

# Impact of Transient Environmental Conditions on Pitting and Cracking

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# List of Abbreviations

| AK                                                  | Aspect Katio                                                                                                                                                                                                                                                                                                                           |
|-----------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| BCC                                                 | Body Centered Cubic                                                                                                                                                                                                                                                                                                                    |
| BCT                                                 | Body Centered Tetragonal                                                                                                                                                                                                                                                                                                               |
| BE                                                  | Binding Energy                                                                                                                                                                                                                                                                                                                         |
| BSE                                                 | Back-scattered Electron                                                                                                                                                                                                                                                                                                                |
|                                                     |                                                                                                                                                                                                                                                                                                                                        |
| CCD                                                 | Charged Coupled Device                                                                                                                                                                                                                                                                                                                 |
| CE                                                  | Counter Electrode                                                                                                                                                                                                                                                                                                                      |
| CF                                                  | Corrosion Fatigue                                                                                                                                                                                                                                                                                                                      |
| CGR                                                 | Crack Growth Rate                                                                                                                                                                                                                                                                                                                      |
| CPT                                                 | Critical Pitting Temperature                                                                                                                                                                                                                                                                                                           |
| CR                                                  | Corrosion Rate                                                                                                                                                                                                                                                                                                                         |
| CV                                                  | Coefficient Of Variation                                                                                                                                                                                                                                                                                                               |
|                                                     |                                                                                                                                                                                                                                                                                                                                        |
| DC                                                  | Direct Current                                                                                                                                                                                                                                                                                                                         |
|                                                     |                                                                                                                                                                                                                                                                                                                                        |
| DCPD                                                | Direct Current Potential Drop                                                                                                                                                                                                                                                                                                          |
| DCPD<br>DIC                                         | Direct Current Potential Drop<br>Digital Image Correlation                                                                                                                                                                                                                                                                             |
| DCPD<br>DIC                                         | Direct Current Potential Drop<br>Digital Image Correlation                                                                                                                                                                                                                                                                             |
| DCPD<br>DIC<br>EAC                                  | Direct Current Potential Drop<br>Digital Image Correlation<br>Environmentally Assisted Cracking                                                                                                                                                                                                                                        |
| DCPD<br>DIC<br>EAC<br>ECN                           | Direct Current Potential Drop<br>Digital Image Correlation<br>Environmentally Assisted Cracking<br>Electrochemical Current Noise                                                                                                                                                                                                       |
| DCPD<br>DIC<br>EAC<br>ECN<br>EDM                    | Direct Current Potential Drop<br>Digital Image Correlation<br>Environmentally Assisted Cracking<br>Electrochemical Current Noise<br>Electrical Discharge Machining                                                                                                                                                                     |
| DCPD<br>DIC<br>EAC<br>ECN<br>EDM<br>EIS             | <ul> <li>Direct Current Potential Drop</li> <li>Digital Image Correlation</li> <li>Environmentally Assisted Cracking</li> <li>Electrochemical Current Noise</li> <li>Electrical Discharge Machining</li> <li>Electrochemical Impedance Spectroscopy</li> </ul>                                                                         |
| DCPD<br>DIC<br>EAC<br>ECN<br>EDM<br>EIS<br>EN       | <ul> <li>Direct Current Potential Drop</li> <li>Digital Image Correlation</li> <li>Environmentally Assisted Cracking</li> <li>Electrochemical Current Noise</li> <li>Electrical Discharge Machining</li> <li>Electrochemical Impedance Spectroscopy</li> <li>Electrochemical Noise</li> </ul>                                          |
| DCPD<br>DIC<br>EAC<br>ECN<br>EDM<br>EIS<br>EN<br>EN | <ul> <li>Direct Current Potential Drop</li> <li>Digital Image Correlation</li> <li>Environmentally Assisted Cracking</li> <li>Electrochemical Current Noise</li> <li>Electrical Discharge Machining</li> <li>Electrochemical Impedance Spectroscopy</li> <li>Electrochemical Noise</li> <li>Electrochemical Potential Noise</li> </ul> |

| FEA Finite Ele | ement Analysis |
|----------------|----------------|
|----------------|----------------|

FEG Field Emission Gun

- FFT Fast Fourier Transform
- FIB Focused Ion Beam
- FWHM Full Width Half Maximum
- HAZ Heat Affected Zone
- HE Hydrogen Embrittlement
- HFW Horizontal Field Width
- HPST High Pressure Steam Turbine
- IPST Intermediate Pressure Steam Turbine
- KE Kinetic Energy
- LCSM Laser Confocal Scanning Microscopy
- LEFM Linear Elastic Fracture Mechanics
- LPR Linear Polarisation Resistance
- LPST Low Pressure Steam Turbine
- OM Optical Microscopy
- PDM Point Defect Model
- PEEK Polyether Ether Ketone
- PFIB Plasma Focused Ion Beam
- PI Pitting Index
- PREN Pitting Resistance Equivalent Number
- PSB Persistent Slip Band
- RE Reference Electrode
- RoI Region Of Interest
- SCC Stress Corrosion Cracking
- SCE Saturated Calomel Electrode

| SCF | Stress Concentration Factor      |
|-----|----------------------------------|
| SE  | Secondary Electron               |
| SEM | Scanning Electron Microscope     |
| SS  | Stainless Steel                  |
| TEM | Transmission Electron Microscope |
| WE  | Working Electrode                |
| WSE | Working-sense Electrode          |
|     |                                  |
| XCT | X-ray Computed Tomography        |
| XPS | X-ray Photoelectron Spectroscopy |
| XRD | X-ray Diffraction                |
|     |                                  |
| ZRA | Zero Resistance Ammeter          |

## Abstract

#### Impact of Transient Environmental Conditions on Pitting and Cracking

Philip J ALDHOUS, The University of Manchester, Doctor of Philosophy, 2021

Coal-fired power stations that were originally designed to provide the baseload energy are now required to operate a two-shifting procedure; to better match consumer demand. The procedure involves switching between periods of on-load operation and off-load shutdown. This results in transient excursions in the chemistry of the steam due to the ingress of species such as oxygen and chloride. The synergistic combination of these species results in the initiation of corrosion pits which are known crack initiation sites in the corrosion fatigue (CF) process. Corrosion pits initiate in the low pressure steam turbine (LPST) of the energy extraction system, where the blades are commonly made from 12Cr stainless steel (SS). A major challenge in an industrial plant is the quantitative prediction of pitting, pit-crack transition and CF, defining inspection intervals and lifetime prediction of components and structures. By investigating the effects of transient environment conditions on corrosion pit initiation and observing the pit-crack transition, this PhD research project contributes towards understanding some of the challenges faced.

Current research has utilised a full immersion setup to simulate a LPST by controlling the water chemistry and performing electrochemical measurements, such as corrosion potential (E<sub>corr</sub>) monitoring. Further work is needed to understand the implications of environmental ageing on the development of the passive film, as there are results which suggest a superior passive film was developed as a result. By utilising additional electrochemical and characterisation techniques, such as electrochemical noise (EN) and X-ray photoelectron spectroscopy (XPS), this research supports claims that a more protective passive film forms, even after a short exposure to a simulated on-load environment. Characterisation of the passive films from different environments has shown that the composition is altered upon exposure to deaerated on-load conditions and provides an explanation for the increased chloride concentration required for pit initiation. Analysis of EN, with a bespoke MATLAB<sup>®</sup> routine, was evaluated as an additional technique for monitoring the electrochemical processes occurring in the simulated LPST environments.

An abundance of research has also shown that corrosion pits act as crack nucleation sites under an applied load, due to the concentration of stress and the impact of local electrochemistry. While most studies have focused on measuring the short and long crack growth rate from such defects, very few have looked at the early stages of crack initiation. More specifically, the location at which a crack nucleates at from a corrosion pit. Two main sites present themselves—the base and the mouth of the corrosion pit due to the concentration of stress and strain. X-ray computed tomography (XCT) work has previously shown that cracks preferentially initiated at the mouth for 3NiCrMoV steel under stress corrosion cracking (SCC) conditions, and this research has identified, with XCT and plasma focused ion beam (PFIB), that the same region is favoured for 12Cr martensitic SS under fatigue loading. The implications of this are that assumptions made about preferred crack nucleation at the base of a pit may not hold true in all cases.

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"I think it is a sad reflection on our civilization that while we can and do measure the temperature in the atmosphere of Venus, we do not know what goes on inside our soufflés."

Nicholas Kurti, 1969

## Chapter 1

## Introduction

#### Contents

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#### 1.1 **Power Generation**

Power stations are industrial facilities that generate electrical power which is utilised in many industrial, commercial, and consumer applications (Fig. 1.1). The global electricity generating capacity in 2011 was 5201 GW and was projected to increase to 6577 GW by 2020 [1].



FIGURE 1.1: An aerial image of Drax power station in Selby, Yorkshire.



FIGURE 1.2: The global generating capacity for each energy type in 2011 and the predicted sizes in 2020 and 2030. Data from Breeze [1].

The largest sources of this energy are currently coal and natural gas, with renewable sources (hydropower, wind, solar) expected to show rapid growth, enabling them to contribute more energy, and ultimately to meet the predicted energy capacity of future decades (Fig. 1.2). However, the sources of energy for solar and wind power plants are intermittent [2], meaning that these plants will be performing well, if they can generate full power for 40 % of the time. Consequently, coal, natural gas, and nuclear power plants will continue to be required to provide a base load of energy and provide additional power when renewable sources cannot.

Accordingly, this makes coal one of the most important sources of electrical power in the world today, responsible for 39% of the world electricity production [3]; despite the UK government plans to close the remaining four coal-fire power stations. To obtain the energy that is stored within the coal, the traditional method is to ignite and burn the fuel in air and capture the heat released during the combustion process. Conventional systems will raise the temperature of water to form steam, which is then used to drive a steam turbine generator that has been designed to extract as much energy as possible from the gas, as shown in Fig. 1.3.



FIGURE 1.3: Schematic of a steam turbine in a power plant. Image from Breeze [3].

Efficiency is the key to modern coal burning technology, in order to produce the cheapest units of electricity that are sold to consumers. Currently, the efficiency of a coal fired power station is in the range 40 % to 45 %. In large power stations, the steam turbine consists of three stages to maximise the amount of extraction, which are a high (HPST), an intermediate (IPST) and a low pressure steam turbine (LPST). To optimise the efficiency of the cycle, the steam is often reheated between the HPST and IPST, in part of the boiler, as represented in Fig. 1.3. Additionally, many power plants are adopting two-shifting cycles to better match the power demand of the national grid, consequently plants are typically on-load for 16 h per day and off-load overnight and at weekends [4, 5]. During an off-load period, the glands of the turbine are no longer sealed, due to the loss of steam pressure, so air leakage occurs, providing sufficient concentrations of oxygen which can facilitate electrochemical processes such as corrosion [6].

As the hot pressurised steam passes over the blades, it forces them to rotate. The action of this converts the heat energy into rotary mechanical energy, where the steam turbine shaft can rotate at 3000 rpm [7]. The blades in the HPST have to be able to withstand both extreme temperature ( $500 \circ C$ - $600 \circ C$ ) and pressure (23 MPa-30 MPa) and resist the abrasive force of the steam [3]. As the pressure and temperature reduces through the



FIGURE 1.4: (A) An image of a low pressure steam turbine. (B) A detailed view of the turbine blade and the fir tree root at the base, that retains the blade in the disk. Images from James et al. [7].

turbine stages, the LPST blades are designed to be longer (1 m), meaning that the 12Cr stainless steel (SS) material chosen has to resist high blade tip speeds and centrifugal forces. An example of a LPST and LPST blade can be seen in Figs. 1.4A and 1.4B respectively.

An additional hazard within the LPST section is that the steam will have cooled sufficiently (120 °C–90 °C) that vapour will start to condense on the surfaces of the blades [6] and a greater amount of condensation occurs when the plant is off-load [4]. Furthermore, solid particles and impurities may have been dragged by the steam flow, which can be deposited onto the blades, causing wear and reducing the turbine efficiency. This has resulted in a significant research programme by the Electric Power Research Institute since the 1930s [8, 9], in order to improve the understanding of these processes. Consequently, the power plants will control and monitor the boiler water, with the intention of minimising the concentration of contaminants in the steam. Nevertheless, significant concentrations of contaminants, including sodium, silica, chloride, sulphate, iron and copper can be found in the steam environment and are coupled with high oxygen concentrations (7.6 ppm at 30 °C) during shut-down [6]. Some of these species (mainly chloride in an aerated environment) will promote corrosion of the LPST blades, which may then lead to stress corrosion cracking (SCC) or corrosion fatigue (CF) failure [10].

#### **1.2** Failure of Steam Turbines

It has long been established that many of the operational issues related to LPST blades are due to impurities, which contaminate the steam condensate, forming at around 90 °C, facilitating corrosion based processes. This matter must be adequately managed in order to ensure the safe and continuous operation of the steam turbine, nevertheless there are numerous reports of turbine failures, which can have catastrophic consequences [10–12]. To improve the resistance to failure, sometimes the main blade and/or the fir tree root will be shot peened to create a compressive residual stress [7], which will oppose the tensile forces required for crack propagation.

In many of these cases, corrosion pits are reported as the precursor to crack initiation and growth, so a comprehensive understanding of the initiation and growth of corrosion pits, the pit-crack transition, and crack growth is required in order to assist in defining inspection intervals and help with the lifetime prediction of components and structures. This sequence of events is known as CF and may be thought of in terms of total lifetime,  $N_{total}$ , where segments are attributed to the stages just mentioned, such that:

$$N_{total} = N_{film \ breakdown} + N_{pit \ growth} + N_{pit-crack} + N_{short \ crack} + N_{long \ crack}$$
 (1.1)

which can be also represented schematically, as shown in Fig. 1.5. It should be noted that a significant proportion of the CF lifetime is spent in the pitting and pit-crack stages.

An understanding of the effects of two-shifting, as well as contamination excursions, is required in order to effectively predict the rate of evolution of damage during each stage. Consequently, this research project will focus on the characterisation of corrosion pitting and the early stages of crack development in the pit-crack transition.



FIGURE 1.5: A schematic showing the stages of corrosion fatigue. Image from Akid [13].

#### 1.3 Aims and Objectives

This PhD research project was undertaken with the intention of providing information and knowledge that would contribute towards predicting the damage evolution of LPST blades during their in-service lifetime. The blades are typically constructed from a 12Cr grade martensitic SS due to the good fatigue and creep properties and adequate corrosion resistance of these types of materials. As previously mentioned, the focus was on two critical areas, the first involving characterisation and quantification of the effects of environmental excursions on corrosion pitting. A flow loop was constructed such that the temperature, flow rate, oxygen and contaminant concentration could be carefully controlled and monitored with in-line conductivity and oxygen probes. This allowed an environment akin to that within the LPST to be recreated in a controlled and safe manner, while enabling electrochemical measurements to be taken simultaneously. Secondly, to aid understanding of the pit-crack transition, interrupted fatigue tests were conducted on specimens containing a corrosion pit so that the evolution of a crack at this location could be observed and characterised by optical microscopy (OM), X-ray computed tomography (XCT) and plasma focused ion beam (PFIB) milling. This would provide clarification on where cracks were likely to initiate from within a corrosion pit to aid with lifetime modelling.

In order to achieve the aims of the project, the following objectives were identified:

- 1. Identify the critical concentrations of contaminants that are required for the initiation of corrosion pits on candidate LPST blade materials.
- Evaluate electrochemical noise (EN) as a technique for monitoring the evolution of corrosion during exposure to a simulated steam environment.
- 3. Develop an understanding regarding the alteration of the material's passive film during simulated two-shifting between on-load and off-load conditions.
- 4. Evaluate possible techniques for creating a single corrosion pit that accurately represents the corrosion pits that initiate in the simulated steam environment.
- Perform interrupted fatigue tests on specimens with single artificial pits and observe the crack initiation behaviour on fine ground and shot peened surfaces using in-situ OM.
- 6. Investigate the location of crack initiation at a corrosion pit by assessing the suitability of XCT and PFIB characterisation.
- 7. Determine whether digital image correlation (DIC) can be used to measure the strain around a corrosion pit at the pit-crack transition.

#### **1.4** Structure and Navigation

This thesis contains eight chapters; with Chapter 2 providing a review of the current literature, focusing on SS, corrosion, fatigue and environmentally assisted cracking (EAC). Following that, Chapter 3 provides a description of the main experimental and characterisation techniques that have been utilised during the completion of this research project.

The subsequent chapters (Chapters 4 to 6) contain information relating to the main experimental work undertaken, as well as the results from such work. Chapter 4 reports on the findings of exposing two 12Cr martensitic SSs (403 and FV566) to a variety of simulated steam turbine environments and the applicability of EN to this setup. The author anticipates that the experiments and results from this chapter will be published in due course. Chapter 5 introduces the electrochemical techniques that were evaluated for creating single artificial corrosion pits to mimic the morphologies of those pits observed in Chapter 4. The creation of single pits would encourage cracks to initiate at a known location in the fatigue testing within Chapter 6. This chapter also contains the findings from using XCT and PFIB to identify the location of crack initiation at a corrosion pit. It is expected that the results within Chapter 5 and Chapter 6 will form a second paper. Finally, in Chapter 7, the main results of the research project are discussed together and evaluated against the project objectives with recommendations for future work made in Chapter 8. At the end of the document are the appendices—the first, Appendix A, provides the MATLAB<sup>®</sup> script that was written to automate the analysis of EN data. Following this, Appendix B presents some initial exploratory results which used DIC to monitor the evolution of strain around a corrosion pit under fatigue loading.

To aid the navigation of this thesis, a table of contents, list of figures and list of tables can be found on pages 6, 11 and 12 respectively. Additionally, a detailed mini table of contents is included at the start of each chapter. If this document is viewed digitally, then cross reference links within the text to chapters, sections, figures, tables, equations, acronyms and references are all interactive. Finally, with the keyboard shortcut Alt + Left, it is possible to return to the previous view if using Adobe Acrobat Reader. For example, this chapter reference takes you to *chapter 2*.

## Chapter 2

# Steam Turbine Design and Degradation

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#### 2.1 Overview

This chapter will provide an introduction to stainless steel (SS) alloys and how they are utilised to form the components of a steam turbine. Additionally, the degradation of key components will then be discussed in terms of corrosion, fatigue and environmentally assisted cracking (EAC) mechanisms. By doing this, it is possible to highlight key pieces of research that have been conducted within this research area as well as identifying pertinent points that this research will aim to address.

#### 2.2 Stainless Steels

#### 2.2.1 Introduction and Background

In the early 20th century, metallurgists had been developing and investigating a new classification of material that has become known as SS. Initially, it was interest in the effects of heat treatments on the mechanical properties and metallographic features of chromiumnickel steels. This was later extended to the evaluation of the material's corrosion resistance by Philip Monnartz in Germany. Following the publication of his work, others found that SS was a commercially viable product—initially being used to make cutlery by Harry Brearley, the initiator of the industrial era of SS [14]. Immediately identifying the practical importance of this discovery, Brearley applied for patents for his "rustless" cutlery that was developed with Ernest Stuart at Messrs. R. F. Mosely in Sheffield [15].

Since then, many SS alloys have been developed that offer a range of mechanical performance and corrosion resistance properties across a wide price range. Critically though, as described by Zapffe [16], the SS alloy must contain at least 12% chromium for there to be no (low) measurable corrosion rate (CR)—in his case—over a ten year period of exposure to 33% nitric acid solution (Fig. 2.1). The effect of the addition of such contents of chromium allows the formation of an adherent and 'self-healing' passive film which sets SS apart from regular carbon steels. The passivity of iron based alloys was first reported by Keir [17] in the 18th century when it was reported that treating iron with nitric acid preserved its "metallic splendour" when trying to precipitate silver from silver nitrate. Later on, this was explained by Faraday and Schoenbein [18] who discussed the formation of an "invisible" oxide layer of iron, this remains the fundamental explanation for the passivating nature of SS.



FIGURE 2.1: Effect of chromium content on corrosion resistance of steel. Exposure of iron-chromium alloys for 10 years to an industrial atmosphere. Reproduced from Zapffe [16].

#### 2.2.2 Passivity of Corrosion Resistant Alloys

Upon exposure to air or aqueous solutions, high performance alloys such as SS and aluminium will spontaneously form a dense passive film that provides protection from corrosion for the underlying metal. Such oxide film on pure polycrystalline iron can be seen by the use of a transmission electron microscope (TEM), as shown in Fig. 2.2. The passive film forms due to the oxidising nature of the environment and, in the case of SSs, forms a duplex layer structure consisting of inner chromium oxide and outer iron oxide with hydroxide at the interface that is in total around 1 nm to 10 nm thick. [19–22].

The passive film will constantly adapt to the surrounding environment and experience film dissolution and growth to accommodate the necessary changes. Therefore, the composition and thickness of the passive film are dependant upon the pH of the environment (in an alkaline solution the solubility of iron is lower than chromium causing an enrichment of chromium in the film [23]), relative humidity, aeration, potential [24], and also the chemical composition of the alloy [23]. The passive layer provides a barrier to the surrounding environment and acts to minimise the CR of the metal substrate beneath it.



FIGURE 2.2: High resolution TEM image of the interface between an iron foil and oxide film roughly 5 nm in thickness. Image taken from Bhargava et al. [21]

Some factors, such as temperature, have been shown to have little effect on the thickness and composition of the passive film when comparing passive films formed in 0.1 mol NaCl solution at 25 °C and 90 °C [25]. Other factors have a greater influence upon the passive film, such as the alloy's chromium content. Chromium has a high affinity for oxygen and readily forms an oxide film. Additionally it has been shown that increasing the atomic percentage of chromium in an alloy will reduce the passive current density as well as increasing the pitting potential to a higher value (Fig. 2.3) resulting in a passive film that is stable over a wide potential range [26].

It has been common to use X-ray photoelectron spectroscopy (XPS) to determine the composition of the passive film. Additionally, angular resolved XPS can provide information about the depth distribution of different species and their corresponding oxidation states [23]. This shows that the inner layer is mainly chromium oxide ( $Cr_2O_3$ ), due to dissolution of the iron compounds in an aqueous environment, which provides the alloy with its observed corrosion resistance. The outer layer of the passive film is composed of a combination of iron and chromium hydroxide.



FIGURE 2.3: Positive relationship between the chromium content in a Fe-Cr alloy and the critical pitting potential. Reproduced from Horvath and Uhlig [26].

#### 2.2.3 Alloy Composition

The nature, composition and stability of the passive film can be altered by including elements that may be added to the iron-chromium alloy, which will, in turn, define the overall apparent corrosion resistance. Common alloying elements may include: nickel, molybdenum, manganese, copper, aluminium, titanium, vanadium, silicon and sulphur with the added concentration, not only affecting the corrosion resistance, but also the microstructural and mechanical properties of the SS alloy. Depending upon the concentration of each alloying element used, the SS alloy will take different crystalline allotropic forms, which in the case of iron based alloys, is normally a body centered cubic (BCC) or face centered cubic (FCC) structure. These two crystalline structures produce a range of properties due to the differing levels of carbon solubility in each crystal structure as shown in the iron-iron carbide eutectoid reaction:

$$\gamma(0.76 \text{ wt\% } \text{C}) \xrightarrow[\text{heating}]{\text{cooling}} \alpha(0.022 \text{ wt\% } \text{C}) + \text{Fe}_3\text{C}(6.70 \text{ wt\% } \text{C})$$
(2.1)

where  $\gamma$  is the austenitic FCC structure,  $\alpha$  is the ferritic BCC structure and Fe<sub>3</sub>C is cementite. This broad range of microstructures and properties means that SS alloys can

be classified into four families, consisting of ferritic (BCC), austenitic (FCC), austeniticferritic (duplex) and martensitic steels. The latter has a metastable body centered tetragonal (BCT) crystal structure which forms due to the rapid quenching of the austenitic FCC structure, from a high temperature, to a highly strained BCT structure due to the restricted period of carbon diffusion out of the FCC octahedral interstitial sites.<sup>1</sup> The addition of nickel to austenitic SSs extends the austenite phase field to room temperature so the FCC structure is retained. Ferritic SSs contain a low concentration of carbon, so on cooling cleanly transforms from the austenitic to a ferritic microstructure. As the concentration of carbon is higher in the martensitic SSs there is some retained austenite in the microstructure. Each family of steels will have different properties, for example, austenitic SSs are non-magnetic whereas ferritic and martensitic SSs are ferromagnetic.

As the alloying elements affect both the microstructure and properties of the SS alloy, they can be summarised in various ways, such as the Schaeffler-Delong diagram shown in Fig. 2.4. The diagram is based upon the ability of the alloying elements to stabilise either the austenite or ferrite phase microstructure at room temperature. Nickel is the main element that promotes the formation of austenite, whereas chromium supports ferrite formation. The other alloying elements will support one of the two microstructures mentioned, which allows a chromium equivalent ( $Cr_{eq}$ ) and nickel equivalent ( $Ni_{eq}$ ) to be calculated by the following two equations [27]:

$$Cr_{eq} = %Cr + 1.5\%Si + \%Mo$$
 (2.2)

$$Ni_{eq} = Ni + 30(NC + N) + 0.5(Nn + Cu + Co)$$
(2.3)

Once calculated, it allows the prediction of the potential microstructure of an alloy when cooled to room temperature, depending upon the concentrations of alloying elements. On the diagram presented, the positions of some of the most common SS alloys are indicated based upon their chemical composition. For example, the most common SS used is an austenitic 304 containing around 18% chromium and 8% nickel, giving a

<sup>&</sup>lt;sup>1</sup>The solubility of carbon in FCC crystals is much higher than BCC due to the difference in size and number of octahedral interstitial sites for the carbon atoms. Therefore if the alloy is cooled at a slower rate carbon will diffuse from the crystal structure as it transitions from FCC to BCC.



FIGURE 2.4: Schaeffler-Delong diagram showing the effect of SS alloying elements, in terms of chromium and nickel equivalent, on the resultant SS microstructure. The two alloys used within this research project have been added to the plot. Figure adapted from Iversen and Leffler [27].
| Grade | Cr    | Мо   | Ni   | С    | Si   | Mn   | Р     | V    | Fe  |
|-------|-------|------|------|------|------|------|-------|------|-----|
| 403   | 11.77 | 0.14 | 0.31 | 0.13 | 0.35 | 0.41 | 0.020 | 0.04 | Bal |
| FV566 | 11.69 | 1.64 | 2.59 | 0.12 | 0.30 | 0.86 | 0.013 | 0.28 | Bal |

TABLE 2.1: Chemical composition of 403 and FV566 martensitic stainless steels provided by NPL (mass %).

 $Cr_{eq}$  of about 18.5 and  $Ni_{eq}$  near to 12.5. Where higher corrosion resistance is required, austenitic alloys such as 316 may be used with increased concentrations of nickel and molybdenum, which raises both  $Cr_{eq}$  and  $Ni_{eq}$ . However, in the case of steam turbine blades, a 12Cr SS is often utilised due to the relatively inert steam environment [28]. As defined by ASTM International in ASTM 982/A982M - 10 [29], such grade of SS material has a composition similar to those given in Table 2.1, where it can be observed that chromium is the main alloying element. Where a more corrosion resistant alloy is desired, FV566 SS can be used as it contains higher concentrations of molybdenum. When calculating the  $Cr_{eq}$  and  $Ni_{eq}$  for the two alloys under study (403 SS—used in USA and FV566 SS—used in Europe respectively<sup>2</sup>) the  $Cr_{eq}$  is calculated as 12.40 and 13.77 and the  $Ni_{eq}$  is 6.19 and 7.45. These values place both alloys in the martensitic region on the left hand side of the Schaeffler-Delong diagram as indicated by the labels in Fig. 2.4.

The alloy composition has been shown to affect the likelihood of producing austenitic or ferritic microstructures in SS alloys. Additionally, the alloying elements will have an impact upon the electrochemical parameters and hence the corrosion properties of the alloy too. The significance of each electrochemical parameter will be discussed in greater detail in a later section (Section 2.3.5). However, as shown in Fig. 2.5, the addition of chromium to the alloy moves the primary passivation potential ( $E_{pp}$ ) in the active direction and extends the pitting potential ( $E_p$ ) to a more noble value which expands the passive potential range [30]. Additionally, the increased chromium concentration will reduce the passive current density ( $i_{pass}$ ) and the maximum current density ( $i_{max}$ ) at the active passive transition. Also evident in the plot is how other elements, such as molybdenum, support the changes to the polarisation curve imparted by the chromium additions. It should also be noted that addition of some elements will have the inverse detrimental effect but these elements are not shown in the diagram.

<sup>&</sup>lt;sup>2</sup>403 SS has a very similar composition to AISI 410 SS. FV566 SS may also be described with the tradename *Jethete M152*.



FIGURE 2.5: Schematic polarisation curve for a passive material showing the effects of alloying elements on the position of the curve. Adapted from Sedriks [30].

To provide further understanding about the effect of alloying elements on corrosion, a simple calculation of the pitting resistance equivalent number (PREN) can be made. This gives a theoretical way of comparing the pitting corrosion resistance of various SS alloys following the equation [31, 32]:

$$PREN = %Cr + 3.3\%Mo + 16\%N$$
(2.4)

however, it does not predict if a certain grade of material will be suitable for a given application or environment. By using the chemical composition of some common alloys, it can be found that the PREN is around 18 for 304 SS and is beyond 25 for 316 SS. Duplex SS have a PREN greater than 30 due to the high chromium and molybdenum content, whereas the 12Cr SS used in this project have a PREN of 13.1 and 17.5, for 403 and FV566 SSs respectively, highlighting the propensity for localised pitting corrosion damage in these martensitic SS alloys.

#### 2.2.4 Families of Stainless Steel

There are four main families into which SSs can be categorised. Each of them is discussed below, outlining the key alloying elements and resulting properties. The alloys used for the steam turbine blades typically have a martensitic microstructure, which is presented in this section, other microstructures are available in resources such as Volume 9 of the ASM handbook [33].

- **Ferritic** Ferritic SS is composed of  $\alpha$ -ferrite phase with a BCC crystal structure. The chromium concentration is usually in the range 14% to 30%—a higher concentration of chromium can be used to resist high-temperature oxidation. To allow stabilisation of the ferritic microstructure to room temperature, no nickel is added and the carbon concentration is kept below 1%. The ferritic alloys tend to have good resistance to corrosion in both MgCl<sub>2</sub> and NaCl environments but become susceptible intergranular corrosion and stress corrosion cracking (SCC) after welding [34]. To improve on these characteristics, new alloys have been developed that incorporate small (<1%) additions of molybdenum, titanium, or niobium. Ferritic SSs show good resistance to chloride SCC but are susceptible to hydrogen embrittement (HE) because of their BCC crystal structure.
- Austenitic The microstructure of austenitic SS consists of  $\gamma$ -phase with FCC crystal structure. This crystal structure has four close packed planes of type {111} with slip occurring in the <111> directions which gives good ductility and toughness properties for these alloys. The most widely used grades are 304 and 316 and they can account for up to 70% of the total tonnage of SS produced [27]. They may have a similar chromium concentration to the ferritic SSs but have additions of nickel and and manganese that assist with stabilising the  $\gamma$ -phase to room temperature. Austenitic SSs are susceptible to chloride SCC as a result of chromium depleted regions around precipitates or grain boundaries [34].
- **Duplex** A dual-phase material is often known as duplex—such as the case with duplex SS where an austenitic-ferritic microstructure exists. Chromium can be added to improve the overall corrosion resistance and nickel can be added to maintain the balance between austenite and ferrite phases as well as improving the mechanical

and physical properties. This results in a microstructure of a continuous ferritic matrix with austenitic islands; often in equal proportions. Duplex SS is often used in environments where a superior level of corrosion resistance is required in conjunction with high tensile and yield strength, such as in the nuclear and oil and gas industries [35].

**Martensitic** If a SS alloy is rapidly cooled (quenched) from the austenitic phase, a new metastable phase called martensite ( $\alpha'$ ) will form. This consists of a super saturated solid solution of carbon in iron, with a BCT crystal structure. The reason for such microstructure is due to the diffusionless (shear) transformation that occurs instantaneously in the transition from the  $\gamma$ -FCC $\rightarrow \alpha'$  phase. Such transformation creates a high density of dislocations in the atomic structure and induces lattice strain due to the retained carbon in the interstitial sites. This produces a very hard material leading to good mechanical properties. However, immediately after quenching, the material is also very brittle, so the as-quenched martensite is often tempered at various temperatures below 996 K to allow diffusion of the carbon from the super saturated solid solution [36]. This carbon precipitates as fine carbides, with Widmanstätten structure, that are evenly distributed throughout the material (Fig. 2.6). As can be seen between the two subfigures (Figs. 2.6A and 2.6B), each of the 12Cr SS has a near identical martensitic microstructure, despite small variation to Mo content. As a result of this microstructure, an increased fracture toughness at similar stresses is provided compared to a pearlitic steel where the carbides are present in thin strips acting as crack initiation locations [37].

To ensure this martensitic structure is achieved, the chromium content needs to be restricted to relatively low levels as shown earlier in the Schaeffler-Delong diagram (Fig. 2.4). As a consequence, the corrosion resistance offered is not as high as other types of SS discussed previously, so these alloys are often used in applications where high-strength, high-toughness materials are required, while offering a relatively low cost. Martensitic SSs offer adequate corrosion resistance to mild atmospheric corrosion and mild chemical environments. Additionally, they can resist short-term exposures to chloride environments but should not be used in continuous chloride exposure conditions such as seawater or marine applications [40].



FIGURE 2.6: Martensitic microstructure of 12Cr stainless steels (A) Grade AISI 410 [38] (B) Jethete<sup>®</sup> FV566 at  $500 \times$  magnification [39].

## 2.2.5 Properties of Stainless Steels

The mechanical properties of metallic materials are defined based upon the results of uniaxial tensile tests. The procedure for carrying out this test is defined in industry standards such as ASTM E8 - 16a [41], where information pertaining to the interpretation of load-displacement data can be found. Once the processing of the data is complete, it is possible to obtain stress-strain curves for the material under test, as shown in Fig. 2.7, where the key regions of the stress-strain curve have been indicated. These regions will be discussed later once the definitions for *stress* and *strain* are considered below. It is possible to observe differences between the properties for transverse and longitudinal testing directions. This is observed in the plot due to the inhomogenous microstructure of the steel and the alignment of inclusions such as manganese sulphide or aluminium oxide during processing of the alloy [42].

When a mechanical test is performed, the specimen will have an initial gauge length of  $L_0$ , a cross-sectional area  $A_0$  and be under an applied load P. The engineering stress  $\sigma_e$  is defined as

$$\sigma_e = \frac{P}{A_0} \tag{2.5}$$

which shows that the engineering stress is directly proportional to the applied load on the specimen. Additionally, if the same load is applied to a smaller cross-sectional area, then the engineering stress will also be higher. However, as a result of the applied load, the cross-sectional area of the specimen reduces as the specimen deforms, meaning that



FIGURE 2.7: An engineering stress-strain curve for FV448 SS—a material representative of those used in low pressure steam turbine blades. Key regions of the plot have been labelled. Adapted from He et al. [42].

Eq. (2.5) becomes increasingly inaccurate as the sample extends [43]. The engineering strain  $\epsilon_e$  is calculated at a specific applied load by measuring the increase in the gauge length of the specimen *dL*, normalised to the initial gauge length of the specimen:

$$\epsilon_e = \frac{dL}{L_0} \tag{2.6}$$

The gauge length will be increasing under load, so a true strain  $\epsilon$  can be defined as

$$\epsilon = \ln(1 + \epsilon_e) \tag{2.7}$$

allowing the true stress  $\sigma$  to be calculated, assuming a constant specimen volume [44], as

$$\sigma = \sigma_e (1 + \epsilon_e) \tag{2.8}$$

Returning now to Fig. 2.7, in the initial region, the relationship between stress and strain is linear for most engineering materials. Additionally within this region, if the load (stress) is removed, the material will unload to its original length ( $L_0$ ) so the material is in a *linear-elastic* region. The relationship between stress and strain can be defined by

Hooke's law as

$$\tau = E\epsilon \tag{2.9}$$

where *E* is the Young's modulus, which for materials such as SSs is around 200 GPa [44].

After a certain applied stress, the engineering material will no longer be able to accommodate the displacement through extension of the interatomic bonds, so the material 'yields' and begins to deform plastically. This means they change their shape in a permanent way and the material enters the *plastic* region. At the point of the onset of plasticity, the yield stress of the material,  $\sigma_y$ , can be defined. This point signifies the movement of crystallographic imperfections called dislocations, which allows for plastic yielding if the material is unloaded above the point  $\sigma_y$  there will be some permanent deformation, i.e.  $\epsilon$  will no longer return to zero as it did within the elastic region. Sometimes  $\sigma_y$  can be hard to identify on the plot, due to gradual material yield, so an alternative measurement is made of the 0.2 % proof stress ( $\sigma_{0.2}$ ) which is defined by constructing a line, with the same gradient as *E*, from a strain of 0.2 % and marking the point of intersection with the stress-strain curve.

