INVESTIGATION OF HYDROGEN INDUCED CRACKING SUSCEPTIBILITY OF
API 5L X65 PIPELINE STEELS

A Thesis Submitted to the
College of Graduate and Postdoctoral Studies
In Partial Fulfilment of the Requirements
For the Degree of Master of Science
In the Department of Mechanical Engineering
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Saskatoon

By

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ABSTRACT

The service environment of oil and gas pipelines often subject them to harsh conditions, such as, very low temperatures, microbial attack, acidic or sour environments etc. These conditions can trigger different failure mechanisms such as corrosion, embrittlement and cracking. The hydrogen induced cracking (HIC) phenomenon often affects pipelines exposed to sour and acidic environments. It involves the ingress of hydrogen atoms into the steel, which leads to the degradation of its mechanical properties such as, strength and ductility as well as embrittlement and cracking of the steel.

This study aims at relating the microstructural and hydrogen diffusion characteristics of steels to their cracking behaviour, and identifying the important microstructural characteristics that influence their hydrogen assisted cracking behaviour. Two X65 pipeline steels were used for this investigation. Firstly, the steels were characterized using optical microscopy, electron backscatter diffraction (EBSD) and mechanical tests. Then, the diffusion and trapping parameters of the steels were evaluated using hydrogen permeation experiments, while the hydrogen microprint technique was used to ascertain the important pathways for hydrogen transport through the steels. Finally, electrochemical hydrogen charging was used to generate cracks in the steels. This facilitated the HIC analysis of the as-received and heat-treated steels, in relation to their microstructural characteristics.

After hydrogen charging, microstructural evaluation revealed cracks at the mid-thickness (segregation zone) of both steels. The cracks initiated and propagated mainly through Si-enriched inclusions and complex precipitates, which are believed to have facilitated crack propagation. However, more severe cracks were observed in plate 1, which had a more strained microstructure, while plate 2 which had a less deformed microstructure and a higher fraction of recrystallized grains, was less severely cracked. The cracking behaviour observed in the steels was related to their hydrogen diffusion and trapping characteristics. The results confirmed that a higher ratio of reversible to irreversible hydrogen trapping sites contributes to increasing HIC severity in steels. Additionally, the hydrogen transport through the investigated steels was most prominent along the grain boundaries, thus, indicating the importance of grain boundary character and distribution to HIC. Finally, the change in microstructure of the heat-treated steels clearly influenced their cracking behaviour. The result confirmed that important factors such as the dislocation density, fraction of deformed and recrystallized grains and grain size distribution are directly related to the resistance of steels to HIC failure.
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Finally, my profound gratitude goes to my parents, Mr. and Mrs. Alaso Jack who have always supported me throughout my academic pursuit. They have always taught me that success is not achieved on a platter of gold, but by the virtue of hardwork.
DEDICATION

To God Almighty
And my family for their support.
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<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>AF</td>
<td>Acicular ferrite</td>
</tr>
<tr>
<td>AIDE</td>
<td>Adsorption-induced dislocation emission</td>
</tr>
<tr>
<td>API</td>
<td>American Petroleum Institute</td>
</tr>
<tr>
<td>ARR</td>
<td>Average rolling reduction</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
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<tr>
<td>CEPA</td>
<td>Canadian Energy Pipeline Association</td>
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<tr>
<td>CSL</td>
<td>Coincidence site lattice</td>
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<td>CFC</td>
<td>Corrosion fatigue cracking</td>
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<td>DC</td>
<td>Direct current</td>
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<td>EBSD</td>
<td>Electron backscatter diffraction</td>
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<td>EDS</td>
<td>Energy dispersive X-ray spectroscopy</td>
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<td>HAGBs</td>
<td>High angle grain boundaries</td>
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<td>HEDE</td>
<td>Hydrogen-enhanced-decohesion</td>
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<td>HELP</td>
<td>Hydrogen-enhanced-local-plasticity</td>
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<td>HIC</td>
<td>Hydrogen induced cracking</td>
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<tr>
<td>HSLA</td>
<td>High strength low alloy</td>
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<td>ISO</td>
<td>International Organization for Standardization</td>
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<td>KAM</td>
<td>Kernel average misorientation</td>
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<td>LAGBs</td>
<td>Low angle grain boundaries</td>
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<td>MLI</td>
<td>Mean lineal intercept</td>
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<tr>
<td>NACE</td>
<td>National Association of Corrosion Engineers</td>
</tr>
<tr>
<td>ND</td>
<td>Normal direction</td>
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<tr>
<td>OM</td>
<td>Optical microscopy</td>
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<tr>
<td>OPEC</td>
<td>Organization of the Petroleum Exporting Countries</td>
</tr>
<tr>
<td>PF</td>
<td>Polygonal ferrite</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
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<tr>
<td>SCC</td>
<td>Stress corrosion cracking</td>
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<tr>
<td>SCE</td>
<td>Saturated calomel electrode</td>
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<tr>
<td>SSC</td>
<td>Sulfide stress cracking</td>
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<tr>
<td>TMCP</td>
<td>Thermomechanical controlled processing</td>
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<tr>
<td>QF</td>
<td>Quasi-polygonal ferrite</td>
</tr>
<tr>
<td>QT</td>
<td>Quenching and tempering</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
<td>--------------------------------------------</td>
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<tr>
<td>RD</td>
<td>Rolling direction</td>
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<td>SWC</td>
<td>Stepwise cracking</td>
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<tr>
<td>TD</td>
<td>Transverse direction</td>
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<td>TEM</td>
<td>Transmission electron microscopy</td>
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LIST OF SYMBOLS

A<sub>r1</sub> and A<sub>r3</sub>  Phase transformation temperatures
C<sub>app</sub>  Apparent hydrogen solubility, mol cm<sup>-3</sup>
D<sub>eff</sub>  Effective hydrogen diffusion coefficient, cm<sup>2</sup> s<sup>-1</sup>
I<sub>∞</sub>  Steady-state current, μA
J<sub>L</sub>  Hydrogen permeability, mol cm<sup>-1</sup> s<sup>-1</sup>
N<sub>T</sub>  Total density of hydrogen trapping sites, cm<sup>-3</sup>
T<sub>L</sub>  Time lag, s
T<sub>nr</sub>  Non-recrystallization temperature
wt%  Weight percentage
α  Ferrite
γ  Austenite
%  Percentage
CHAPTER ONE

INTRODUCTION

1.1 Overview

This chapter presents a brief introduction and background for the current study. It highlights the motivation and objectives of this research. Also, it provides an outline detailing how the entire thesis is arranged.

1.2 Background

Pipelines are used to economically transport crude oil and natural gas through long distances to various locations of interest, such as flow stations and refineries. Pipelines are preferred for the transportation of these resources as against other modes of transport, such as trucks and by rail, because of their speed and reliability and the repetitive nature of the process [1,2]. Steel is commonly used in structures or applications that require a good combination of strength, toughness and cost effectiveness. Thus, steel has been used over the years for the construction of petroleum pipelines, which are associated with high internal pressures during the transportation of high volumes of natural resources [3,4].

Due to the demand for stronger, lighter and more durable pipelines for the improvement of production capabilities, significant advancements have been made in steel processing to obtain quality pipelines to meet diverse application requirements. Over the years, elemental additions and several processing techniques have been used to improve the mechanical properties of pipelines. A significant leap in steel production will be the use of niobium as a strengthener in hot rolled carbon-manganese (C-Mn) steels in the 20th century and the introduction of controlled rolling and thermomechanical controlled processing (TMCP) of steels [4,5]. These niobium containing microalloyed steels were first commercially produced in 1958 [6]. This has given rise to the era of high strength low alloy (HSLA) and microalloyed steels, having a low weight percent combination of the main microalloying elements: niobium, vanadium and titanium. For decades, research into microalloyed steels have been centred on enhancing their strength, toughness and resistance to environmental and service conditions [4,5]. Although the mechanism behind developing good mechanical properties in steels has been well established, the incorporation of these desired properties and failure resistance in pipeline steels has been a real challenge. Thus, research is still ongoing on the development of high strength steels, which
will possess acceptable resistance to several failure mechanisms, with regards to their proposed environment of service. Thus far, various studies have cited several approaches to improve the failure resistance of steels. These include methods such as, microalloying and desulphurization; TMCP; inclusion type and morphology control; microstructure evolution; minimization of segregation and lower hardness values at the segregation zone; crystallographic texture control and other factors [7–9]. Although some uncontrollable factors such as vandalism, earthquakes etc, can also result in pipeline failure incidents, research has shown that devoid of these factors, the integrity of pipelines is largely dependent on its microstructural characteristics.

Advancements in steel research over the last century have subsequently birthed several grades of steel. International standards by the American Petroleum Institute (API) classify carbon steel pipelines used for oil and gas transmissions under the API spec 5L [10]. The API 5L pipelines grades follow a grading system where their identification number corresponds to the minimum yield strength required for that grade in kilo pound per square inch (ksi). Notable instances of these API 5L pipelines include the X42, X46, X52, X56, X60, X65, X70, X80, X100, and X120 grades. Although these pipeline grades are identified by their minimum yield strengths, they are broadly categorized with regards to their composition, mechanical properties and processing specifications [5,10]. Though, most high strength steels such as the X100 and X120 grades are being developed and studied, their implementation potential in key projects is still a challenge but promising [11,12], as their very high strength make them more susceptible to cracking and failure [13]. Hence, pipelines such as the X65 and X70 pipeline steel grades are currently being used in various construction projects.

Even though pipelines are considered a safe and economic way to transport petroleum products, it does not come without its challenges. Often, certain conditions such as the pH value of the multiphase fluid being transported, operational location of the pipeline or even fabrication or cathodic protection processes, subject these pipelines to harsh and/or corrosive environments, which lead to their degradation and subsequent failure [14,15]. The increasing demand for energy globally has led to the exploration of oil and gas in diverse environments, such as acidic environments and areas with sour hydrocarbons. Also, oil wells with reduced or declining production capacity are being rejuvenated using acidizing techniques [16]. These processes and environments tend to initiate severely corrosive and/or embrittling conditions, which can lead to pipeline failure [14,15].
The Canadian Energy Pipeline Association (CEPA), in their 2019 annual report [17], categorized pipeline incidents according to their level of significance and reoccurrence. These categories included: materials, manufacturing and construction defects, cracking, metal loss, external interference, geotechnical movements, and others. The relative frequency recorded for these pipeline incidents over a period of 5 years (2014 – 2018) were 14%, 18%, 41%, 11%, 3% and 13%, respectively. This data is presented in Figure 1.1. This report showed that failures resulting from metal loss and cracking were the main causes of pipeline incidents in Canada, within that period. This information is important because North America (which includes Canada) has about 51% of the global pipeline network currently in pre-construction or construction stages and has the largest global pipeline investment of about $232.5 billion [18].

Fig 1.1. The relative frequency of the causes of pipeline incidents in Canada [17].

Metal loss is usually a surface phenomenon, which has several removal mechanisms such as uniform corrosion, pitting, erosion corrosion etc. However, the corrosion reaction at the steel surface in some cases, such as in sour or acidic environments, leads to the manifestation of internal cracking in steel, which can go unnoticed until failure. These cracks are designated as environmentally induced cracks. There are several environmentally induced cracking mechanisms that cause pipeline failure, most notable of these are stress corrosion cracking (SCC), corrosion fatigue cracking (CFC) and hydrogen induced cracking (HIC) [19]. A schematic of some common pipeline failure mechanisms is shown in Fig 1.2.
Fig. 1.2. Schematic illustration of common pipeline failure mechanisms [20].

SCC is known to occur in the presence of stress, HIC can occur in the absence of applied stress, while CFC occurs under cyclic loading in a corrosive environment. This study will focus on HIC in steel, which has been linked to several pipeline failures, but has not been given adequate research attention like SCC, which has been more extensively studied [7]. HIC involves the ingress of hydrogen (H) into the steels, leading to the degradation of mechanical properties and cracking of the steels. HIC is a phenomenon widespread in sour and acidic environments. It is characterized by the entry of atomic hydrogen and its recombination at various defects, such as inclusions, dislocations or grain boundaries in the steel structure. This recombination causes an increase in gas pressure, which reaches a critical value and initiates cracks in the material without the application of additional load or internal stress [21].

In recent times, various aspects of steel production have been studied in relation to their effect on the susceptibility of various steels grades to HIC. These aspects include their composition, processing route (TMCP parameters), microstructural features, diffusion characteristics. These have been studied at laboratory scale using several techniques, such as H₂S promoted charging (HIC standard test), electrochemical hydrogen charging, hydrogen permeation etc [15]. These studies are important because in the foreseeable future, the transportation of oil and gas resources will largely rely on these steel pipeline. The number of new pipeline constructions has increased progressively for over 35 years, with a large number of pipelines still in the pre-
construction stage [18]. This steady increase in global pipeline networks is because of the demand for higher oil and gas output. According to projections by the Organization of the Petroleum Exporting Countries (OPEC), the petroleum demand is also estimated to increase through the year 2040, following the global population growth [22]. Hence, the development of more failure resistant steels is imperative.

1.3 Motivation for the study

With the increasing number of pipeline networks and a demand for lighter and stronger pipelines to increase productivity, the development of safer and more reliable pipelines has become essential. Since pipelines run through very long distances, failures might occur at hard to access areas and severe environmental conditions at several locations can affect pipeline integrity. These failures are often devastating and expensive, and attract direct and indirect costs. Some notable costs implications associated with pipeline failures include: catastrophic damage such as explosions, loss of life, environmental degradation, fines, compensation, replacement cost etc [15]. Pipelines have a zero tolerance for abrupt failure and they are pivotal to the success of global economies. Pipeline constructions usually attract a lot of political interest and very high investment costs. Hence, the production of different grades of pipeline steel with a good balance of mechanical properties and failure resistance is necessary.

To achieve this feat, it is important to understand the relationship linking the microstructural characteristics, mechanical properties and failure susceptibility of the various grades of pipeline steel. Although HIC in steels has been investigated in the past, most studies often consider effects of specific or isolated microstructural features on the HIC mechanism in steels. Also, some reports in literature have given contradictory accounts and views on this subject. Thus, there is a need to generate and report more experimental observations on the HIC phenomenon. In addition, a correlation of the microstructural and diffusion characteristics of steels and a holistic study of HIC, taking all relevant parameters into consideration will help offer a better understanding of HIC in pipeline steels.

In this study, the hydrogen induced cracking susceptibility of two X65 pipeline steel plates, in relation to their mechanical properties, microstructural features and diffusion characteristics was examined. This work aims at offering a more general understanding of the damaging effects of hydrogen on steels and how the characteristics of steels influence the cracking behaviour. This study was carried out using several experimental techniques such as
electrochemical hydrogen charging, hydrogen permeation experiment and the hydrogen microprint technique.

1.4 Research objectives

The main goal of this research was to investigate the hydrogen induced cracking susceptibility of two formulations of X65 pipeline steels. This was achieved by pursuing the following specific objectives:

1. To identify the important microstructural characteristics that influence hydrogen assisted crack initiation and propagation in the two steels.
2. To determine the role of hydrogen trapping and its influence on the HIC susceptibility of the two X65 steels.
3. To relate the diffusion and microstructural characteristics of the X65 steels to their cracking behaviour.

1.5 Thesis arrangement

This thesis is divided into five chapters. The current chapter (Chapter 1) contains a brief introduction, the motivation and objectives of this study. The second chapter presents a summarized literature review on the subject matter. Detailed descriptions of the pipeline steels used and experimental procedures for this study are covered in Chapter 3. The results obtained are then analysed and discussed in Chapter 4. Lastly, Chapter 5 contains a brief summary of this work, the key conclusions drawn from the study as well as recommendations for future works.

Some of the information and results presented in this work are already published in a journal, and used with permission from Elsevier. The copyright permission to use the information in the published journal article [23]: T.A. Jack, R. Pourazizi, E. Ohaeri, J. Szpunar, J. Zhang, J. Qu (2020) “Investigation of the hydrogen induced cracking behaviour of API 5L X65 pipeline steel,” International Journal of Hydrogen Energy, vol 45, no. 35, pp. 17671-17684, can be found in Appendix A. Also, photographs of some important machines and equipment used in this study are presented in Appendix B.
CHAPTER TWO

LITERATURE REVIEW

2.1 Overview

This chapter begins with an account of the uptake and trapping of atomic hydrogen in steels. A brief review of the HIC phenomenon is also given, focusing on its cause and effect on pipeline steels. Several theories postulated to explain the hydrogen embrittlement process are also briefly reviewed. The key factors that influence the HIC susceptibility of steels, such as composition, TMCP, microstructure, mechanical properties etc are discussed in this chapter, detailing their individual effects on hydrogen related failure in steels. Finally, the main experimental techniques to be employed for this research are reviewed, specifying reasons for their usage.

2.2 Hydrogen degradation of pipeline steels

Pipeline steels are widely used in oil and gas transmission systems because of their good combination of strength, toughness and weldability. These properties facilitate the transport of these natural resources over long distances. However, pipelines in service can be exposed to hydrogen producing environments, which facilitates the absorption of hydrogen into the steel to cause hydrogen embrittlement. Hydrogen embrittlement in steels often manifests with a degradation of the mechanical properties of steels, and also formation of internal cracks and blisters on the surface. Over time, these all contribute to the failure of the pipeline [15,24].

HIC has caused pipeline failures for decades, with the first reports of HIC in pipelines linked to the service failure of transmission pipelines in the mid – 20th century (1940’s - 1960’s). Stepwise cracking, delamination and blistering were observed during the failure analysis of these pipelines subjected to sour service or hydrogen producing environments [25]. Since then, more pipeline and pressure vessels have also been reported to fail in a similar fashion. These incidents initiated at diverse locations, such as, the body of the pipeline or vessel or the heat affected zone of repair welds; with some of these incidents leading to catastrophic failures and fatalities. Hydrogen damage at these locations not only degraded their mechanical properties by more than half, but also comprised of physical features, both internal and external. Blisters and delamination were observed on the surface of the pipelines and vessels, often causing a visible bulge and internal stepwise cracks which are induced by the absorbed hydrogen in the
steel [25]. This absorbed hydrogen is fundamental to the initiation and the propagation of these internal cracks (HIC) which often go unnoticed until failure [15,21]. However, since it has been established that HIC is dependent on the entry of hydrogen into steels, it is important to understand how this occurs and what transpires during the transport of this hydrogen through the steel.

2.2.1 Hydrogen evolution and admission in pipeline steels

Hydrogen is usually produced during the corrosive reaction between the steel surface and a sour or acidic environment. Also, during uncontrolled cathodic protection processes on pipelines, the applied potentials can lead to the evolution of hydrogen on the steel surface through the cathodic reaction [15,26]. Apart from pipelines in service, hydrogen can also come in contact with steel during fabrication and steel processing stages. For instance, during arc welding with coated electrodes hydrogen is produced and absorbed by the steel [14]. Although, several classes of low hydrogen electrodes have been developed to mitigate the occurrence of HIC during this process. Also, during steel pickling with acids, hydrogen absorption may occur due to the corrosive reaction on the steel surface [14,15,27]. However, reports have shown that catastrophic failures from hydrogen attack usually occur in service, since the accumulation of hydrogen within the steel happens over time [21].

