 1.377 1.343	1.334 1.365 1.352	12.04	12.02	12.03	8.11	18.02 6.64
	X100CO ₂ -25b	95	4.914	3.722	18.53	18.52	18.53	1.394 1.396 1.334	1.334 1.368 1.327	1.324 1.347 1.331	12.03	12.02	12.02	8.14	17.93 6.68
	X100CO ₂ -Notched	80	4.955	3.763	18.50	18.52	18.51	1.339 1.341 1.339	1.349 1.387 1.350	1.329 1.374 1.361	12.02	12.01	12.02	8.13	18.00 6.67

Table B-6 - 3-point bent-beam specimen's dimensions exposed in solution with CO₂ at 5 °C solution temperature.

Material grade	Specimen #	Y.S., %	Weight of specimens, g		Length, mm	Wall thickness (middle section), mm	Wall thickness (edge sections), mm		Width (middle section), mm	Width (edge sections), mm		Surface area, cm ²
			Pre-exposed	Post-exposed			1	2		1	2	
X70	X70CO ₂ -3P-5a	80	17.320	16.585	102.01	1.088 1.094 1.090	1.089 1.090 1.091	1.086 1.089 1.087	20.01	20.02	20.01	42.5297
	X70CO ₂ -3P-5a-R	80	17.542	16.811	101.90	1.102 1.103 1.103	1.102 1.102 1.103	1.101 1.100 1.099	19.97	19.95	19.97	42.413

X100	X100CO ₂ - 3P-5a	80	17.486	15.098	102.16	1.125 1.128 1.131	1.039 1.057 1.069	1.133 1.134 1.135	20.05	20.02	20.03	42.7942
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Table B-7 - 3-point bent-beam specimen's dimensions exposed in solution with CO₂ at 25 °C solution temperature.

Material grade	Specimen #	Y.S., %	Weight of specimens, g		Length, mm	Wall thickness (middle section), mm	Wall thickness (edge sections), mm		Width (middle section), mm	Width (edge sections), mm		Surface area, cm ²
			Pre-exposed	Post-exposed			1	2		1	2	
X70	X70CO ₂ - 3P-25a	80	17.552	15.818	101.97	1.104 1.104 1.102	1.102 1.103 1.102	1.103 1.102 1.103	20.03	20.03	20.05	42.5937
	X70CO ₂ - 3P-25a-R	80	17.539	15.798	102.00	1.104 1.103 1.102	1.102 1.102 1.101	1.103 1.102 1.100	20.04	20.02	20.02	42.5842
X100	X100CO ₂ - 3P-25a	80	18.020	13.607	102.15	1.133 1.140 1.126	1.136 1.136 1.138	1.135 1.134 1.133	20.04	20.05	20.03	42.7543

B.3 Appendix: Dimensional, pre- and post-exposure weight measurements of C-rings samples exposed in solution with O₂/N₂ at 5 °C and 25 °C.

Table B-8 - C-rings specimen's dimensions exposed in solution with O₂/N₂ at 5 °C solution temperature.

Material grade	Specimen #	Y. S., %	Weight of specimens, g		O.D. (mid. sect.), mm	O.D. (edge sections), mm		Wall thick. (mid. sect.) mm	Wall thick.(edge sections), mm		Width (middle section) mm	Width (edge sections), mm		Mouth opening/O.D., mm	
			Pre-exp.	Post-exp.		1	2		1	2		1	2	Bef. str.	M.O aft. str./O.D.
X65	X65O ₂ /N ₂ -5a	80	4.809	4.662	18.51	18.51	18.52	1.296 1.301 1.306	1.299 1.322 1.313	1.281 1.301 1.328	12.02	11.99	12.01	8.10	7.13 18.15
	X65O ₂ /N ₂ -5b	95	4.868	4.717	18.50	18.51	18.51	1.319 1.332 1.341	1.312 1.331 1.318	1.302 1.324 1.342	11.97	11.97	11.96	8.06	6.97 18.06
	X65O ₂ /N ₂ -Notched	80	4.843	4.716	18.49	18.50	18.48	1.335 1.322 1.330	1.299 1.326 1.308	1.318 1.332 1.308	11.97	11.96	11.96	8.04	7.04 18.14
X70	X70O ₂ /N ₂ -5a	80	4.918	4.767	18.51	18.51	18.50	1.332 1.328 1.330	1.341 1.366 1.344	1.325 1.349 1.328	11.99	11.96	11.98	8.20	7.32 18.13
	X70O ₂ /N ₂ -5b	95	4.884	4.792	18.51	18.52	18.53	1.307 1.306 1.314	1.310 1.344 1.309	1.307 1.331 1.302	12.03	12.00	12.02	8.09	7.13 18.08
	X70O ₂ /N ₂ -Notched	80	4.854	4.722	18.48	18.53	18.51	1.314 1.311 1.312	1.286 1.297 1.284	1.318 1.340 1.313	12.00	12.01	12.01	7.94	6.91 18.13
X80	X80O ₂ /N ₂ -5a	80	4.821	4.732	18.49	18.49	18.48	1.331 1.339	1.282 1.304	1.312 1.341	12.02	12.02	12.00	7.99	6.82

