An Investigation of Bent-Beam Stress-Corrosion Test for Titanium Alloys

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Materials Engineering, master's level
2019

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Abstract

Titanium alloys are highly resistant to all types of corrosion due to their excellent ability to form an oxide film on the surface. However, under certain circumstances, these alloys may experience an environmental degradation which could potentially, under the application of mechanical stress, lead to a complete failure of the material. One of these cracking processes is stress-corrosion cracking (SCC). SCC has an embrittling effect on otherwise ductile materials under tensile stress. Since titanium alloys are frequently used in the aerospace industry and it is therefore of interest to test these alloys in different environments in order to prevent any future accidents. SCC testing is frequently tested at GKN Aerospace and a new testing method is of interest. The main objective with this work was to gain knowledge of the testing method.

Bent-beam testing method has been used to investigate stress-corrosion cracking (SCC) of titanium alloys in a laboratory based experiment. The bent-beam testing method was of type 2-point bent beam test, where a saline solution was applied at the apex of the specimen. The specimens were loaded to a range of stresses from 40%, to 95% of the materials yield strength and the salt concentration in the saline solution was 1wt% and 3wt%. By doing so, a relative susceptibility of the different alloys could be established. Three different titanium alloys were tested: Ti-6Al-4V, Ti-8Al-1Mo-1V, and Ti-6Al-2Sn-4Zr-2Mo. The testing method was able to cause cracking on all titanium alloys, where Ti-6Al-4V was found to be the least susceptible to SCC. Ti-8Al-1Mo-1V, and Ti-6Al-2Sn-4Zr-2Mo showed an overall high susceptibility to SCC as cracking occurred in all testing configurations. Cracking was observed on both the surface of the specimen as well as in the cross sections, where the cracks grew perpendicular to the surface. SEM was also used to evaluate the crack propagation in Ti-8Al-1Mo-1V, and Ti-6Al-2Sn-4Zr-2Mo, and it was found that the cracks grew mostly along the grain boundaries.

Keywords: Hot-salt, Stress-corrosion cracking, titanium alloy, hydrogen embrittlement, brittle fracture.
Acknowledgements

The work presented in this report was conducted between September 2018 and February 2019 at the chemical and mechanical engineering department at GKN Aerospace Sweden AB.

First and foremost, I would like to show my greatest gratitude to GKN Aerospace and Karin Ericson for giving me the opportunity to conduct my master thesis at their facilities.

I would like to thank my supervisors: Monica Skog Brönnestam, Per-Henrik Danielsson, and Joel Mattsson for their constant support and guidance during the execution of this master thesis. A special thanks to Dr. Pia Åkerfeldt at Luleå university of technology for her constant encouragement and knowledge throughout the whole project. I would also like to thank Johan Johansson for his assistance with the operation of the furnace, and all the engineers at the materials laboratory for providing an inspiring and encouraging atmosphere, thank you.

Daniel León Zapata
If everything seems under control, you’re just not going fast enough.

Mario Andretti
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1

Introduction

This master thesis was conducted at the facilities of GKN Aerospace Sweden AB in Trollhättan. This chapter will therefore briefly introduce the company, give background to this project and introduce the problem formulation, Aim, objective, Scope and limitations of this study and lastly give an outline of how this report is structured.

1.1 GKN Aerospace

GKN is a global engineering company and its origins can be traced back to the birth of the industrial revolution as it was founded in the south of Wales in 1759. Over the course of 260 years, GKN has developed into a world leading technology company with approximately 58,000 employees in 30 countries. GKN is divided into five different divisions: Aerospace, Driveline, Powder Metallurgy, Off-Highway Powertrain, and Wheels & Structures.[1]

GKN Aerospace is one of the worlds largest suppliers to the aviation industry, both commercial and military, with more than 17,000 employees in around 50 manufacturing sites distributed over 15 countries. The products consists of aerostructures, engine components, and special products. The production site in Trollhättan with approximately 2000 employees, is the head quarters of the subdivision Engine Systems. In addition to Sweden, GKN Aerospace Engine Systems also has production sites in USA, Norway, and Mexico. The technology produced by GKN Aerospace Engine systems can be found in 90% of todays commercial aircrafts flights.[1] Figure 1.1 presents an aero-engine and its different key components.
1. Introduction

Figure 1.1: Schematic view of an aero-engine.[1]

1.2 Background

The high demand on performance drove the military and civil supersonic aircraft industry to go from wood structured aircrafts, in the beginning of the twentieth century [2], to all-metal structures in post-world war II.[15] The high mechanical properties of metals made the material an excellent candidate for airframe and gas turbine applications. By going from natural based materials, the metallic aircraft components possessed more consistent properties and eliminated problems of moisture and fungus found in wooden structures. However, metals suffer from their own type of environmental degradation in form of corrosion, hydrogen embrittlement and stress corrosion cracking (SCC).[15]

Stress corrosion cracking has been a worrying concern to the aerospace industry for almost 60 years and most of the SCC service failures were on aluminum alloy components. For titanium alloy components however, there are no reports of SCC service failures. Titanium possesses excellent corrosion resistance attributed to its ability to create a protective barrier on its surface when in contact with oxygen and is therefore considered to be highly resistant to stress corrosion cracking. However, the lack of in-service failures is a mystery since the phenomenon has been observed in laboratory testing, when the material has been exposed to certain environments. The discrepancy between the results of laboratory testing and actual in-service observations are not fully understood, even though several explanations have been proposed[34, 35].

Nevertheless, the aerospace industry still has an urge to map all possible environments which may induce SCC in aerospace materials to avoid potential accidents and other unforeseen failures, specially with the recent renewed interest of space exploration along with the constant development of new alloys. A laboratory testing is usually the way to go for mapping SCC susceptibility of materials, since it is often unpractical to test actual structural components.
1.3 Problem Formulation

Stress corrosion cracking has been tested at GKN Aerospace using a testing method which required Ti-8Al-1Mo-1V as testing material. The alloy, however is no longer available for purchase. Besides, the old testing method was of the type 'U-bend method' which gave an extreme way of testing since the actual components never experience that type of plastic deformation. Furthermore, the test method had some difficulties in validation of the test and it was common that the test was rejected and re-run several times. GKN Aerospace initiated this work to explore a new testing method for SCC.

The testing method of interest is a two-point bending test method which belongs to the group 'bent-beam test'.

1.4 Scope of Work

The thesis centers around the two-point testing method for stress-corrosion cracking. The primary objective has been to gain knowledge of the testing method and to assess whether or not the method is applicable to titanium alloys. The following subtasks were carried out in order to reach this objective:

- Performing a literature study to fully understand the methods advantages and drawbacks.
- **Validation of the methods** capability to induce SCC in titanium alloys for SCC assessment. The main focus of this subtask was to find parameters for which the alloys are susceptible to SCC with this test method.
- **Investigation of the SCC behavior** of the chosen alloys. To see how the different titanium alloys behave in comparison to each other when tested under the same conditions.
- **Verify the results** to the literature. Are the results dependent on the type of testing method?
- **Evaluate a substitute for Ti-8Al-1Mo-1V**. Due to the unavailability of the titanium alloy, it is of interest to find a substitute alloy.

1.5 Limitations

The project was conducted in 20 weeks and required some limitations. The set limitations are formulated below.

- Three titanium alloys were considered in this work: Ti-6Al-4V, Ti-8Al-1Mo-1V, and Ti-6Al-2Sn-4Zr-2Mo.
- 2 parameters were varied: Mechanical stress and salt concentrations.
- Temperature and time were held constant.
- This work only investigates the 2-point bending test method.
1.6 Thesis outline

This report is divided into 6 different chapters

- Introduction - This chapter aims in introducing the reader to the project by giving a brief presentation to GKN Aerospace, background information to the project and the problem formulation tied it.
- Theoretical Background - this chapter covers the fundamentals necessary for further understanding the work presented in the project.
- Experimental - The practical part of the work is presented in this chapter. This chapter describes the chosen testing method, the methodology of said method, the materials used in present work, specimen preparation, and examination.
- Results - The results from the testing methods are presented in this chapter.
- Discussion - The results are discussed based on the knowledge gained from the theoretical background chapter.
- Conclusion & Furtherwork.
2 Theoretical Background

This chapter covers the fundamentals necessary for understanding the project. The material used in this work, titanium and its alloys are firstly introduced. This is followed by an introduction to the fundamentals of the broad term stress-corrosion cracking and its different mechanisms.

2.1 Titanium Alloys

Titanium was discovered by William the British reverend in 1791 by producing titanium oxide from magnetic sand from a local river. Martin Heinrich Klaproth found titanium oxide independently four years later from a Hungarian mineral and named it 'rutile'. The name titanium was given by Klaproth where he found inspiration from the children of Uranos and Gaia, the titans, in Greek mythology. The production of pure titanium had to wait more than 100 years, before Matthew Albert Hinter succeeded to isolate the metal in 1910. The commercialization of titanium begun with Wilhelm Justin Kroll (often referred as the father of the titanium industry) who managed to produce titanium by combining TiCl$_4$ with a reducing agent, in a process called 'Kroll process'. The DuPont company was the first to produce titanium commercially in the year 1948 and by the 1950’s, titanium was considered a key material for aircraft engines. [3] Titanium is still to date an important material in the military and aerospace industry and with the recent interest in additive manufacturing of titanium and its alloys indicates that the titanium market might by heading to a bright future.[5, 6]

2.1.1 Properties & Applications

Titanium is considered to be part of the category 'light metals', along with metals e.g aluminium, magnesium, and beryllium. In fact, with a density of 4.51 g cm$^{-3}$, titanium is the heaviest light metal in this category (Figure 2.1a), doubling the weight of aluminium. [3] However, titanium and its alloys have a higher strength-to-weight ratio (specific strength) than most metals up to temperatures of 500-600°C, making them particularly attractive to the aerospace industry and explains why it is the largest consumer of the material.[3, 4, 5] The high strength at elevated temperatures give titanium an important advantage over other aerospace materials. Figure 2.1b shows the specific strength of different materials and how it is affected by temperature. It can be seen that titanium alloys have high specific strength at high temperatures and only at temperatures below 300°C do carbon fiber reinforced plastic...
(CFRP) have a higher specific strength in comparison to titanium alloys.[3] For this reason, titanium is often selected for components with a service temperature that is too high for aluminium alloys or composite materials, but with sufficiently low loads where the use of steel or nickel superalloys are not required. These components are gas turbine engines, fuel storage tanks, and other high-temperature applications. The strength of the titanium gradually reduces as temperature increases. The maximum application temperature of titanium (400-450°C) is dependent on the oxidizing behavior of the material.[3] Above this point, the material loses its strength, as seen in Figure 2.1b.