Irrespective of the source of hydrogen, the presence of hydrogen around the inner or outer wall of steel will allow the atomic hydrogen diffuse into the steel. The ingress of hydrogen into steel is believed to follow these steps [5,25,28]:

1. Physical adsorption of hydrogen on the steel surface
2. Chemisorption and dissociation of hydrogen
3. Absorption of atomic hydrogen
4. Diffusion and trapping of hydrogen atoms within the steel

After the production of hydrogen from the corrosive reaction on the steel surface, the hydrogen adsorbs to the steel surface almost immediately. Here, weak van der Waal’s bonds are created between the adsorbate and the steel’s surface (adsorbent) and this is a reversible process. Due to the electron transfer associated with the corrosion process, a chemical adsorption (reaction) between the hydrogen molecules and the steel surface occurs, leading to the formation of covalent bonds and the dissociation of hydrogen molecules to atomic hydrogen [5]. In a sour environment, the hydrogen sulphide (H$_2$S) acts as a recombination poison further minimizing
the formation of hydrogen molecules, thus, promoting the formation of atomic hydrogen on the steel surface [29]. Finally, the atomic hydrogen is absorbed into the steel’s crystalline matrix, leading to diffusion and trapping within the steel. It is known that atomic hydrogen in steel tends to be attracted to areas of stress [25,30], this is usually termed stress driven diffusion [21]. Stress driven diffusion facilitates trapping and hydrogen accumulation. Fig. 2.1 shows a schematic illustration of the corrosion reactions between pipeline steel and an acidic environment (sour environment), and the subsequent absorption of atomic hydrogen into the steel. Fig. 2.2 illustrates the stages involved during hydrogen entry in steels.

Fig. 2.1. Schematic illustration of the hydrogen evolution reactions, hydrogen absorption, potential trapping sites and stress driven diffusion in pipeline steel [21].

Fig. 2.2. Stages of hydrogen ingress into pipeline steel [5].
2.2.2 Hydrogen trapping in pipeline steels

Since iron (Fe) and its alloys possess large enough interstitial sites, the absorbed hydrogen atoms can diffuse through the steel to various lattice defects such as inclusions, dislocations, grain boundaries, voids, precipitates [5,31], second-phase particles (cementite) [32], where they are trapped. Hydrogen atoms tend to be attracted to these defects. These microstructural defects are termed as hydrogen trapping sites or hydrogen traps and they impede hydrogen transport through steels. The susceptibility of steels to HIC has been studied with respect to the trapping characteristics of steels [5,31].

Hydrogen traps are broadly classified as reversible or irreversible traps, according to their binding energies and hydrogen retention capabilities [33]. Reversible traps are hydrogen trapping sites that temporarily store hydrogen and have a lower binding energy of less than about 35-60 kJ/mol. Reversible traps mostly include grain boundaries and dislocations. Conversely, irreversible traps store hydrogen for a much longer time and usually have higher binding energies. Examples of irreversible traps are inclusions and precipitates [33]. However, the coherency of these precipitates and second phase particles with the steel matrix influences their binding energies and in turn, their hydrogen retention capabilities. It has been observed that coherent and semi-coherent precipitates act as reversible trapping sites due to their low binding energy with hydrogen, whereas incoherent precipitates are irreversible traps. Therefore, some inclusions and precipitates can also act as reversible and irreversible traps based on their binding energy with hydrogen [33,34]. Hydrogen atoms trapped in irreversible traps can be released at higher temperatures. An increase in temperature (heating) usually leads to thermal de-trapping and a general decrease of hydrogen occupation of these irreversible traps [35,36]. However, Grabke and Riecke [27] claimed that hydrogen diffusivity in Fe alloys and steels decreases significantly by trapping at temperatures less than 200 °C, i.e. hydrogen binds to traps at energy levels lower than that of the normal interstitial sites at these temperatures.

Most researchers have reported that reversible traps play a vital role in influencing hydrogen diffusion and HIC susceptibility in steels [34,37]. It is believed that the susceptibility of steels to HIC increase with an increase in the density of reversible traps [33,38,39]. Also, a uniform dispersion of fine irreversible traps has also been reported to result in a reduction in susceptibility to hydrogen embrittlement by balancing the harmful effect of the reversible traps. Thus, an increase in density of innocuous irreversible traps will be beneficial in reducing hydrogen induced damage [40]. Most importantly, hydrogen traps alter the diffusion
characteristics of steels, and the susceptibility to hydrogen related failure is largely dependent on the hydrogen transport behaviour. The trapping characteristics of steels have been seen to be altered by and are dependent on factors such as, alloying and thermomechanical treatment schedules [33].

2.3 Mechanisms of hydrogen embrittlement

The presence of trapped atomic hydrogen within steels leads to hydrogen embrittlement. Thus, hydrogen embrittlement occurs in both stress corrosion cracking and hydrogen induced cracking scenarios, that is, in the presence of stress or devoid of applied stresses, respectively [7]. It is well known that service induced loads tend to concentrate stresses at certain points within the steel microstructure. A good example will be at a microcrack tip, this stress concentration and possible stress driven diffusion can accelerate crack propagation. Some researchers are of the opinion that without applied stresses, such as in the HIC scenario, cracks can initiate and propagate following the build-up of internal pressure within the steel microstructure, at lattice defects. Hydrogen in steels results in loss in ductility by significantly decreasing the elongation and reduction in area of steels [14]. Experimental works have shown that the void growth and void coalescence reduces the effective cross-section of the metal and result in the reduction of the elongation and is followed by cracking [14,24]. It is believed by some researchers that the void growth and coalescence is facilitated by the internal pressure of trapped hydrogen, other researchers suggest that the void growth and coalescences of these voids is accelerated by hydrogen dilatation and strain localization. These hypotheses are backed up by several mechanisms that have been postulated over the years to explain hydrogen embrittlement, as well as, crack initiation and propagation in metals [14].

The hydrogen embrittlement phenomenon which encourages the cracking and blistering of steels is a complex phenomenon and over the years, several mechanisms have been postulated to explain it and its related failure. Most notable of these are the hydrogen-enhanced-decohesion (HEDE), adsorption-induced dislocation emission (AIDE) and hydrogen-enhanced-local-plasticity (HELP) [5,41].

2.3.1 Hydrogen-enhanced-decohesion (HEDE)

The HEDE mechanism is one of the oldest mechanisms proposed. It was proposed several decades ago (1920’s) and it hypothesizes that the presence of hydrogen in the steel weakens the strength of its metallic bonds, resulting in decohesion [41]. This decohesion reduces the
gross cohesive strength significantly through a dilatation of the atomic lattice and reduction of the fracture energy [14]. Although a charge transfer from Fe atoms to the H atoms is quite possible, direct experimental evidence for the reduction in metal-metal (Fe-Fe) bond strength is still lacking [41,42].

2.3.2 Adsorption-induced dislocation emission (AIDE)

The AIDE mechanism was first proposed by S.P. Lynch in the late 1970’s, using experimental tests of nickel single crystals to study hydrogen embrittlement [41,43]. The author proposed that the diffusible hydrogen atoms adsorb to surface defects in regions of stress concentration, such as, at the crack tips and this causes the movement and emission of dislocations ahead of the crack tips, causing crack growth through the linkage of micro voids, as well as causing deformation around the crack during propagation [5,41].

2.3.3 Hydrogen-enhanced-local-plasticity (HELP)

The HELP mechanism which is considered a better mechanism than the AIDE, was proposed by a group of researchers in Illinois, United States around the late 1980’s and early 1990’s [41]. It is also centred on the movement of dislocations induced by the hydrogen in the steel [5,14]. However, in this mechanism, the hydrogen in solution, which is ahead of the crack and not the hydrogen adsorbed at the crack tip, is responsible for the localized plastic deformation. Using transmission electron microscopy (TEM) observations, the Illinois research group observed that the segregation of hydrogen to dislocations, which is sensitive to strain rate and temperature, have elastic interactions which form Cottrell atmospheres. When the hydrogen segregates to dislocations, it reduces their energy per unit length as well as the range of elastic interactions between dislocations [41]. This segregation makes the dislocations have a weaker interaction with strain fields within the steel structure. The plasticity of the steel will be affected due to the presence of hydrogen, causing minimized obstructions and enhanced dislocation mobility. This dislocation motion leads to some localized plastic deformation. As dislocations continue to move and interact, the Cottrell atmospheres trigger a resistance to dislocation motion, which is similar to the theory of solute drag. Hence, this results in a pile-up of dislocations. The plastic instability in that local region will lead to ductile fracture. Using atomistic simulations, Song and Curtin [44] reported the movement of dislocations and subsequent pile-ups, as a result of absorbed hydrogen in α-Fe. The authors reported that over a wide range of hydrogen concentrations, the Cottrell atmospheres which form due to the
presence of hydrogen, follow the moving dislocations. However, some other researchers are of the opinion that the correlation between the reduced elastic interactions between dislocations and the dislocation mobility is less obvious, except when viewed as work hardening, where elastic interactions between dislocations on parallel slip planes impede their motion. Although the HELP mechanism has some experimental evidence, it does not explain all experimental observations [41].

The HELP mechanism assumes that there is an existing microcrack or stress concentration in the metal, and the hydrogen is not uniformly distributed in the metal. Hence, it can be said to agree with the creation of hydrogen induced cracks from the internal pressure accumulation and the HELP mechanism exists during crack propagation. In a review of HIC in steels and the internal pressure theory, Chattoraj [25] reported that some researchers believe that the dislocation pile-up can also initiate cracks but under the influence of external stresses. Also, the generation of Cottrell atmospheres around dislocations because of the presence of hydrogen, and their transportation along with dislocations had also been earlier observed by some researchers in the 1950’s. This review gives some credibility to the idea of the HELP mechanism facilitating the propagation of cracks initiated by critical pressures attained by the accumulation of hydrogen.

More recently, Nagumo [42] proposed a new mechanism based on his experimental observations, where he noted that strain induced an increase in hydrogen absorption capacity in steels of different microstructures, and this was linked with their susceptibility to hydrogen related failure. The author proposed that the enhanced creation of vacancies and the accumulation of these vacancies leads to the decrease in ductile crack growth resistance. Thus, moving the main cause of degradation from hydrogen atoms to the vacancies formed, while the formation and stabilization of these vacancies is enhanced by hydrogen. However, it is currently believed that there is no one mechanism that comprehensively explains the hydrogen embrittlement phenomenon in all observed cases [15,24]. Some researchers are of the opinion that more than one mechanism can jointly help explain the process [45,46]. At present, following several experimental observations reported, this might be a possibility.

2.4 Hydrogen induced cracking in pipeline steels

HIC is often considered as one form of hydrogen embrittlement, but it is distinguished from the other forms of hydrogen embrittlement by the appearance, morphology, cracking sites and
the mode of crack propagation. Hydrogen induced cracks are often accompanied by surface blisters and the cracks usually have a planar appearance, with different cracks linked in a step-wise fashion. Hence, the common term stepwise cracking (SWC) [25]. Although, some researchers believe that lattice decohesion occurs with the accumulation of the hydrogen atoms [28,47], which weakens the cohesive forces within the pipeline steel. The initiation of hydrogen induced cracks is widely believed to occur due to the accumulation of pressure at various trapping sites. The trapped hydrogen atoms coalesce to form hydrogen molecules (H₂). The build-up of this hydrogen molecules around lattice defects or trappings sites in the steel generates internal pressure within the lattice. At critical accumulation levels, H₂ is capable of generating sufficient pressure at these defects to cause crack initiation with or without the application of external load or stresses [7,21,38]. It is also believed that more hydrogen supplied around the crack tip will facilitate crack propagation. This theory is termed the internal pressure theory, and was first proposed by C.A. Zapffe and C.E.Sims [48]. It is widely accepted with several researchers attributing their experimental findings and observations to this concept [21,40,49,50]. The initiation and propagation of hydrogen induced cracks, according to the internal pressure theory can be illustrated using the cyclic flow diagram in Fig. 2.3.

![Diagram](image)

**Fig. 2.3.** Schematic illustration of the HIC initiation and propagation process, according to the internal pressure theory [21].

From Fig. 2.3, following the absorption and trapping of atomic hydrogen, there is a recombination and build of hydrogen molecules at these traps. The pressure within these
trapping site, such as inclusion or incoherent precipitate, leads to crack initiation. Depending on the stress level around the crack tip, the hydrogen-affected fracture toughness of the steel can be reached and the HIC process further advances. Finally, crack extension occurs with the supply of hydrogen through stress driven diffusion and is temporarily suppressed by the drop in pressure when volume of the cavity increases. The cycle continues until failure occurs [21]. Pressouyre and Bernstein [40] in their study, showed that finely distributed inclusions reduce HIC susceptibility by moderating the accumulation of atomic hydrogen at the potential crack initiation sites, by increasing the time it would take to reach a critical concentration level or dispersion of hydrogen to limit build-up and to ensure a critical localized concentration of hydrogen is not reached.

In recent years, HIC has been studied in a variety of pipeline steel grades to enhance the existing knowledge of the factors that directly influence the vulnerability of steels. Some focus has been on locating the probable sites for crack initiation and the propagation and arrest mechanisms of these cracks. Researchers have also made attempts to link the HIC susceptibility of steels to their diffusion characteristics and some microstructural features such as microstructural phases, inclusion type and morphology, dislocation density and so on. However, the results show that there is still more work to be done, as contradictory observations have been reported with regards to the effects of certain parameters on HIC susceptibility [15].

2.5 Factors affecting HIC susceptibility of steels

Several factors affect the HIC susceptibility of steels, these mainly involve the service environment and the characteristics of the steel. However, research has shown that the microstructural characteristics largely influence the behaviour of steels in the same environment. Ohaeri et al. in two separate studies [51,52], showed that steels of similar composition but differently thermomechanically processed, exhibited different resistance levels to hydrogen degradation (HIC, surface corrosion). The authors attributed these differences to the microstructure and crystallographic texture of the steels. Thus, it would be of interest to review the influence of these steel characteristics on HIC susceptibility. The characteristics of steel in this context, involves the chemical composition, processing, mechanical properties, and microstructural features of the steels such as, the microstructural phases, grain boundary character, crystallographic orientation (texture) etc. However, these factors are largely co-related and co-dependent. For instance, the microstructure of steel is jointly dependent on the chemical composition and processing technique. Although, it has been
cited that the design of the chemical composition of steels is more important than the rolling parameters or conditions employed [53], every stage of steel manufacturing is essential to obtain failure resistant steels. The factors affecting steel vulnerability to failure, have been studied on a case-by-case basis by researchers over the years, in a bid to understand their individual effect on steels. This current investigation obtained conclusions from these individual studies, to explain the experimental observations in this study, offering a more holistic view of the problem.

2.5.1 **Steel composition and microalloying additions**

The first factor to be considered in the manufacturing of steel is the chemical composition, as this will form the basis for all other factors. Steel which is primarily an alloy of Fe and carbon (C), has evolved over the years involving elemental additions such as manganese (Mn) and chromium (Cr) in the 19th century and microalloying elements, such as niobium (Nb), titanium (Ti), and vanadium (V) in the 20th Century [5]. Microalloying involves adding small quantities of different elements in steels to achieve desired properties (enhancing grain refinement and strengthening) for various applications [3,4]. The chemistry of steels is critical to their physical and mechanical properties, hydrogen diffusion characteristics and precipitate and inclusion formation. In addition, all these factors are essential in determining the susceptibility of steels to HIC. Hence, the effect of the steel composition on these subfactors will be briefly reviewed.

2.5.1.1 **Effect of steel composition on its properties**

Pipeline steels generally require a good combination of specific mechanical properties which make them suitable for the transmission of petroleum. These properties include strength, toughness, formability, corrosion resistance, weldability etc [3]. Although the processing of the steel also plays a vital role in determining these properties, the chemical composition of the steel lays the foundation upon which all other steel characteristics or factors function. For it is well known that carbon is a strong ferrite strengthener in steels, however, when the carbon content is reduced, the formability and weldability of steels improve [3]. This is because a high carbon content increases the steel’s tendency to form martensite. Thus, reduced carbon contents are being used in contemporary high strength pipeline steels, with other alloying elements to compensate for the drop in carbon. High sulphur (S) content in steels has been observed to have a negative influence on the toughness of steels and leads to the formation of manganese sulphide (MnS), which have been reported to be potential crack initiation sites. However, controlled
additions of S are being allowed to improve the machinability [4,5]. Desulfurization techniques have been able to reduce sulphur levels and have been developed to minimize MnS formation and facilitate the production of steels with high strength and excellent toughness [5]. In a review of the guidelines for producing HIC resistant pipeline steels, Stalheim and Hoh [54] recommended low levels of sulphur, phosphorus (P) and manganese contents be employed for pipeline steels to be used for low pH or sour applications (less than 0.0015 wt%, 0.018 wt% and 1.5 wt%, respectively). Similarly, Matsumoto et al. [53], stated that an increase of the C equivalent or P content in pipeline steels tends to harden the mid-thickness region of the steel (segregation zones) after controlled rolling. However, reducing the C content to about 0.01 - 0.05 wt% will significantly reduce the hardness of the segregation zone and HIC susceptibility, with little regard to the action of the other alloy elements. In addition, the authors also reported that ≥ 1.0 wt% Mn and low P content in API 5L X60 and X65 steel grades will enhance HIC resistance and mechanical properties.

Also, small additions of copper (Cu), nickel (Ni), silicon (Si) or chromium (Cr) to steels can help improve their corrosion resistance by forming protective layers [3,27,55]. Finally, microalloying elements such as Nb, Ti and V are usually added in small quantities to improve strength, microstructure and enhance the controlled rolling process of steels. In the presence of nitrogen (N) and carbon (C), the formation of strain induced precipitates, such as carbides, nitrides and carbonitrides, (Ti, V, Nb) (C, N) is promoted during hot deformation. These nano-precipitates pin down the austenitic grain boundaries, restricting grain growth at high temperatures and suppressing the austenite-ferrite transformation of steels. They subsequently impede the movement of dislocations and lead to strengthening of steel [3–6]. These precipitates also play key roles in the diffusion and trapping characteristics of steels. The discovery of the influence of additional elements on the retardation of the austenite recrystallization, led to the introduction of controlled rolling and thermomechanical controlled processing [5]. Other elements such as molybdenum (Mo) and aluminium (Al) have also been reported to have retardation effects on the austenite recrystallization of steels, however, Nb has been seen to have a more significant effect [5,6,56]. Mn and P can also affect the microstructure formed during annealing through precipitation strengthening and pinning effect on recrystallized grains [57].

The production of contemporary high strength steels generally involves the optimization of chemical composition and processing. This includes solid solution strengthening by Mn, Si, Cu, Ni, Cr, Mo additions, microstructure refinement through thermomechanical controlled
processing and precipitation strengthening by microalloying (Nb, Ti, V) additions [5,15]. Table 2.1 helps summarize some of the information, as regards the effect of elemental additions to the properties of steel. It shows some alloying elements commonly used in modern pipeline steels and their effects on some of the characteristics of steels. The data in the table covers the elements present in the pipeline steel plates used in this study.

