

**INVESTIGATION OF STRESS CORROSION CRACKING OF
STORAGE TANKS USED TO STORE METHANOL FOR GAS
HYDRATE INHIBITION**

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Materials Science and Engineering
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In Partial Fulfilment of the Requirements for the Degree of

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By

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Abuja, Nigeria

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CERTIFICATION

This is to certify that the thesis titled “Investigation of Stress Corrosion Racking of Storage Tanks Used to Store Methanol for Gas Hydrate Inhibition”, submitted to the School of Postgraduate Studies, African University of Science and Technology (AUST) in Abuja, Nigeria, for the award of the Master's degree, is a record of original research carried out by Daniel Iramofu Amune in the Department of Materials Science and Engineering.

**INVESTIGATION OF STRESS CORROSION CRACKING OF STORAGE TANKS
USED TO STORE METHANOL FOR GAS HYDRATE INHIBITION**

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ABSTRACT

Methanol is normally used in the oil and gas industries for inhibiting gas hydrate. Before use, the methanol is normally stored in tanks often made of carbon steels and stainless steels, and these tanks are prone to corrosion when exposed to methanol.

Many investigations have been carried out by researchers to understand the phenomenon of stress corrosion cracking (SCC) in ethanol. Very few investigations have, however, been carried out on methanol stress corrosion cracking. Even the work that has been done, has involved performing slow strain-rate tests, so the contribution of residual stress alone has not been investigated. This work, therefore, focuses on investigating the effect of residual stress brought about by elevated temperatures, arising from welding processes, on carbon steel during construction of methanol storage tanks.

The samples used during the test were made from X65-grade carbon steels, and the test was performed at ambient temperature. The samples were immersed in aerated methanol and purged methanol; and the results obtained suggest that the use of nitrogen in the purging of methanol plays an active role in localized corrosion of carbon steels, as indicated by Fourier Transform Infrared (FTIR) peaks. Cracks were found to have been initiated by pit coalescence and propagated by crack coalescence along the surface of the samples studied. SEM analysis revealed cracks through the thickness that were covered by corrosion product. EDS analysis of the corrosion product formed on samples exposed to purged methanol can be used to confirm the active role of nitrogen in the localized corrosion of the samples.

Keywords: Stress Corrosion Cracking, Methanol, Residual Stress, Carbon steel.

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DEDICATION

I dedicate this work to God almighty, who is my pillar of strength, my rock and my way-maker, and to my parents and brothers, and to Hope.

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LIST OF ABBREVIATIONS

FTIR	Fourier Transform Infrared
SEM	Scanning Electron Microscopy
EDS/EDX	Energy Dispersive Spectroscopy/Energy Dispersive X-ray spectroscopy
MEG	MonoethyleneGlycol
DEG	DiethyleneGlycol
TEG	TriethyleneGlycol
SCC	Stress Corrosion Cracking
K_{Ic}	Critical Stress Concentration Factor
V_{SHE}	Standard Hydrogen Electrode Potential
FRSD	Film Rupture and Slip Dislocation
BWR	Boiling Water Reactor
SS	Stainless Steel
SAW	Submerged Arc Welding
HAZ	Heat-affected Zone

CHAPTER ONE: INTRODUCTION

1.1 Background

Among the many problems faced by the oil and gas industries is the flow assurance problem called gas hydrate formation. Failure of pipelines and flow lines in offshore operations can result from gas hydrate plugs (Figure 1.1). These failures can be catastrophic, leading to loss of lives and property. Gas hydrate, when formed, normally necessitates the shutting down of operations to allow the equipment to warm, a situation that results in the loss of considerable amounts of time and money (O'Brien, Addington & Mejorada, 2016). One of the solutions to this problem is the use of hydrate inhibitors such as methanol, MEG (Monoethylene Glycol), DEG (Diethylene Glycol) and TEG (Triethylene Glycol). Methanol is commonly used because it is cheaper than the other aforementioned inhibitors. Low viscosity and surface tension are a function of the temperature of methanol relative to other solvents, making it especially well suited to the application when compared with other solvents. When these inhibitors have been produced, it is necessary to store them for use. Many problems have occurred in the past due to storage of oil and gas products. Chang and Lin (2006) reviewed 242 accidents at storage tanks that occurred in industrial facilities over the past 40 years. The results show that 74% of accidents occurred at petroleum refineries, oil terminals or storage facilities. Fires and explosions account for 85% of the accidents.



Figure 1.1: Hydrate plug



Figure 1.2: Large welded API-grade storage tank (Cembell Industries, 2017)

There were 80 accidents (33%) caused by lightning and 72 (30%) caused by human error, including poor operations and maintenance. Other causes (37%) were equipment failure, sabotage, cracking and rupture, leak and line rupture, static electricity, open flames, etc. (Chang & Lin, 2006). Some of the cracking and rupture cases may be attributed to Stress Corrosion Cracking (SCC). The corrosion of materials causes great loss in industrial applications, especially under some extreme conditions, i.e., the corrosive atmosphere and high temperature (Zhang & Tang, 2009). Oil and gas fluids contain solid particulates such as sodium chloride, potassium chloride, other salts, carbonates, sulphates, partially polymerized oils including waxes and paraffin, as well as silica, dirt and greases. Some of these particulates dissolve in the fluid, while some remain in suspension (Master Bond, 2017). These contaminants can drive the corrosion process of a pure non-corrosive fluid.

A type of corrosion caused by methanol, known as methanol-induced corrosion, is a recognized problem in the gas and oil industries.

Methanol-induced corrosion occurs in pipelines and pipeline components, such as valves, and other metallic components. It has also been linked to corrosion in methanol storage tanks. Stress corrosion cracking (SCC) has been observed in absolute methanol.

1.2 Aims and objectives

Although much work has been done to study the effects of alcohol on SCC, the majority of the work focused particularly on ethanol; even the reports on methanol-induced SCC mostly simulate methanol SCC caused by external stress and environment. There exists little research on methanol SCC caused by residual stresses. The aim of this work was to study the effect of microstructural alteration caused by elevated temperature during welding, and of methanol on the SCC of X65 steel. It was also intended to perform Fourier Transform Infrared (FTIR) analysis of the corrosion products, in the event of any forming on a steel sample. Scanning Electron Microscopy (SEM) was done to understand the nature of the crack initiation and growth mechanism.

1.3 Scope of work

This research is focused on experimentation to produce cracks in X65 steel samples by immersing the samples in aerated and de-aerated methanol. Characterization was done to study the surface morphology and cracks using a scanning electron microscope. Corrosion products formed on the steel surface were analysed using FTIR spectroscopy and energy dispersive x-ray spectrometry (EDS/EDX).

1.4 Outline of thesis

Chapter one gives a brief overview of the background, research objective, scope and justification for the research.

Chapter two presents an extensive literature review on SCC of metals, and methanol SCC. It also highlights the factors that cause SCC generally, modes of SCC, the role of methanol in gas hydrate inhibition, methanol storage, effect of impurities on the SCC of metals in methanol, and the nitrogen blanketing process.

Chapter three presents details of the experimental method for preparing the samples and producing cracking for analysis.

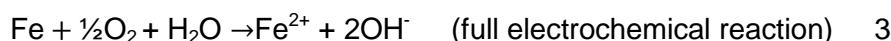
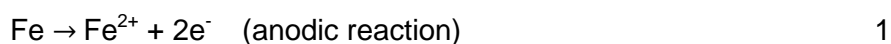
Chapter four presents and discusses the results obtained from the experiments.

Chapter five presents salient conclusions drawn from this work, along with recommendations for future research.

CHAPTER TWO: LITERATURE REVIEW

2.1 Corrosion

For an electric current to flow, a complete circuit must be available, otherwise it will not flow. In a similar manner, electrochemical corrosion cannot occur without a complete circuit. What forms this corrosion circuit includes: (1) the anode –at the anode, oxidation half reaction occurs; (2) the cathode – reduction half reaction occurs at the cathode; (3) electrolytes, which include soil, water, moisture, etc.; and (4) and electrical connection between anode and cathode by wire, metal wall, etc. (Bell, n.d.). For example, the corrosion of a metal in an aqueous environment will occur according to the following reactions:



Most metals suffer from corrosion as they tend to revert back to their thermodynamically stable state as ores. A few metals such as gold and platinum do not, however, suffer corrosion, but remain in their natural state not as ores, but as metals. This class of metals is generally called noble metals. Other metals such as stainless steel, aluminium, etc., have the tendency to form passive films as a corrosion product and these films cover the surface of the metal and become a barrier to further corrosion of the metal. The type of corrosion mechanism, and its rate of attack, depend on the nature of the environment (air, soil, water etc.) in which the corrosion takes place. Understanding the chemistry between environments and materials in the environment, and hence the class of corrosion, can be vital in developing or selecting the correct type of corrosion prevention methods. Whereas some environmental conditions can increase the rate of corrosion, others help control it; hence industrial products and waste can be either corrosion inhibitors or catalysts (ASM, 1992). Various environmental variables such as pH (acidity), temperature (heat transfer), concentration (solution constituents), oxidizing power (potential) and velocity (fluid flow) are known to have an effect on the corrosion of metals in aqueous environments (Silverman & Puyear, 1987).

There are a large number of mechanisms by which corrosion occurs, if the broad definition of corrosion is considered as the deterioration of materials by reaction with the environment. The corrosion process cannot be directly measured *in situ* because it may be slow and normally occurs at a microscopic level. Thus, corrosion observations are normally made by inference from indirect mechanical and electrochemical measurements; and from physical and microstructural observations. Aside from the electrochemical method, corrosion can be evaluated by digital image processing of morphology: colour, texture and shape. Machine vision methods can be applied to the analysis of corrosion surface damage (Choi & Kim, 2005).

2.2 Classification of corrosion

Corrosion can be classification in many ways. For example, corrosion can be classified based on temperature, as low-temperature and high-temperature corrosion. Other methods include direct combination (or oxidation); electrochemical corrosion; and wet and dry corrosion. As the name implies, wet corrosion occurs in the presence of liquid, while dry corrosion occurs in the absence of liquid in the corrosion environment (Fontana, 1987).

Corrosion can be grouped into five different classes as general corrosion; localized corrosion; metallurgically influenced corrosion; mechanically assisted corrosion; and environmentally induced cracking (Adebola, 2014; ASM, 1992). While general corrosion involves uniform thinning of the metal, localized corrosion is classified by an increased corrosion rate at specific sites across the metal's surface.

Metallurgically influenced corrosion involves all corrosion types that occur as a result of the microstructure of a metal. Table 1.1 shows the ASM international classification of corrosion.

Table 1.1: ASM classifications of corrosion types

Classes	Forms
General corrosion	Corrosion dominated by uniform thinning that proceeds without appreciable localized attack, for instance: Atmospheric corrosion Galvanic corrosion Stray-current corrosion

	<p>General biological corrosion</p> <p>Molten salt corrosion</p> <p>Corrosion in liquid metals</p> <p>High-temperature corrosion</p>
Localized corrosion	<p>Characterized by high rates of metal penetration at specific sites, normally insidious, and can lead to premature failure of a structure by rapid penetration with little overall weight loss, for instance:</p> <p>Crevice corrosion</p> <p>Filiform corrosion</p> <p>Pitting corrosion</p> <p>Localized biological corrosion</p>
Metallurgically influenced corrosion	<p>Affected by metallurgical factors including alloy chemistry and heat treatment. These factors influence the relative stability of the components of an alloy, metallic phases, metalloid phases, such as carbides, and local variations in composition in a single phase, for instance:</p> <p>Dealloying</p> <p>Selective leaching</p> <p>Parting</p> <p>Intergranular corrosion</p>
Mechanically assisted degradation	<p>Corrosion with a mechanical component. It is defined as any type of degradation that involves both a corrosion mechanism and a wear or fatigue mechanism, for instance:</p> <p>Erosion corrosion</p> <p>Fretting corrosion</p> <p>Cavitation and water drop impingement</p> <p>Corrosion fatigue</p>
Environmentally induced cracking	<p>All of these phenomena are generally dependent on yield strength and applied stress. As both of these factors increase, resistance to SCC, hydrogen damage, liquid metal embrittlement and solid metal induced embrittlement decreases, for instance:</p> <p>Stress corrosion cracking (SCC)</p> <p>Hydrogen damage (also known as hydrogen embrittlement)</p> <p>Liquid metal embrittlement</p> <p>Solid metal induced embrittlement</p>

(Source: ASM, 1992)

Although there are many forms of corrosion, two or more classes or forms can occur together on a particular metal in the same medium. Pitting corrosion, a form of corrosion related to this research, is briefly discussed below.

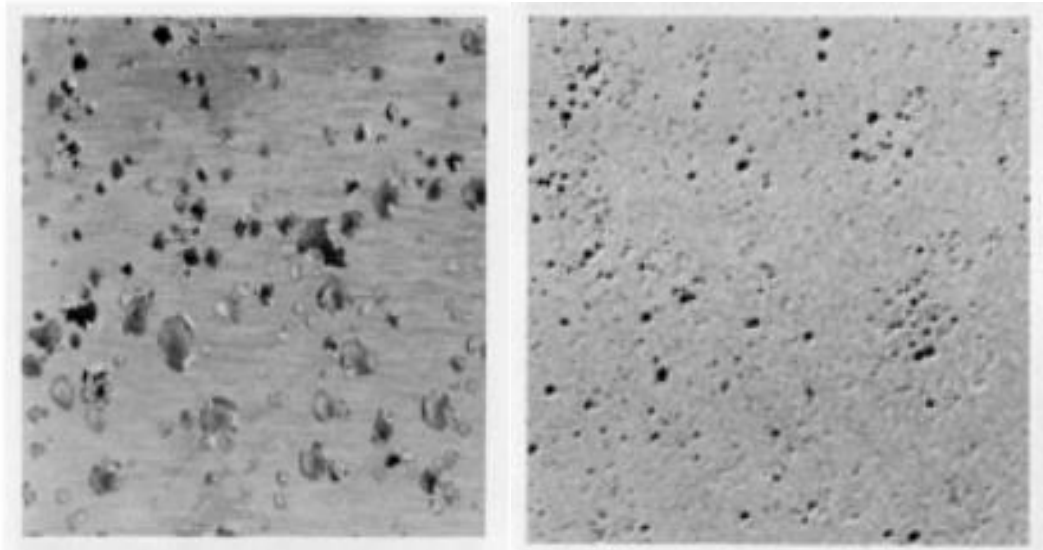
2.2.1 Pitting corrosion

Pitting is an insidious and highly localized form of corrosion that normally results in holes or pits in metals. The diameter of the pits may be small or large (Fontana, 1987). A small corrosion product normally forms a cap over the pit (Cheng & Luo, 1999a), while the damage continues through the thickness of the metal. Pitting in metals can be initiated by surface defects such as scratches on the metal surface, breaking of passive films, or local change in microstructure leading to galvanic sites. Difference in microstructure can result from inclusions such as sulphides. Among sulphide inclusions in stainless steel, manganese sulphides, especially those containing central oxide cores, are the most favourable sites for pitting corrosion (Sedriks, 1983).

Aggressive anions such as chlorides, fluorides, thiosulphates and iodides are some known environmental species that can participate in driving the pitting process. Pitting is normally initiated by a self-stimulating, self-sustaining process known as an autocatalytic process. This autocatalytic process is characterized by the breakdown of passive films – migration of anions into the formed pits, to combine with the very positive oxidized pit, to achieve electro-neutrality. Thus, the excess metal chlorides formed react with water to produce hydrogen chloride and hydrogen ions, thereby sustaining the pitting process. The pit is normally free of oxygen, while the oxygen undergoes cathodic reaction at the metal's surface.

A maximum has been found to exist in the potential dependence of the pit initiation rate. Metastable pit growth is controlled by the ohmic potential drop, mainly across the cover over the pits. It has also been shown that re-passivation of metastable pits is favoured by the increase in potential. The ratio of peak pit current to pit radius, known as the pit stabilisation criterion, must exceed $6 \times 10^{-2} \text{ Acm}^{-1}$ during pit growth to avoid re-passivation (Cheng & Luo, 1999b).