The highest stress reached by the material before the onset of necking is defined as the material's ultimate tensile strength ( $\sigma_{UTS}$ ). After this point, the material is able to extend further as the cross-sectional area reduces in a localised area, but the applied force remains close to constant, so the stress does not increase any further once necking has begun before the final fracture of the specimen occurs. Between the positions of  $\sigma_y$  and  $\sigma_{UTS}$ , there is a period of *work hardening* where an increasing applied force is needed to induce further strain in the plastic region. Such increase in strain results in strengthening and hardening of the material, so a larger force is required to maintain the strain increase. This effect is attributed to the interaction and obstruction of dislocations attempting to glide along the slip planes of the material's crystal structure [44].

As a result of the different alloy compositions for SS, a wide variety of mechanical

| AISI        |           | Mecha                     | nical properties        |                  |                                      |  |  |
|-------------|-----------|---------------------------|-------------------------|------------------|--------------------------------------|--|--|
| number      | Condition | Tensile strength<br>(MPa) | Yield strength<br>(MPa) | Ductility<br>(%) | Typical applications                 |  |  |
| Ferritic    |           |                           |                         |                  |                                      |  |  |
| 409         | Annealed  | 380                       | 205                     | 20               | Automotive exhaust components        |  |  |
| 430         | Annealed  | 450                       | 260                     | 20               | Domestic appliances, decorative trim |  |  |
| Austenitic  |           |                           |                         |                  |                                      |  |  |
| 304         | Annealed  | 515                       | 205                     | 40               | Chemical processing equipment        |  |  |
| 316         | Annealed  | 485                       | 170                     | 40               | Welding, construction                |  |  |
| Martensitic |           |                           |                         |                  |                                      |  |  |
| 410         | Annealed  | 425                       | 275                     | 20               | Cutlory ist anging parts             |  |  |
|             | Q&T       | 825                       | 620                     | 12               | Cutiery, jet engine parts            |  |  |
| FV566       | Q&T       | 1007                      | 829                     | 25               | Steam turbine blades                 |  |  |

TABLE 2.2: Designation, condition, mechanical properties and typical applications of common SS grades. Adapted from Callister and Rethwisch [45] to include FV566 SS mechanical properties provided by NPL.

properties can be produced as shown in Table 2.2 for various grades of stainless. To produce good mechanical properties for ferritic and austenitic grades, they must be strengthened and hardened by cold working, which causes dislocation pile-up as mentioned earlier, as the alloys cannot be easily heat treated without losing the microstructure. Martensitic SS can be quenched and tempered (Q&T) to produce a fine lathe structure which essentially produces a very small grain size, increasing the yield strength as each boundary acts as an obstacle to dislocation motion—known as the Hall-Petch effect [45].

# 2.3 Corrosion

## 2.3.1 Introduction and Background

Whether it is the rusting of automotive body panels or an old iron fence, we can assume that everyone is at least a little familiar with corrosion. It can be generally defined as the destruction or degradation of a material, usually a metal, and its properties because of a reaction with its environment [46]. Consequently, corrosion affects many of today's main industries such as the oil and gas sector, nuclear, aerospace, automotive and defence industries. A recent review of current structural integrity research gaps still lists "Materials and degradation" as one of the most critical factors in the integrity of a component or structure [47].

The power generation industry within the UK, follows rigorous guidelines produced by the Government's Health and Safety Executive on the design and operation of power plants. This includes a strict maintenance and inspection programme with the objective of enabling the safe operation of these vital assets for as long a duration as possible. Due to the thorough design, testing and maintenance of these systems, the likelihood of a failure of a component in the system is reduced; but not eliminated entirely. As will be discussed in this and the following sections, degradation can occur over the useful lifetime, sometimes leading to catastrophic failure—such as that at Hinkley Point 'A' in Sept 1969 [12] or that investigated by Stifanese et al. [10]. The report identifies SCC of the disc steel, where a combination of a susceptible microstructure, applied or residual load and corrosive environment all contributed towards the failure of the component. Each contributing aspect will be explored in the subsections that follow.

In metallic materials, deteriorative mechanisms exist that lead to the loss of material from a component. This loss is in the form of a nonmetallic scale or film due to oxidation or actual material loss by dissolution during the physicochemical phenomena of electrochemistry known as corrosion. Corrosion is defined in NACE/ASTM G192-12 [48] as

The deterioration of a material, usually a metal, that results from a chemical or electrochemical reaction with its environment...

meaning that corrosion is a naturally occurring process due to the interaction of materials with the environments surrounding them.

Such deterioration of the material used to form key industrial components will have an economic impact due to the direct costs such as replacement and protection of parts and the indirect costs which include management and monitoring of corrosion, loss of product or revenue due to downtime, reliability and reputation. There are various reports of the cost of corrosion that include: reported losses to the United Kingdom of £1.365 billion, equating to 3.5% of of the UK's Gross National Product [49], estimated as 5% of an industrialised nation's income [50] as well as two studies by NACE [51, 52] which estimate the cost to be increasing from 3.1% to 3.4% of the Gross Domestic Product for the USA in the 14 year period between reports. There is clearly a significant economic impact from corrosion, and some of this has been directly attributed towards corrosion fatigue (CF) and SCC of turbines in the fossil and nuclear sector [53]. This equates to a cost of \$792 million—the fifth highest cost of those identified in the EPRI report [54].

#### 2.3.2 Aqueous Corrosion Overview

To extract metals from their ores, a great amount of energy is required to allow the metastable metallic state to be reached. Once the metallic materials are exposed to an environment again, it is only natural for them to return to their natural state in order to reduce their overall free energy [53]. The metallic materials that constitute a component, such as the blades in a low pressure steam turbine (LPST), experience the electrochemical process known as aqueous corrosion. That is, corrosion in the process of an electrolyte which can provide reactants and remove products for the redox reactions taking place in such a system. It is typical that the metal substrate is oxidised, leading the loss of electrons (oxidation) which are consumed in the corresponding reduction reaction. During these redox reactions, the reactants will undergo a change in oxidation state, so both types of reactions must be occurring simultaneously for charge neutrality to be maintained.

### **Anodic Reactions**

The electrochemical dissolution of iron from steel is the main anodic reaction of concern in the field of corrosion as it leads to the loss of metal. These reactions are of the form

$$\mathbf{M} \longrightarrow \mathbf{M}^{n+} + \mathbf{n}\mathbf{e}^{-} \tag{2.10}$$

where *M* denotes a metallic material that is oxidised resulting in it becoming an n+ positively charged ion, that is losing *n* valence electrons (e-) from the metal's electronic structure. Therefore, in the case of iron, common anodic oxidation reactions are

$$Fe \longrightarrow Fe^{2+} + 2e^{-}$$
 (2.11)

where Fe<sup>2+</sup> will dissolve in the electrolyte giving the process the term *anodic dissolution*. The electrons generated in this reaction are transferred to a second site where they are consumed in a cathodic reaction.

## **Cathodic Reactions**

To maintain the charge neutrality that was mentioned previously, the  $e^-$  generated in the anodic reaction must be consumed in a reduction reaction. During such an event,

a chemical species will gain electrons in the reaction. If corrosion is taking place in an acidic solution, there will be an abundance of H<sup>+</sup>, so the cathodic reaction is of the form

$$2 H^+ + 2 e^- \longrightarrow H_2 \tag{2.12}$$

where the  $H^+$  ions are reduced to hydrogen gas. Without a significant concentration of  $H^+$ , the reduction of water will likely occur instead by

$$2 H_2 O + 2 e^- \longrightarrow H_2 + 2 O H^-$$
(2.13)

If the solution is aerated (containing dissolved oxygen), then the oxygen reduction reaction

$$O_2 + 4 H^+ + 4 e^- \longrightarrow 2 H_2 O \tag{2.14}$$

is likely to occur in a low pH environment. In the case of a LPST though, the pH is not expected to be acidic, as it is carefully controlled at around pH 8 or pH 9 due to the contaminants in the steam [6, 55]. Additionally, corrosion is only likely to occur when the plant is off-load and air can enter the turbine, providing a sufficient concentration of oxygen to facilitate the reaction of

$$O_2 + H_2O + 4e^- \longrightarrow 4OH^-$$
(2.15)

all of which occur at the cathodic site of the corrosion process [50]. Additionally there can be cathodic reactions where the metal ion is reduced if it has more than one valence state. In the case of iron this could be

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}$$
 (2.16)

In the absence of oxygen, the main cathodic reaction will be the hydrogen evolution reaction, shown in Eq. (2.12), and this will control the overall reaction rate. This effect is known as cathodic control as the cathodic reaction limits the rate at which the anodic reaction occurs.



FIGURE 2.8: Schematic diagram showing the sites at which the anodic and cathodic reactions occur during the corrosion of iron in a an aerated neutral solution.

## **Overall Process**

All corrosion reactions are a combination of one, or more, anodic and cathodic reactions occurring on the metal surface, as shown in Fig. 2.8, for iron in a neutral or alkaline solution. There can be no net electrical charge accumulation, which means that all electrons generated in anodic reactions must be consumed in equal proportions in cathodic reactions.

# 2.3.3 Forms of Aqueous Corrosion

When a corroded metal is optically inspected, it is possible to classify the corrosion mechanism responsible for its degradation. Each form of corrosion is unique with characteristics that are specific to the type of corrosion observed. There are eight forms of corrosion that are generally accepted which are presented in Table 2.3.

## 2.3.4 Aqueous Corrosion in Steam Turbines

A schematic diagram of a steam turbine is shown in Fig. 2.9, where the HPST, IPST and a LPST sections are indicated; where the temperature ranges from 500 °C to 30 °C and pressure from 15500 kPa to 12 kPa [6]. The turbine disk and blade shown are housed within the low-pressure section of the steam turbine which is susceptible to corrosion. The variety of forms of corrosion found within the steam turbine, as summarised by

TABLE 2.3: The eight most common forms of corrosion. Adapted from Callister and Rethwisch [50].

| Туре                  | Characteristics                                                                                                                    | Example                                                                 |  |  |
|-----------------------|------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------|--|--|
| Uniform<br>attack     | Occurs over the entire exposed surface.<br>Create scale or film on surface.                                                        | General rusting of iron.                                                |  |  |
| Galvanic              | Preferential corrosion of the more active<br>metal when two or more are joined in an<br>electrical couple.                         | Joining of copper and steel tubing.                                     |  |  |
| Crevice               | Localised corrosion caused by differences<br>in concentrations of ions or dissolved gases.                                         | Corrosion around a rivet.                                               |  |  |
| Pitting               | Highly localised attack of metals with pas-<br>sive films. Cavities form beneath the metal<br>surface.                             | Pitting of stainless steel in chloride solution.                        |  |  |
| Intergranular         | Preferential corrosion along the grain boundaries due to Cr depletion.                                                             | Sensitisation of stainless<br>steel when heat treated<br>or weld decay. |  |  |
| Selective<br>leaching | One element is preferentially corroded in a solid solution alloy.                                                                  | Dezincification of brass.                                               |  |  |
| Erosion<br>corrosion  | Combined action of chemical and mechani-<br>cal attack. Particles maybe erode protective<br>film leaving susceptible to corrosion. | Piping bends and el-<br>bows.                                           |  |  |
| Stress<br>corrosion   | Combined action of stress and a corrosive environment.                                                                             | Chloride SCC of<br>austenitic stainless<br>steel.                       |  |  |



FIGURE 2.9: Schematic diagram of a steam turbine showing the high, intermediate and low-pressure sections. The main forms of corrosion for the low pressure blades and disks are indicated in the labels. Figure adapted from Zhou and Turnbull [6].

Zhou and Turnbull [6], are indicated on the diagram and mainly include pitting, CF and SCC.

The reason for these types of corrosion is condensation of the steam onto the turbine blades and disks to form droplets or a thin liquid film which are concentrated with contaminants. Over time, the concentration can build up, such that a threshold is reached that facilitates pitting corrosion of the material when oxygen is present during a shutdown period. The initiated corrosion pits then act as stress concentration sites where cracks are likely to initiate during the mutli-axial fatigue loading experienced under normal turbine conditions. As the steam turbine environment chemistry is critical in understanding the initiation of corrosion pits, further details pertaining to the steam turbine operating conditions are presented in Section 2.5.3.

## 2.3.5 Pitting Corrosion

Structural alloys with a passive film, such as SSs and aluminium alloys, will generally have an acceptable corrosion resistance in a variety of aqueous environments. However, in the presence of aggressive anionic species (usually chloride ions), the passive film can experience localised breakdown allowing corrosion of the metal beneath to occur resulting in cavities or holes forming. If this type of attack occurs on an open surface, it is known as pitting corrosion [56] and can lead to accelerated failure of structural components. This can either be due to perforation or the corrosion pits acting as initiation sites for cracking of the component. As such, pitting is considered to be an insidious type of corrosion, which is more dangerous than uniform corrosion as a small amount of material loss can result in material failure [53].

Upon the formation of a corrosion pit, the cathodic reaction, Eq. (2.15), quickly consumes the oxygen within the pit, so the reaction proceeds at the surface surrounding the pit where the reactant remains in plentiful supply. The anodic dissolution of the metal, Eq. (2.10), continues within the pit producing an excess of  $Cr^{3+}$  and  $Fe^{2+}$ . To maintain charge neutrality, the anions electromigrate ( $Cl^-$  diffuse quickly) into the pit; finally forming a metal salt of iron(II) chloride (FeCl<sub>2</sub>) which hydrolyses in water by the reaction:

$$FeCl_2 + H_2O \longrightarrow Fe(OH)_2 \downarrow + H^+Cl^-$$
 (2.17)

forming an insoluble iron hydroxide and a proton which may also form by the two-step reaction, described by Frankel [56], of

$$\operatorname{Fe}^{2+} + 2\operatorname{H}_2\operatorname{O} \longrightarrow \operatorname{Fe}(\operatorname{OH})^+ + \operatorname{H}^+ + \operatorname{H}_2\operatorname{O} \longrightarrow \operatorname{Fe}(\operatorname{OH})_2 \downarrow + 2\operatorname{H}^+$$
(2.18)

The chromium ions will also hydrolyse by the reaction:

$$Cr^{3+} + 2Cl^{-} + H_2O \longrightarrow Cr(OH)_3 + 3H^+Cl^-$$
(2.19)

forming chromium hydroxide and lowering the pit pH through the formation of H<sup>+</sup> ions.

As a result, the pH within the pit solution will decrease towards zero [57], further stimulating the dissolution of the metal and electromigration of chloride into the pit. Consequently, pitting corrosion is known as an auto-catalytic process [46]. The solubility of oxygen also decreases towards zero in the concentrated pit solution, ensuring that the cathodic reaction (oxygen reduction) occurs on the surface surrounding the pit. This essentially protects the material in the close vicinity of the pit from corrosion. The overall



FIGURE 2.10: Schematic diagram of the autocatalytic nature of corrosion pitting. The anodic reaction proceeds at the base of the corrosion pit and the cathodic reaction occurs on the surrounding surface. Image taken from Fontana [46].

pitting process is represented schematically in Fig. 2.10 and has recently been observed with synchrotron radiography to extract key kinetic parameters by Ghahari et al. in [58, 59].

Due to the complex nature of pitting corrosion and the variety of electrochemical processes that are active, a number of factors are known to affect the rate of pitting corrosion. These factors include temperature (critical pitting temperature (CPT)) [60], pH [61], microstructural inclusions (such as manganese sulphide) [62–64], chloride and sulphate concentration [65], surface roughness [66] and alloy composition [11]. To understand how each of these affects the rate of pitting corrosion, it is necessary to understand how the process is initiated. Pitting begins with passive film breakdown, followed by metastable pitting and finally the growth of large stable corrosion pits which will be explored below.



FIGURE 2.11: Schematic illustrations of the three possible mechanisms for passive film breakdown. (A) Adsorption, (B) penetration and (C) breakdown. Adapted from Böhni [67].

## **Passive Film Breakdown**

The development of a corrosion pit occurs due to fulfilment of a multi-stage process that begins with the breakdown of the protective oxide film on the passive material. As described by Böhni [67] in 1987, there have been a number of theoretical models that are used to describe the nucleation or initiation stage that leads to passive film breakdown of 'perfect' passive films. The models are described as *adsorption* of aggressive anions, *penetration* and ion migration models, and finally *mechanical* film breakdown theories as shown in Fig. 2.11. In alloys, such as SS, there will often be flaws such as voids, inclusions, dents, scratches, forging laps and folds and areas of microstructural inhomogeneity that will present sites for pit initiation due to the flawed passive film.

The adsorption model (Fig. 2.11A) was discussed by Kolotyrkin [68] in 1963. It was based upon the theory that aggressive anions would displace oxygen within the oxide film at localised sites. Consequently, this would lead to a thinning of the oxide, the formation of a metal-chloride complex, and finally, localised active dissolution i.e. pitting. Later investigations by Khalil et al. [69] with XPS showed that halide ions such as Cl<sup>-</sup> would in fact thin the oxide film by a relatively slow process.

The transport of the aggressive anions through the passive film to the metal/oxide interface is described by the penetration model (Fig. 2.11B) that was proposed by Hoar et al. [70]. Upon reaching the interface, the anions react with the metal leading to localised dissolution. The migration of the anions through the passive film supports the idea of an induction time after  $Cl^-$  are introduced into an otherwise inert electrolyte [56]. The rate of migration is controlled by the electric field within the passive film—which can be of the order  $10^6 \,\mathrm{V \, cm^{-1}}$  to  $10^7 \,\mathrm{V \, cm^{-1}}$ . However, contradicting evidence exists from



FIGURE 2.12: Processes occurring that lead to passive film breakdown according to the point-defect model. Figure from Macdonald [73].

Szklarska-Smialowska et al. [71] who studied the passive films on iron formed in chloride containing solutions with electron spectroscopy techniques and found little evidence of Cl<sup>-</sup> incorporation into the oxide layer.

A similar approach was taken by the point defect model (PDM), developed by Macdonald and co-workers [72, 73] in the 1980s (Fig. 2.12). The PDM discusses the growth and breakdown of a passive film depending upon the behaviour of point defects within the passive film. The defects discussed include electrons, holes and metal/oxide vacancies ( $V_M/V_O$ ) where the role of  $V_O$  is critical. It was proposed that the cation vacancies migrate from the film-solution interface to the metal-film interface and the cations migrate in the opposite direction. If the rate of vacancy annihilation at the metal interface is low, then a local accumulation of anion vacancies will occur at the metal-film interface, creating vacancy condensate within the passive film, ultimately leading to film rupture and pitting. Furthermore, they included an explanation for the effect of Cl<sup>-</sup> on the process, as the ion is of similar size to the oxide ion, so would therefore be adsorbed into the anion vacancies leading to a concomitant increase in the concentration of cation vacancies ( $V_M$ ) at the metal/film interface [22].

The final proposed mechanism of pit initiation is described by mechanical film breakdown (Fig. 2.11C). The theory was introduced by Sato [74] where breakages within the film would give the electrolyte (and anions) direct access to the unprotected metal surface. Sato [74] calculated the tensions induced in the oxide film by electrostriction due to the electric field and concluded that these were high enough to produce mechanical breakdown. Additionally, film rupture is thought to be a direct consequence of the passive films nature to constantly adapt and evolve to the surrounding environment; leading to breakdown and repair. This is mentioned within Galvele [75]'s critical acidification model, where for a small defect around  $10^{-6}$  cm in size, a current density of  $1 \,\mathrm{A \, cm^{-2}}$  was identified as the necessary value to allow a critical pH to be reached for sustained pit growth [75]. However, in the case of SS, Frankel [56] states that

... the local chloride concentration is probably more important than the local

pH in terms of stabilizing pit growth and preventing repassivation...

On the other hand though, the chloride concentration will roughly scale with acidity so it may still be useful to predict pit stability.

Due to the short duration, small scale and scarcity of pit initiation events, it has always made direct observation of such occurrence difficult. However, there have recently been some successful attempts of microscopic *in situ* high-resolution observation of an electrode surface under electrochemical control [76–78]. As a consequence, it is also important to appreciate the stages occurring after localised breakdown of the passive film.

### **Metastable Pitting**

Metastable pit is a term given to a corrosion pit that initiates and grows for a limited period before repassivating. Most pits repassivate as the local chemistry required for the continued growth of the corrosion pit cannot be sustained. Early work by Pickering and Frankenthal [79] and Galvele [75], identified the local pit chemistry changes that were occurring within a simplified unidirectional corrosion pit model for iron in the passive state (pH 10) assuming only the first step of Eq. (2.18) occurs. The changes to the localised pit chemistry were presented for a given bulk pH as a function of a pit stability product  $x \cdot i$ , where x is the length of pit, with x = 0 at the opening of the pit and i is the current density. The plots produced allowed prediction of the concentration for different species (H<sup>+</sup>, Fe(OH)<sup>+</sup>, Fe<sup>2+</sup>) in corrosion pits of two different sizes with the same current density or two pits of equal size with different current densities at a pH deemed to facilitate pitting corrosion from the Fe Pourbaix diagram. The H<sup>+</sup> concentration that



FIGURE 2.13: Concentrations of  $H^+$ , Fe(OH)<sup>+</sup> and Fe<sup>2+</sup> as a function of the product of the pit depth *x* and the current density *i* for iron in a 1 mol NaCl solution at pH 10. The critical  $H^+$  concentration, corresponding to corrosion, is marked by the cross (a). Figure from Alvarez and Galvele [80].

corresponds to the required pH is marked on Fig. 2.13 at the cross marked 'a', giving an  $x \cdot i$  of  $10^{-6}$  A cm<sup>-1</sup>. The current density when pitting starts is around 1 A cm<sup>-2</sup> [80], so pits as small as 0.01 µm would be able to initiate.

Additionally, the effects of altering the external pH could be calculated successfully. It was shown that increasing the external pH resulted in the H<sup>+</sup> curve being shifted to higher  $x \cdot i$  values. This means that for a fixed value of x, a higher current density (higher pitting potential) would be required to obtain the same pit acidification.

The geometry of the corrosion pit can lead to a restriction in mass transport, resulting in different chemistries within the pit compared to the bulk solution. A comprehensive review of the experimental methods that can be used to investigate such electrochemical conditions is provided in [81]. "Direct" methods involve the use of micro-electrode test probes within the corrosion pit, while avoiding perturbation of the pit environment and salt film formation. Closely related are "semi-direct" methods that either sample the solution from the pit environment or make electrochemical measurements in the close vicinity of the pit mouth. Through such methods it has been possible to measure a reduced pH (2–3) in the vicinity of a pit, considerably lower than the bulk pH. Additionally, in systems involving stainless steel, a micro-capillary tip has been used to measure the potential in real corrosion pits. It is reported that the potential at the bottom of a corrosion pit, in 18Cr-12Ni-2Mo-Ti austenitic SS, decreased linearly by 480 mV to 136 mV (vs. saturated calomel electrode (SCE)) with a solution pH of 1.3 [81]. This larger potential difference results in an increased driving force for corrosion pitting. Similar reports of potential drop and acidification of the pit environment, due to dissolved metal chlorides, for many systems are reported in the review. Chromium and ferric ions are reported to have the most significant impact on reducing the pit pH.

Another characteristic associated with metastable pitting is that of electrochemical noise (EN). The initiation, growth and repassivation of a corrosion pit will generate transient fluctuations in the electrochemical current noise (ECN) and electrochemical potential noise (EPN). This can occur at potentials below  $E_p$  and during the induction time before stable pitting at potentials above  $E_p$ . For SS in chloride solution, the metastable pits are covered by a remnant of the passive film and upon rupture of this cover the localised pit environment that has developed is diluted and the pit repassivates [82].

Associated with such events is a change in the ECN, which has some characteristic features. As shown in Fig. 2.14, the initiation of the corrosion pit results in a steady increase in the current above the background passive current. Once the film ruptures and the pit repassivates, the current quickly decreases back to the background current level [83]. Such event also affects the EPN, where a typical shape would consist of a rapid drop in potential followed by a slow increase in potential due to the capacitance of the double-layer between metal and electrolyte [84]. Similar transients in EPN may also be associated with the nucleation and propagation of SCC in SS [85]. The transients due to rupture of the oxide film were in the range 1 mV to 2 mV, whereas a more intense signal (>20 mV) was observed due to the presence of SCC. Cuevas Arteaga et al. [86] has used EN to analyse the performance of 410 SS (another 12Cr SS used for turbine blades) in a synthetic seawater environment. They achieved positive indication from the results, that differences in potential and current noise would be observed for pitting, mixed and uniform corrosion. Additionally, they use a localisation index (current noise standard



FIGURE 2.14: A plot of current vs. time showing examples of current spikes due to metastable pitting events. Image from Burstein et al. [82].

deviation over the root mean square of the current value) to show that this statistic gives a good indication of corrosion processes occurring in the system as the uncracked samples had a value close to 0.1 and the cracked samples had higher values.

Frankel [56] reported that the pit current (*I*) increases proportionally to  $t^2$  during metastable pit growth, assuming that the shape is hemispherical and that the current density is approximately constant as well. Others found that the current would vary in a power-law relationship ( $I \sim t^n$ ) but with *n* equal to 0.5 [87]. This would indicate that the propagation of metastable pits was under ohmic control due to the porous pit cover resistance.

As the localised environment becomes more aggressive (higher concentrations of H<sup>+</sup> and Cl<sup>-</sup>), the likelihood of repassivation becomes less. The remainder of the passive film (lacy cover) is eventually no longer required to sustain the concentration gradient, as this can be provided by the depth of the corrosion pit alone and, if present, the salt film at the base of the pit can provide a buffer of ionic species to reconcentrate the environment. However, recent work has shown that a salt film is not required for pit stabilisation and that the film is just a consequence of a pit achieving diffusion-controlled growth [88, 89].

Recently, Frankel et al. [90] has provided a perspective that either the protectiveness



FIGURE 2.15: Schematic diagrams of the cross-sectional shapes of corrosion pits. Image from Roberge [53].

and initial breakdown of the passive film or the stabilisation of pit growth can be the critical step depending upon the electrolyte chemistry. In less aggressive solutions (low  $Cl^-$  concentration) the breakdown of the passive film will be slow but at a high potential, so the breakdown of the passive film is deemed to be rate controlling and will be followed by rapid pit growth. When the concentration of  $Cl^-$  is higher, the rupture of the film will happen very quickly, so pit stability considerations will determine pit growth and become rate controlling. As the contaminant concentrations within the steam turbine environment are usually carefully controlled, it can be assumed that the breakdown of the passive film will be the controlling process.<sup>3</sup>

### **Corrosion Pit Morphology**

Once a high rate of anodic dissolution is maintained, a corrosion pit will form in the metallic material. The resulting pit geometries vary widely, as shown in Fig. 2.15, depending upon the rate-controlling reactions taking place during the growth of the pit, which will either impose diffusion, charge transfer or ohmic limitations [67]. For SS, the shape of the pit is usually either narrow and deep, shallow and wide, elliptical/hemispherical or subsurface.

<sup>&</sup>lt;sup>3</sup>Further details are given about the steam turbine environment in Section 2.5.3.



FIGURE 2.16: Part of a polarisation curve of a passive material showing the locations of the pitting potential  $E_p$ , the repassivation potential  $E_r$  and inhibition potential  $E_i$ . Figure adapted from Galvele [93].

#### **Electrochemical Parameters for Pitting**

The use of electronic instruments, such as the potentiostat, has allowed several potential values, characteristic of pitting corrosion, to be identified. The most pertinent is perhaps the pitting potential  $E_p$ , as it was found that stable pitting would not be observed below this potential.<sup>4</sup> On the other hand, once the potential is above  $E_p$  stable pitting will either commence immediately or begin after a short induction time as for SS [91, 92]. A typical anodic polarisation curve is shown in Fig. 2.16 for an alloy in chloride-containing solution where  $E_p$  is shown. The electrode potential is changed at a constant scan rate, while the current is recorded and an increase in current indicates pitting at a corresponding value of  $E_p$ .

Additionally shown in Fig. 2.16, is the repassivation potential  $E_r$ , which is another characteristic potential of the pitting process that was first described by Pourbaix [94]. It was noted that when pitting commences at a  $E_p$ , the pits will continue to grow even if the potential is lowered back below  $E_p$ . The growth of corrosion pits only arrests once the potential is taken below a certain potential corresponding to the value of  $E_r$ . Additionally, if the potential is raised further beyond  $E_p$ , there may be a point at which the pits

<sup>&</sup>lt;sup>4</sup>Metastable pits can initiate below  $E_p$  but will not propagate into stable growing corrosion pits.

repassivate, known as the pitting inhibition potential  $E_i$  and can be observed for stainless steel in chloride solutions containing nitrates. However,  $E_i$  has little practical application as applying such a high potential would make the material susceptible to crevice corrosion [80]. Additionally, at high potentials, the chromium rich passive film will dissolve, due to formation of soluble chromate ions meaning the metal is no longer in a passive condition so pitting cannot occur—the process is known as transpassive corrosion. The temperature of the solution and alloy composition can affect the electrochemical parameters, as well as the rate of scanning [95]. This was shown in the 1960s by Horvath and Uhlig [26], where they found  $E_p$  was 0.5 V higher at 0 °C compared with 25 °C and that additions such as molybdenum could either increase or decrease  $E_p$  depending upon the temperature under study.

Related to this phenomenon is a parameter known as CPT, which provides a way to rank different grades of SS alloys. This was introduced by Brigham and Tozer [60] in 1973 and is defined as the lowest temperature at which the growth of stable corrosion pits is possible. If the temperature is below the CPT, then no stable pitting can occur. As a result of this observation, it was possible to rank SS alloys resistance to pitting corrosion as a higher CPT would indicate an alloy that is more resistant to pitting. The CPT of many SS alloys lie within the range of 10 °C to 90 °C and can be accurately measured by using an Avesta cell, which eliminates the possibility of crevice corrosion which would otherwise interfere with the measurement. Recently, Li et al. [96] have suggested that CPT is not an intrinsic material property and is a statistically distributed value based upon the behaviour of many pitting events.

#### **Effects of Environment and Surface Condition**

A wide variety of anions are known to be 'aggressive' for SSs—including Cl<sup>-</sup>, Br<sup>-</sup> and SCN<sup>-</sup>. Each of these ions will produce metal compounds that are soluble in the pit electrolyte, produce strong acids and do not interfere with hydrolysis reactions; all which promote acidification of the pit [80]. As such,  $E_p$  for a metal will vary with the concentration of anions in solution. A higher concentration of anions will lower the value of  $E_p$  by the equation

$$E_p = A - B \log C_x \tag{2.20}$$

where *A* and *B* are constants and  $C_x$  is the concentration of the aggressive anion. The value of *B* is reported at around 200 mV [80, 97].

As will be discussed in detail in Section 2.5.3, the adoption of two-shifting in power plants, in order to better match consumer demands, results in regular cycling of the environment solution chemistry between on-load (deaerated) and off-load (aerated) conditions at elevated (90 °C) and ambient temperature respectively. Critically, the off-load environment provides conditions in which corrosion pits can initiate if the concentration of contaminants (chloride) reaches a critical concentration. Research published by Zhou and Turnbull [4] and Salzman et al. [98] has demonstrated that two-shifting will impact upon the corrosion potential of LPST materials: 3NiCrMoV steel and 403 SS respectively. In both cases, a sluggish response of corrosion potential was noted when the chloride containing solution was deaerated; simulating a start-up procedure to on-load conditions. However, the response of the corrosion potential was faster when the solution also contained sulphate ions which the author suggests may be due to some contribution from SCC behaviour. Additionally, the sluggish response in corrosion potential may increase the risk of pitting corrosion as a higher potential is sustained for longer periods. However, in the study conducted by Salzman et al. [98], they noted that corrosion pits that formed in the aerated 35 ppm chloride solution would either arrest or grow very slowly during subsequent exposures to the aerated solution due to the effects of exposure to deaerated conditions. They attribute this effect towards a more protective passive film that develops during the deaeration periods, but there was limited attempt to quantify the composition of such film or the chloride concentration required to promote further corrosion pitting. Furthermore, as only measurements of changes to the corrosion potential were made during these investigations, there is no information relating to the CR. As will be discussed in Section 3.3.4, EN offers itself as a possible technique to further evaluate the behaviour of steam turbine materials under the simulated environmental conditions.

Additionally, the breakdown of passivity on 403 SS, due to chloride, was studied by Zhang et al. [99] and Rybalka et al. [100]. The results in [99] show that the value of  $E_p$  decreases linearly with increasing logarithm of chloride activity for deaerated NaCl



FIGURE 2.17: A micrograph of a typical corrosion pit that initiated on 403 SS in 1 mol NaCl solution at 20 °C in tests conducted by Rybalka et al. [100].

solutions of concentrations 0.028 mol to  $0.5 \text{ mol.}^5$  Rybalka et al. [100] carries out similar investigations at open circuit potential and reports a corrosion potential,  $E_{corr}$ , of -0.2 V vs. standard hydrogen electrode for NaCl concentrations 0.1 mol to 1 mol and a higher  $E_{corr}$  of -0.1 V in 0.001 mol to 0.01 mol NaCl. They also note a cathodic shift in  $E_{corr}$  due to the formation of the initial corrosion pit.

Furthermore, the results also include micrographs of the morphology of corrosion pits that form in a 1 mol NaCl solution, as shown in Fig. 2.17. The author notes that there is a single large pit with a small surrounding, lightly etched area and surrounding this is a larger area that is protected from corrosion (due to local cathodic reaction activity) and at the outer boundary of this region there is a semicircular band of general corrosion.

The surface condition of the alloy can also affect the susceptibility to pitting corrosion. This has been reported by Ezuber and Newman [87] who looked at the effect of two surface finishes; namely 600-grit and 4000-grit, with the latter providing a smoother surface. Their results showed that a rougher surface had deeper micro-crevices, which stabilised the growth of corrosion pits. This was supported by additional work from Burstein et al. [66, 101] who concluded that a smoother surface reduced the number of metastable pitting sites capable of pit growth. However, they noted that a metastable pit on the

<sup>&</sup>lt;sup>5</sup>This equates to a parts per million (ppm) concentration ranging from 993 ppm to 17727 ppm.

smooth surface had a greater probability of growing to a stable pit as it was not diffusion limited by the surface roughness. Ezuber et al. [102] also noted more recently that  $E_p$  was lowered as the surface roughness was increased. Additionally, like Burstein and Pistorius [66], they reported that there were fewer metastable events on the smoother surface due to the reduction in available sites.

# 2.4 Fatigue

## 2.4.1 Introduction and Background

Failure of engineering materials and structures is a result of complex interactions of the applied loads, duration and environment in which they were designed for. Fatigue is a failure mechanism resulting from repeated dynamic, cyclic or fluctuating loading. As a result, it is possible for failure to occur at a cyclic stress level considerably lower than the material's yield strength under constant static load. The fatigue process occurs, first by initiation and then propagation of cracks until failure as described by the International Organization for Standardization [103]:

... the term "fatigue" relates to the initiation and growth of cracks in metallic materials due to the repeated application of mechanical stresses or strains ...

As a consequence of the ubiquity of materials under variable load, around 50-90% of mechanical failures can be attributed to fatigue. With the majority of these failures being unexpected, due to stress levels often being below the static yield strength of the material. The associated cost of fatigue in the USA in 1978 was \$119 billion, around 4 % of the countries GDP [104].

Fatigue has perhaps been reported since about the mid-19th century in the railway industry, when Wöhler [105] published results on his experimental attempts to determine the forces acting on the axles of rail cars. Through simulating the effects of irregularities in the train tracks, the axle-like specimens experienced large dynamic rotating bending forces, which are more commonly known as fatigue. Wöhler's studies also elucidated the existence of a limiting fatigue range–now known as the *fatigue limit*, below which failures would not occur and introducing stress versus life (S-N) diagrams.



FIGURE 2.18: A fully reversed fatigue stress cycle.