Table 2.1. Common alloying elements used in pipeline steels

<table>
<thead>
<tr>
<th>Element</th>
<th>wt %</th>
<th>Effects on steel</th>
<th>Ref.</th>
</tr>
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</table>
| C       | < 0.25| • Strengthens steel  
          |         | • High tendency to segregate and form harder phases  
          |         | • Enhances weldability at lower compositions                                       | [3] [15] |
| Si      | 0.1 - 0.5 | • Deoxidizer in molten steel during casting                                        | [3]      |
|         |       | • Solid solution strengthener in steels                                            |          |
| Mn      | 0.5 - 2.0 | • Strengthens steel through solid solution strengthening  
          |         | • Reduces ductile to brittle transition temperature  
          |         | • Strong segregation tendency which rises HIC concerns  
          |         | • High tendency to form sulfides, MnS  
          |         | • Delays the austenite decomposition during accelerated cooling.               | [3][15] |
| P       | < 0.018| • Increased concentrations will lower steel toughness, percentage of ductility and susceptibility to HIC but increase ductile to brittle transition temperature  
          |         | • Increased concentrations also increase corrosion of steels                   | [54][58] |
| S       | < 0.0015 | (in low pH)  
          |       | • Increased concentrations will lower toughness, percentage of ductility and susceptibility to HIC but increase ductile to brittle transition temperature  
          |         | • Increased concentrations also increase corrosion of steels                   | [54][58] |
|         | < 0.003 | (in high pH)     
          |         | • Increased concentrations will lower toughness, percentage of ductility and susceptibility to HIC but increase ductile to brittle transition temperature  
          |         | • Increased concentrations also increase corrosion of steels                   | [27] |
|         |       | • Increased concentrations will lower toughness, percentage of ductility and susceptibility to HIC but increase ductile to brittle transition temperature  
          |         | • Increased concentrations also increase corrosion of steels                   | [27] |
| Nb      | 0.02 - 0.06 | • Very strong strengthener of steel through precipitate strengthening         | [3][6]   |
• Ready formation of carbides and carbonitrides during processing, Nb (C, N)
• Facilitates grain refinement
• Retards austenite-ferrite transformation

<table>
<thead>
<tr>
<th>Element</th>
<th>Range</th>
<th>Properties</th>
</tr>
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</table>
| Ti      | 0 - 0.06 | • Grain size control by the formation of nitrides, TiN
• Strengthener of steels |
| Cr      | 0 - 1.25 | • In combination with Cu, it usually increases atmospheric corrosion resistance
• Reduces susceptibility to hydrogen assisted cracking by hindering the uptake of atomic hydrogen |
| Ni      | 0 - 0.5  | • Enhances fracture toughness
• Enhances corrosion resistance |
| Cu      | 0 - 0.55 | • Enhances corrosion resistance
• Strengthener in steels |
| Mo      | 0 - 0.3  | • Strengthener in steels
• Promotes bainite formation
• Increases hardenability |
| N       | < 0.012 | • Strong former of nitrides and carbonitrides with microalloyed elements |

The chemistry of steels and their resulting precipitates also plays a vital role in texture evolution and grain boundary character formation. The presence of C and N in the solid solution of steel has a significant effect on the formation of recrystallized grains, prompting the formation of low energy grain boundary, as against the generation of high energy boundaries. Also, \{111\} or more random grains are formed in the early stages of annealing depending on the amount of C in solid solution. A low carbon content will encourage a wide-ranging and quick restoration of deformed grains, that are activated from different nucleation sites that leads to the formation of \{111\} texture. Conversely, a high carbon content will slow down the restoration process, as C-Mn dipoles restrain dislocations [57]. This is of importance because several reports suggest that crystallographic texture and grain boundary character influence failure behaviour of steels [38,59].
2.5.1.2 Effect of steel composition on its diffusion characteristics

It is clear that alloying elements in low alloy steels collectively contribute to improving the properties of the steel. However, elemental additions or omissions can also have negative effects, especially by influencing its crack susceptibility. The absence of Ti in solid solution limits carbide precipitation and weakens resistance to hydrogen degradation in steels [15,57]. Elements which form nitride, carbide and carbonitride precipitates such as, Mo, V, Nb, Cr and Ti reduce hydrogen diffusion through the steel lattice, as these act as trapping sites (often irreversible) within the steel [14,15]. Grabke and Riecke [27] also reported that the quantity of hydrogen dissolved is considerably enhanced by the alloying elements, but they observed that it follows the following sequence: Mo < V < Nb < Ti < Zr. The same authors reported that the main microalloying elements decrease permeability in the sequence: V > Ti > Nb. They also observed that Si decreases hydrogen solubility and permeability while Cr increases hydrogen trapping in Fe alloys and steels.

Shi et al. [60] observed nano-scale Cu-precipitates in novel Cu-bearing pipeline steels. The authors believed that these precipitates contributed to the precipitation strengthening which resulted in achieving a high strength pipeline of API X120 grade. They observed that the uniform dispersion of these precipitates within the steel structure acted as beneficial irreversible traps, thus, reducing the HIC susceptibility of the novel high strength steel. Cu has also been reported to lower hydrogen diffusion and corrosion susceptibility in steels by a few researchers; it is speculated that the protective layer retarded hydrogen uptake as well as protected against corrosion [61]. It is also believed that Ni, which is known for its corrosion resistance, has a similar effect on hydrogen absorption into the steels [14]. While S, P, and Mn increase hydrogen activity and absorption in steels [14].

Following the observations and reports in literature, it is quite clear that during the manufacturing of pipeline steels, it is essential to strike an informed balance among all the alloying elements to obtain failure resistant steels that possess the required properties. The information on the effects of some alloying elements on hydrogen uptake in Fe alloys and pipeline steels are summarized as follows: C – Increases, Si – Decreases, Mn – Increases, P – Increases, S -Increases, Nb – Increases, Cr – Decreases, Ni – Decreases, Cu – Decreases. [14,15,27]
2.5.1.3 Inclusions and precipitates in steels

The chemical composition of steels significantly determines the type of inclusions and precipitates that are found in the steel’s microstructure. Although, the morphology of these precipitates has also been observed to be dependent on thermomechanical treatment applied. Carbides, nitrides and carbonitrides of the main alloying elements popularly depicted as (Nb, Ti, V) (C, N) precipitates as well as inclusions (usually non-metallic oxides and multi-elemental inclusions) usually act as crack initiation sites in steels when they coarsen or are formed in large sizes [7,62,63].

However, some inclusions have been observed to be more detrimental to crack resistance than others. This difference can be with regards to the coherency, size, type or morphology of the inclusion or precipitate. Research on titanium carbide (TiC) precipitates have shown that they can exist in steels as coherent, semi-coherent and incoherent precipitates. The incoherent precipitates have much higher binding energies than the coherent and semi-coherent ones [40,64]. The diffusion and trapping characteristics of TiC precipitates in the steels have been studied, showing the difference in hydrogen trapping between semi-coherent and incoherent TiC precipitates, with respect to their interaction energy with hydrogen and their hydrogen capacity [36,65]. Wei et al. [66] also examined the hydrogen trapping behaviour of the nano-carbide precipitates of Nb, Ti and V. They observed that the coherent and semi-coherent carbide precipitates had trapping capacities in this sequence: NbC > TiC > VC. Lastly, they stated that incoherent NbC and VC precipitates are unable to trap hydrogen while coherent and semi-coherent NbC and VC precipitates exhibit a surface area dependence on their hydrogen trapping capacity. This dependence of hydrogen trapping on the effective surface area of carbides rather than the volume fraction was also reported by other researchers who studied VC precipitates in steels [67]. This implies that for a given volume fraction smaller precipitates constitute a better trapping system.

The effects of other nano-sized carbides have also been studied, such as, the effect of nano-sized (Ti, Mo)C precipitates on the hydrogen embrittlement of a high-strength, tempered lath martensitic steel. Reports on the effects of these nano-precipitates conform with popular opinions which suggest that these finely distributed precipitates improve hydrogen-related damage resistance of steel, as they act as innocuous irreversible traps. However, they only delay the on-set of hydrogen embrittlement for higher concentrations of hydrogen. It is suggested that upon saturation of these traps, susceptibility to hydrogen embrittlement is
expected to return/increase [68]. The production of these (Ti, Mo)C precipitates during TMCP of Ti-Mo bearing steels has been reported severally in literature. In addition to their trapping capabilities and nano-size (as low as 3 nm), researchers have also cited their precipitation hardening effect and indicated that the formation of these (Ti, Mo)C precipitates is a normal occurrence in Ti-Mo bearing steels [69,70].

With regards to the type and morphology of inclusions, calcium (Ca) has been reported to effectively modify inclusion type and morphology, and also to desulfurize steels forming calcium sulphides (CaS) in a bid to check the HIC susceptibility of steels. This is achieved due to the preferential formation of spherical CaS instead of MnS, although the HIC resistance only improves for stoichiometric ratios (Ca:S) greater than 1.25 [71]. A review of elemental additions in HIC resistant pipeline steels [54] suggested a Ca/S mass ratio of 2:1, when the S content is below 10 – 15 ppm. Also, the use of zirconium (Zr), boron (B) and some rare earth metals have also been reportedly used for the control of inclusions [5].

Different kinds of inclusions are formed during slab solidification, and often segregate around the mid-thickness zone. Spinal-shaped inclusions such as elongated manganese sulphide (MnS), rectangular-shaped and globular (spherical) shaped inclusions mostly comprising of complex multi-elemental inclusions (Mn-S-Al-Nb-N) aid crack initiation. The MnS inclusions which usually appear in a spinal shape, present a ready crack tip for easy crack propagation, while globular shaped inclusions were observed to have less cracking susceptibility and mainly affect mechanical properties such as strength and ductility [72]. Mohtadi-Bonab et al. [7], while investigating the HIC failure mechanism in X70 steel, observed cracks in regions with MnS inclusions and complex carbonitride (Ti, Nb, V)(C, N) precipitates. These regions were mostly at the mid-thickness of the plate and this was attributed to the segregation of elements to this region, a common phenomenon during slab solidification or TMCP. However, Jin et al. [73] in their study of non-metallic inclusion effects on HIC, observed that hydrogen induced cracks are more related to inclusions enriched with Si and Al than MnS inclusion, even though MnS still pose HIC risks in pipeline steels. Thus, it is noteworthy that most of the steels used in contemporary pipeline steel research have very low sulphur content, which will reduce the presence of MnS inclusions significantly. This could be a plausible explanation for the report by Jin et al [73]. Complex Al- and Si- enriched oxide inclusions have also been reported to act as vital crack initiation sites by several researchers, and appear in multi-elemental configurations. Examples of these complex inclusions include Si-Ca-Al-Mg-O and Al-Ca-Ti-
O [74], Al-Mg-Ca-O and Al-Mg-O [75]. However, in the present study some of these elements, such as Ca, Mg, V, Zr etc, are not present in the investigated steels, thus, it would be of interest to see the hydrogen related degradation, as it relates to the type and morphology of the inclusions in the investigated steels.

2.5.2 Steel processing

The final microstructure of steel is highly dependent on the processing route or technique employed. Over the years, several processing techniques have been applied to steels, with regards to their desired application. However, casting and rolling of steel slabs is the conventional method used for the processing of pipeline plates. The major advancement in pipeline steel processing came in the 20th century, with the development and continuous improvement of the thermomechanical processing of steels. TMCP involves slab reheating, controlled rolling of steel, (which is usually in two stages: rough rolling and finish rolling), and also accelerated cooling, to support grain refinement [5]. Heat treatment schedules have also been applied to pipeline steels in a bid to improve their failure resistance. They have been noted to lead to an evolution of microstructure, crystallographic texture and mechanical properties in steels, and it is well-known that these factors directly influence failure resistance [76,77]. However, these heat treatments are considered not to be as effective as TMCP.

TMCP is regarded to be one of the most effective ways to simultaneously increase the strength and toughness of steels. Strengthening in pipeline steels is primarily through grain refinement, solid solution strengthening and precipitation strengthening. Solid solution strengthening in steels is directly related to the alloying content of the steel, while grain refinement (microstructure formation) and precipitation strengthening are largely dependent on both the microalloying elements and thermomechanical controlled process applied [3,5]. Grain refinement involves the regulation of grain growth during recrystallization and austenite-ferrite transformation. It usually involves the reduction of the Ar1 and Ar3 transformation temperatures through microalloying. This enhances the toughness and strength of steels, as the yield strength will be expected to increase with the reduction of grain size, following the well-known Hall-Petch relationship. The ultimate goal of TMCP improvement is to obtain optimum rolling parameters to process a specific steel composition, which will produce desired physical and mechanical properties in failure resistant steels. This will help avoid time consuming heat treatment techniques (annealing, normalizing, quenching and tempering) which often improves one property at the expense of the other or might hamper steel properties [3,5]. A schematic
illustration of the temperature profile of the steel rolling process (TMCP) is presented in Fig. 2.4.

Fig 2.4 Schematic illustration of the TMCP of steel with resulting microstructures [3,5].

The effect of TMCP on steels is greatly affected by different parameters, such as rolling reduction, passing strain, rolling temperature, cooling rate and coiling temperature [70]. By controlling these rolling and cooling parameters, the microstructure and subsequently, the mechanical properties of the steel can be altered. For instance, deformation in the dual phase region (γ + α) followed by air-cooling produces a structure with larger grain sizes than that obtained when finish rolling is conducted above the Ar₃ transformation temperature, followed by accelerated cooling [5].

Kim et al. [78] conducted several rolling schedules to study the effect of rolling temperatures on microstructure and mechanical properties of steel. The authors observed that conducting the rough and finish rolling in the austenite recrystallization region provided the highest precipitation hardening by preventing strain induced precipitation. However, this high rolling temperature above the non-recrystallized temperature (T_nr) allowed the growth of recrystallized austenite grains, thus, reducing grain refinement and consequently the strength of the steel.
Also, while rolling in the austenite non-recrystallization region (below the $T_{nr}$), the formation of an elongated “pancaked” austenite grain structure was observed. This is as a result of the retardation or prevention of austenite recrystallization during the rolling process. The pancaked grains and deformation bands will lead to the nucleation of a ferrite structure with a more refined grain size. These refined grains will enhance the strength of the steel. The authors went further to roll in the dual phase region (below the $Ar_3$), they observed that the austenite - ferrite phase transformation process during rolling gave rise to even smaller grains. However, they claimed that the clustering of interphase precipitates significantly reduced precipitation hardening effect, thereby degrading the strength of the steel when compared to steels rolled below the $T_{nr}$ but still above the $Ar_3$. In relation to hydrogen degradation, rolling at low temperatures (very low ferritic temperatures) has been reported to have a negative effect on crack resistance in sour environments [5], as well as corrosion resistance [79].

Steel production usually involves the casting of steel slabs, which are subsequently, thermomechanically processed. During slab solidification and TMCP, there is a tendency for elemental segregation towards the mid thickness of the slab. Thus, the mid thickness of steel have more inclusions, precipitates and harder phases, which make this region very susceptible to HIC [53,55]. Every step in the steel production process is crucial to its final properties and failure resistance. Stalheim and Hoh [54] in their guide for HIC resistant steels recommended that a low superheat above the liquidus (i.e. less than 20 °C above the liquidus temperature) should be targeted for casted steels to minimize elemental segregation during solidification. Matsumoto et al. [53] reported that rolling at relatively lower temperatures increases the hardness of the center segregation zone, which will increase HIC susceptibility. They also cited the homogenization treatment of steels as an effective method for decreasing the hardness of the center segregation zone. Another study [55], identified that fast cooling rates (greater than 15 °C/s) and terminating the cooling process at a temperature range of 400 – 550 °C during TMCP, allowed a reduction of the segregation of elements and the formation of phases such as martensite and upper bainite within the mid-thickness region of steels. Minimizing the presence of these harder phases will lower the risks of HIC. However, very fast or rapid cooling rates are well known to produce martensitic structures in steels which increase the HIC susceptibility. Thus, the cooling rate must be increased in moderation, with regards to rolling parameters and steel chemistry.
The microstructures formed during TMCP can influence the HIC behaviour of steels, through their mechanical properties, precipitates and microstructural phases formed. The microstructural phases formed in steels have been seen to be highly dependent on the cooling rate or route chosen [3]. However, for precipitates, several kinds are formed at various stages of TMCP such as, while reheating, during deformation, during or after the austenite to ferrite ($\gamma - \alpha$) transformation, with regards to the microalloying composition [3,4]. As earlier discussed, the precipitates formed during TMCP, could be coherent, semi-coherent or incoherent with the crystalline lattice of steel. These precipitates and microstructural phases formed can significantly influence trapping and HIC susceptibility of steel. Hence, a careful selection of the TMCP parameters is needed to achieve failure resistant steels with the desired mechanical properties, making TMCP of steels a very crucial step in steel production.

2.5.3 Microstructure of steels

It has been well established that thermomechanical processing is critical for the development of an optimum steel microstructure and mechanical properties [80], as well as the control of their hydrogen trapping behaviour [81]. TMCP can result in fine or large grain sizes with largely recrystallized or more deformed structures, which consist of varying steel phases. Commonly encountered steel structures include ferrite/pearlite, polygonal ferrite, quasi-polygonal ferrite, acicular ferrite, bainite and martensite microstructures; their formation largely depends on the cooling rate applied during steel processing [15]. Even the hardness of the structure formed is dependent on the cooling rate applied, because a more refined microstructure will be harder than a less refined one. Also, the hardest microstructural phase in steel being the martensitic structure, is obtained during very rapid cooling schedules, while a relatively softer pearlite structure results from the application of slower cooling rates. Generally, it is well known that harder phases in steels tend to increase its susceptibility to cracking [82,83]. Martensite which is a metastable phase in steel, usually has a strained and saturated structure as a result of the trapped carbon within the lattice. This phase in steel encourages hydrogen damage and has been reported to be the most susceptible to cracking [15,84]. Park et al. [81] showed that varying finish rolling and cooling parameters of X65 pipeline steel can produce different microstructures with ferrite/degenerated pearlite, ferrite/acicular ferrite and ferrite/bainite structures. The authors concluded that acicular ferrite phase was the most resistant to cracking, whereas martensite/austenite islands and inclusions acted as crack initiation sites. Similarly, Li et al. [85] studied the effect of the microstructure
of X100 pipeline steel on stress corrosion cracking in acidic environment. The authors reported that stress concentration in the hydrogen-producing environment facilitated formation of microvoids at the interface of the martensite/austenite islands and the steel matrix, which could promote initiation and propagation of SCC microcracks through the coalescence of these microvoids. The authors also observed that cracks preferred propagating along upper bainite laths, whereas acicular ferrite and quasi-polygonal ferrite showed more resistance to crack propagation. The resistance of acicular ferrite to hydrogen-related cracking such as HIC and sulfide stress cracking (SSC) has also been observed by several other researchers [86].

Dunne et al. [87] and Saleh et al. [88] conducted a two-part study on the effect of microstructure on HIC and blistering. They concluded that hydrogen trapping and HIC susceptibility of steels is highly dependent on the microstructure of steels. Dunne et al. [87] showed that the hydrogen trapping efficiency of steel varied with microstructure, and decrease in this order: banded ferrite/pearlite, ferrite-granular bainite, equiaxed ferrite/pearlite, and bainitic ferrite microstructures. Saleh et al. [88] reported that the banded ferrite/pearlite microstructure exhibited a high susceptibility to hydrogen-related damage. This was attributed to the banding of the microstructure, as they observed most of the crack initiation sites at the ferrite-pearlite interfaces as well as around oxide inclusions.