Pits can be shallow or deep, depending on the resultant area of pit surface with respect to the fixed area of the metal surface that is considered. If appreciable attack is confined to a relatively small fixed area of metal acting as an anode, the resultant pits are described as deep (Figure 2.1a). If the area of attack is relatively larger and not so deep, the pits are called shallow (Figure 2.1b) (Asphahani & Silence, 1987).



(a)

(b)

Figure 2.1: (a) Deep pitting and (b) shallow pitting (adapted from Asphahani & Silence, 1987)

The main role of Cl^{-1} in pitting is to increase the chance of the breakdown of the passive film, rather than to inhibit surface re-passivation (Cheng & Luo, 1999b).

2.3 Mechanisms of stress corrosion cracking

Stress corrosion cracking (SCC) is a type of environmentally induced cracking (ASM, 1992). It is a form of localized corrosion that produces cracks in metals by the simultaneous action of a corrodent and tensile stress on a susceptible material. This is shown schematically in Figure 2.2.

It follows from the definition of SCC that the absence of one of these conditions will prevent the occurrence of SCC of the metal. Stress corrosion cracking normally occurs in an environment that is mildly corrosive to the metal itself.

Crevice loads, as a result of stress concentration, can cause these stresses, or the stress can occur as a result of the type of assembly, or residual stress from materials fabrication (e.g., cold working, welding, etc.). Stress relieving of the residual stress can be achieved by annealing or other surface treatments (Munnings, Badwal & Fini, 2014). If the three components of SCC do not function simultaneously, for example, pre-corrosion followed by loading, there will not be significant crack propagation (Aly & Neto, 1995). Corrosion alone in the absence of stress does not cause SCC. SCC occurs at points of stress (Schweitzer, 2013).

The minimum stress below which SCC will occur is called the “threshold stress”, but this may be as low as 10% of the yield stress in some systems. The critical stress concentration (K_{IC}) required to fracture the metal in an inert environment (absence of one of the conditions for SCC) is greater than the critical stress concentration in a corrosive environment (K_{ISCC}), i.e., threshold stress beyond which SCC will occur in an active environment (simultaneous and synergistic combination of the three conditions for SCC).

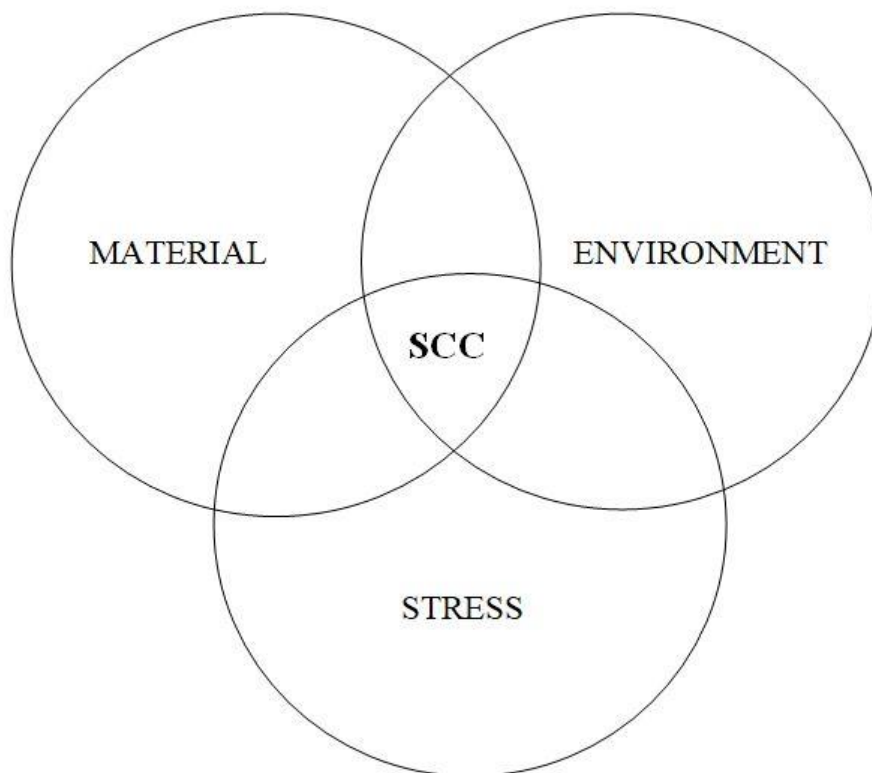


Figure 2.2: Schematic representation of the three primary conditions for stress corrosion cracking

The stresses required to cause SCC are tensile in nature and small, usually below the macroscopic yield stress (Aly & Neto, 1995). In many environments where steels are susceptible to SCC, a frequent precursor to crack initiation is pitting corrosion. In these environments, when stresses – either applied or residual – are relatively low, pitting ultimately produces failure. As the stress level increases, however, SCC can become the controlling mode of failure (Jones & Ricker, 2013). Pits sometimes result in environment-assisted cracking such as SCC and corrosion fatigue, by providing sites of stress concentration (Schweitzer, 2013). The presence of sulphides is likely to affect the SCC process (Elboudjaini & Revie, 2009). SCC initiation normally results from features such as pits, fabrication defects and intergranular corrosion. These features are easily observed and identified, but there are few well-developed models of SCC initiation, for several reasons. Although it is not difficult to detect the location from which a growing crack has emanated, the initiation of a crack is difficult to measure experimentally.

The fracture mechanics concept of design assumes pre-existing flaws in materials, although these may not be surface flaws that can become stress corrosion cracks (Jones & Ricker, 2013). In addition, SCC should not be mistaken for corrosion fatigue, as both phenomena are similar. The fundamental difference between them is that SCC occurs when the metal is subjected to static loading, while corrosion fatigue results from cyclic loading of the material. Some environments that can cause SCC at high pH are sodium hydroxide (NaOH), carbonates and bicarbonates at moderately basic pH values, and possibly amines. Steel can also suffer SCC at lower pH, but this behaviour is less prevalent. Examples of these environments are hydrogen fluoride (HF) vapours and hydrogen sulphide (H₂S). The mechanism in these cases may be that of hydrogen embrittlement (ASM, 1992). SCC cracking modes can be intergranular, transgranular or mixed. Stress corrosion cracking occurs practically without material loss and visible corrosion product, and it normally produces a brittle-type failure surface. It is an insidious type of corrosion and the failure resulting from SCC can be catastrophic. SCC is normally “river branched”, existing as a primary branch with tributaries. There are various stages in the SCC process: (1) incubation; (2) initiation; and (3) coalescence. When the SCC stress intensity factor (K_{ISCC}) is reached, a fast increase in propagation is observed (Parkins, 1980).

Depending on the nature of the environment, microstructure of the material and stress involved, SCC can be dominated by any of these three factors. Environments that cause SCC are usually aqueous and can be either condensed layers of moisture or bulk solutions. SCC is alloy/environment-specific; that is, it is frequently the result of a specific chemical species in the environment. Various combinations of temperature, degree of aeration and/or concentration of species can cause SCC in such ways that there is virtually an infinite environment that causes SCC.

2.3.1 Modes of stress corrosion cracking

There are three modes of SCC: intergranular; transgranular; and mixed SCC. Intergranular corrosion normally occurs at high pH. It is, thus, usually referred to as high pH SCC. The low pH and near neutral pH environments normally favour a transgranular mode of stress corrosion cracking. Stress Corrosion Cracking has been found to be transgranular when the stress exceeds yield strength (Sridhar, Price, Buckingham & Dante, 2006). Intergranular SCC is often related to the existence of some chemical heterogeneity in the grain boundary, such as a segregated impurity element, which can provide an electrochemically active path for the corrosion process to occur. Transgranular SCC invariably has a brittle, cleavage-like appearance (Sieradzki & Newman, 1987). Intergranular SCC corresponds to crack propagation along the grain boundary, and transgranular SCC corresponds to crack propagation across the grain boundary.

The rate of SCC is normally affected by stress intensity, temperature and potential. Several reports have shown that the electrochemical potential regime for SCC falls within a small range of potentials near the active-passive transition. In a report on the SCC behaviour of cold-worked mild steel in a hot NaOH solution, using fracture mechanics techniques, it was shown that SCC occurred under both freely corroding potentials ($E_{\text{corr}} \sim -1.00 V_{\text{SHE}}$) and potentiostatic potentials of $-0.76 V_{\text{SRM}}$ near the active-passive transition. Cracking was transgranular at E_{corr} and intergranular at $-0.76 V_{\text{SRM}}$ (Singbeil & Tromans, 1982).

2.3.2 Effect of films and impurities on SCC

Above a particular passivation potential, corrosion product formed on the metal surface may adhere to the surface, thereby forming a protective film that reduces the rate of subsequent corrosion. This protective film normally adheres to the metal surface at near neutral pH ($5 < \text{pH} < 9$). At strongly acidic conditions ($\text{pH} < 5$) there is a high corrosion rate characterised by metal dissolution. Also, at strongly basic conditions ($\text{pH} > 9$) the corrosion rate increases with pH (Silverman & Puyear, 1987).

Dissolution of non-adherent corrosion product has been shown to increase the rate of corrosion. Impurities are also known to cause SCC of steels. After the fabrication process of metals, impurities adhering to the metal can also have a major effect on the corrosion resistance of the metal. Sulphide inclusions in the form of conductive metal sulphides can act as local cathodes in steel and can promote corrosion.

Huy Ha Le and Ghali (1993) studied the effect of impurities (organic species) in Bayer liquor on SCC of ASTM A516 steel by conducting slow strain rate tests, and showed that these impurities have effects on the susceptibility and embrittlement of A516 steel. They also showed that among all these impurities, aluminate ions have the most important effect.

Qin, Li, Chen and Qu (2016) conducted an experimental study on the SCC propagation rate of FV520B in CO_2 and H_2S solution (one of the main corrosion failure modes for FV520B in industrial transportation of natural gas). The test results showed that the crack propagation rate rises with increasing the crack opening displacement. Under the condition of different initial loading, K_{ISCC} generally shows a decreasing tendency with an increase in H_2S concentration, and the crack propagation rate shows a substantial increasing trend. For the enrichment of sulphide ions in cracktip-induced pitting corrosion, the pit defects gradually extend and connect with the adjacent pit to form a small crack, leading to further propagation until cracking occurs. Table 2.1 shows different metallic alloy and environment combinations, and the resulting films that form at the crack tip. These films normally give an indication of the cause of crack initiation (Jones & Ricker, 2013).

Table 2.1: Alloy/environment combinations and the resulting films that form at the crack tip (Jones & Ricker, 2013)

Metal/Alloy	Environment	Initiating layer
Iron-chromium nickel	Chloride Hydroxide and high-temperature water	Dealloyed layer (Au) Dealloyed layer Oxides Dealloyed layer or oxide
Ferritic steels	High-temperature water Phosphate Anhydrous ammonia CO/CO ₂ /H ₂ O CS ₂ /H ₂ O	Oxide Oxide (?) Nitride Carbide Carbide
α-Brass	Nitrite	Oxide
Copper	Nitrite	Oxide
Aluminium alloys, steel	Various media	Near surface hydrogen
Titanium alloys	Chloride	Hydrides
α-Brass, copper-aluminium	Ammonia	Dealloyed layer (Cu)
Gold-copper	FeCl ₃	Dealloyed layer (Au)

Some models are available that explain different crack mechanisms. Some of these models include slip dissolution, film rupture, environmentally-assisted cleavage and hydrogen-assisted cracking (Ford, 1989). In general there are two basic mechanisms of SCC: One based on localized dissolution of metals, which has been postulated since SCC involves a corrosive environment; and the other, known as cleavage mechanism, has also been postulated because of the brittle feature appearance of the SCC cracked metals (Chatterjee, 1995).

2.3.2.1 Dissolution mechanisms

According to the dissolution mechanism, a crack advances by preferential dissolution at its tip. This dissolution is limited by a process attributed to either a pre-existing active path or a strain-generated active path.

In the pre-existing active path mechanism, grain boundary segregation creates a local cell which facilitates SCC. Segregated solutes or precipitated phases may act as an anode in the local cell or, by acting as an efficient cathode, may cause the dissolution to be localized upon the immediately adjacent matrix. The role of stress here is to keep the crack open for the accessibility of the corrosive medium to the crack tip.

Strain-generated active path mechanisms hold for a metal that does not have a pre-existing crack. Two models that explain these mechanisms are the film rupture and slip dissolution models. According to the film rupture model, the stress opens up the crack and the localized plastic deformation at the crack tip ruptures the passivating film, exposing the bare metal which dissolves rapidly, resulting in crack extension. The crack tip remains bare if the rate of film rupture at the crack tip exceeds the rate of repassivation. If the situation is reversed, the crack tip repassivates completely and is periodically ruptured by the emergence of slip steps. The bare slip step sustains dissolution until the next repassivation (Chatterjee, 1995).

2.3.2.2 Cleavage mechanisms

Several mechanisms have been postulated to explain the cleavage-type cracking encountered in SCC. These are: hydrogen-assisted cracking, tarnish rupture, film-induced cleavage, adsorption-induced cleavage and atomic surface mobility mechanisms.

In the hydrogen-assisted cracking, atomically dissolved hydrogen acts to weaken the inter-atomic bond in the plain strain region of the crack tip by lowering the surface energy; embrittlement would then result from dislocations on the intersecting slip plane. Hydrogen-assisted crack growth in the manner described has been suggested as the SCC mechanism for ferritic steels, nickel base alloys, austenitic stainless steels, aluminium alloys and intermetallic compounds. The most probable source of atomic hydrogen that enters into the metal is the cathodic reduction of hydrogen ions accompanying the anodic dissolution in aqueous environments.

In a film-induced cleavage mechanism, it is assumed that dissolution leads to the formation of a surface film and a crack growing in the film propagates further into the underlying metal. From an initial arrest position, the crack advances by cleavage for a limited distance, after which the crack becomes progressively blunted by plastic deformation until the propagation stage is repeated. The film may be a dealloyed layer or oxide in which nano-porosity is considered to be the key feature leading to the injection of sharp cracks into the substrate (Chatterjee, 1995).

For high pH SCC, it has been accepted that the crack wall is passive or inert compared to the crack tip, where periodic film rupture and slip dissolution occur, and the SCC growth follows the Film Rupture and Slip Dissolution (FRSD) mechanism (Javidi & Bahalaou Horeh, 2014).

The SCC of carbon steel in alcohols appears to be more closely tied to anodic than to hydrogen-related SCC mechanisms. The mechanism of high pH SCC of ferritic steels is attributed to anodic dissolution and the repeated rupture of passive films that form over the crack tip (Zhu et al., 2014). It is suggested that alcohols are oxidized electrochemically in cracks to a mixture of products which, depending on other factors, may lead to a dissolution type of intergranular SCC or a more complex, but still anodically controlled, transgranular SCC analogous to CO-CO₂-H₂O SCC. Specifically, the transgranular SCC seen in the presence of chloride seems to ally the cracking with CO-CO₂-H₂O and anhydrous ammonia SCC; these systems are very peculiar and may involve special cleavage mechanisms (Newman, 2008).

2.3.3 Effect of temperature on SCC

For transgranular SCC, cracking has been observed at all temperatures between 50 °C and 350 °C, and all conceivable cracking mechanisms have been proposed at one time or another (Sieradzki & Newman, 1987). Some combinations of pH and temperature can result in SCC in some metals (Silverman & Puyear, 1987). Nakano et al. (2014) conducted a cracking growth test in high-temperature water containing hydrogen peroxide (H₂O₂) at 561–423 K to evaluate the effects of H₂O₂ on SCC of stainless steel (SS) at a temperature lower than the Boiling Water Reactor (BWR) operating temperature.

They showed that for an oxide formation at 561- 423 K, the boundary between Fe_2O_3 and Fe_3O_4 , and between Fe_2O_3 and NiFe_2O_4 , shifts gradually towards high pH levels with a decrease in temperature. They concluded that the amounts of Fe^{3+} and OH^- can be expected to contribute to the extension of the Fe_2O_3 phase because of a decrease in the thermal decomposition of H_2O_2 .