![Figure 2.1: Comparison of the properties of titanium and its alloys to other materials.](image)

Besides high strength, titanium alloys also have good fatigue resistance, creep resistance at high temperature and excellent corrosion resistance. The resistance to corrosion is due to ability of titanium to react to oxygen and instantly form a thin protective oxide film on its surface when exposed to air. This oxide layer is resistant to most corrosive agents. Furthermore, the resistance to corrosion of titanium is better than that of high-strength aluminium alloys. For this reason, titanium is often used, instead of aluminum, in aircraft structures when the corrosion resistance is prioritized. [4]

In the late 1980’s, 80% of the produced titanium was used in the aerospace industry. This value has decreased to 50% since the demand of titanium in other sectors have increased.[5] The biocompatibility of the metal and in combination to corrosion resistance, makes titanium attractive for medical use. In fact, titanium is often the choice when producing artificial knees, hip-joints and teeth.[6]

### 2.1.2 Crystallography & Metallurgy

Titanium is an allotropic material, meaning that it has two crystalline phases. The stability of the crystal structure is dependent on the temperature. For pure titanium, hexagonal close packed (HCP) $\alpha$-titanium is stable in room temperature and
at temperatures up to 882±2°C. Above this temperature, an allotropic transformation occurs where the α-titanium (or α-phase) transforms to a body-centered cubic (BCC) phase, referred as β-titanium (or β-phase). Figure 2.2 shows the unit cells of α- and β-titanium along with their most densely packed planes. [3]

Figure 2.2: The two crystalline phases of titanium. Hexagonal close packed to the left and Body-centered cubic to the right.[3]

The α to β phase transformation temperature is known as the β-transus temperature and is strongly dependent on the purity of the material. The incorporating of alloying elements into the solid solution can affect the material in three different ways: (i) Stabilization of the α-phase, (ii) stabilization of the β-phase, or (iii) solid solution strengthening.[6] The β-transus temperature is thus risen or lowered depending of alloy. Interstitial elements such as carbon, aluminium, and oxygen increases the β-transus temperature and thus stabilizes the α-phase. Moreover, a two-phase α+β field is also created by incorporating α-stabilizers. Elements like hydrogen and molybdenum, on the other hand, act as β-stabilizers and hence lowers the β-transus temperature. Furthermore, β-stabilizers can be divided into two subgroups: β-isomorphous and β-euctectoid elements, where the elements with high solubility in titanium belong to β-isomorphous group, and the elements with limited solubility and form intermetallics belong to β-euctectoid groups. An illustration on how the elements affect the β-transus temperature can be seen in Figure 2.3.[3, 4, 5]

The β-transus temperature is of great importance since it takes place during thermomechanical processing of the material and affects the final microstructure of the material, and thus the materials final properties. [3, 4, 6]
2. Theoretical Background

2.1.3 Alloy Classification

There exist more than 100 known titanium alloys, where 20-30 have reached commercial status. The alloys are divided into different classes depending on the phase dominating the alloy at room temperature. The three main classes of titanium alloys are: \( \alpha \), \( \alpha + \beta \), and \( \beta \) alloys. Moreover, \( \alpha \) and \( \beta \) alloys can be further divided into two subclasses: near-\( \alpha \) and near-\( \beta \).[3] Figure 2.4 gives the properties of different titanium alloys. It can be seen that even though the chemical composition is more or less identical, their different crystal structures give the different alloys different properties. This means that \( \alpha \)-titanium and \( \beta \)-titanium are applicable in different parts of an aerospace engine depending on the requirements of the component and/or the material.[4]

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<td>1000</td>
<td>128</td>
</tr>
<tr>
<td>Carbon-epoxy composite*</td>
<td>1.7</td>
<td>50</td>
<td>29.4</td>
<td>760</td>
<td>450</td>
</tr>
</tbody>
</table>

Figure 2.4: Properties of Different Alloys. [4]
2.1.3.1 \( \alpha \) & near-\( \alpha \) alloys

Characteristic properties of \( \alpha \)-alloys are: excellent resistance to corrosion, good workability and good weldability.\[5\] The primarily use of \( \alpha \)-alloys are therefore in the chemical and process engineering industry. Commercially pure (CP) titanium belongs to this class, where the differences between grades are their content of oxygen. Oxygen is an \( \alpha \)-stabilizer and the incorporation of the interstitial element affect the materials mechanical properties. Oxygen increases the strength of the alloy but simultaneously reduces the ductility. Near-\( \alpha \) titanium alloys contain a small amount of \( \beta \)-stabilizers, e.g Mo and V. This type of alloy have excellent creep resistance and high strength, making them very suitable for high-temperature applications, with an upper operation limit of 500-550\( ^{\circ} \)C.\[3\] \( \alpha \) and near-\( \alpha \) alloys contain \( \alpha \)-stabilizers like aluminium and oxygen, elements that have been shown to increase susceptibility to stress-corrosion cracking.\[5\] Titanium alloys such as Ti-8Al-1Mo-1V and Ti-6Al-2Sn-4Zr-2Mo belong to this class.

2.1.3.2 \( \alpha + \beta \) alloys

Alloys in this class have an equilibrium of two phases (\( \alpha \) and \( \beta \)) present in the microstructure at room temperature by the addition of both \( \alpha \)- and \( \beta \)-stabilizers. As a result, this type of alloy have a superior combination of strength and ductility in comparison to the two other classes of titanium alloys. The amount of \( \beta \)-phase can vary and is dependent on the amount on \( \beta \)-stabilizers and the thermomechanical process.\[6\] Furthermore, the susceptibility of stress-corrosion cracking can vary depending on the amount of \( \beta \)-phase present in the microstructure, since the \( \beta \)-phase has been shown to increase the resistance to stress-corrosion cracking.\[5\] Ti-6Al-4V belongs to this class and is the most common titanium alloy in use today. It is by far the most tested titanium alloy and is mainly used in the aerospace industry.\[3\]

2.1.3.3 \( \beta \) & near-\( \beta \) alloys

This class is also referred as metastable \( \beta \) titanium alloys since the phase is in a metastable state, where cold working or heating the alloy may result in partial transformation to \( \alpha \)-phase.\[5, 6\] The phase is usually stabilized by \( \beta \) isomorphous stabilizers, e.g: V, Nb, Cr and Mo, and a minimum of 10% of solutes is required in order to stabilize the phase during quenching. As a result, the stabilization of the \( \beta \)-phase suppresses the martensitic transformation upon fast cooling. \( \beta \) alloys exhibit the highest strength to weight ratios and have good combination of strength, toughness and fatigue resistance. Some drawbacks in comparison to \( \alpha + \beta \) alloys are high density, small processing window, and higher cost.\[3\]

2.1.4 Oxidation of Titanium Alloys

The maximum service temperature of titanium alloys are closely related to the oxidation behavior of the material. The oxidation of titanium alloys occurs when the material is exposed to elevated temperatures in oxygen containing environments.
During oxidation, two reactions occurs simultaneously: (i) the formation of an oxide film and (ii) inward diffusion of oxygen into the base material.[9]

### 2.1.4.1 Oxide Film

It was mentioned earlier that titanium has the ability to form a protective oxide film when in contact with oxygen. In fact, it is this property that makes titanium and its alloys to possess a high resistance to corrosion. The formation of the oxide film, or scale, begins with the decomposition of oxygen molecules at the metal surface. Subsequently, the oxygen atoms are adsorbed onto the metal surface. The adsorption can either be physical, where oxygen atoms bond with the metal surface with weak Van der Waals forces, or through chemisorption, where stable chemical bonds are formed.[7] Once the metal surface is saturated with adsorbed oxygen atoms, oxide nuclei are formed. The nuclei grows laterally until a compact and uniform oxide film is created. The oxide film covers the metal surface completely and separates the metal from the environment, hence protecting the base material. The further growth of the oxide film is mainly controlled by mass transport through the oxide film. [3] The four different steps in the oxidation of titanium are illustrated in Figure 2.5.

![Figure 2.5: Schematic illustration on the formation of the oxide film on a metallic surface.][3] (a) Oxygen adsorption, (b) formation of nuclei, (c) lateral growth of nuclei, and (d) further growth of the oxide film.

The growth of the compact oxide film is allowed trough mass transportation of charged elements, i.e electrons and ions, thus behaving like a semiconductor. The conductivity of the oxides is largely dependent on the defects, i.e vacancies, of the metal oxides and are classified into n- and p-type semiconductors. Which type of semiconductor the oxide is, depends on the imperfections and the conductivity of the metal oxides.[3] In general, n-type oxides tend to grow inwards into the bulk material, whereas the p-type oxides grow outwards. Titanium oxidize and forms a n-type oxide film which act as a diffusion zone. As a result, the oxygen ions diffuse through the oxide film until reaching and reacting further with the bulk material, hence growing the oxide film inwards.[7, 9]

Titanium can form different types of thermodynamic stable oxide films depending on temperature and pressure. However, rutile TiO$_2$ is the only oxide reported for
titanium alloys oxidizing at temperatures below 1000°C and at near-atmospheric pressures [7], even though thermodynamical calculations of ternary Ti-Al-O phase diagrams have shown that Al₂O₃ should (in theory) be more stable than rutile. The reason for the discrepancy between experimental and thermodynamic calculated Ti-Al-O phase diagram is believed to the neglection of oxygen solubilities in the various Ti-Al phases by the thermodynamic calculations. [3] Moreover, at exposure to temperatures above 480°C, Ti-6Al-4V has shown to have a multilayered structured oxide film consisting of TiO₂ and Al₂O₃.[9]

2.1.4.2 Alpha Case

The oxidation of titanium in high temperatures also involve the formation of an oxygen enriched subsurface layer which is often referred as alpha case. When the titanium alloy is exposed to temperatures above 480°C in an oxygen containing environment, the diffusion rate of oxygen into the region adjacent to the exposed surface increases rapidly. Oxygen has a high solubility of about 14.5 wt% in α and it will therefore diffuse into the α-phase by occupying free interstitial positions, preferably in the octahedral interstitial positions, in the hexagonal close-packed crystal structure.[7] Since oxygen is an α-phase stabilizer, the incorporation of the element contributes to the raise of the β-transus temperature and promotes the β to α phase transformation. As a result, an oxygen enriched α-phase region (hence the name alpha case) is created. The formation of alpha case has a detrimental effect on the surface of the material as it affects its ductility and fatigue resistance significantly.[10] This is due to the solid strengthening effect produced by the oxygen in the crystal lattice. Figure 2.6 illustrates the alpha case in two different titanium alloys. The alpha case can be seen as the bright layer near the surface.

![Figure 2.6: Optical micrographs showcasing alpha case in (a) Ti-6Al-2Sn-4Zr-2Mo and (b) Ti-6Al-4V.][11]

2.1.5 Chemical Milling

The manufacturing process of titanium alloys in aerospace applications involves many different types of thermomechanical operations and post processing heat treatments which are all normally performed in elevated temperature and in an oxygen containing environment.[12] As mentioned earlier, titanium alloys are highly reactive
with oxygen under such conditions and forms an oxide film and an oxygen enriched layer commonly known as alpha case. It is common in the aerospace industry to turn to chemical milling (often referred as etching) in order to eliminate surface and subsurface oxygen contamination, i.e. oxide film and alpha case, since it is well known the detrimental effects that oxidation can have on the mechanical properties of the surface of titanium alloys. An ideal chemical milling treatment removes all the oxygen impurities without dissolving the base material and thus leaving an acceptable surface finish with no post processing operations.[7] The passive film formation ability of titanium alloys makes the material resistant to most oxidizing reagents. Hydrofluoric acid (HF) has been found to effectively remove oxygen contamination in titanium alloys and is conventionally used for this purpose. HF has the ability to remove the protective oxide film of the material through a combination of chemical and electrochemical reactions. The dissolution process occurs at the metal/acid solution interface via the following chemical reactions[7, 12]:

\[
\begin{align*}
TiO_2(s) + 6HF(aq) & \rightarrow [TiF_6]^{2-} + 2H_3O^+ \quad (2.1) \\
Ti(s) + 6HF(aq) & \rightarrow H_2TiF_6(aq) + 2H_2(g) \quad (2.2) \\
3H_2(g) + 2HNO_3(aq) & \rightarrow 2NO(g) + 4H_2O(l) \quad (2.3) \\
3TiO_2(s) + 18HF(aq) + 4HNO_3(aq) & \rightarrow 3H_2TiF_6(aq) + 4NO(g) + 8H_2O(l) \quad (2.4)
\end{align*}
\]

In reaction 2.1, HF attacks the passive oxide film (TiO$_2$) by dissolving it and resulting in formation of soluble titanium hexafluoro complexes. Once the HF reaches the base material, a reaction will occur where once again, a titanium hexafluoro complex is formed along with hydrogen gas (Eq.2.2). The formation of hydrogen gas is undesired since it could lead to hydrogen embrittlement due to hydride formation. It is therefore common practice to add HNO$_3$ into the etching solution in order to hinder the formation hydrogen gas. [7, 12] Reaction 2.3 shows how HNO$_3$ reacts with the hydrogen gas and oxidizes it into water and NO$_x$ gases (a mixture of NO and NO$_2$ gases).[12] A merging of reactions 2.1, 2.2 and 2.3 are presented in reaction 2.4. Furthermore, HNO$_3$ also reacts with the substrate material by oxidizing it and re-forming a passive film which is contaminated by nitric groups.[7, 12]

\[
3Ti(s) + 10HNO_3(aq) \rightarrow 2TiO(NO_3)_2(aq) + 5H_2O(l) + 4NO(g) \quad (2.5)
\]