Microstructural banding is a phenomenon that manifests itself with alternating layers of two different microstructures in steel. Although banding is known commonly to occur with alternating layers of ferrite and pearlite structures in steels, other configurations such as, the banding of ferrite/martensite, ferrite/bainite, bainite/martensite, pearlite/bainite as well as pearlite/martensite have also been reported [89]. It occurs due to the micro-segregation of alloying elements during solidification of the steel slab [89,90]. Domizzi et al. [9] also observed cracks extending along pearlitic bands at the mid-thickness of steels, as shown in Fig 2.5 which was adapted from their work. The authors drew our attention to the fact that very low S contents in steels do not necessarily mean the steel will be HIC resistant. This is because HIC is dependent on several other factors, which has been recognized so far in this review. Finally, the authors also related the cracking susceptibility of the mid-thickness region to the hardness of steels and discovered that the banded region had a relatively higher hardness value than the rest of the steel’s cross-section. This can serve as a confirmation for several observations in literature which have related increasing cracking susceptibility to higher hardness in steels [74].
Fig. 2.5 (a) Banded microstructure (b) Optical micrograph and (c) Electron micrograph of crack propagating along mid-thickness band in steel [9]

However, microstructural banding seems to be largely dependent on steel composition and elemental segregation, as a reduction of the C and Mn content in X65 steels has been reported to help eliminate microstructural banding [91]. Conversely, Chatzidouros et al. [92] in their study mentioned that among the steels examined, the steel with the banded ferrite-pearlite microstructure showed the best resistance to hydrogen-related damage. The authors studied the effect of microstructure on hydrogen-related damage in low carbon X52, X65 and X70 pipeline steels having a banded ferritic-pearlitic structure, ferritic-bainitic structure and a banded ferritic-mixed bainitic-pearlitic structure, respectively. It is possible that other microstructural features or factors such as the mechanical properties influenced this behaviour.

2.5.4 Mechanical properties

The determining factor which makes steels suitable for any desired application is its mechanical properties. Pipeline steels require good strength, toughness, formability and weldability. Most of the previous studies have extensively looked at achieving various mechanical properties in steels, however, more recent studies are mainly focused on achieving these properties as well as failure resistance [5,15]. Given the sensitive nature of pipelines and their zero tolerance for abrupt failure, mechanical properties required for adequate performance of pipelines have to be evaluated alongside failure resistance in the intended environment of service. This is indeed a challenge, since mechanical properties such as strength and hardness of steels have a direct relationship with their susceptibility to HIC [13,74]. This implies that a higher strength steels (higher grades) are considered to be more susceptible to HIC failure than steels with lower strength. This has been reported by various researchers [93,94]. The reason being that higher strength in steels is usually associated with harder phases such as (martensite and bainite),
increased dislocation density or small or very fine grains. These will certainly influence the diffusion characteristics of steels and increase their HIC susceptibility.

It is well established that upon the ingress of hydrogen atoms into the steel, a degradation of the mechanical properties leads to failure [15]. Hydrogen related degradation involves a reduction of strength [51], loss of ductility [13,14,51], temporary increase in hardness [95], reduction of elasticity and an increased susceptibility to brittle fracture [24]. Khatib Zadeh Davani et al. [95] reported a temporary increase in hardness immediately after a hydrogen charging experiment. This takes place because of the segregation of hydrogen around dislocations, which reduces their elastic range and suppresses the sliding of screw dislocations; this results in hardening when multiple slip systems are activated [5]. However, the measurements taken at different time intervals after the hydrogen charging indicated a decline of the increased hardness value recorded immediately after charging [95]. This is possibly due to the discharge of hydrogen from the reversible traps.

2.5.5 Grain boundary character and grain size

Grain boundaries are interfaces between gains in polycrystalline materials. They are considered two-dimensional defects within the material lattice and they act as reversible traps for hydrogen. Grain boundaries are mainly categorized based on their axis of rotation or their degree of misorientation. Based on axis of rotation, they can either be tilt or twist boundaries, when the axis of rotation is parallel or perpendicular to the boundary plane, respectively. However, more commonly, they are categorized as high angle and low angle grain boundaries, based on their degrees of misorientation. With high angle grain boundaries (HAGBs) being angles greater than 15° and low angle grain boundaries (LAGBs) being sub-grain boundaries usually less than 15° but greater than 5°. The grain boundaries have interfacial energies roughly proportional to their degrees of misorientation. HAGBs have high interfacial energies, while LAGBs have low interfacial energies. However, there are special boundaries which are termed as coincident site lattice (CSL) boundaries. CSL boundaries are grain boundaries with misorientations that result in some degree of periodicity being retained by a network of grain boundary dislocations. They are characterized by sigma numbers (Σ), which is the volume ratio of the coincidence unit to the crystal unit. They usually have lower energies than the HAGBs [51,96]. The grain boundary character and the size of grains in metals can be altered through thermomechanical processing.
2.5.5.1 Grain boundary character

Thermomechanical processing can enhance the formation of LAGBs, Telang et al. [97] reported an increase of 38 – 73 % in LAGB formation after thermomechanical processing of an Inconel alloy 600. The formation of LAGBs and CSL boundaries in steels is encouraged because there have been reports of the ability of these low energy boundaries to arrest cracks within the steel structure. Arafin and Szpunar [98] investigated the role of grain boundary character on intergranular SCC, using an in-service X65 pipeline steel. They reported that LAGBs and CSL boundaries, especially Σ11 and Σ13b CSL boundaries, were crack resistant and led to the arrest of intergranular cracks. The authors also observed that HAGBs were more vulnerable to crack propagation. This view on the increased susceptibility of HAGBs, as a result of their higher energy has also been noted by Venegas et al. [99]. The same authors, (Venegas et al.) in another study [100], reported that HIC and intergranular crack resistance in steels can be improved significantly by increasing the CSL boundaries and LAGBs between grains oriented with the {111}∥ND texture fibre. Here, the authors also observed that CSL boundaries with low sigma values (i.e., Σ11, Σ13b and Σ29a) showed good resistance to HIC. Similar results have been presented by Masoumi et al. [101], who stated that increasing the fraction of LAGBs and CSL boundaries around low {hkl} indexing and densely packed planes such as, {111} and {110} planes are targeted in the grain boundary engineering to improve HIC resistance. This is because CSL boundaries around these planes tend to be more efficient in retarding crack nucleation and propagation than CSL boundaries around less densely packed planes such as the {001} plane. From these reports, apart from the grain boundary character, the crystallographic orientation (texture) of grains within the steel structure also influence the cracking behaviour of steels.

2.5.5.2 Grain size

Grain boundaries serve as reversible traps within the steel structure; thus, the difference in grain size and character of the grain boundaries will certainly affect the diffusion characteristics of steels. LAGBs and CSL boundaries generally have lower diffusion rates compared to HAGBs. While, larger grain sizes will mean less grain boundaries and trapping site per surface area, possibly leading to a higher diffusion rate. However, there have been contradictory views on the role played by grain refinement and grain size as it relates with hydrogen diffusion and HIC susceptibility. For instance, Takasawa et al. [102] concluded that grain refinement is effective in reducing the susceptibility of steel to hydrogen embrittlement. The authors made this
conclusion using notched tensile specimens made of HSLA steel, in a pressurized hydrogen environment. Similarly, Zan et al. [103] using average grain sizes in the range of 4 µm to 45 µm, in a slow strain rate test with steel samples pre-charged with hydrogen, observed that hydrogen embrittlement susceptibility increased with grain size. Contrary to these views, Masoumi et al. [104] using slow strain rate tests on martensitic ultra-high strength reported that very fine grains with higher grain boundary densities are more susceptible to hydrogen embrittlement. The authors attributed this to the grains exhibiting a decrease in the fraction of CSL boundaries and an increase of HAGBs in very fine-grained specimens. This view was further reinforced by Mohtadi-Bonab et al. [7] using electrochemical hydrogen experiments. They reported that fine grain colonies (less than 3.5 µm) usually with {001}||ND orientations are more susceptible to HIC. These fine grain colonies form necklace like structures in steel and facilitate crack propagation. Masoumi et al. [105] also observed more HIC propagation along regions consisting of fine grains.

The effect of grain size has also been studied in relation to hydrogen diffusion through steel. It is well-known that low diffusivity and permeability in steels signifies high density of traps and higher susceptibility to failure [75,106]. Yazdipour et al. [107] studied the effect of grain size on hydrogen diffusion in X70 steel, using computational modelling techniques. They claimed that grain size has a two-fold effect on the diffusion rate i.e., very fine and very coarse (large) grains will have slow diffusion rates. Thus, implying that there is an optimum intermediate grain size which will be optimum for diffusion in pipeline steels. In a recent study, Thomas and Szpunar [108] studied the effect of grain size on hydrogen diffusion in steels, using several annealing treatments to obtain varying grain sizes (average grain size range of 2.5 – 12 µm). Their hydrogen permeation results proved that increase in grain size reduces hydrogen trapping (apparent solubility) and increases diffusivity and permeability in steels.

It will be of importance to clarify this discrepancy on the role of grain size and grain boundaries in the diffusion and HIC susceptibility of steels. Because, grain refinement is important for mechanical property enhancement, and its role in failure susceptibility should not be shrouded in uncertainty. However, important deductions from the review of grain boundary size and character reveal that a good balance has to be struck during grain refinement to obtain good strength properties, which will not make the steel vulnerable to hydrogen degradation.
2.5.6 Crystallographic texture

Crystallographic orientation basically refers to the way atomic planes in crystalline materials are positioned relative to a fixed reference. The tendency for a large percent of the grains to be oriented in a certain way in most metals is often termed preferred orientation or crystallographic texture [96]. Texture in steels has been reported to have significant effects on various properties such as strength, ductility, magnetism, electrical conductivity etc [96,109]. It has also been linked to hydrogen related degradation, such as, corrosion and cracking in steels [52,99]. Hence, there are suggestions in literature that crystallographic texture control during processing can enhance failure resistance of pipeline steel. Crystallographic texture in steels have been observed to evolve during TMCP and heat treatment schedules [59,77,110]. Omale et al. [110] studied the microstructure and texture evolution of steels produced through warm rolling. The authors reported that the finish rolling temperature plays a vital role in the development of the microstructure and texture. They claimed that finish rolling at a temperature of 700 °C (warm rolling) promoted the development of the gamma-fiber texture with majority of the recrystallized grains oriented towards the \{111\}||ND. Venegas et al. [111] also had a similar observation and reported that the \{111\}||ND fibre textures significantly increases the HIC resistance of pipeline steels. While \{001\}||ND and close-to-random textures make steels more susceptible to HIC [100,111,112]. Thus, implying that the development of pipeline steels with the preferred \{111\} grain orientation will potentially improve crack resistance.

The report on the increased susceptibility to failure of \{001\}||ND grains was supported by Mohtadi-Bonab et al. [7], who reported that very fine grain colonies with predominantly \{001\}||ND orientation are more prone to HIC, because they have substantially lower hydrogen diffusion rate. However, the same authors also concluded that cracking can occur in a wide range of grain orientations including \{123\}||ND, \{112\}||ND and also \{111\}||ND, which has been considered to be resistant to cracking. Similarly, other researchers [59] noticed cracks propagating along the \{111\}||ND. This discrepancy suggests that the role of crystallographic texture in cracking has not been resolved. It has been speculated that this could be due to other factors coming into play. For instance, crack resistant grains could become more susceptible to cracking due to the energy of the surrounding grain boundaries. Thus, in spite of the fact that a grain has a crack resistant orientation, the crack might continue to propagate because of the high energy associated with their boundaries (HAGBs), which can facilitate crack propagation [15].
2.5.7 Dislocation density and lattice misorientation

Dislocations are linear defects within a crystalline material, which indicate an abrupt change in the arrangement of atoms. They are generated during solidification, plastic deformation or as a result of rapid cooling. Dislocations in steels are usually studied using high resolution transmission electron microscopy (TEM), however, the lattice misorientation within grains qualitatively measured using electron backscatter diffraction (EBSD) has been used over the years to estimate the dislocation density in materials. The local misorientation or kernel average misorientation measures the misorientation between a certain point within a grain relative to the surrounding area in that grain. It can be used to approximate the amount of induced deformation or stored energy in the material.

As earlier mentioned, dislocations act as reversible hydrogen traps, thus, an increase in the dislocation density of metals by deformation (cold rolling) will lead to an increase in the hydrogen solubility and hydrogen trapping in the steel. This has been extensively reported in literature and in addition, the increased susceptibility to hydrogen damage of cold worked steels has also been observed by several researchers [39,106,113–115]. The notion is that the increase in dislocation density increases the metals hydrogen retention capacity (solubility) by increasing the number of hydrogen traps. In this case, reversible trapping will be the dominant trapping mechanism in the steel, thus, ensuring enough hydrogen atoms are contained in the steel [116]. This large hydrogen concentration in the steel will certainly accelerate hydrogen-related failure through crack initiation, crack propagation and blistering. Cold deformation not only increases the dislocation density, it modifies the grain boundary characteristics and local misorientation within the metal. These changes significantly affect hydrogen diffusion and trapping in steels. However, the diffusion can be improved through thermal treatments [106,115], which are used to control the grain size and reorganize the dislocation network in steels.

Laureys et al. [50] studied the hydrogen-related damage of three ultra-low carbon steels. Their results showed that hydrogen damage (cracking and blistering) was the highest for the cold worked steel, followed by the partially recrystallized steel, before the recrystallized steel. This report illustrates the increased resistance of recrystallized grains to failure in hydrogen environment. A high dislocation density indicates high stored strain energy, highly deformed fraction and high local misorientation within the steel. Mohtadi-Bonab et al. [38] also suggested a better HIC resistance for steels with higher fractions of recrystallized grains, in a comparative
study between an X60SS and X60 pipeline steels. In their work, they reported that the X60SS specimen (which was designated for use in a sour environment) showed no cracking, even after being subjected to similar hydrogen charging conditions as the X60 steel. This resistance to cracking of the X60SS steel was attributed to the lower local misorientation, very high recrystallized fraction and the grain boundary character of the steel. The high recrystallized fraction observed in the X60SS steel indicates low stored energy within its microstructure. High energy stored at HAGBs and that stored in dislocations within steels facilitate crack propagation.

2.6 Experimental methods for the investigation of HIC susceptibility

Several experimental techniques have been used to study HIC susceptibility and the diffusion characteristics of steels [15]. However, this brief review will focus on the experimental methods that will be employed in the present study. These include electrochemical hydrogen charging, hydrogen permeation and the hydrogen microprint technique. The electrochemical hydrogen charging which is often used to generate cracks in the steel samples while the hydrogen permeation and microprint techniques are used to determine the diffusion characteristics and image the diffusion pathways of hydrogen in the steels.

2.6.1 Electrochemical hydrogen charging

Electrochemical hydrogen charging which is often called cathodic charging, is an experimental technique often used to induce hydrogen cracks in steel specimens. In recent years, it has been used extensively in HIC studies, as a reliable substitute for the standard method for evaluating HIC susceptibility in pressure vessel and pipeline steels. The standard method proposed by the National Association of Corrosion Engineers (NACE) under the designation NACE TM-0284, involves H₂S promoted charging [15]. There have been reports that the results from cathodic charging have good correlation with those obtained during the standard H₂S promoted charging method [117]. Over the years, cathodic charging has been used extensively in hydrogen-related studies, it gained popularity because of its ease of operation and curbing the hazards associated with H₂S gas handling [8].

Electrochemical hydrogen charging uses the principle of the electrolysis of water, containing an electrolyte solution and a hydrogen recombination poison. The electrolyte solution ensures that the current flows through the electrochemical cell while the recombination poison reduces hydrogen recombination on the steel surface, thereby promoting hydrogen absorption. The
electrolyte solution and charging current used in various studies differ, but nevertheless, the
goal is mostly to generate cracks in the specimen and establish a comparison. So, the same
charging conditions are usually applied to all the specimens to establish a basis for comparison.
Commonly encountered recombination poisons encountered in literature include, ammonium
thiocyanate (NH₄SCN) [38,72], thiourea [50] and arsenic trioxide (As₂O₃) [95,118]. Also,
several studies have shown that the effect of hydrogen embrittlement increases with an increase
in charging current [5,73,119]. This is plausible as a higher charging current will lead to an
increase of hydrogen formation and ingress into the steel. The charging time has also been
observed to have an effect on the embrittlement and HIC behaviour of steels [120]. Dong et al.
[118] studied the HIC behaviour of X80 pipeline steel using electrochemical hydrogen
charging. They varied charging current and charging time and observed that an increase in any
of these parameters results in an increase in hydrogen content within the steel. This will
certainly affect the cracking behaviour of the steel. They also noted a degradation of
mechanical properties such as, a significant reduction in strength and ductility after longer
exposure times. However, in this study, fixed parameters will be used to analyse the steels, to
obtain a good basis for comparison.

2.6.2 Hydrogen permeation experiment (Devanathan - Stachurski method)

The hydrogen permeation experiment is an electrochemical technique used to evaluate the
diffusion characteristics of metals. It uses a dual-electrochemical cell, often referred to as the
Devanathan-Stachurski cell. M.A.V Devanathan and Z. Stachurski developed the hydrogen
permeation experiment in the early 1960’s, with a study of hydrogen permeation through a
palladium membrane [121]. Since then it has been used extensively to study hydrogen diffusion
through metals [8,15]. A global standard for the measurement of hydrogen permeation and
determination of hydrogen uptake in metals has been enacted by the International Organization
for Standardization (ISO) and has been reviewed over the years. The hydrogen permeation set-
up as shown in the ISO 17805 standard [122] is presented in Fig. 2.6.

The diagram in Fig. 2.6, shows the dual cell of the hydrogen permeation set-up, consisting of
a charging cell and an oxidation cell, with the test sample in-between these two cells. The
permeation experiment helps to determine the diffusion parameters of metals, such as, the
effective diffusivity, permeability and density of traps. These parameters can aid in estimating
the susceptibility of the material to hydrogen-related damage [15]. In the hydrogen permeation
experiment, hydrogen atoms are generated at the surface of the sample in the charging cell.
These hydrogen atoms diffuse through the metal to the oxidation side. The use of a palladium coating on both sides of the sample is commonly used to control formation of oxide film and enhance the oxidation of hydrogen atoms. Palladium is also known to facilitate the dissociation of hydrogen molecules into atomic hydrogen [123]. A steady current is applied to initiate hydrogen transport and changes in the oxidation current, which relates to the hydrogen flux is monitored as a function of time [122].

Fig 2.6. Hydrogen permeation cell (Devanathan-Stachurski cell) [122]

However, similar to the electrochemical hydrogen charging, there are some experimental factors that can influence the hydrogen permeation experiment. These include mainly the temperature, presence of palladium coating on the steel and charging current. It has been observed that an increase of the charging current increases the rate of permeation for the same steel sample with the same thickness. Also, as a result of high cold rolling reductions, the diffusivity reduces [114]. This is due to the increased dislocation density and grain boundary characteristics in the steel. Kazum and Kannan [124] reported an increase in hydrogen diffusivity with an increase in charging current. They observed a 37 % and 135 % increase of the effective diffusivity of mild steel, when charging current was increased from 10 mA cm$^{-2}$ to 20 mA cm$^{-2}$ and 30 mA cm$^{-2}$. However, the same authors recorded only a slight increase in
diffusivity for two nanostructured bainitic steels. This is possibly due to the high trapping efficiency of bainitic structures, and in addition, the nano-structure will provide more grain boundaries to enhance hydrogen trapping. Also, Choo [125] developed a model showing that the hydrogen diffusivity varies linearly with the square root of the charging current density, implying that both parameters are directly proportional.