Very little work has been done to determine the influence of ambient temperature on SCC. What is known generally is that an increase in temperature increases acidity of the electrolyte.

2.4 Metal welding processes

There are various welding processes used to join materials. Examples are:

- Arc welding processes which include:
 - Gas metal arc welding (GMAW)
 - Submerged arc welding (SAW)
 - Gas tungsten arc welding (GTAW)
 - Flux cored arc welding (FCAW)
- Beam welding technology
- Friction and resistance welding processes
- Hybrid welding technology.

Storage tanks are normally welded at the bottom and the surface. In this work the welding process adopted was submerged arc welding.

2.4.1 Submerged arc welding (SAW)

Submerged arc welding (SAW) is an arc welding process in which the arc is concealed by a blanket of granular and fusible flux (Figure 2.3). Heat for SAW is generated by an arc between a bare, solid-metal (or cored) consumable wire or strip electrode and the workpiece. By maintaining the arc in a cavity of molten flux, the weld is refined and protected from atmospheric contamination. Alloy ingredients in the flux may be present to enhance the mechanical properties and crack resistance of the weld deposit (ASM International, 1993; Rehal & Randhawa, 2012).

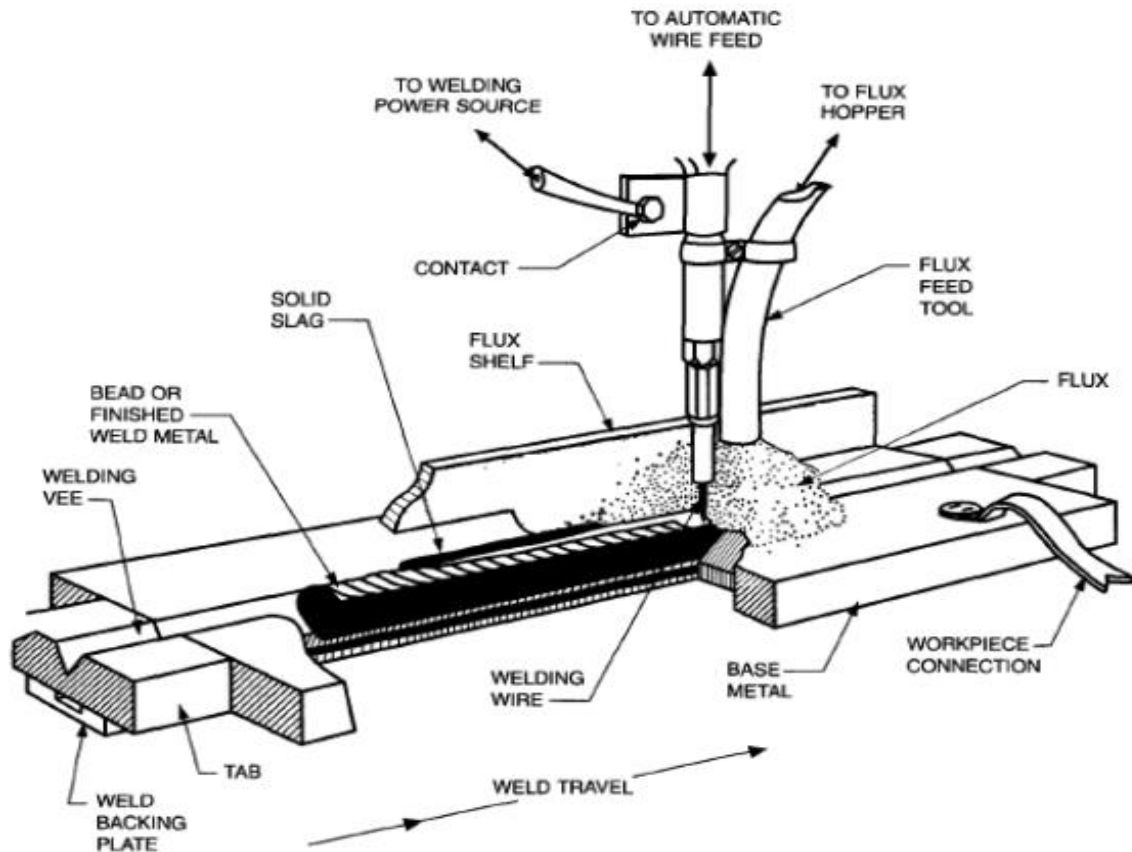


Figure 2.3: Schematic view of the submerged arc welding process

In plate and structural work such as bridge building, ship building and pressure vessel fabrication, assuming the work pieces can be properly positioned and the equipment accurately guided, SAW is the most efficient fusion welding process (Kah & Martikainen, 2012).

Certain qualities such as: ease of control of process variables; high quality; deep penetration; smooth finish; capability to weld thicker sections; and prevention of atmospheric contamination of the weld pool, make SAW a preferred method (Houldcroft, 1989). Atmospheric protection from contamination is important in corrosion prevention.

Each chemical constituent element of a flux has been found by other investigators to influence the quality of the weld, even perhaps increasing the strength of the resulting welds. The composition selected depends on its utility.

SAW is generally performed on butt joints in flat positions, and also on fillet joints in both flat and horizontal-vertical positions. For circumferential joints, the workpiece is normally rotated simultaneously with the welding process, the welding taking place in a flat position. Although SAW is ideally suited for longitudinal and circumferential butt and butt welds, the operations described are carried out particularly because of the high fluidity of the weld pool, molten slag and loose flux layer.

The fact that SAW is a high-heat input process under a protective blanket of flux greatly decreases the chance of weld defects. Defects such as lack of fusion, slag entrapment, solidification cracking, hydrogen cracking or porosity do, however, occasionally occur.

Submerged arc welding is most commonly used to join plain carbon steels. Alloy steels can be readily welded with SAW if care is taken to limit the heat input, as required to prevent damage to the Heat-affected Zone (HAZ). Maintaining proper preheat and interpass temperature is also important when welding alloy steels, to prevent weld metal and HAZ cracking, and to develop the required mechanical properties in the weld deposit. Because SAW is used to join thick steel sections, it is primarily used in ship building, pipe fabrication, pressure vessels and structural components of bridges and buildings. Other than joining, SAW is used to build up parts and overlay with stainless or wear-resistant steel (for example, rolls for continuous casting steel, pressure vessels, rail car wheels and equipment for mining, mineral processing, construction and agriculture) (ASM International, 1993).

2.4.1 Metallurgically induced SCC

Several investigations have been carried out to understand the cause of SCC in welded steels. During welding or mechanical working of steel, residual stresses are normally induced in the steel and, if the resultant stress at any particular area in the steel is tensile and above the stress level required to cause SCC (i.e., the threshold stress) then SCC can be expected when the steels are used in an active environment.

In engineering practice, the maximum residual stresses produced in the welding process may be higher than the yield strength of material, so that they can induce SCC without the aid of applied stresses (Lu, Chen, Luo, Patchett & Xu, 2005).

Reports have shown that the most commonly affected area of welded steels is the Heat-affected Zone (HAZ). The parent metal and the weld are, however, also sometimes affected. SCC attack is less common in welds due to the corrosion-resistant nature of the high-purity weld metal. There are also many instances in which the weld exhibits corrosion resistance superior to that of unwelded base metal. One or more of the following factors are often the reason why welds corrode: Welding sequence, weldment design, welding practice, fabrication technique, moisture contamination, organic or inorganic chemical species, weld slag and spatter, oxide film and scale, porosity, incomplete weld penetration or fusion, cracks (crevices), high residual stresses, final surface finish and improper choice of filler metal.

During welding the cycle of heating and cooling that occurs normally alters the microstructure and surface composition of metal at both the weld region and in the base metal. Consequently, the corrosion resistance of autogenous welds and welds made with matching filler metal may be inferior to that of properly annealed base metal because of: micro-segregation; formation of unmixed zones; precipitation of secondary phases; volatilization of alloying elements from the molten weld pool; recrystallization and grain growth in the weld heat-affected zone (HAZ); and contamination of the solidifying weld pool.

Corrosion resistance can usually be maintained in the welded condition by: balancing alloy compositions to inhibit certain precipitation reactions; shielding molten and hot metal surfaces from reactive gases in the weld environment; removing chromium-enriched oxides and chromium-depleted base metal from thermally discoloured (heat-tinted) surfaces; and by choosing the proper welding parameters (ASM, 1992).

2.5 SCC preventive measures

Since it is known that SCC cannot occur without the simultaneous effect of the three factors that contribute to its occurrence (tensile stress, corrosive environment and susceptible material), it follows that corrosion can be prevented by interrupting this combination. The most effective measure is to remove residual stresses or prevent the application of tensile stresses. By proper design and installation techniques, many tensile stresses can be avoided (Schweitzer, 2013).

Stress induced in the metal during manufacturing/fabrication can be relieved by annealing or shot peening. Although this stress-relieving method can be applied to a wide range of metals, shot peening is more suitable for metals that can be sensitized, such as stainless steels. Corrosion coating and corrosion inhibition are methods that can also be used to prevent SCC. Another option, when practical and economically feasible, is the selection during manufacturing of materials that are non-susceptible to corrosion in the environment where they will be used (Schweitzer, 2013).

2.6 Hydrate formation

Gas hydrate formation is one of the major challenges facing the oil and gas industries. Hydrates are crystalline compounds that occur when water forms a cage-like structure around smaller guest molecules (Sloan, 1991). In 1934, Hammerschmidt discovered that natural gas hydrates were responsible for blocking gas pipelines. He classified the causes of hydrate formation as (1) primary and (2) secondary. He showed that natural gas hydrate formation depends primarily on the temperature, pressure and composition of the gas. Secondly, hydrate formation is promoted by any force that tends to mix or stir the melt, because any such agitation increases the probability of bringing a critical number of molecules into the correct position required for crystallization.

Both high velocities and pressure pulsations impart a mixing action to the droplets of condensed moisture (Hammerschmidt, 1934). When water molecules and guest gas molecules combine under favourable conditions, usually at low temperatures and elevated pressures, it can lead to the formation of hydrates.

The guest molecules that are most frequently present are methane, hydrogen sulphide, propane, carbon dioxide, nitrogen, ethane, isobutane and normal butane, of which methane is the most abundantly occurring compound in natural hydrates (Bahadori, 2011).

A way to prevent hydrate formation is by keeping the temperature and pressure of the gas hydrate outside the hydrate formation zone. Two ways to achieve this is by: (1) injection of thermodynamic hydrate inhibitors such as methanol and glycol; and (2) heating the production facilities. The latter method has some challenges in that production facilities cannot be warmed during long periods of shutdown of facilities (Peytavy, Bourg & Larribau, 2008).

2.7 Role of methanol in gas hydrate inhibition

Gas hydrate formation has been prevented through the following thermodynamic means (Sloan & Fleyfel, 1991):

1. Removal of free water as well as reducing the water contained in the hydrocarbon phase;
2. Ensuring that the temperature of the system remains above the hydrate formation temperature;
3. Ensuring that the pressure of the system remains below the hydrate formation pressure; and
4. Injection of inhibitors to shift the equilibrium, such that the temperature and pressure are kept outside the hydrate formation range. Chemicals most commonly used for this purpose are thermodynamic inhibitors such as methanol, Monoethylene Glycol (MEG) and Diethylene Glycol (DEG), commonly referred to as glycol (Bahadori, 2011; Sloan & Fleyfel, 1991).

Methanol has long been used to inhibit hydrate formation in the oil and gas industries (Sloan & Fleyfel, 1991). The inhibitors act like molecular sieves that dehydrate the system, thereby preventing the occurrence of the hydrate. Hydrate suppression systems are commonly located at gathering or pipeline systems and gas processing facilities. Hydrate suppressing systems are also commonly used in natural gas liquid extraction facilities or refrigeration plants.

The low viscosity and surface tension (as a function of temperature) of methanol relative to other solvents make it especially well-suited to this application when compared to other solvents.

The greatest disadvantage of methanol is its high vapour pressure (which is significantly higher than that of the traditional glycols) which can result in potentially high losses under certain conditions. In addition to hydrate suppression, methanol has other uses and benefits in the gas processing industry. Methanol has been used successfully in acid gas removal, hydrocarbon dew point control and dehydration.

Methanol forms a fully hydrogen-bonded network when it is used as a hydrate inhibitor, but water reorientation takes place much more easily than in pure ice and in most clathrate hydrates (Nakayama et al., n.d.). Methanol is not a component of the hydrocarbon systems, but today is intentionally introduced by producers into hydrocarbon systems to either scavenge H₂S or inhibit gas hydrate formation. The primary use of methanol in the natural gas liquid industry is, however, in hydrate inhibition (O'Brien et al., 2016).

2.8 Methanol storage tanks

Methanol is manufactured, transported, stored, processed and utilized for a wide variety of purposes and applications, including: in chemical feed stock; hydrate control in oil and gas production; as a motor fuel additive; as primary motor fuel (M-100); as a source of carbon for waste water denitrification; in the manufacture of bio-fuels; in methanol-based hydrogen fuel cells; and many others. The array of operating parameters and circumstances is equally wide-ranging. Each application has unique material requirements (Methanol Institute, n.d.).

Methanol is a colourless, volatile, flammable and odourless liquid readily miscible in water, and with a boiling point of ~ 65⁰C. Methanol easily dissolves in other alcohols and chlorinated hydrocarbons, but has limited solubility in diesel, vegetable oils and aliphatic hydrocarbons (Basak, Nirmla & Biswas, 2010). A number of materials can be used to construct methanol storage tanks. Carbon steel or 300 series austenitic stainless steels such as ASTM 304, 304L, 316 or 316L are, however, preferred choices in terms of structural strength, corrosion resistance, form of corrosion and

life cycle cost. The service life of carbon steel tanks in methanol service is ≈ 20 years (≈ 30 years for 300 series austenitic stainless steel tanks), depending on factors such as inspection frequency, maintenance and effectiveness of cathodic protection.

Although a suitable choice for tank fabrication materials, steels are not necessarily the best choice for tank covers. Properly designed aluminium alloy components have high strength-to-weight and stiffness-to-weight ratios compared to steels. The high strength-to-weight ratio and stiffness of aluminium alloys; the lower relative buoyancy of steel; and the fact that floating roof service is a static, non-flowing service, make aluminium a candidate material for floating roofs, particularly if the floats are coating protected (Methanol Institute, 2012).

2.9 Nitrogen blanketing

Tank blanketing, also known as padding, is the introduction of an inert gas into the vapour space of a storage tank. The pressure of the blanketing gas, usually nitrogen, is slightly higher than atmospheric pressure. The pressure requirement is low because higher pressures do not significantly improve results and waste expensive blanketing gas. Also, storage tanks have thin walls which are not designed for high-pressure containment applications (Swagelok, 2017).

Blanketing helps protect plant personnel, products and plant assets by reducing the oxygen content in the vapour space of a storage tank or process vessel. This eliminates the possibility of fire or explosion, decreases evaporation and protects the tank from structural corrosion damage caused by air and moisture. It also prevents air, moisture or other contaminants from entering the vapour space and causing product degradation.

Nitrogen is the most commonly used gas for blanketing because it is inert, widely available, and relatively inexpensive on virtually any scale. Other gases such as carbon dioxide or argon are also occasionally used; however, carbon dioxide is more reactive and argon is about five to ten times more expensive, depending on the volume and location (Yanisko, Zheng, Dumoit & Carlson, 2011).

By providing the proper level of nitrogen in the system, methanol can be kept below the minimum oxygen concentration (MOC) of <10% and in the safety range (Methanol institute, n.d.).

From Figure 2.4 below, it can be seen that reducing oxygen to less than 10% will prevent explosions.

Methanol storage in tanks must be protected from water absorption. This is achieved by storing methanol in a fixed-roof tank with an internal floating roof. Nitrogen blanketing of the tank headspace also provides additional protection against any penetrating moisture (Groysman, 2015; Methanol institute, n.d.).