The HF dissolves the newly formed passive film in reaction 2.5, into soluble hexafluoro complexes and NO$_x$ gas. Reaction 2.4 happens continuously resulting in a continuous metal dissolution. An overall chemical reaction of this process can be seen below[7]

\[
Ti + nHF + HNO_3 \rightarrow TiF_{n(4-n)} + N_2O + 2\frac{1}{2}H_2O + (n - 4)H^+ \quad (2.6)
\]

The dissolution rate of the metal is affected by several factors and by controlling these, a controlled removal rate can be achieved. Factors affecting the removal rate are molar concentration between the two acids, temperature, agitation, and age of the bath solution.[7] HF promotes the dissolution rate of the material and the increase of HF in the etching solution has shown to increase the removal rate. On the
other hand, the increase of HNO\textsubscript{3} have opposite effect on the dissolution rate. It is therefore important to have a good ratio between HNO\textsubscript{3}/HF in the etching solution. For Ti-6AL-4V, it has been found that in order to achieve acceptable surface finish and fatigue properties after chemical milling in the aviation industry, the HNO\textsubscript{3} should be kept below 20\% and HF below 2.5\%.[13] The temperature also influences on the dissolution rate. As the temperature increases, so does the removal rate of the etching solution on the material. However, at temperatures above 55\(^\circ\)C and excessive formation of toxic NO\textsubscript{x} gas might lead to increase of surface roughness. The agitation of the etching solution contributes to a uniform attack on the surface of the material, hence a better surface finish.[7]

2.2 Stress-Corrosion Cracking

Stress-corrosion cracking (SCC) is a slow mechanical-environmental failure mechanism caused by a combined simultaneous interaction between mechanical and chemical forces. The result is a brittle failure of an otherwise ductile material caused by relatively low stresses. In fact, the stresses necessary to propagate a crack under SCC conditions can be as low as 5\% of the yield stress.[14, 15] The stresses involved in SCC may be externally applied or may also be residual stresses caused by manufacturing of the material. Moreover, residual stresses are usually the cause of most SCC failures.[14] Three simultaneous conditions need to be satisfied for SCC to occur: A susceptible alloy, an aggressive corrosive environment and a static tensile stress (Fig. 2.7). These conditions work in synergy, meaning that if either the stress or the corrosive media were suppressed, the result would not be the same. Hence, these factors do not cause SCC independently.

![Venn Diagram for Stress-corrosion cracking.](image)

There is a similar form of corrosion called corrosion fatigue (CF) where the key difference is that CF requires a cyclic stress, instead of a static stress. SCC is a process that occurs inside the material, where the cracks propagate inside the internal structure. Often, the outer surface is left unharmed, making the detection of SCC difficult. This makes it a dangerous form of corrosion since a catastrophic failure may occur at stress levels within the service stress range of the material. The threshold stress-intensity factor, \(K_{ISCC}\), depicts the minimum required stress for the crack to propagate under SCC conditions. Below \(K_{ISCC}\), no crack propagation occurs. \(K_{ISCC}\) is dependent on the alloy and the service environment and is typically much less than the critical stress intensity factor, \(K_I\). This suggest that, under SCC
conditions, cracking may occur at stress levels much lower than for cracking in an inert environment. Figure 2.8 shows the crack propagation rate plotted against the stress intensity, \( K_I \), and three regions can be distinguished. Region I shows a dependency between the crack propagation rate and \( K_I \). In this region, the crack propagation rate increases rapidly with increasing of \( K_I \). Region II exhibit a plateau, showing little to no dependency of the crack propagation on \( K_I \). In region III, the crack propagation rate exhibits, once again a dependency on \( K_I \). The crack propagation rate increases rapidly as \( K_I \) approaches to the critical stress-intensity level, \( K_{IC} \), for mechanical fracture in an inert environment. Once \( K_{IC} \) is reached, the fracture ends in a catastrophic failure.[14]

![Figure 2.8: Typical crack propagation rate as a function of stress intensity factor.[14]](image)

### 2.2.1 Crack Initiation

Surface discontinuities and flaws caused by machining, e.g grooves, laps or burrs, have been found to act as initiation sites for SCC. Other initiation sites for SCC are corrosion pits and/or intergranular corrosion that occurs during exposure to a corrosive environment during service. Crack initiation mechanisms are often complicated and few well-developed models have been established. The reasons are many to why that is the case, e.g the lack of definition to when a pit becomes a crack or difficulty in determining when intergranular corrosion becomes intergranular corrosion caused by SCC. [14]

### 2.2.2 Crack Propagation Mechanisms

SCC cracks tend to propagate perpendicular to the direction of the stress and can propagate either intergranular och transgranular. In fact, both types have been observed on the same fracture surface caused by SCC.[14] Different mechanisms have been proposed for describing the crack propagation during SCC but there
is, however, no mechanism to date that describes all cases of SCC. The different propagation mechanisms of SCC can be categorized into two sections:

- Dissolution Based Mechanisms
- Mechanical Based Mechanisms

Below follows the most used mechanisms that describes SCC crack propagation. These mechanisms can contribute to SCC alone or in collaboration with one another. [14, 17]

2.2.2.1 Dissolution Based Mechanisms

This mechanism refers to when the crack propagation is driven by an anodic reaction at the crack tip, resulting in a dissolution of the material.

Active Path Dissolution

An active path is a narrow path inside the material that is more susceptible to corrosion in comparison to the relatively more passive bulk material. The reason to the increase in corrosion susceptibility is due to the local segregation of corrosion resistant alloying elements caused by manufacturing process. An example of this is sensitized austenitic steels which precipitates chromium carbides along the grain boundaries. This results in a local depletion of corrosion resistant element chromium in the solid solution, and an increase in a local corrosion susceptibility along the grain boundary is created, hence creating an active path. Active path dissolution can happen without any stress. In the presence of stress, the crack tip is opened and increasing the dissolution rate since corrosion products are allowed to transport away easier from the crack tip. In this example, the crack would be referred as intergranular SCC.[18]

Film Rupture Model

A passive film forms at the surface on the material when the material is exposed to a corrosive environment, and thus protects the material. The stress associated with SCC ruptures this protective film at the crack tip, typically in a brittle manner, exposing the base material and consequently allowing dissolution. [14, 17, 18] There are two different version of this model. The first one assumes that once the passive film at the crack tip is ruptured, the dissolution rate is higher than the re-passivation rate, resulting in a continuous crack propagation. For the second version, the passive film is restored. The passive film is ruptured periodically by the emergence of slip steps, leading to a discontinuous crack propagation. The discontinuity in the crack propagation leaves crack arrest markings.[14, 17] Figure 2.9 illustrates both versions of the film rupture model.
2. Theoretical Background

Figure 2.9: Schematic representation of film rupture model. (a) Crack propagation occurs in a continuous manner. (b) Crack propagates in a step-wise (discontinuous) manner. [17]

The dissolution models "Active path" and "Film rupture" are generally accepted mechanisms to describe most cases of intergranular SCC.[14, 17]

2.2.2.2 Mechanical Fracture models

These models suggest that the fracture occurs due to stress concentrations rather than dissolution of the material. Several mechanisms have been proposed but only the more prominent are presented.

The Adsorption-Induce Brittle Fracture
This models is also referred as the Stress-sorption model and suggest that adsorption of environmental species lowers the interatomic bond strength and the stress required for cleavage fracture. The crack propagation proceeds by weakening of the already strained atomic bonds at the crack tip, rather than by chemical or electro-chemical dissolution.[42]

Tarnish-Rupture Model
This model was originally proposed to explain the discontinuous transgranular crack growth. The model suggest that a brittle surface film forms on the surface on the metal and fractures when stress is applied. In the same process, a small crack is also created in the metal. The bare metal is consequently exposed to the environment, which rapidly re-forms the surface film. The crack propagates by this cycle of growth and fracture of the film. The model was later modify for intergranular SCC, where it was proposed that the tarnish penetrates along the grain boundary ahead of the crack tip.[14]

The Corrosion Tunnel Model
This model explains a combination of dissolution and mechanical fracture. A fine array of small corrosion tunnels at emerging slip steps are assumed to form. The tunnels grow in a diameter and length until the stresses in the remaining ligaments
are large enough to cause a ductile deformation and fracture. However, grooves and microvoids should be present on the fracture surface according to the model, which has not been experimentally observed. The model has thus been modified, where it was suggested that the application of tensile stress results in a change in the morphology of the corrosion damage from tunnels to thin, flat slots.[14]

2.2.3 Factors Affecting Stress-Corrosion Cracking

There are several factors that contribute to SCC and these factors can be tied to the material or alloy system, the environment and mechanical attributes. Altering any of the factors may alter the corrosion rate by either reducing or increasing the rate of propagation. [14] Extensive research have been conducted by American Society for Metals (ASM) on the SCC behavior relative to alloy systems and it was concluded that nearly all structural alloys are susceptible to SCC in the right conditions, e.g alloy chemistry, metallurgical, and service conditions.[20] Table 2.1 lists some of the factors that affect SCC.

Table 2.1: Different factors affecting SCC.

<table>
<thead>
<tr>
<th>Materials Factors</th>
<th>Environmental Factors</th>
<th>Mechanical Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>Temperature</td>
<td>Stress</td>
</tr>
<tr>
<td>Microstructure</td>
<td>pH</td>
<td>Strain rate</td>
</tr>
<tr>
<td>Contaminants</td>
<td>Electrochemical Potential</td>
<td></td>
</tr>
<tr>
<td>Grain size</td>
<td>Solute species</td>
<td></td>
</tr>
<tr>
<td>Grain orientation</td>
<td>Solute concentration</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oxygen concentration</td>
<td></td>
</tr>
</tbody>
</table>

The environment is tied to a specific alloy, meaning that an environment that causes SCC on one alloy, may not cause SCC on another alloy. Table 2.2 presents the most common observed alloy-environment combination exhibiting SCC. The temperature also affects differently as an alloy can be immune to corrosion in one temperature, but the same alloy may be susceptible to SCC when exposed to another temperature.

Table 2.2: Alloy-environment systems exhibiting SCC. [14]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Steel</td>
<td>Hot nitrate, hydroxide, and carbonate/bicarbonate solutions</td>
</tr>
<tr>
<td>High-strength steels</td>
<td>Aqueous electrolytes, particularly when containing H₂S</td>
</tr>
<tr>
<td>Austenitic stainless steels</td>
<td>Hot, concentrated chloride solutions; chloride-contaminated steam</td>
</tr>
<tr>
<td>High-nickel alloys</td>
<td>High-purity steam</td>
</tr>
<tr>
<td>a-brass</td>
<td>Ammoniacal solutions</td>
</tr>
<tr>
<td>Aluminium alloys</td>
<td>Aqueous Cl⁻, Br⁻, and I⁻ solutions</td>
</tr>
<tr>
<td>Titanium alloys</td>
<td>Aqueous Cl⁻, Br⁻, and I⁻ solutions; organic liquids; N₂O₄</td>
</tr>
<tr>
<td>Magnesium alloys</td>
<td>Aqueous Cl⁻ solutions</td>
</tr>
<tr>
<td>Zirconium alloys</td>
<td>Aqueous Cl⁻ solutions; organic liquids; I₂ at 350°C</td>
</tr>
</tbody>
</table>
2.3 Stress-Corrosion Cracking of Titanium Alloys

Titanium have great resistance to all types of corrosion due to its ability to passivate by forming a tenacious, self-healing oxide film of primarily TiO$_2$. Most commercial titanium alloys exhibit excellent resistance to SCC in most service environment concerning aerospace applications. However, several unique conditions have been found to promote SCC. [19] The first report of SCC of titanium alloys was in 1953 by Keifer and Harple [23], where cracking in commercially pure titanium in red fuming nitric acid was observed. A couple of years later, in the mid 1950’s, "hot-salt cracking" of titanium alloys was discovered in turbine blades when being creep tested.[23] In 1965, Brown was the first to report SCC of titanium alloy in an aqueous environment at room temperature, where its was discovered that Ti-8Al-1Mo-1V alloy was susceptible to SCC in sea water.[19, 23] These findings lead to an intensification of the investigation of the susceptibility of titanium alloys in the 1960’s due to the high interest of the development of supersonic transport and deep-sea submersibles. [23]

Titanium alloys are overall considered to be highly resistant to stress-corrosion in comparison to other engineering materials, and their susceptibility is dictated by alloy composition and metallurgical conditions. In certain environments, however, the protective oxide film can be broken down with no possibility of re-passivation due to absence of oxygen or water species. Environments such as certain liquids and solids, anhydrous methanol, molten halide salts, and hot halide salts residues, have shown to result in cracking in titanium alloys which have been attributed to SCC.[19] In the aerospace industry, chlorides and/or chlorines of one form or another are titanium alloys most likely to encounter during their journey from ingot to the aircraft. The encounter of chlorides and/or chlorines may be during manufacturing of an engine component, where it may have been degreased or lubricated with chlorinated hydrocarbon. Another possible source of contamination may be human sweat (which contains NaCl) during handling of the component.[25] During service, the salt residues in combination of a susceptible material and the increase in temperature provided by the operating engine, may result in hot-salt stress-corrosion cracking.