The necessity of the palladium coating on the sample has been cited by a few researchers, and it is also included in the ISO 17805 standard for hydrogen permeation measurements. Manolatos et al. [126] conducted permeation experiments with and without the palladium coating. They observed that applying a higher potential at the oxidation cell is not adequate to ensure the complete oxidation of the diffused hydrogen atoms. This is because some of the diffused hydrogen atoms recombine at the oxidation side to give molecular hydrogen, and thus, they are not captured in the anodic oxidation current recorded in the oxidation cell. This will certainly result in an unreliable measurement of the hydrogen flux. On the other hand, with the palladium coating, oxidation of hydrogen atoms was observed to be completed, offering a more reliable measurement. However, some researchers [127] have shown that hydrogen transport slightly reduces with increasing palladium coating thickness. They showed this using palladium coatings of 10 nm, 20 nm and 30 nm thickness. This implies that to ensure adequate hydrogen flow and control the formation of oxide films during the permeation experiment, the palladium coating thickness needs to be optimized.

Another factor to be considered during hydrogen-related experiments is temperature. Temperature as earlier mentioned affects the hydrogen trapping characteristics of materials. Thus, with the change of experimental temperature, diffusion characteristics are expected to change. Several studies have shown that the increase in experimental temperature will increase hydrogen flux and permeation through metals [128,129]. Wang et al. [129] studied the effect of temperature on the hydrogen permeation in steels in wet H₂S environment. They used test temperatures of 30 °C, 35 °C and 40 °C, to show that the steady-state current density, flux and the hydrogen permeation rate increases with increase in temperature. These findings suggest that temperature has a role to play in the susceptibility of pipelines to hydrogen-related failure. However, like in the electrochemical charging, all the parameters for the hydrogen permeation experiments in the present study are fixed.
2.6.3 Hydrogen microprint technique

The hydrogen microprint technique (HMT) is an experimental method used to detect and visualize hydrogen diffusion through metals. It is often called the silver decoration technique. The hydrogen microprint technique was reportedly first used by T.E. Pérez and J. Ovejero-García in the early 1980’s [130]. Since then, this hydrogen detection experiment has gained some prominence, perhaps due to its ease of operation and precision. Earlier applications of the microprint technique were usually done on samples previously charged with hydrogen. Immediately after charging the steels, an emulsion containing silver bromide (AgBr) crystals will be used to cover the sample so the discharging hydrogen can reduce the silver ions in the emulsion to obtain metallic silver [131]. The reduced silver can then be visualized using an electron microscope. This silver reduction occurs according to the following reaction:

$$\text{Ag}^+ + \frac{1}{2} \text{H}_2 \rightarrow \text{Ag}^0 + \text{H}^+ \quad (2.1)$$

Using pre charged samples, Horikawa et al. [132] investigated the effects of exposure time and temperature on the hydrogen diffusion behaviour in low alloy steels using the microprint technique. They reported an even distribution of silver particles in the steel matrix, suggesting a uniform diffusion. Also, they observed silver particles at the periphery of second phase particles such as inclusions. Thus, revealing that hydrogen atoms diffuse through the interface between these particles and the matrix and do not go through the particles. Also, the authors acknowledged that the size of the silver particles visibly increased when the exposure time after hydrogen charging increased or when the exposure temperature was higher than the room temperature.

However, the microprint experimental procedure has been modified to accommodate direct charging of the samples and a subsequent reaction with the emulsion. This configuration utilizes only the charging cell of the permeation setup. Ichitani et al. [133] used this new configuration and they were able to show that the ferrite phase was the main diffusion path in the hypo-eutectoid steel studied. The authors observed prominent diffusion along the ferrite/cementite interface in pearlite, which they attributed to the trapping effect within that interface. Luu and Wu [134,135] in two separate studies reported that the lattice, carbide/ferrite interfaces and the inclusion/matrix interfaces are the main diffusion pathways through steels. And the authors stated that diffusion along grain boundaries was not observed in carbon steel. A slightly different opinion was noted by Mohtadi-Bonab et al. [74] who reported a uniform
diffusion through the steel lattice, however, they observed preferential diffusion through the grain boundaries of two pipeline steels investigated, X60 and X70. This preferential diffusion through grain boundaries and triple joints was confirmed by other researchers, who also reported the detection of diffusion through cementite [108]. A few other researchers have reported preferential diffusion through different phases in steel. Like Ronevich et al. [136] showed a preferential diffusion through the ferrite phase than through the austenite and martensite/austenite structures. More recently, Thomas and Szpunar [108] using the modified hydrogen microprint set-up and high resolution electron images, showed preferential hydrogen diffusion in steels at grain boundaries, triple junctions, through cementite and around inclusions and precipitates.

Following the reports in literature, it would be of interest to establish the pathways of hydrogen transport through steels. This is important because the failure susceptibility of pipeline steels depends on the uptake, diffusion and trapping of atomic hydrogen within the steels. Thus, gaining knowledge of the actual travel path through steels will offer a better understanding of the hydrogen transport phenomenon and failure mechanics.
CHAPTER THREE

EXPERIMENTAL MATERIALS AND METHODOLOGY

3.1 Overview

In this chapter, the materials and experimental methodology employed in this study are described. The main experimental methods include: material characterization, hydrogen permeation experiment, hydrogen microprint technique, electrochemical hydrogen charging and heat treatment of the steels. The sample preparation for these experiments is also described. The chemicals and reagents used in all the experiments were reagent grade (sufficient purity), also, the experiments were conducted at room temperature.

3.2 As-received pipeline steels

The materials used for this study are two API 5L X65 pipeline steel plates, which were produced and supplied by the Institute of Research of Iron and Steel, ShaSteel Group in Jiangsu Province, China. The chemical composition of both steels is given in Table 3.1.

Table 3.1. Chemical composition of X65 steel plates

<table>
<thead>
<tr>
<th>Plates</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Nb</th>
<th>Ti</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plate 1</td>
<td>0.05</td>
<td>0.2</td>
<td>1.15</td>
<td>0.009</td>
<td>0.0012</td>
<td>0.019</td>
<td>0.016</td>
<td>0.18</td>
<td>0.29</td>
<td>0.19</td>
<td>-</td>
</tr>
<tr>
<td>Plate 2</td>
<td>0.06</td>
<td>0.21</td>
<td>1.13</td>
<td>0.007</td>
<td>0.0011</td>
<td>0.018</td>
<td>0.015</td>
<td>0.19</td>
<td>0.19</td>
<td>0.19</td>
<td>0.09</td>
</tr>
</tbody>
</table>

The steels were hot rolled using the TMCP parameters presented in Table 3.2, which indicates the temperatures for each treatment stage.

Table 3.2. Thermomechanical processing parameters for X65 steel plates

<table>
<thead>
<tr>
<th>Plates</th>
<th>Reheating temperature</th>
<th>Roughing temperature</th>
<th>Finish rolling temperature</th>
<th>Cooling temperature</th>
<th>Cooling rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(°C)</td>
<td>(°C)</td>
<td>(°C)</td>
<td>(°C)</td>
<td>(°C/s)</td>
</tr>
<tr>
<td>Plate 1</td>
<td>1200</td>
<td>1042</td>
<td>935 – 844</td>
<td>815 – 485</td>
<td>20</td>
</tr>
<tr>
<td>Plate 2</td>
<td>1200</td>
<td>1042</td>
<td>927 – 843</td>
<td>812 – 472</td>
<td>20</td>
</tr>
</tbody>
</table>

The X65 steels were subjected to similar thermomechanical treatments, during the slab reheating and rough rolling stages. However, the finish rolling, and cooling temperatures were
slightly varied as shown. Fig 3.1 shows a schematic diagram of the rolling process, highlighting the rolling parameters, which are the same for both steel plates. The plates were rough rolled from 220 mm slabs to 70 mm slabs in five passes, with an average rolling reduction (ARR) of 20.4%; and subsequently, finish rolled to a thickness of 20 mm in seven passes with an average rolling reduction of 21.5%.

Fig 3.1. Schematic illustration of the rolling process for the steel plates

3.3 Mechanical test

3.3.1 Tensile test

The tensile tests for the pipeline steels were also conducted at the Institute of Research of Iron and Steel in China. Tensile tests were performed according to the ASTM E8/E8M [137] standard. The tensile specimens were machined along the transverse direction (TD) of the rolled plate, and tested using a strain rate of $4.2 \times 10^{-3}$ s$^{-1}$. Each test was conducted three times to ensure consistent results with a reasonable margin of error, which is presented as supplied in the Results and Discussion (Chapter 4) of this work.

3.3.2 Microhardness measurements

Vickers microhardness measurements were conducted in accordance with the ASTM E384-17 [138] standard. The sample preparation for the microhardness evaluation followed the well-
established procedure for metallographic examination. The steel surface was polished to a mirror-like finish, before tests were performed using an MVK-H1 Mitutoyo Vickers hardness tester set at the 1 kg load with a resident time of 12 s. The common errors associated with hardness measurements were avoided; these include indenting too close to the edge of test samples or too close to a previous indentation. Six measurements were taken to determine the average microhardness value for each steel.

3.4 Microstructural evaluation

Before hydrogen related experiments were conducted on the plates, microstructural examination of the supplied plates was carried out. This was done using an optical microscope and a scanning electron microscope (SEM). Optical images of the microstructure of the steels were taken, while EBSD measurements were done using the SEM. The sample preparation for both microscopy observations involved cutting samples from the supplied plates, hot mounting the specimens using a conductive resin and polishing to obtain a smooth surface finish.

3.4.1 Optical microscopy

Samples were cut from the as-received plates to analyse the RD – TD, TD – ND and RD – ND planes of the steels. The samples were hot mounted using a Buehler SimpliMet XPS1 automatic compression mounting system. Then, they were polished with 180, 320, 400, 600, 800 and 1200 grit silicon carbide (SiC) paper to obtain a smooth surface. This was followed by diamond polishing using the 3 μm Struers MD-Dac disc and 1 μm Struers MD-Nap disc to obtain a mirror-like surface finish. The polishing was done using a LaboPol-20 manual polishing machine. After polishing, the samples were etched with 2% nital solution, to reveal their microstructures. The microstructure examination was done using a Nikon Eclipse MA100 inverted optical microscope interfaced with the PAX-it image analysis software. The average grain size was first estimated manually through mean lineal intercept method (Heyn’s Technique), using the obtained optical micrographs.

3.4.2 Electron backscatter diffraction

EBSD scans were done on the TD – ND planes. Samples cut from the steel plates were hot mounted and polished similar to the metallographic procedure used for the samples for optical microscopy, up until the mirror-like surface finish achieved using the 1 μm Struers MD-Nap disc. Then, to obtain a suitable stress-free surface for the EBSD measurements after diamond
polishing, the samples were vibratory polished using a Buehler Vibromet 2 vibratory polisher with a 0.04 μm colloidal silica slurry. The samples were allowed to chemo-mechanically polish for 10 hrs, then rinsed with water, ethanol and dried, before placing them in a vacuum chamber in preparation for the EBSD measurements. A Hitachi SU6600 scanning electron microscope (SEM) equipped with an Oxford Instruments HKLNordlys EBSD detector and an energy dispersive X-ray spectroscopy (EDS) detector was used for the investigation of the steels. The SEM was interfaced with the AZTEC 2.0 data acquisition software to acquire the backscattered electron maps. The SEM was operated at an accelerating voltage of 30 kV and scans were conducted with a binning of 8 x 8 pixels. A schematic illustration of the sample configuration for orientation imaging through EBSD is shown in Fig. 3.2.

Fig. 3.2. Schematic illustration of the sample configuration for orientation imaging using EBSD

All EBSD measurements were analysed using the Oxford Instruments Channel 5 post-processing software. The post-processing was done to obtain the grain boundary maps, crystallographic orientation maps, kernel average misorientation (KAM) maps, recrystallized and deformed fraction maps for the steels. The KAM depicts misorientation angles of Θ < 5° within the same grain, while the LAGBs are categorised as grains with low misorientation angles, 5° < Θ < 15°, and the HAGBs are misorientation angles in the range of 15° < Θ < 62.5°. Finally, using the EBSD direct grain area measurement, the grain size of the steels was determined and compared with that obtained using the mean lineal intercept technique. Also, a grain size distribution plot for both plates was generated using the data obtained.
3.5 Hydrogen permeation experiment

Hydrogen permeation experiments were used to analyse the hydrogen diffusion in the steels. The experiments were conducted according to ISO 17081 standard [122], using the Devanathan–Stachurski permeation set-up. The experimental set-up is given in Fig. 3.3.

![Schematic diagram of the hydrogen permeation experimental set-up](image)

Fig. 3.3. Schematic diagram of the hydrogen permeation experimental set-up

Test samples were cut from the as-received plate, revealing the TD – ND plane in the following dimensions: 20 mm (TD) x 20 mm (ND) x 2 mm (RD). The samples were polished to a mirror-like surface on both sides in line with the metallographic procedure described for the microstructure evaluation up until the 1 μm MD-Nap disc. A very smooth surface is required to ensure accurate measurements of hydrogen oxidation current. The polishing process also reduced the thickness of the samples to ~1 mm. After polishing, a palladium coating with a thickness of ~20 nm was deposited on both polished sides of the steel samples by sputtering in a vacuum. The coating was done using a Quorum Q150T turbomolecular-pumped coating system. The high permeability and excellent corrosion resistance of palladium makes it a good coating for this application. The palladium coating on the oxidation side of the samples enhances the oxidation of diffused hydrogen, and also improves the repeatability of the results obtained. It also controls oxide formation, which is often associated with this technique. The setup used for this experiment covers a circular portion of about 100 mm² of the steel sample on both the charging and oxidation sides.
The electrolyte solution for the charging cell was a 250 ml solution of 0.1 M sulfuric acid (H₂SO₄) and 3 g/L ammonium thiocyanate (NH₄SCN) dissolved in distilled water, while the oxidation cell contained a 250 ml solution of 0.1 M sodium hydroxide (NaOH) in distilled water. A graphite counter electrode was connected to both sides of the double-cell. In addition, the oxidation cell contained a saturated calomel electrode (SCE) containing 3 M potassium chloride (KCl) as the reference electrode. Argon gas was used to simultaneously deaerate the charging and oxidation cells, while a charging current of 5 mA was maintained with an Instek direct current (DC) power source [49,51,74,139]. Also, a G750 Gamry potentiostat was used to supply a constant voltage of 250 mV to the oxidation cell. The oxidation current, which is statistically equivalent to the diffused hydrogen from the charging cell was measured in the oxidation cell relative to the SCE and monitored using the Gamry software. First, the current of the oxidation cell was allowed to stabilize below 1 µA before activating the charging cell. To ensure adequate results, the experiments were conducted twice on both plates.

The permeation experiment creates a hydrogen concentration gradient between the two sides of the steel sample. Hydrogen is produced in the charging cell and is allowed to diffuse to the oxidation cell. Atomic hydrogen diffuses through the steel showing an upward trend until it reaches a saturation point. At this point, the curve starts to plateau signifying a saturation of all the hydrogen traps. At this time, the charging cell was deactivated to allow the trapped hydrogen diffuse out of the steel. Also, this is evident by a decline in the permeation current. From the resulting permeation curves, steady-state current (I∞) and time lag (tL) are read and used to determine the diffusion parameters of the steels, such as, the permeability coefficient (J∞L), effective diffusion coefficient (D_{eff}), apparent solubility (C_{app}) and total density of hydrogen-trapping sites (N_T).

The steady-state current is the highest point on the permeation curve, that is, the region where the curve forms a plateau. It is measured in microamperes (µA). The time lag is the time elapsed during the charging process to achieve 0.63 of the steady-state current density (i.e., time to achieve 0.63 I∞). And it is measured in seconds (s). The diffusion coefficient and permeability are measures of the rate of hydrogen flux passing through the steel sample, with the effective diffusion coefficient measured in squared centimeters per second (cm² s⁻¹) and permeability in moles per centimeter per second (mol cm⁻¹ s⁻¹). The apparent solubility depicts the lattice concentration of hydrogen as a function of position and time. It is measured in moles per cubic centimeters (mol cm⁻³). The total density of hydrogen-trapping sites shows the combined
number of reversible and irreversible traps in the steel. These parameters were calculated based on the following equations [74,122].

\[
J_\infty L = \frac{I_\infty L}{FA} \quad (3.1)
\]

\[
D_{\text{eff}} = \frac{L^2}{6k_L} \quad (3.2)
\]

\[
C_{\text{app}} = \frac{J_\infty L}{D_{\text{eff}}} \quad (3.3)
\]

\[
N_T = \frac{n C_{\text{app}}}{3} \left( \frac{D_L}{D_{\text{eff}}} - 1 \right) \quad (3.4)
\]

where, \( L \) (cm) and \( A \) (cm\(^2\)) are the thickness of steel membrane and area of the sample exposed to charging; Faraday’s constant, \( F = 96500 \) cm mol\(^{-1}\), lattice diffusion coefficient, \( D_L = 1.28 \times 10^{-4} \) cm\(^2\) s\(^{-1}\) and the number of electrons per mole, \( n = 6.02 \times 10^{23} \) electrons per mole.

When the first charging cycle is complete and the current begins to plateau, the power source connected to the cell is switched off to allow hydrogen discharge and the current to reduce to about 1 µA. The electrolyte solution in the charging cell is also sucked out to prevent further charging. Once it is below 1 µA, the power source is switched on to commence the second charging cycle. At this stage, it is believed that only the reversible traps participate in hydrogen trapping. This is because all the traps are filled up when the first charging cycle reaches saturation and during discharge only the reversible traps give up hydrogen. During the second cycle, only the reversible traps are filled. The number of irreversible traps was obtained by subtracting the total number of traps in the second charging cycle from the total of the first cycle [75].

### 3.6 Hydrogen microprint technique

The hydrogen microprint technique uses an emulsion to detect and visualize hydrogen diffusion path of hydrogen through the steel samples. The microprint setup in this study uses only one half of the permeation double cell (the charging cell). Hydrogen is produced in the charging cell and allowed to diffuse through the steel sample which is coated with an emulsion on the other side. The reaction of hydrogen with the emulsion can then be easily detected using the SEM, after the unreacted portions of the emulsion is carefully washed away.

The sample dimension and preparation were similar to that for the hydrogen permeation experiment, except that one polished surface was etched using 2 % nital solution to reveal the
grain boundaries. An emulsion was prepared using reagent grade, silver bromide (AgBr) manufactured by Alfa Aesar. It was applied on the etched side of the sample. The emulsion comprised of 5 g of AgBr powder and 10 ml solution of 1.4 M sodium nitrite (NaNO₂) [74,131]. This concentration of sodium nitrite is used to suppress the corrosion of the etched side of the sample during the experiment. The reaction of diffused hydrogen and the emulsion can lead to corrosion of the sample, if not inhibited. A metal wire loop was used to apply a mono-granular layer across the etched surface of the samples. After depositing the emulsion on the sample, it was left to dry for about 20 minutes before it was inserted into the experimental set-up for charging. A schematic illustration of the hydrogen microprint technique is shown in Fig. 3.4.