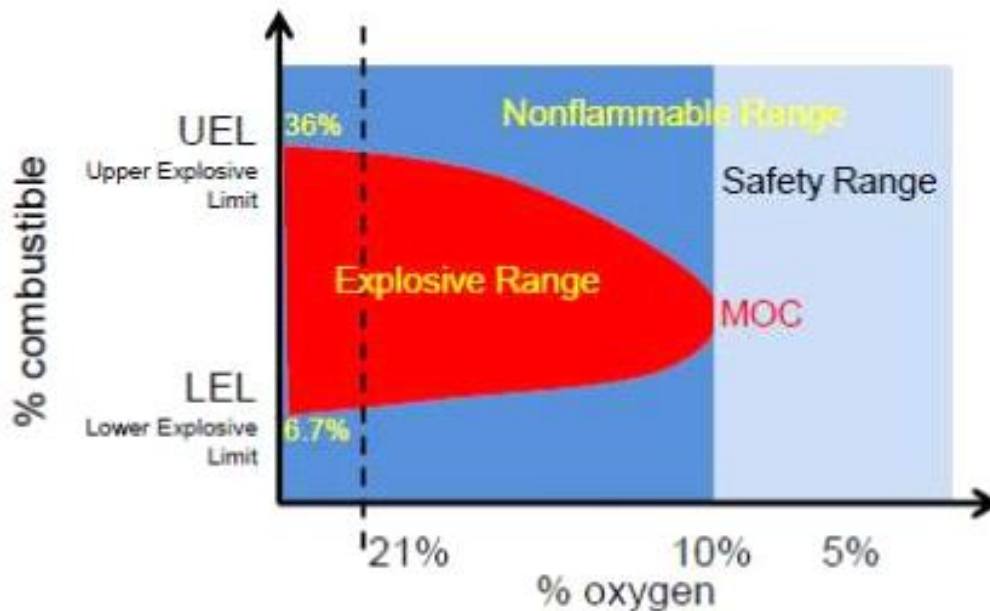


Figure 2.4: Relationship between oxygen and combustibility (Methanol institute, n.d.)

Nitrogen can be used to blanket a product and reduce the oxygen concentration. It can also be used to displace air and its associated moisture content. The replacement of moist air with dry nitrogen will prevent water contamination of the product. This water can sometimes lead to corrosion of vessels and piping. The purity of nitrogen is also important in maintaining the quality of the stored product (Methanol Institute, n.d.).

While nitrogen blanketing of methanol is done in order to reduce corrosion by expelling oxygen and replacing water with dry nitrogen, impurities in the nitrogen may even increase the rate of corrosion above that which it would have been without nitrogen blanketing. Figure 2.5 illustrates a nitrogen blanketing system.

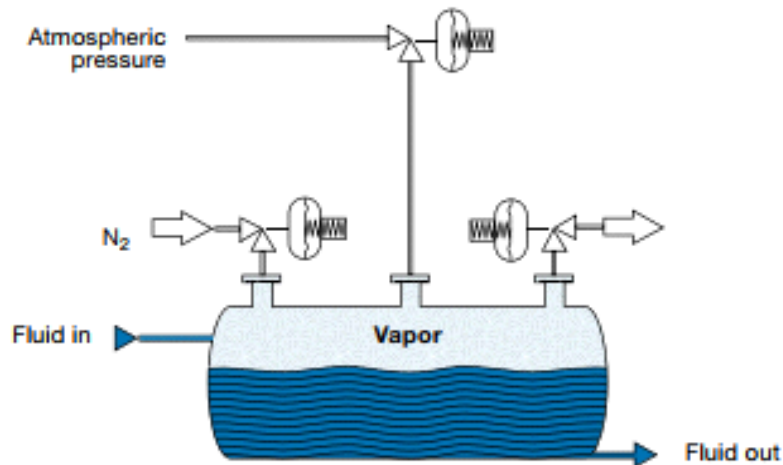


Figure 2.5: Nitrogen blanketing system (Swagelok, 2017)

2.10 Mechanisms SCC of carbon steels in alcohol

Several similarities have been established between organic (alcoholic) and aqueous media. One such similarity is that water and alcohol are polar protic liquids capable of undergoing protonation (i.e., accepting electrons or giving out electrons and dissociation of hydrogen). An important factor in corrosion is the protic or aprotic property of pure solvents. The presence of H⁺ ions brings about, in MeOH, the complete and rapid dissolution of the protective oxide film (Farina, Faita & Olivani, 1978). The existence of a one-phase or multi-phase liquid state is crucial.

Additionally, the electrode potential of the media is similar, as shown in Figure 8. Therefore, in most cases, it would be expected that the corrosion processes and galvanic interactions be thermodynamically similar in alcohol and aqueous media. Variables such as dissolved water and oxygen, acids, bases, ions, microorganisms, temperature, fluid regime and velocity, associated with alcohol and aqueous media, may produce a similar corrosion effect on metals in contact with these media (Maldonado & Kane, 2008).

Figure 2.6 provides a comparison of electrode potentials of metals in different solvents including water, methanol and ethanol.

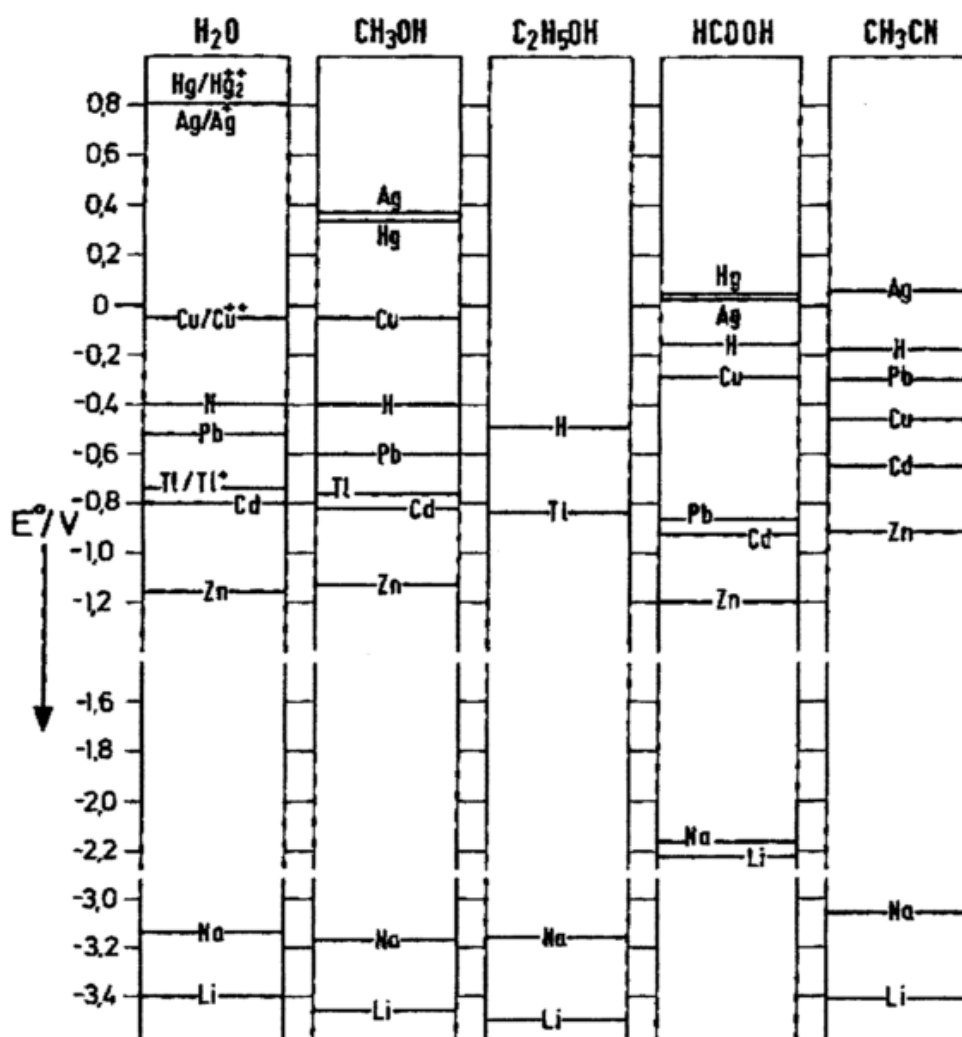


Figure 2.6: Comparison of electrode potentials of metals in different solvents including water, methanol and ethanol (Maldonado & Kane, 2008)

Another major similarity between these liquids is their physical properties. The conductivity of an ethanolic solution is lower than that of either water or methanol. The solubility of oxygen in water is less than that of methanol and ethanol, and the solubility of oxygen in methanol is more than that in ethanol, as shown in Table 2.2 (Groisman, 2014, 2015).

**Table 2.2: Solubility of inorganic oxygen-containing solvents at 293 K
(Groysman, 2015)**

Solvent	Chemical formula	Solubility of oxygen at (Pa)		
		L ^a	101,325 ^b	
		21278.25 ^c	ppm ^d	
Methanol	CH ₃ OH	0.247	415	87
Ethanol	CH ₃ CH ₂ OH	0.243	413	86
1-Propanol	CH ₃ CH ₂ CHOH	0.214	343	72
2-Propanol	CH ₃ CHOHCH ₃	0.247	418	88
1-Butanol	CH ₃ (CH ₂) ₃ OH	0.212	348	73
Methyl acetate	CH ₃ COOCH ₃	0.269	384	80
Ethyl acetate	CH ₃ CHOOCH ₂ CH ₃	0.214	318	67
Diethyl ether	C ₂ H ₅ OC ₂ H ₅	0.450	839	176
Water	H ₂ O	0.033	44	9.2
Ethylene glycol	C ₂ H ₆ O ₂	0.014	16.75	3.5
1,2,3- Propanetriol	C ₃ H ₈ O ₃	0.008	8.45	1.8

Alcohols are hygroscopic (i.e., they have a high tendency to absorb water from the atmosphere). Data show a radical increase in water content of ethanol after 30 days of exposure to a humid environment (Kane, Maldonado & Klein, 2004). A measure to control corrosion of tanks containing alcohol is to carefully isolate the tanks from the atmosphere. Alcohols themselves are not known to have any particular aggressive effect on iron, so a reasonable hypothesis is that the alcohol is being oxidized in cracks into formic acid (HCOOH), acetic acid (CH₃COOH) and carbon monoxide (CO), which cause SCC (Methanol Institute, 2012). Pure methanol is non-corrosive to most metals at ambient temperatures; exceptions include magnesium and lead. Methanol can contain contaminants such as ethanol, acetone, water, acids, chlorides, sulphur and iron (Table 2.3). Methanol can be oxidized on metallic surfaces with the formation of corrosive formic acid, especially at high temperatures (Groysman, 2015).

Table 2.3: Quality specification for methanol (IMPCA, 2012)

Substance or property	Limit (ppm max.)
Ethanol	50
Acetone	30
Water	1,000
Sulphur	0.5
Chloride (as Cl ⁻)	0.5
Acidity (as acetic acid)	30
Total iron	0.1

Because methanol is a polar solvent, galvanic corrosion is more prevalent in methanol than in other commonly used motor fuels (Element 1 Hydrogen Generators, 2013). Table 2.4 shows types of corrosion of some metals and alloys in methanol.

Table 2.4: Corrosion of some metals and alloys in methanol (Groysman, 2014)

Contaminants in fuel	Metal/alloy	Type of corrosion attack	T (°C)	Prevention of corrosion
Methyl formate Carbon steel,	Carbon steel, Zinc	General corrosion	20–25	Elimination of formate
< 0.05% H ₂ O	Aluminium	General corrosion, pitting	BP (64.7 °C)	Add 1% H ₂ O
Chlorides	Titanium	SCC, HE	20–25	Elimination of chlorides and adding of H ₂ O

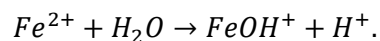
Sridhar et al. (2006) reported on the effect of various impurities such as water, oxygen, chloride, corrosion inhibitors, acetic acid (CH₃COOH), denaturant and corrosion products on the SCC of steel in ethanol. A greater potential effect was shown on the corrosion of steels in ethanol, as it is influenced by oxygen. The availability of oxygen for corrosion in methanol is, however, more than that in ethanol, since methanol has higher oxygen solubility, as shown in Table 2.4. Presumably, corrosion of metal in contact with methanol should be greater than in ethanol, when oxygen is the only variable.

The factors leading to SCC of carbon steel in fuel ethanol are: dissolved oxygen (the main reason); the presence of chlorides (even less than 5 ppm); and methanol in ethanol and its blends with gasoline; and the existence of scale and rust on carbon steel surfaces. Presumably, factors such as dissolved oxygen, presence of chlorides and methanol, and existence of scale and rust on carbon steel, could also result in SCC of the carbon steel in methanol (Groisman, 2015).

Impurity inclusions can act as catalysts for ethanol oxidation, or as nucleation sites for ethanol SCC (Hänninen, Hirsi & Torkkeli, 2011). Water has a significant effect on the SCC capability of metals in alcohol. Most of what can be inferred has come from investigations involving steel in methanolic solutions, with the assumption that these environments are mechanistically similar. In solutions of methanol and water in the range of 200 to 460 ppm, the natural (air-formed) oxide film on the surface is not stable and partially dissolves, leading to the following reaction in the protic medium (Farina et al., 1978):



Oxide-free areas on the steel's surface will rapidly dissolve according to the following reaction:



Johnston, Johnson, Ecord and Castner (1967) presented the results of fatigue, constant load, ultimate tensile strength and cathodic protection tests on Ti-6Al-4V-STA alloy exposed to various fluids, including methanol. They showed that in 6Al-4V-STA alloy, while simultaneously under stress and in contact with methanol, small amounts of moisture (one percent or greater) contained in the methanol inhibited the adverse effect of the fluid on stressed Ti-6Al-4V-STA alloy. Metallurgical factors can also affect SCC of steel in alcohol.

Ethanol SCC can occur in the ethanol piping applications when some external stresses (in addition to weld residual stresses) and subsequent localized plastic strains occur in the pipe weldments (Hänninen et al., 2011).

In a report (Sridhar et al., 2006) it was shown that SCC of steel in ethanol was intergranular when the chloride concentration in ethanol (laboratory and field samples) was low (less than one ppm) and it was transgranular when the chloride concentration was high (32 mg/L). The SCC in liquid ammonia and methanol has been reported to be essentially transgranular.

Padgett, Norfleet & Ironside (2016) investigated three in-service leaks on a crude oil pipeline operating in Canada to identify their metallurgical cause(s). They concluded that the likely crack-initiating mechanism was methanol-induced SCC, based on some observations common to all three locations of the leaks: (1) the axial directionality of the cracks; (2) the short crack length; (3) the crack location adjacent to girth welds; (4) the circumferential location of the cracks; and (5) the intergranular crack morphologies.

CHAPTER THREE: METHODOLOGY

3.1 Materials selection for the experiment

The specimens used in this experiment were made out of X65 grade carbon steel with chemical composition and mechanical properties shown in Table 3.1 and Table 3.2 respectively. The dimensions of the samples were: length 50 mm; width 20 mm; and thickness 20 mm. The material was welded using welding with a cup and cone-shape seam weld type. The electrode used for the welding had a chemical composition very similar to the welded steel. Specimens were finished with 600 grit size emery paper on Ecomet™ 250 Pro V2/Ecomet™ 300 Pro V2 Grinder-polisher that had an Automet™ 250/Automet™ 300 power head. After grinding and polishing, the samples were degreased in ethanol and acetone before testing. The surfaces to be studied were prepared up to surface finish to remove scratches in order to prevent SCC nucleating from the scratches.

The specimens were contained in glass cells closed with rubber stoppers, through which the oxygen was expelled during venting. The cells contained ports for bubbling nitrogen through the solution. All specimens were examined by metallography after completion of the test. At the conclusion of the tests, surfaces of the specimens were examined using SEM and EDS/EDX.