								1.316	1.286	1.325					18.04
	X80O ₂ /N ₂ -5b	95	4.83 1	4.741	18.49	18.51	18.50	1.307 1.312 1.305	1.322 1.336 1.312	1.323 1.342 1.328	12.04	12.02	12.01	8.07	6.73 17.97
	X80O ₂ /N ₂ -Notched	80	4.83 2	4.726	18.48	18.50	18.51	1.323 1.310 1.330	1.343 1.341 1.347	1.315 1.307 1.318	12.01	12.00	11.99	8.01	6.84 18.04
X100	X100O ₂ /N ₂ -5a	80	4.87 9	4.759	18.51	18.50	18.49	1.312 1.316 1.321	1.319 1.344 1.311	1.320 1.346 1.330	11.98	11.96	11.97	8.08	6.83 18.02
	X100O ₂ /N ₂ -5b	95	4.94 5	4.772	18.51	18.52	18.51	1.340 1.335 1.340	1.335 1.360 1.340	1.340 1.360 1.332	12.00	11.99	11.97	7.97	6.67 17.90
	X100O ₂ /N ₂ -Notched	80	4.94 8	4.811	18.49	18.48	18.49	1.349 1.351 1.352	1.340 1.360 1.345	1.356 1.372 1.347	12.01	12.00	11.98	8.10	6.82 8.01

Table B-9 - C-rings specimen's dimensions exposed in solution with O₂/N₂ at 25 °C solution temperature.

Material grade	Specimen #	Y.S., %	Weight of specimens, g		O.D (mid. sect.), mm	O.D. (edge sections), mm		Wall thick. (mid. sect.), mm	Wall thick. (edge sections), mm		Width (mid. sect.), mm	Width (edge sections), mm		Mouth opening/O.D., mm	
			Pre-exp.	Post-exp.		1	2		1	2		1	2	Bef. str.	M.O aft. str./O.D.
X65	X65O ₂ /N ₂ -25a	80	4.857	4.690	18.50	18.49	18.50	1.286 1.283 1.287	1.350 1.356 1.338	1.309 1.340 1.302	11.97	11.97	11.97	7.99	6.95 18.13
	X65O ₂ /N ₂ -25b	95	4.828	4.656	18.51	18.51	18.50	1.309 1.300	1.300 1.325	1.362 1.327	11.99	11.98	11.99	8.02	6.92

								1.278	1.302	1.347					18.06
	X65O ₂ /N ₂ -Notched	80	4.841	4.643	18.48	18.47	18.50	1.308 1.296 1.290	1.320 1.337 1.311	1.287 1.290 1.280	12.00	11.99	12.01	7.97	6.92 18.14
X70	X70O ₂ /N ₂ -25a	80	4.846	4.656	18.48	18.48	18.49	1.285 1.299 1.286	1.295 1.300 1.293	1.311 1.335 1.312	12.03	12.02	12.02	8.04	7.03 18.15
	X70O ₂ /N ₂ -25b	95	4.933	4.737	18.48	18.46	18.47	1.336 1.351 1.346	1.347 1.354 1.334	1.298 1.308 1.302	12.02	12.01	12.00	7.98	6.89 18.06
	X70O ₂ /N ₂ -Notched	80	4.895	4.728	18.47	18.46	18.47	1.312 1.316 1.318	1.317 1.327 1.312	1.299 1.316 1.307	12.02	12.00	12.01	7.96	6.94 18.13
X80	X80O ₂ /N ₂ -25a	80	4.897	4.647	18.48	18.47	18.48	1.325 1.332 1.340	1.324 1.332 1.320	1.331 1.336 1.339	11.99	12.01	11.99	7.79	6.46 18.06
	X80O ₂ /N ₂ -25b	95	4.818	4.573	18.47	18.46	18.49	1.297 1.300 1.291	1.278 1.272 1.277	1.299 1.305 1.292	12.02	12.00	11.99	8.08	6.59 17.97
	X80O ₂ /N ₂ -Notched	80	4.829	4.627	18.48	18.48	18.47	1.300 1.296 1.291	1.306 1.335 1.296	1.296 1.325 1.300	11.97	11.98	11.99	7.92	6.49 18.06
X100	X100O ₂ /N ₂ -25a	80	4.840	4.624	18.46	18.49	18.47	1.307 1.310 1.309	1.317 1.341 1.314	1.310 1.338 1.317	12.00	11.99	12.01	8.20	6.56 18.01
	X100O ₂ /N ₂ -25b	95	4.904	4.642	18.48	18.48	18.47	1.322 1.331 1.333	1.333 1.355 1.326	1.326 1.353 1.328	12.01	12.02	12.00	8.11	6.66 17.93
	X100O ₂ /N ₂ -Notched	80	4.908	4.663	18.50	18.48	18.48	1.318 1.321 1.327	1.333 1.354 1.321	1.324 1.347 1.333	12.00	11.99	11.99	7.99	6.58 18.02