![Schematic illustration of the hydrogen microprint technique](image)

**Fig. 3.4.** Schematic illustration of the hydrogen microprint technique

The charging process is also carried out at a constant current supply of 5 mA for a predetermined time, which is supplied by a DC power source. Fig. 3.4 also illustrates a flow diagram showing how the set-up allows atomic hydrogen to diffuse through the thin steel sample and react with the emulsion on the opposite side of the sample. The reaction between hydrogen and the emulsion leads to the reduction of the silver ions in the emulsion according to equation (3.5) [130,131].

\[
\text{AgBr} + \frac{1}{2} \text{H}_2 \rightarrow \text{Ag}^0 + \text{H}^+ + \text{Br}^-
\] (3.5)

For this study, a charging and discharging time of one hour each was used. After one hour of charging, the power source was switched off and the charging electrolyte sucked out of the cell.
to facilitate the discharging process. After charging and subsequent discharging, the samples were dipped for one minute in a fixing solution containing 0.6 M sodium thiosulfate (Na$_2$S$_2$O$_3$) and 1.4 M sodium nitrite (NaNO$_2$). This process helps to remove the unreacted emulsion, and leaves only the reduced silver as white particles on the steel substrate. The samples were also dipped in distilled water for 30 secs before drying [74,108]. Adequate caution was taken throughout the experiment to avoid touching the etched surface or emulsion. Finally, the SEM was used to visualize and image the hydrogen diffusion path through the steel samples. The diffusion pathways will be microprinted and easily detected in high resolution as white silver particles.

### 3.7 Electrochemical hydrogen charging

Steel blocks with the following dimensions: 25 mm (RD) x 20 mm (TD) x 20 mm (ND) were cut from the supplied plates for hydrogen charging. The electrochemical hydrogen charging method was used to induce cracks in the charged steels; this is because of its good result correlation with the standard H$_2$S charging [117]. A schematic diagram of the experimental set-up is show in Fig. 3.5.

![Schematic diagram of the electrochemical hydrogen charging set-up](image)

**Fig 3.5.** Schematic diagram of the electrochemical hydrogen charging set-up

The key components of the set-up are the inert electrode, which was a platinum wire in this case (anode), the steel block to be charge with hydrogen (cathode), DC power source and the electrolyte solution. The electrochemical cell follows the principle of the electrolysis of water,
where in the presence of an electrolyte, oxygen is produced at the anode while hydrogen is deposited at the cathode.

Each steel block was continuously charged for 24 hours using the electrochemical cell shown in Fig. 3.5. The cell was connected to an Instek DC power supply, which was set at a constant current density of 20 mA cm\(^{-2}\) [30,51]. Hydrogen charging was achieved by fully immersing the steel block into an electrolyte solution of 0.2 M H\(_2\)SO\(_4\) and 3 g/L NH\(_4\)SCN dissolved in distilled water. The NH\(_4\)SCN was added as a recombination poison in the solution, to facilitate the entry of hydrogen atoms into the steel and minimize the formation of hydrogen gas (H\(_2\)) at the steel surface. The following equations (Eqs. 3.6 - 3.8) describe the oxidation and reduction reactions that take place during this electrochemical process.

**Oxidation at anode:**

\[
2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4\text{e}^- \quad (3.6)
\]

**Reduction at cathode:**

\[
4\text{H}^+(aq) + 4\text{e}^- \rightarrow 2\text{H}_2(g) \quad (3.7)
\]

**Overall chemical reaction:**

\[
2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g) \quad (3.8)
\]

After hydrogen charging, the steel blocks were sectioned to reveal the TD – ND planes. These surfaces were then again, hot mounted and polished, in preparation for EBSD and EDS scans along the cracked region of the samples. The sample preparation for EBSD was the same with that for the as-received samples. The EBSD raw data obtained, were also analysed using the Oxford Instruments Channel 5 post-processing software. Also, the samples with the hydrogen induced cracks were etched and analysed using an optical microscope to evaluate the length and width of visible crack in both steels.

### 3.8 Heat treatment of steels

There are an infinite number of possible heat treatment schedules which can be applied to steels. This is because several parameters can be varied during the heat treatment. These include, solution temperature, cooling medium (brine, water, oil, air, furnace), tempering temperature, holding time for all the stages and so on. However, leveraging on previous experience and trials by our research group at the University of Saskatchewan, in both published [77] and unpublished works; a stress-relieving heat treatment and three quenching and tempering (QT) heat treatment schedules were applied in this study.
The stress-relieving was done to relief the internal stresses in the plates. It usually involves heating of steels to temperatures below their lower critical temperature (eutectoid), and this temperature is maintained for a specified time, before the steel is cooled. Since the stress-relieving temperature lies in the ferritic region, there will be no major change in microstructure of the steels, except some rearrangement of dislocations to obtain a less strained microstructure. It would be of interest to see how a reduction in the strain level of the steels will affect HIC.

For the QT heat treatment, it was done to investigate the effect of microstructure evolution on the HIC behaviour of the steels. The QT heat treatment involves a solution temperature which heats the steel to the austenitic region and it is quenched after a specified time, using a selected cooling medium. Then again, the steels will be tempered at a ferritic temperature for a specific period of time before cooling again.

The heat treatments were done using a Thermo Scientific Thermolyne F48028 muffle furnace. The four heat treatment schedules were done on steel blocks with dimensions similar to those used during the electrochemical hydrogen charging: 25 mm (RD) x 20 mm (TD) x 20 mm (ND). Schematics of the heat treatment schedules applied on the steels are shown in Fig. 3.6. The four heat treatment schedules which were performed on both steels as illustrated in Fig. 3.6 are explained as follows:

1. In Fig. 3.6 a, Stress relief heat treatment at 550 °C for one hour, followed by air cooling. This steel is designated as 550SR.
2. In Fig. 3.6 b, QT heat treatment with initial heating to 800 °C for one hour, followed by water quenching. Then, tempered at 550 °C for 15 minutes, followed by air cooling. This steel is labelled as 800QT-water.
3. In Fig. 3.6 c, QT heat treatment with initial heating to 800 °C for one hour, followed by oil quenching. Then, tempered at 550 °C for 15 minutes, followed by air cooling. This steel is designated as 800QT-oil.
4. In Fig. 3.6 d, QT heat treatment with initial heating to 900 °C for one hour, followed by water quenching. Then, tempered at 550 °C for 15 minutes, followed by air cooling. This steel is defined as 900QT-water.
Fig 3.6. Schematic illustration of the (a) stress relief and (b, c, d) quenching and tempering heat treatment schedules applied on the two steels.

After the heat treatments, the heat-treated steel blocks were electrochemically charged with hydrogen, in a similar fashion as described in section 3.7. The resulting microstructure and the hydrogen induced cracking behaviour of the heat-treated steels on their TD – ND planes, were also evaluated using the optical microscopy and EBSD.
CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Overview

In this chapter, the results of the experiments and tests conducted in this study are presented and discussed. The presentation of the results begins with the characterization of the as-received X65 steels, using optical microscopy, EBSD and mechanical tests. This is followed by the observations and analysis of the hydrogen permeation and hydrogen microprint experiments. Finally, the results from the hydrogen charging tests conducted on the as-received and heat-treated steels are also discussed.

4.2 Microstructure and mechanical properties of the as-received X65 steels

Microstructure is a key determinant of the physical and mechanical properties of materials. Identifying the microstructural differences between both steels will help illustrate the effect of microstructure on HIC susceptibility and also help in understanding the mechanism of hydrogen assisted failure. Optical micrographs were taken on the three principal planes of both steels, the RD – TD, TD – ND, and RD – ND planes. While the grain size measurements and EBSD scans were conducted on the plane of interest, the TD – ND plane.

4.2.1 Optical imaging of the as-received steels

The optical micrographs of the microstructure of both plates are presented in Fig. 4.1. A visual assessment of the micrographs indicates the coexistence of ferrite and pearlite in the structure of both steels. Since a combination of both phases commonly occurs in X65 pipelines, distinguishing them would be of interest. The darker pearlitic regions are prominently dispersed within the boundaries of the brighter ferrite grains. More pearlite is seen in plate 2 when compared to plate 1, this is mostly because the formation of pearlite is strongly dependent on carbon content. Considering the chemical composition of the steel plates given in Table 3.1, higher fraction of carbon is present in plate 2 compared to plate 1. Although high strength steels often contain low amount of alloying elements, it is worth mentioning that carbon enriched regions of austenite can easily transform into pearlite during processing [140]. Also, the grains in plate 2 are observed to be relatively larger than those in plate 1 across the three planes that were examined. The microstructure of plate 1 consists of pearlite, and mostly fine and
elongated ferrite grains that have similar sizes on all planes. On the other hand, the microstructure of plate 2 mainly consists of pearlite, quasi-polygonal ferrite (QF) and sizable polygonal ferrite (PF) or block ferrite grains. In the plane of interest, TD – ND plane, these block ferrite grains are more prominent and evenly spread out through the microstructure. The PF grains are characterised by smoother boundaries in comparison to the QF with rather irregular boundaries, also there is a small presence of elongated grains in plate 2, especially on the RD – ND plane. However, these elongated grains in plate 2 are not observed as much as those in plate 1, as plate 1 is dominated by these structures.

![Plate 1](image1)
![Plate 2](image2)

Fig. 4.1. Optical micrographs for (a, b, c) plate 1, and (d, e, f) plate 2, showing the RD – TD, TD – ND and RD – ND planes, respectively.
4.2.2 Grain size determination for the steels (mean lineal intercept)

The grain size of the steels was first estimated using the mean lineal intercept (MLI) method, which is commonly known as the Heyn’s technique. It is one of the most widely used methods for grain size determination and it was done in accordance to the ASTM 112 standard [141] for determining the average grain sizes of materials. The average grain size of the steels was measured from their TD – ND planes, using the obtained optical micrographs.

The mean lineal intercept method involves the use of test lines, magnification and the number of intersections (grain boundaries) cut by the test lines. The sets of test lines were used because of the somewhat non-equiaxed structure of the plates. Also, the precision of the measurement will increase with an increase in number of test lines and length of test lines, a lower magnification is also advisable to get more grains with the measurement field. A total of ten (10) test lines with equal length were used in this case to estimate the average grain size of the steels. The mean lineal intercept or the average grain diameter is given by the following formula:

\[
MLI = \frac{L_T}{PM}
\]

(4.1)

where \(L_T\) is the total length of the test lines, \(P\) is the total number of grain boundary intersections and \(M\) is the magnification (which can be obtained using the scale bar of the micrograph).

The result from the mean lineal intercept method estimated the average grain size from the micrographs of plate 1 and 2 to be about 3.2 (~3) \(\mu\)m and 4.6 (~5) \(\mu\)m, respectively.

4.2.3 Mechanical properties of the steels

The mechanical properties of pipeline steels depend on their microstructure, and the microstructure can be controlled by altering their chemical composition and TMCP parameters. It is known that the composition of microalloying elements significantly affects the non-recrystallization temperature (\(T_{nr}\)) range of steels, and rolling within and outside this region affects the microstructure of the steel [3]. The thermomechanical treatment conditions adopted for processing each plate are responsible for the differences in mechanical properties and microstructural features such as grain morphology, grain orientation, grain boundary character distribution of the as-received steels. The yield and tensile strength values as well as the average microhardness of the steels are given in Table 4.1.
Table 4.1. Mechanical properties of X65 plates

<table>
<thead>
<tr>
<th>Mechanical Properties</th>
<th>Plate 1</th>
<th>Plate 2</th>
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</thead>
<tbody>
<tr>
<td>Yield strength (MPa)</td>
<td>535 ± 4</td>
<td>501 ± 5</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>605 ± 7</td>
<td>620 ± 8</td>
</tr>
<tr>
<td>Microhardness (HV)</td>
<td>250 ± 4</td>
<td>228 ± 2</td>
</tr>
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</table>

Previous research [142] has reported that finish rolling at higher temperatures promotes the nucleation of small ferrite grains through recovery and recrystallization. Also, Ni and Mn are known to open the austenite field of steels, leading to lower $A_{r1}$ and $A_{r3}$ transformation temperatures. While carbide forming elements such as Mo, Cr etc, tend to close the austenite field [143]. From Table 3.1, plate 1 has a higher Ni content than plate 2 and only plate 2 contains Mo, while the other elements are moderately similar for both plates. This can help explain the smaller grain size observed in plate 1 after rolling at an elevated temperature range (935 – 844 $^\circ$C) in comparison to plate 2 (927 – 843 $^\circ$C), assuming that the austenite field is larger for plate 1. However, a lower average grain size, higher yield strength and hardness values are recorded for plate 1. It is well-known that an increase in grain size decreases the hardness of a material. This is logical because the higher number of grain boundaries per surface area creates obstacles for dislocation motion. Also deformation will be more difficult since the hardness values often have a direct relationship with the strength of the material [144]. The higher yield strength in plate 1 was expected because of the largely elongated grains observed in the steel structure, which resemble acicular ferrite (AF) structures. AF structures are usually more effective barriers to dislocations than PF structures, this is because of their usually fine interlocking nature which can resist dislocation motion. Nevertheless, recrystallization seems to be incomplete in this case, as more elongated grains are observed on every plane in plate 1. This high fraction of elongated ferrite grains in plate 1 suggests that it has a more strained microstructure than plate 2. Thus, it would be important to evaluate the dislocation density or stored strain in the steels.

4.2.4 EBSD measurements of as-received X65 steels

The as-received plates were analysed using backscattered diffraction, to get an idea of the crystallographic orientation, grain boundary character, local misorientation, deformed and recrystallized fraction of the steels. The EBSD maps showing these steel characteristics are presented in Fig 4.2.
Fig. 4.2. EBSD orientation map, grain boundary character map, KAM map, deformed and recrystallized fraction map of the TD - ND plane for (a, b, c, d) plate 1 and (e, f, g, h) plate 2, respectively.
Thermomechanical processing influences the formation of the final microstructure, which is accompanied by crystallographic texture development in steels. Hence, large areas along the mid-thickness of the steels were analysed using EBSD to gain knowledge of the differences in texture along this region. EBSD scans of areas on the TD – ND plane of both steels, around the mid-thickness region were done using a scan step size of 0.8 µm. The scans were used to generate EBSD orientation maps, grain boundary character maps, kernel average misorientation maps, deformed and recrystallized fraction maps, as well as to determine the average grain size and grain size distribution of the two plates.

From Fig. 4.2 a and e, the EBSD orientation maps of the scanned area on both plates show a quite similar texture. Although, scans of smaller areas might differ, as the statistics of texture tends to differ on a surface when smaller areas are probed. However, the other EBSD maps yielded interesting results, as both steels showed obvious differences. Fig. 4.2 c and d, clearly shows a more strained microstructure in plate 1, with greater degrees of misorientation and a larger deformed fraction. This depicts more stored energy in the plate due to plastic deformation during TMCP. Due to these large degrees of misorientation in plate 1, more subgrain boundaries are observed in plate 1 despite having smaller grains, as shown in Fig. 4.2 b and f. This confirms that larger degrees of misorientation exist within the grains in plate 1, which is also clearly shown by the KAM map. The KAM map approximates the dislocation density in the steel, thus, indicating a higher dislocation density in plate 1 and hence, the very high deformed fraction recorded, as shown in Fig. 4.2 d and h. The relative frequencies of the kernel average misorientation, as well as the deformed, recovered and recrystallized fractions for both plates are plotted in Fig. 4.3.

Fig. 4.3. Relative frequency of the (a) kernel average misorientation and (b) deformed and recrystallized fraction of both steels
Fig. 4.3a shows that the misorientations in plate 1 are at much higher angles than plate 2, which is skewed towards lower angles of misorientation. While Fig. 4.3b shows a large disparity between the recrystallized fractions in both plates. It would be of interest to see how these factors affect the HIC behaviour of the steels, as greater recrystallized fractions in low carbon steels have been reported to increase resistance to hydrogen-related damage [50].

Using the EBSD direct grain area measurement, the average gain sizes of plate 1 and plate 2 were also determined to be approximately 3 µm and 5 µm, respectively. Comparing these values to those obtained through the Heyn’s technique and our visual assessment of the microstructure of the steels, we can conclude that plate 2 has a larger average grain size than plate 1. The grain size distribution for the both plates are presented in Fig. 4.4.

![Grain size distribution plot](image)

**Fig. 4.4. Grain size distribution for both steels**

The grain size distribution plot in Fig. 4.4 shows that plate 1 has a larger percent of smaller grains than plate 2. Also, plate 2 has some very large grains up to 30 µm, which are absent in plate 1. This helps confirm the visual observation of the large polygonal ferrite (block ferrite) grains observed in the TD – ND plane of plate 2 in Fig. 4.1

### 4.3 Hydrogen diffusion and trapping behaviour of as-received X65 steels

The hydrogen diffusion behaviour of the steels was evaluated using the hydrogen permeation experiment. This was done by measuring the permeation current during hydrogen transport
through the steels. It is believed that during the first charging cycle, all the hydrogen traps (reversible and irreversible) contribute to the result of the diffusion process until the steel matrix reaches saturation. And during the second charging, only the reversible traps participate in the process. The permeation curves for the first and second charging cycles for the steels are presented in Fig 4.5.

Parameters from the permeation curves which are given in Table 4.2, such as the time lag and steady-state currents were used to calculate the hydrogen diffusion parameters, using equations 3.1 – 3.4. Here, the thickness of the samples used for the permeation experiments after polishing both sides for plate 1 and plate 2 were both ~1 mm (about 1.25 mm and 1.27 mm, respectively). Table 4.2 also contains the calculated diffusion parameters, such as, the permeability, effective diffusivity, and the apparent solubility of the first and second charging cycles of both steels. Similarly, the values describing the trapping characteristics of the steels were evaluated and are given in Table 4.3.

![Fig. 4.5. Hydrogen permeation curves for the steel plates](image-url)
Table 4.2. Hydrogen permeation parameters for the steel plates

<table>
<thead>
<tr>
<th>Diffusion Parameters</th>
<th>Plate 1</th>
<th>Plate 2</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>First charging</td>
<td>Second charging</td>
</tr>
<tr>
<td>Steady-state current, $I_\infty$ ($\mu$A)</td>
<td>55.4</td>
<td>43.4</td>
</tr>
<tr>
<td>Time lag, $t_i$ (s)</td>
<td>962</td>
<td>1278</td>
</tr>
<tr>
<td>Permeability, $J_\infty L \times 10^{-11}$ (molcm$^{-1}$s$^{-1}$)</td>
<td>7.67</td>
<td>6.01</td>
</tr>
<tr>
<td>Effective Diffusivity, $D_{\text{eff}} \times 10^{-6}$ (cm$^2$s$^{-1}$)</td>
<td>2.79</td>
<td>2.1</td>
</tr>
<tr>
<td>Apparent Solubility, $C_{\text{app}} \times 10^{-6}$ (molcm$^{-3}$)</td>
<td>27.49</td>
<td>28.62</td>
</tr>
</tbody>
</table>

Table 4.3. Hydrogen trapping characteristics of the steel plates

<table>
<thead>
<tr>
<th>Trapping Characteristics</th>
<th>Plate 1</th>
<th>Plate 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total density of traps $\times 10^{19}$ (cm$^3$)</td>
<td>34.44</td>
<td>15.82</td>
</tr>
<tr>
<td>Density of reversible traps $\times 10^{19}$ (cm$^3$)</td>
<td>24.76</td>
<td>3.62</td>
</tr>
<tr>
<td>Density of irreversible traps $\times 10^{19}$ (cm$^3$)</td>
<td>9.68</td>
<td>12.2</td>
</tr>
</tbody>
</table>

Fig. 4.5 shows a clear difference between the steady-state current of the first and second charging cycles for the both plates. This is due to the difference in the character of traps participating in the charging cycles, reversible and irreversible in the first charging cycle and only the reversible in the second charging cycle. After the first charging cycle, a reduced rate of hydrogen permeation is observed in plate 1. This is supported by the decrease in permeation current and the significant reduction of the effective diffusivity. Fig. 4.5 shows a spike in the current during the first charging for plate 2, which indicates higher permeability.