Table 3.1: Chemical composition of the steel samples

Element	% composition
C	0.968
Si	<0.001
Mn	1.752
P	0.006
S	0.008
Cr	0.011
Mo	<0.002
Ni	3.056
Nb	0.010
Al	0.431
Cu	<0.001

Co	<0.002
B	<0.0005
Ti	0.009
V	<0.001
W	0.005
Mg	0.0014
Ca	0.0006
Ce	<0.002
La	<0.005
As	<0.005
Pb	0.008
Sn	0.039
Sb	0.048
Te	0.003
Zn	0.009
Zr	0.216
N	0.007
Fe	93.409

Table 3.2: Mechanical properties of the steel samples

Energy (toughness) (J)	Resilience (J/cm)	Tensile strength (MPa)	Yield strength (MPa)
155.2	155.2	531	448

3.2 Experimental conditions

The test environment simulates actual conditions in which methanol is stored for use in the oil and gas industry. The environmental parameters included ambient temperature (25 °C) and constant pressure; and the experiment was run in an anaerobic environment. Three samples were each immersed in the media, which consisted of methanol blanketed or purged by nitrogen to deoxygenate the media. Also, three samples were each immersed in the media, which consisted of unpurged methanol.

The specimens were placed in a nitrogen-blanketed environment. Nitrogen was purged through the solution after first passing through a filter to prevent contaminants from entering the flask. Tests were conducted in 250-mL flasks that had ports for introducing the specimen and the gas (Figure 3.1).



Figure 3.1: Experimental set-up showing methanol being purged with nitrogen

The test final-sample exposure period was seven days. The immersion periods for samples 1–5 were 48, 96, 120, 144 and 168 hours, respectively. After the test, specimens were examined visually using SEM and optical microscopy.

3.3 Welding

A cup and cone seam weld type was introduced on X65 carbon steel using the submerged arc welding method. The weld was made with low carbon solid filler wire, Ba-s2Mo, which had a composition matching the X65 steel throughout the welding process. The flux type used was Lincoln weld SP X80. After welding, the metal was cut to the required dimensions and then cleaned immediately to avoid corrosion by the cutting fluid utilized (Figure 3.2).

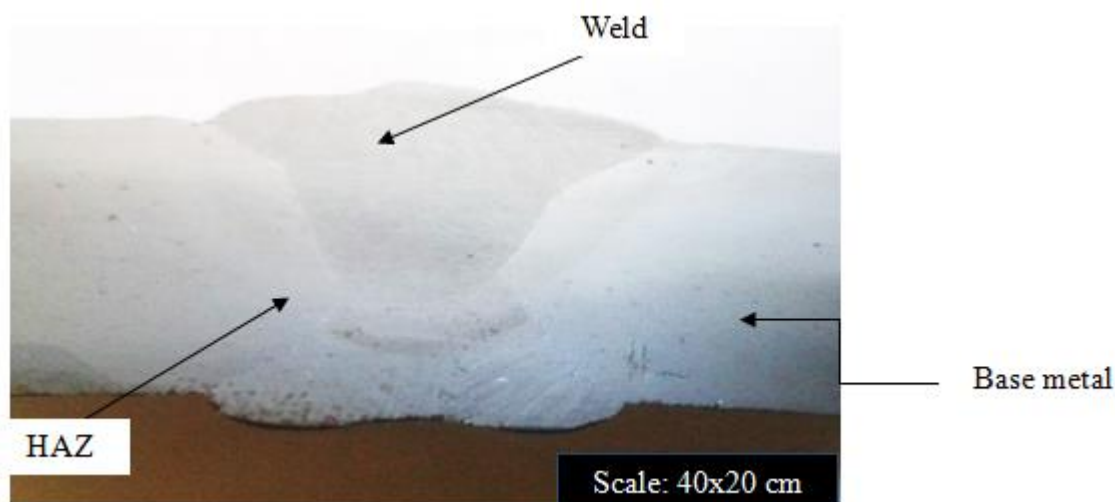


Figure 3.2: Double U-weld on X65 carbon steel

3.4 FTIR sample preparation

In order to prepare the sample for FTIR analysis, the corrosion product on the metal surface was carefully scraped from the metal sample using a scapula. The corrosion product was then added to heated potassium bromide (KBr) with a concentration of 0.2% to 1%, mixed and grinded to a fine powder. After grinding, the mixture was pressed using a compactor to form a pellet. The pellet was then held with the FTIR sample holder for characterisation.

3.5 SEM sample preparation

The specimens used for SEM analysis were cut from the original samples exposed to methanol. Small sections of the samples ($1 \times 1 \text{ cm}^2$) were cut out using a diamond saw.

To ensure low deformation of the profile region, corroded surfaces were covered with epoxy resin before cutting and mounting. The samples were then mounted properly for polishing. The surface of the specimens to be characterised was prepared by finishing using 250, 320, 400, 600 and 1200 grit size emery paper on Ecomet™ 250 Pro V2/Ecomet™ 300 Pro V2 grinder-polisher that had an Automet™ 250/Automet™ 300 power head, operated at a speed of 350 RPM. Finally, the specimens were polished with emery cloths to which various polishing fluids containing different micro-sized abrasive particles were applied. The samples were cleaned with water

and acetone and dried immediately before mounting on the Carl Zeiss Evo LS10 scanning electron microscope which had EDS/EDX attached to it.

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1 Introduction

During the experiment it was expected that the samples in the de-aerated medium should not corrode, since methanol was purged with nitrogen to remove oxygen, which is known to be an important corrodent in most media. However, corrosion did occur on the samples in the de-aerated medium (Figure 4.1). Thus FT-IR was performed on the corroded surface of the samples to ascertain the composition of the corrosion product.

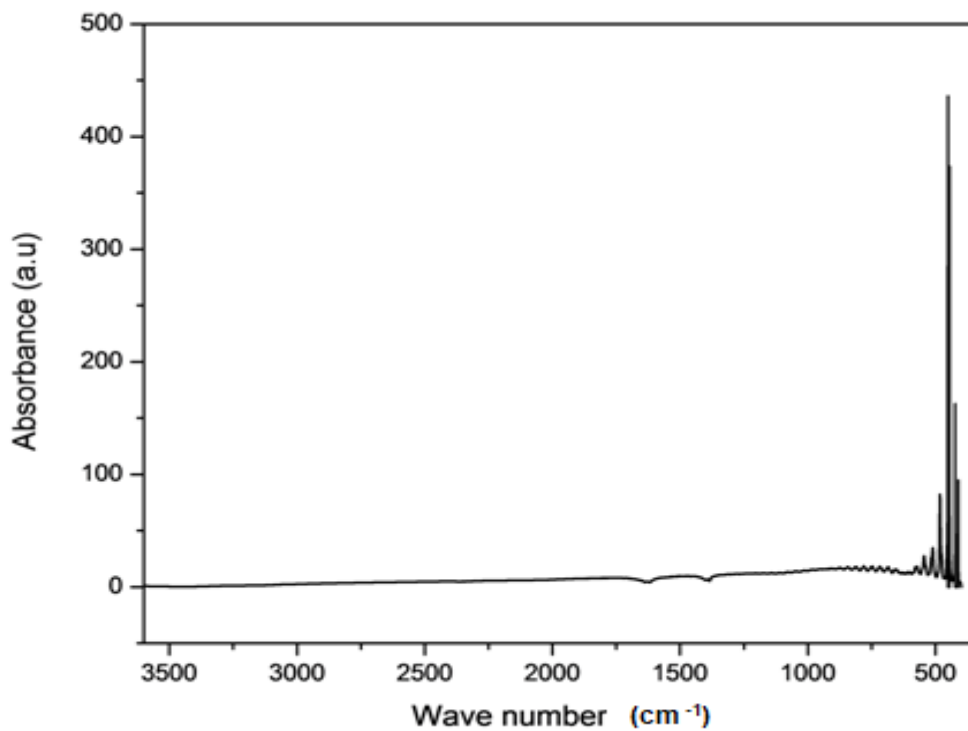


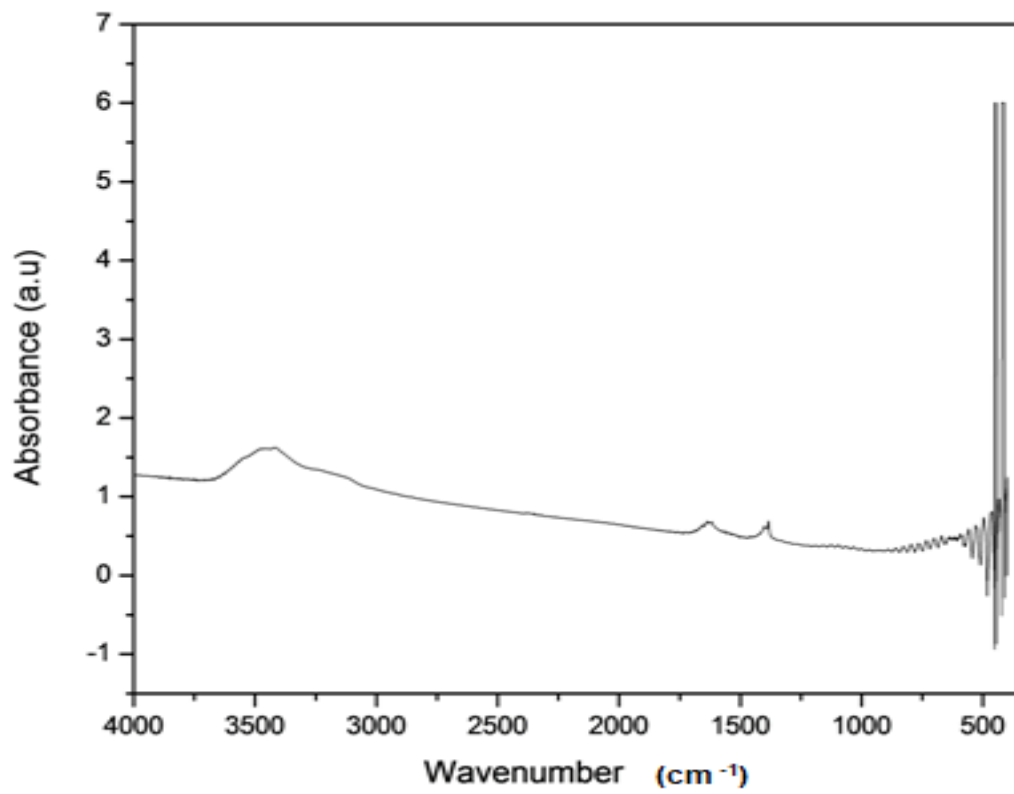
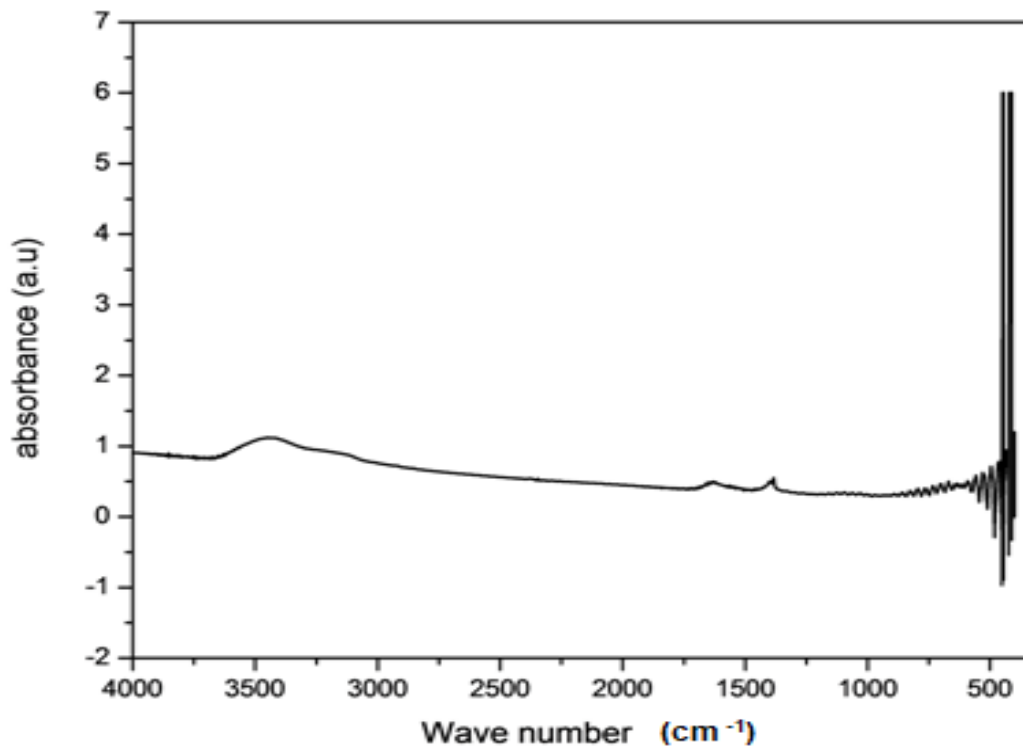
Figure 4.1: Corroded steel from the de-aerated methanol medium

4.2 FT-IR spectroscopy

FT-IR spectrographs of corrosion products on samples D1–D5 are shown in Figure 4.2; and there are similarities between all the spectra. The presence of amides in the corrosion products was detected due to the characteristic IR bands at 1636 cm^{-1} ; this corresponds to NH out of plane. The peak at 698 cm^{-1} corresponds to out of plane C–H bonds; and the peak at 3415 cm^{-1} corresponds to stretching of the O–H bond. The peak at 1384 cm^{-1} is evidence of the presence of alkane, $-\text{CH}_3$ group and N–O nitro compound in the corrosion product formed.

All these peaks, combined indicate that nitrogen, used for blanketing, is a reactant that took part in the corrosion process. The IR absorption peak at 3415 cm^{-1} corresponds to a secondary amide N–H stretch. The peak may be an indication of the vibrations of NH_2 species bonded to Fe sites developed after H_2 adsorption, which provides evidence that atomic nitrogen in Fe_2N reacts with hydrogen to produce $-\text{NH}_2$ species. Thus a probably valid hypothesis that explains the reaction mechanism could be that during nitrogen purging, iron nitride (Fe_2N) might have formed at anodic potentials on various sites of high-stress concentration.