B.4 Appendix: Dimensional, pre- and post-exposure weight measurements of C-rings samples exposed in solution with O₂/CO₂ at 5 °C, 15 °C and 25 °C.

Table B-10 - C-rings specimen's dimensions exposed in solution with O₂/CO₂ at 5 °C solution temperature.

Material grade	Specimen #	Y.S., %	Weight of specimens, g		O.D (mid. sect.) mm	O.D (edge sections), mm		Wall thick. (mid. sect.), mm	Wall thickness (edge sections), mm		Width (mid. sect.), mm	Width (edge sections), mm		Mouth opening/O.D., mm	
			Pre-exp.	Post-exp.		1	2		1	2		1	2	Bef. str.	M.O aft. str./O.D.
X65	X65O ₂ /CO ₂ -5a	80	4.847	4.618	18.49	18.47	18.49	1.311 1.312 1.311	1.325 1.321 1.320	1.323 1.333 1.326	11.99	12.00	11.98	8.04	7.24 18.14
		95	4.852	4.575	18.49	18.51	18.50	1.322 1.326 1.335	1.323 1.331 1.341	1.306 1.321 1.318	11.98	11.97	11.96	8.13	7.34 18.08
		80	4.839	4.612	18.52	18.50	18.48	1.324 1.310 1.311	1.333 1.336 1.338	1.316 1.321 1.322	12.02	12.00	12.01	7.98	7.26 18.13
	X70O ₂ /CO ₂ -5a	80	4.876	4.672	18.47	18.48	18.46	1.299 1.301 1.312	1.293 1.302 1.320	1.296 1.303 1.316	12.02	12.01	12.02	7.97	7.24 18.14
		80	4.888	4.680	18.49	18.51	18.49	1.318 1.317 1.319	1.316 1.320 1.332	1.324 1.333 1.316	12.02	12.01	12.01	7.99	7.25 18.13
		95	4.915	4.720	18.47	18.46	18.47	1.309 1.311 1.306	1.311 1.308 1.311	1.307 1.305 1.308	12.02	12.00	12.01	8.03	7.32 18.06

	X70O ₂ /CO ₂ - Notched	80	4.871	4.661	18.47	18.50	18.49	1.314 1.328 1.329	1.327 1.326 1.325	1.315 1.311 1.308	12.01	12.00	12.02	8.10	7.37 18.13
X80	X80O ₂ /CO ₂ - 5a	80	4.849	4.640	18.49	18.51	18.49	1.326 1.346 1.335	1.330 1.341 1.331	1.335 1.345 1.334	12.02	12.01	12.01	8.01	6.96 18.04
	X80O ₂ /CO ₂ - 5b	95	4.872	4.633	18.52	18.50	18.49	1.312 1.318 1.323	1.320 1.325 1.321	1.316 1.321 1.325	12.03	12.01	12.03	7.98	6.85 17.95
	X80O ₂ /CO ₂ - Notched	80	4.848	4.605	18.51	18.49	18.50	1.307 1.315 1.314	1.297 1.346 1.301	1.343 1.346 1.382	12.05	12.06	12.07	7.91	6.91 18.06
X100	X100O ₂ /CO ₂ - 5a	80	4.896	4.516	18.46	18.46	18.47	1.323 1.343 1.332	1.347 1.351 1.330	1.340 1.348 1.328	12.04	12.01	12.02	7.97	7.07 18.00
	X100O ₂ /CO ₂ - 5b	95	4.924	4.441	18.51	18.51	18.50	1.361 1.360 1.355	1.357 1.363 1.340	1.356 1.367 1.332	12.03	12.01	12.02	8.06	6.99 17.93
	X100O ₂ /CO ₂ - Notched	80	4.943	4.498	18.48	18.49	18.51	1.353 1.351 1.342	1.353 1.356 1.350	1.346 1.358 1.345	12.01	12.01	12.01	8.08	7.17 18.02