Hot-salt stress-corrosion cracking will be briefly introduced in this section along with other environment known to promote SCC in titanium alloys. Table 2.3 present some the types of environments that are known to promote SCC in titanium alloys.
Table 2.3: Known environments to cause SCC in Titanium alloys. [17]

<table>
<thead>
<tr>
<th>Environment</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitric acid (red-fuming)</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Nitrogen tetroxide</td>
<td>30-75</td>
</tr>
<tr>
<td>Methyl alcohol (anhydrous)</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Ethyl alcohol (anhydrous)</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Chloride and other halide salts</td>
<td>230-430</td>
</tr>
<tr>
<td>Cadmium (solid + liquid)</td>
<td>25-600</td>
</tr>
<tr>
<td>Mercury (liquid)</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Seawater/NaCl solution</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Distilled water</td>
<td>Room temperature</td>
</tr>
</tbody>
</table>

2.4 Hot-Salt Stress-Corrosion of Titanium alloys & The Role of Hydrogen

The susceptibility of titanium alloys to hot-salt stress corrosion cracking (HSSCC) was first reported in 1955 by Hadley et.al [22], where cracks were found in the post-test surface of a high temperature test specimen. It was later found that the cracks were due to salt residues from a fingerprint. Subsequently, extensive investigations on the susceptibility of titanium alloys to HSSCC were conducted, and National Aeronautic and Space Administration (NASA) was one of many performing such studies.[26, 27, 28, 29, 33] A major concern for NASA was that titanium alloy sheet materials were considered to be used as skin materials for a supersonic transport airplane which operated at speeds up to Mach 3. This type of airplane would operate in airports located along sea coasts, and thus had a high probability of salt accumulation in its structure. The airplane skin was expected to be subjected to high stresses and high temperatures up to 316°C, giving the perfect conditions for HSSCC.[26] Apart from NASA, other companies like Boeing were also interested in conducting similar investigations of HSSCC susceptibility of titanium alloys.[23, 24]

The salt residues which have been reported to promote HSSCC are chloride, bromide, and iodide salts. The aggression of the attack seem to increase with the cation type. This can clearly be seen with different chloride salts were the attack severity increase as follows: MgCl₂ < SrCl₂ < CsCl < CaCl₂ < BaCl₂ < NaCl < LiCl.[19]

2.4.1 The Role of Hydrogen

The complexity of the process of stress-corrosion cracking have made it difficult to conclude the nature of the phenomenon. Over the years, many investigations have been made with conflicting reports among different authors. However, after more than sixty years of investigations of the phenomenon, there is today a gen-
eral consensus that monoatomic hydrogen is responsible for failures during HSSCC investigations.[24] The anodic reaction associated with stress-corrosion cracking must have a corresponding cathodic reaction. Hydrogen is believed to participate in this cathodic reaction in HSSCC by experiencing an electrochemical reduction. The small monoatomic hydrogen is absorbed into the metal lattice, introducing additional pressure to the already stressed lattice. The phenomenon is called hydrogen embrittlement and is part of the umbrella term hydrogen-damage. There are several models proposed to explain the phenomenon. The crack initiating and propagation of HSSCC is thus believed to be a combination of stress-corrosion (anodic) and hydrogen embrittlement (cathodic) mechanisms.[14]

There are many evidence supporting the idea that hydrogen play an important role in HSSCC. Rideout et.al [41] suggested the cracking associated with HSSCC was due to the production of hydrogen since it was found that the hydrogen was concentrated in the crack areas. Rideout reported in the same study that the initiation of cracking was highly dependent on the presence of moisture. Gray[27] conducted an investigation where salt coated samples were tested at different strain rates, at different temperatures. It was found that specimens coated with salt experienced a more pronounced embrittlement when tensile tested at slow strain rates in lower temperatures. At higher strain rates (1 cm/min), the salt coated samples experienced no loss in ductility. Regions adjacent to the fractures surfaces were measured for hydrogen content. It was found that in these regions the material exhibited an elevated hydrogen content in comparison to the substrate material.

Ondrejcin and Louthan[33] tested unsalted titanium alloy specimen in hydrochloric acids and hydrogen atmospheres at elevated temperatures and found that fracture surfaces of HCl cracking were very similar to those of HSSCC. Furthermore, it was found that cracking occurred faster in HCl than for HSSCC. In the study, it was argued that the rapid cracking viewed in HCl environments was due to the constant supply of HCl. For HSSCC, on the other hand, an incubation period is required for cracking to occur, hence resulting in a slower embrittlement. Ondrejcin and Louthan also concluded that hydrogen was the sorbing species since no evidence of HCl or any other corrosion products were found on any of the fracture surfaces.

It can thus been concluded by the studies mentioned above and many other studies, that there are strong evidence suggesting that hydrogen plays an important role during cracking of titanium alloys when exposed to HSSCC conditions.

2.4.2 Models for HSSCC Mechanism

Since the first discovery of a crack attributed to HSSCC, extensive research have been made in order to fully understand the mechanism behind crack initiation and propagation associated with HSSCC. It is generally accepted that the cause of cracking in HSSCC of titanium alloys is attributed to hydrogen embrittlement.[27, 30, 33, 44] The mechanism of the hydrogen generation, however, is not fully understood. Many models have been proposed over the years but unfortunately, no proposed model to
date is able to fully describe HSSCC of titanium alloys in a satisfactory manner.\[^{35}\]

In reality, HSSCC is due to many factors which collectively contribute to the phenomenon. Such factors may be chemical and electrochemical reactions.\[^{35}\]

The proposed models can in general be divided into two different classes. The first class involves the models that consider the formation of the embrittlement species to be a result of the direct interaction between salt-atmosphere-substrate.\[^{44}\] The second class is for models which considers the generation of embrittling species a result from electrochemical processes. The two most comprehensive models from each class are Rideout’s pyrohydrolysis model\[^{41}\] and Ripling’s electrochemical model\[^{43}\], which take part of class one and two respectively. Said models will be briefly introduced in this section along with their flaws. Furthermore, the improved electrochemical model proposed by Myers and Hall \[^{45}\] is considered to be the most consistant and adequate model which describes the mechanism of HSSCC.\[^{35}\] The model will therefore also be described in this section in more detail. Besides the already mentioned models, other suggested models for the description of the mechanism of HSSCC are stress sorption model\[^{42}\] and Garfinkel’s hybrid electrochemical model\[^{44}\].

### 2.4.2.1 Rideout’s Pyrohydrolysis Model

This model proposes that the direct reaction between the salt, atmosphere, and base material is responsible for the cracking associated with HSSCC. The pyrohydrolysis reaction can be divided into several step-reactions.

\[
Ti + 2NaCl + 2H_2O \rightarrow TiCl_2 + 2NaOH + 2H
\] (2.7)

In this first step the salt deposits are oxidized and resulting in the formation of titanium dichloride.

\[
TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl
\] (2.8)

In the second reaction, titanium dichloride hydrolyzes at elevated temperatures and forms hydrogen chloride.

\[
Ti + 4HCl \rightarrow TiCl_4 + 4H
\] (2.9)

The formed hydrogen chloride subsequently reacts with the base material to form hydrogen and additional titanium chloride. The newly formed titanium chloride then continues to react with water and a thus a new hydrogen generation cycle begins.

The model proposed by Rideout \[^{42}\] has however some drawbacks. The reaction associated with this model is thermodynamically unfavorable. Also, the reaction requires the formation of hydrochloric acid which should get neutralized by the hydroxide ions which are being produced simultaneously by the reaction.

### 2.4.2.2 Ripling’s Electrochemical Model

Lingwall and Ripling \[^{43}\] proposed that stress-corrosion cracking is an electrochemical process and the reaction occurred in an oxygen concentration cell, where the
salt-metal-air interface is always one electrode of the cell. The oxygen is involved in a cathodic reaction and is reduced by the following reaction:

$$2e^- + \frac{1}{2}O_2 + H_2O = 2OH^-$$  \hspace{1cm} (2.10)

While the metal is dissolved in the anode reaction:

$$Ti = Ti^{n+} + ne^-$$  \hspace{1cm} (2.11)

Even though Lingwall and Ripling argued in their study that the fracture was probably due to hydrogen embrittlement. They failed to provide the source for hydrogen formation required for HSSC.[43]

2.4.2.3 Improved Electrochemical Model

It was earlier mentioned that many models which attempt to describe HSSCC mechanisms have been proposed over the years. Out of all proposed models[41, 42, 43, 44], Myers and Hall’s[45] improved electrochemical model is considered to be the relatively most consistent and adequate to apply when it comes to describing the generation of hydrogen associated with HSSCC.[34]

Crack Initiation

The model assumes that an oxygen differential aeration cell is present at the surface of the material. A salt deposit (usually sodium chloride) is placed on the passive oxide layer created when titanium alloys react with oxygen. The combination of salt, temperature and surface strains result in a localized break down of the physical barrier (passive oxide film) between the substrate and the corrosive medium. The high concentration of chloride impedes the re-formation of the passive film, exposing the substrate material to the corrosive medium. The anodic reaction would occur under the salt deposit where there is a deficiency in oxygen according to the following:

$$Ti = Ti^{n+} + ne^-$$  \hspace{1cm} (2.12)

The cathodic reaction occurs in the oxygen rich electrolyte adjacent to the salt deposit, according to the following reaction:

$$O_2 + 2H_2O + 4e^- \rightarrow OH^-$$  \hspace{1cm} (2.13)

As a result, a pit is formed. The pit is then filled with electrolyte by capillary action. Subsequently, a positive charge is developed in the pit due to dissolution of the metal. Titanium ions will bond with chloride ions and produce titanium chlorides which in turn will be pyrohydrolized according to the following reaction:

$$TiCl_n + nH_2O \rightarrow Ti(OH)_n + nH^+ + nCl^-$$  \hspace{1cm} (2.14)

The concentration of H$^+$ will increase in the pit which allows a secondary cathodic reaction where the hydrogen ions are reduced by the following reaction:

$$H^+ + e^- \rightarrow H$$  \hspace{1cm} (2.15)
Crack Propagation:
The monoatomic hydrogen produced during the secondary cathodic reaction would diffuse into the titanium allow and concentrate in the base of the pit, where the stress concentration is the highest. The hydrogen will be thus localized in this region. Subsequently, as the hydrogen content is increased and reaches and exceeds a concentration of 1000 ppm, the fracture toughness of said region will start to the decrease, hence embrittling the region. The stress intensity factor will eventually exceed the fracture toughness (Figure 2.8) in the hydrogen concentrated region, resulting in propagation of crack. The crack propagation will succeed until the crack tip reaches a region with significantly less hydrogen concentration. New accumulation of hydrogen will occur at the crack tip, which would allow further propagation of the crack, until a new region is reached with low hydrogen content. The sequence will then be repeated until the remaining substrate is not able to support the applied load and fail catastrophically.

Even though Myers and Hall argued that the model is consistent with the observations made on HSSCC of titanium alloys, there are still assumptions made in this model that has not yet been proven. The model assumes that the presence of an electrolyte and implies that the pit will be filled in by capillary forces. This assumption contradicts reports, which state that no liquids were found in stress-corrosion cracks. Furthermore, HSSCC does not require high amounts of water vapour which would impede the existence of an electrolyte.