In general, it is now accepted that there are three types of stress-time models representing the different types of load fluctuations. Perhaps the most complex would be random fluctuations in both amplitude and frequency due to the accumulation of differing imposed 'damage' at each step. The majority of fatigue tests use the simplest representation of fatigue loading, which is, a time-dependent sinusoidal wave (Fig. 2.18). The experimental setup may necessitate that the sample is exposed to both tensile and compressive forces or the maximum and minimum stress are asymmetrical relative to a mean applied stress  $\sigma_m$ ; as was the case in this research project. The mean stress is defined as the average of maximum and minimum stresses in the cycle:

$$\sigma_m = \frac{\sigma_{max} + \sigma_{min}}{2} \tag{2.21}$$

Several other parameters are used to characterise the fluctuating stress cycle, including the range of stress,  $\Delta\sigma$ , which is the difference between maximum and minimum stress

$$\Delta \sigma = \sigma_{max} - \sigma_{min} \tag{2.22}$$

The stress amplitude,  $\sigma_a$  is one half of  $\Delta \sigma$ 

$$\sigma_a = \frac{\Delta\sigma}{2} \tag{2.23}$$

Finally, the stress ratio, *R*, is the ratio between maximum and minimum stress, where R = -1 represents a fully reversed cycle as in (Fig. 2.18).

$$R = \frac{\sigma_{min}}{\sigma_{max}} \tag{2.24}$$

Under the application of sufficient stresses and cycles a material may fail by fatigue,



FIGURE 2.19: The three mode of crack displacement. (A) Mode I - tensile or opening, (B) mode II - sliding and (C) mode III - tearing. Images from Callister and Rethwisch [50].

the process begins by the initiation and subsequent propagation of cracks. Normally the fracture surface will be perpendicular to the direction of applied load [50].

# 2.4.2 Modes of Crack Surface Displacement

When a sufficient load is applied to a material, it may begin to fail through initiation and growth of a crack. Depending upon the orientation of the applied load relative to the crack face and direction, three different modes of crack displacement are defined; as shown in Fig. 2.19.

- **Mode I: Fig. 2.19A** This is the most common mode of crack displacement and occurs through the application of tensile forces. As a consequence, it is known as *opening* or *tensile* mode and the crack grows perpendicular to the applied load. Tensile and fatigue crack growth is most commonly seen to occur by this mode.
- **Mode II: Fig. 2.19B** The load is applied in a shear mode and the displacement occurs inplane. The crack surfaces move over one another in a direction that is parallel to the applied force, so this mode is known as *sliding*. As described in Section 2.4.3, short cracks usually initiate in this mode and it also the mode in which material can be removed from a workpiece that rotates on a lathe.
- **Mode III: Fig. 2.19C** The load is applied in a shear direction which is perpendicular to the crack growth direction, so is known as a *tearing* mode. This mode of crack displacement is common when cutting paper with scissors.

### 2.4.3 Stages of Fatigue Damage

The stages of fatigue can be characterised by three distinctive stages and the growth of a crack is subdivided into two stages based upon the relative size of the plastic zone at the crack tip and the microstructure, giving the following order:

- 1. Crack initiation
- 2. Crack propagation
  - (a) Stage I short crack propagation.

The plastic zone size is large compared to the microstructure

(b) Stage II - long crack propagation.

The plastic zone is smaller in size than the microstructure

Final failure

Cracks are most likely to initiate at a location of stress concentration, which can include: surface scratches, sharp fillets, keyways, threads, dents, notches, voids and pits [50]. A crack may also nucleate on a 'smooth surface', where the cyclic loading generates surface discontinuities due to a favourably orientated slip system providing the largest shear stress. Once the crack has initiated on the surface of the material, it will progress through stage I and stage II crack growth as shown in Fig. 2.20. Once the dominant crack grows to a critical size, the remaining ligament will have insufficient strength to sustain the next cycle of load and there will be final failure/fracture of the material or component.

The following subsections explores each of the reported stages in more detail to highlight pertinent contributions to failure at each stage.

#### Crack Initiation

As previously mentioned, cracks initiate at localised stress and strain concentrations that do not necessarily have to be a surface defect.

When a polycrystalline material is subject to tensile (or compressive) load, the grains experience a resulting shear stress. The near-surface grains follow the same mechanism that a single crystal (comprised of a single grain) would. The anisotropic deformation is characterised in terms of the resolved shear stress  $\tau_R$ . The shear strain acts on a specific



FIGURE 2.20: Schematic of the formation of persistent slip bands at the surface of the material. Followed by fatigue crack growth through stage I crack growth by the shear mode and stage II crack growth in tensile mode in a polycrystalline material. Adapted from Lawrence and Jones [106].

slip plane along a specific slip direction depending upon the crystal structure of the microstructure [107]. The slip plane normal and slip direction are orientated at angles of  $\phi$ and  $\lambda$  respectively, with respect to the loading axis. The applied load can be angularly resolved to find  $\tau_R$  by the equation:

$$\tau_R = \sigma \cos \phi \cos \lambda \tag{2.25}$$

if this resolved shear stress is greater than a critical value, then the crystal undergoes plastic deformation. Under the application of a uniaxial applied load, the maximum value of  $\tau_R$  is found when  $\phi$  and  $\lambda$  are 45° to the loading axis. This means that slip occurs preferentially in those grains with slip planes corresponding to this angle by mode II crack displacement (Fig. 2.19B). The resulting deformation at these specific orientations appears as microscopic bands in the grain, known as persistent slip bands (PSBs). Due to the applied cyclic load, the increase in dislocation density induces work hardening creating boundaries between hard and soft regions. Fatigue cracks then initiate at these sites as they have introduced an area of discontinuity and stress concentration to the material.



FIGURE 2.21: Schematic of crack speed vs. crack length for a material with grain sizes which are (A) small and (B) large. Adapted from Miller and Akid [109]

In commercial alloys, such as SS, sites such as voids, inclusions, dents, scratches, forging laps and folds and areas of microstructural inhomogeneity act as stress concentrators, increasing the chance of cracking at these sites. Additionally, these materials are also affected by their surrounding environment, as the newly formed slip step that forms during the tensile portion of a fatigue cycle may adsorb embrittling species or form an oxide layer on the fresh surface that inhibits the reverse slip. This exacerbates the ease of the formation of PSBs and therefore facilitating crack nucleation [107].

## **Stage I - Short Crack Propagation**

Under the continued cycling of load, fatigue cracks grow and coalesce along the planes of maximum shear stress (45°) in stage I crack propagation as shown in Fig. 2.20. This microstructurally short crack growth continues until the crack is decelerated by microstructural barriers, *d*, as shown in Fig. 2.21, these barriers include grain boundaries, inclusions or pearlitic zones [108]. There can be several different microstructural barriers to crack growth in a single material causing a repeated increase and decrease in the crack growth rate (CGR).

If any of these stage I cracks arrest at such microstructural barriers, then these cracks are termed as *non-propagating* cracks. A rise in the stress level is required to overcome



FIGURE 2.22: A plot of crack length vs. stress range showing the regions within which different fatigue methodologies can be applied. Short cracks may propagate at stresses below the fatigue limit but arrest at microstructural barriers and long cracks can be modelled with fracture mechanics approaches. This plot from Miller [110] is conventionally known as a Kitagawa-Takahashi diagram.

each barrier *d* (see Fig. 2.22), achieved by increasing the dislocation density, thus allowing crack propagation to continue and an increase in the CGR [110]. Consequently, procedures such as grain boundary refinement can improve a material's apparent fatigue resistance by introducing many of these microstructural barriers. The effect of this represented in Fig. 2.21A, where there are more oscillations in crack speed due to the smaller grain size. There may also be multiple microstructually short cracks propagating at a time. If these grow in adjacent grains, then the crack on the optimum slip plane will continue to grow while the growth of the second crack is retarded. After the crack has successfully propagated over a few grains, the influence of the microstructural boundaries is minimised and the crack transitions to stage II of crack propagation, where the crack now grows perpendicular to the applied load in mode I crack displacement (Fig. 2.19A).

## Stage II - Long Crack Propagation

As the length of the crack and local stress increases, slip develops in different planes to those of maximum resolved shear stress and the crack propagates in mode I. Due to the continued application and removal of load during fatigue cycling, the crack tip is continuously sharpened and blunted, which as a consequence, forms striations. These are only visible under scanning electron microscope (SEM) observation of the fracture surface, as concentric ridges where the spacing between them is proportional to the stress range [50]. These marks should not be confused with beachmarks, which are visible to the naked eye on a fracture surface as semicircular patterns where the width is controlled by the duration of fatigue loading, i.e. a machine that only operates during regular working hours. Consequently, due to the different length scales, there may be thousands of striations within a single beachmark which can aid in diagnosing the cause of failure for a component.

## **Final Failure**

Finally, depending upon the mechanical properties of the material, unstable crack growth, i.e. fracture, will occur by either ductile or brittle mechanisms. Brittle fracture occurs with a very low amount of plastic deformation, so the observed fracture surface is very flat due to rapid crack propagation. This is often unfavourable as it gives little warning of imminent failure. Fortunately, most engineering alloys will fail in a ductile fashion, which can generate extensive plastic deformation and produced a fast fracture region of characteristic *cup-and-cone* fracture surface due to shear deformation at 45°—corresponding to maximum shear stress.

Such process occurs when the stress intensity factor *K*, reaches a critical value termed  $K_{Ic}^{6}$  in the relationship

$$K_{Ic} = Y \sigma \sqrt{\pi a} \tag{2.26}$$

where *Y* is a dimensionless shape parameter defined by the crack and specimen geometries,  $\sigma$  is the applied stress and *a* is the crack length. For a material with known  $K_{Ic}$ , such expression explains the difference in fast fracture zone size, as under a high applied load (high value of  $\sigma$ ) the critical crack length required to reach  $K_{Ic}$  is lower so the fast fracture zone is larger. The inverse applies to a lower applied load [108]. The value of *K* may also be estimated from 3D volume imaging if the size and shape of the crack can be accurately measured [111].

<sup>&</sup>lt;sup>6</sup>The *I* subscript denotes that the crack displacement is by a tensile mode.



FIGURE 2.23: Stress vs. the log of number of cycles to failure for a type 403 stainless steel. The material displays a fatigue limit when tested in air, but the fatigue limit is lost and N is reduced (fewer cycles to failure for the same applied load) upon testing in 0.01 mol NaCl solution. Plot adapted from Shalaby and Gouda [114].

## 2.4.4 Fatigue Life Prediction Models

In order to successfully design against the impact of fatigue, two common methodologies are followed to evaluate the total fatigue lifetime of a material or component. The two main approaches are discussed in the following subsections.

#### **Total-Life Approach**

The original approach to fatigue testing is now termed as the total-life approach, where materials are characterised by their fatigue life from a series of fatigue tests. The specimens are subjected to a large  $\Delta \sigma$ , but below  $\sigma_y$ , in a high-cycle fatigue test which may be under stress or strain control, as described in the industry standards ASTM E606-12 [112] and E466-14 [113], where the number of cycles (*N*) until specimen failure (*N*<sub>f</sub>) is recorded. After a number of tests have been conducted at different values of  $\sigma_{max}$ , it is conventional to plot the data as Stress-Life (S-N) or Strain-Life (E-N) with respect to the number of cycles to failure. Completion of such testing yields the plot shown in Fig. 2.23.

As the testing of the material is below  $\sigma_y$ , the material exhibits macroscopic elastic behaviour owing to the high number of cycles required for failure of the specimen. The plot shows how an increased applied  $\sigma_{max}$  results in fewer cycles to failure. As the stress
range is reduced, it can be observed that the curve for specimens tested in air begins to plateau corresponding to the fatigue limit of the ferrous materials. This material property defines the largest value of fluctuating stress that will *not* cause fatigue failure over an infinite number of cycles. It should be noted that most nonferrous alloys do not manifest a fatigue limit, so the curve continues on a downward trend and a nominal value of 10<sup>7</sup> is often taken as the fatigue limit [45]; although more recent studies use have used up to 10<sup>9</sup> cycles [115]. This number of cycles had also originally been regarded as the limit below which cracks fail to initiate, however, due to improvements in crack observation, it is accepted that cracks may initiate but will arrest at microstructural barriers and become non-propagating [116]. For the FV566 SS used in the fatigue limit is around 700 MPa for a fine ground surface at a stress ratio of 0.1 and is unaffected by the cyclic frequency used. The fatigue limit of 403 SS is 675 MPa [98].

From S-N plots, it is possible to estimate the expected fatigue life as long as the stress range for a given application is known. However, the scatter in results provides design uncertainties, as for a given stress range, the measured value of *N* will show some variation. This can be due to a range of specimen and test parameters such as specimen fabrication, surface preparation, microstructure variation and specimen alignment for testing. It can also be noted from the plot, that the combination of fatigue loading within a test environment can lead to a reduction in cycles to failure and loss of a fatigue limit. This will be discussed further in Section 2.5.3.

This stress-based methodology embodies the damage evolution, crack nucleation and crack growth stages of fatigue into a single, experimentally characterised formulation. This makes differentiating the lifetime spent on crack initiation and crack growth difficult, unlike defect-tolerant methods which consider the fatigue life to be that in which a pre-existing flaw is propagated to a critical size.

#### **Defect-Tolerant Approach**

An alternative approach to using S-N plots is based upon the application of linear elastic fracture mechanics (LEFM) to characterise the fatigue crack propagation. This approach assumes that there are pre-existing defects in the material or structure, from which cracks

will initiate and grow. The driving force for crack growth was introduced previously, as the stress intensity factor *K*. When *K* reaches a critical value,  $K_{Ic}$ , crack propagation is rapid and is more commonly referred to as the fracture toughness of a material—see Section 2.4.3 and Eq. (2.26) for details.

Under cyclic fatigue conditions, cracks will grow from a defect at values of *K* below  $K_{Ic}$ . Paris and Erdogan [117] proposed that the growth of a crack under cyclic load would be governed by the equation:

$$\frac{da}{dN} = C\Delta K^m \tag{2.27}$$

where  $\frac{da}{dN}$  is the change in length *a* of the crack per load cycle, *N* is the number of fatigue cycles, *C* and *m* are empirical constants depending upon the material's properties and microstructure, fatigue frequency, stress ratio, environment, stress state and test temperature [107] and  $\Delta K$  is the stress intensity factor range:

$$\Delta K = K_{max} - K_{min} \tag{2.28}$$

From the Paris law, the fatigue life or number of fatigue cycles to failure can then be calculated by integrating Eq. (2.27) from a measured initial defect size  $a_0$  to a critical defect size  $a_c$ .

This empirical crack growth law is the most widely used for characterising fatigue CGR as it allows for a wide variety of materials and environments and is commonly plotted as  $\frac{da}{dN}$  vs.  $\Delta K$  on a log-log scale plot as shown in Fig. 2.24.

For most engineering alloys, such a plot will exhibit sigmoidal variation with three distinct regimes of crack growth that can be identified. The first, labelled as stage I, shows that there is a minimum threshold value  $\Delta K_0^7$  needed for measurable crack growth. This corresponds to an actual CGR of  $10^{-10}$  m/cycle as defined by ASTM E647-15 [119]. Below  $\Delta K_0$ , cracks are either dormant or grow at an undetectable rate. Once above  $\Delta K_0$ , cracks begin to grow and are strongly influenced by the microstructure, mean stress, frequency and environment. In stage II, there is a linear relationship, corresponding to the Paris law introduced earlier in Eq. (2.27). From the plot, it is possible to obtain the values for *C* and

<sup>&</sup>lt;sup>7</sup>This threshold value may also be referred to as the abbreviation  $\Delta K_{th}$ 



Cyclic stress intensity factor range ( $\Delta K$ )

FIGURE 2.24: A plot of crack growth rate vs. stress intensity factor range for LEFM based crack growth. A minimum stress intensity is required for crack initiation in stage I which is followed by a linear Paris growth region before final fracture. Schematic from Zerbst et al. [118]

*m* by extending the straight line to  $\Delta K = 1 \text{ MPa}\sqrt{\text{m}}$  and calculating the gradient of the line respectively [104]. Due to the increase in crack length, the microstructure has less impact than within stage I; instead, the environment influences the macroscopic CGR. Stage III lifetime is often very short due to the high and unstable CGRs associated with it as *K* begins to approach the fracture toughness of the material (*K*<sub>*Ic*</sub>) which depends upon microstructure and mean stress.

The Paris law is only applicable to stage II, so integration of Eq. (2.27) over the whole range of the sigmoidal curve often gives a conservative fatigue crack growth life, which may be satisfactory in some cases. If a less conservative calculation is needed, then software models such as NASGRO cover the entire curve [120]:

$$\frac{da}{dN} = C \left[ \left( \frac{1-f}{1-R} \right) \Delta K \right]^n \frac{\left( 1 - \frac{\Delta K_{th}}{\Delta K} \right)^p}{\left( 1 - \frac{K_{max}}{K_c} \right)^q}$$
(2.29)

where *C*, *n*, *p* and *q* are the parameters of the material, *R* is the load ratio and *f* is the ratio of crack opening stress intensity factor to  $K_c$ .

In many situations involving the design of engineering components, it is possible to compare the fatigue CGR of different materials by use of LEFM and  $\Delta K$ . However, it

has been established [121–124] that when a crack is in the very early embryonic stages of growth (Stage I crack propagation—microstructurally short), LEFM cannot be applied as the similitude concept breaks-down due to the large plastic zone size of short cracks.<sup>8</sup>

# **Short Fatigue Cracks**

In Fig. 2.22, which was presented earlier, it can be seen that LEFM can only be used to predict cracks with a crack length that is greater than l, as the negatively sloped straight line segment is representative of  $\Delta K_0$ ; below this threshold cracks should be non-propagating. Additionally, the horizontal line, at short crack lengths, defines the fatigue limit of smooth specimens, below which an infinite number of cycles can be completed without continuous fatigue crack propagation. The curved region between the two straight line segments thus defines a region where a range of small crack lengths cannot easily be defined by either LEFM or fatigue limit analysis. This behaviour leads to cracks growing below the long crack threshold of  $\Delta K_0$  and the fatigue limit leading to non-conservative life predictions [104].

One possible way to define the curve between the fatigue limit and  $\Delta K_0$  lines, is to combine both of the equations and solve for the crack length  $a_0$  at which the two lines intersect, giving

$$a_0 = \frac{1}{\pi} \cdot \left(\frac{\Delta K_0}{Y \cdot \Delta \sigma_0}\right)^2 \tag{2.30}$$

where  $\Delta K_0$  is the threshold stress intensity factor needed for long crack propagation by LEFM and  $\Delta \sigma_0$  is the fatigue limit of smooth specimens as reported by Schönbauer et al. [125]. Their tests, conducted on 403 12Cr martensitic SS, showed that specimens did fail below  $\Delta K_0$  and Eq. (2.30) provided a sufficient estimation of the true fatigue limit.

The plots, such as those in Fig. 2.22, are described as Kitagawa-Takahashi diagrams [126] and are useful in helping to explain the short crack problem and the elimination of the fatigue limit under CF conditions [127]. Additionally, the diagram shows that a microstructurally short crack of length  $d_1$  will not be able to propagate to failure unless  $\Delta \sigma$  is raised above the fatigue limit. However, the short crack may grow rapidly to sizes

<sup>&</sup>lt;sup>8</sup>The plastic zone size should be greater than or equal to one-fiftieth of the crack length for LEFM to be applicable, as reported by Miller [121].

 $d_2$  and  $d_3$  if  $\Delta \sigma$  is sufficient for the crack to overcome the microstructural barrier and initiate crack growth in neighbouring grains, despite the stress intensity factor being below  $\Delta K_0$ . Therefore, any predictions made with sigmoidal curve akin to that in Fig. 2.24, will give non-conservative estimates of the CGR so should not be used where fatigue life is dominated by microstructurally short crack growth at high  $\Delta \sigma$  [109].

Evidently, the microstructure will play an important role in determining the behaviour of short fatigue cracks, resulting in the development of microstructure-sensitive models [128]. Of these, crystal plasticity models require a large amount complex analysis, calibration and processing, making them impractical in many engineering cases. The microstructural fracture mechanics models are less complex and can be used to explain short crack growth microstructure-dependence and can be used in situations when LEFM is not applicable [129]. In order to understand the microstructure effect on short crack growth, techniques such as X-ray computed tomography (XCT) have been used to capture the tortuosity of a corrosion pit and the particles in the near vicinity [130]. The results can be used in simulations to predict the most probable locations of crack initiation in corroded material. More recently, a micromechanical model has been developed and validated for short fatigue crack initiation and growth at corrosion pits [131].

# 2.4.5 Fatigue Crack Initiation from Notches and Pits

In a machined specimen, fatigue cracks will usually initiate within the material's microstructure, at localised stress concentrations such as PSBs, as described in Section 2.4.3. However, it is not unusual for material structures to contain defects or flaws, such as a notch, which would generate a much higher localised increase in stress concentration, therefore acting as a preferred crack initiation site [132].

In the case of a cross section of material containing an internal crack under a tensile load, the bulk of the material will be under the nominal stress  $\sigma_0$ ; equal to the ratio between the load and the cross-sectional area. Due to the flaw within the material (internal crack), the magnitude of stress is amplified by the defect in such a way that the maximum

stress  $\sigma_{max}$  is found by the relationship

$$\sigma_{max} = 2\sigma_0 \left(\frac{a}{\rho_t}\right)^{\frac{1}{2}} \tag{2.31}$$

where *a* represents half the length of an internal crack and  $\rho_t$  is the radius of curvature of the crack tip. Clearly, for a relatively long crack, with small tip radius the value of  $\sigma_{max}$  will be very large compared to  $\sigma_0$  [50]. The value of  $\sigma_{max}$  diminishes at distances away from the crack tip to the value of  $\sigma_0$ .

When a passive material succumbs to pitting corrosion, as described in Section 2.3.5, the corrosion pits will each act as a stress concentration site increasing the localised stress and strain in a similar way to a notch. The severity of a corrosion pit as a stress concentration site can be estimated by calculating the stress concentration factor (SCF),  $K_t$ . Cerit et al. [133] provide such calculation of SCF based upon the pit aspect ratio (AR) a/2c, where *a* is the depth and *c* is the pit radius, in the relationship

$$K_t = \frac{\left[1 + 6.6\frac{a}{2c}\right]}{\left[1 + 2\frac{a}{2c}\right]} \tag{2.32}$$

Other relationships between the pit AR and *K*<sup>*t*</sup> exist, such as [134]

$$K_t = 1 + 1.25 \sqrt{\frac{2}{1 + (\frac{2c}{a})^2}}$$
(2.33)

The use of such equations would give values of  $K_t$  as 2.15 and 1.79, respectively, for a hemispherical pit where a = c. Cerit et al. [133] also shows with finite element analysis (FEA) that the stress distribution changes depending upon the AR of the corrosion pit and that pits with lower ARs have maximum stress at the bottom of the pit. Upon increasing the AR towards narrower and deeper pits, the location of the highest stress shifts to a location slightly below the pit mouth; providing some indication about the location where cracks may initiate under fatigue loading in the presence of corrosion pits.

Indeed, there have been many studies pertaining to that of measuring or modelling crack initiation at corrosion pits with a variety of techniques [38, 111, 135–143]. A section following this will introduce the combined effects of CF and discuss the mechanisms



FIGURE 2.25: Micrographs of crack initiation at a corrosion pit. (A) Optical image captured during fatigue loading where arrows indicate the direction of applied load. (B) SEM image of the fracture surface after sample failure [115].

of nucleation and growth for both corrosion pits and fatigue cracks. As can be seen in Fig. 2.25, when a fatigue specimen, containing a corrosion pit, is subject to cycling loading cracks will grow perpendicular to the applied load—ultimately leading to fracture of the specimen. The optical image in Fig. 2.25A, was captured using an in-situ optical microscope attached to a fatigue rig as described later in Section 6.2.3.

## 2.4.6 Surface Treatments to Resist Fatigue

As has been discussed in previous sections, fatigue is a consequence of localised surface phenomena leading to crack initiation and growth. Therefore, by altering the nature of the surface condition of a component, it is possible to assist with resisting fatigue crack initiation. Mechanical treatments, such as shot peening, are one such method that would alter the surface region; due to the transfer of energy from the shot material to the targeted surface. As a result of the impact of the shot with the target, the material undergoes plastic deformation and induces a residual compressive stress in the nearsurface layers. Guidelines on shot peening are available in ASTM B851 - 04 [144] and ASM handbook vol. 5 [145], where definitions are provided for the composition, shape, size and hardness of the shot material. Additionally, the intensity (a function of velocity, flow rate, time and traverse speed) and coverage of the shot peening process are defined in terms of a standard *Almen strip*. The height of the curved arc that forms when the test strip is subjected to the stream of shot defines the Almen number. Excessively high shot peening intensity may cause unnecessary surface roughness and undue tensile stresses in the core of a work piece. However, insufficient application of intensity may fail to provide the desired resistance to fatigue crack initiation. In the power generation industry, it is not uncommon for either or both of the fir tree root and blade to be processed in this way, following the procedure S170 8-12A—typical of industrial practice for turbine blades [7, 146, 147].

The impact of the abrasive media imparts a residual compressive stress at the nearsurface and a nanocrystalline layer [148, 149], which oppose and nullify the surface tensile stress needed to initiate a fatigue crack. The compressive residual stresses have been measured as up to 700 MPa, for 12Cr SS used in turbine blades [147, 149], extending to around 300 µm into the bulk of the material. Additionally, the shot peening process causes surface nanocrystallisation, essentially reducing the grain size to tens of nanometers, which increases the number of microstructural barriers [150]. As was shown earlier, these microstructural barriers can reduce the fatigue CGR [109].

The benefits of shot peening on fatigue lifetime are well reported and for 12Cr SS used in steam turbines many comprehensive studies have been undertaken that demonstrate the extension to fatigue life [42, 140]. In general, a higher number of cycles must be completed before crack initiation occurs and the fatigue limit of the material is increased to a higher stress range. This is represented in the Kitagawa-Takahashi type plot from Turnbull et al. [147] (Fig. 2.26), illustrating the results of shot peening on the fatigue strength at 10<sup>7</sup> cycles as a function of corrosion pit depth.

They show that shot peening increases the resistance to fatigue, except for at very high stress ranges (small defect size of  $30 \,\mu\text{m}$ ) where significant plastic deformation is expected. Additionally, the Kitagawa-Takahashi plot allows an estimation of the minimum stress required to initiate cracks at corrosion pits of depth 50  $\mu$ m in both fine-ground and



FIGURE 2.26: Effect of pit depth on the fatigue strength at 10<sup>7</sup> cycles for FV566 stainless steel with different surface finishes. The lines delineate regions where cracks are non=propagating and regions where cracks develop causing failure. Reproduced from Turnbull et al. [147].

shot peened materials. For fine-ground material this corresponds to a  $\Delta \sigma$  of 600 MPa, and assuming the same *R* ratio of 0.1, gives a  $\sigma_{max}$  of 660 MPa or roughly 80 % of FV566 SS  $\sigma_y$ . This increases beyond 90 % of  $\sigma_y$  for shot peened material.

# 2.5 Environmental Assisted Cracking

The term EAC is used to described the combined and simultaneous effects of environment, stress and material properties. For instance, some materials may exhibit superior corrosion resistance during electrochemical testing but may fail rapidly if the specimens are also subject to stress, be it applied or residual.

The effects of corrosion and stress can generally be classified into three forms, which are outlined in the ensuing sections:

- hydrogen embrittlement (HE)
- stress corrosion cracking (SCC)
- corrosion fatigue (CF)

#### 2.5.1 Hydrogen Embrittlement

Through dissolution of the metal, hydrogen ions are generated, as was shown in Eq. (2.18). The electrochemical process of metal dissolution<sup>9</sup> may facilitate the incorporation or pickup of atomic hydrogen into a metallic structure where it may diffuse, combine and produce molecular hydrogen [151, 152]. Due to its small molecular size, the hydrogen is able to occupy the interstitial sites in the crystallographic microstructure of steel, at either tetrahedral or octahedral sites. Additionally, the hydrogen may also diffuse towards microstructural defects, termed *traps*, which include vacancies, dislocations, grain boundaries and inclusions.

The accumulation of hydrogen in a material's microstructure can be detrimental to its mechanical properties. Gaseous hydrogen may form blisters in the structure which act as stress concentration sites; more commonly though, hydrogen alters the fracture mechanism of high-strength steels from a ductile to brittle fracture as the material cannot deform as much due to interstitial hydrogen [153]. Such changes to mechanical properties are undesirable, as a component that originally would fail in a ductile fashion, giving time for repair, may now fail in a brittle manner at much lower stresses than anticipated. The propensity for HE is affected by the strength of alloy, temperature, source of hydrogen, exposure time, alloy composition and microstructure [154].

# 2.5.2 Stress Corrosion Cracking

Failure of material can occur by the combined effect of a susceptible microstructure, sustained tensile stress (applied or residual) and a specific corrosive environment in a process known as SCC. This has been an intensive research area for many years [155] due to the vast quantities of SS alloys used in a wide variety and increasing number of applications. Like HE, cracking usually occurs at a stress below  $\sigma_y$  of the material due to the aggressive nature of the environment—in the case of SS this is often when chloride ions are present. The SCC cracks are normally of branch-like appearance and can be intergranular or transgranular, depending upon the environment system [156].

<sup>&</sup>lt;sup>9</sup>The anodic dissolution of iron produces electrons, which enables the reduction of water molecules to form atomic hydrogen and hydroxide ions.

Experimental studies are often carried out with either self-loaded cylindrical specimens [157] or U-bend specimens [158], to ensure that the constant load is applied to the specimens while they are exposed to a test environment. As reported by Horner et al. [157], SCC will preferentially initiate at corrosion pit sites, below  $\sigma_y$ , due to the localisation of stress and strain around the pit mouth. Exposure tests of up to 668 h (~ 1 month) were required to initiate cracks at these sites, demonstrating that a significant period of time is attributed to the crack initiation stage of overall crack growth.

# 2.5.3 Corrosion Fatigue

Due the nature of applied loads in a steam turbine, the blades are normally subjected to fluctuating cyclic stresses in a hot steam environment [6]. As such, the turbine blades (and other components) are susceptible to EAC in the form of CF. The nature of CF means that the synergistic combination of both (cyclic stress and corrosive environment) acting together is more detrimental than that of either one acting separately [104]. Furthermore, it is defined within NACE/ASTM G193-12 [48] as

... the process wherein a metal fractures prematurely under conditions of simultaneous corrosion and repeated cyclic loading at lower stress levels or fewer cycles than would be required to cause fatigue of that metal in the absence of the corrosive environment...

An example of the detrimental impact that the combined effect of environment and cyclic load has on fatigue life was presented earlier in Fig. 2.23. Additionally, many comprehensive studies into the effects of CF on component lifetime have shown that there is a considerable reduction in the number of cycles to failure and an elimination of the fatigue limit, which is often observed in air [38, 139, 140, 143, 159–161].

The presence of the aggressive environment can encourage the initiation and growth of fatigue cracks, due to stimulating the initiation and growth of corrosion pits which are known localised stress concentration sites (see Section 2.4.5). Additionally, the environment may also assist crack growth overcome barriers that would otherwise retard crack growth, such as microstructural features. Due to the complexity of interactions between the many possible microstructure and environment combinations, numerous mechanisms are possible including HE, film rupture, dissolution and repassivation, enhanced localised plasticity, interactions of dislocations with surface dissolution [159, 162].

#### **Corrosion Fatigue Mechanisms**

Of those mechanisms mentioned, it is anodic slip dissolution and HE that are the two main CF mechanisms. HE was discussed within Section 2.5.1, so only anodic slip dissolution is presented in this section. In the case of SS, the process involves the diffusion of the active species (H<sub>2</sub>O and Cl<sup>-</sup>) to the tip of the crack and the rupture of the protective passive film, under an applied load, by mode II crack displacement on a slip plane [32]. The small anodic area of bare metal is then subjected to anodic dissolution, which is enhanced by the aggressive environment resulting in sharpening of the crack tip. As a consequence, this increases the value of *K* by reducing the crack tip radius, facilitating the continued growth of the crack.

Due to the cyclic nature of fatigue loading, a number of factors will influence the rate of anodic dissolution. These include the oxide rupture rate, solution renewal at the crack tip and repassivation rate. The fretting contact between mating crack faces can break the oxide and the tensile cyclic load can assist in 'pumping' fresh solution towards the crack tip. Consequently, the cyclic frequency and type of waveform will impact upon the propensity of CF damage; under fatigue alone these factors would not be as significant [32, 107]. Waveforms that do not provide for sufficient time for environmental interactions will not affect the CGR. These types of waveforms include square and negative sawtooth as the loading occurs rapidly in a single step and prevents continuous exposure of the crack tip to the aggressive environment. Conversely, sinusoidal, triangular and positive sawtooth would have a detrimental effect on the CGR due to the environment interaction.

## **Stages of Corrosion Fatigue**

In Section 1.2 and Fig. 1.5, it was shown that the CF process can be treated as a series of sequential events, consisting of: passive film breakdown—allowing for pit initiation, growth of the corrosion pits, transition from metastable to stable pitting, pit-to-crack transition i.e the initiation of a crack at a corrosion pit, the growth of the fatigue crack until



FIGURE 2.27: Schematic representation of the stages in corrosion fatigue.

fracture—which can be separated into short and long crack growth. The process of these events is shown in Fig. 2.27 and to be able to reliably predict and model the effects of CF requires a comprehensive and quantitative understanding of each stage [163].

As discussed previously in Section 2.3.5, engineering alloys such as SS and aluminium are protected by a passive oxide film that resists metal dissolution by electrochemical processes. However, species such as chloride are known to facilitate the breakdown of the passive film and encourage the initiation and growth of a corrosion pit. As such, the offload steam turbine environment (discussed later in Section 2.5.3) offers an environment that will allow the nucleation and growth of corrosion pits. These pits will initiate at locations like grain boundaries, surface flaws, mechanical damage sites, or inclusions. There are numerous reports that inclusions, such as MnS, will act as sites for corrosion pit initiation in SS and the 12Cr grades used for blades within the LPST due to them being more anodic than the steel matrix [28, 139, 142, 160, 164, 165].

Once the corrosion pit has initiated, a localised environment is needed to sustain the growth of a pit beyond that of the metastable stage; otherwise the pit will die and the surface repassivate. Additionally, the applied cyclic load, during CF, will assist the pit growth rate due to the induced degree of plasticity within neighbouring grains [31]. The combined effect of environment and load encourages corrosion pits to grow to a size that begins to impart some stress and strain localisation.

As the corrosion pit grows in size, so does the severity of stress concentration, as was presented in Section 2.4.5. Consequently, when a pit is of significant size, the associated stress concentration will be high enough to facilitate crack initiation [138, 166, 167]. The minimum pit size for crack initiation will ultimately depend upon the stress levels, but a minimum size has been reported around 50 µm by Turnbull and Zhou [166] and other

authors [157, 168]. In addition to exceeding a threshold stress intensity factor ( $\Delta K_{th}$ ), the growth rate of the crack  $(\frac{da}{dt})_{crack}$  must also exceed the growth rate of the pit  $(\frac{da}{dt})_{pit}$ ; which was originally proposed by Kondo [169] in their competition model:

$$\Delta K \ge \Delta K_{th}$$
 and  $(\frac{da}{dt})_{crack} \ge (\frac{da}{dt})_{pit}$  (2.34)

As such, there are two criteria that determine the early stages of CF crack growth [170]; initially it is the growth of the corrosion pit that dominates, which is then replaced by fatigue crack growth. When the the CF process is controlled by pit growth, the lifetime of the material is controlled by the time-dependent corrosion processes for the majority of the total lifetime. The controlling factor transitions to a mechanics dominated and cycle-dependant mechanism once crack initiation has begun.

However, such approach essentially equates a three-dimensional corrosion pit as an effective two-dimensional crack so that a value for *K* can be calculated. The main drawback to this is that a considerable proportion of the total lifetime, which should include the duration of pit growth, crack initiation and short crack growth is not included; only long crack growth from a critical size is measured. As was shown in Section 2.4.4, the use of  $\Delta K$  for short cracks leads to a breakdown of LEFM conditions, so the use of *K* has been questioned despite its continued use over many years [171]. The review by Larrosa et al. [171] highlights how efforts were made to account for the fact that fatigue cracks may initiate from pits, even when the pit is small enough to result in *K* values that are below the LEFM threshold. Improvements to the models were made by separating the CF process into discrete stages that would separate short crack and long crack growth. This allowed different LEFM models, such as corner crack growth, to be used in addition to a surface crack model once the crack is of longer length, but this will be affected by the AR of the pit.

To account for the effect of stress on the growth of the corrosion pit, Sriraman and Pidaparti [172] modified previously presented models such that the equation for pit depth growth rate includes a stress amplitude component in the form

$$a_p = \left(\frac{3M}{2\pi n F \rho}\right)^{\frac{1}{3}} (I_p)^{\frac{1}{3}} (A')(t)^{\frac{1}{3}}$$
(2.35)

where  $a_p$  is the pit depth, M is the atomic mass of the alloy, n is the valence of the atoms, F is Faraday's constant,  $\rho$  is the density of the alloy,  $I_p$  is the pitting current, t is time and A' is equivalent to  $1.01^{\sigma_a}$ , where  $\sigma_a$  is the stress amplitude. This meant that for lower stress amplitudes, a significant period of component lifetime would elapse before the pit reaches a critical depth for crack initiation; matching observations from aluminium alloys. The model was developed to take into account the accelerated fatigue damage produced in a corrosive environment and the modification of the fatigue curve due to the synergistic effect of pitting and fatigue.