Table B-11 - C-rings specimen's dimensions exposed in solution with O₂/CO₂ at 15 °C solution temperature.

Material grade	Specimen #	Y.S., %	Weight of specimens, g		O.D (mid. sect.), mm	O.D (edge sections), mm		Wall thick. (mid. sect.), mm	Wall thickness (edge sections), mm		Width (mid. sect.), mm	Width (edge sections), mm		Mouth opening/O.D., mm	
			Pre-exp.	Post-exp.		1	2		1	2		1	2	Bef. str.	M.O aft. str./O.D.
X65	X65O ₂ /CO ₂ - 15a	80	4.817	4.480	18.48	18.50	18.48	1.307 1.341 1.332	1.337 1.364 1.332	1.288 1.316 1.292	11.98	11.99	12.00	8.03	6.68 18.13

	X65O ₂ /CO ₂ -15b	95	4.853	4.514	18.47	18.49	18.50	1.320 1.323 1.325	1.313 1.329 1.310	1.347 1.367 1.319	12.00	11.99	11.98	8.16	6.42 18.07
X70	X70O ₂ /CO ₂ -15a	80	4.914	4.303	18.50	18.52	18.51	1.312 1.316 1.315	1.331 1.363 1.322	1.307 1.335 1.317	12.03	12.02	12.02	8.00	6.62 18.15
	X70O ₂ /CO ₂ -15b	95	4.899	4.373	18.47	18.47	18.49	1.313 1.317 1.332	1.334 1.363 1.328	1.317 1.362 1.333	12.01	12.03	12.00	8.13	6.38 18.05
X80	X80O ₂ /CO ₂ -15a	80	4.796	4.471	18.50	18.49	18.53	1.302 1.307 1.316	1.309 1.324 1.292	1.303 1.326 1.296	12.01	11.99	12.00	8.08	6.35 18.03
	X80O ₂ /CO ₂ -15b	95	4.814	4.487	18.48	18.50	18.48	1.324 1.335 1.334	1.293 1.296 1.312	1.311 1.336 1.324	11.99	12.00	12.00	8.06	6.27 17.97
X100	X100O ₂ /CO ₂ -15a	80	4.877	3.603	18.48	18.47	18.47	1.334 1.318 1.329	1.328 1.339 1.321	1.335 1.353 1.347	11.98	12.01	11.99	8.01	6.48 18.00
	X100O ₂ /CO ₂ -15b	95	4.927	3.815	18.46	18.49	18.51	1.326 1.332 1.337	1.340 1.361 1.347	1.335 1.365 1.337	12.00	12.00	12.01	8.14	6.46 17.93

Table B-12 - C-rings specimen's dimensions exposed in solution with O₂/CO₂ at 25 °C solution temperature.

Material grade	Specimen #	Y. S, %	Weight of specimens, g		O.D (mid. sect.), mm	O.D (edge sections), mm		Wall thick. (mid. sect.), mm	Wall thickness (edge sections), mm		Width (mid. sect.), mm	Width (edge sections), mm		Mouth opening/O.D., mm	
			Pre-exp.	Post-exp.		1	2		1	2		1	2	Bef. str.	M.O aft. str./O.D
X65	X65O ₂ /CO ₂ -25a	80	4.851	3.992	18.48	18.46	18.50	1.347 1.346	1.326 1.345	1.325 1.352	12.01	12.01	12.01	8.13	7.50