The sequence of events suggested by Myers and Hall’s improved electrochemical model can be observed in Figure 2.10. A more detailed view of the embrittling of the base of the pit is illustrated in Figure 2.11.
2. Theoretical Background

Figure 2.10: Sequence for crack initiation and propagation according to the improved electrochemical model proposed by Myers and Hall. a) Salt deposit on passive titanium alloy, b) Localized breakdown of passive passive film under salt deposit, c) creation of pit, d) concentration of hydrogen at the base of the pit, e) crack propagation. [45]

Figure 2.11: Detailed illustration of the concentration of hydrogen at the base of the pit [45]
2.4.3 HSSCC Susceptibility of Titanium Alloys

Most titanium alloys are considered to be more or less susceptible to HSSCC in the temperature range 200-500°C. Over the years, several factors have been established to occur and/or contribute to HSSCC of titanium alloys. Jackson and Boyd [32] proposed that the greatest susceptibility was in the temperature range 288-427°C (550-800°F) and that HSSCC has not been observed in temperatures below 260°C. Below this temperature, the incubation periods required for cracking would be extended extremely. At higher temperatures, over 510°C, cracking is not expected due to the creep limitation of titanium alloys.[45] Apart from temperature, HSSCC has also been found to depend on factors such as stress and time. In fact, time to failure has been found to decrease when temperature or stress levels are increased.[32] On the other hand, the introduction of small cathodic currents have shown to significantly extend the time to failure. Furthermore, it has also been established that there must exist an incubation time before crack initiation, a threshold stress is required, and that cracks propagate primarily intergranularly in titanium alloys. Lastly, oxygen and a small amount of moisture is required for HSSCC [44] and the moisture may come from the atmosphere or fluid retained in the salt.[45]

In general, it has been found that the most susceptible titanium grades are alpha and near alpha-phase alloys. Alpha-beta alloys are considered less prone to HSSCC and their susceptibility may increase if the amount of aluminium content in the alloy is increased.[32] Ondrejcin [33] reported that aluminium in the alpha-phase is preferably attacked by the hot salt. On the other hand, molybdenum, vanadium and tin have shown to improve HSSCC resistance due to their ability to stabilize β-phase.[35]

Ti-8Al-1Mo-1V alloy in the duplex annealed condition was early investigated due to its desirable strength and stiffness properties and thus making it a good candidate for aerospace applications. It was soon found that such alloys were highly susceptible to HSSCC. Hugh R. Gray [28] investigated the relative susceptibility to HSSCC of seven different titanium alloys by first exposing static loaded salt-coated specimens in test temperatures 320°C to 480°C for 100 hours. The samples were then tensile tested at room temperature at a constant low strain rate. It was found that Ti-8Al-1Mo-1V was ranked in second place over the most susceptible material to HSSCC in the study. Another study conducted by Dick M. Royster[26] reported that tensile elongation properties of Ti-8Al-1Mo-1V decreased significantly when salt-stress corrosion cracks were developed. Moreover, the threshold stresses of the material were found to decrease as temperature and time increased. Similar findings were reported by D. Sinigaglia[30] where it was found that the alloy (Ti-8Al-1Mo-1V) was found to be the most susceptible to HSSCC out of all the titanium alloys tested. It was also found that the increase in tensile stress applied to the samples increases the susceptibility to HSSCC, under the same conditions of temperature and for the same alloy. Another well studied titanium alloy for HSSCC susceptibility is Ti-6Al-4V. Ti-6Al-4V is relatively more resistant to HSSCC in comparison to Ti-8Al-1Mo-1V. Furthermore, when tested at 287°C and at 345 MPa, Ti-6Al-4V did not fail after 3200 h of exposure. Ti-8Al-1Mo-1V on the other hand, failed within 1000 h when
exposed to a temperature of 288°C and 275 MPa.[31] In the same study of Hugh R. Gray [28], it was concluded that Ti-6Al-4V and Ti-6Al-2Sn-4Zr-2Mo had low susceptibility of HSSCC out of the seven tested materials, where the latter showed the highest resistance to HSSCC. Similar findings have been reported showing that Ti-6Al-2Sn-4Zr-2Mo seem to be less susceptible to HSSCC than Ti-6Al-4V and Ti-8Al-1Mo-1V, when compared to the materials critical stress.[8] Figure 2.12 presents the measured critical stress under SCC conditions of Ti-6Al-4V, Ti-8Al-1Mo-1V, and Ti-6Al-2Sn-4Zr-2Mo.

![Figure 2.12: Comparative critical stress in 425°C][8]

### 2.4.4 Service Failures Attributed to SCC

Interestingly, despite extensive laboratory investigations demonstrating susceptibility of SCC of titanium alloys, service failures in the aerospace industry exclusively attributed to SCC are rare. In fact, only one reported incident of a failure of a titanium component attributed to SCC has been found.[29] A part from this report, no mention in any other reviewed literature could be found on the observence of SCC service failures. The non-observance of SCC during service is not fully understood and many theories have been proposed. Dinnappa [35] proposed that the reason for the lack of observance of hot-salt stress-corrosion cracking in aero gas turbines was due to the high velocity of the air stream flowing through the compressor components, cyclic stresses and thermal fluctuations. Dinnappa argued that due to said factors, the HSSCC conditions experienced by the material were less severed than in a laboratory test. Furthermore, the incoming air stream could potentially remove the corrosion produced hydrogen chloride and thus prevent the formation of hydrogen. As a result, the incubation time for pitting to cause crack initiation would increase significantly. Dinnappa further elaborated that hydrogen embrittlement in titanium alloys was found to be non-cumulative and reversible. This means that if HSSCC conditions are interrupted prior to the formation of the cracks critical
size, the hydrogen may dissipate from the stress concentrated area (the crack tip) and hence incubation time to cause HSSCC is increased. In other words, the duration of flights will be relatively small and will not exceed incubation period since re-establishment of HSCC conditions will be required after each flight.

2.5 Test Methods

The lack of early detection of SCC before a catastrophic structural failure gave an early urge to characterize different materials in different environments under stress. Even though the interest peak for understanding SCC was in the mid 60’s to mid 70’s, it is still considered an important corrosion topic mainly due to the constant development of new materials.[20] Testing for SCC is therefore crucial for reducing the likelihood of unexpected failures in service. Even though advantageous, it is often unpractical to test actual structural components when testing a material in a certain environment. Laboratory testing is more often the way to go for the prediction of combinations of material and environment that result in SCC.

The principle of SCC tests consists in stressed specimens being exposed to an aggressive environment. The testing parameters, e.g materials, environmental conditions, and actual service load history, need to be taken into account when designing a test, for the test to have relevance to service operations. Moreover, the test are often needed to be accelerated since SCC typically occurs over long periods of time. The test may be accelerated by exposure of more severe environments, higher mechanical stresses, higher temperatures, or applying anodic or cathodic polarization. However, since the main purpose of the test is to screen out material based on their susceptibility to SCC, the SCC mechanisms in the accelerated test should be the same as for that occurring in service. Otherwise, the test may exclude materials that are safe during service. [16]

Over the years, several standardized tests have been developed by American Society for Testing and Materials (ASTM), the International Organization for Standardization (ISO) and the National Association of Corrosion Engineers (NACE). The development of the test methods was focused on the purpose and application of the test and there is thus no single test method that is superior to all other tests. Instead, many different test methods have been developed where each method has its specific advantage in a specific condition.[21] SCC tests are usually divided into two categories: smooth specimens, and pre-cracked (or notched) specimens. In both categories, either static or dynamic loads may be applied.

2.5.1 Smooth specimens

Smooth specimens are used to study the whole SCC life, including the crack initiation and propagation. The testing can be performed under constant strain, constant load or strain rate.
2. Theoretical Background

2.5.1.1 Constant Strain

Constant strain testing is performed on smooth specimens and this is a widely used test method since it does not require any complex test fixtures, the specimens are easy to fabricate, and a large amount of specimens can be tested at one time. The simple geometry of the specimen allows the initial stress to be calculated and subsequently the threshold stresses. However, the results are not always reproducible. The initial calculated stress will decrease as the crack starts to propagate since a relaxation will occur. The severity of the test will therefore decrease as the crack propagates. There are several variation to the test, where most common test specimen being bent-beam, U-bend, C-ring, and tensile type specimens.[48]

2.5.1.2 Constant Load

The application of a constant load will maintain the load at the crack tip as the crack propagates, in contrary to constant strain tests. The test will therefore be more severe, leading to earlier failure and lower estimates of threshold stress. This loading may reflect a more realistic scenario for the material and what it might experience in actual service. However, the threshold stresses are strongly dependent on the method of loading and cannot be considered a material property. Moreover, constant loading test require more sophisticated jig fixtures.[48]

2.5.1.3 Slow Strain Rate Tests

A slow dynamic strain rate above the elastic limit is applied for initiation of SCC. Consequently, SCC is accelerated which provides the evaluation of the susceptibility of materials in a relatively short period of time. This test requires standard tensile machines capable of applying loads at the required strain rate. [48]

2.5.2 Pre-Cracked Specimens

Pre-cracking of specimen for SCC evaluation resembles fracture mechanics testing where it is assumed that all engineering materials contain cracklike flaws. By introducing a crack with a known geometry, stress analysis can be performed with a fracture mechanics approach and thus a relationship between applied stress, crack length, and crack growth in a corrosive environment, can be made. [48]
3
Experimental

This section presents alloys considered for this project along with their respective material specification. Furthermore, the test method of concern is presented and the methodology is described in a step-by-step manner.

3.1 Materials

Three different types of titanium alloys in sheet form were studied in this project: Ti-6Al-4V, Ti-8Al-1Mo-1V, and Ti-6Al-2Sn-4Zr-2Mo. The sheet materials were produced according to the Society of Automotive Engineers (SAE) aerospace standards, and their respective material specifications are presented in Table 3.1. The reason to the choice of material is based on the materials used in ASTM F945, which requires Ti-6Al-4V and Ti-8Al-1Mo-1V. Ti-6Al-2Sn-4Zr-2Mo was included since it is a common alloy in the aerospace industry.

Table 3.1: The chemical compositions in weight percentage of the titanium alloys used in this work. The material specification is abbreviated as MS.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>MS</th>
<th>Ti</th>
<th>Al</th>
<th>Zr</th>
<th>Mo</th>
<th>Sn</th>
<th>V</th>
<th>Si</th>
<th>Fe</th>
<th>O</th>
<th>N</th>
<th>H</th>
<th>Yttrium</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti64</td>
<td>AMS4911</td>
<td>5.50-6.75</td>
<td>-</td>
<td>-</td>
<td>3.58-4.50</td>
<td>-</td>
<td>0.30</td>
<td>0.20</td>
<td>0.08</td>
<td>0.050</td>
<td>&lt;0.015</td>
<td>0.005</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>Ti811</td>
<td>AMS4916</td>
<td>Balance</td>
<td>7.35-8.35</td>
<td>-</td>
<td>0.75-1.25</td>
<td>-</td>
<td>0.38</td>
<td>0.12</td>
<td>0.08</td>
<td>0.05</td>
<td>&lt;0.015</td>
<td>0.005</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>Ti6242</td>
<td>AMS4919</td>
<td>Balance</td>
<td>5.50-6.50</td>
<td>0.65-1.40</td>
<td>1.80-2.20</td>
<td>1.80-2.2</td>
<td>-</td>
<td>0.06-0.10</td>
<td>0.25</td>
<td>0.12</td>
<td>0.05</td>
<td>0.0150</td>
<td>0.005</td>
<td>0.30</td>
</tr>
</tbody>
</table>

3.2 Test Method

The chosen test method in this work is a 2-point bending test adapted from the standard method developed by Pratt & Whitney, PWA:MCL E-205.[46] The method consist in introducing a static stress on the surface of a rectangular sheet of a specific length by introducing a constant deflection on the specimen. The specimen is loaded in a 2-point bend rig, which has a smaller holder span than the length of the specimen, hence creating a deflection when the specimen is loaded into the rig. An illustrative image of a loaded specimen can be observed in Figure 3.1.
3. Experimental

Figure 3.1: Schematic illustration of the experimental set-up of 2-point bending method.[29]

3.2.1 Calculation of Specimen Dimensions

The dimensions of the specimens were calculated according to equation 3.1[47], where it can be seen that the resulting stress is highly dependent on the thickness and length of the specimen.

\[
L = \left( \frac{ktE}{\sigma} \right) \sin^{-1} \left( \frac{H\sigma}{ktE} \right)
\]

(3.1)

Where \( L \) is the specimen length, \( \sigma \) is the maximum stress, \( E \) is the Young’s modulus, \( H \) is the holder span, \( t \) is the thickness of the specimen, and \( k \) is an empirical constant that is equal to 1.280. Equation 3.1 is only valid when \( \frac{H\sigma}{ktE} \) is less than 1.0. In the present study, the thickness, \( t \), and holder span, \( H \), is kept constant, whilst the length of the specimen is varied in order to vary the stress obtained at the apex of the bent specimen. The test method is designed for stresses below the yield strength of the material, hence within the elastic region of the material. This needs to be taken into consideration when varying the length of the specimen since at stresses above the yield strength, Eq. 3.1 is no longer valid. To verify that the error of stress is within acceptable limits, the thickness and holder span should give a value between 0.01-0.5 for \( (L-H)/H \).