A relatively high concentration of hydrogen is detected within plate 1. This is demonstrated by the high apparent solubility observed. The increased solubility during the second charging cycle indicates that the ratio of reversible traps in plate 1 is higher than that of the irreversible traps. This is confirmed by the result of the trapping characteristics in Table 4.3. Previous studies have related the increase in HIC susceptibility in steels to low diffusivity and permeability [74,81]. Also, some correlations have been established between the increase in apparent solubility and KAM with HIC susceptibility, due to the significant hydrogen retention within the lattice defects [39,114,145]. The results in Table 4.2 show that plate 1 has the capacity of accumulating more hydrogen, which consequently reduces diffusion through the steel structure. The reason for this behaviour is not far-fetched considering that plate 1 has a
more strained structure and more grain boundaries per unit area, resulting in a high density of reversible traps, more than eight times the value calculated for plate 2. Also, most of the trapping sites in plate 1 were reversible, while plate 2 had mostly irreversible trapping sites. This can be offered as an explanation for the small increase in permeation current recorded when testing plate 1 as against plate 2, during the second charging cycle. Going by the results in Fig. 4.2, the high misorientation in plate 1, which estimates a high dislocation density in the plate, is the possible reason for this high ratio of reversible to irreversible traps observed. Also, the formation of nanosized (Ti, Mo) C precipitates in Ti and Mo bearing steels or other innocuous precipitates could also be the reason for the high irreversible trap density observed in plate 2. Previous findings of these innocuous nanosized precipitates reported in literature, indicate that they can be as fine as 3 nm, which can be observed at very high resolution, using TEM [68–70]. These results confirm the observations reported in literature that reversible trapping sites play a greater role than irreversible traps in determining the HIC susceptibility of steels [33,74]. This is because the reversible traps control hydrogen transport through the steels, which can result in the accumulation of hydrogen around the crack tips, to aid crack propagation [74]. The permeation results are important to gain knowledge on the diffusion and trapping characteristics of the investigated steels, however, the transport of hydrogen atoms, noting the important pathways through the steel matrix still needs to be clarified.

4.4 Detection of diffused hydrogen in the steels

The hydrogen diffusion path through the steels was visualized using the very sensitive hydrogen microprint technique. The production of hydrogen atoms and its diffusion through the steels was done simultaneous in this study. The charging and discharging stages were done for an hour each, enough time to ensure hydrogen sufficiently reacts with the emulsion. This configuration will ensure that the intensity of diffusion through the steels will be clearly detected to determine the main pathways for hydrogen.

After the experiment, the etched sample surfaces that reacted with the emulsion were examined using the SEM equipped with an EDS detector. After carefully rinsing the samples in a fixing solution, white silver particles usually spherical in nature, are expected around the regions where the reduction reaction has occurred. The electron micrographs for the both steels, showing white silver particles produced during the reduction of the AgBr emulsion are presented in Fig. 4.6.
Fig. 4.6. SEM images of (a, b, c) plate 1, and (d, e, f) plate 2 after hydrogen microprint experiment

The results clearly show hydrogen diffusion through the grain boundaries and phase interfaces in both samples. The differences observed in the hydrogen detection efficiency can be related to the differences in grain boundary character distribution, as the diffusion through low angle and coincident site lattice (CSL) boundaries would be lower than that through high angle grain boundaries because of the difference in free volume. Certainly, it is observed that the grain boundaries and phase interphases are the preferred path for hydrogen discharge from the steel samples. This has also been reported by other researchers [74, 108, 131]. However, some others have reported a more uniform diffusion through the steel matrix [134–136]. This is plausible, as these researchers have shown electron images from their microprint experiments and the
observations in this study also noted some diffusion through the lattice. But there is clearly more diffusion through the interphases and grain boundaries which act as reversible traps. Hence, making them the main diffusion pathways for hydrogen in the steels. This observation supports the well-known notion which states that the activation energy for lattice diffusion has a greater order of magnitude than the activation energy for diffusion through the grain boundaries. This large difference in activation energy implies that diffusion will be lower through the lattice structure than through the grain boundaries and interfaces. Fig. 4.7 presents an EDS scan showing diffusion through the steel, and the white spherical particles observed are metallic silver reduced during hydrogen diffusion.

Fig. 4.7. EDS scan showing the detection of metallic silver on the steel surface.

This result showing that the grain boundaries are the main diffusion path in steels implies that finer grains, which have higher number of boundaries will have lower effective diffusion due to more hydrogen traps per surface area. Higher dislocation densities will also lower the effective diffusion, as dislocations also act as reversible traps. On the contrary, larger grains will have higher hydrogen diffusion rate with less trapping sites per surface area. This result also reinforces the diffusion and trapping characteristics evaluated for the steels, as plate 1 with higher dislocation density and smaller grains exhibited lower diffusion and high density of reversible traps as a result. This has been similarly confirmed by Thomas and Szpunar [108].
who showed that the increase of grain size in pipeline steels increases diffusivity and permeability and reduces hydrogen solubility.

Furthermore, a circular pattern of hydrogen diffusion is seen around the inclusions and precipitates in both plates, as shown in Fig. 4.6 c and f. This occurrence has been reported severally in literature [108,131,134]. This is probably related to the matrix distortion and high local misorientation usually observed around inclusions. This high degree of misorientation and distortion can be seen in Fig. 4.8, which shows a KAM map around an inclusion in steel.

![Image of KAM map showing high misorientation around an inclusion in steel](image)

Fig. 4.8. KAM map showing high misorientation around an inclusion in steel

This distortion and high degrees of misorientation may create microvoids in the steel matrix, which in turn act as reversible traps. This is a plausible explanation for the circular area of hydrogen diffusion often reported around inclusions and incoherent precipitates in steels.

4.5 Microstructure evaluation of the steels after hydrogen charging

After hydrogen charging, the specimens were sectioned from the charged steel blocks to reveal the TD – ND planes. The examination of the cross-section of both specimens revealed hydrogen induced cracks across the mid thickness of the specimens. All the cracks propagated parallel to the plate surface, with occasional deflections along the normal direction, hence a stepwise cracking. However, the crack characteristics for the both plates were clearly different, with plate 1 showing more severe cracking than plate 2. It is well known that the mid thickness at the cross-section of steel plates is the zone, where elements such as manganese, titanium, sulphur, carbon migrate during solidification of the casted steel slab and TMCP. Also, hard phases tend to form around this region due to this segregation [55]. Thus, this study focuses on
understanding the microstructural factors that facilitate cracking around the mid-thickness region. It is also of interest to determine the role of grain orientation, grain size, grain boundary character, and local misorientation in crack propagation, using the difference in crack characteristics of the two steels as a case study.

4.5.1 EBSD measurements of the steels after hydrogen charging

EBSD scans were conducted along the crack path in the mid thickness region of both steels. These scans are smaller scans than those done on the as-received steels, but at a higher resolution to obtain finer details. Some of the results obtained after post-processing of the EBSD raw data are presented in Fig. 4.9, showing the band contrast maps, EBSD orientation maps and grain boundary distribution maps of the steels.

![EBSD results showing the band contrast, EBSD orientation map and grain boundary distribution map for (a, b, c) plate 1 and (d, e, f) plate 2, respectively.]

Fig. 4.9. EBSD results showing the band contrast, EBSD orientation map and grain boundary distribution map for (a, b, c) plate 1 and (d, e, f) plate 2, respectively.
The band contrast maps (Fig. 4.9 a and d) show smaller grains in plate 1 when compared to plate 2. The average grain sizes around the crack path in plate 1 and plate 2 were obtained as 1.5 and 2.1 µm, respectively, using the EBSD direct grain area measurement. This might be an indication of grain fragmentation during cracking [38], especially in plate 1 which shows a severe transgranular crack. But most importantly, Fig. 4.9 clearly shows a more severe crack in plate 1 in comparison to plate 2. The EBSD orientation maps collected from the TD – ND planes of the steels along the crack path are presented in Fig. 4.9 b and e. Plate 1 has more {110}-oriented grains and the transgranular crack is observed to run through grains of this orientation. Also, a few {100}-oriented grains are observed along the crack path. Plate 2 consists mainly of {111} and a few {100} oriented grains. The crack observed was less severe and intergranular. Grains with {111} orientation are often considered as more resistant to HIC [8,112]. Therefore, it is likely that the crack intensity in plate 2 was hindered by the high fraction of {111} oriented grains around this mid-thickness region. However, it is also possible that other factors contributed to the difference in the observed crack behaviour. This is because other researchers have reported cracks propagating through {111} oriented grains [7,59]. The as-received steels showed a largely similar texture in both steels, while other features such as their microstructure, dislocation density, residual stresses and so on were quite different. Hence, the effect of these features on the cracking behaviour were also examined.

The grain boundary distribution for the both steels are presented in Figs. 4.9 c and f. Considering the differences in the distribution of the grain boundary type in both specimens, the crack might have been facilitated by the higher fraction of HAGBs in plate 1. There are reports of preferential crack propagation along HAGBs, while LAGBs are more crack resistant [88,98,146]. This view is rather unclear in this study, due to the severity of the cracks observed, especially in plate 1. However, clusters of very fine grains with HAGBs are seen around the crack region in plate 1. The accumulation of high energy boundaries in plate 1 implies that the grains are highly misoriented relative to one another. These boundaries provide higher local grain boundary energy and higher free volume for hydrogen trapping sites, which will facilitate HIC through stress driven diffusion [38]. This observation agrees with reports in literature, which suggest that colonies of fine grains in steels can lead to increased susceptibility to HIC [7,59,104]. Perhaps, there is indeed an optimum average grain size that would be suitable for hydrogen diffusion and crack resistance, as suggested in literature [59,107]. Nevertheless, in this case, the transgranular type of cracking was dominant and more severe in plate 1, which had finer grains around the crack path in the mid-thickness region.
The kernel average misorientation (KAM) map was used to approximate the dislocation density around the crack area in the two steels. The KAM describes the average misorientation between a certain point on the EBSD scan and its surrounding points within the same grain. It helps to qualify the local strain retained in the samples after deformation. From the earlier scan of the as-received steels, we have established that plate 1 had a higher dislocation density than plate 2. Thus, after hydrogen charging, it would be necessary to see the KAM distribution around the crack path. Fig. 4.10 shows the KAM maps of the steels around the crack path.

From Fig. 4.10, it is obvious that there is a high local misorientation around the crack path. This high matrix distortion was probably increased during crack propagation. Generally, cracks reduce accumulated energy, but store local elastic distortion during propagation. However, away from the crack path, high KAM is still observed in plate 1. This high local misorientation, which was also observed in the as-received steel, suggests the retention of residual stresses with a high dislocation density. This is the most likely cause of the severe cracking behaviour observed in plate 1. Plate 1 has a high density of dislocations, stored energy is higher and there are more reversible trapping sites, therefore, the energy required for crack propagation is lower.

The build-up of strain in steels generally indicates incomplete recrystallization. This means that the steel plate may require some stress relieving treatment, or annealing to facilitate recrystallization. Unfortunately, the development of strain free grains can compromise mechanical properties such as strength and toughness. Thermomechanical processing is considered a more effective way to simultaneously improve properties such as strength and toughness [3,54]. Thus, a proper planning of the steel rolling schedule is essential.
The distribution of the recrystallized, recovered (sub-structured) and deformed fractions in plates 1 and 2 are presented in Fig. 4.11. A clear correlation is seen between the KAM maps in Fig. 4.10 a and b, and the deformed and recovered areas in Fig. 4.11 a and b.

![Fig. 4.11. EBSD results showing the recrystallization and deformed fraction distribution for (a) plate 1 and (b) plate 2](image)

Although low recrystallized fractions were observed in the both scans in Fig. 4.11, this might be as a result of the small area of the steels scanned. However, the large deformed fraction in plate 1 is still observed. The larger scans of the as-received steels in Fig. 4.2 show a significantly higher recrystallized fraction for plate 2 and a much higher deformed fraction for plate 1. Laureys et al [50] examined the effect of a recrystallized, partially recrystalized and deformed structure in steels on hydrogen induced damage (cracking and blistering), using electrochemical hydrogen charging. They observed that hydrogen damage was less severe when recrystallized fraction increased. This suggests that recrystallized grains pose a higher resistance to hydrogen damage than deformed steels. Thus, it can be inferred that the higher percentage of deformed grains in plate 1 contributed to the severity of the observed cracks. The energy and dislocation density will induce some hardening of steel as seen in the hardness results in Table 4.1. In addition, accumulated dislocations can also temporary store up hydrogen, which will further contribute to hardening after hydrogen charging and facilitate crack propagation [95]. Reports in literature have clearly shown that the mechanical properties of steel, especially hardness, have a direct relationship with the HIC susceptibility [74]. Thus, these EBSD observations help to explain the severe cracking observed in plate 1. However, during the initial probe of the mid-thickness cracks, several inclusions were observed around
the crack path, with some acting as crack initiation points and aiding crack propagation. It would be of interest to determine the elemental composition, type and morphology of these inclusions to gain more knowledge of their role in the cracking of steels.

4.5.2 EDS scans of the steels after hydrogen charging

Energy dispersive X-ray spectroscopy (EDS) scans were done at selected sites along the crack path at the mid-thickness of both steels. The mid-thickness of pipeline steel which is often tagged the segregation zone, usually contains a high concentration of various elements. This segregation zone usually has harder phases, more inclusions and precipitates, which are instrumental in the initiation and propagation of cracks, leading to higher HIC susceptibility of pipeline steel [7,54,55]. The result of the EDS scans, showing the composition of some inclusions at selected sites in the both plates are shown in the following figures. More scans were done on plate 1 because of the severity of the crack and more features of interest.

Fig. 4.12 displays sites within the severe crack which shows fragmented complex carbonitrides in plate 1. These precipitates clearly played a role in crack propagation and its possible initiation. In the same vein, fragmented Si-enriched carbide inclusions (Si-O-C) were also observed within the severe crack in plate 1. This is presented in Fig. 4.13, which also includes higher resolution EDS maps as a sub-set to Fig. 4.13 to show a clearer image of the fragmented carbides. These higher resolution maps suggest that the crack propagated along these carbide inclusions. Also, an EDS scan of plate 1 showing a rectangular-shaped multi-elemental inclusion (Ti-Nb-P-N-Si) along the crack path is presented in Fig. 4.14. This multi-elemental inclusion helps illustrates the effect of elemental segregation. It is believed that it aided crack propagation, as the crack cuts through its interface with the steel matrix. Mohtadi-Bonab et al. [147] in a study using finite element modelling suggested that while cracks initiate around inclusions based on the internal pressure theory, propagation is aided by the linking of these cracks to get longer cracks in the presence of diffusible hydrogen atoms. This seems to be the case, as these inclusions are found within the large crack. Results in literature have reported that carbonitrides, carbide and non-metallic inclusions and precipitates act as crack initiation sites in steels [7,73], which has also been observed in this study. Finally, the less severe cracks in plate two were observed to initiate from Si-enriched non-metallic oxide inclusions. An example of this is shown in Fig. 4.15. The crack initiation image from plate 2 is quite consistent with the internal pressure theory. The delayed cracking in plate 2 enabled the imaging of crack initiation around an oxide inclusion (non-metallic inclusion).
Fig. 4.12. EDS maps showing fragmented complex carbonitride precipitates within the crack in plate 1.
Fig. 4.13. EDS maps showing carbide precipitates within the crack in plate 1.

Fig. 4.14. EDS maps showing multi-elemental inclusion along crack path in plate 1.

Fig. 4.15. EDS maps showing Si-enriched oxide inclusion (crack initiation site) in plate 2.
These results reveal that HIC initiated and propagated through Si-enriched areas. Although precipitates of Ti and Nb were found in plate 1, they were almost not present in plate 2. This might be as a result of their reduced fraction in plate 2 (see the composition of the steels in Table 3.1). Also, it is worth mentioning that there were not many MnS inclusions in both plates. This can also be attributed to the moderate Mn and low S content of the investigated steels.

Considering the type and morphology of inclusions, it is possible for hydrogen to initiate cracks around a wide range of inclusions and precipitates, such as, oxide inclusions, angular precipitates, and/or elongated sulphides. For instance, HIC has been observed to start at multi-elemental inclusions comprising of (Mn -S -V -Nb -Ti -N) [72], (Ti-Nb) N, Al-Mg-Ca [148] and MnS, (Ti, Nb, V)(C, N) precipitates [7,63]. Inclusions and precipitates store hydrogen more permanently, in addition, microvoids often exist in the steel matrix around these inclusions and precipitates. This has been shown using the hydrogen microprint experiment. Since hydrogen will tend to concentrate at less coherent interfaces, therefore, cracks can easily initiate as the pressure from hydrogen continues to build up within the voids. Du et al [149] also proposed that the attraction of hydrogen towards inclusions in a ferrite-pearlite structured steel results in crack initiation and propagation. They attributed such behaviour to the weakening of Fe-Fe bonds leading to decohesion.

**4.5.3 Evaluation of HIC severity after hydrogen charging**

The specimens used for the EBSD measurements were etched and examined using an optical microscope. Table 4.4 presents a statistical account of the visible cracks spotted using an optical microscope, according to the number and dimensions of cracks. While, Fig. 4.16 shows the optical micrographs of selected crack sites along the mid-sections of the investigated steels.

Table 4.4. Account of cracks observed in the steels

<table>
<thead>
<tr>
<th></th>
<th>Number of cracks</th>
<th>Average Length (µm)</th>
<th>Average Width (µm)</th>
<th>Length of Longest Crack (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Plate 1</strong></td>
<td>5</td>
<td>2053 ± 489</td>
<td>7 ± 1.3</td>
<td>2413</td>
</tr>
<tr>
<td><strong>Plate 2</strong></td>
<td>2</td>
<td>647 ± 356</td>
<td>1 ± 0.4</td>
<td>898</td>
</tr>
</tbody>
</table>

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As mentioned earlier, plate 1 showed greater HIC susceptibility than plate 2. Longer and wider cracks are seen in plate 1 (Fig. 4.16 a and b), while plate 2 (Fig. 4.16 c and d) showed less prominent cracks at different magnifications. From the results, there are strong indications that the microstructural characteristics of the steels influenced their crack pattern and severity. The severe cracks in plate 1 suggests that more hydrogen accumulated within the steel, hence, enhancing crack propagation. This fact has been confirmed using the hydrogen permeation tests. The higher density of reversible traps in plate 1, which is largely a result of the high dislocation density increased the hydrogen solubility of the steel. This retention of more hydrogen atoms within the steel will ensure that there is sufficient hydrogen around the crack tip through stress driven diffusion to accelerate crack propagation. Also, this can make the critical hydrogen saturation point in plate 1 to be attained faster, leading to an early onset of HIC in the steel. Finally, since plate 2 contains larger grains, it is more likely to experience delayed cracking [150].