Once a fatigue crack has initiated at a corrosion pit, the environment can assist with continuous growth through many grains. Previously, for fatigue in air (Section 2.4.3), it was shown that cracks may become non-propagating due to microstructural barriers such as grain boundaries due to their differing orientation of slip planes. It has been shown by Akid and Miller [116], that the environment assists the short crack growth overcome these barriers through metal dissolution, with the effect becoming less as the crack grows; perhaps due to the restricted diffusion of species as the crack becomes longer. However, it is generally agreed that the effects of the environment will lead to an overall increase in the CGR [110, 173]. Furthermore, for fatigue in air, around 80 % of the lifetime is spent in the crack initiation stage (crack length <100  $\mu$ m), whereas the presence of the environment reduced the proportion of time for initiation and the majority of the fatigue life is predominantly crack propagation [32].

The crack grows until it reaches a size that can be quantified by LEFM methods (see Section 2.4.4). It is possible to characterise the effect of the environment on the rates of fatigue crack growth by measuring the sigmoidal variation of fatigue crack growth as a function of the stress intensity factor range. If the environment does impact upon crack growth behaviour, then an increased value of  $\frac{da}{dN}$  will be measured for a given value of  $\Delta K$  and  $\Delta K_0$  is reduced; as reported in [107, 122, 159].

Additionally, transient environmental conditions may impact upon the growth rate of cracks, as reported by Turnbull and Zhou [174]. They found that the CGR may change depending upon the temperature of a chloride-containing environment. For both 321 and 316L SS, SCC cracks would initiate at elevated temperatures of 130 °C and continue to grow only in 321 SS when the temperature was lowered to 40 °C. Clearly, the general expectation that kinetic reactions are slower at lower temperatures does not apply in this situation and further research would be needed to find if similar effects were present when testing other grades of SS used in steam turbines.

#### **Corrosion Fatigue in Steam Turbines**

The operating environmental conditions of a steam turbine were reviewed by Zhou and Turnbull [6] in order to establish an understanding of the chemistry of condensates on turbine components. In the LPST section of a fossil-fired steam turbine, condensation of steam starts to occur at 90 °C when the blade's surface temperature is below that of the steam saturation point.

Under normal operating conditions, the water chemistry of the steam, is tightly controlled through pre-treatment and monitoring at dosing points. However, there are unfavourable circumstances that may arise when the water treatment is ineffective, there are leaks from other systems or transient chemistries during startup/shut down that allow increased concentrations of impurities into the steam. Once the impurities are dissolved within the steam, they can be deposited onto the metal surface either by deposition or condensation. Subsequent deliquescence of the salt allows the formation of droplets or a continuous liquid film on the turbine surface [175]. The precise concentration of salt in this film is hard to measure in service. However, guidelines suggest that under normal operation, the concentration of chloride (steam cation conductivity) should not exceed 3 ppb. Through the use of thermodynamic data, Zhou and Turnbull [6] calculated that this would equate to a chloride concentration between 300 ppb and 100 ppb for a steam wetness of 1 % and 3 % respectively.

Another key species in the condensate is oxygen, as the concentration of this will influence the rate of corrosion. If there is no air leakage in the system, then the only source of oxygen is that of dissolved oxygen within the feedwater. Calculation of the oxygen content in the water phase depending on the inlet steam oxygen concentration showed that the concentration is < 1 ppb even for inlet steam containing 8 ppm oxygen. However, in regions where the steam pressure is less than the atmospheric pressure (final stage of the LPST), there may be leakage of air into the turbine through the gland seals allowing concentrations up to 2.5 ppm depending on the partial pressure of air and the temperature in the turbine.

Further consideration regarding oxygen concentration was identified as the effect of two-shifting [6]; that is, switching between on-load and off-load conditions at evenings and weekends to better match consumer demand. When the steam turbine is operational (on-load), the concentration of oxygen will be low (< 1 ppb), as the glands are sealed by steam pressure. However, during shut down (off-load), the steam is no longer supplied, so air leakage occurs. Depending upon the shut down duration, the oxygen concentration may reach up to 3.7 ppm overnight at 70 °C and 7.6 ppm at 20 °C during a longer weekend shut down. Consequently, when restarting the system after a shut-down there is a critical period where the steam has formed a condensate containing a high concentration of oxygen. Coupled with earlier information regarding contaminants in the steam, it is possible to produce an aqueous environment that is potentially damaging to the steam turbine components.

The operating environment conditions can therefore be defined as follows [4]:

- On-load
  - Deaerated
  - Low concentration (300 ppb to 600 ppb) of anionic impurities (Cl<sup>-</sup>) for 1% steam wetness
  - Temperature of 90 °C when steam condensation begins
  - Temperatures reducing to 40 °C at later stages in LPST
  - Exposure periods of around 16 h per day
- Off-load
  - Air saturated
  - Pure water condensate
  - Anion concentration < 3 ppb</li>
  - Temperature around 70 °C overnight
  - Dropping to 20 °C at weekends

During operation there are a range of forces acting upon the LPST blade. The main forces to consider are centrifugal forces due to rotation, bending forces due to the fluid pressure and change of momentum and bending forces due to centrifugal action [176].

# **Crack Initiation Location at Corrosion Pits**

In the previous section, various models were presented that represent the CF process, to include the initiation and growth of a crack at a corrosion pit once a threshold criteria is reached. The corrosion pit presents two main sites as possible locations for crack initiation, namely, the base and mouth of the pit, shown in Figs. 2.28A and 2.28B respectively. Prior to the work of Horner et al. [157], the general perspective was that cracks would develop from the base of a corrosion pit due to the concentration of stress at this location. Through the use of XCT, the 3D visualisation of pits and SCC in 3NiCr-MoV SS (Fig. 2.29A) showed that for the vast majority, the crack initiated close to the pit mouth and not at the base. The research also went further and showed, with FE analysis (Fig. 2.29B), that the dynamic strain introduced by the growth of the pit, and reduced constraint around the pit mouth, resulted in the strain being maximised just below the pit mouth as opposed to the base, where stress was maximised due to redistribution [150, 177]. The high concentration of strain at the pit mouth was the proposed explanation for crack initiation at this location. Consequently, it may be possible to use surface observation techniques, such as in-situ optical microscopy (OM) and digital image correlation (DIC), to capture the early stages of crack initiation at the mouth of corrosion pits [142, 178]. In the work of Evans et al. [178], they were able to show, with DIC, that the value of threshold strain for crack initiation remained was unaffected by the depth of the corrosion pit. This suggests that the measured value of 0.24% strain



FIGURE 2.28: Schematic diagrams of the relation between pit *P* and crack *C* with (A) showing crack initiation at the base of a pit, (B) crack initiation at the mouth of a corrosion pit and (C) a developed crack due to crack coalescence once the crack growth rate exceeds the pit growth rate. Adapted from Horner et al. [157].



FIGURE 2.29: (A) An XCT image of the inside surface of a corrosion pit showing SCC nucleation near the mouth of the pit [157]. (B) FE analysis map showing localisation of plastic strain just below the pit mouth [177].

could be an intrinsic material property for crack initiation.

However, in the steam turbine environment it has been reported [6] that the oxygen concentration will be very low (<5 ppb). Therefore, the possibility of corrosion pit growth during normal operation is reduced, so it is unlikely that there will be dynamic strain evolution during this time and it may be possible to only consider fatigue crack initiation at corrosion pits that formed during previous periods of shut-down; although environment effects on CGR would not be obtained.

Contrary to these findings, there are also numerous cases in which crack initiation is located at the base of corrosion pits [133, 140, 179–181]. This could be due to a lower applied stress range or a change to the aggressive environment making the base of the pit more susceptible to crack initiation. Additionally, different ARs, residual stress and microtopographical features will result in a wide variety of stress intensity factors which may make the base or mouth of pits a preferred crack initiation location [150, 182]. Schönbauer et al. [115] provide values of the geometry factor *Y*, used in Eq. (2.26), from a range of authors and show that *Y* and consequently the stress intensity factor is maximised at the surface and minimum at the deepest part of the pit.

Also evident from Fig. 2.29A and reported in [142], is the fact that a crack may start from one side of the corrosion pit and then grow in size before observation of crack initiation on the opposite side is apparent. In this case, it is difficult to define which will be the dominant crack because as they each grow, their growth rate may exceed that of the pit growth rate, meaning they may coalesce to form a single crack which extends beyond the sides and base of the corrosion pit; as shown in Fig. 2.28C [183].

Additionally, in Section 2.4.6, the benefits of shot peening a surface to resist fatigue crack initiation were introduced. Apart from recent studies by Turnbull et al. [147] and Guo et al. [149], there is little understanding about whether the residual stress layer, induced by shot peening, will still have a beneficial impact when the depth of the corrosion pit is of equal or greater depth (around  $300 \,\mu$ m). It was just presented that crack initiation was most likely near the mouth of the corrosion pit, but for a shot peened surface this would also correlate to the highest amount of residual compressive stress. There appears a lack of understanding as to whether the residual stress will influence the crack initiation location at corrosion pits on shot peened material, i.e. cracks initiating at the base of the pit where the residual stress is lower.

Finally, those who have adopted the Kondo [169] model must be aware of the limitations by assuming the pit and crack to be the same size at the transition point, as this will not take into account early stage crack initiation and growth at opposite sides of the mouth, crack coalescence or consideration of the 3D crack tortuosity [183]. Additionally, the more recent models highlighted [171], tend to treat CF as a two-stage process of pit growth followed by crack growth. As was shown in Fig. 2.27, the process of CF involves five defined stages which cannot be accurately represented by the two-stage models presented here as additional knowledge about the underlying mechanisms involving pit-to-crack transition and short crack growth is required. Additionally, the models tend to adopt the assumption that the pit can be treated as an equivalent crack to allow  $\Delta K_0$ calculation based upon LEFM even though a considerable portion of the CF lifetime is attributed towards the corrosion-dominated pit growth process. While much research presented has also shown that short cracks will be initiate and grow at values below  $\Delta K_0$ measured from long crack experiments.

# 2.6 Literature Review Summary

The above sections have presented a comprehensive review of all aspects involved with steam turbine design and degradation mechanisms. This has included a review of SS engineering alloys that are used and the corrosion, fatigue and EAC of these alloys which is summarised below.

# 2.6.1 Main Findings from Literature Review

- The LPST blades are commonly made from a 12Cr type martensitic SS due to its good mechanical properties and adequate corrosion resistance. However, due to the relatively low concentration of chromium and molybdenum, these alloys are susceptible to localised corrosion in a contaminated aerated condensate.
- The LPST blades are susceptible to pitting corrosion due to the condensation of a contaminated steam environment onto the material during start-up and shut-down periods, leading to the formation of a contaminated condensate that provides an environment for localised corrosion.
- Chloride is consistently reported as a contaminant that stimulates and supports the initiation and growth of corrosion pits. The effects are exacerbated by the industrial desire to better match consumer power needs by switching regularly between onload and off-load conditions, which allows a build-up of contaminants and oxygen into the turbine cavities.
- Initial research by Salzman et al. [98] has demonstrated some of the effects of twoshifting, but further work could be done to identify chloride concentrations for pitting and how two-shifting affects the passive film composition.
- The main failure mechanism for LPST blades is CF due to the repeated variable load during operation and the prescence of a steam environment, which results in a reduction in the number of cycles to failure.
- The CF process consists of a series of sequential steps which are passive film breakdown, growth of corrosion pit, pit-to-crack transition, short crack growth and long

crack growth until failure.

- Under regular operation, corrosion pits which initiated and grew during water chemistry excursions are consistently reported as fatigue crack initiation sites due to the localisation of stress and strain around the site.
- The transition from a pit to a crack is often defined as the point at which the growth rate of the crack exceeds that of the pit and the stress intensity factor of the pit is above a threshold.
- CF is a complex and multistage process with the majority of lifetime spent on timedependant corrosion-dominated processes. However, most CF models adopt a simpler two-stage approach of pit growth followed by crack growth using various forms of a threshold *K* which is required for transition between stages.
- Surface treatments such as shot peening can be used to improve the resistance to fatigue damage, but the effectiveness of this when corrosion pits exceed the depth of the compressive residual stress layer requires some clarity.
- It has been common to assume that the crack and the pit are the same size at the point of transition, but SCC work by Horner et al. [157] with XCT has shown that this is not always the case and embryonic fatigue cracks initiate at either side of the pit mouth before growing and coalescing into a single dominant crack.
- The research by Turnbull et al. [177] used FE to show that the reason for crack initiation at the mouth of a corrosion pit was likely to be due to the localisation of plastic strain in this region rather than at the pit base.
- The location of crack initiation at a corrosion pit may be related to the corrosion pit AR, but some research has shown with DIC that the same critical strain is required for crack initiation [178].
- Due to incorrect assumptions about crack initiation at pits, models based on the previous assumption often unreliably predict the growth rate of short cracks, which is often much faster than that of the corresponding long CGR.

- The growth of long cracks can be effectively calculated through use of the stress intensity factor *K* and LEFM.
- A significant amount of data has been published by Salzman et al. [137], Ebara [140], Turnbull et al. [142], Schonbauer et al. [168] and others relating to CGRs from corrosion pits and the construction of Kitagawa-Takahashi type diagrams so it may not be necessary to repeat these measurements.

# 2.6.2 Research Gap

- The critical concentrations of chloride required to induce corrosion pit initiation in a steam turbine environment are not widely available. Furthermore, the full effect of cycling between on-load and off-load environmental conditions and the impact of water chemistry excursions on initiation, growth and repassivation of corrosion pits is unknown.
- Additional electrochemical techniques, such as EN, could be utilised to support the data reported by [4, 98] and evaluate other materials which are used for the steam turbine blades.
- The effect of cycling between on-load and off-load conditions on the composition of the passive film that protects the component requires further investigation.
- Various methods exist for producing artificial corrosion pits making it easier to ensure cracks initiate in a desirable location, but which method produces the most representative could be clarified.
- Recent opinions, suggest that Kondo's assumption that cracks would initiate at the base of the corrosion pit due high localised stress may be incorrect. Crack initiation at the pit mouth has been visualised with XCT for static load, SCC of 3NiCrMoV and similar may be possible with 12Cr SS under dynamic fatigue loading.
- More recent developments in non-destructive techniques, such as XCT, may enable better visualisation of embryonic crack growth at corrosion pits or other microscopy

techniques such as plasma focused ion beam (PFIB) milling could be used to confirm the crack initiation location.

- Comparative studies, to those reported by Evans et al. [178], could be performed to determine if the critical strain for crack initiation is an intrinsic material property.
- Further studies to those of Turnbull et al. [147], Guo et al. [149] are required to evaluate the effectiveness of shot peening when corrosion pit depths are similar to the depth of residual compressive stresses.

# Chapter 3

# **Experimental and Characterisation Techniques**

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# 3.1 Overview

Throughout this research project, a wide variety of experimental and characterisation techniques were utilised, in order to study both the initiation of corrosion pits and nucleation of cracks at these sites in a simulated low pressure steam turbine (LPST) environment. Characterisation techniques were required that would allow the geometry of the corrosion pit to be determined and electrochemical techniques were required in order to measure the corrosion kinetics in a simulated steam turbine environment to determine the impact of contaminants and produce representative corrosion pits on fatigue specimens so crack initiation could be investigated. To reveal the sub-surface crack initiation location, techniques were chosen that would provide insight into internal features using X-rays or destructive milling. The chart shown in Fig. 3.1 summarises the research programme and the experimental and characterisation techniques used for each area of investigation; this chapter will provide a description of such techniques and the experimental procedures are found within Chapters 4 to 6.

This chapter aims to outline the techniques used within each area of investigation, provide background information and describe the principles of operation. Further details pertaining to the experimental methods adopted whilse completing this research are given in the chapters that follow this one.



FIGURE 3.1: Outline of overall research areas, experimental and characterisation techniques.

# 3.2 Microscopy Techniques

# 3.2.1 Laser Confocal Scanning Microscopy

The extensive use of the laser confocal scanning microscopy (LCSM) allowed measurement of the corrosion pits that initiated in the simulated steam turbine environment and those produced via artificial electrochemical methods. The data obtained provided both quantification of the corrosion pit geometry (diameter and depth) and allowed a 3D representation of the pit morphology to be produced.

# Background

LCSMs are often equipped with both white and laser light sources providing colour and laser intensity details. A LCSM has the ability to generate a sharper image with greater depth of field than a traditional optical microscope. The white light is detected by a charged coupled device (CCD) camera to provide the colour information for each pixel in the focal plane. More importantly, the laser light source provides a high intensity, monochromatic and coherent beam, meaning that the waves travel in phase, causing no interference. To extract height information from the sample, the use of pinholes within the laser optics is utilised as this only allows light from the focal plane to reach the photoreceptor. Light from other planes is rejected as unwanted scattered waves would interfere with the in-focus image created by the coherent waves [184].



FIGURE 3.2: Schematic diagram of the Keyence VK-X200K laser confocal scanning microscope [185].

A modern LCSM is able to build up an image of a rough or pitted surface by capturing a sequence of images at different heights determined by the Z-axis pitch. The X-Y scan optics and objective lens are used to focus the laser waves onto the selected area and the intensity for each pixel is stored for that plane. The lens then moves in the Z-axis to scan the next focal plane and the process is repeated until all planes have been imaged and stored. Once the scan is complete, the stored pixel intensities of each plane are combined by the software to construct colour, laser and height intensity maps.

A labelled schematic of the Keyence VK-X200K 3D LCSM used in this study is presented in Fig. 3.2. The laser light source is a violet laser with  $\lambda$  = 408 nm and the display resolution is 0.5 nm in the Z-direction and 1 nm in the X and Y-direction. The images captured by the system have a resolution of 2048 × 1536 pixels for superfine resolution [185].

The possibility to generate 3D images of uneven surfaces and the enhanced illumination provided by the laser light source makes LCSM an attractive technique to image small and concave defects such as corrosion pits. Through analysis of the height maps, it is possible to determine the pit depth, while the colour and laser images can be used to measure the pit geometry.

# Operation

To measure the geometry of a corrosion pit using a LCSM,<sup>1</sup> a series of steps were followed to obtain accurate and reliable data which are outlined below:

- 1. The sample to be measured was placed onto the measurement stage and an appropriate objective lens was selected to allow magnification of the pit.
- 2. The lower and upper bounds of the z-axis position were set so that the surface of material and base of corrosion pit were within the measurement range.
- 3. The auto-gain wizard was run to allow the brightness and number of scans to be set; dependant upon the reflectivity of the surface and depth of the corrosion pit.<sup>2</sup>
- 4. A macro, in the VK-Analyser software, was run so that the image was processed with the following modules to reduce errors associated with the measurement:
  - (a) auto eliminate noise normal
  - (b) height cut level normal
  - (c) correct tilt auto plane tilt
- 5. The diameter of the corrosion pit and height change (depth of corrosion pit) were measured using the profile from a straight measurement line placed onto the image.

# 3.2.2 Scanning Electron Microscopy

A scanning electron microscope (SEM) is an instrument that provides high resolution digital images of the sample under observation. Within this project, the use of SEM has enabled the observation of the corrosion pits that were grown onto the gauge section of fatigue specimens, the fracture surfaces and capture of successive images of the cross sectioned surface during plasma focused ion beam (PFIB) milling through corrosion pits.

#### Background

The SEM offers higher resolution images and a better depth of field than optical or confocal techniques due to the electrons having a shorter wavelength than light viz. 0.001 nm to 0.01 nm (electrons) vs. 400 nm to 700 nm (light). The resolution of a modern SEM is

<sup>&</sup>lt;sup>1</sup>The LCSM was operated through VK-Viewer and subsequent analysis in VK-Analyser software provided by the manufacturer.

<sup>&</sup>lt;sup>2</sup>A dual scan allowed a high brightness to be used to image the base of the corrosion pit where it was difficult for light to reach and a lower brightness for the reflective metallic surface.



FIGURE 3.3: Schematic diagram of the main components of an SEM [187].

1 nm to 20 nm, although a resolution of 0.4 nm at 30 keV was achieved with a Hitachi S-5500 in 2009 [186]. Although not as high as the resolution achieved with a transmission electron microscope (TEM), this is a significant improvement over an optical system which would have a resolution close to 300 nm; around half the wavelength of light.

The electrons needed to image at these resolutions are generated from a field emission gun (FEG) or tungsten filament electron gun source under vacuum. The latter produces electrons with a wider energy spread (1 eV to 2 eV) than the former, meaning FEG sources are now preferred as they provide a lower energy spread of electrons to the SEM allowing improved resolution [187]. The electrons are accelerated to an energy of 1 keV to 30 keV before being focused by the condenser and objective lenses (shown in Fig. 3.3) to a spot size of 1 nm to 10 nm on the sample surface. Upon reaching the surface, the incident beam interacts with the sample. The depth of interaction depends upon the accelerating voltage chosen, in turn producing different types of signals, most of which can be detected. X-rays interact the least, so are not easily absorbed and can come from a region several micrometres in diameter [187].

The region penetrated by the electrons is known as the interaction volume (Fig. 3.4A)



FIGURE 3.4: (A) The interaction volume of the primary electron beam and the regions from which secondary electrons, backscattered electrons and X-rays may be released. (B) Some of the common signals released from the sample in an SEM [187].

and within this region the incident electrons can be scattered either elastically or inelastically releasing characteristic electrons and X-rays from the sample (Fig. 3.4B). The SEM has the ability to detect and measure the radiation escaping from the specimen—the most utilised are the back-scattered electrons (BSEs) and secondary electrons (SEs). The BSEs originate from the incident beam and have been scattered multiple times within the sample, so much so, that they are directed back towards the SEM lenses. Consequently, the energy of the BSEs is close to the incident beam (60 % to 80 %) and is ultimately determined by the material's atomic number, meaning that BSE images can be used to distinguish between areas of differing chemical composition. Closer to the surface of the material, SEs are released by ionisation due to the impact of the primary beam - a form of inelastic scattering. Only 'knocked out' electrons with sufficient energy are able to escape the material and as such these electrons come from the upper few nm of the surface, which means SE images produce excellent sample topographical details. SEM imaging was carried out to characterise the morphology of corrosion pits initiated during exposure testing and those produced by artificial methods. It was also used to image the cracks that initiated at corrosion pits during fatigue testing. The imaging was mainly conducted on a TESCAN MIRA3 FEG-SEM and FEI Helios DualBeam<sup>™</sup> PFIB-SEM.

# 3.2.3 Plasma Focused Ion Beam Microscopy

A focused ion beam (FIB) instrument has a similar setup to that of a conventional SEM. The procedure is carried out within a chamber under high vacuum, with specimens mounted on a sample stage and detectors positioned within the close vicinity to record emitted signals. Consequently, the FIB setup is frequently combined with SEM to give a FIB-SEM dual platform instrument capable of 'slice and view' serial sectioning. Traditionally, using a Ga<sup>+</sup> FIB, only a small volume (tens of cubic microns) could be excavated and serial sectioned. Recent developments of the PFIB have enabled much larger volumes of material to be excavated with automated serial sectioning routines within a feasible time frame [188]. It has long been established that by capturing sequential 2D images, a considerable amount of information can be inferred about the examined sample's 3D structure while providing high spatial resolution and sub-micron resolution. This is particularly useful when wanting to capture information on damage mechanisms, such as crack initiation sites at a corrosion pit. Previously, due to the limited small volume that could be serial sectioned with FIB, the operator would need prior knowledge about the volume from which to make their measurement. The increased milling rate of the PFIB means that a volume of around  $(300 \,\mu\text{m})^3$  can be excavated, with each slice sequentially imaged with an automated serial sectioning routine. As a consequence, it is possible to mill through a corrosion pit, in its entirety, without concern of losing sub-surface information that may otherwise go unnoticed, i.e. cracks that have nucleated near the base of a corrosion pit.

# Background

The FIB is an instrument for sequential imaging and milling of material at the sub-micron scale. Traditionally, the FIB has used a liquid metal ion source (Ga<sup>+</sup>) which was developed by Seliger et al. [189] in 1979. More recently, efforts have been made to utilise a

noble gas, such as xenon, to generate a plasma ion beam of Xe<sup>+</sup> to allow the development of PFIB-SEM dual beam microscopes [190]. The main advantage of a Xe<sup>+</sup> ion source over a more traditional Ga<sup>+</sup> ion source is the exceptionally high milling rate of a wide variety of materials [191]. This is due to the Xe<sup>+</sup> plasma ion source being able to produce a probe current in excess of 1  $\mu$ A, while also maintaining a small spot size and limiting the damage introduced by the ion beam. As a result, the milling rate that can be achieved is 20–60 times greater than FIB, allowing for a much larger 3D volume of material to be milled and imaged by SEM within a similar period.

Observation of the sample is possible with the ion beam in a similar manner to the use of an electron beam in SEM. The notable difference is that rather than an electron beam rastering over the surface of the sample, it is the  $Ga^+/Xe^+$  ion beam instead [192]. The *large* ion atoms bombard the surface of the solid material, resulting in energy being transferred to the target atoms through multiple collisions. As a result, surface atoms may be ejected and produce SEs; both of which can be detected to form an image of the sample under study [193].

# Operation

The FEI Helios PFIB-SEM dual beam microscope used within this research project utilises the FEI Slice and View<sup>TM</sup> software to automate the milling and imaging process of a defined block. In order to define the block for 3D serial sectioning, side and front trenches are excavated with the ion beam. The width of these must be approximately  $\frac{1}{5}$  of the trench length, i.e. for a Z-axis side trench that is 150 µm in length, a width of ~30 µm should be used. An additional benefit of the trenches is that the material removed by the milling process has a volume in which to re-deposit without interfering with the imaging of the cross sectioned slice. Thus, a block of material (or region of interest (RoI)) is now defined for serial sectioning as shown in Fig. 3.5.

The Xe<sup>+</sup> ion beam is positioned parallel to the cross sectioned face in order to mill and reveal successive, equally spaced and parallel slices. The milling rate is not uniform across the surface, due to differences in the orientation of grains and second phase particles. This can generate large channels in the milling direction known as 'curtains' which obscure the microstructure beneath (Fig. 3.6). To alleviate this, a rocking polish  $\pm \sim 5^{\circ}$ 



FIGURE 3.5: Schematic diagram showing a block of material that is to be sectioned by the ion beam with a SE image after each successive slice. The ion beam is parallel to the surface that is being imaged by the electron beam at a tilt angle of 52°. Tracking fiducials (o and ×) are milled behind the RoI to assist with identifying the milling location.

can be used, the precise angle used is determined by the Y-Axis depth of the cross section [194]. Additionally, the RoI that is to be serial sectioned is protected by depositing a platinum layer, which is 1  $\mu$ m to 5  $\mu$ m thick, which can also reduce the curtaining effect as it creates a uniform surface for the initial impact of the Xe<sup>+</sup> ion beam.

To image the cross sectioned face after each milling step, the ion and electron columns are arranged so that with the sample in the eucentric position the focus of both beams is coincident. As such, when the ion beam is normal to the surface of the sample the electron beam is at an angle of 52° [195]. This allows consecutive steps of milling and imaging without moving the sample—just rotation between the milling and imaging modes. To assist with placement of the milling and imaging locations, tracking fiducials were made directly behind the RoI in the form of  $\circ$  and  $\times$  markers. This ensured that the correct position and orientation was maintained during the automated routine.

An FEI Helios FEI Helios DualBeam<sup>™</sup> PFIB-SEM was used within this project to characterise the location of cracks that had initiated at corrosion pits which had been subjected to fatigue cycling.



FIGURE 3.6: An example of how PFIB milling can generate channels within a cross section slice due to the none uniform milling rate of different grain orientations. The 'curtaining' effect masks the microstructure and other features beneath, a rocking polish is used to minimise this effect.

# 3.3 Electrochemical Techniques

# 3.3.1 Potentiometry

By passively measuring the potential difference between two electrodes, it possible to obtain the corrosion potential,  $E_{corr}$ ,<sup>3</sup> a measurement that is extensively used in corrosion based experiments. When the corroding system is at equilibrium, the reduction and oxidation reactions are occurring at the same rate. Consequently, the opposing anodic and cathodic currents are equal, meaning that the net current flow is zero. At this point, without application of current or voltage, it is possible to measure the voltage difference between the working-sense electrode (WSE) and reference electrode (RE) to provide a value for  $E_{corr}$  (Fig. 3.7A). This is reported as V vs. RE, where RE indicates the type of RE used in the experiment (a saturated calomel electrode (SCE) is common), allowing comparison between data sets as the potential differences between common RE are known [196].

It is possible to record  $E_{corr}$  as a function of time and changes to  $E_{corr}$  can provide information about the reactions occurring at the working electrode (WE) under study.

<sup>&</sup>lt;sup>3</sup>It may also be defined as the open circuit potential (OCP), electrode potential, free corrosion potential or electrochemical corrosion potential.



FIGURE 3.7: Electrode connections for a: (A) corrosion potential measurement, (B) two electrode setup and (C) three electrode setup.

An example would be an  $E_{corr}$  shift to a more negative potential which would indicate either an increase in anodic reaction or a decrease in cathodic reaction. In this project, such a shift in  $E_{corr}$  would be a suitable indication for the onset of localised corrosion, in the form of pitting, during exposure experiments to simulated steam turbine operating conditions (Chapter 4). This potentiometry method was chosen over dynamic methods (such as electrochemical impedance spectroscopy (EIS)) due to the low conductivity of the steam turbine environment (~20 µS) that would generate a large IR drop arising from the high solution resistance.

# 3.3.2 Galvanostatic Polarisation

With the use of a potentiostat, it is possible to control and apply a current to the sample under study and measure the potential reached by the sample. This is known as galvanostatic polarisation. The RE is not used in the control loop of the applied current but can be used to measure the potential in the electrochemical cell relative to the WSE connection. Due to the controlling current being between the WE and counter electrode (CE), it is possible to connect the RE to the CE in a two electrode setup as shown in Fig. 3.7B. Within this project, such a setup was used to generate an artificial corrosion pit on a fatigue specimen (WE) within a droplet of sodium chloride solution using a platinum wire as the CE/RE (Details of this technique are given later in Section 5.2.2).
### 3.3.3 Potentiostatic Polarisation

Additionally, a potentiostat can also be used to control the potential at the WE with respect to the RE. A CE facilitates the desired working potential at the WE by being driven to a suitable potential. The resultant current flow between the WE and CE can be recorded in order to generate a plot of current vs. time during the potentiostatic polarisation. This three electrode setup is shown in Fig. 3.7C and was used within the project to initiate an artificial corrosion pit with the micro-electrochemical cell (Section 5.2.1). The sample acted as the WE, the platinum flag was the CE and an Ag/AgCl RE was used. By choosing a potential that is above the pitting potential of the material, it is possible to remove the material electrochemically and generate a pitted region as the repassivation rate is retarded when above the pitting potential.

Due to the resistance of the solution between the electrodes a voltage drop (IR drop) is always included in the measured value [196]. As a result of this solution resistance, when a voltage is applied the peak voltage at the WE is reduced producing inaccurate measurements. It is possible to minimise the IR drop by reducing the distance between the WE and RE with a Luggin-Haber capillary, however some uncompensated resistance usually remains. Due to the low conductivity of the steam turbine environment polarisation experiments were not deemed appropriate in this project as the IR drop would be too high.

### 3.3.4 Electrochemical Noise

Electrochemical noise (EN) refers to the analysis of fluctuations in potential or current from natural variations in the electrochemical rate kinetics during a corrosion process. It is possible to monitor and record the evolution of a corrosion process on two coupled electrodes by using an instrument that applies no external signal. After collecting the EN data, various mathematical and statistical methods can be applied to analyse the electrochemical signals [197]. EN was identified as a suitable technique that can measure an electrochemical system without the need to apply a potential or current, which in the system studied here, would be limited due to the IR drop of the high solution resistance of the steam turbine environment used in the experiments.

### Background

The fluctuations in potential or current from a corroding electrode have long been observed, but it was always thought of as a source of error, rather than a useful signal. The acceptance and use of EN has increased steadily since the publication of work by Iverson [198] and Tyagai and Lukyanchikova [199] in 1968. Since then, its popularity has increased due to its potential application as an *in-situ* industrial corrosion monitoring method for metallic systems. However, caution must be exercised when relying solely upon EN measurements, it is often advised to combine EN with other electrochemical techniques such as  $E_{corr}$ , linear polarisation resistance (LPR) or EIS for support of the results.

### Fundamentals

It is possible to obtain EN data either with potentiostatic, galvanostatic or free corrosion potential techniques. In the first two cases, there is only one measured parameter that varies with time, as the other is controlled, making it simpler to analyse. However, by imposing an applied potential or current, there may be subsequent effects on the actual corrosion mechanisms under study. Consequently, measurements are often taken from the freely corroding system and modern potentiostats allow the changes in corrosion potential and current flow between coupled electrodes to be measured simultaneously. In order to make this type of measurement, the configuration shown in Fig. 3.8 is normally adopted. The two WEs are electrically connected via a zero resistance ammeter (ZRA) to allow the current flowing between the WSE and ground connections to be logged. Simultaneously, the potential difference between the RE and WE is recorded by using a potentiostat.

The ZRA acts to maintain a 0 V potential difference between the inputs from the two WEs and measures the current required to do this via a low resistance feedback resistor, *R*. The voltage output, *V*, of the ZRA is related to the current, *I*, flowing through the system by the equation:

$$V = IR \tag{3.1}$$

In this setup, two identical electrodes are used, as in principle, this means there should be



FIGURE 3.8: Electrochemical noise electrode connections.

no net current flow between the two electrodes. In practice though, due to the stochastic nature of the corrosion processes, there is variation between the corrosion rates (CRs) of each electrode's surface, so current flow (current noise) and potential changes (potential noise) are observed.

One of the challenges in EN measurement is deciding on a satisfactory acquisition frequency and number of data points. Choosing a frequency of 1 Hz may mean that pit initiation events are not detected due to their sub-second lifetime (Fig. 2.14). Additionally, enough data points must be recorded to ensure that the data is representative of the electrochemical processes occurring in the system under study [200]. Modern multichannel potentiostats have the ability to record a large number of data points at a high frequency. Therefore, data was acquired continuously throughout testing, at a frequency of 5 Hz, as others have done [201], and then analysed in segments of 256 data points.

### Sources of Electrochemical Noise

Corroding systems may generate EN due to the electrochemical reactions taking place in the system. Possible mechanisms include stress corrosion cracking (SCC), crevice corrosion and pitting corrosion which are discussed in more detail below [202].

SCC is the degradation of a susceptible material under the combined effect of a load (applied or residual) and a corrosive environment. The cracks in SCC may propagate by discontinuous or continuous processes, which will have quite different EN characteristics [179, 197, 201]. In discontinuous crack growth, current transients will be observed each time a new surface at the crack tip is exposed to the corrosive environment. Conversely, if the crack growth is continuous, the noise levels will be more consistent and only show variation due to random fluctuations in the crack growth rate (CGR). As the crack grows in length, it will become more effective at shielding the crack tip from the external circuit used to measure the EN. As a result, this presents a limitation in using EN to measure SCC [203].

Crevice corrosion occurs at locations that allow for differential aeration due to restricted diffusion between two electrically connected passive materials. Examples of such locations would be gaskets, couplings or joints. During the onset of crevice corrosion, there will be a large drop in the potential as the active crevice polarises the external passive surface. If this surface is able to sustain the current needed to maintain the crevice in its active state, then the potential will fall and remain low. This allows for simple visual analysis of the data as this large permanent drop in potential was probably caused by the initiation of crevice corrosion.

During pitting, initiation, growth and death of metastable corrosion pits produce current transients that are detectable by EN monitoring. This process will be observed as a slow rise in the current followed by a sharp current fall for stainless steel (SS) or a slower fall for carbon steel and aluminium alloys [203]. Such changes in the current are a direct consequence of the breakdown and repassivation of the passive film. If the anodic dissolution of the metal can be maintained, then the recovery of the potential ceases and transients can be seen to last for a few minutes [204]. These changes in current and potential make EN analysis an attractive solution for monitoring SS samples for evidence of corrosion pitting activity.