In the present study, the stresses of interest were set to be 40%, 60%, 85%, and 95% of the materials yield strength and their corresponding length were then calculated using Eq. 3.1. The lengths of the specimens for each material are presented in Table 3.2 along with other measurements.
Table 3.2: Dimensions of specimens for 2-point bending method.

<table>
<thead>
<tr>
<th></th>
<th>Stress (%)</th>
<th>Length (mm)</th>
<th>Thickness (mm)</th>
<th>Width (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMS4911</td>
<td>40</td>
<td>141,721</td>
<td>1,318</td>
<td>12.7</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>144,792</td>
<td>1,318</td>
<td>12.7</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>150,424</td>
<td>1,318</td>
<td>12.7</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>153,969</td>
<td>1,318</td>
<td>12.7</td>
</tr>
<tr>
<td>AMS4916</td>
<td>40</td>
<td>141,387</td>
<td>1,274</td>
<td>12.7</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>143,663</td>
<td>1,274</td>
<td>12.7</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>148,380</td>
<td>1,274</td>
<td>12.7</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>151,086</td>
<td>1,274</td>
<td>12.7</td>
</tr>
<tr>
<td>AMS4919</td>
<td>40</td>
<td>141,828</td>
<td>1,306</td>
<td>12.7</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>144,843</td>
<td>1,306</td>
<td>12.7</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>151,403</td>
<td>1,306</td>
<td>12.7</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>155,410</td>
<td>1,306</td>
<td>12.7</td>
</tr>
</tbody>
</table>

3.2.2 Preparation of Specimens

In order to achieve the dimensions shown in Table 3.2, long strips with the correct width and thickness for each material were first cut by water-jet at Ottossons mekaniska AB. The strips were cut from a large sheet, hence all the strips of the same material have the same thickness as seen in Table 3.2. According to the standard, the long axis of the strip was set to be perpendicular to the sheets rolling direction. The lengths of the specimen were then cut in the materials lab at GKN Aerospace, where a hacksaw was used to achieve the desired length of the specimen. Caution was taken to handle the specimen with gloves in order to not cause any damage on the surface of the specimen. A schematic illustration of the strips can be seen in Figure 3.2.

Figure 3.2: Schematic illustration of the strip.
3.2.3 Test Procedure

Once the test specimens were ensured to have the correct dimensions according to Table 3.2, they were marked with a vibrating pen. The surface of the specimens was examined in an optical microscope at 10X. No surface imperfections of any kind were allowed. If no surface defects were detected, the specimens were immersed in acetone and ultrasonically cleaned for 15 minutes. Once cleaned, the specimens were handled with cotton gloves to avoid salt residuals from fingerprints. The clean specimens were loaded into the specimen holder by gently bending the specimen into place. A small space was left between each specimen to avoid cross contamination. 50µL NaCl-solution was applied on the apex of the test specimen and then dried at 50°C. A solid residue of NaCl-solution should remain on the test specimen, as seen in Figure 3.3. The loaded specimen holder was then placed into an air-circulating furnace and heat treated at 482±10°C for 100±1h. Once the heat treatment was complete, the loaded specimen holder is removed from the furnace and air cooled down to room temperature.

![Salt residue on the apex of the test specimens.](image)

3.2.4 Examination & Metallography

The loaded specimens were firstly examined for breaks or gross cracks. The specimen were then unloaded from the holder and abrasive blasted with aluminum oxide grit in order to remove residual salt solution so that subtle cracks could be revealed. The particle size of the abrasive was 320-grit. Once the salt residues was removed, the specimens were etched in etching reagent containing 150 mL nitric acid (HNO₃), 30 mL hydrofluoric acid (HF), and 30 mL sulfuric acid (H₂SO₄). A deviation from the standard was made were the temperature of the etching solution was not heated to 54-66°C. Instead, the etching occurred at the temperature generated from the exothermic reaction from when the different chemicals (HNO₃, HF, and H₂SO₄) were mixed. To compensate, the time of immersion of each specimen was increased from 30 seconds to 40-45 seconds. Directly after immersion, the specimens were immersed in a water containing cup and subsequently rinsed in running tap water in order to stop the reaction.
Once air dried, the specimens were firstly visually examined for cracks. The top surface (the apex) of the specimen was then inspected for cracks with light optical microscopy (LOM) at a low magnification of 5X. Figure 3.5 shows an example of an image taken on the apex surface of the test specimen treated with salt solution. The cross-section of the bend was also inspected by carefully cutting the specimen according to the arrows in Figure 3.4. The cutting was performed on a Struers Secotom-50 cutting machine using aluminum oxide cut wafers. One half of the specimen was then mounted, ground and polished. The machine used for hot mounting was Buehler SimpliMet 4000. The principle of grinding is that abrasive particles removed damaged material from the surface without causing more deformation. The grinding and polishing was performed on Buehler Phoenix 4000 grinding machine. In this project, the abrasive papers used were: 120, 500, 800, 1000, 2000, 4000. The principle of polishing is the same as for grinding. however, instead of using abrasive paper, a fine OP-S colloidal silica particles were used as suspension final polish of the surface. The samples were carefully washed with soap and water between each step during grinding and polishing in order to fully remove particles that could scratch the surface when moving on to a grid paper/suspension with smaller particles. The different parameters used for grinding and polishing are presented in Table 3.3.

Figure 3.4: Illustration of the cross-section on the specimens.

Figure 3.5: Top view of the surface of test sample of Ti-8Al-1Mo-1V treated with 3 wt\% NaCl-solution. Image taken at 5X.
3. Experimental

Table 3.3: Grinding and polishing steps for evaluating the metallography.

<table>
<thead>
<tr>
<th>Step</th>
<th>Surface</th>
<th>Suspension</th>
<th>Lubricant</th>
<th>Time</th>
<th>Rotation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>120 Grid SiC</td>
<td>-</td>
<td>water</td>
<td>1 min</td>
<td>Co-rotating</td>
</tr>
<tr>
<td>2</td>
<td>500 Grid SiC</td>
<td>-</td>
<td>water</td>
<td>1 min</td>
<td>Co-rotating</td>
</tr>
<tr>
<td>3</td>
<td>800 Grid SiC</td>
<td>-</td>
<td>water</td>
<td>1 min</td>
<td>Co-rotating</td>
</tr>
<tr>
<td>4</td>
<td>1000 Grid SiC</td>
<td>-</td>
<td>water</td>
<td>1 min</td>
<td>Co-rotating</td>
</tr>
<tr>
<td>5</td>
<td>2000 Grid SiC</td>
<td>-</td>
<td>water</td>
<td>30 sec</td>
<td>Co-rotating</td>
</tr>
<tr>
<td>6</td>
<td>4000 Grid SiC</td>
<td>-</td>
<td>water</td>
<td>30 sec</td>
<td>Co-rotating</td>
</tr>
<tr>
<td>7</td>
<td>Microcloth</td>
<td>OP-S colloidal silica</td>
<td>-</td>
<td>2 min</td>
<td>Counter-rot</td>
</tr>
</tbody>
</table>

The cross-sections were carefully evaluated with LOM at magnifications up to 100X. If cracks were found during inspection, they were documented. Figure 3.6 shows the typical appearance of a cracks created from stress-corrosion.

Figure 3.6: Image of the cross-section of Ti-6Al-2Sn-4Zr-2Mo revealing a crack. Image taken at 20X.

3.2.5 Crack Characterization

The cracks found in the optical microscope were further characterized with an electron scanning microscope (SEM) in order to investigate the propagation nature of the crack. In order to achieve images of high quality and resolution, the surfaces of the mounted samples were gold sputtered. A thin layer of gold was deposited on the surface of the sample in a process called physical vapor deposition (PVD). The film deposition was conducted in a low pressure chamber filled with argon gas and the thin gold layer is created when the gold is bombarded with a high energy plasma. Subsequently, the gold evaporates and condenses onto the sample surface to be coated. Gold sputtering were performed on the samples due to the non-conductive resin used during mounting. The non-conductive material would decrease the image quality and resolution by acting as electron traps. The electrons are then accumulated (or charged) in the non-conductive material resulting in extra-white regions on the sample, hence giving low quality images. One of the gold sputtered samples can be seen in Figure 3.7.
Figure 3.7: Gold sputtered sample.
4 Results

This chapter presents the most relevant results obtained from the experimental part. The chapter contains only the most relevant figures and tables and the appendix is used as compliment.

4.1 Metallographic Evaluation

This section presents the metallographic evaluation for the titanium alloys used in this work. Table presents the summarized results obtained using the test method for all titanium alloys.

4.1.1 Ti-6Al-4V

The results of the SCC two-point load testing method for Ti64 are summarized in Table 4.1. The testing conditions consisted in varying the salt concentration between 1-3 wt%, and the applied stress between 40-95%σYS. The stress applied on the test specimen was obtained by varying the length and was calculated with equation 3.1. The results presented in Table 4.1 are divided in the in salt concentration and the location of cracking, surface cracking (SC) and cross section cracking (CSC). The validity of the test method was established by testing untreated (reference) specimens under the same conditions as the test specimens. No evidence of cracks or breaks on any of the reference specimens were acceptable. The test would otherwise be rejected and rerun.
4. Results

Figure 4.1: Visual inspection of two salt-treated specimens (Left) and two untreated specimens (right).

The test specimens were removed from the test fixture after exposure to 482°C for 100 hours and were visually inspected. At first glance, the test specimen treated with salt did not show any apparent damage on the surfaces. As seen in Figure 4.1, corrosion products and oxidation covered any potential damage on the salt-treated surface. Moreover, white islands consisting of conglomerated crystals can be seen on the salt-treated specimens which formed a circle pattern. The size and position of the white salt crystals correspond well with the location of the applied saline solution before the specimen was heat treated. The white salt crystals forming a circular pattern were present in all salt treated specimens.

The surfaces of the untreated specimens were covered with a smooth coating in blue colour. It is worth noting that some of the untreated specimen exhibited white spots, as seen in Figure 4.1.

To fully reveal any damage caused by HSSCC, all samples were abrasive blasted and chemically etched according the test plan. The specimens were then examined with optical microscopy.

Table 4.1: Overview of the results of Ti-6Al-4V.

<table>
<thead>
<tr>
<th>Salt concentration (wt%)</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stress (%σYS)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>No Cracking</td>
<td>No Cracking</td>
<td>No Cracking</td>
</tr>
<tr>
<td>60</td>
<td>No Cracking</td>
<td>No Cracking</td>
<td>No Cracking</td>
</tr>
<tr>
<td>85</td>
<td>No Cracking</td>
<td>No Cracking</td>
<td>Cracking</td>
</tr>
<tr>
<td>95</td>
<td>Cracking</td>
<td>Cracking</td>
<td>Cracking</td>
</tr>
</tbody>
</table>
4. Results

4.1.1.1 Surface Cracking

Ti64 showed an overall high resistance to HSSCC with this method. In fact, there was almost no cracking on the salt-treated surface at a low salt concentration (1wt%). A high stress of $\sigma_{95\%YS}$ was required in order to induce cracks. Figures 4.2a, 4.2c, 4.2e, 4.2g, presents the optical micrographs from the salt-treated surface at low salt concentrations after grit blasting and etching. It can be seen that no cracks can be observed on the salt-treated surface when the specimens were treated with low concentration of salt solutions for stresses $\sigma_{40\%YS}$, $\sigma_{60\%YS}$, and $\sigma_{85\%YS}$. Moreover, several dark spots (indicated by red arrows) are present on the surfaces and they seem to increase as the stress is increased. These spots were identified as pits suggesting that pitting corrosion is present during testing and increases with stress. The first sign of cracks may be seen in the specimens when a stress of $\sigma_{95\%YS}$ was applied, as seen in Figure 4.2g. Furthermore, the cracks in these specimens were few, sparse and parallel to the direction of rolling of the sheet.