### 4.6 Microstructure evaluation of the heat-treated steels

The microstructures of the heat-treated steels were examined using optical microscopy and EBSD measurements. The electrochemical hydrogen charging procedure for the heat-treated steels was similar to that conducted on the as-received steels. Thus, a similar mode of
evaluation was applied to the heat-treated steels. However, the discussion of results focuses only on a few observations of interest. The optical micrographs of the heat-treated steels for plate 1 and 2 are presented in Fig. 4.17.

Fig. 4.17. Optical micrographs showing the TD – ND planes of the heat-treated samples of (a, b, c, d) plate 1, and (e, f, g, h) plate 2.
4.6.1 Microstructure evaluation of the 550SR steels

From Fig. 4.17 a and e, which show optical micrographs of the stress relieved steels (550SR), the microstructure is observed to be somewhat similar to that of the as-received steels. This is because the stress relieving schedule did not significantly change the microstructure of the plates. However, more polygonal ferrite grains are observed in 550SR plate 1 than in the as-received plate 1 (Fig 4.1 b), while plate 2 still mainly consists of polygonal ferrite grains.

Interestingly, after hydrogen charging, the cracking behaviour was similar to that observed for in the as-received steels. 550SR plate 1 still showed a more severe hydrogen induced crack than 550SR plate 2. Thus, EBSD measurements were conducted on the crack path of the stress relieved steels, to estimate the stored strain in the steels after the heat treatment. Fig 4.18 shows the electron micrograph and the results of EBSD scans taken along the cracks observed in the stress relieved steels.

Fig 4.18. Electron micrograph of cracks and EBSD maps showing the EBSD orientation map and KAM map for (a, b, c) 550SR plate 1 and (d, e, f) 550SR plate 2, respectively.

It is worth mentioning that despite the reduction of stored strain in the steels, the cracking behaviour is somewhat similar, indicating that although it is a contributing factor, there are still other factors that come into play during crack propagation. Perhaps, a change or evolution of the microstructure will show a much more different cracking behaviour as suggested in
literature [87,88]. Also, the severity in the crack in 550SR plate 2 seems to slightly increase with difference in crystallographic texture around the crack path.

### 4.6.2 Microstructure evaluation of the 800QT-water steels

From Fig 4.17 b and f, which show the optical micrographs of the 800QT-water steels, the microstructure of both steels mainly consist of well spread-out polygonal ferrite structures with some pearlite along the grain boundaries of the ferrite structures. 800QT-water plate 2 is observed to have more pearlite structures than 800QT-water plate 1, this can also be attributed to its higher carbon content.

After hydrogen charging, no visible cracks were observed along the mid-thickness region in both plates. This is probably due to the polygonal ferrite grains in their microstructure, which have been hinted to inhibit crack propagation. Li et al. [85] observed in their study of SCC in X100 pipeline steels that acicular ferrite and quasi-polygonal ferrite showed more resistance to crack propagation. However, results in this present study have suggested that the cracking behaviour in steels is actually influenced by several contributing factors. So, to gain more knowledge to explain the absence of cracking at the mid-thickness region after 24 hours of hydrogen charging, EBSD scans were conducted along this region in both steels. The scans were done to ascertain the level of lattice strain and deformed grains as well as crystallographic texture in this region. The EBSD maps are presented in Fig. 4.19.

Fig 4.19. EBSD maps showing the EBSD orientation maps, grain boundary distribution, KAM map and recrystallized fraction for (a, b, c) 800QT-water plate 1 and (d, e, f) 800QT-water plate 2, respectively.
The EBSD maps in Fig 4.19 show a similar situation for both 800QT-water steels. They both comprise of a similar texture, similar distribution of grain boundary character and grain size, as well as, very low local misorientation and very low deformed fractions. The polygonal ferrite grains observed in these 800QT-water steels are also relatively larger than those seen in the as-received steels. It is plausible that these factors jointly contributed in increasing the HIC resistance of the steels, since it has been established that lower dislocation density and higher recrystallized fractions enhance the resistance of pipeline steel to hydrogen related damage [39,50,114]. However, despite the resistance to mid-thickness cracking, further probing of the samples revealed small cracks, which were evidently created during the quenching process. These quench cracks were mainly observed in 800QT-water plate 1, and are shown in Fig. 4.20.

Fig. 4.20. (a, b) Quench cracks observed in plate 1 (c) subset showing the EBSD maps within the quench crack.

The quench cracks observed in plate 1 are given in Fig. 4.20 a and b, while Fig. 4.20 c shows the EBSD maps around the crack observed in Fig. 4.20a. As widely observed in the 800QT-water steels and confirmed by Fig. 4. 19, the steels generally have low dislocation density, as well as, low deformed and high recrystallized fractions. However, during quenching in water, which is quite rapid, thermal stresses as well as transformation stresses were set-up in the steel and these stresses resulted in the cracks observed [143]. Within the quench crack, very small and highly deformed grains were observed, and these grains seems to have higher dislocation
density and stored energy within this region than the rest of the steel matrix. It is noteworthy that these cracks which initiated away from the mid-thickness region did not propagate into longer cracks even after 24 hours of charging, as seen in the mid-thickness of the as-received steels. This could be because of the reduced fraction of precipitates and inclusions around this region, which would have prevented further initiation and joining of cracks. Also, the microstructure was somewhat favourable and less strained. Nevertheless, quench cracks were observed, which could grow in time, if the pipeline steel was in service. Thus, a slower cooling was applied at the same temperature to possibly avoid these mini-cracks being set-up by the quenching process.

4.6.3 Microstructure evaluation of the 800QT-oil steels

From Fig. 4.17 c and g, which show the optical micrographs of the 800QT-oil steels, the microstructures of both steels consist of more homogenous polygonal ferrite structures. However, the morphology of the 800QT-oil plate 2 has more of equiaxed - polygonal ferrite structures. As expected, after hydrogen charging, no visible cracks were observed along the mid-thickness region in both plates and away from the mid-thickness region no visible quench crack was spotted in both steels. The steels showed the best resistance to HIC. The oil quenching which is a much slower mode of quenching due to the thermal conductivity of oil relative to water, helped mitigate the effects of thermal stress build-up within the steels. This created a smooth microstructure devoid of cracks after quenching and subsequent hydrogen charging. The EBSD maps for the 800QT-oil steels are presented in Fig. 4.21.

Fig. 4.21 also shows a similar microstructure for both plates, with less strained microstructures, and very low deformed fractions. These results confirm that indeed microstructure optimization can aid in increasing the resistance of steels to HIC. It also helps to identify the important factors which make steels more resistance to HIC, such as the reduction of dislocation density and homogenous grain distribution. Although, crystallographic texture has been reported to play a vital role in determining the susceptibility of steels to failure. In this study, its role was rather unclear, as cracking seemed to be highly dependent on microstructure. Perhaps, a study using steels with clearly different crystallographic texture, will facilitate a clearer evaluation of the role of crystallographic texture in the cracking of steels.
The results so far inspired a question regarding the possible microstructure that will be formed at higher heat treatment temperatures and the HIC behaviour of the structure. Thus, a higher solution temperature of 900 °C was applied and quenched in water, before tempering.

![Fig. 4.21. EBSD maps showing the EBSD orientation maps, grain boundary distribution, KAM map and recrystallized fraction for (a, b, c, d) 800QT-oil plate 1 and (e, f, g, h) 800QT-oil plate 2, respectively.]

4.6.4 Microstructure evaluation of the 900QT-water steels

From Fig 4. 17 d and h, which show the optical micrographs of the 900QT-water steels, the microstructures of both steels mainly comprised of bainitic structures, with evidence of the formation of martensite in both plates. Previous research has shown that the elemental composition of steels plays a major role in determining the phase transformation temperature of the steel. The interactions between substitutional alloying elements in steels such as Si-Cr, Si-Mo, Mn-Cr, Mn-Mo and so on, have been reported to have significant effects on reducing the martensite start temperature [151]. Hence, the variations in the elemental composition of the investigated steels, such as, the addition of Mo in plate 2, will certainly affect the transformation behaviour of the steels. 900QT-water plate 1 showed a more bainitic structure than 900QT-water plate 2, which still presented some polygonal ferrite grains in its microstructure. This result confirms that for the investigated steels, the temperature of 800 °C lies somewhere in the dual phase region of the steels, while 900 °C is most likely within the austenitic region. This is evident from the microstructures formed after quenching from these temperatures. Bainite usually forms due to the decomposition of prior austenite grains. Thus,
given that a large portion of bainite was observed, it can be inferred that a larger portion of the steel was converted to austenite during the heating process. This is expected as the alloying composition of the steels, especially plate 1, contain elements such as Ni, which helps to reduce the transformation temperatures.

After hydrogen charging, no visible cracks were observed in 900QT-water plate 2, however, some cracks were observed in 900QT-water plate 1. The cracks detected were much smaller and less severe than the ones seen in the as-received steels and the stress relieved steels. Fig. 4.22 shows the EBSD maps along the mid-thickness region of the 900QT-water steels, while Fig. 4.23 shows the electron image and the crack observed in 900QT-water plate 1.

![Fig. 4.22. EBSD maps showing the EBSD orientation maps, grain boundary distribution, KAM map and recrystallized fraction for (a, b, c, d) 900QT-water plate 1 and (e, f, g, h) 900QT-water plate 2, respectively.](image1)

![Fig. 4.23. Electron micrograph of crack and EBSD maps showing the EBSD orientation map and KAM map for (a, b, c) 900QT-water plate 1](image2)
It is believed that the greater resistance posed by the 900QT-water steels is because of the tough bainitic microstructure formed. This is supported by a less strained microstructure, with a very low deformed fraction, perhaps a slightly slower cooling rate will yield better results as observed in the 800QT-oil steels. It is worth mentioning that in Fig. 4.22c, 900QT-water plate 1 showed a higher dislocation density, which resulted in less recrystallized fraction in Fig. 4.22d. This is possibly due to the rapid quenching and the formation of a largely bainitic structure. However, this increase is not observed in 900QT-water plate 2. This could be a contributing factor to the cracks observed in 900QT-water plate 1 (Fig. 4.23). Also, the discontinuous crack observed in Fig. 4.23b, seems to selectively cut through certain grains, mainly {110} and {100} oriented grains. The {100} planes have been reported to be more susceptible to HIC [7]. However, going by the results of this study, more studies have to be done on the subject to fully make an assertion on the role of crystallographic texture in crack propagation.

With the changes in grain size, microstructural phases and dislocation density the mechanical properties of these steels will be altered, these will largely affect the implementation of the steels. However, this study focuses on identifying the important parameters which influence the HIC susceptibility and cracking behaviour of the investigated steels. Ultimately, it has been established that heat treatment schedules which alter the microstructure of steels have an effect on the cracking behaviour in steels. The cracking behaviour is largely dependent on microstructure as well as the dislocation density and recrystallized fraction. These factors can be linked to the diffusion and trapping behaviour within the steel; hence, they jointly influence the HIC susceptibility of steels.
CHAPTER FIVE

CONCLUSION

5.1 Overview

This concluding chapter briefly summarizes the works done in this study, highlights the key findings of this investigation and gives a few recommendations for future works.

5.2 Summary

The susceptibility of two X65 pipeline steel plates to hydrogen induced crack was investigated. The study commenced with the characterization of the as-received steels to gain knowledge of their mechanical properties and microstructure. This was done using mechanical tests as well as optical and scanning electron microscopy techniques. The optical micrographs helped in identifying the type and morphology of the dominant microstructural phases in the steels, which were mainly elongated ferrite structures and polygonal ferrite structures in plate 1 and plate 2, respectively. EBSD measurements were taken to ascertain several microstructural characteristics of the steels such as, their crystallographic orientation, grain boundary character distribution, grain size, local misorientation (which qualitatively approximates the dislocation density) as well as the deformed and recrystallized fraction of the steels. The plane of interest for the investigated steels was their TD – ND planes, thus, most examinations and tests in this study were conducted on that plane. After establishing the microstructural characteristics of the steels, hydrogen permeation and hydrogen microprint experiments were performed on the steels, to evaluate the diffusion and trapping characteristics, and to visualize the pathways of hydrogen through the steels.

The diffusion and trapping characteristics showed a clear correlation with the microstructural characteristics of the both steels investigated. Plate 1 with higher degrees of local misorientation (dislocation density) and smaller grain size had lower effective diffusivity, and higher hydrogen solubility than plate 2. As a result, the reversible trap to irreversible trap ratio was higher than that of plate 2. Also, the hydrogen microprint results clearly showed a high amount of hydrogen diffusion through the grain boundaries and through steel/inclusion interfaces, with less visible diffusion through the lattice (grains) of the steels investigated. Thus, indicating an important role of grain size and grain boundary character in the hydrogen diffusion and transport through steels.
Further tests were conducted to discover the cracking behaviour of the steels. Electrochemical hydrogen charging generated cracks in the steels. Both steels showed stepwise cracks (hydrogen induced cracks) mainly along their mid-thickness region. This is a common phenomenon, which has been attributed to the segregation of alloying elements during steel solidification and processing. However, the cracks interestingly differed in severity in both plates, with plate 1 showing a severe transgranular type crack while plate 2 exhibited less severe (less visible) cracks, which were mainly intergranular. Using EBSD scans around the crack path, several observations and deductions were made. These include the obvious difference in deformed and recrystallized fraction of the steels, which translated to a higher dislocation density in plate 1 and the presence of very fine grains and high angle grain boundaries around the crack path in plate 1. These observations corroborate the lower diffusion and high hydrogen solubility in plate 1. Hence, the microstructural features of plate 1 are believed to be responsible for the longer hydrogen residence in the steel, which in turn can locate existing microcracks through stress driven diffusion and accelerate crack propagation. The EDS scans of several crack sites also revealed the presence of complex carbide and carbonitride inclusions within the crack especially in plate 1 and some multi-elemental inclusions along the crack path. The presence of these precipitates and inclusions suggests that crack initiates around their interface with the steel matrix and propagates by linking with other cracks with the presence of diffusible hydrogen atoms. Also, an EDS scan of a crack initiation site in plate 2, confirmed the initiation of cracks in steels from non-metallic oxide inclusions. Most of the inclusions were also observed to be Si-enriched.

Several heat treatments, birthed from personal and research group experiences, were applied to the steels and their effect on HIC susceptibility was also studied. These treatments were performed to gain more knowledge on the role of microstructural transformation and the role of deformed and recrystallized fractions in steels. These heat treatments comprised of one stress relief schedule and three quenching and tempering schedules. The stress relief heat treatment was conducted at 550 °C for 1 hour followed by subsequent cooling in air. While during the three quenching and tempering treatments, the steels were: heated for one hour at 800 °C then quenched in water, heated for one hour at 800 °C then quenched in oil and finally, heated for one hour at 900 °C then quenched in water. All the quenched steels were tempered at 550 °C for 15 minutes, and then cooled in air.
The heat treatment schedules yielded more significant differences in microstructure and cracking behaviour for the quenched and tempered steels than in the stress relieved steels, which did not show significant change in microstructure. Thus, confirming that hydrogen induced cracking susceptibility is highly dependent on the microstructure of steels. However, an interesting observation after EBSD scans of the heat-treated steels revealed that HIC propagation is indeed influenced by the stored energy within the structure and grain size distribution. This is because with the reduction of the deformed fraction (low stored energy), and increase in the recrystallized grain fraction as well as a more homogenous microstructure, no visible crack was observed in both steels.

The investigations of the role of microstructure, hydrogen diffusion, and trapping allowed the determination of the HIC susceptibility of the steels. However, in this study, the correlation between the HIC behaviour and crystallographic texture was rather unclear. Further studies will be required to fully ascertain its role in HIC susceptibility.

### 5.3 Conclusions

Based on the material characterization, evaluation of diffusion parameters, and crack assessment of the two X65 pipeline steels, the following conclusions were drawn from this study.

1. The segregation zone at the mid-thickness region was identified as the most susceptible region to cracking in the investigated steels. Both plates exhibited hydrogen induced cracks across the segregated zone in the mid-thickness region parallel to the plate surface. The cracks initiated and propagated mainly through Si-enriched inclusions and complex carbide and carbonitride precipitates.

2. The most important microstructural characteristics related to crack formation (propagation) in the investigated steels were identified as grain size distribution and strain energy stored in the microstructure. Plate 1 with a smaller grain size (with areas having very fine grains) and higher lattice misorientation, had more severe transgranular cracks, while plate 2 with less stored strain exhibited more resistance to crack propagation.

3. The smaller grain size and strained microstructure of plate 1, resulted in a higher density of hydrogen trapping sites (especially reversible traps) than plate 2. This is because the
small grains and strained microstructure present more grain boundaries per surface area and a higher dislocation density.

4. High density of hydrogen traps, especially the reversible traps was clearly linked to the severity of HIC in investigated steels. The highly strained microstructure (high dislocation density) and high-volume fraction of HAGBs around the crack path contributed to the propagation of the severe cracks observed in plate 1.

5. The HIC behaviour in steels is related to their hydrogen diffusion and trapping characteristics. The reversible traps played a very important role in determining the severity of HIC in steels. While irreversible traps act as crack initiation sites, reversible traps supply hydrogen which facilitates crack propagation. Higher density of reversible traps reduces the hydrogen permeability and diffusivity and also increase apparent solubility of hydrogen in steels, hence, increasing their HIC susceptibility.

6. The hydrogen microprint results confirmed that the grain boundaries and phase interfaces are the main diffusion pathways for hydrogen transport through pipeline steels. This implies that an increase in grain boundaries per surface area will increase hydrogen solubility in steels.

7. Heat treatments which generated lower stored energy (dislocation density) and a more homogenous grain size in the steels helped to eliminate mid-thickness cracks. HIC susceptibility is highly dependent on the microstructure of the steel. However, contributing factors such as the stored energy (dislocation density) and grain size tend to influence the cracking behaviour, because of their links to hydrogen diffusion and trapping in steels.

5.4 Recommendations for future works

The observations in this study encouraged the identification of some potential research areas.

1. High resolution TEM investigation of plate 2 in this work, will help determine if the formation of fine innocuous and dispersed precipitates, like the (Ti,Mo)C precipitates (usually found in Ti and Mo bearing steels), contributed to the high density of irreversible traps recorded for the steel and their role in HIC resistance.

2. The mechanical properties and failure resistance of the heat-treated steels with no mid-thickness cracks in this study, should be further evaluated and compared with similar microstructures obtained through TMCP.
3. The role of crystallographic texture in HIC susceptibility should be studied using steels having similar composition and microstructure but distinctly different crystallographic texture. Macrotexture and microtexture should be considered during the study.
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APPENDIX A

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APPENDIX B

EXPERIMENTAL MACHINES AND EQUIPMENT

Photographs of some important machines and experimental set-ups used in this study are presented below.

Fig. B.1. (a) Buehler SimpliMet XPS1 automatic compression mounting system (b) LaboPol-20 manual polishing machine (c) MVK-H1 Mitutoyo Vickers hardness tester

Fig. B.2. Hitachi SU6600 scanning electron microscope
Fig. B.3. (a) Photograph of the hydrogen permeation experimental set-up (b) photograph of the permeation current recorded by Gamry software

Fig. B.4. (a) Nikon Eclipse MA100 inverted optical microscope (b) Buehler Vibromet 2 vibratory polisher (c) Thermo Scientific Thermolyne F48028 muffle furnace