### **Interpretation of Results**

There are various ways in which the EN data can be analysed and interpreted, some of which are detailed within Appendix X1 of ASTM G119-09 [205] and within ISO 17093:2015 [206]. Possible methods include examination of the raw time vs current/potential noise records, as differentiating features may be apparent due to the effects of localised pitting corrosion. Additionally, a mathematical approach can be adopted to extract statistical information from the time records of fluctuations in electrochemical current noise (ECN) and electrochemical potential noise (EPN). However, the direct current (DC) drift must be removed before any of these calculations are made [207]. The DC drift is usually in one



FIGURE 3.9: 403 SS in 20 ppm chloride solution at 90 °C. Potential vs. time record, over a period of 1 h, showing the raw potential vs. SCE (top) and the detrended EPN signal (bottom) with the yellow line representing the polynomial that was used to detrend the data.

direction and is caused by a DC source, such as the potential shift of the test coupon during exposure to the test environment [200]. There are many options available for DC drift removal such as moving average removal, linear detrending, polynomial detrend fitting or high-pass filtering [208]. As recommended by Bertocci et al. [208], polynomial detrending was chosen to remove the DC drift from the EN data that was collected in this study. This was done within a MATLAB<sup>®</sup> script (provided in Appendix A) using the *detrend* function, with n = 2, to remove a quadratic trend function from the data. As EN data was continuously acquired, breakpoints were included in the function so that the quadratic trend was calculated for smaller segments of 256 data points, i.e. 2<sup>8</sup>—the smallest window size suggested in [200]. An example of the outcome from the detrend function is shown in Fig. 3.9. In the top figure, the original values of potential vs. time are shown with an overlaying yellow line representing the quadratic trend that was calculated for every 256 points. The resulting detrended signal is shown in the plot below and from this detrended data, it is possible to compute statistical information, such as the standard deviations of potential and current,  $\sigma_E$  and  $\sigma_i$  respectively. This allows the electrochemical noise resistance  $R_n$  to be calculated, assuming that the area, A, of the electrodes is known:

$$R_n = \frac{\sigma_E A}{\sigma_i} \tag{3.2}$$

Generally, it is accepted that  $R_n$  is comparable to polarisation resistance,  $R_p$ , calculated from LPR [200, 203, 209, 210]. As a consequence, it would be possible to calculate a CR in mm year<sup>-1</sup> once the equivalent weight, *EW*, of the alloy has been calculated as:

$$EW = \frac{1}{\sum \frac{n_i f_i}{W_i}}$$
(3.3)

where *i* represents each element with mass fraction >1 %, *n* is the valence , *f* is the mass fraction and *W* is the atomic weight. Using *EW* (Eq. (3.3)) and the equation provided in [211], it is possible to calculate CR as:

$$CR (mm year^{-1}) = \frac{K_1 i_{corr} EW}{\rho}$$
(3.4)

where  $K_1$  is a constant, equal to 3272 mm/(A cm year),  $\rho$  is the density of the material and  $i_{corr}$  is the corrosion current density, which can be calculated from:

$$i_{corr} = \frac{B}{R_p} \tag{3.5}$$

assuming that  $R_p \equiv R_n$  (as calculated in Eq. (3.2)) and that *B*, the Stern-Geary coefficient, is equal to

$$B = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)} \tag{3.6}$$

where  $\beta$  represents the Tafel gradient constant from the *a*, anodic and *c*, cathodic regions of a polarisation curve [212]. When a value for *B* has not been calculated, it is common to use a value of 26 mV for activation controlled systems and 52 mV when the cathodic reaction is limited by diffusion [213]. However, the use of these values assumes that both anodic and cathodic reactions must obey Tafel's law meaning they must be under activation control. During the growth of corrosion pits the anodic reaction is under diffusion control so will not obey Tafel's law. Furthermore, it is assumed that the electrochemical reactions will be uniformly distributed over the electrode surface i.e. general corrosion is occurring. Due to the passive nature of SS alloys only localised corrosion i.e. pitting or crevice corrosion is likely, so further errors in calculation of the corrosion rate are introduced [214]. Consequently, it was not deemed suitable to calculate a CR from the data collected as it would be inaccurate.

As information on localised corrosion (pitting) is pertinent to this research project, the additional calculations of pitting index (PI) and coefficient of variation (CV) were included in the evaluation of EN data. From the current noise data, PI is calculated using the following expression:

$$PI = \frac{\sigma_i}{I_{rms}}$$
(3.7)

where  $I_{rms}$  is the root mean square of the current noise. The calculated values of PI range from 0 to 1. A value of PI that is above 0.6 may be indicative of localised pitting corrosion. Additionally, the CV was calculated as:

$$CV = \frac{\sigma_i}{I_{mean}} \tag{3.8}$$

where  $I_{mean}$  is the absolute value of the mean average coupling current. This would show the deviation of the current from the mean value and a greater value of CV would indicate a higher level of corrosion activity taking place.

Mathematical and statistical analysis of ECN and EPN data was utilised in this study to identify localised corrosion activity on test coupons during exposure to simulated steam turbine environments with variable concentrations of contamination.

### 3.4 X-ray Techniques

### 3.4.1 X-ray Computed Tomography

### Background

X-ray computed tomography (XCT) is becoming increasingly attractive as a characterisation technique due to the ability to image internal features without destroying the sample [215–218] i.e. cross sectional analysis. As a result, standards have recently been issued



FIGURE 3.10: Schematic drawing of the XCT process: data acquisition, reconstruction and extraction of 2D slices. Reproduced from Landis and Keane [225].

to provide a framework for the use of XCT as a non-destructive technique [219–223]. By capturing a range of projections at different viewing angles, it is possible to reconstruct the internal features of the sample of interest as shown in Fig. 3.10. In this study, X-ray absorption tomography was utilised to determine the geometry of corrosion pits and the location of any associated cracks. Other forms of tomography, such as X-ray diffraction tomography are emerging and have the potential to be used to provide high-resolution grain maps of polycrystalline materials [224].

Whilst the use of X-rays to image internal features is not a new concept, with Röntgen discovering them in 1898 and Hildebrandt making use of them to image projectile and shrapnel injuries in World War I, it was in the early 1970s when Hounsfield developed a commercial CT system for the medical industry. There were some limitations within the medical industry though—mainly limiting the dosage of X-rays received by the patient achieved through a short scan time of several seconds with the added benefit that this reduces the amount of blurring caused by movement of the patient during the scan. These limitations are readily avoidable when scanning inanimate objects, however, allowing much higher X-ray intensities to be used over a longer measurement period. As a result, this greatly improves the signal-to-noise ratio achievable [226, 227].

Early industrial and medical XCT systems were able to resolve features on the millimetre scale. This generated significant interest in developing systems able to detect features on the microstructural scale of an engineering material—around 1 µm to 10 µm. This would allow materials and components to be inspected non-destructively, being especially useful in manufacturing process control [228].

### **Fundamentals**

XCT relies on the constant production of X-rays which are generated using an X-ray tube. Electrons leave the tungsten filament of the tube, under the effect of the applied potential and are accelerated towards a target material that is normally Cu, Mo, Ag or W. As the electrons strike the target, they decelerate, with the majority of energy loss being converted to heat while a small fraction (1%) is converted into X-rays [229]. The spot size is the area within which the electron beam interacts with the target material, this should be as small as possible as it determines the end resolution—which is directly proportional to spot size.

Two main types of radiation are observed: namely, Bremsstrahlung (continuous) and characteristic, represented as *B* and *K* on Fig. 3.11, respectively. The continuous X-rays are generated from an incident electron passing the nucleus of an atom in the target anode resulting in a change of trajectory due to the electrostatic interaction. Due to the deceleration of the electron, it loses energy which is emitted as an X-ray photon. The incident electrons pass at various distances from the nucleus so will be decelerated at different amounts forming a continuous spectrum. The characteristic X-rays are produced by an entirely different mechanism—if the incident electron instead strikes an electron from the innermost shell (K) of the atom, this may be ejected leaving a vacancy in the electron shell structure. An electron from an outer shell then transitions to fill the K-shell losing energy as it does so that is of X-ray radiation wavelength. As the electron shells are quantized, the characteristic X-rays generated have discrete values for each transition from an outer shell into the K-shell producing sharp peaks in the spectra.

Additionally, the energy spectrum of the X-rays can be altered by positioning a filter between the X-ray source and the sample. The filter material will attenuate low-energy X-rays as shown by curve *F* in Fig. 3.11. It is important to remove these low energy X-rays as it is unlikely that they will be transmitted through the sample, instead just saturating the detector in areas where the X-rays pass around the specimen reducing the overall contrast achievable.



FIGURE 3.11: Schematic of X-ray tube spectra - intensity (I) as a function of energy (E). Each dashed lines (B) shows continuous spectra at increasing X-ray tube voltages (kVp). The peak (K) represents one characteristic X-ray peak. The solid curve *F* shows the impact of filtering the beam to eliminate lower energy photons from the spectra. Reproduced from Stock [226].

As the X-rays pass through the adsorbing sample, their energy gradually decreases such that the intensity decreases exponentially as a function of the material's attenuation coefficient as shown in Eq. (3.9), the Beer-Lambert law. In general, attenuation increases with the atomic number of the sample and is greater at lower X-ray energies.

$$I = I_0 \cdot e^{-\mu x} \tag{3.9}$$

where *I* is the intensity (number of photons) of the X-ray beam with an initial intensity  $I_0$ , after traversing a distance of *x*, through a material with linear attenuation coefficient of  $\mu$ .

### Operation

Within a laboratory X-ray imaging facility, the object of interest is located on an x-yz rotating stage between the X-ray source and a 2D flat panel detector. Standard 2D detectors have a resolution of  $2048 \times 2048$  pixels and each pixel is 200 µm in size [228].

The cone-shaped beam generated by the laboratory X-ray tube (parallel beam for synchrotron sources) creates two competing geometrical phenomena. The first is geometrical magnification where the divergent beam from the X-ray source spreads a feature within the object to a greater width on the detector and as such allows smaller features to be seen on the projected images as seen in the first example of Fig. 3.12. Also evident in this



FIGURE 3.12: Schematic diagram to represent the effects of geometrical magnification and blurring due to the positioning of the object in relation to the source and detector. Reproduced from Kruth et al. [228].

figure is the blurring created due to the finite source size. As the beam crosses over at the object, it spreads the contrast over a larger area on the detector, introducing penumbral blurring to the images [230]. To avoid this blurring, the X-ray source size should be minimised (by reducing the beam current) and the detector can be brought close to the sample whilst still making benefit from a lesser amount of geometrical magnification as shown in the second example of Fig. 3.12.

The amount of geometrical magnification (*M*) is calculated by:

$$M = \frac{D_{sd}}{D_{so}} \tag{3.10}$$

where  $D_{sd}$  equals the source-to-detector distance and  $D_{so}$  equals the source-to-object distance. From the magnification it is possible to estimate the pixel size ( $P_s$ ) of the radiographs through the relation between M and the pixel pitch ( $P_p$ ), which was 200 µm for the 2D panel detectors used in this study:

$$P_s = \frac{P_p}{M} \tag{3.11}$$

As the X-rays pass through the object, some of the photons are attenuated and this loss is measured on the photo detector in the form of a radiograph. The sample is then rotated by a small rotation step and a new radiograph captured. The rotation step used is normally in the range 0.1° to 1°. This process repeats for the full 360° and the series of projections obtained can be used to reconstruct a 3D volume formed from a sequence of 2D slices.

### 3.4.2 X-ray Photoelectron Spectroscopy

### Background

X-ray photoelectron spectroscopy (XPS) is a surface sensitive analysis technique.<sup>4</sup> Therefore, it can be used to determine the elemental/chemical composition of the topmost layer (10 nm) of the sample under study . The ability to assign chemical states to the detected atoms within the first few atomic layers makes it a very powerful analytical tool used throughout the world. XPS was first developed by Kai Siegbahn at the University of Uppsala, Sweden, in the mid-1960s, winning him the Nobel Prize for Physics in 1981.

Analysis of a surface by XPS involves irradiating the solid with monochromatic X-rays *in vacuo* and analysing the emitted photoelectrons as a function of energy. The spectrum recorded provides details of the number of detected electrons at each energy interval vs. their kinetic energy (KE) which generates a unique spectrum for each element [231]. Quantitative data can be obtained from the peaks of the spectrum by modelling them with line shape functions and then calculating the area and heights of these peaks.

### Fundamentals

A surface is analysed with XPS by irradiating the sample with a monochromatic X-ray source—Al K $\alpha$  ( $h\nu$  = 1486.7 eV) as used in this research programme. These *soft* X-rays have limited penetrating power and the mean free path of electrons in a solid is low, so as a consequence, the photoelectrons originate from the near surface region. The X-ray photon, with an energy of  $h\nu$ , interacts with the electron structure by the photoelectric

<sup>&</sup>lt;sup>4</sup>It may also be known as electron spectroscopy for chemical analysis.



FIGURE 3.13: Schematic diagrams of (A) the photoelectric effect where the incoming X-ray photon is shown to excite a core level electron such that a photoelectron is ejected from the structure. (B) Due to the formation of a core electron vacancy an electron from a higher energy level may fall into this vacancy. The KE that needs to be lost to facilitate this transition is transferred to a neighbouring electron which is emitted as an Auger electron.

effect [232], where the emitted photoelectrons have a measured *KE* given by:

$$KE = h\nu - BE - \Phi \tag{3.12}$$

where *BE* is the binding energy (BE) of the elemental orbital from which the electron originated<sup>5</sup> and  $\Phi$  is a spectrometer work function which is calibrated to become zero. The X-ray photon will interact with electrons from the inner shell as shown in Fig. 3.13A generating a photoelectron. This will have a BE that will depend upon the final photoelectron state upon leaving a specific type of atom owing to a broad range of measurable KEs. As every chemical element has a unique electron configuration, they will produce specific KE that are well tabulated [233].

The photoemission peaks generated are described by the electron quantum number with the nomenclature  $nl_j$  [234]. Where n is the principal quantum number (1,2,3,...) relating to the electron shell (K,L,M,N,...), l is the angular momentum giving the shape of the orbital (0,1,2,3...but to avoid confusion with n, letter notation of the form s, p, d, f,... is used) and j relates to the spin of the electron ( $|l \pm \frac{1}{2}|$ ). For all orbital levels, apart from the s-orbital (spherically symmetric around the nucleus, so l = 0), there will be

<sup>&</sup>lt;sup>5</sup>Electrons in shells closer to the nucleus have higher BEs



FIGURE 3.14: (A) High resolution photoelectron spectrum of the Cr 2p peak showing the area ratio of 1:2 between the  $Cr 2p_{1/2}$  and  $Cr 2p_{3/2}$  orbitals due to spin orbit peak splitting. (B) Example of a wide angle photoelectron spectrum showing the main elements present across the binding energy range measured. Auger electron peaks from oxygen and iron can be observed at higher binding energies.

a doublet peak at different BE due to spin-orbit splitting. This is observed in the 2p configuration where *n* is equal to 2 and *l* is 1 giving values of *j* as  $\frac{1}{2}$  or  $\frac{3}{2}$ . Therefore, the area ratio between the spin-orbit peaks of  $2p_{1/2}$ :  $2p_{3/2}$  will be 1:2 (2 electrons in  $2p_{1/2}$  and 4 electrons in  $2p_{3/2}$ ) as shown in Fig. 3.14A [202].

Previously, the peaks were modelled using a single fitted curve, as in the work by Fierro et al. [235]. However, it is now known that a spectral feature that can be observed is due to the interaction of a newly unpaired electron, if photoionisation of a core level electron has occurred, with an unpaired electron in the valence band (outermost shell). This creates multiplet peaks due to the many possible energies of the final state configurations [231].

Another feature observed due to the irradiating X-ray source, is the production of Auger electrons. When a photoelectron is ejected from an inner shell electron an outer electron may fall into the inner orbital vacancy (Fig. 3.13B). The required energy loss is transferred to a second electron that is simultaneously emitted [234]. This Auger electron will have KE that when combined with the KE of the photoelectron does not exceed the energy of the radiation source. The ejected Auger electrons are much more likely to interact with matter than the photoelectrons, so undergo inelastic scattering (loss of energy) and form the background of the spectra. Only Auger electrons that are ejected from close to the surface are likely to be escape without energy loss, producing useful peaks within

the XPS spectra. For example, Auger peaks from oxygen and iron contributions are presented in Fig. 3.14B, where the label O KLL denotes the filling of a K-shell vacancy by an electron from the L-shell which has ejected an energy loss electron from the L-shell.

### **Quantification of XPS Spectra**

It has been shown how the photoelectron spectrum will reproduce the electronic structure of an element quite accurately due to the unique BE of each electron. Additionally, information about the chemical state can also be obtained as the BE of an atom's core electrons is affected by the chemical environment of the atom [234]. In the case of iron, this means that the spectra of  $Fe^0$ ,  $Fe^{2+}$  and  $Fe^{3+}$  will all appear at slightly different BEs as each chemical state represents a different total number of electrons (26, 24 and 23 electrons for the three states of iron given previously).

To quantify the chemical information provided by the XPS spectra, line profiles are modelled in software<sup>6</sup> to match the shapes of each peak. A region around the peak is defined and a 'Shirley type' background is usually used to remove the effects of inelastic scattering from photoelectrons and Auger electrons. The peak is then defined in terms of full width half maximum (FWHM), its shape and is positioned at a BE appropriate for the chemical state it will represent (values available online [233]). The shape of the curve is often a Voigt function comprising of Gaussian peak shape with the addition of up to 30 % Lorentzian character [234]. For metals, the shape becomes asymmetric due to the excitation of the 'free' electrons within the conductance band. As a consequence, metals are better modelled by an asymmetric modified Lorentzian line shape.

By correcting each of the peak intensities to a normalised peak intensity, using relative sensitivity factors, it is possible to extract the concentration of the element or chemical it represents. This allows the area of the peak intensities to be converted into quantitative information about the measured sample. The results of XPS were used to determine the oxidation states of chemical elements. From XPS alone, it is not possible to infer which compounds are present, i.e. it is possible to quantify the concentration of Fe<sup>2+</sup>, but distinguishing between its presence in FeO or FeCr<sub>2</sub>O<sub>4</sub> (chromite) is not possible. This

<sup>&</sup>lt;sup>6</sup>CasaXPS [236] version 2.3.19 was used in this work.

process was utilised in this research project to investigate the different SS passive films that formed during exposure to simulated steam turbine environment conditions.

# Chapter 4

# **Corrosion Pitting in a Simulated Steam Turbine Environment**

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### 4.1 Introduction

The safe and continuous operation of a power plant requires all of its components to function with minimum risk of failure. Additionally, the turbine must efficiently extract the energy produced by the combustion of coal or natural gas. The fuel releases heat which raises the temperature of the water which is circulating through the drum-type boiler, such that the water vaporises to steam. This steam is then directed through a multi-stage turbine (high, intermediate and low pressures) within which the blades are forced to rotate by the steam as it passes to extract the energy.

The steam is known to contain a small, but significant, concentration of impurities such as chlorides and sulphates [237]. These may deposit within droplets, forming a condensate on the low pressure steam turbine (LPST) blades, ultimately leading to a loss in efficiency of the energy extraction process. Additionally, these sites are preferential areas in which localised corrosion (pitting) may occur. As a result, reports [8, 9] suggest that the majority of outage hours have been assigned to this issue in order to avoid major turbine failure due to crack initiation at corrosion pits during operation.

Ascertaining a full understanding of the steam turbine operating conditions is a complex problem that varies between power plants due to differences in the types of plants and standard operating procedures. However, there will be similarities in the temperatures and conditions at which the steam will condense onto the turbine blades and the composition of the deposits left once any condensate has evaporated.

There is little reported information about the specific concentration of contaminants required to induce corrosion pit nucleation in a steam turbine environment. Additionally, there have been few attempts to quantify the impact the regular operating environment will have on the development of the material's protective passive film. Or how previously initiated corrosion pits will behave in subsequent periods of susceptibility to corrosion when the turbines are inactive. This work aims to answer some of these key issues by simulating an operating steam environment and exposing coupons of common LPST blade materials to this environment.

The experimental and results sections of this chapter are split into four subsections. The first aims to identify the critical chloride concentration, [Cl]\*, needed for pit initiation. Next, the effect of environmental ageing is examined to determine if this will impact upon [Cl]\*. The final two subsections study the behaviour of nucleated corrosion pits in subsequent exposure to the operating steam environment. It is proposed that the findings from this chapter will assist inspection engineers to ascertain a greater level of confidence during assessment of turbine blades that may show signs of corrosion pit damage.

### 4.2 Experimental

### 4.2.1 Sample Preparation

Flat coupons (40 mm  $\times$  50 mm  $\times$  2 mm) of 403 stainless steel (SS) and (24 mm  $\times$  53 mm  $\times$  2 mm) FV566 12Cr martensitic SS were used to investigate the effect of environment excursions on corrosion pit initiation behaviour. The chemical composition of each material was given in Table 2.1 and typical microstructure of these 12Cr martensitic SS is shown in Fig. 4.1, with prior austenite grain size  $\sim$ 25 µm.

The coupons were mounted in  $3M^{\otimes}$  Scotch-Weld<sup>®</sup> structural Epoxy Adhesive EC-9323 B/A leaving one face exposed; a spot-welded nickel wire encased in polyether ether ketone (PEEK) tubing allowed an electrical connection. Once coated, the coupons were cured for 12 h at 90 °C and then ground with SiC abrasive papers of grade P600, P800 and P1200. The final coupons were stored in a desiccator until use and examples of the 403 SS coupons are shown in Fig. 4.2. Upon exposure to the environment, some coupons suffered crevice corrosion which would affect  $E_{corr}$ , and in turn affect pit initiation and growth. This crevice corrosion was at a bubble or cavity at the interface between the metal and epoxy adhesive, the crevice develops due to depletion of oxygen in the cavity leading to increased anodic dissolution, consequently these coupons were not used for further analysis.



FIGURE 4.1: Martensitic microstructure of 12Cr FV566 stainless steel
(A) LCSM image once etched with Vilella reagent—etchant 80 in ASTM E407-07 [238] for alloys with composition Fe + 4–12 Cr. (B) SEM image taken during plasma focused ion beam milling.



FIGURE 4.2: (A)  $50 \text{ mm} \times 40 \text{ mm} \times 2 \text{ mm}$  coupons of 403 SS and (B)  $50 \text{ mm} \times 24 \text{ mm} \times 2 \text{ mm}$  coupons of FV566 SS mounted in  $3M^{\text{(B)}}$  epoxy that were used for pit initiation studies after the final grinding stage with P1200 SiC abrasive paper. The dashed square represents the orientation from which the microstructure is presented in Fig. 4.1.

For X-ray photoelectron spectroscopy (XPS), the coupon's size was limited to  $10 \text{ mm} \times 10 \text{ mm}$ , so a Dremel multi-tool, with a cutting wheel was used to extract XPS samples from the larger test coupons. During cutting, the coupon was regularly cleaned with deionised water and sprayed with compressed air to minimise heating of the surface and protect the integrity of the passive film.

### 4.2.2 Steam Turbine Environment Simulation

Clearly, it is not possible to run a complete steam turbine within a university laboratory, so some compromises must be made to best simulate these conditions in a safe and consistent manner. A condensing steam setup would be the most applicable choice as the review showed the steam condensed onto the turbine components to form droplets and a thin liquid film. However, simulation and control of the temperature gradient required to achieve this is difficult to implement. Furthermore, regulating the chemistry of the condensate that would form on the coupons is an additional challenge and would lead to unknown concentrations of impurities within the condensate. By using a full immersion setup, the ability to carefully monitor and control the chemistry and temperature of the solution is relatively straightforward. Additionally, electrochemical measurements of test coupons can be taken during exposure. However, the thin film characteristics and the surface deposits that build up due to on-load/off-load cycling will be lost. The desire of a carefully controlled environment chemistry meant that a full immersion setup was used.

A large reservoir (301), constructed from type 316 SS, was used to contain the test solution which was heated to 90 °C; as this was the identified temperature at which condensation of the steam starts to occur onto turbine components. The chemistry of the solution was initially nearly pure water to represent a well controlled, fully operational plant. Contaminants, such as chloride, could then be dosed into the reservoir as required to reflect different compositions of water chemistry excursions. The use of 316 SS tubing and fittings throughout the flow loop (Fig. 4.3) ensured that oxygen concentration could also be controlled during testing. The system could be completely deaerated, using nitrogen, to simulate regular on-load conditions with oxygen concentration < 5 ppb and then the gas supply could be changed to air to mimic an overnight or weekend shut



FIGURE 4.3: Controlled water chemistry flow loop used to circulate heated solution from the reservoir to the test cells with on-line oxygen concentration and conductivity monitoring of test solution.

down. Coupons were mounted within each of the four SS test cells, on hot plates, using Conax sealing glands and each cell could be isolated individually from the rest of the loop to allow inspection of the coupons after a desired exposure period. A Grundfos  $DDE^{TM}$  diaphragm dosing pump circulated the solution from the reservoir into each of the test cells at a speed that resulted in the solution of each cell being replaced about three times per hour. An oxygen and a conductivity probe were mounted on the solution return line, allowing real time measurement of the water chemistry system and a multichannel potentiostat was used to make electrochemical measurements of the coupons during testing. To limit the diffusion of chloride from the reference electrode (RE) into the, initially, pure water solution, a double-junction AgCl RE was mounted outside the test cell—connected by a custom made PEEK adaptor.

Due to the complexity involved with the design, purchase and assembly of the controlled water chemistry flow loop, the majority of these experiments were performed at the Teddington site of NPL during two placements. As a result of the limited availability of flow loop a test could typically only be repeated twice and the most appropriate results were selected for complete analysis as variation between tests was low. In latter stages of the project, the flow loop could be used in Manchester and was commissioned by further repeating some of the initial critical chloride concentration experiments on the two materials under study. Overall, a number of experiments were performed using the controlled water chemistry flow loop which are described in more detail in the sections below; a short summary is provided here. The main objectives and questions were:

- Identify a critical chloride concentration, [Cl]\*, needed for pit initiation on freshly ground coupons of 403 and FV566 SSs
- Does [Cl]\* for pit initiation change after a long period of exposure to on-load conditions?
- If corrosion pits initiate on a test coupon, do they continue to grow in subsequent exposure periods or do further corrosion pits initiate at new sites?

### 4.2.3 Threshold Chloride Concentration for Pit Initiation

The first objective was to identify a baseline threshold concentration of chloride, [Cl]\*, that was required to initiate corrosion pits on the two materials (403 and FV566 SSs). The results from these tests may help identify whether or not the increased molybdenum and nickel content within FV566 SS significantly impact on the chloride concentration required to initiate corrosion pits.

In each test, eight test coupons, ground to a P1200 finish with SiC abrasive paper, were distributed evenly between the test cells. The initial exposure environment was aerated 0.3 ppm chloride solution at 90 °C (Step 1, Table 4.1), representing well controlled plant operation. After a 24 h exposure to that concentration of chloride, the chloride concentration was then increased, in a step-wise fashion, by adding a small volume of concentrated NaCl stock solution to the reservoir. Three concentrations of stock solution were available—660 ppm, 3300 ppm and 77 000 ppm chloride. The method for calculating the volume of stock solution,  $V_{stock}$ , required for a specific increase in chloride concentration

| Step  | Environment<br>(ppm chloride) | Conductivity<br>(µS/cm) | Duration<br>(h) | Total duration<br>(h) |
|-------|-------------------------------|-------------------------|-----------------|-----------------------|
| 403 s | TAINLESS STEEL                |                         |                 |                       |
| 1     | 0.3                           | 19.9                    | 24.1            | 24.1                  |
| 2     | 1.5                           | 63.7                    | 22.1            | 46.3                  |
| 3     | 6                             | 210.4                   | 23.8            | 70.0                  |
| 4     | 12                            | 401.6                   | 23.8            | 93.8                  |
| 5     | 20                            | 664.1                   | 48.0            | 144.8                 |
| FV56  | 6 STAINLESS STE               | EL                      |                 |                       |
| 1     | 0.3                           | 19.3                    | 24.8            | 24.8                  |
| 2     | 3                             | 104.0                   | 23.9            | 48.7                  |
| 3     | 6                             | 203.4                   | 25.7            | 74.4                  |
| 4     | 12                            | 402.2                   | 21.9            | 96.0                  |
| 5     | 20                            | 665.8                   | 23.7            | 120.0                 |
| 6     | 50                            | 1385.0                  | 24.0            | 144.1                 |
| 7     | 100                           | 2682.0                  | 24.2            | 168.3                 |
| 8     | 250                           | 4710.0                  | 24.1            | 192.4                 |

TABLE 4.1: Exposure intervals used, for each material, to determine the threshold chloride concentration for pit initiation ([Cl]\*). Tests were conducted at 90  $^{\circ}$ C in aerated (1.8 ppm) solution.

is shown below:

$$V_{stock} = \frac{(C_N - C_{N-1}) \times V_{system}}{C_{stock}}$$
(4.1)

where *N* is the step number, *C* is the concentration of chloride at step *N*,  $V_{system}$  is the total volume of solution in the flow loop and  $C_{stock}$  is the concentration of chloride stock solution to be added. Once the stock solution was injected into the reservoir there was a 2 h period in which the ions diffused throughout the solution in circulation. This was recorded as the time period in which it took the conductivity (measured on the solution return to the reservoir) to increase to a stable value.

To detect evidence of corrosion pit initiation, the corrosion potential  $E_{corr}$  was monitored vs. a double junction RE at a recording frequency of 1 Hz. Additional tests were performed following ASTM G199-09 [205] and BS EN ISO 17093:2015 [206] on electrochemical noise (EN) with an Ametek PARSTAT multi-channel potentiostat, with a minimum current and voltage resolution of 238 fA and 1.2 µV respectively. This allowed simultaneous measurement of the electrochemical current noise (ECN) and electrochemical potential noise (EPN) at a rate of 5 Hz (Section 3.3.4). The benefit of this was that fluctuations occurring in the potential and current between the two coupons as a result of spontaneous changes in the instantaneous corrosion rate (CR) over very short (< 1 s) time periods could be detected. After the EN data had been collected, it was processed in a MATLAB<sup>®</sup> script that would automatically: remove the direct current (DC) drift from the data, plot figures of the raw and detrended ECN and EPN for each hour, calculate and plot trends of pitting index (PI), coefficient of variation (CV),  $R_n$  and CR for each day that data was collected—see Appendix A for the full script. It may also be possible to evaluate the electrochemical processes through the use of other non-destructive methods such as acoustic emission analysis as others have done [239].

Additionally, test cells were isolated from the loop at desired concentrations of chloride so that the coupons inside could be inspected. The coupons were cleaned with acetone in an ultrasonic bath before the location and geometry of each corrosion pit was measured with a Keyence VK-X200k laser confocal scanning microscopy (LCSM). This would allow comparison between the electrochemical observations and measurements of corrosion pit number and size.

# 4.2.4 Impact of Environmental Ageing on Threshold Chloride Concentration for Pit Initiation

When a power plant operates under its design operating conditions, the water chemistry of the condensate will be low in contaminants and the oxygen concentration will be below 5 ppb [4, 6]. During this period of regular 'on-load' operation, the passive film of the SS components will be developing due to the lower oxygen concentration and reduced cathodic reaction rate. Within the power generation industry, this process is known as 'ageing' of the passive film and should not be confused with artificial ageing during the treatment of a metal alloy at elevated temperature.

Salzman et al. [98] have previously reported that the deaerated environment drastically reduced the growth rate of corrosion pits and that [Cl]\* for pit initiation or reactivation had increased as a consequence of the exposure period to deaerated 'on-load' conditions. They attribute this observation to the formation of a shiny black film (magnetite Fe<sub>3</sub>O<sub>4</sub>) that is more resistant to localised corrosion. However, no further work was completed to identify the new concentration of [Cl]\* or to characterise the passive film formed during exposure to 'on-load' deaerated conditions.

| Step | Environment<br>(ppm chloride) | Conductivity<br>(µS/cm) | Duration<br>(h) | Total duration<br>(h) |
|------|-------------------------------|-------------------------|-----------------|-----------------------|
| 1    | 0.3                           | 2.1                     | 18.0            | 18.0                  |
| 2    | Deaerated 0.3                 | 2.1                     | 660.3           | 678.3                 |
| 3    | 0.3                           | 2.1                     | 6.7             | 685.0                 |
| 4    | 1.5                           | 6.6                     | 13.5            | 698.5                 |
| 5    | 6                             | 20.6                    | 25.0            | 723.5                 |
| 6    | 12                            | 40.1                    | 25.6            | 749.1                 |
| 7    | 20                            | 64.3                    | 41.7            | 790.8                 |
| 8    | 35                            | 112.3                   | 23.5            | 814.3                 |
| 9    | 50                            | 162.8                   | 23.7            | 838.0                 |
| 10   | 100                           | 326                     | 28.0            | 866.0                 |
| 11   | 150                           | 492                     | 24.0            | 890.0                 |
| 12   | Test complete                 |                         | 96.0            | 986.0                 |

TABLE 4.2: Exposure intervals used to determine the impact of blade ageing (exposure to 'on-load' deaerated solution) on [Cl]\*. Tests were conducted at 90 °C in aerated (1.8 ppm) solution unless otherwise stated. For deaerated solution  $[O_2] < 5$  ppb.

Therefore, to investigate the impact of environmental ageing on [Cl]\* for pit initiation, test coupons of 403 SS (Fig. 4.2) were exposed to *both* off-load (aerated) and on-load (deaerated) conditions—as described in Table 4.2. The initial environment (Step 1) was aerated 0.3 ppm chloride solution at 90 °C to simulate the conditions expected during turbine startup with well controlled water chemistry. As the steam pressure within the turbine increases, the gland seals are forced shut and the environment becomes deaerated. This was simulated under laboratory conditions by switching the gas flow into the reservoir from air to nitrogen which, in turn, gradually decreased the oxygen concentration. The result of this procedure is shown in Fig. 4.4 and after 18 h the oxygen concentration had dropped below 5 ppb.

A power plant may be operational for a significant period before a shut down occurs to allow for inspection and maintenance. Therefore, the coupons were exposed to the, now, deaerated solution for a period of 27.5 d. In turn, this would also allow significant development of the shiny black film observed by Salzman et al. [98]. After this period, the gas supply to the reservoir was switched back to the air pump, representing shut down of the power plant as air would be allowed to enter the turbine (Step 3 - Table 4.2). To establish if the period of deaeration had impacted on [Cl]\*, the chloride concentration



FIGURE 4.4: Response of the oxygen concentration to switching the gas supply from air to nitrogen. Within 18 h the solution becomes deaerated with the  $[O_2] < 5$  ppb.

was increased daily from 0.3 ppm to 150 ppm as detailed in Steps 4–12. The corrosion potential of two coupons from one, of four, test cell(s) was sampled at a rate of 1 Hz. The corrosion potentials of the other coupons were recorded intermittently throughout the experiment in order to monitor changes to  $E_{corr}$  in response to the transient environmental conditions. As each test cell could be isolated individually, the test coupons could be removed from the test at predetermined concentrations of chloride to inspect their surfaces for any indication of localised pitting corrosion.

# 4.2.5 Effect of Chloride Excursion on Threshold Chloride Concentration for Pit Initiation

During the shut down of a power plant, contaminants such as chloride, are known to initiate corrosion pits within the aerated condensate that forms on the turbine blade as the steam cools. If there is significant contamination (35 ppm chloride), then the depth of the corrosion pits increases with time according to the equation cited by Salzman et al. [98], Turnbull et al. [240]:

$$a = \alpha t^{\beta} \tag{4.2}$$

where *a* is the pit depth expressed in meters and *t* is the time in seconds. The values of  $\alpha$  and  $\beta$  are based on the solutions to deterministic equations and a Monte Carlo method to achieve statistical variability by Turnbull et al. [240]. The value of  $\beta$  can be increased in magnitude to reflect the larger number of possible combinations of conditions in the system leading to corrosion, i.e. deaerated pure water would have a lower value of  $\beta$  compared to an aerated environment containing chloride. Based on this model, Salzman et al. [98] provides values for  $\alpha$  and  $\beta$  of  $1 \times 10^{-5}$  and 0.27, respectively, for coupons that were exposed to an aerated 35 ppm chloride solution.

As a consequence of such chloride contamination, the SS blade within the LPST will contain a number of corrosion pits. The risk of continuing to use a pitted steam turbine blade is that the corrosion pits will act as stress concentrators. If the pit is of a considerable size, then the stress concentration factor (SCF) will be significant enough that cracks may initiate at these sites during loading under normal operation. However, if the duration of shut down was short and/or the chloride contamination was low, the initiated corrosion pits may only measure a few tens of microns in depth. As such, they will not be recorded as a significant defect that would require the turbine blade to be replaced—a timely and costly procedure due to the operational downtime lost and additional costs of labour and replacement parts.