The optical micrographs of the salt-treated surfaces at high salt concentrations (3wt%) after grit blasting and etching are presented in Figures 4.2b, 4.2d, 4.2f, and 4.2h. The cracking behavior at this salt concentration level is very similar to the one at lower concentration levels. However, a slight increase in susceptibility was found when the salt concentration was increased since cracking was discovered at lower stresses. The first sign of cracking was found at $\sigma_{85\%YS}$ and the cracks were found to be small, sparse and parallel to the direction of rolling of the sheet.

4.1.1.2 Cross Section

The specimens were cut, mounted, grounded and polished according to the test plan in order to evaluate their cross sections. Figures 4.3a, 4.3c, 4.3e, and 4.3g present the optical micrographs of the specimens treated at low salt concentrations. The cross sections of the specimens showed no cracking when the stresses where varied between $\sigma_{40\%YS}$, $\sigma_{60\%YS}$, and $\sigma_{85\%YS}$. At stresses of $\sigma_{95\%YS}$, cracks were observed and documented, as seen in Figure 4.3e. Furthermore, the cracks were oriented perpendicular to the applied tensile stress in the material. The cracks found in this environment are however very few and with a total average crack length of 31,15 $\mu$m.

The optical micrographs of the cross sections of the salt-treated surface at high salt concentrations are presented in Figures 4.3b, 4.3d, 4.3f, and 4.3h. No cracking was observed when the stress $\sigma_{40\%YS}$ was applied in this environment. Cracking was observed in the specimen where the remaining stresses were applied. Just as for the case in low salt concentration environment, the cracks were oriented perpendicular to the applied stress. The total average crack length for stresses $\sigma_{60\%YS}$, $\sigma_{85\%YS}$, and $\sigma_{95\%YS}$ were found to be 20,71 $\mu$m, 20,57 $\mu$m, and 28,2 $\mu$m respectively.

Notable for all observed cracks is that they seem to originate from a pit which is most likely due to corrosion.
4. Results

Figure 4.2: Optical micrographs of the top view of Ti-6Al-4V. All images are taken at 50X.
4. Results

Figure 4.3: Optical micrographs of the cross sections of Ti-6Al-4V. All images are taken at 500X.
4. Results

4.1.2 Ti-8Al-1Mo-1V

The results of the SCC two-point load testing method for Ti811 are summarized in Table 4.2. The testing conditions consisted in varying the salt concentration between 1-3 wt%, and the applied stress between 40-95% \( \sigma_{YS} \). The stress applied on the test specimen was obtained by varying the length and was calculated with equation 3.1. The results presented in Table 4.2 are divided in the in salt concentration and the location of cracking, surface cracking (SC) and cross section cracking (CSC). The validity of the test method was established by testing untreated (reference) specimens under the same conditions as the test specimens. No evidence of cracks or breaks on any of the reference specimens were acceptable. The test would otherwise be rejected and rerun.

![Figure 4.4: Visual inspection of two salt-treated specimens (Left) and two untreated specimens (right).](image)

Figure 4.4 shows the SCC tested Ti811 specimens after removal from the furnace. Just like in the case for Ti64, no apparent evidence of cracking could be observed on the salt-treated surfaces due to corrosion products and oxidation covering any potential damage on the salt-treated surface. Moreover, white islands consisting of conglomerated crystals in a circle pattern formation can be seen on the salt-treated specimens. The size and position of the white salt crystals correspond well with the location of the applied saline solution. The white salt crystals forming a circular pattern were present in all salt treated specimens.

The surfaces of the untreated specimens were covered with a smooth coating in blue
and purple colour. White spots were present in the untreated specimen just like in the case of Ti64, as seen in Figure 4.4.

To fully reveal any damage caused by HSSCC, all samples were abrasive blasted and chemically etched according the test plan. The specimens were then examined with optical microscopy.

Table 4.2: Overview of the results of Ti-8Al-1Mo-1V.

<table>
<thead>
<tr>
<th>Stress (%σYS)</th>
<th>Salt concentration (wt%)</th>
<th>1</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SC</td>
<td>CSC</td>
<td>SC</td>
</tr>
<tr>
<td>40</td>
<td>Cracking</td>
<td>No Cracking</td>
<td>Cracking</td>
</tr>
<tr>
<td>60</td>
<td>Cracking</td>
<td>Cracking</td>
<td>Cracking</td>
</tr>
<tr>
<td>85</td>
<td>Cracking</td>
<td>Cracking</td>
<td>Cracking</td>
</tr>
<tr>
<td>95</td>
<td>Cracking</td>
<td>Cracking</td>
<td>Cracking</td>
</tr>
</tbody>
</table>

4.1.2.1 Surface Cracking

Figures 4.5a-4.5h, presents the optical micrographs from the salt-treated surface at low salt concentrations after grit blasting and etching. Ti811 showed an overall high susceptibility to HSSCC since cracking was found on all the salt treated surfaces regardless of the salt concentration of the applied saline solution. Interestingly, the number of cracks seen on the samples seem to be more dependent on the applied stress rather than the salt concentration of the saline solution. Hence, the amount of cracks observed seemed to increase with increase of applied stress, as seen in Figures 4.5a-4.5h. Furthermore, the cracks are oriented parallel to the rolling direction of the sheet material.

4.1.2.2 Cross Section

The high susceptibility of Ti811 to HSSCC was also reflected in the cross sections of the specimen. Large cracks were observed in all tested samples except for samples treated at $σ_{40\%YS}$-1% NaCl. The cracks were perpendicular to the applied mechanical stress in the material and the cracks were visible at low magnifications. Similar to the reports of Ti64, all the observed cracks seem to have originated from corrosion pits.
4. Results

(a) $\sigma_{40\%YS-1\% \ NaCl}$  
(b) $\sigma_{40\%YS-3\% \ NaCl}$  
(c) $\sigma_{60\%YS-1\% \ NaCl}$  
(d) $\sigma_{60\%YS-3\% \ NaCl}$  
(e) $\sigma_{85\%YS-1\% \ NaCl}$  
(f) $\sigma_{85\%YS-3\% \ NaCl}$  
(g) $\sigma_{95\%YS-1\% \ NaCl}$  
(h) $\sigma_{95\%YS-3\% \ NaCl}$

Figure 4.5: Surface cracking in Ti811. Cracking occurred along the rolling direction.
4. Results

Figure 4.6: Cracking in the cross sections of Ti811. Cracks propagated perpendicular to the tensile stress.
4. Results

4.1.3 Ti-6Al-2Sn-4Zr-2Mo

The results of the SCC two-point load testing method for Ti6242 are summarized in Table 4.3. The testing conditions consisted in varying the salt concentration between 1-3 wt%, and the applied stress between 40-95% $\sigma_{YS}$. The stress applied on the test specimen was obtained by varying the length and was calculated with equation 3.1. The results presented in Table 4.3 are divided in the in salt concentration and the location of cracking, surface cracking (SC) and cross section cracking (CSC). The validity of the test method was established by testing untreated (reference) specimens under the same conditions as the test specimens. No evidence of cracks or breaks on any of the reference specimens were acceptable. The test would otherwise be rejected and rerun.

![Figure 4.7: Visual inspection of two salt-treated specimens (left) and two untreated specimens (right).](image)

Figure 4.7 shows a typical view Ti6242 specimens after removal from the furnace for the SCC testing method. Previously, reports on the other two tested alloys in this work have shown no apparent cracking before etching and grit blasting due to oxidation and residues of the saline solution. Similar findings were observed for
4. Results

Ti6242 for all samples except one. At $\sigma_{95\%YS}$-3% NaCl, one of the duplicate samples exhibited severe cracking roughly in the middle of the sample, where the mechanical stresses are expected to be the largest. Figure 4.8b shows how the crack splits the circle-patterned conglomerated salt crystals in one of the duplicated samples. Furthermore, the depth of the cracking is also severe as it almost cuts the specimen in half, as seen in Figure 4.8a.

Just like the reports found on the other two materials, the size and position of the white salt crystals correspond well with the location of the applied saline solution. The white salt crystals forming a circular pattern were present in all salt treated specimens.

The surfaces of the untreated specimens were covered with a smooth coating in blue colour. The blue colour for this material was slightly lighter than the one seen for Ti64.

To fully reveal any damage caused by HSSCC, all samples were abrasive blasted and chemically etched according to the test plan. The specimens were then examined with optical microscopy.

![Image](image.png)

(a) Severe cracking seen from the side.  (b) Severe cracking seen from above.

**Figure 4.8:** Images showing severe cracking seen in one of the duplicate specimens when treated at $\sigma_{95\%YS}$-3% NaCl.

**Table 4.3:** Overview of the results of Ti-6Al-2Sn-4Zr-2Mo.

<table>
<thead>
<tr>
<th>Salt concentration (wt%)</th>
<th>Ti-6Al-2Sn-4Zr-2Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>SC</td>
<td>SC</td>
</tr>
<tr>
<td>CSC</td>
<td>CSC</td>
</tr>
<tr>
<td>40</td>
<td>Cracking</td>
</tr>
<tr>
<td>60</td>
<td>Cracking</td>
</tr>
<tr>
<td>85</td>
<td>Cracking</td>
</tr>
<tr>
<td>95</td>
<td>Cracking</td>
</tr>
</tbody>
</table>
4. Results

4.1.4 Surface Cracking

The cracks investigated on the surface of the salt treated specimens were present in all samples for all applied stresses and salt concentrations. The cracks were oriented parallel to the rolling direction of the sheet material.

The cracks were very few for the specimens tested at $\sigma_{40\%YS}$, in particular for $\sigma_{40\%YS}$-1% NaCl. The amount of cracks observed on the surface increase significantly when the stress was increased to $\sigma_{60\%YS}$ and above, regardless of the salt concentration.

The test was performed twice for $\sigma_{40\%YS}$-3% NaCl since no surface cracks were present on any of the duplicate specimens. Since cracking have been present at lower salt concentrations, new specimens were prepared and the test was rerun. For the second test, one of the duplicate specimens had very few cracks on the test region whilst the other specimen exhibited no cracks at all.

4.1.5 Cross Section

The optical micrographs of the cross sections of the samples can be seen in Figures 4.10a-4.10h. In general, Ti6242 had difficulties exhibiting cracks at $\sigma_{40\%YS}$. Interestingly, cracking was observed for $\sigma_{40\%YS}$-1% NaCl whilst no cracking was observed for $\sigma_{40\%YS}$-3% NaCl, despite the higher salt concentration in the saline solution for the latter. However, the crack displayed in Figure 4.10a is the only crack found and it was on one of the duplicate specimens. The other duplicate specimen had no cracks.

The cross section of the large crack presented earlier (Figure 4.8) is presented in Figure 4.10h. The depth of this crack was measured to be 1044.16 $\mu$m.
4. Results

(a) $\sigma_{40\%YS-1\% \text{NaCl}}, 100X$

(b) $\sigma_{40\%YS-3\% \text{NaCl}}, 500X$

(c) $\sigma_{60\%YS-1\% \text{NaCl}}$

(d) $\sigma_{60\%YS-3\% \text{NaCl}}, 200X$

(e) $\sigma_{85\%YS-1\% \text{NaCl}}, 100X$

(f) $\sigma_{85\%YS-3\% \text{NaCl}}, 100X$

(g) $\sigma_{95\%YS-1\% \text{NaCl}}, 200X$

(h) $\sigma_{95\%YS-3\% \text{NaCl}}, 100X$

Figure 4.9: Surface cracking in Ti6242. Cracking occurred along the rolling direction.
4. Results

(a) $\sigma_{40\%YS-1\% \text{NaCl}}$

(b) $\sigma_{40\%YS-3\% \text{NaCl}}$

(c) $\sigma_{60\%YS-1\% \text{NaCl}}$

(d) $\sigma_{60\%YS-3\% \text{NaCl}}$

(e) $\sigma_{85\%YS-1\% \text{NaCl}}$

(f) $\sigma_{85\%YS-3\% \text{NaCl}}$

(g) $\sigma_{95\%YS-1\% \text{NaCl}}$

(h) $\sigma_{95\%YS-3\% \text{NaCl}}$

Figure 4.10: Cross sections of showing cracking in Ti6242. Cracks propagated perpendicular to the applied tensile stress.
4. Results

4.2 Cracking Properties

During the investigation of the cross sections, the encountered cracks were measured and documented.