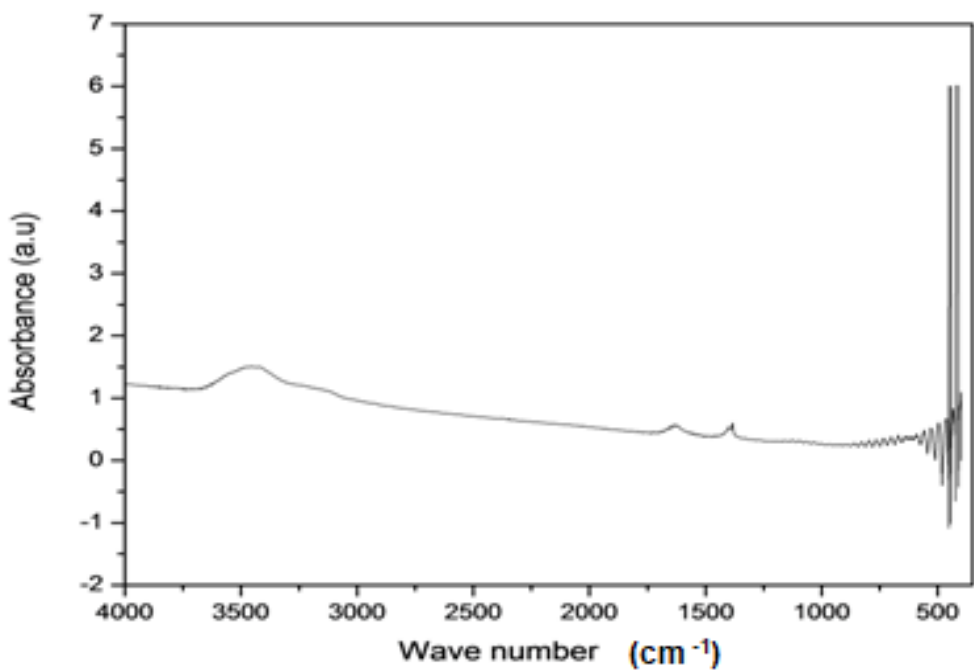
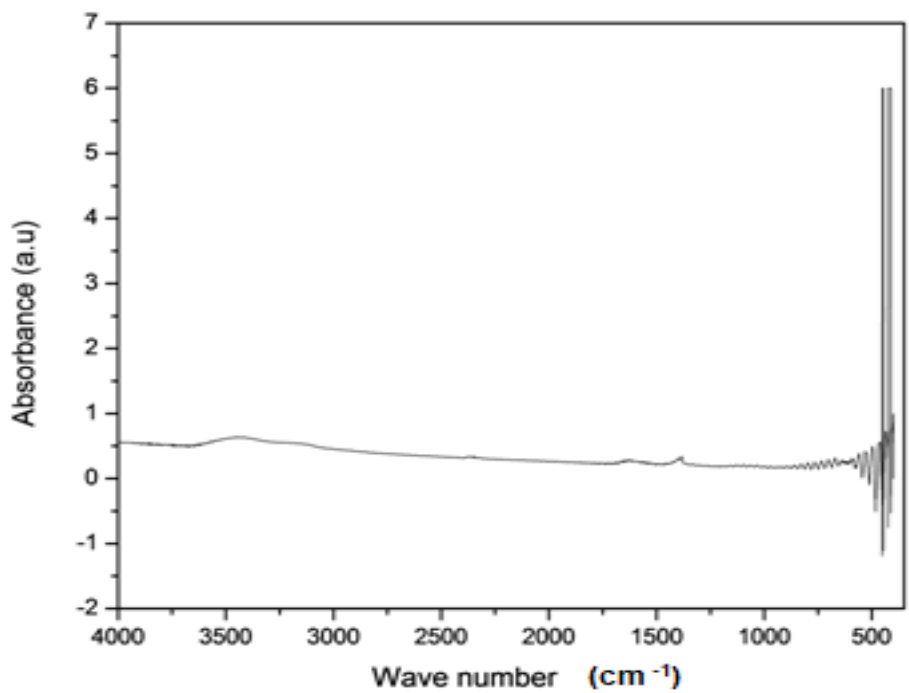


Figure 4.2: FTIR spectrograph of samples (D1–D5) exposed to de-aerated methanol

Environmental conditions (such as pH), to which the steel was subjected, normally have an influence on the corrosion process.

Figure 4.3 provides an indication of the possible influence of pH on this corrosion phenomenon. The pH of methanol before immersing the samples was found to be 7.407.

From Figure 4.3 it can be seen that the pH of aerated methanol during all exposure periods was lower than that of de-aerated methanol, and also lower than the initial pH of methanol before commencement of the test. For de-aerated methanol there was a continuous increase in pH with exposure time, which may have resulted from a decrease in hydrogen production during purging. The result is, however, different for an aerated methanol solution where there is a decrease in pH, followed by an increase; and then a further decrease. The fact that the severity of corrosion was independent of exposure time, as evidenced in the SEMs (Figure 4.4), may be correlated to this behaviour. This decrease in pH suggests that the production of hydrogen increased acidification.

Table 4.1: pH of aerated and de-aerated methanol at various exposure periods of samples

Sample	Solution type	Exposure time (hrs)	pH of the solution
A-1	Aerated	48	7.108
A-2	Aerated	96	7.199
A-3	Aerated	120	7.202
A-4	Aerated	144	7.149
A-5	Aerated	168	7.023
D-1	De-aerated	48	7.498
D-2	De-aerated	96	7.582
D-3	De-aerated	120	7.602
D-4	De-aerated	144	7.706
D-5	De-aerated	168	7.728

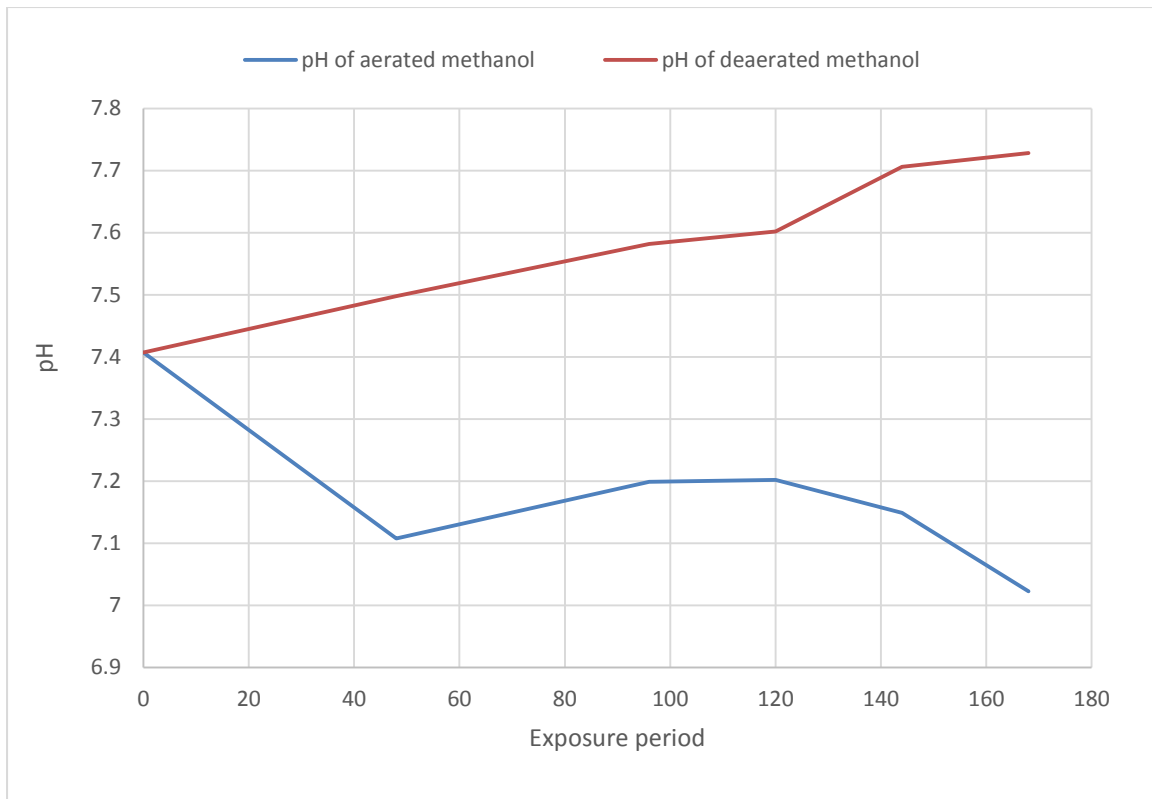
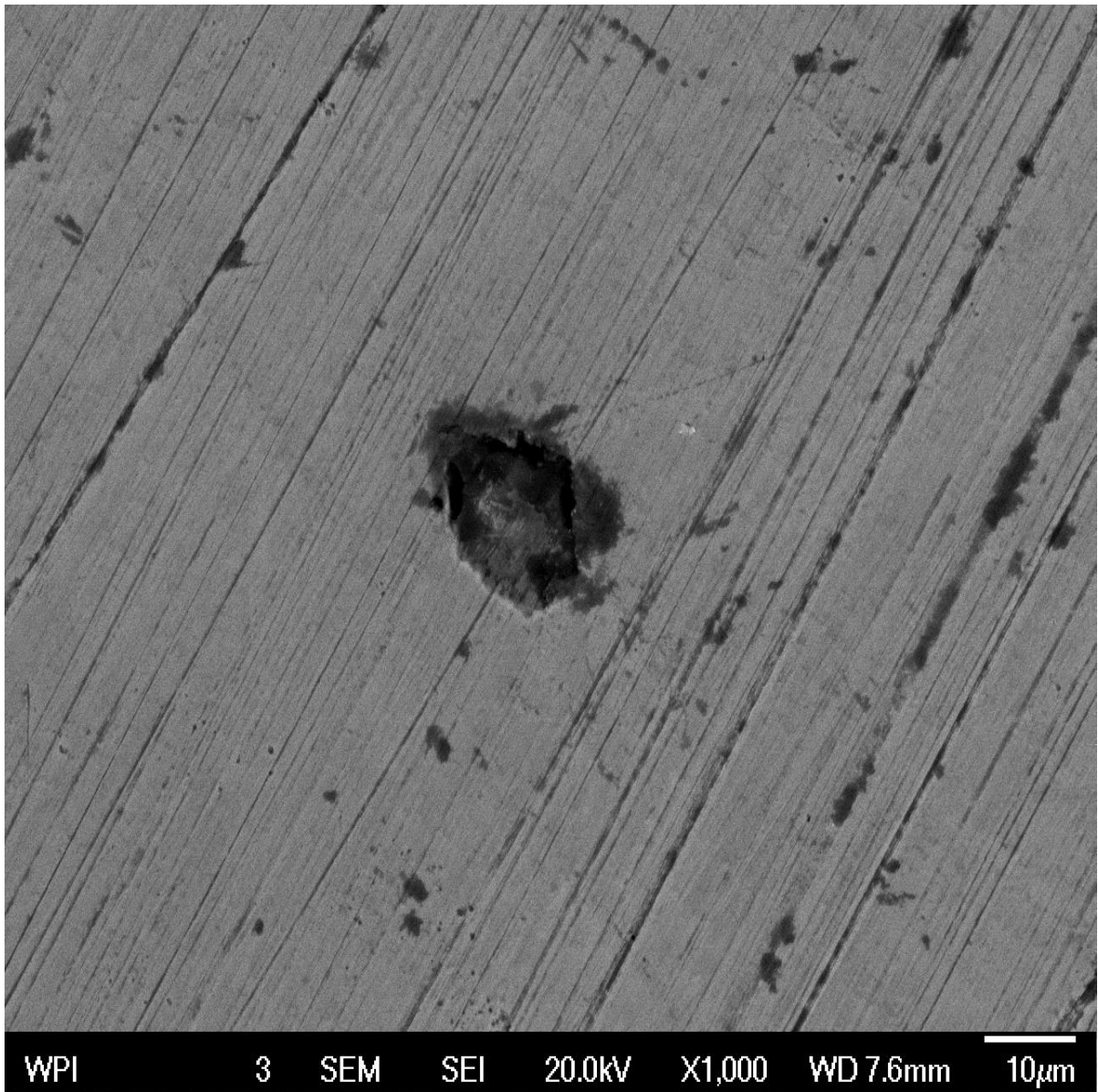


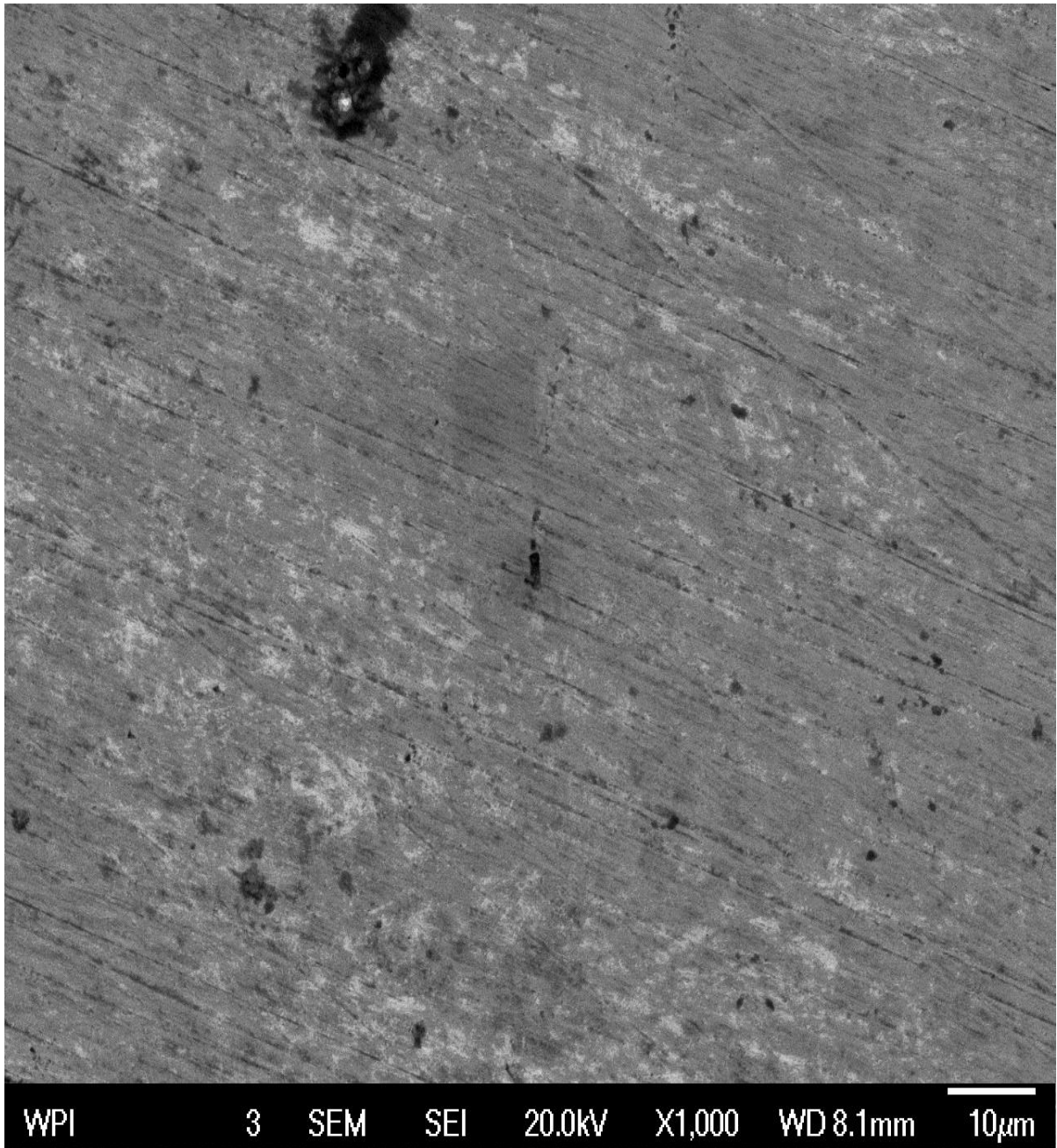
Figure 4.3: Comparison between pH of aerated and de-aerated methanol after a period of sample exposure, each sample removed at different periods for both aerated and de-aerated methanol