If the choice is made to continue using the blades with small corrosion pits, it remains unclear how these corrosion pits will develop during subsequent periods of water chemistry excursions in an aerated environment. For example, will the previously initiated corrosion pits continue to grow (reactivation) or will further corrosion pits initiate at new sites on the blade's surface?

In order to investigate this, a series of exposure periods to aerated 35 ppm were performed as outlined in Table 4.3. Initially, in Step 1, all four coupons were exposed to 35 ppm chloride solution for a duration of 6 h to initiate some corrosion pits on the surface of the ground coupons (shown previously in Fig. 4.2). After this exposure, the coupons were removed from the environment and immediately washed with deionised water and then cleaned, ultrasonically, with ethanol for 10 min. This process represented the blade being inspected by an engineer who would rinse the turbine blade before observation but

| Step | Coupons  | Environment<br>(ppm chloride) | Conductivity<br>(µS/cm) | Duration<br>(h) | Total duration<br>(h) |
|------|----------|-------------------------------|-------------------------|-----------------|-----------------------|
| 1    | All      | 35                            | 114.0                   | 6.0             | 6.0                   |
| 2    | 3.1, 3.2 | 35                            | 119.1                   | 24.4            | 30.4                  |
| 3    | 3.1, 3.2 | 35                            | 120.5                   | 72.2            | 102.6                 |
| 4    | 3.3, 3.4 | 35                            | 120.9                   | 121.0           | 127.0                 |

TABLE 4.3: Exposure intervals used to determine the impact of a chloride excursion on [Cl]\*. Tests were conducted at 90 °C in aerated (1.8 ppm) solution.

would not use chemicals as they may contaminate the environment. Once the coupon had been washed and dried, the geometry of each corrosion pit was recorded by measuring with a Nikon MM-60 optical microscope.

Once imaged, the four coupons were split between two test cells on the flow loop (Fig. 4.3) and exposed again to 35 ppm chloride solution. One of the test cells (containing coupons 3.1 and 3.2) was removed from the flow loop and inspected after 24 h (Step 2) before been exposed for a final period of 72 h (Step 3). The other cell (coupons 3.3 and 3.4) remained exposed to 35 ppm chloride solution for the total duration of 121 h (Step 4). During each of the steps, the corrosion potential was recorded (vs. saturated calomel electrode (SCE)) to ascertain whether there was any change in its value that would indicate the initiation of corrosion pits. When coupons were removed from the cells at the end of a step, they were processed as previously described, so the number and size of corrosion pits could be recorded.

## 4.2.6 Combined Effect of Environment Ageing and Chloride Excursion on Threshold Chloride Concentration for Pit Initiation

As discussed previously in Section 4.2.4, the turbine blades will be aged during exposure to the 'on-load' deaerated conditions. The ageing of the blades results in the development of the passive film; such that the material becomes more resistant to corrosion pit initiation in successive periods of power plant shut down, as reported by Salzman et al. [98]. Additionally, Zhou and Turnbull [4] have showed that shifting between on-load and off-load conditions can impact upon the response of  $E_{corr}$  to the change in environment.

If the environment becomes such that it allows corrosion pits to initiate, there is little

| Step | Environment<br>(ppm chloride) | Conductivity<br>(µS/cm) | Duration<br>(h) | Total duration<br>(h) |
|------|-------------------------------|-------------------------|-----------------|-----------------------|
| 1    | 35                            | 119.2                   | 6.0             | 6.0                   |
| 2    | 0.3                           | 2.6                     | 22.1            | 28.1                  |
| 3    | Deaerated 0.3                 | 4.5                     | 100.4           | 128.5                 |
| 4    | 0.3                           | 5.2                     | 5.4             | 133.9                 |
| 5    | 6                             | 25.2                    | 16.7            | 150.6                 |
| 6    | 12                            | 46                      | 28.0            | 178.6                 |
| 7    | 20                            | 73                      | 67.3            | 245.9                 |
| 8    | 35                            | 126                     | 24.7            | 270.6                 |
| 9    | 50                            | 180                     | 24.4            | 295.0                 |
| 10   | 100                           | 348                     | 23.7            | 318.7                 |
| 11   | 150                           | 519                     | 24.3            | 343.0                 |
| 12   | Test complete                 |                         | 72.1            | 415.1                 |

TABLE 4.4: Exposure intervals used to determine the impact of a chloride excursion on [Cl]\* on an 'aged' blade. Tests were conducted at 90 °C in aerated (1.8 ppm) solution unless otherwise stated. For deaerated solution  $[O_2] < 5$  ppb.

information about how these corrosion pits will respond in the subsequent two-shifting conditions of the power plant. The previous section looked at how the corrosion pits would respond in ensuing excursions of chloride concentration and identified whether the initiated corrosion pits would reactivate and continue to grow or further pits would nucleate at new sites. However, this did not take into account the possible important effect of exposure to the deaerated on-load environment as this is known to affect the passive film composition and resulting value of [Cl]\*.

To determine whether the on-load conditions had a significant impact on the corrosion pit behaviour, coupons of 403 SS were first exposed to a contaminated aerated environment (representing a water chemistry excursion) containing 35 ppm chloride solution (Step 1 - Table 4.4). The location, number and size of corrosion pits on the coupons were recorded using an optical microscope. The coupons were then exposed to a simulated start up procedure where the environment gradually became deaerated, as per Section 4.2.4. Additionally, to determine the importance of the duration of the exposure period to the deaerated solution, the duration was reduced from 27.5 d, used previously, to 4 d. This would reveal whether a shorter exposure to on-load conditions would have a similar impact on [Cl]\*.

Finally, to ascertain whether the pits on the coupons would continue to grow after onload environment simulation, the chloride concentration was gradually increased daily in an aerated environment (Steps 4–12 in Table 4.4). Test cells were isolated and coupons removed from the test cells when a change in  $E_{corr}$  (vs. SCE) was observed.

# 4.2.7 X-ray Photoelectron Spectroscopy: Impact of Exposure to Simulated Operating Steam Environment on Passive Film Composition

The corrosion resistance of the SS material is achieved by the formation of a thin and protective passive film (1 nm to 10 nm) on the surface. The material is dependant upon the stability and strength of this passive film in order to perpetuate its low CR when exposed to a variety of environments. As a result of transients in environmental conditions, the passive film will adapt to meet the demands of the current environment, meaning that the film may grow, dissolve or alter in composition. Various techniques exist that will allow for characterisation of the passive film, which include: glow discharge optical emission spectroscopy [241], environmental scanning electron microscopy [242], Raman spectroscopy [243] or XPS, as used in this research.

Here, the 403 SS was exposed to two differing simulated steam environments: the first, in Section 4.2.3, was an off-load environment. This environment simulated operating conditions during an overnight or weekend shutdown where the steam would aerate due to the reduction in steam pressure. The second, in Section 4.2.4, was a long period of exposure to on-load conditions, consisting of a high purity and deaerated steam environment.

The current understanding of passive film behaviour in different solutions would suggest that the passive films from these two environments will have some variation due to the different concentrations of oxygen in each system.<sup>1</sup> In order to quantify the differences in the breakdown resistance to chloride species, a study with XPS was undertaken. Comparative spectra from samples exposed to on-load or off-load environments were acquired to evaluate the different passive film compositions.

<sup>&</sup>lt;sup>1</sup>In the aerated environment the oxygen concentration was 1.8 ppm and was < 5 ppb in the deaerated solution. Both environments were at 90 °C.

### 4.3 **Results and Discussion**

### 4.3.1 Threshold Chloride Concentration for Pit Initiation

The corrosion potential of a cell was recorded for the duration of exposure to chloride solutions of increasing concentration at 90 °C. The chloride concentration was initially 0.3 ppm, simulating a well controlled plant operating within its design criteria. The concentration of chloride can increase beyond this level if there is sufficient contamination of the feedwater or leaks from other parts of the turbine system. To investigate the impact of increased concentrations of chloride on the material and identify [Cl]\* for each material, the concentration was gradually increased at each 24 h interval. Initially, the corrosion potential (vs. SCE) of 403 SS had stabilised between -10 mV and -20 mV, as shown in Fig. 4.5, and remained within this region as the concentration to 12 ppm that a rapid decrease in potential to -80 mV is observed, suggesting that the protective oxide film had begun to breakdown allowing for increased anodic activity. A further increase in chloride concentration to 20 ppm results in another decrease in potential to -105 mV and increased noise in the potential signal, this is due to the increased frequency of stable and metastable pitting events [197].

Additionally, EN measurements were taken from two identical coupled coupons of 403 SS and a RE<sup>2</sup> for the same concentrations and exposure periods, with an additional day at 20 ppm chloride. An example of the raw potential (Fig. 4.6A) and current (Fig. 4.6B) vs. time plots in 1.5 ppm chloride solution are represented by the blue line plots in the top of each subfigure. Applying the *detrend* function<sup>3</sup> within the MATLAB<sup>®</sup> script (provided

<sup>&</sup>lt;sup>2</sup>Sentek R2 AgCl 3 mol KCl double junction RE

<sup>&</sup>lt;sup>3</sup>See Section 3.3.4 for details about the interpretation of EN data.



FIGURE 4.5: Example corrosion potential vs. SCE plot for 403 SS coupon (one of eight). The chloride concentration was increased, step-wise, every 24 h from 0.3 ppm to 20 ppm. Time zero represents the transfer start time of the 0.3 ppm chloride solution from the reservoir to the four test cells.

in Appendix A), with a quadratic fitting over segments of 256 data points, yielded the detrended EPN and ECN data; with the yellow line in the plots representing the calculated trend across segments.

From the example of EN data presented for coupons in 1.5 ppm chloride solution (Fig. 4.6), we can see that the EN data exhibited very frequent fluctuations, the EPN varies  $\pm 1 \text{ mV}$  and ECN varies  $\pm 0.5 \text{ nA}$ . This provides us with confirmation that the EN fluctuation intensities are within the resolution of the potentiostat used.

From the ECN data, it is possible to obtain information that would indicate localised pitting corrosion may be occurring on the coupons. The ratio between the standard deviation and the root mean square of the current noise, shown earlier in Eq. (3.7), provides a PI value between 0 and 1. A value above 0.6 may indicate localised corrosion. The PI can be plotted for each exposure period, with the value of PI being calculated for each hour to provide an indication of the probability of localised corrosion. In Fig. 4.7, the PI for each day is presented corresponding to increasing concentrations of chloride in the simulated steam turbine environment.



FIGURE 4.6: Plots of the raw and detrended data vs. time for (A) voltage and (B) current in 1.5 ppm chloride solution. A quadratic trend was calculated in each case for segments of 256 data points—represented by the yellow curve.



FIGURE 4.7: Calculated values of the pitting index for 403 SS coupons in chloride containing solutions of increasing concentration. Day two - 1.5 ppm, day three - 6 ppm, day four - 12 ppm, day five onward - 20 ppm. A PI greater than 0.6 may indicate localised corrosion activity.

The initial environment (day one) was 0.3 ppm chloride. No corrosion was expected in this solution as the concentration of contaminants was the same as that expected under normal operating conditions of a steam turbine in service [6]. However, the calculated PI for this day displayed an initial large increase to 0.8; perhaps due to error associated with the development of the passive film during the initial exposure to the environment solution or the low conductivity of the 0.3 ppm chloride solution (19 µS). Therefore, this day is not presented within the plot. Day two corresponds to a chloride concentration of 1.5 ppm and the value of PI initially is around 0.30, dropping below 0.20 by the end of the day, suggesting that there is no localised corrosion occurring. On day three ([Cl] = 6 ppm), the calculated value of PI remained fairly stable throughout the day but at a slightly higher average PI value of  $0.36 \pm 0.05$ , indicating again that no pitting should be expected at this concentration of chloride. Therefore, the values of PI are so far in agreement with the measured corrosion potential of the coupon (Fig. 4.5). There had been no observed reduction in E<sub>corr</sub> at the same chloride concentrations—such reduction would correspond to pit initiation. It is only after increasing to 12 ppm that a drop in E<sub>corr</sub> occurred on day four. Additionally, the PI plot (Fig. 4.7) shows that the average PI is



FIGURE 4.8: Plots of the raw and detrended current vs. time in 12 ppm chloride solution. A quadratic trend was calculated in each case for segments of 256 data points—represented by the yellow curve.

now  $0.62 \pm 0.07$ . Following the guidance in ASTM G199-09 [205], this would suggest that localised corrosion could be occurring, generating larger variation in the ECN signal. The increase in ECN can be observed in Fig. 4.8, where the peak-to-peak amplitude of ECN is now of the order 20 nA.<sup>4</sup>

The PI further increases to an average of  $0.84 \pm 0.11$  on day five, at which the chloride concentration was increased to 20 ppm and  $E_{corr}$  reached the lowest value of -105 mV. Interestingly, once the potential had dropped, the average value of PI also decreases on days six and seven to  $0.07 \pm 0.01$  and  $0.08 \pm 0.01$ , respectively. This would suggest that the initiated corrosion pits become dominant and grow in a stable manner giving a constant high corrosion current. As consequence, the small ECN signal of any new corrosion pits is no longer detected, so the calculated PI is low.

Additionally, information about localised corrosion can also be obtained from calculating the ratio between the standard deviation of ECN and the absolute value of the mean coupling current. This produces a parameter named the CV. An increase in CV would indicate an increase in localised pitting corrosion compared to the uniform

<sup>&</sup>lt;sup>4</sup>The peak-to-peak amplitude was 1 nA in 1.5 ppm chloride solution.


FIGURE 4.9: Calculated value of coefficient of variation for 403 SS coupons in chloride containing solutions of increasing concentration. Day two - 1.5 ppm, day three - 6 ppm, day four - 12 ppm, day five onward - 20 ppm.

CR [197]. A plot of CV vs. time for each day of different chloride concentrations is shown in Fig. 4.9 and follows a similar trend to that of the PI plot. In the 1.5 ppm chloride solution, CV is, on average, equal to  $0.21 \pm 0.04$ . The value of CV increases by a factor of two on each of the next two days to an average value of  $0.86 \pm 0.11$ . On day five, when the chloride concentration reaches 20 ppm, there is a sharp rise in CV to an average value of  $1.79 \pm 0.65$  and a maximum of 3.65. After this day, CV is then calculated as  $0.07 \pm 0.01$ ; this value is below the value obtained on day two and indicating that localised corrosion activity has reduced as per the observations made from the PI data.

Alternative information regarding the general CR can be gained by calculating the electrochemical noise resistance ( $R_n$ ) for the material in each solution of differing chloride concentrations. The value of  $R_n$  is found by the ratio of the standard deviations of the potential and current noise multiplied by the area of the coupon, as shown earlier in Eq. (3.2). The calculated value of  $R_n$  for each hour of testing is presented in Fig. 4.10 and demonstrates a trend in decreasing values of  $R_n$  as the concentration of chloride is increased in the solution. Initially, on day two,  $R_n$  is the highest (above  $5 \times 10^7 \,\Omega \text{cm}^2$ ) suggesting that the rate of corrosion would be very low due to the inverse proportionality.



FIGURE 4.10: Calculated value of electrochemical noise resistance for 403 SS coupons in solutions of different chloride concentrations. Day two - 1.5 ppm, day three - 6 ppm, day four - 12 ppm, day five onward - 20 ppm.

As the chloride concentration is increased to 6 ppm,  $R_n$  drops slightly to  $1.5 \times 10^7 \,\Omega \text{cm}^2$ and falls one order of magnitude more when the concentration is increased to 12 ppm on day four. The lowest  $R_n$  was observed on the final day of exposure to 20 ppm chloride solution which was  $2.1 \times 10^5 \,\Omega \text{cm}^2$ .

Additionally, coupons were removed for inspection from the simulated steam turbine environment at different chloride concentrations. This allowed comparison to the electrochemical data to see if  $E_{corr}$  changes are in agreement with evidence of corrosion pitting on the coupons. As shown in Fig. 4.11, the coupon removed at a chloride concentration of 6 ppm displays no evidence of crevice or pitting corrosion. The coupons removed after exposure to 12 ppm chloride show a small corrosion pit on one sample, whilst the other is free of corrosion—perhaps due to local variation in microstructure and passive film. This would suggest that the value of [Cl]\* is close to this concentration, whilst justifying the increase in PI beyond the threshold of 0.6. The coupons removed at a chloride concentration of 20 ppm all show evidence of corrosion pitting.

The corrosion pits in Fig. 4.12 are visually similar to those presented in [100] and Fig. 2.17 with the same lightly etched, local region in the vicinity of the active corrosion



(A) Coupon 1.2 - 6 ppm Removed after step 3



(C) Coupon 1.7 - 20 ppm Removed after step 5



(B) Coupons 1.3 and 1.4 - 12 ppm Removed after step 4



(D) Coupons 1.5 and 1.6 - 20 ppm Removed after step 5

FIGURE 4.11: Macrographs of ground 403 SS coupons that were removed at increasing chloride concentrations at 24 h intervals as described in Table 4.1. Red arrows indicate an initiated corrosion pit.



FIGURE 4.12: (A) A micrograph showing typical appearance of corrosion pit initiated in NaCl solutions at 90 °C. (B) A schematic diagram of the regions shown in the micrograph: *red*—active corrosion pit, *blue*—lightly etched area, *green*—protected region, *orange*—area of spectral colours due to thin film interference.

pit. Surrounding this, there is a protected region where the surface looks as polished. At the perimeter of the protected region is a coloured band which forms due to the effect of thin film interference. The light waves are reflected by the inner and outer surfaces of the thin film and as a result travel slightly different distances causing both constructive and destructive interference which produces the different colours observed on the surface.

From these coupons, the number and geometry of each corrosion pit was measured using a LCSM in order to ascertain the severity of the corrosion pitting. Clearly, a high concentration of corrosion pits with large geometries would be more detrimental to the integrity of a component than fewer smaller corrosion pits. As shown in Fig. 4.13, the depth of the corrosion pits ranges from  $4\,\mu\text{m}$  to  $45\,\mu\text{m}$  with aspect ratios (ARs) from 0.17 to 1.5. There is a general trend that the AR increases towards one with greater pit depth. The majority of the pits are less than 20 µm deep and most pits (15) had an AR between 0.2 and 1, classifying them as 'Wide and Shallow' pits (described in detail later in Section 5.3.1).

A second material commonly used to construct LPST blades from is FV566 SS. This is another 12Cr martensitic SS with a similar composition to 403 SS but containing a higher concentration of molybdenum and nickel and is widely used throughout Europe. The coupons were arranged in the same manner as for the previous tests and the same



FIGURE 4.13: Aspect ratio of pits as a function of the pit depth in coupon 1.7 in aerated solution at 90 °C containing 0.3 ppm to 20 ppm chloride for a total duration of 144.8 h.

environment step changes were followed (Table 4.1).

On the first day, the PI gradually decreases as the passive film develops after immersion in the simulated steam environment solution (Fig. 4.14). After 2 h, the calculated PI drops below 0.02 and the PI averages 0.04 for the remainder of the exposure period to 0.3 ppm chloride solution. On days four and five, the PI had increased to an average of  $0.37 \pm 0.18$  and  $0.30 \pm 0.03$ , which was still below the threshold value of 0.6; this inferred that pitting corrosion was not occurring on the test coupons. Therefore, there was already some indication that FV566 SS is more resistant to localised pit initiation than 403 SS, as the PI for 403 SS had already reached 0.86 when exposed to 20 ppm chloride solution on day five. To surpass the threshold value of 0.6, the chloride concentration needed to be increased to 100 ppm on day seven where PI was  $0.75 \pm 0.13$ . Similarly to the 403 SS material, once the corrosion pits have initiated, the PI dropped rapidly (after 5 h on day eight), suggesting that the ECN and EPN are dominated by the stable pit growth and small fluctuations from new pits are not resolvable.

The change in ECN signals due to the different chloride concentrations of 12 ppm and 100 ppm on days four and seven, respectively, is evident in the plots of the detrended



FIGURE 4.14: Calculated values of the pitting index for FV566 SS coupons in chloride containing solutions of increasing concentration. Day one -0.3 ppm, day four - 12 ppm, day five - 20 ppm, day six - 50 ppm, day seven -100 ppm, day eight - 250 ppm. A PI greater than 0.6 may indicate localised corrosion activity.

data in Fig. 4.15. The peak-to-peak amplitude of the ECN on day four is 40 nA compared to 80 nA on day seven. This increased intensity of ECN is due to an escalation in localised pitting corrosion.

Another source of information on localised pitting corrosion is the CV—the ratio between the current's standard deviation and absolute mean. The CV for FV566 SS at each of the chloride concentrations tested is shown in Fig. 4.16. Immediately, it is evident that the range of CV values is greater in FV566 SS than that from the 403 SS plot (Fig. 4.9) i.e., the highest value of CV is 91.8 compared to 3.65. The high value of CV compared to the CV for 403 SS could be due to the exposure to a higher concentration of chloride (250 ppm vs. 20 ppm). Indeed, looking at the CV in this plot at lower concentrations of chloride they are comparable to those from the 403 SS. In the initial 0.3 ppm chloride solution, CV is 0.07 and increases to around 0.4 once the chloride concentration reaches 12 ppm. This is a similar value to that calculated for 403 SS in 6 ppm chloride solution. The value of CV then remains around 0.4 as the concentration is further increased to 20 ppm and 50 ppm. Comparatively, CV was close to 2 for 403 SS in 20 ppm chloride solution. On days seven



FIGURE 4.15: Plots of the raw and detrended current EN data vs. time in (A) 12 ppm and (B) 100 ppm chloride solution. A quadratic trend was calculated in each case for segments of 256 data points—represented by the yellow curve.

and eight, a higher CV is calculated, suggesting that these are the concentrations at which localised pitting corrosion occurs in the FV566 SS, indicating that it is more resistant to localised pitting corrosion than 403 SS.

However, the calculated values of  $R_n$  (Fig. 4.17) are much lower than those for 403 SS at the lower chloride concentrations investigated, i.e., <20 ppm chloride. This is summarised in Table 4.5, where the average electrochemical noise resistance ( $\overline{R_n}$ ) was calculated at each chloride concentration to which the coupons were exposed at. In chloride concentrations between 0.3 ppm and 1.5 ppm,  $\overline{R_n}$  is the highest (5 × 10<sup>7</sup>  $\Omega$ cm<sup>2</sup>) for the 403 material but reduces to  $1.5 \times 10^6 \Omega$ cm<sup>2</sup> as the concentration reaches 12 ppm. The lowest value of  $\overline{R_n}$  (2.13 × 10<sup>5</sup>  $\Omega$ cm<sup>2</sup>) was calculated on the final day of exposure to the 20 ppm chloride solution, suggesting the highest CR at this concentration. As a comparison, the value of  $\overline{R_n}$  for FV566 SS is lower (around 10<sup>6</sup>  $\Omega$ cm<sup>2</sup>) at the lower concentration to 20 ppm to 100 ppm, the  $\overline{R_n}$  is in the same order of magnitude to that measured with 403 SS in 20 ppm chloride, suggesting that the passive film of the FV566 SS still provides adequate resistance to metal dissolution at higher concentrations of chloride. It is only at the highest concentration (250 ppm) that the  $\overline{R_n}$  of FV566 SS decreases to a lower value of  $5.49 \times 10^4 \Omega$ cm<sup>2</sup>.

In summary, the electrochemical data presented shows that [Cl]\* for 403 SS is between



FIGURE 4.16: Calculated values of the coefficient of variation for FV566 SS coupons in chloride containing solutions of increasing concentration. Day one - 0.3 ppm, day four - 12 ppm, day five - 20 ppm, day six - 50 ppm, day seven - 100 ppm, day eight - 250 ppm.



FIGURE 4.17: Calculated value of electrochemical noise resistance for FV566 SS coupons in solutions of different chloride concentrations. Day one - 0.3 ppm, day two - 1.5 ppm, day four - 12 ppm, day five - 20 ppm, day six - 50 ppm, day seven - 100 ppm, day eight - 250 ppm.

| [Cl]                   | $\overline{R_n}$ ( $\Omega$ cm <sup>2</sup> )                 |                   |  |
|------------------------|---------------------------------------------------------------|-------------------|--|
| (ppm)                  | 403                                                           | FV566             |  |
| 0.3                    | $6.51 	imes 10^7$                                             | $5.72 	imes 10^6$ |  |
| 1.5                    | $5.48	imes10^7$                                               | _                 |  |
| 3                      | _                                                             | $9.36	imes10^5$   |  |
| 6                      | $1.52 	imes 10^7$                                             | $1.11 	imes 10^6$ |  |
| 12                     | $1.54	imes10^6$                                               | $4.17 	imes 10^5$ |  |
| 20 <sup><i>a</i></sup> | $\begin{array}{c} 7.97\times10^5\\ 2.13\times10^5\end{array}$ | $3.60 	imes 10^5$ |  |
| 50                     | _                                                             | $2.15	imes10^5$   |  |
| 100                    | _                                                             | $1.01 	imes 10^5$ |  |
| 250                    | _                                                             | $5.49	imes10^4$   |  |

TABLE 4.5: The average electrochemical noise resistance for 403 and FV566 SSs in aerated solution containing different concentrations of chloride.

<sup>*a*</sup> Two values of  $\overline{R_n}$  are given for 403 SS that correspond to exposure after 24 h and 72 h respectively

6 ppm to 12 ppm as this corresponded to the reduction in  $E_{corr}$  by 80 mV and the increase in PI and CV beyond the threshold value of 0.6. Additionally,  $\overline{R_n}$  decreases as the chloride concentration reached these values, which would suggest an increased general CR. Conversely, the value of [Cl]\* for FV566 SS is estimated to be much higher—>100 ppm chloride based upon the value of PI remaining below 0.6 until this concentration was reached within the environment. Furthermore, the value of  $\overline{R_n}$  for FV566 SS is the same order of magnitude at chloride concentrations 12 ppm to 100 ppm, as it was for 403 SS at 20 ppm. On balance, FV566 SS provides the greatest resistance to corrosion pit initiation over a broader range of chloride concentrations in an aerated solution compared with 403 SS. However, the 403 SS did exhibit the highest values of  $\overline{R_n}$  at lower concentration suggesting the overall CR may be lowest at the contamination levels typically expected during normal operation of a power station.

# 4.3.2 Impact of Environmental Ageing on Threshold Chloride Concentration for Pit Initiation

The coupons of 403 SS were initially exposed to a simulated turbine start up procedure where the environment was transitioned from 'off-load' to 'on-load' water chemistry. During this environment alteration, the oxygen concentration fell below 5 ppb and as a



FIGURE 4.18: Response of corrosion potential to deaeration of the 0.3 ppm chloride solution simulating startup of steam turbine after shut down to on-load operation.

consequence there was a cathodic shift in the corrosion potential (Fig. 4.18) as others have reported [244]. The value of  $E_{corr}$  in the aerated 0.3 ppm chloride solution was -0.1 V (vs. SCE).  $E_{corr}$  fell to -0.68 V (vs. SCE) in the 'on-load' environment, although it can be noted that coupons with the solid markers and lines took longer to reach this potential than the others. This is attributed to different coupon storage durations between the final grinding stage and immersion in the test solution. Those that had been ground nearer to the time of immersion readily decreased in corrosion potential value as their passive film was freshly developed and thinner than those than had been stored. Despite this, all coupons reached the same value of  $E_{corr}$  at the end of Step 2.

In order to simulate the shut down of the power plant, the environment was aerated after 678 h. The oxygen concentration quickly recovered to 1.7 ppm; 8 h later as shown in Fig. 4.19. In a similar time frame,  $E_{corr}$  also increased rapidly to an average of -0.13 V for the eight coupons—slightly lower than the initial value measured prior to the on-load period ( $\Delta V = 30$  mV).

Salzman et al. [98] had predicted that the period of deaeration would impact on [Cl]\* for corrosion pit initiation. Therefore, to quantify the new [Cl]\* for pit initiation, the



FIGURE 4.19: Response of corrosion potential to switching the gas supply from nitrogen to air after 27.5 d representing a weekend shut down or inspection period.

chloride concentration within the environment was gradually increased under aerated conditions. The effect of increasing the chloride concentration to moderate levels of contamination is presented in Fig. 4.20; the vertical dashed lines indicate the time point at which concentrated chloride solution was added to the reservoir. The chloride concentration was increased incrementally, approximately once per 24 h, from 1.5 ppm to 50 ppm. It was observed that E<sub>corr</sub> gradually increased towards 0.04 V (vs. SCE) for the majority of coupons due to the development of the passive film in the chloride containing solutions. It was noted that two coupons (2.1 and 2.4) showed a gradual decrease in  $E_{corr}$ . Upon visual inspection of these coupons, once removed from the test, crevice corrosion was present, so these coupons were discarded from further analysis. An important comparison must be made here, with respect to the previous test (Section 4.3.1), which was conducted in only an aerated environment without any environmental ageing-[Cl]\* was 6 ppm to 12 ppm whereas these coupons are exposed to higher concentrations (50 ppm) without showing any indication of localised pitting corrosion<sup>5</sup> indicating that the period of exposure to on-load deaerated conditions has improved the resistance of the passive film to pit initiation.

<sup>&</sup>lt;sup>5</sup>A large decrease in E<sub>corr</sub> would indicate the onset of pitting.



FIGURE 4.20: Response of corrosion potential to increasing the chloride concentration from 1.5 ppm to 50 ppm representing chloride contamination during an off-load aerated period.

To determine the required value of [Cl]\* for initiation of new corrosion pits, the concentration of chloride needed to be increased further. Consequently, the chloride concentration was increased to 100 ppm, at which point  $E_{corr}$  of coupon 2.5 dropped suddenly (Fig. 4.21). The test cell containing this coupon was isolated so the coupon could be visually inspected, which showed it was crevice corrosion that cause the reduction in potential. The test was continued with chloride concentration increased to 150 ppm causing  $E_{corr}$  of coupon 2.7 to drop by 0.15 V.

When inspecting the coupons removed from the test cells at different chloride concentrations, the darkening of the surface, observed by Salzman et al. [98], is noticeable (Fig. 4.22). The period of exposure to the 'on-load' conditions has altered the passive film in such a way that the surface of the coupons appears much darker when compared to those coupons exposed only to a chloride contaminated 'off-load' environment as per the previous test (Fig. 4.11).

Also observable from Fig. 4.22, is that at chloride concentrations of 20 ppm, 50 ppm and 100 ppm, there is no evidence of localised pitting corrosion on the coupons. Only the coupon removed at the highest concentration (150 ppm) presents a single corrosion pit



FIGURE 4.21: Response of corrosion potential to increasing the chloride concentration from 100 ppm to 150 ppm representing significant chloride contamination during an off-load aerated period.

on the surface (Fig. 4.22D). Corrosion around the pit site was evident due to the diffusion of the concentrated acidic pit solution to the surrounding area.

From the electrochemical data presented and the inspection for localised corrosion on the test coupons, the exposure to an 'on-load' environment for 27.5 d increased [Cl]\* for pit initiation from around 12 ppm to >100 ppm. The reason for this appears to be an alteration to the protective passive film during exposure to deaerated conditions as the coupons are noticeably darker than previous studies.

# 4.3.3 Effect of Chloride Excursion on Threshold Chloride Concentration for Pit Initiation

In order to investigate the impact of a chloride excursion on pitting behaviour during subsequent transients in environmental conditions, coupons of 403 SS were initially exposed to an environment that represented a water chemistry excursion. This consisted of an aerated 35 ppm chloride solution at 90 °C as previous results showed that this concentration was greater than [Cl]\* (Section 4.3.1).

As shown in the plot of Fig. 4.23, many corrosion pits initiated upon exposure to the



FIGURE 4.22: Macrographs of four of the coupons removed after different steps indicated in each subcaption and detailed in Table 4.2. Only coupon 2.7 in (D) that was exposed to 150 ppm chloride has succumbed to pitting corrosion. All test coupons (exposed to both deaerated and then aerated solution) appear duller and darker than coupons just exposed to aerated solution (Fig 4.11).



FIGURE 4.23: Aspect ratio of pits as a function of the pit depth formed in an aerated solution, at 90  $^{\circ}$ C, containing 35 ppm chloride for a duration of 6 h.

35 ppm chloride solution for 6 h. The depths were typically in the range 20 µm to 80 µm with an AR > 1, meaning the shape of corrosion pits was akin to a truncated spheroid, as observed by Turnbull et al. [142]. Using the equation from Salzman et al. [98] in Eq. (4.2), the calculated pit depth in a 6 h exposure would be 148 µm, so the constants used in the equation over estimate the pit depths measured here. A better fit to the experimental data would be altering the constant,  $\alpha$ , to a value of  $5 \times 10^{-6}$ , which would give a pit depth of 74 µm in the 6 h exposure. The difference in growth rate and subsequent value of  $\alpha$  could be due to the difference in the grade of SiC paper used for the final grinding stage. In this work the final step was with P1200 SiC paper. Salzman et al. [98] used a final paper of 180 grit—a much rougher surface. This may allow corrosion pits to initiate more readily on the surface as the surface roughness provides a higher number of sites for metastable pit growth [66, 101, 102].

When the coupons were re-exposed to the test environment, after imaging, the value of  $E_{corr}$  was also monitored in order to ascertain whether there was any change in the value that would indicate corrosion pit initiation. As can be seen in the plot of Fig. 4.24, the potential of all four coupons was just above -0.1 V upon immersion in the 35 ppm



FIGURE 4.24: Corrosion potential of coupons re-exposed to aerated 35 ppm chloride solution at 90 °C. The coupons had been initially exposed to the same conditions for 6 h as described in Table 4.3. The green and red lines represent the beginning and end of a step. Coupons were removed and visually inspected at the end of a step—as shown in Figs. 4.25 and 4.27.

chloride environment. Within the next 24 h,  $E_{corr}$  of all four coupons reduced by around 35 mV to 40 mV—a slightly smaller  $\Delta V$  than previous results.<sup>6</sup> This may be due to the coupons previous exposure to 35 ppm chloride solution for 6 h.

To see if the drop in  $E_{corr}$  was the result of localised pitting corrosion, the cell containing coupons 3.1 and 3.2 was removed, with coupons being washed and dried after a 24 h exposure period (Step 2). When looking at the differences between Figs. 4.25B and 4.25C, it was noted that additional corrosion pits had initiated during the second exposure period to the chloride containing solution—represented by the red arrows in the figures. This shows us that if a component has become pitted during a shut down period, that further corrosion pits may initiate on the surface during subsequent shut downs i.e., an increase in pit density on the surface.

To see if the number of corrosion pits would increase further, two coupons (3.1 and 3.2) were exposed for a third time (Step 3 - Table 4.3) to 35 ppm chloride solution. During this exposure,  $E_{corr}$  remained stable at around -0.13 V (Fig. 4.24), indicating that all

<sup>&</sup>lt;sup>6</sup>The  $\Delta V$  for [Cl]\* was 60 mV to 85 mV vs. SCE.



FIGURE 4.25: Macrographs of coupons 3.1 and 3.2 (left and right hand side respectively of each subfigure) after different exposure steps to 35 ppm chloride solution as detailed in Table 4.3. (A) after final grinding with P1200 SiC paper, (B) after 6 h, (C) after 24.4 h and (D) after 72.2 h. The red arrows indicate sites where corrosion pits have initiated at new sites.



FIGURE 4.26: Example micrographs of corrosion pits measured on the surface of a test coupon after step 3. (A) is of pit 3, with diameter of 61 µm on coupon 3.1 and (B) is of pit 7, with diameter of 18 µm on coupon 3.2.

the most active sites for pit initiation (MnS inclusions) may have been exhausted making further pitting at this concentration of chloride unlikely. Upon visual inspection of the coupons again, after a cumulative exposure time of 102.6 h, it was observed that the number of additional corrosion pits that initiated was one (Fig. 4.25D) supporting the observations made from the electrochemical data.

The surface appearance of the corrosion pits that initiated during exposure to the 35 ppm chloride solution are shown in the micrographs of Fig. 4.26. They appear to be fairly circular—they have a consistent radius and there is some discolouration to the surface around the pit site. This is most likely due to effects of thin film interference. The light waves are reflected by the inner and outer surfaces of the thin film and as a result travel slightly different distances. As a result of this, there is both constructive and destructive interference which produces the different colours observed.