								1.349	1.327	1.344					18.15
	X65O ₂ /CO ₂ -25b	95	4.828	4.057	18.48	18.50	18.50	1.331 1.332 1.343	1.309 1.345 1.328	1.304 1.318 1.301	12.02	11.99	12.01	8.00	7.01 18.07
	X65O ₂ /CO ₂ -Notched	80	4.857	4.196	18.47	18.50	18.48	1.309 1.304 1.302	1.340 1.333 1.332	1.337 1.351 1.329	12.00	11.99	11.99	7.97	7.31 18.13
X70	X70O ₂ /CO ₂ -25a	80	4.866	3.665	18.46	18.45	18.47	1.300 1.302 1.302	1.337 1.359 1.353	1.350 1.335 1.353	12.04	12.04	12.04	8.03	7.57 18.13
	X70O ₂ /CO ₂ -25a-R	80	4.863	3.607	18.47	18.47	18.46	1.313 1.308 1.309	1.314 1.344 1.322	1.318 1.360 1.327	12.01	11.98	11.97	8.13	7.45 8.14
	X70O ₂ /CO ₂ -25b	95	4.850	3.597	18.46	18.45	18.45	1.323 1.342 1.345	1.309 1.339 1.309	1.320 1.319 1.330	12.00	12.02	12.00	8.04	7.45 18.06
	X70O ₂ /CO ₂ -Notched	80	4.870	3.629	18.47	18.50	18.48	1.324 1.338 1.313	1.325 1.330 1.329	1.313 1.335 1.338	11.98	12.00	12.00	8.05	7.34 18.16
X80	X80O ₂ /CO ₂ -25a	80	4.827	3.964	18.51	18.49	18.51	1.308 1.303 1.304	1.309 1.316 1.324	1.318 1.321 1.319	12.03	12.03	12.02	8.09	7.21 18.05
	X80O ₂ /CO ₂ -25b	95	4.828	3.978	18.50	18.49	18.50	1.305 1.304 1.310	1.325 1.296 1.294	1.299 1.307 1.326	12.02	12.01	12.01	8.04	6.89 17.95
	X80O ₂ /CO ₂ -Notched	80	4.853	3.927	18.51	18.50	18.52	1.292 1.295 1.296	1.284 1.293 1.295	1.341 1.343 1.319	12.03	12.04	12.03	8.07	7.02 18.04
X100	X100O ₂ /CO ₂ -25a	80	4.934	2.839	18.49	18.48	18.48	1.333 1.336 1.344	1.348 1.355 1.342	1.340 1.350 1.339	12.02	12.02	12.02	8.12	6.93 18.02
	X100O ₂ /CO ₂ -25b	95	4.851	2.820	18.48	18.48	18.49	1.317 1.322	1.326 1.324	1.315 1.328	12.03	12.01	12.02	8.14	6.87

								1.319	1.320	1.318					17.91
	X100O ₂ /CO 2-Notched	80	4.927	3.124	18.50	18.49	18.51	1.337 1.340 1.337	1.332 1.349 1.341	1.330 1.346 1.318	12.00	12.01	12.01	8.03	7.01 18.02

Appendix C : Chiller and heating tape set temperatures to achieve solution temperatures.

Table C-1 - Chiller calibrations to achieve 5 °C solution temperature.

Ambient temperature, °C	Set chiller temperature, °C	Test water temperature, °C	Duration to reach solution temperature	Target water temperature, °C
22	0	15	1.40 hrs	5
22	-3	8.5	2.20 hrs	5
22	-5	6.5	1.45 hrs	5
13	-5	5.5	1.45 hrs	5
13	-5	0	21 hrs (next day)	5
13	-2	1 (test water temp. still not stable)	2.05 hrs	5
11	-2	4.5	2.20 hrs	5
12	-2	1.5	45 hrs	5
12	0	2.5 (test water temp. still not stable)	2.10 hrs	5
13	0	5	2.30 hrs	5
13	0	4.5	22 hrs (next day)	5
13.5	0 (With N ₂ at 5 ml/min)	4.0	46 hrs	5
14	1 (With N ₂ at 10 ml/min)	4.5	165 hrs	5
14	2	4.8	24 hrs	5

Table C-2 – Heating tape calibrations to achieve 25 °C solution temperature.

Ambient temperature, °C	Set heating tape temperature, °C	Test water temperature, °C	Duration to reach solution temperature	Target water temperature, °C
22	30	28	2.20 hrs	25
22	30	28	2 hrs	25
13	32	28	1.45 hrs	25
13	30	27	21hrs (next day)	25
13	30	26 (test water temp. still not stable)	2hrs	25
11	30	24	2.30 hrs	25
12	30	26	45 hrs	25
12	28	24 (test water temp. still not stable)	2 hrs	25
13	28	23.5	2.45 hrs	25
13	28	25	22 hrs (next day)	25