4.2.1 Average Crack Length

The average crack lengths for each material was also determined with the same procedure as previous. All the cracks found in the duplicate specimens were compiled and an average was calculated. The average crack lengths (ACL) of Ti64, Ti811, and Ti6242 are presented in Figures 4.11a, 4.11b, and 4.11c respectively. In general, it can be seen that the ACL seem to increase with applied mechanical stress. Furthermore, the applied mechanical stress seem to play a dominant role for the ACL, whilst the salt concentration plays a more recessive role. This is displayed in the graphs (Figures 4.11) were ACL increases significantly with the increase in stress, whilst the difference between ACL when altering the salt concentration, is minimal. This is perhaps best illustrated in Figure 4.11b.
4. Results

(a) Ti64

(b) Ti811

(c) Ti6242

Figure 4.11: Average cracks lengths of the different titanium alloys investigated in this work.
4.2.2 Average Crack Density

Figure 4.12 presents the evolution of the average crack density (ACD) and how it is affected by the applied mechanical stress. The ACD was determined by calculating the amount of cracks over a unit length. To determine the ACD of a given material, the ACD was first calculated on the two halves for each specimen, and this was performed for both of the duplicated specimens. An average crack density was then calculated.

In general, the ACD increases as the applied mechanical stress increases, as seen in Figure 4.12. For Ti64, the increase in ACD is minimal regardless of the salt concentration where the highest value for ACD was found for $\sigma_{85\%YS} - 3\% \text{ NaCl}$. The value was however very close to zero ($\sim 0.2\text{mm}^{-1}$). Ti811, and Ti6242 exhibited very similar behavior in regards to the ACD at $\sigma_{90\%YS}$. In fact at this stress level, Ti811 (high salt concentration) and Ti6242 (high and low salt concentrations) had the same ACD value of $\sim 1.5\text{mm}^{-1}$. Interestingly, Ti811 exhibited the highest ACD value of $\sim 1.8\text{mm}^{-1}$ when tested at low salt concentrations. At stresses $\sigma_{85\%YS}$ and $\sigma_{95\%YS}$, Ti811 clearly exhibits a higher ACD for both salt concentrations, in comparison to Ti6242. Furthermore, the ACD values for Ti6242 are very similar despite the change in salt concentration. For Ti811 on the other hand, a significant scatter in ACD values were found, where the highest difference can be found at $\sigma_{85\%YS}$. Noteworthy, the ACD seem to be higher when the alloys were tested at lower salt concentration, rather than the expected higher salt concentration. This was the case at stresses $\sigma_{60\%YS}$, $\sigma_{85\%YS}$, and $\sigma_{95\%YS}$.

![Figure 4.12: Average crack density for the different titanium alloys.](image_url)
4.2.3 Crack Morphology

The cracks obtained from HSSCC using the 2-point loading method were further characterized with SEM. Extensive research on the cracking behavior for Ti64 and Ti811 in regards to HSSCC, have been made throughout the years. For Ti6242 on the other hand, few scientific articles were found on the alloys cracking behavior under HSSCC mechanisms. In this work, the alloys Ti811 and Ti6242 gave similar results when the method 2-point load method was used. It was therefore of interest to further investigate, characterize, and compare the cracks obtained in these alloys (due HSSCC).

Figures 4.13 and 4.14 present two typical appearance of the HSSCC of Ti811 when in contact to Sodium chloride. The equivalent images for Ti6242 are presented in Figures 4.15 and 4.16. The BS-SEM images reveal a clear distinction between the phases as the alpha matrix (grey) with dispersed beta (beta) can be observed. The features of the phases were obtained by compositional contrast used in the BS-SEM images. The examination of the cross sections revealed that cracking was predominately intergranular with some limited regions of transgranular crack propagation for both Ti6242 and Ti811. Both cracking mechanisms can clearly be seen in Figure 4.16. The cracks had in general little branching even though it was present. The branching seems to be more occurring in Ti811 when compared to Ti6242.

![Figure 4.13: BS-SEM of Ti811.](image)

Figure 4.13: BS-SEM of Ti811.
4. Results

Figure 4.14: BS-SEM of Ti811.

Figure 4.15: BS-SEM images of Ti6242.
Figure 4.16: BS-SEM images of Ti6242.
5

Discussion

5.1 HSSCC Susceptibility

For a long time, the rule of thumb for determining the susceptibility of a titanium alloy to HSSCC was the aluminium and/or oxygen content. The lower the aluminium and/or oxygen, less beta is stable, and thus the alloys are more susceptible to HSSCC. Even though it is a good guidance, the susceptibility of a titanium alloy to HSSCC is more complex than that, as is reflected in the results of this current work. Ti811 and Ti6242 showed a similar cracking behavior where the former was slightly more susceptible to HSSCC since cracking occurred in almost all configurations. The similar behavior in cracking between the alloys is quite surprising since Ti64 and Ti6242 both have the same aluminum content and are both classified as $\alpha+\beta$ alloys. Ti811 on the other hand, is a near-alpha alloy with a greater aluminum content, and thus expected to be the most susceptible alloy. Hugh R. Gray [28] investigated the relative susceptibility of seven different titanium alloys and concluded that Ti64 and Ti6242 showed a similar behavior. The same materials with similar heating history as the one in this current work, were used in Grays study. However, the test method was different. Grey used a mechanical fracture approach where a tensile testing method with slow rate strain was used. The factor comparing the different alloys were thus the stress intensity factor. In the present study, the comparing factor between the alloys is made through the relative stress in regards to their yield and not their stress intensity factor. When Gray compared the susceptibility of the alloys based on the crack threshold stress as a percentage of the creep strength of the alloys, Ti64 was ranked as the superior alloy to resist HSSCC. Ti6242 and Ti811 were found to be significantly more susceptible to HSSCC, where the latter had a slightly higher susceptibility. These results are coherent with the results found in this work. The comparison in susceptibility between alloys is more meaningful since a materials strength is a limiting design factor.

5.1.1 Salinity and Stress

The increase in salt concentration did indeed have some effect on the susceptibility of the material in regards to the surface cracking. It was clear that cracking started to occur at higher salinity levels when the applied stresses were kept constant and this phenomenon was seen for all alloys. However, the salinity showed to have little to no effect on the crack density in all alloys as they had more or less the same value regardless of the salt concentration. The results from the literature also indicate that the salt concentration have a minor influence on the susceptibility of the tested
titanium alloys.[28, 37] However, it should be mentioned that the results in ACD deviated for stresses $\sigma_{85\%YS}$ and $\sigma_{95\%YS}$, since a significant difference in values were observed. The observed difference in ACD at these stresses are not fully understood but one could argue that they could be due to the limited producibility in the nature of the test. The saline solution is applied on the apex of the loaded sheet specimen since it is in this region the pre-calculated stress is found. A slight misalignment in the application of the saline solution would mean that the test would operate at a slightly lower stress than the one intended for that specific specimen. This might explain why the ACD for Ti811 exhibited a difference between the two salt concentrations. Thus the right applied stress is essential the testing of HSSCC susceptibility of titanium alloys with this method. This was reflected in the results as the density of cracks found on the surface of the cracks seem to increase as the applied stress is increased. The mechanical stress also affected the ACL and ACD, in a similar way.

5.1.2 Rolling Orientation

The rolling direction for the sheet specimens was in this work oriented perpendicular to the specimen length (Figure 3.2). Striations were observed in all the specimen for all alloys and they were oriented parallel to the rolling direction. Since these are in fact surface flaws, the question arises whether or not the surface flaws attribute to pre-existing damage of the specimen. Previous reports have shown that crack initiation is rather insensitive to pre-existing surface flaws.[38] Furthermore, another investigator concluded that the orientation of the rolling direction had no influence on cracking on Ti64 [38] but found a greater deterioration of the tensile properties in the transverse direction for Ti811.[39] Furthermore, another investigator found that cracking was more severe in the transverse specimen when testing Ti-5Al-2.5Sn. The susceptibility of an titanium alloy to the rolling direction seem thus to depend on the type of alloy which is being tested.

5.2 Cracking Mechanism

The images obtained from the optical microscope showed that all cracks stemmed from a corrosion pit. This suggests that the cracking mechanism present in this alloys, when tested with this method, gives a cracking mechanisms similar to the one suggested by Myers and Hall[45]. However, the crack characterization conducted in this work is limited and thus makes it difficult to draw any conclusions. Moreover, SEM images taken from Ti811 and Ti6242, revealed that the crack propagation occurred mostly along the grain boundaries. Similar results have been reported for Ti811 [40].

5.3 Anomalies

Several white spots were found on some of the untreated specimens after being subjected to HSSCC conditions. Similar findings were reported by A. K. Wong et
5. Discussion

al. [29] where the same method was used. The conclusion was that the spots were
due to spot pitting from unintentional contamination. The cause of contamination is
unknown, but one possible source which may explain the occurrence of spot pitting
in the untreated specimens, may be the air flow inside the furnace. If the saline
solution had not completely dried after application, and the specimens were placed
too close to one another, drops of the saline solution could possibility have reached
the untreated specimens with the assistance of the circulating air. This may be
prevented by decreasing the airflow inside the furnace. The airflow has been reported
to have a minor influence on the susceptibility [37]

5.4 Comparison between Ti811 and Ti6242

Since the testing method requires that the applied stresses are within the elastic
region of the chosen testing material, a liaison between the testing alloys could be
made. This liaison facilitates the comparison to the different alloys by testing their
relative susceptibility to hot salt. Figure 5.1 presents a compilation of all the results
based on alloy, stress applied, salt concentration, and inspection plane. It is clear
that Ti811 and Ti6242 experience a similar susceptibility to hot salt when tested
with a two-point bending test method within the chosen testing range of this work.

<table>
<thead>
<tr>
<th>Material</th>
<th>Stress/salt conc.</th>
<th>Ti811</th>
<th>Ti811</th>
<th>Ti6242</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No cracks</td>
<td>No cracks</td>
<td>No cracks</td>
<td>No cracks</td>
</tr>
<tr>
<td>0%</td>
<td>No cracks</td>
<td>No cracks</td>
<td>No cracks</td>
<td>Cracking</td>
</tr>
<tr>
<td>0%</td>
<td>No cracks</td>
<td>No cracks</td>
<td>No cracks</td>
<td>Cracking</td>
</tr>
<tr>
<td>0%</td>
<td>No cracks</td>
<td>No cracks</td>
<td>No cracks</td>
<td>Cracking</td>
</tr>
</tbody>
</table>

**Figure 5.1:** Overall result for all tested titanium alloys
Conclusion

The following conclusions can be drawn from the obtained results:

- This test method provides a simple evaluation of susceptibility of sheet material with minimum sample preparation. The test method apparatus is inexpensive and provides multiple test specimens to be tested at the same time.
- The high resistance of Ti64 to SCC was also present in this work, where the test method had difficulty inducing cracks where hot salt was used as test environment.
- T811 and Ti6242 showed to be highly susceptible to HSSCC for the test configurations conducted in this work.
- Increased stresses produced more harmful effects and seem in general to affect the susceptibility more than the variation of salt concentration.
- The crack propagation in Ti811 and Ti6242 seem to occur along the grain boundaries. However, more crack characterization is required.

6.1 Future Work

The environment chosen for this testing method was hot salt. In order to get a more versatile testing method, it would be of interest to test other environments. An attempt of crack characterization was performed in this work. However, due to time restrictions only optical and electron microscopy could be used. In order to fully understand the crack mechanism occurring in the materials by using this testing method (and environment), further characterization is needed. From a statistical point of view, it would be interesting to repeat the test multiple times and see if there is any discrepancies in the results.
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https://doi.org/10.5006/0010-9312-33.7.252