Furthermore, the second cell that was exposed to the chloride solution for the entire duration shows that the number of initiated corrosion pits is not a time dependant process. Upon comparison of the surfaces after the initial 6 h exposure (Fig. 4.27B) and subsequent 121 h exposure (Fig. 4.27C), the total number of corrosion pits does not increase any higher than the coupons from the other cell. The final geometry of the corrosion pit was also comparable to other coupons. This suggests that the process of removing the



FIGURE 4.27: Macrographs of coupon 3.3 and 3.4 (left and right hand side respectively of each subfigure) after different exposure steps to 35 ppm chloride solution as detailed in Table 4.3. (A) after final grinding step with P1200 SiC paper, (B) after 6 h and (C) after 121 h. The red arrows indicate sites where corrosion pits have initiated at new sites.

coupons from the environment and drying them out makes them more susceptible to pitting, as  $E_{corr}$  is initially at a higher value at the beginning of the next exposure period i.e. after 6 h in Fig. 4.24, but gradually falls. The subsequent 40 mV reduction in  $E_{corr}$  is thought to be due to the initiation of corrosion pits at new sites. Once new corrosion pits initiate in the second exposure, it is proposed that this exhausts all the lowest activation pit nucleation sites (MnS inclusions), so the same effect is not observed during a subsequent procedure of removal, drying and re-exposure (Step 3 - Fig. 4.24) which is why the  $E_{corr}$  is constant. Consequently, this means that there is a critical period when the turbine blades may be more susceptible to corrosion pit initiation. This is when the power plant has been shut down for a long enough period that the condensate on the blades has dried out. When the plant begins its start-up procedure, fatigue cycling commences and steam will begin to condense again on the blades and this point is identified as the period at which the materials are more susceptible to pit initiation.

Additionally, the surface geometry of the corrosion pits was measured through optical microscopy (OM) to determine if previously initiated pits had continued to grow in subsequent excursions—representative of 'corrosion pit reactivation'. The bar charts in Fig. 4.28 show the growth rate of the corrosion pits on coupons that were in the cell that was inspected at three different time periods. From these plots, it is observable that the corrosion pits that initiated in the first 6 h exposure (blue bars) did not continue to grow during exposure periods two and three. In the longer second exposure, the new pits that did initiate grew to a similar final size, making them independent to the exposure at which they initiated. As a result, the calculated pit growth rate was much less in exposures two and three.

The observation made here: that the pits all grew to a similar final size supports the argument that new corrosion pits are likely to initiate as opposed to old pits becoming reactivated and growing further. Removing the coupons from the test environment for inspection, at the end of each exposure would most likely change or remove the localised pit chemistry, which is why the pits do not appear to 'reactivate'. This is a pertinent result for the industry as they seek information relating to the likelihood of corrosion pits that have been identified during an inspection to continue to grow to a significant size that the SCF will be high enough that cracks initiate at a pit during loading. Additionally, observations made of the number of *new* corrosion pits initiated during each exposure period would suggest that once all sites of the lowest activation energy (MnS inclusions) have been activated, further pitting is unlikely at the same chloride concentration. Possibly explaining the high number of pits initiated within the first exposure compared with exposures two and three.

# 4.3.4 Combined Effect of Ageing and Chloride Excursion on Threshold Chloride Concentration for Pit Initiation

During service, it is likely that the composition of the steam condensate will contain impurities such as chloride at some stage. This could be due to a leak from the gland seal or contamination during routine inspection. As a consequence, when the turbine is shut down, some corrosion pits may initiate on the surface of the turbine blades within the aerated environment. If the size of the corrosion pits is judged to be small and the likelihood of them acting as nucleation sites for cracks is low, then the component will remain in operation. During the subsequent running of the power plant, the environment will be deaerated 'on-load' conditions, meaning the blades will experience ageing where the passive film is known to develop [98]. In the following shut down procedures of the power plant, it is not known how the corrosion pits on the blade will behave. There are three main possible outcomes: that the corrosion pits will *reactivate* and continue to grow, corrosion pits will initiate at new sites on the blade, or no corrosion pit activity and a higher concentration of contamination would be needed to initiate pits.

To establish which of these was the most likely outcome, coupons were exposed to



FIGURE 4.28: Pit growth rate and the final pit diameter of each individual corrosion pit during the first, second and third exposures in aerated 35 ppm chloride solution at 90 °C.



(A) Coupon 4.1 (L) and 4.2 (R)

(B) Coupon 4.3 (L) and 4.4 (R)



(C) Coupon 4.5 (L) and 4.6 (R)

(D) Coupon 4.7 (L) and 4.8 (R)



a 35 ppm chloride solution for a period of 6 h. This ensured some corrosion pits would initiate on the coupons as the concentration of chloride was above [Cl]\*. The appearance of the coupons after the initial exposure is shown in Fig. 4.29 and the corrosion pits are apparent due to the discolouration around each of their sites.

The coupons were loaded back into the four test cells and the initial environment of 0.3 ppm chloride solution was circulated to fill the cells. The corrosion potential of the coupons was allowed to stabilise for 8 h at -0.05 V (vs. SCE) before a simulated startup procedure was undertaken. The gas supply was switched from air to nitrogen in order to completely deaerate the solution in circulation. As can be seen Fig. 4.30, the oxygen concentration dropped below 10 ppb after 14 h. As a consequence, the E<sub>corr</sub> of coupons dropped to a value of -0.64 V (vs. SCE) after a test duration of 100 h—a similar E<sub>corr</sub> to that which was measured for freshly ground coupons in an earlier subsection (Section 4.3.2). This indicates that the presence of corrosion pits on the surface of the coupons has little impact on the E<sub>corr</sub> of 403 SS in 'on-load' deaerated 0.3 ppm chloride solution.



FIGURE 4.30: Response of corrosion potential, on pitted coupons, to oxygen transients simulating a period of 'on-load' exposure to deaerated 0.3 ppm chloride solution followed by an 'off-load' period with chloride contamination. See Table 4.4 for more details of environments.

The gas entering the reservoir was reverted to air after an on-load period of 100 h. Consequently, the oxygen concentration rapidly increased to 1.7 ppm within 6 h. Within the same period, the  $E_{corr}$  of the coupons increased to -0.11 V (vs. SCE), which was 60 mV lower than when the coupons were first exposed to the environment and a similar change to that reported in a previous section (Section 4.3.2).

The, now aerated, 0.3 ppm chloride solution represents the conditions that are predicted when the turbine is shut off and air is able to enter the chambers. The presence of oxygen facilitates the initiation of corrosion pits if the concentration of chloride is sufficient to induce the breakdown of the passive film. In earlier sections, [Cl]\* was found to be 6 ppm to 12 ppm (Section 4.3.1) in the absence of any exposure to a simulated operating steam environment and an increase to 100 ppm was observed when the 'on-load' environment was introduced (Section 4.3.2).

Due to the reintroduction of oxygen into the environment and increasing the chloride concentration, at regular intervals to 6 ppm and 12 ppm, the measured value of  $E_{corr}$ increases to -0.07 V due to the progressively more passive nature of the material. This potential is maintained as the concentration of chloride is increased further to 20 ppm, 35 ppm and 50 ppm. This would suggest that the deaeration period has improved the material's resistance to corrosion pit initiation (the same effect as previously observed) in a reduced exposure period of just 100 h; notably, 15 % of the previous experiment's exposure time. Additionally, the corrosion pits sites from the initial 35 ppm chloride excursion appear to have little to no impact on the stability of the passive film.

For coupon number 4.7, a reduction in  $E_{corr}$  of 100 mV was recorded when the chloride concentration was increased to 100 ppm which would indicate localised corrosion. The second coupon (number 4.8) required a higher concentration of 150 ppm chloride before  $E_{corr}$  again dropped by 100 mV.

The coupons were inspected following removal from their test cells, as shown in Fig. 4.31—again the darkening of the passive film is noticeable due to the 'on-load' exposure. The coupons in Fig. 4.31A were removed when the concentration was increased to 35 ppm and it is evident that no further pits have initiated on these samples and microscopic examination confirmed that the pits had not grown further. The other sets of coupons were removed at higher concentrations of chloride (100 ppm or 150 ppm) and half of the samples exhibited corrosion pit initiation at new sites and very little evidence that the previous pits had grown any further.

These results clearly indicate that the period of on-load water chemistry exposure can be short ( $\sim 4 d$ ) whilst still affecting the passive film composition. As a result, the coupons surface appears darker and a higher concentration of chloride is needed to initiate corrosion pits.

### 4.3.5 X-ray Photoelectron Spectroscopy: Impact of Exposure to Simulated Operating Steam Environment on Passive Film Composition

Coupons from an on-load or off-load simulated steam environment were analysed with XPS in order to quantify the observed differences in resistance to localised pitting corrosion. The wide angle XPS spectra of the two conditions are presented in Fig. 4.32 with the main spectral elements labelled.



(C) Coupon 4.5 (L) and 4.6 (R) – 100 ppm

(D) Coupon 4.7 (L) and 4.8 (R) – 150 ppm





FIGURE 4.32: Wide angle XPS spectra of passive films from aerated and deaerated environments. The main spectral elements visible have been labelled.

Both coupons analysed have prominent peaks due to the presence of carbon and oxygen. Additionally, peaks corresponding to chlorine, nitrogen, chromium and iron were also identified in both cases. Some differences can be noted regarding the intensity and shape of the chromium and iron peaks between coupons. In order to evaluate these differences, higher resolution scans of the O1 s,  $Cr 2 p_{3/2}$  and  $Fe 2 p_{3/2}$  peaks were performed. These spectra are presented in Fig. 4.33, where a number of differences are observed concerning the original spectrum (solid black line), mainly, the absence of a peak corresponding to the zero oxidation state metal signal (Fe<sup>0</sup> and Cr<sup>0</sup>) in the sample from the on-load conditions and the doublet O 1s peak in the coupon from aerated conditions.

To model the photoelectron peaks in the high resolution data, CasaXPS software [236] version 2.3.19 was utilised. First, the binding energy (BE) scales were calibrated by referencing to the C 1s peak at 284.4 eV. Afterwards, the Shirley method was applied to subtract the background around each region of the high resolution spectra. Numerous peaks were fitted to the spectra consisting of Gaussian-Lorentzian (30 % Lorentzian) line shape functions for the photoelectron peaks and asymmetric modified Lorentzian (LA( $\alpha$ ,  $\beta$ , m)) line shapes for the zero oxidation state metal components. Where the values of  $\alpha$  and  $\beta$  control the spread of the Lorentzian tails and m defines the width of Gaussian used. The best fit parameters (BE and full width half maximum (FWHM)) used for each component are given in Table 4.6 [245, 246]. Additionally, by summation of the calculated areas under each multiplet peak, the atomic percentage of each oxidation state can be determined, allowing the ratio between XPS core levels to be presented for each environmental condition.

As can be seen in the O 1s spectra, in the top row of Fig. 4.33, three peaks have been fitted with G-L functions. The first peak, at lowest BE, corresponds to lattice oxide ( $O^{2-}$ ) and has a FWHM that is narrower than the other two peaks. The next peak up corresponds to the hydroxides ( $OH^{-}$ ) and has a FWHM equal to the final peak at 532.8 eV. This final peak represents any adsorbed water or organic species in the surface film [246].

Below the O 1s spectra are the spectra for the  $Cr 2 p_{3/2}$  component. The peak observed at the lowest BE (574.1 eV) is attributed to the core level of metallic chromium ( $Cr^0$ ) and



 $\begin{array}{l} \mbox{FIGURE 4.33: XPS spectrum fitted with parameters from Table 4.6 for O1s, } \\ \mbox{Cr}2p_{3/2} \mbox{ and Fe}2p_{3/2} \mbox{ peaks from coupons exposed to (A) only aerated 'on-load' environment and (B) simulated deaerated 'on-load' conditions and then aerated solutions containing chloride. \end{array}$ 

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| $\begin{array}{c cccc} \hline \text{Dinding energy (eV)} & FWHI \\ \hline \mathbb{C}r_{\text{oxide}}^{2} & 574.1 & \mathbb{C} \\ \mathbb{C}r_{\text{oxide}}^{3+} & 574.1 & \mathbb{C} \\ \mathbb{C}r_{\text{oxide}}^{3+} & 575.9 & \mathbb{C} \\ \mathbb{C}r_{\text{oxide}}^{3+} & 577.6 & \mathbb{C} \\ \mathbb{C}r_{\text{oxide}}^{3+} & 577.6 & \mathbb{C} \\ \mathbb{C}r_{\text{OH}}^{3+} & 577.2 & \mathbb{C} \\ \mathbb{C}r_{\text{OH}}^{3+} & 577.2 & \mathbb{C} \\ \mathbb{C}r_{\text{OH}}^{3+} & 706.8 & \mathbb{C} \\ \mathbb{R}e^{2^{+}} & 709.0 & \mathbb{C} \\ \hline \end{array}$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | M (eV) 0.8<br>0.9 |      |                     |           |      |
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| $\begin{array}{cccc} Cr_{\text{oxide}}^{3+} & 575.9 & 0 \\ 576.9 & 576.9 & 0 \\ 577.6 & 0 \\ 578.6 & 0 \\ 579.0 & 0 \\ Cr_{\text{oH}}^{3+} & 577.2 & 2 \\ 2r_{\text{oH}}^{3+} & 577.2 & 2 \\ 2r_{\text{oH}}^{3+} & 706.8 & 0 \\ 2r_{\text{e}}^{2+} & 709.0 & 1 \end{array}$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | 0.9               | 0.2  | 575.3               | 0.8       | 1.2  |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                   |      | 576.0               | 0.9       |      |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 0.9               |      | 577.0               | 0.9       |      |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 0.9               | 3.8  | 577.8               | 0.9       | 8.3  |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 0.9               |      | 578.8               | 0.9       |      |
| $\begin{array}{cccc} Cr_{OH}^{3+} & 577.2 & 2\\ Re^{0 \ b} & 706.8 & 0\\ Re^{2+} & 709.0 & 1 \end{array}$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | 0.9               |      | 579.2               | 0.9       |      |
| $\frac{1}{2} \frac{1}{2} \frac{1}$ | 2.5               | 3.1  | 577.4               | 2.6       | 16.3 |
| $r_{e}^{2+}$ 709.0 1                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 0.9               | 1.6  | 707.6               | 0.9       | 0.5  |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | 1.4               |      | 708.5               | 1.4       |      |
| 710.3 1                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 1.6               |      | 709.8               | 1.6       |      |
| 711.5 1                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 1.6               | 6.6  | 711.0               | 1.6       | 3.6  |
| 712.7 2                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 2.9               |      | 712.2               | 2.9       |      |
| 716.0 2                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 2.5               |      | 715.5               | 2.5       |      |
| ie <sup>3+</sup> 709.9 1                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | 1.2               |      | 709.5               | 1.2       |      |
| 710.9                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | 1.3               |      | 710.5               | 1.3       |      |
| 711.8 1                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 1.4               | 101  | 711.4               | 1.4       | L 0  |
| 712.9 1                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 1.4               | 10.4 | 712.5               | 1.4       | 7.1  |
| 714.0 1                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 1.9               |      | 713.6               | 1.9       |      |
| 719.4 2                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 2.7               |      | 719.0               | 2.7       |      |
| Drganics 532.8 1                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | 1.9 1             | 6.1  | 533.0               | 2.0       | 13.8 |
| DH <sup>-</sup> 531.4 1                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 1.9 2             | 28.6 | 531.4               | 2.0       | 29.6 |
| D <sup>2-</sup> 529.9 1                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 1.2 2             | 21.6 | 530.0               | 1.7       | 17.2 |
| ∃e/Cr ratio                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                   | 3.7  |                     |           | 0.5  |

is fitted with a modified Lorentzian line shape function. Additionally, there is a contribution from the hydroxide component  $(Cr_{OH}^{3+})$  which is fitted with a broad peak with a FWHM of at least 2.5. The contribution from the oxide  $(Cr_{oxide}^{3+})$  requires multiple peaks to be added due to the effects of multiplet splitting. This phenomenon arises when the atom contains an unpaired electron in its outer shell (unpaired d electrons in this case). When photoionisation of core electrons occurs, a core electron vacancy will form which can couple with with the unpaired electron from the outer shell. This process is known to create a number of final states which are apparent in the photoelectron spectrum [246]. The five multiplet splitting G-L peaks are all fitted with equal FWHM (0.9), which is of similar value to the  $Cr^{0}$  component. As reported by Biesinger et al. [246], it may also be possible to include multiplet fitting peaks for chromite (FeCr<sub>2</sub>O<sub>4</sub>) at BEs similar to those used for  $Cr_{oxide}^{3+}$ . However, in order to get meaningful separation between these components, a very low signal-to-noise ratio is required, so the chromite features have not been considered further. Nevertheless, chromite could be present and further analysis would need be completed in order to confirm this.

Finally, the bottom row of the figure shows the Fe 2  $p_{3/2}$  spectra. At lowest BE (~707.0 eV) there is a single Lorentzian line shape function attributed to the contribution from core level metallic iron (Fe<sup>0</sup>). At BEs in the range 709.0 eV to 719.4 eV, there are numerous components that originate from the Fe(II) (Fe<sup>2+</sup>) and Fe(III) (Fe<sup>3+</sup>) oxidation states. Both of these components require fitting with a multiplet structure [247] with the average values taken from Biesinger et al. [246]. They consist of 5 and 6 G-L functions for Fe<sup>2+</sup> and Fe<sup>3+</sup>, respectively. The multiplet structures have increasing FWHM as the BE reaches a higher value in the range of 1.2 to 2.7. From the fitting of these curves, it is apparent that the photoemission from Fe<sup>3+</sup> is dominant in both coupons measured.

The high resolution spectra of O 1s,  $Cr 2 p_{3/2}$  and  $Fe 2 p_{3/2}$  have been presented from two environment systems with fitted line shape functions for the species present in each case. The first passive film (Fig. 4.33A) was formed when coupons were exposed only to off-load aerated environment with no on-load exposure. Conversely, the second passive film analysed (Fig. 4.33B) was exposed to on-load conditions for 27.5 d followed by a short period of exposure to off-load conditions. In order to compare the composition of these two passive films, it is necessary to calculate the ratio between chromium and

iron-containing components to present a Fe/Cr ratio. For the first passive film, the ratio of Fe/Cr was calculated at a value of 3.7. Simply put, this means that the film contained a higher number of iron containing species than chromium containing species. After a period of exposure to the deaerated on-load environment, this ratio decreases to 0.5. Thus, the composition of the passive film has changed, such that it has become impoverished in compounds containing Fe<sup>2+</sup> and Fe<sup>3+</sup> ions and enriched with Cr<sup>3+</sup> oxide and hydroxide components. This enrichment of Cr<sup>3+</sup> compounds at the surface of the passive film would corroborate the observation that a higher concentration of chloride was needed to initiate corrosion pits after the period of on-load exposure. The Cr<sup>3+</sup> compounds offer an increased resistance to pit initiation compared with iron species. The decrease in the size of the Cr<sup>0</sup> and Fe<sup>0</sup> peaks could also suggest that the passive film had increased in thickness-either due to the increased total exposure time or an additional effect of the deaerated environment. The thicker passive film would reduce the photoemission peak from the metal substrate beneath the passive film. To further quantify the composition of the passive film, it may be possible to combine XPS with depth profiling or to utilise Raman spectroscopy, as others have done [243, 248], in order to quantify the compounds contributing to the changes observed in O 1s,  $\operatorname{Cr} 2 p_{3/2}$  and  $\operatorname{Fe} 2 p_{3/2}$  spectra.

### 4.3.6 Summary of findings

In total, four experiments were conducted in order to identify the threshold concentration of chloride needed to initiate corrosion pits—[Cl]\*. Additionally, the impact of exposure to simulated on-load conditions on the value of [Cl]\* was examined and finally the effect of previous chloride excursions that generated corrosion pits was studied. A summary of the results from these four tests conducted using 403 SS is shown in Table 4.7.

The initial value of [Cl]\* was identified around 12 ppm for 403 SS and in excess of 100 ppm for FV566 SS. For the 403 SS, the effect of the environmental ageing was to increase the value of [Cl]\* beyond 100 ppm. Additionally, it was observed that corrosion pits may initiate during a period of exposure to aerated conditions and then become deactivated upon re-exposure. It was found that these dormant corrosion pits did not hinder the nucleation of new corrosion pits in subsequent water chemistry excursions, until all lowest activation pit initiation sites are exhausted.

| Test                | Coupon ID | Max [Cl]<br>(ppm) | Total immersion time<br>(h) | Outcome      |
|---------------------|-----------|-------------------|-----------------------------|--------------|
|                     | 1.1       | 6                 | 69.8                        | crevice      |
|                     | 1.2       | 6                 | 69.8                        | no corrosion |
|                     | 1.3       | 12                | 93.8                        | one pit      |
| [Cl]* for pit       | 1.4       | 12                | 93.8                        | no corrosion |
| initiation          | 1.5       | 20                | 141.8                       | two pits     |
|                     | 1.6       | 20                | 141.8                       | five pits    |
|                     | 1.7       | 20                | 144.8                       | one pit      |
|                     | 1.8       | 20                | 143.8                       | crevice      |
| Impact of           | 2.1       | 20                | 814.1                       | crevice      |
|                     | 2.2       | 20                | 814.1                       | no corrosion |
|                     | 2.3       | 50                | 862.3                       | no corrosion |
| impact of           | 2.4       | 50                | 862.3                       | crevice      |
|                     | 2.5       | 100               | 886.7                       | crevice      |
| [CI]*               | 2.6       | 100               | 886.7                       | no corrosion |
|                     | 2.7       | 150               | 986.0                       | one pit      |
|                     | 2.8       | 150               | 986.0                       | no corrosion |
| Effect of           | 3.1       | 35                | 102.0                       | new pits     |
| pitting on<br>[Cl]* | 3.2       | 35                | 102.0                       | new pits     |
|                     | 3.3       | 35                | 127.3                       | new pits     |
|                     | 3.4       | 35                | 127.3                       | new pits     |
|                     | 4.1       | 35                | 288.5                       | no corrosion |
| Combined            | 4.2       | 35                | 288.5                       | no corrosion |
| effect of           | 4.3       | 150               | 408.3                       | one new pit  |
|                     | 4.4       | 150               | 408.3                       | no corrosion |
| agoing on           | 4.5       | 100               | 336.7                       | two new pits |
|                     | 4.6       | 100               | 336.7                       | no corrosion |
|                     | 4.7       | 150               | 409.1                       | one new pit  |
|                     | 4.8       | 150               | 409.1                       | no corrosion |

TABLE 4.7: Summary table of 403 SS coupons used in each test, detailing the maximum chloride concentration they were exposed too, total immersion time in solution and outcome of testing.

### 4.4 Conclusions

Chapter 4 has provided a comprehensive investigation into the impact of transient environmental conditions on corrosion pit initiation. From this work, a number of important conclusions can be drawn about how the steam turbine environment can affect the steam turbine blade's susceptibility to corrosion pit initiation.

- The critical chloride concentration for pit initiation was identified between 6 ppm and 12 ppm and >100 ppm for 403 and FV566 SSs, respectively.
- Monitoring of the corrosion potential, coupled with EN analysis and visual inspection all provided reliable information relating to the initiation of localised pitting corrosion.
- The PI for 403 SS reached the threshold value of 0.6 when the chloride concentration reached 12 ppm. Comparatively, the PI of FV566 SS was 0.37 in the same concentration solution; a concentration of 100 ppm was required to surpass the threshold PI value.
- The *R<sub>n</sub>* of 403 SS was higher than FV566 SS at lower concentrations of chloride, inferring a lower CR. However, the EN resistance of FV566 SS remained stable over a much greater concentration of chloride concentrations, indicating its superior corrosion resistance across a broader range of chloride concentrations.
- Differences between the microstructures of 403 and FV566 SS, may explain the differences in [Cl]\* measured, future work could involve a more detailed characterisation of the microstructure as this was not a focus within this research.
- Exposure to simulated on-load conditions had a significant impact on the critical chloride concentration needed for pit initiation in 403 SS. The critical chloride concentration increased from 12 ppm to 100 ppm. The appearance of the surface was dull and darker compared to the coupons from just the off-load environment, which agreed with the observations from Salzman et al. [98].
- Analysis of the passive films from the off-load or on-load environment by XPS revealed significant differences in the composition of the passive film. A Fe/Cr ratio

was calculated for each passive film of 3.7 and 0.5 for the off-load and on-load environments, respectively. The film formed in the on-load environment contained a much higher percentage of  $Cr^{3+}$  oxide and hydroxide components, explaining the enhanced corrosion resistance performance.

- An XPS measurement of the passive film of FV566 SS material should aid in explaining the higher value of [Cl]\*. It is expected the passive film would contain a significant contribution from the molybdenum within the alloy composition. This would be performed in order to publish the results of this chapter.
- Additional future work could utilise Raman spectroscopy to identify and quantify compounds in the passive films in order to explain the reason for enhanced resistance to passive film breakdown and the changes observed in the high resolution XPS measurements [243, 248].
- Investigations into the behaviour of initiated corrosion pits in subsequent environmental excursions revealed that corrosion pit reactivation is unlikely. Instead, corrosion pits initiated at new sites on the material, increasing the corrosion pit density. This is a key finding as it will assist inspection engineers decide on the possibility of corrosion pits continuing to grow to a critical size that would allow cracks to initiate in service.
- A combined study of ageing and a pitted surface showed that a very short exposure to on-load conditions had the same impact on increasing the critical chloride concentration for pit initiation. Additionally, the previous corrosion pits did not grow further in subsequent periods of water chemistry excursions.

# **Chapter 5**

# **Controlled Growth of Corrosion Pits**

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### 5.1 Introduction

During a power plant's shutdown period, chloride contamination may cause multiple corrosion pits to initiate on the surface of the low pressure steam turbine (LPST) blade, from which multiple cracks can grow during on-load fatigue cycling. For that reason, it is desirable to be able to grow a single corrosion pit in a known and measurable location allowing observation of crack initiation from this site. Methods such as drilling [249] and spark erosion [167] have been used previously but may introduce residual stresses or changes to the material's microstructure. Consequently, electrochemical techniques [250–252] have become more popular for generating single corrosion pits as they eliminate these two factors and corrosion pitting is a natural electrochemical process [253].

The aim of this chapter is to identify a suitable technique which would allow the production of a single corrosion pit in a desirable location on the material. The pit morphology should be representative of those pits that initiated in the studies reported within Chapter 4, so an electrochemical technique should be chosen. Two techniques will be compared below and the rationale for the chosen technique is presented. The technique chosen to produce single corrosion pits will then be used within the experimental procedures of Chapter 6, where the location of crack initiation at the pit site is investigated. The benefit of having corrosion pits of a desirable size in a chosen location is that the largest pit can be observed, optically, during fatigue cycling; which allows the mechanical test to be interrupted when a crack of sufficient size is visible.

### 5.2 Experimental

### 5.2.1 Micro-electrochemical Cell

The micro-electrochemical cell, designed by Evans et al. [178], comprised of a PMMA body with two insert ports for a micro-pipette and mini reference electrode (RE). The micro-pipette allowed the body to be filled with 0.6 mol NaCl solution while the ALS RE-3V (Ag/3m AgCl) RE was used during polarisation with a flag of platinum sealed into the top of the PMMA body to act as the counter electrode (CE). The sample (working electrode (WE)) was ground to a P4000 finish with SiC abrasive paper and a 300 µl pipette tip located the solution onto the sample surface as shown in Fig. 5.1.

A potentiostatic programme (Section 3.3.3) was used with a Princeton Applied Research VersaSTAT 4 at a potential of 1.5 V vs. Ag/3M AgCl with the duration varying from 0.5 h to 12 h.

After the pit had been created, the sample was cleaned in acetone in an ultrasonic bath for 5 min to remove corrosion product from the surface. Finally, the pit was measured with a Keyence VK-X200K laser confocal scanning microscopy (LCSM) and VK-Analyser software was used to calculate the pit geometry. For each pit, four line profiles were taken across the pit mouth (Fig. 5.2) and then the depth and width from each of these were used to calculate the average.



FIGURE 5.1: The micro-electrochemical cell used to generate a corrosion pit at the boundary between the wall of the pipette tip and the surface of the fatigue specimen.



FIGURE 5.2: A diagram of the four line scans made across a corrosion pit from which profiles were taken to determine the pit geometry.


FIGURE 5.3: The droplet cell that was used to electrochemically initiate a corrosion pit within the NaCl droplet on the surface of the fatigue specimen. (A) A macrograph and (B) a schematic diagram of the setup used for the droplet cell.

# 5.2.2 Droplet Method

A second method of single pit generation, developed by Turnbull et al. [142], is shown in Fig. 5.3 and described in ISO 21153:2018 [254]. A Drummond Wiretrol<sup>®</sup> II glass capillary micropipette of volume 2 µl to 5 µl was used to locate a small droplet of 0.1 mol (fine ground surface) or 0.5 mol (shot-peened surface) sodium chloride solution on the specimen surface within a cell to limit the rate of evaporation. The process of depositing the droplet is akin to the procedure followed in performing a contact angle measurement [255]. By assuming a hemispherical droplet of volume 3 µl, the contact surface area of the droplet would be  $\sim 4 \text{ mm}^2$ ; consequently, the droplet would cover a large number of grains (grain size  $\sim 25 \text{ µm}$ ), within which a pit may initiate. Pit initiation at the perimeter of the droplet was not common due to the high oxygen concentration of the surrounding air, encouraging cathodic reactions. A 0.1 mm diameter platinum wire acted as the CE/RE and was positioned within the droplet using a Uniscan SECM370 or clamp stand.

A galvanostatic programme (Section 3.3.2) was used, in which the specimen (WE) was anodically polarised using a galvanostatic current ranging from  $20 \,\mu$ A to  $50 \,\mu$ A. This would drive the potential of the specimen beyond the pitting potential, allowing a single pit to initiate due to the limited current applied, and, as a result, the potential would drop

below the pitting potential preventing formation of more than one pit. The duration of anodic polarisation time was varied between 5 min and 600 min and once complete, the specimen and pit were cleaned and measured as before.

# 5.3 **Results and Discussion**

## 5.3.1 Corrosion Pit Geometry

Within this work, the geometry of the corrosion pit is an important detail. Therefore, the corrosion pit geometry was defined as follows:

- **Depth (a)** The average of the deepest position on each of the four lines scans across the corrosion pit.
- Width (2c) The average of the four distances between each side of the pit from the line scans.
- Aspect ratio (AR) The average depth divided by half the average width of each pit.

The possible classifications of pit profiles are shown in Fig. 5.4. A pit AR of one would represent a *hemispherical* pit, where the radius of the pit is equivalent to the depth. An AR greater than one would describe a *narrow and deep* pit where the depth exceeds the radius; while an AR less than one would represent a *wide and shallow* geometry.

# 5.3.2 Micro-electrochemical Cell

A potentiostatic method was used with the micro-electrochemical cell to create corrosion pits of different geometries. A potential of 1.5 V vs. Ag/3M AgCl was used with 0.6 mol NaCl solution with polarisation time ranging from 0.5 h to 12 h.



FIGURE 5.4: Schematic diagram showing the classification of pit profiles depending upon the calculated aspect ratio where AR = a/c.



FIGURE 5.5: Plots of (A) pit depth vs. polarisation time, and (B) aspect ratio vs pit depth for pits produced with micro-electrochemical cell.

The relationship between the maximum pit depth measured for each polarisation time is shown in Fig. 5.5A and the resulting pit ARs for each pit depth are given in Fig. 5.5B. From these plots, it was observed that the pit depth increases with longer periods of polarisation and the curve follows a  $x = \sqrt{y}$  trend, i.e., as the polarisation time increases, the rate of increase in pit depth decreases. A maximum pit depth of just over 300 µm was achieved after 12 h polarisation which produced significant corrosion products within the pipette tip. This would limit the diffusion of oxygen and chloride ions towards the metalelectrolyte interface, retarding further growth of the corrosion pit by metal dissolution.

The pit AR vs. pit depth follows a linear relationship from 0.1 to 0.8 as the width of each pit produced was approximately equal to the width of the plastic pipette tip ( $\sim$ 700 µm). This meant that the AR for all pits produced with this method was < 1, categorising them as 'Wide and Shallow' pits.

The pit surface (shown in Fig. 5.6) has a smooth elliptical shape, similar to the profiles used for modelling, but unlike a 'real' corrosion pit which has microtopographical wall features. Evans [256], who developed the micro-electrochemical cell, stated that the smooth pit wall was advantageous as it removed random stress concentration features from the pit which would create scatter in his crack initiation studies.

It is apparent that this method allows for metal dissolution over the entire area that is in contact with the electrolyte enclosed in the pipette tip. Therefore, the ARs of pits produced by the micro-electrochemical cell do not accurately represent corrosion pits



FIGURE 5.6: Surface plot of a corrosion pit produced using the microelectrochemical cell after 12h potentiostatic polarisation taken from a LCSM image.

that were observed during the pit initiation studies in Chapter 4, these pit ARs were in the range of 1-2 for a pit of just 50 µm in depth (Fig. 4.23). The AR could be altered by using a pipette tip of smaller diameter, but then the orifice would become blocked more easily due to the corrosion product and limit the pit depths producible.

#### 5.3.3 Droplet Method

A galvanostatic method was used with the droplet technique to create singular corrosion pits of variable geometries depending on the polarisation times.

The galvanostatic polarisation time was varied from 5 min to 10 h with larger droplets of NaCl solution used for longer durations (up to 5  $\mu$ l). A galvanostatic current of 20 or 40  $\mu$ A was selected for fine ground and shot peened, respectively. This applied current increased the potential beyond the pitting potential, allowing a corrosion pit to initiate; once initiated, the potential drops preventing further corrosion pits from initiating. A typical galvanostatic curve is shown in Fig. 5.7 with the inset plot showing detail of the initial drop in potential over the first 200 s—corresponding to the initiation of a corrosion pit. As a result of anodic dissolution of the metal, corrosion product forms and the potential rises due to the increased solution resistance. For fine ground surfaces, a 0.1 mol



FIGURE 5.7: Galvanostatic polarisation curve for a 3 µl droplet of 0.1 mol NaCl solution at 20 µA over a period of 10 h.

NaCl solution was used and this concentration was increased to 0.5 mol for shot peened surfaces.

The shot peened surface was more resilient to pit initiation with the droplet technique as both an increased current and chloride concentration were needed to initiate corrosion pits. A similar effect was observed by Azar et al. [257] in shot peened 316L material. They reported that a duration of shot peening greater than 25 min reduced the corrosion current density to a value lower than the ground material; although limited explanation was given for the possible mechanism. However, as reported by Turnbull et al. [147], the shot peening procedure induced a 10 µm deep nanocrystalline layer in the near surface microstructure of these FV566 stainless steel (SS) samples. It has been well reported in the literature [148, 258–260] that the nanocrystalline layer formed on Fe-Cr and zirconium alloys can improve the corrosion properties by allowing greater chromium diffusion and formation of a more compact and chromium rich oxide film. It is likely that the effect of the nanocrystalline is hindering the ease at which the droplet technique can initiate a corrosion pit, explaining why an increased concentration of sodium chloride solution and applied current was required for shot peened material.

Graphs showing how corrosion pit depth changes with applied charge (time  $\times$  current) are shown in Fig. 5.8A. For both surface conditions of fine ground and shot peened,



FIGURE 5.8: Plots of (A) corrosion pit depth vs. applied charge (current of  $20 \,\mu\text{A}$  and  $40 \,\mu\text{A}$ ), and (B) aspect ratio vs. pit depth for pits produced with droplet technique.

it was possible to produce corrosion pits with a maximum depth of 50 µm to 225 µm where a greater applied charge was needed to produce deeper pits. However, this increase in pit depth with applied charge is not linear but follows closely to a  $x = \sqrt{y}$  function, meaning that as the applied charge increases, the resulting increase in depth slowly decreases. The galvanostatic method maintains a constant applied current during the duration of polarisation period and also, theoretically, a constant metal dissolution rate. This is achieved by increasing the potential as the solution resistance increases within the droplet due to the formation of corrosion products.

The AR of corrosion pits produced with the droplet method was always > 1 and often closer to 2 as shown in Fig. 5.8B. Therefore, these pits would be classified as 'Narrow and Deep' pits and more closely match the AR of those observed in earlier pit initiation work (Fig. 4.23).

An example of one such pit is shown in Fig. 5.9 corresponding to a pit with an AR of 2.27, meaning it is slightly deeper than the diameter of the pit. This surface plot also reveals these pits are not as smooth as pits produced with the micro-electrochemical cell and have a rough microtopographical pit wall. The surface plot shows the corrosion pit to have vertical sides below the pit mouth, despite a common feature of corrosion pits being their undercutting geometry [53]. As this LCSM measurement technique is a line of sight process, it will be unable to detect any pit undercutting surrounding the pit mouth as it is covered by material above and an alternative technique such as cross



FIGURE 5.9: Surface plot of a corrosion pit produced using the droplet technique after 10 h galvanostatic polarisation taken from a LCSM image.

sectional analysis or X-ray computed tomography (XCT) would be needed to measure the real pit geometry. However, this technique can still be used to measure the pit depth as the deepest part of the pit normally sits directly below the centre of the pit mouth.