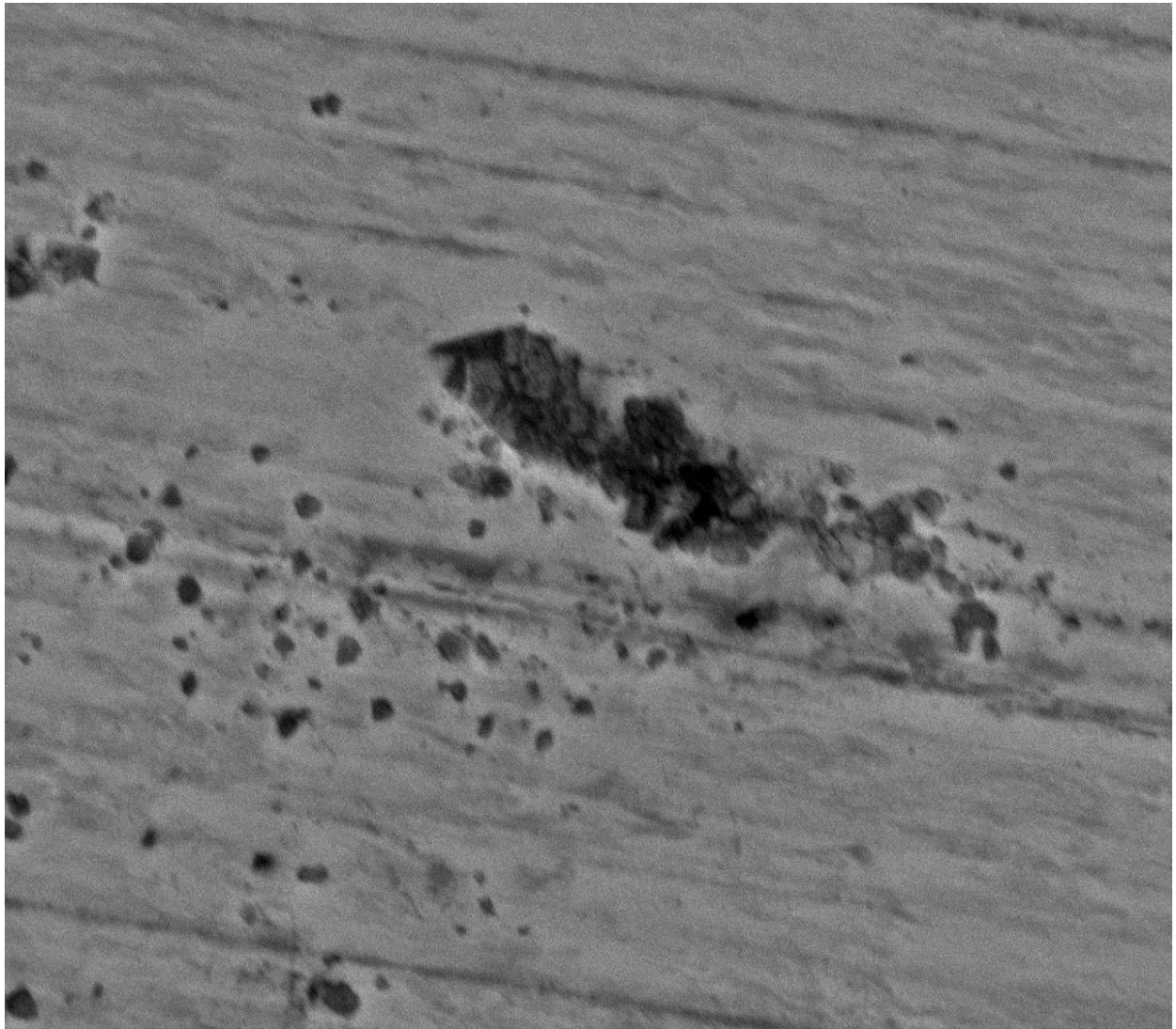
4.3 SEM analysis

The images obtained from SEM carried out on the samples are shown in Figure 4.4. Profile and cross-sectional views of the samples were obtained at various magnifications. From the SEM images shown, it can be seen that pitting corrosion is the dominant damage mechanism, whereas for the samples exposed to de-aerated methanol, pitting corrosion was not present; rather, a different localised corrosion mechanism occurred. This corrosion is found to be very severe in some samples and minimal in others, as can be seen from the micrographs. The overall conclusion, however, is that time had a dominant effect, but that other variables, such as level of impurities or concentration effect, could have resulted in the differences observed. Several phenomena are observed from the SEM results. In Figure 4.4 (sample A3), cracking appears to have been initiated inside the pit that was first formed; while in Figure 14 (sample A1), cracking apparently resulted from pit coalescence.

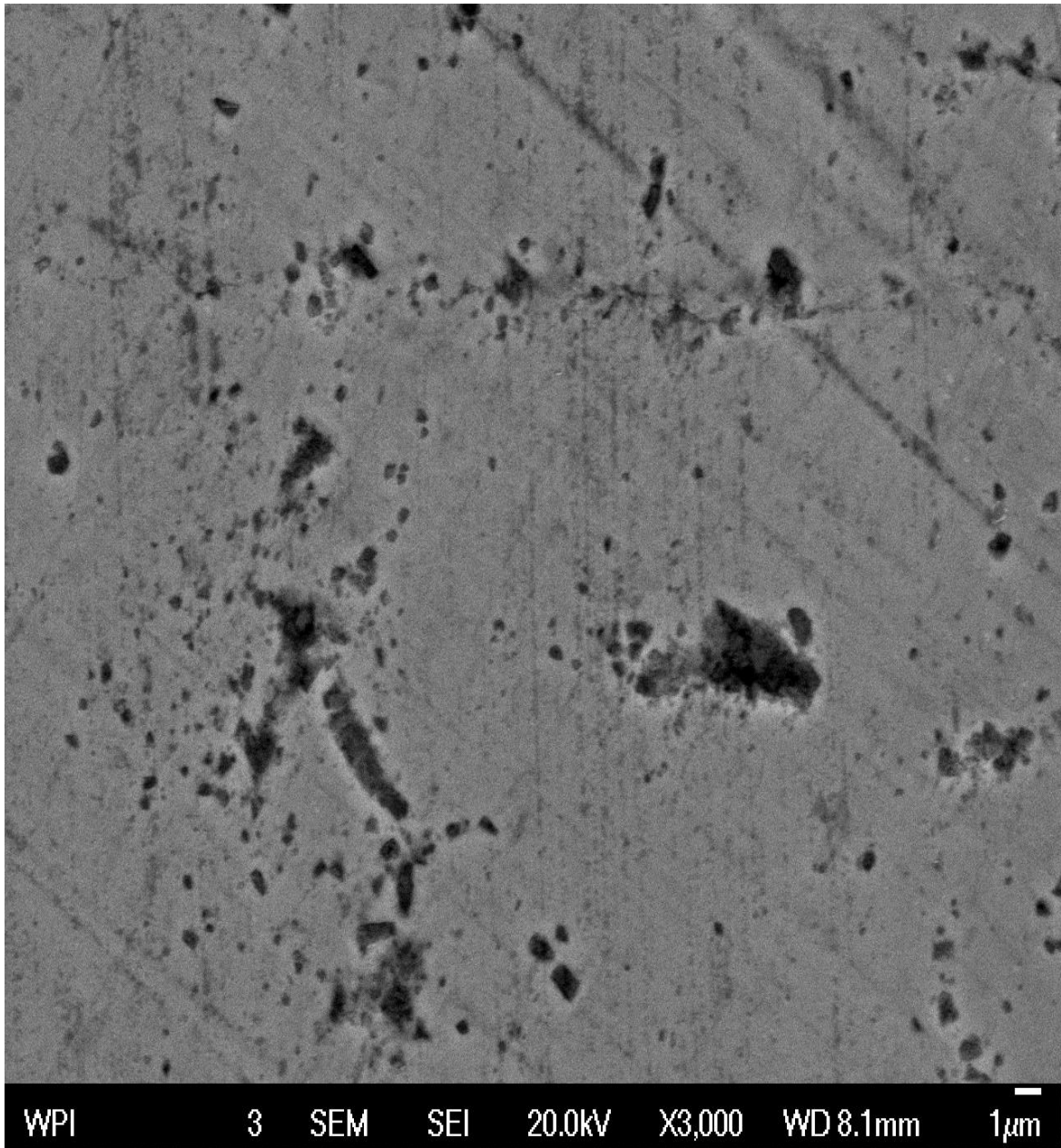
Scanning Electron Microscopy (SEM) of the cross-section of the samples revealed no pitting or cracking, probably due to the short test exposure time.

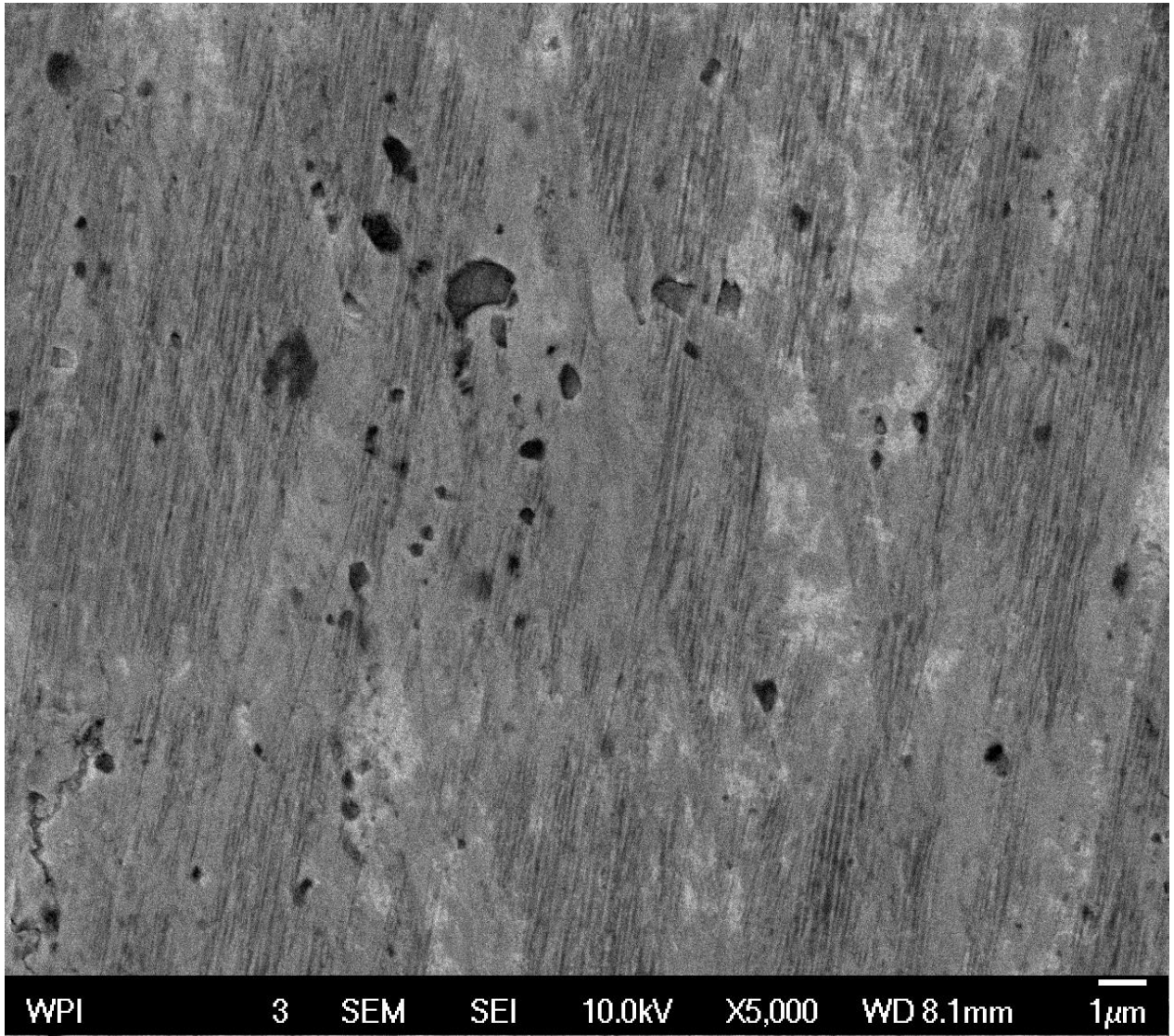


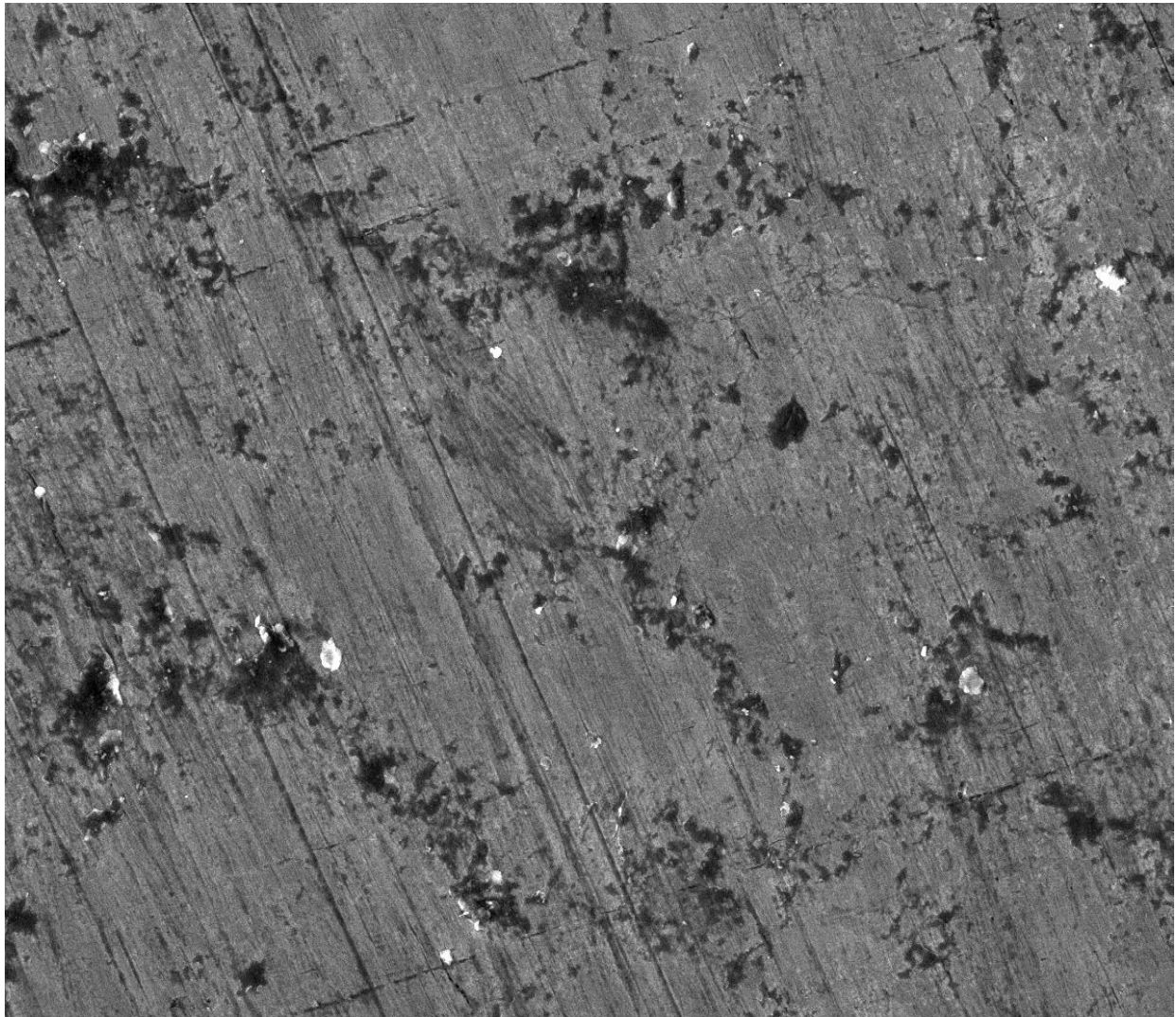




WPI 3 SEM SEI 20.0kV X3,500 WD 6.6mm 1 μ m







WPI

3

SEM

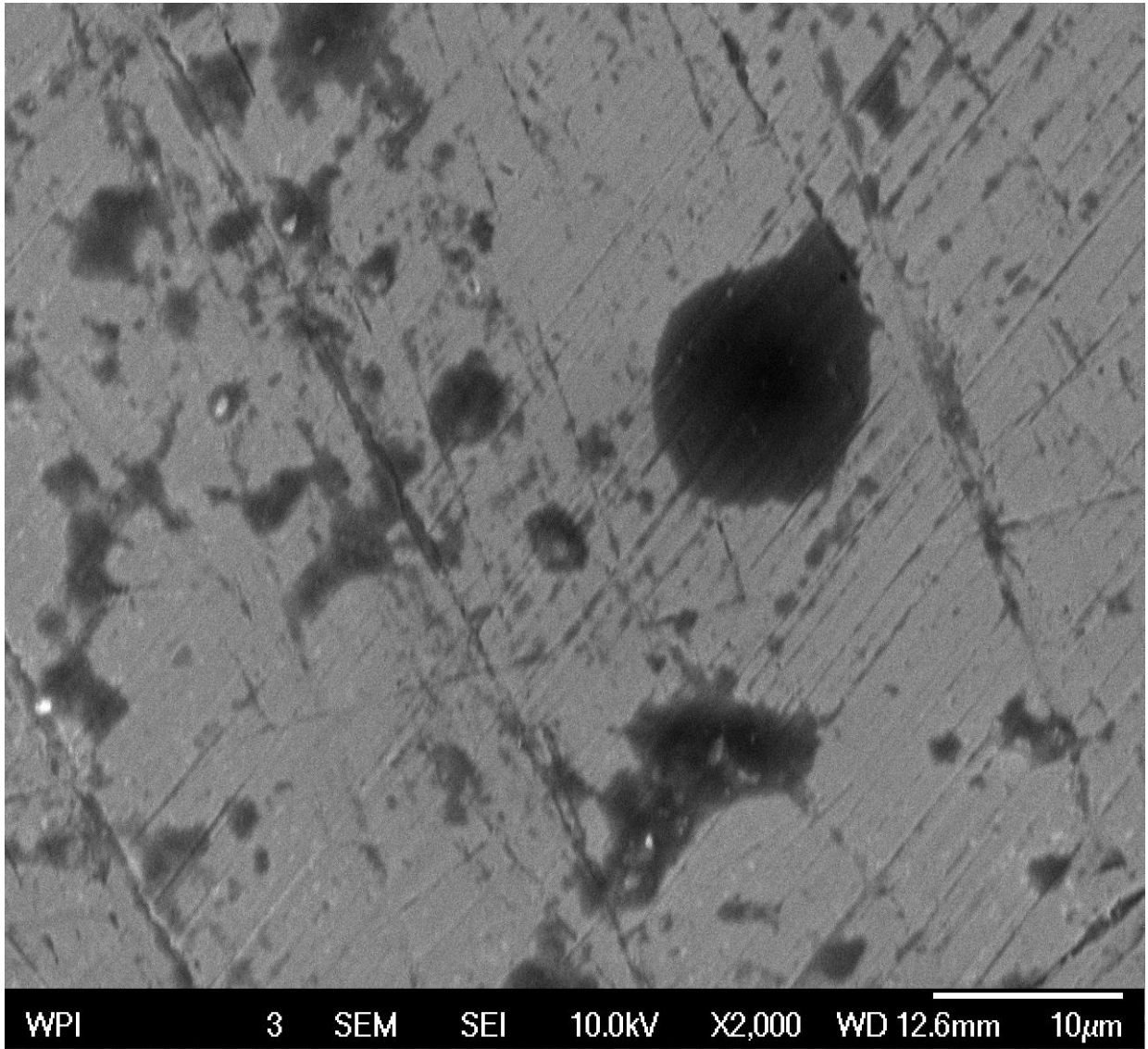
SEI

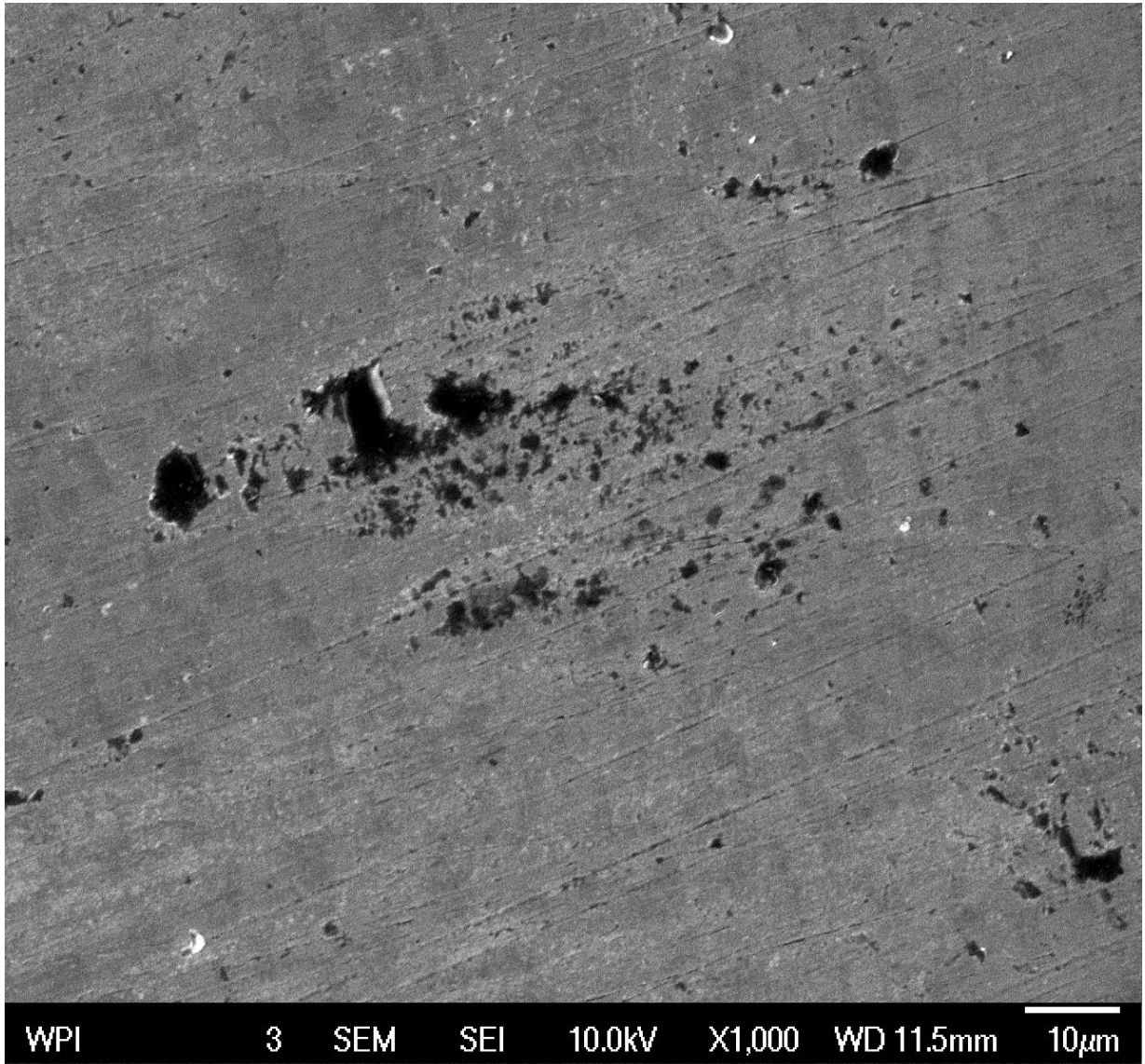
10.0kV

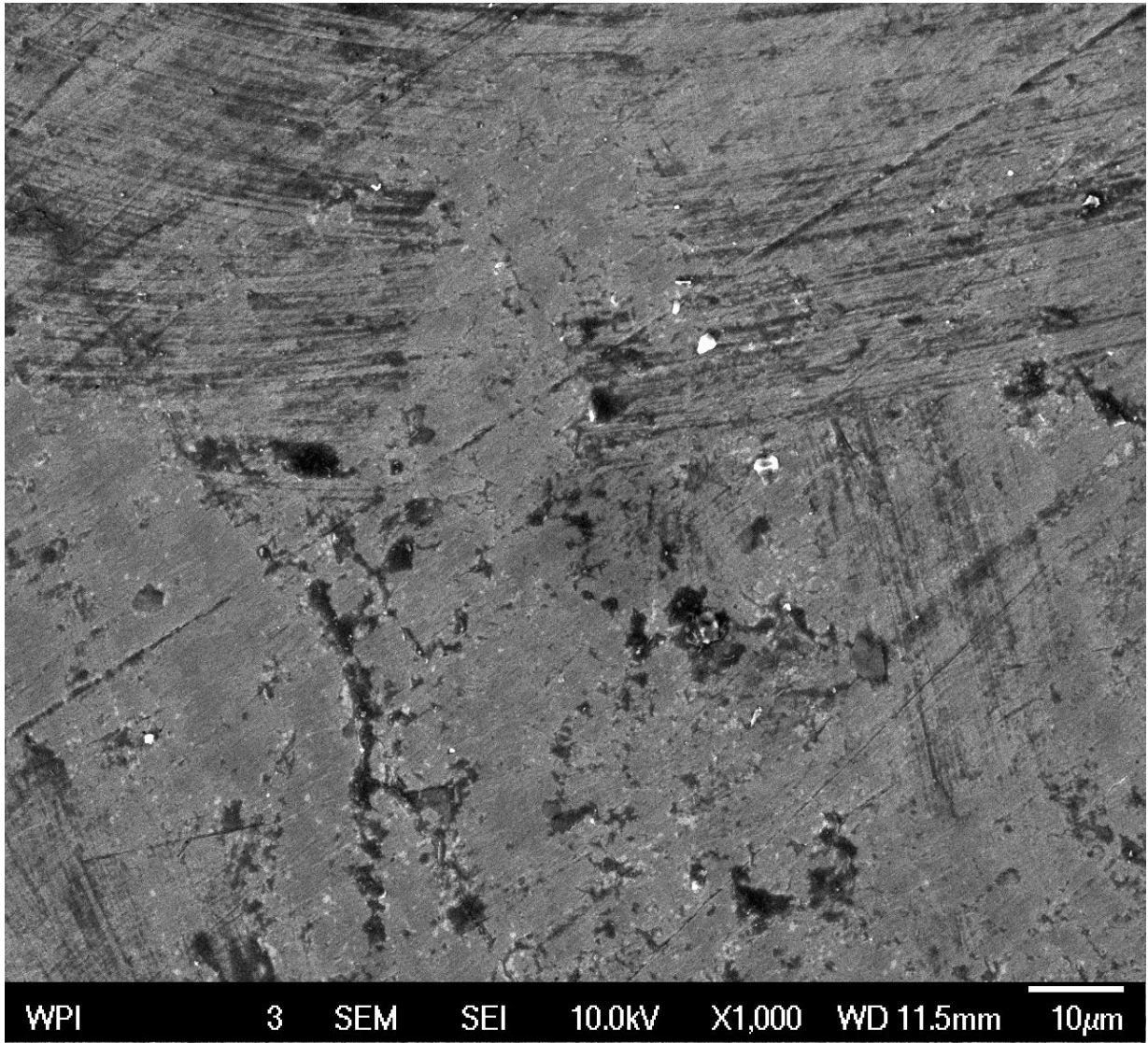
X1,000

WD 11.1mm

10 μ m







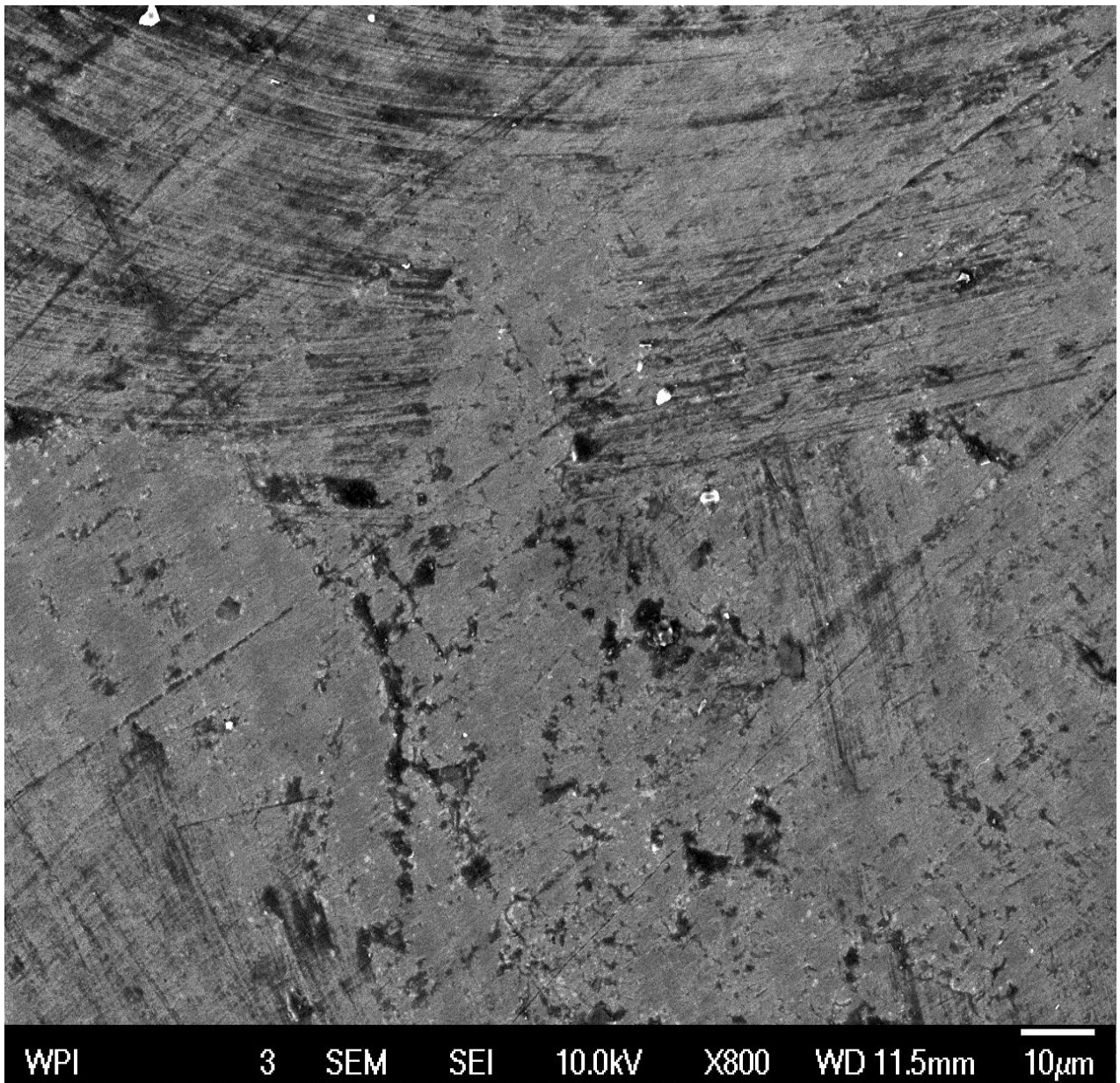


Figure 4.4: SEM images of samples exposed to aerated methanol (A1-A5) and samples exposed to de-aerated methanol (D1-D5)

From the results of the SEM analysis performed, it was observed that neither cracks nor pits were initiated on samples exposed to de-aerated methanol. For samples in aerated methanol, features which look like cracks, probably formed by coalescence of pits, were observed in some of the samples. This cannot be verified, however, due to low magnification. Generally, all the samples exposed to aerated methanol had pits whose sizes varied with period of exposure.

If this claim happens to be true, then the crack may be said to have been formed probably by an anodic dissolution mechanism resulting from oxidation of pits.

FTIR analysis of corrosion product formed on each sample exposed to de-aerated methanol revealed that oxygen was not a major participant in the corrosion process; rather the corrosion occurred due to some reactions that may have been facilitated by impurities, probably emanating from the nitrogen gas or the methanol.

Unfortunately, due to time constraints and certain challenges with the equipment, the purity of the methanol and nitrogen gas could not be ascertained.

CHAPTER FIVE: CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The results obtained show that:

- There is a likelihood that residual tensile stress alone, without applied tensile stress, can result in SCC of low-carbon steels when exposed to methanol in a favourable environment, as evidenced by the crack-like feature observed in the SEM images.
- Whereas neither cracks nor pits were formed on the samples in the de-aerated methanol, pitting was more prevalent in the samples exposed to aerated methanol.
- Crack-like features observed in the SEM images could not be verified due to low magnification. Cracks may be found at higher magnification and imaging of suspected areas. A clear profile of cracks might probably be more obvious if longer test-exposure time is considered. In future work, I will seek to overcome these unavoidable constraints.
- Purity of the purging gases is very important as it could lead to another type of corrosion mechanism.

5.2 Recommendations

- That extended coupon exposures be tested over a longer period.
- That slow strain rate tests, with electrochemical monitoring (including potential monitoring, current monitoring and EIS) be applied to monitor the surface and film behaviour when a tensile force is applied to the sample.
- Test for purity of methanol purging gases.
- High-resolution SEM analysis.

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