Similar pits were produced by Ghahari et al. [58, 59], on 20 µm foils of 304 SS under galvanostatic control. Through observation of the sample with synchrotron X-ray imaging methods, they were able to observe pit growth *in situ* and study the development of the pit profile. They saw that the pits propagated by uniform growth in all directions into a bulbous shape with rough interior surface; similar to the corrosion pits produced here. As the amount of current is limited, while the pit and surface area are growing, the current density gradually decreases and becomes insufficient to maintain a concentrated solution in the pit, so gradually repassivates, explaining why these pits grow to a finite size. The limited current also determines the profile of pits produced under galvanostatic conditions as they adjust to a circular shape to provide the least electrical resistance.

As the droplet of NaCl solution that is located onto the specimen is of limited volume and remains static during the galvanostatic polarisation, there is the tendency for corrosion products to form within the solution. Initially, the rate of metal dissolution is the rate determining step in pit growth. However, as corrosion products form from the metal ions, these precipitates build up hindering the diffusion of chemical species into and out of the pit electrolyte, hence, acting as the rate-determining step at greater applied charges and pit depths. The corrosion product that formed was observed to be red-brown in colour. Similar observations of the formation of this type of corrosion product were made by Makar and Tromans [261] during their chloride induced pit initiation studies on pure iron and they identified it as Fe<sub>2</sub>O<sub>3</sub> or Fe(OH)<sub>3</sub>. It is likely the same corrosion products are formed during pit initiation on 12Cr SS using the droplet technique.

# 5.4 Conclusions

This chapter has provided an insight into possible techniques that could be used to produce artificial corrosion pits. The ability to do so in a desirable location with controlled geometry, was evaluated.

- Both the micro-electrochemical cell and droplet techniques allowed the production of single corrosion pits by potentiostatic or galvanostatic polarisation.
- A range of pit depths could be produced depending upon the polarisation period.
- Both techniques were susceptible to retardation of pit growth at longer polarisation times due to the effects of corrosion products formed during the process.
- The micro-electrochemical cell produced pits with a diameter akin to the pipette tip. This meant that the ARs of pits produced by this method were < 1, as the diameter was much greater than the depth.
- The corrosion pits produced by the micro-electrochemical cell had smooth internal morphology. They were lacking in the microtopographical features and local stress concentration sites observed in real corrosion pits.
- Using the droplet cell, a galvanostatic current of 20 µA could be used to initiate corrosion pits within the NaCl droplet on a fine ground surface. A greater current of 40 µA was needed to initiate corrosion pits on a shot peened surface due to the formation of a nanocrystalline layer induced by the shot peening procedure. This layer consists of a more compacted and enriched chromium oxide film improving the corrosion resistance of the material.

- The applied current caused an increase in the potential beyond the pitting potential, allowing a corrosion pit to initiate. Consequently, the potential would then drop back below the pitting potential, eliminating the possibility of multiple corrosion pits forming.
- The use of the droplet technique yielded pits with morphologies similar to those observed within Chapter 4 of this research project. The ARs were in the range of 1–2.5 and the pits were irregular in shape.

# Chapter 6

# Fatigue Crack Initiation at Corrosion Pits

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# 6.1 Introduction

Within Chapter 4, it was shown that transients in environmental conditions may facilitate the initiation of corrosion pits. Once a corrosion pit has initiated and grown in size, it is widely accepted that these areas of localised corrosion are favourable crack initiation sites in the early stages of the corrosion fatigue (CF) process [115, 140, 157, 160, 166, 262]. The reason for this is the localisation of stress and strain around this defect in the material when under an applied cyclic load. As a consequence, cracks are more likely to initiate at these sites than other regions of a component. Crack initiation from a corrosion pit can happen very quickly and pre-pitted fatigue specimens can have their fatigue life significantly reduced—up to 70% [161, 168, 180]. The application of shot peening to a component's surface can improve the fatigue life as the residual compressive stresses mitigate then tensile stresses generated from fatigue loading [7, 42, 147, 149, 257, 263]. Whether this effect is still prevalent fully, when a corrosion pit extends beyond the depth of the compressive layer is not clear.

In order to understand the importance of the presence of a corrosion pit and its role in crack initiation in a steam turbine, it may be acceptable to test without an environmental cell during high frequency fatigue. This is based upon the water chemistry of the turbine being carefully controlled, such that the steam should only contain a very low level of deleterious components such as chloride and should have an oxygen level below 5 ppb. Therefore, it is very unlikely that further corrosion activity will be possible during the cyclic loading encountered during operation and only existing pits will act as crack nucleation sites.

Using the technique identified in Chapter 5, it has been possible to produce single corrosion pits, of different desired pit depths, onto the gauge section of fatigue samples. The precise location of each pit is determined by the positioning of the NaCl droplet onto the surface, allowing direct observation of each singular corrosion pit during fatigue testing. Essentially, this allows the nucleation and growth of cracks from the corrosion pit to be monitored as a function of fatigue cycles, allowing for tests to be interrupted at the precise moment cracks become visible with a microscope. There are numerous reports of cracks initiating from both the shoulder/mouth region of the corrosion pit or at the base [115, 149, 157, 177, 181, 264, 265]. Often this is predicted through finite element analysis (FEA) and confirmed by examination of fracture surfaces. However, little work has been previously presented that identifies the site of embryonic crack growth at corrosion pits as this is difficult to detect through conventional surface observation techniques. The use of novel techniques such as X-ray computed tomography (XCT) and plasma focused

ion beam (PFIB) enables the internal features of the corrosion pit to be seen post test, allowing direct comparison between the crack initiation point and the corrosion pit region. Ultimately, different aspect ratios (ARs) of corrosion pits can be grown to investigate whether the pit geometry impacts on the location of crack initiation at a corrosion pit and the number of cycles needed to initiate cracks.

# 6.2 Experimental

#### 6.2.1 Fatigue Sample Preparation

Flat dog bone fatigue specimens of FV566 stainless steel (SS) (Table 2.1) were machined by Kay Engineering, Middlesex, to a P4000 finish giving an average surface roughness,  $R_a$ , of 0.1 µm. Shot peening, of the 20 mm gauge section, was carried out by Curtiss-Wright Surface Technologies, Newbury, following the procedure S170 8-12A, typical of industrial practice for turbine blades. The residual stress profile of both ground and shot peened surfaces (Fig. 6.1) was measured by NPL using X-ray diffraction (XRD) with a Pulstec  $\mu$ -X360 diffractometer using Cr K $\alpha$  radiation, combined with layer removal by electropolishing [147]. The final fatigue specimens had a 20 mm × 4 mm × 4 mm parallel gauge section, an overall size of 165 mm × 25 mm × 4 mm and are shown in Fig. 6.2.

#### 6.2.2 Controlled Growth of Corrosion Pits

In order to further understand the effect of pit geometry on crack initiation, a range of pit sizes were produced on the front and reverse of the 20 mm parallel gauge section of the fatigue specimens.<sup>1</sup> The reasoning behind this was that only the largest corrosion pit would be observed during fatigue until crack growth was obviously visible with the microscope. It was anticipated that whilst cracks nucleating from the larger corrosion pits might be fully developed; thus making identification of the precise crack nucleation location difficult, the smaller corrosion pits would have less developed cracks that would reveal the crack nucleation location. Using the droplet technique presented in Chapter 5 (Fig. 5.3) and a range of galvanostatic polarisation times, between 5 min and 10 h, it was possible to produce pit depths ranging from 50 µm to >200 µm. A 0.1 mol or 0.5 mol NaCl solution was used with a current of 20 µA or 40 µA for the ground and shot peened

<sup>&</sup>lt;sup>1</sup>Shown later in Figs. 6.14 and 6.15.



FIGURE 6.1: Longitudinal residual stress profile of shot peened ( $R_a$  - 2.7 µm) and fine ground ( $R_a$  - 0.1 µm) FV566 stainless steel determined by X-ray diffraction. Figure re-plotted from Turnbull et al. [147].



FIGURE 6.2: (A) Computer generated 3D representation of fatigue sample geometry. (B) Macrographs of the fine ground (top) and shot peened (bottom) fatigue specimens.

| Pit ID  | Droplet volume | Polarisation time | Current | Pit depth <sup>1</sup> | Aspect |
|---------|----------------|-------------------|---------|------------------------|--------|
|         | (µl)           | (min)             | (µA)    | (µm)                   | ratio  |
| Front   |                |                   |         |                        |        |
| F1      | 2              | 5                 | 20      | 52                     | 1.67   |
| F2      | 2              | 45                | 20      | 103                    | 1.41   |
| F3      | 3              | 180               | 20      | 162                    | 1.85   |
| F4      | 3              | 300               | 20      | 162                    | 1.73   |
| F5      | 3              | 600               | 20      | 163                    | 2.18   |
| F6      | 5              | 600               | 40      | 206                    | 2.27   |
| Reverse |                |                   |         |                        |        |
| R1      | 3              | 15                | 20      | 88                     | 1.95   |
| R2      | 3              | 60                | 20      | 121                    | 1.89   |
| R3      | 3              | 120               | 20      | 149                    | 1.81   |
| R4      | 3              | 240               | 20      | 181                    | 1.80   |
| R5      | 5              | 360               | 20      | 184                    | 2.04   |
| R6      | 5              | 480               | 20      | 206                    | 2.15   |
| R7      | 3              | 30                | 20      | 103                    | 1.93   |
| R8      | 3              | 10                | 20      | 67                     | 1.65   |
| R9      | 3              | 90                | 20      | 136                    | 1.65   |
| R10     | 3              | 360               | 40      | 188                    | 2.01   |

TABLE 6.1: The depth of each corrosion pit on the front and reverse sides of the fine ground gauge section of the fatigue sample AFTX-124. The parameters used to produce each pit using the droplet cell technique are also given for reference.

<sup>1</sup> Measured by LCSM

surfaces, respectively. The geometries of the corrosion pits created are given in Tables 6.1 and 6.2 along with the NaCl droplet volume, polarisation time and current applied.

#### 6.2.3 Fatigue Testing and Optical Microscope Rig Set-up

Constant stress amplitude fatigue cycling [113] of the pitted specimens was performed using an Instron 8801 fatigue testing system with a 100 kN load cell and metallic loading pins. From an earlier Kitagawa-Takahashi plot (Fig. 2.26), reported by Turnbull et al. [147], the stress range  $\Delta\sigma$  required for failure due to crack initiation and growth at a corrosion pit of a given depth was already known. Testing at a lower stress may result in no cracks initiating from the smaller corrosion pits where the stress concentration factor is lower compared to the larger corrosion pits. As such, both fine-ground and shot peened samples were tested with a sinusoidal waveform with an  $F_{max}$  corresponding to 85%  $\sigma_{0.2}$ ,<sup>2</sup> resulting in a  $\Delta\sigma$  of 634.18 MPa. A stress ratio of R = 0.1 and cyclic frequency of 5 Hz to 20 Hz was used; previous work with this SS alloy reported no significant effect of

<sup>&</sup>lt;sup>2</sup>The mechanical properties of FV566 SS were included in Table 2.2 earlier.

| Pit ID  | Droplet volume<br>(µl) | Polarisation time<br>(min) | Current<br>(µA) | Pit depth <sup>1</sup><br>(µm) | Aspect<br>ratio |
|---------|------------------------|----------------------------|-----------------|--------------------------------|-----------------|
| Front   |                        |                            |                 |                                |                 |
| F1      | 3                      | 5                          | 40              | 66                             | 1.77            |
| F2      | 3                      | 30                         | 20              | 107                            | 2.75            |
| F3      | 5                      | 360                        | 40              | 161                            | 1.55            |
| F4      | 3                      | 120                        | 40              | 216                            | 1.78            |
| F5      | 5                      | 600                        | 40              | 232                            | 1.83            |
| F6      | 3                      | 15                         | 40              | 51                             | 1.13            |
| Reverse |                        |                            |                 |                                |                 |
| R1      | 3                      | 60                         | 40              | 145                            | 1.04            |
| R2      | 3                      | 90                         | 40              | 184                            | 1.85            |
| R3      | 3                      | 180                        | 40              | 100                            | 1.42            |
| R5      | 3                      | 300                        | 40              | 221                            | 2.01            |
| R6      | 5                      | 420                        | 40              | 218                            | 1.58            |
| R7      | 3                      | 540                        | 40              | 157                            | 1.66            |

TABLE 6.2: The depth of each corrosion pit on the front and reverse sides of the shot peened gauge section of fatigue sample AFTX-88. The parameters used to produce each pit using the droplet cell technique are also given for reference.

<sup>1</sup> Measured by LCSM

frequency on fatigue life [39]. Although a higher  $\Delta\sigma$  of close to 700 MPa was reported for failure of the shot peened samples by Turnbull et al. [147] (Fig. 2.26), it was hoped that the chosen  $\Delta\sigma$  would be high enough to initiate cracks, although they would become non-propagating, and thus still inform about crack initiation location.

WaveMatrix software from Instron was used to program the testing method and incorporate an electrical voltage signal every 3600 cycles that was monitored in a LabVIEW program (Fig. 6.3). This would send a trigger signal to the digital camera to capture an image. A National Instruments USB-6009 DAQ device was used to monitor the voltage that was being sent from the Instron's analogue output port. Once the voltage signal went above a threshold value (5 V), the output of the comparison function switched from 'false' to 'true'. The Boolean crossing function would detect this transition at its input and as a result would move and click the computer mouse to trigger the camera shutter within Sony's Remote Camera Control software and increase the image counter by one. This programme allowed for automation of image capture at F<sub>max</sub>.

For image capture, an SP80 Metallurgical optical microscope from Brunel, UK, was



FIGURE 6.3: Screen capture of the LabView programme that was used to track and trigger camera images comprising of (A) block diagram view and (B) front panel view.



FIGURE 6.4: The optical microscope mounted to an x–y–z stage to allow direct observation and image capture of a corrosion pit during a fatigue test. The fatigue sample geometry is shown in Fig. 6.2.

machined to remove the mechanical stage and base and mounted on its side on to an xy-z micro-translation stage from Edmund Optics, UK. A custom-built platform allowed the microscope and translation stages to be attached to the Instron 8801;  $5 \times$  or  $10 \times$  long WD Mitutoyo objective lenses provided observation of a selected pit through the microscope. A Sony Alpha A77 II digital camera was connected to the camera for digital image capture during fatigue tests. The complete setup is shown in Fig. 6.4.

The fatigue tests, once started, were only interrupted and ended once a crack around  $10 \,\mu\text{m}$  to  $50 \,\mu\text{m}$  was visible from the chosen corrosion pit being observed with the microscope.

#### 6.2.4 Post-Fatigue Analysis

Once embryonic cracks had been observed to initiate from the corrosion pits, the fatigue test was interrupted and micrographs of each pit were captured with a TESCAN MIRA3 scanning electron microscope (SEM).

In order to be able to capture information relating to the crack initiation sites below the surface of the pits, two analysis techniques were employed; one non-destructive and one destructive. The benefit of these successive techniques was that the non-destructive XCT scans could be used as a 3D map to visualise and measure the volume of material to be extracted with the destructive PFIB technique. Both techniques required that the fatigue specimen be reduced in size in order to achieve a high enough resolution to be able to resolve the features of the crack in the results.

#### X-ray computed tomography

The use of X-rays allows the sub-surface structure and features of a corrosion pit or crack to be seen on the radiographs captured. The background details of XCT were given in Section 3.4.1 and this section focuses on how samples were prepared for each XCT scan performed.

As the voxel size (a three-dimensional pixel) and blurring of the data set is dependant on the ability to reduce the distances between the source, object and detector, it is desirable to minimise the dimensions of the object.

Initially, to begin to reduce the sample size, the gauge section from the fatigue sample was removed using electrical discharge machining (EDM); this is shown in Fig. 6.5A. These samples were used for 'macro-' XCT scans on two Nikon systems—an XTEK XTH 225kV and High Flux Nikon XTEK bay which were maintained and calibrated by Nikon engineers. The parameters used for each scan and resulting approximate voxel size are given in Table 6.3.

To achieve a higher resolution (smaller voxel size), the sample dimensions needed to be reduced further. In order to do this, a 3D-Micromac microPREP (microscopy preparation) was employed to extract cylinders around each corrosion pit. Using ultra-short



(A) Macro-XCT

(B) Micro-XCT

FIGURE 6.5: (A) Fatigue sample after 1 mm slices of the gauge section had been removed from the bulk specimen by EDM for macro-XCT. (B) Cylinder (diameter of  $500 \,\mu$ m) extracted with laser cutter from samples in (A) around each individual corrosion pit. Each cylinder was mounted on an Al rod and held by a pin vice base on the micro-XCT stage.

| Step           | Settings                      | А      | В      |
|----------------|-------------------------------|--------|--------|
|                | Source                        | W      | W      |
|                | Voltage (kV)                  | 140    | 220    |
|                | Current (µA)                  | 43     | 23     |
|                | Power (W)                     | 5.2    | 5.1    |
| Acquisition    | Exposure time (s)             | 1.42   | 1.42   |
| -              | Filter material               | Cu     | Al     |
|                | Filter thickness (mm)         | 0.25   | 2      |
|                | Source-sample distance (mm)   | 75.46  | 53.03  |
|                | Source-detector distance (mm) | 967.32 | 942.50 |
|                | Voxel size (µm)               | 9.907  | 5.627  |
| Reconstruction | Beam hardening                | 0      | 0      |
|                | Noise reduction               | 0      | 0      |

TABLE 6.3: Nikon systems data acquisition settings

| Power            | 2 W                                   |
|------------------|---------------------------------------|
| Spot diameter    | 10 µm                                 |
| Pulse distance   | 15 µm                                 |
| Line distance    | 5 µm                                  |
| Scan regime      | Layer by layer                        |
| Vector direction | Bidirectional                         |
| Area dose        | $40 \mathrm{pulses}/\mathrm{\mu m}^2$ |
| Number of layers | 30                                    |

TABLE 6.4: Laser cutting parameters for 3D-Micromac microPREP used to produce cylinders for XCT and ablate part of the cylinder prior to PFIB.

and high energy pulses, it is possible to ablate many kinds of materials, including SS, at a high rate while restricting the depth of the heat affected zone (HAZ) to  $<1 \mu m$  [266– 268]. Initially, a  $1 \text{ mm} \times 1 \text{ mm}$  square section was cut around each corrosion pit from the EDM prepared gauge section with an automatic metallographic abrasive cutting machine. Each square section was then mounted onto an SEM stub to allow laser preparation in the chamber of the microPREP. A cylinder is the ideal shape for XCT as it gives near uniform transmission to X-rays during rotation through 360°. Therefore, a 'pillar' recipe was used in conjunction with the parameters given in Table 6.4 to produce a cylinder measuring 500 µm in diameter with a single corrosion at the centre of the top surface as shown in Figs. 6.5B and 6.6.

The 500  $\mu$ m diameter pillars enabled the object to detector distance to be minimised for the 'micro-' XCT scans on the Zeiss VersaXRM520 as shown in Fig. 6.7. In addition, optical magnification on this system allowed further reduction of the voxel size to <1  $\mu$ m using the parameters given in Table 6.5. To confirm the actual resolution achieved in an XCT scan, a JIMA resolution chart can be placed into the position of the object and a radiograph of the chart captured using the same settings with which the sample will be imaged. Part of a JIMA chart is shown in Fig. 6.8A with the graduations getting progressively closer. When a line probe is performed along the length of the chart (Fig. 6.8B), it is possible to see the peaks and troughs which correspond to crossing graduation marks. The difference in greyscale value is still discernible to around 850 pixels along the line probe. This results in a real resolution of between 1  $\mu$ m and 2  $\mu$ m for a 0.566  $\mu$ m voxel size.

The reduced voxel size allows better resolution of the object being scanned as it is



FIGURE 6.6: Metal cylinder (suitable for micro-XCT scans) extracted from the gauge section of the fatigue samples by microPREP laser system. The cylinder has final dimensions of height equal to 1 mm and a diameter of 500 µm. (A) Optical image of the cylinder surface and corrosion pit mouth.
(B) An image showing the metal cylinder reconstructed and segmented from XCT data.



FIGURE 6.7: View inside the cabinet of a Zeiss VersaXRM520 X-ray CT scanner. (A) The position of the source, object and detector. (B) A magnified view of the object next to the detector.

| Step           | Settings                      | С           | D           |
|----------------|-------------------------------|-------------|-------------|
|                | Source                        | W           | W           |
|                | Voltage (kV)                  | 80          | 150         |
|                | Power (W)                     | 7           | 10          |
|                | Exposure time (s)             | 37          | 220         |
| Acquisition    | Filter                        | LE4         | HE2         |
|                | Binning                       | 1           | 1           |
|                | Optical magnification         | $10 \times$ | $20 \times$ |
|                | Source-sample distance (mm)   | 37          | 30          |
|                | Source-detector distance (mm) | 41          | 33          |
| Reconstruction | Voxel size (µm)               | 1.144       | 0.566       |
|                | Beam nardening                | 0.55        | 0.55        |

TABLE 6.5: Zeiss Versa XRM520 data acquisition settings



FIGURE 6.8: (A) Radiograph of 2D JIMA resolution chart with the line probe region in red. (B) Line probe across JIMA chart. Each trough represents crossing one black band in the JIMA chart. Actual resolution between  $1 \,\mu\text{m}$  and  $2 \,\mu\text{m}$ .



FIGURE 6.9: (A) Line probe path on radiograph starting in the corrosion pit and ending in the metal. (B) A plot of grey values across the line probe.

possible to distinguish between points that are closer together. In order to separate the components out though, the image must be segmented into relevant groups, often based on their greyscale value. Segmentation is the process of identifying the discrete phases that exist in an image<sup>3</sup> and separating these into individual regions of interest. If the object scanned by XCT contains just two high-contrast phases, then the histogram of the data will contain two well-defined peaks separated by a valley. This allows the grouping together of regions due to a distinctive greyscale value corresponding to the unique adsorption of each phase. Problems arise when these peaks are overlapped or are over a broad range as defining the boundary between each region is more difficult. A line probe passing through the corrosion pit (A) and metal (B) is shown in Fig. 6.9A, highlighting the effect of a broad distribution of intensity values. The corrosion pit has intensity around 10000 and the metal is above 40 000 (Fig. 6.9B). There is also an intermediate region between the two phases containing a broad range of greyscale values that are difficult to allocate to a specific label based on greyscale thresholding alone.

Software is available to assist with the segmentation process and Thermo Scientific Avizo 9.7.0 was used to analyse the XCT and PFIB data in this project. Avizo is a leading high-performance 3D visualisation and analysis package allowing state of the art image data processing, exploration and analysis of features contained within an intuitive work-flow and easy to use graphical interface (Fig. 6.10).

<sup>&</sup>lt;sup>3</sup>A stack of 16-bit TIFF radiographs in this project with greyscale values ranging from 1 to 65536.



FIGURE 6.10: Screen captures of (A) Avizo 9.7.0 Graphical User Interface. (B) Avizo segmentation editor



FIGURE 6.11: Avizo segmentation flow chart.

The radiograph sequence is loaded into the work-space of Avizo and different modules are applied to the data-set in order to assign the voxels of different regions to each particular material label. The radiographs of the pillars had two main regions of interest; the metal and the corrosion pit, so two material labels were used. Due to the transition region between the metal and the pit (see Fig. 6.9) it was not possible to use only a simple thresholding selection to define each region. Therefore, a watershed segmentation routine was developed to mark initial seed points in each region and then 'flood' the regions until they reach the watershed line. The process is shown in the flow chart of Fig. 6.11 and this would assign voxels of the metal phase to one material label. After this, the lasso tool was used to capture voxels that represented the corrosion pit by marking the intersection between the top surface of the pillar and the air.

#### **Plasma Focused Ion Beam**

To further investigate the location of crack initiation at a corrosion pit, a volume of material was milled using an FEI Helios PFIB Dual Beam FIB-SEM. This destructive technique follows an automated routine of sequential rocking-milling and SEM imaging through the 'Slice and View' programme within the FEI software. A major benefit of using a Xe<sup>+</sup> beam over a Ga<sup>+</sup> beam is the increased material removal rate [195], which in turn allows a larger volume of material to be examined. For this reason, it was possible to slice through all of, or a large proportion of the pit, as well as the crack. Ultimately allowing better visualisation of the crack position relative to the corrosion pit wall.

The largest and smallest corrosion pits from the ground specimen were chosen as a comparison due to the differing ARs.<sup>4</sup> The larger pit was deeper than it was wide and the smaller pit was the opposite, corresponding to ARs of 2.27 and 1.67, respectively; the AR would equal 2 when pit width equals pit depth. From the XCT scans, it was known that a pixel size in the range of 30 nm to 50 nm was needed to see the cracks. The secondary electron (SE) SEM image was  $6144 \times 4096$  pixels, so this limited the horizontal field width (HFW) to a maximum of 300 µm. As the pillar containing the largest pit, shown previously in Fig. 6.6, was greater in size than the maximum HFW, the pillar needed to be further reduced in size. It is also advisable to limit the total number of slices in the project to around 400 and with the intention of keeping the slice thickness in the range 200 nm to 250 nm, the total milling distance was limited to around 100 µm. Ultimately, this meant that the entire volume of the largest pit could not be milled without making alterations to the operating parameters. Interest was, however, mainly focused on the relationship between the crack and the corrosion pit wall, so this was not seen as an issue. To reduce the size of the pillar, so as to be suitable for PFIB, the 3D-Micromac microPREP was used to ablate a segment of the metal and corrosion pit. This would leave a rough front face within the pit, from where the PFIB milling would begin, as can be seen in Fig. 6.12. The reduced dimensions of the smaller pit meant that the whole pit could be milled using the same parameters as for the larger pit. As a consequence, the microPREP was used to ablate a segment of the pillar so that the face it produced was close (10  $\mu$ m) to the crack tip. It was desirable to be as close to the crack tip as possible so to avoid milling through material containing no useful information.

Once the pillars had been machined with the microPREP, they were prepared for PFIB

<sup>&</sup>lt;sup>4</sup>See Section 5.3.1 for the definition.



(B)

FIGURE 6.12: (A) Top surface view and (B) Cross section view at  $52^{\circ}$  after laser cutting the largest pit. The inset image shows the surface crack with a length of  $33 \,\mu$ m.



FIGURE 6.13: Secondary electron image of the smaller corrosion pit with front face and side trenches prepared by PFIB milling to create a block for serial sectioning. A platinum layer protects the area of interest and minimises curtaining effects. The tracking fiducials are visible at the back of the block to assist placement of the milling location.

within the instrument's chamber. A high current Xe<sup>+</sup> beam cut a front trench and produced a clean cross section view. Trenches were also milled on either side of the pit to prevent shadowing in images due to re-deposition of expelled material during the slicing process. Following this, a platinum layer was deposited over the region to be milled to protect the structure beneath and limit the amount of the vertical curtaining effect (discussed in Section 3.2.3). A fully prepared block containing the smaller corrosion pit is shown in Fig. 6.13.

# 6.3 **Results and Discussion**

## 6.3.1 Controlled Growth of Corrosion Pits

With the ability to produce corrosion pits with depths ranging from  $50 \,\mu\text{m}$  to  $225 \,\mu\text{m}$  using the droplet technique (Chapter 5), a number of pits were made along the gauge section of the ground and shot peened fatigue specimens. The location of each corrosion pit along the 20 mm gauge section can be seen in Figs. 6.14 and 6.15. Due to the random nature of pitting corrosion, the pits were not guaranteed to nucleate in the centre of the

droplet, hence it can be observed that some pits are further away from the central line than others. The microtopographical roughness around each pit mouth can be seen in the SEM images presented in the sub figures encircling the central image. These features act as local stress concentrations and preferential sites for cracks to initiate.

#### 6.3.2 Crack Growth from Fatigue Testing

The fatigue tests were carried out on ground and shot peened fatigue specimens (as described in Section 6.2.3) and interrupted when a crack(s) had nucleated from the corrosion pit being observed. The first cracks were observed after 3600 cycles and 111 600 cycles for the ground and shot peened samples, respectively. The effect of the compressive residual stress layer from shot peening at resisting crack nucleation is clearly evident (see Section 2.4.6).

Figures 6.16 and 6.17 show micrographs of the observed corrosion pit before and after fatigue cycling; the white arrows represent the sites where cracks initiated.

As cracks had initiated within the first 3600 cycles for the ground specimen (Fig. 6.16), it is not possible to present any data on the rate of growth of these cracks. However, it was possible to measure the length of cracks that had initiated from each corrosion pit by capturing images at  $F_{max}$  at the end of fatigue testing, i.e., after 3600 cycles. From Fig. 6.18, it can be observed that cracks had initiated on both the left and right hand sides of each corrosion pit on the front face of the fatigue specimen (corresponding to pits F1– F6 in Table 6.1). For corrosion pits up to a depth of 103 µm, the cracks grew to around 10 µm in length on the surface. Two of the pits with depth of 160 µm grew slightly larger cracks ranging from 24 µm to 37 µm. The other pit with similar depth exhibited slightly different crack initiation behaviour as the right hand side crack dominated, growing to a final length of 87 µm with the left hand side crack only growing to 13 µm. This could be due to the subsurface morphology of the pit not being hemispherical; creating a localised stress/strain region that would favour crack initiation.

The topography generated by shot peening obscured the crack path in each micrograph (Fig. 6.17), making it hard to observe when a crack had nucleated. To be sure that a crack had nucleated at the corrosion pit, the cycling was continued beyond the



 $\label{eq:Figure 6.14: Optical micrograph of 20\,mm\times4\,mm fine ground fatigue gauge section with SE SEM images of each corrosion pit.$ 



(C) F1

 $\label{eq:Figure 6.15: Optical micrograph of 20\,mm\times4\,mm \ shot \ peened \ fatigue \ gauge \ section \ with SE SEM \ images \ of \ each \ corrosion \ pit.$ 



FIGURE 6.16: Optical micrographs at  $F_{max}$  of a corrosion pit on a fine ground surface (A) before fatigue cycling and (B) after 3600 cycles with white arrows indicating initiated cracks.



FIGURE 6.17: Optical micrographs at  $F_{max}$  of a corrosion pit on a shot peened surface (A) before fatigue cycling and (B) after 111600 cycles with white arrows indicating initiated cracks.



FIGURE 6.18: Left and right hand side crack lengths vs pit depth from corrosion pits F1–F6 of the ground fatigue specimen. Crack lengths measured from micrographs captured at  $F_{max}$  at the end of fatigue testing.

point at which it was first thought a crack had initiated, with an image being captured every 3600 cycles. The complete sequence of images was aligned using the TurboReg FIJI plugin [269] and could be viewed in reverse to identify the crack initiation position. For this sample, one crack initiated on either side of the corrosion pit. The crack on the left hand side appears to nucleate first; within the first 3600 cycles. It continues to grow over the next 21 600 cycles at a rate of 3.64 nm/cycle before arresting at a length of 92 µm due to the crack reaching a microstructural barrier. Examples of such barriers are grain or twin boundaries, non-metallic inclusions or other precipitates or second-phase particles, each contributing towards a reduction in the crack growth rate (CGR) of short cracks [110, 270].<sup>5</sup> After 14 400 more cycles, the microstructural barrier is overcome allowing continuation of crack propagation, until it ultimately reaches a final crack length of 173 µm after 111 600 cycles at a rate of 1.07 nm/cycle. The growth of the crack is represented graphically as the blue line in Fig. 6.19.

The crack on the other side of the pit is not visible on the surface until 64800 cycles

<sup>&</sup>lt;sup>5</sup>The martensitic microstructure of this FV566 SS alloy was presented in Fig. 4.1. The lathe structure essentially provides a very high number of grain boundaries.



FIGURE 6.19: Crack length vs number of cycles for the two cracks growing from a corrosion pit in shot peened FV566 SS.

have completed. It can then be seen at 93  $\mu$ m from the edge of the corrosion pit, suggesting that this crack initially grew subsurface or its path was obscured by the topography of the shot peening. Over the next 39 600 cycles, the crack grew a further 10  $\mu$ m before a larger increase in crack length to 136  $\mu$ m, at which point the test was stopped.

#### 6.3.3 X-ray Computed Tomography

The XCT scans produced a stack of 2D radiographs, reconstructed by VG Studio and CT Pro software into a .TIFF image sequence. To segment and visualise the data, the complete data set was loaded into Avizo 9.7.0 on a Dell Precision Tower 7910 PC, with Intel Xeon CPU E5-2687W 10 core processor and 256 GB RAM.

The first macro-XCT scan was of the pitted dog bone sample prior to fatigue testing (Setting 'A' in Table 6.3). The raw data set, shown in Fig. 6.20A, consisted of 2254 slices at a bit depth of 16 bit, occupying 33 GB of memory. To reduce the data set size, and therefore processing time, a region of interest (RoI) containing the square fatigue cross section was cropped from the data set. The two ends of the data set were also cropped to remove possible edge effects, which left a volume with a physical size of  $4.3 \text{ mm} \times 4.3 \text{ mm} \times 20 \text{ mm}$  stored in 730 MB of memory as shown in Fig. 6.20B.



FIGURE 6.20: (A) The original XCT radiographs of 2254 slices and data size of 33 GB. (B) Cropped data measuring  $4.3 \text{ mm} \times 4.3 \text{ mm} \times 20 \text{ mm}$  and 730 MB in size. Voxel: 9.907 µm.

Following the processing routine in Fig. 6.11, it was possible to segment the metal gauge section from the surrounding air due to the different greyscale values of the two phases. This generates the surface view shown in Fig. 6.21A, where the location of each corrosion pit can be seen in the surface despite the relatively large voxel size (9.9 µm). The large voxel size becomes more apparent when one of the corrosion pits was viewed from within the metal volume as shown in Fig. 6.21B. The pit wall is constructed of block like, sharp segments corresponding to each voxel, rather than a smoother profile that was expected. This internal view of the largest pit also reveals the complex geometry of the corrosion pits produced by the droplet method that is missed with line of sight techniques such as laser confocal scanning microscopy (LCSM). The pit in the foreground (F6 in Table 6.1) consists of a primary pit with a larger secondary pit that appears to have initiated at the base. The other pit shown (F5 in Table 6.1) has a similar complex structure but with a smaller secondary corrosion pit.

This complex coupling of corrosion pits makes predicting crack initiation locations more difficult due to the presumed variation in localised stress and strain concentrations this would cause. Some authors [150, 182] have reported stress and strain localisation due to the peak and trough features attributed to microtopography, so it is assumed a



FIGURE 6.21: (A) Surface view of the segmented gauge section showing the sites of the corrosion pits. (B) An internal view of the metal surface showing the complex geometry of corrosion pits produced from the droplet technique.

secondary pit would only exacerbate the severity of these and make predicting the location of fatigue crack initiation challenging. Consequently, caution should be exercised when only taking measurements from FE analysis using idealised smooth shaped pits as they may not give similar results if the real corrosion pits contain a significant number of large features [177, 271, 272].

After the fatigue test had been completed, a second XCT scan was performed using settings 'B' in Table 6.3. This scan was performed on a reduced gauge section in Fig. 6.5A that was extracted by EDM in order to improve the obtained pixel size by reducing the distance between objects (source, sample and detector).

As per the first XCT scan, the collected data set was cropped in Avizo to reduce the overall file size and computational time. An example of the radiographs obtained from this scan is given in Fig. 6.22 which shows the  $4 \text{ mm} \times 1 \text{ mm}$  EDM extracted gauge section. Due to the differences in attenuation coefficients between the metal and the surrounding air, the metal corresponds to the areas of high intensity (white) and the darker areas represent the air. The dark pore within the metal shows the location of a corrosion pit within the metal.


FIGURE 6.22: Radiograph of cropped data set from XCT scan of part of the ground gauge section removed by EDM. The dark spot corresponds to a corrosion pit in the metal.

Following the processing routine, the selected voxels corresponding to the metal phase were added to the matching label in the segmentation editor of Avizo. Any unassigned voxels within the boundary of the metal could then be allocated to the corrosion pit labels. Additionally, due to the spacing between the corrosion pits, it was possible to segregate the slice range related to each pit. This made it possible to highlight the location and geometry of each pit (Fig. 6.23). From using the label analysis function in Avizo, the volume of each corrosion pit could be calculated from the individual pit labels shown in Fig. 6.24. These reconstructed images of each corrosion pit provide a much clearer representation of the true size and morphology of each corrosion pit compared to LCSM. The corrosion pits on the top row are hemispherical in shape and only the pit in (C) begins to show some undercutting. The corrosion pits on the bottom row of Fig. 6.24 have much more complex geometry. The images show that it is possible for secondary corrosion pits to nucleate towards the base of the initial corrosion pit; similar to early observations made by Ernst and Newman [57]. This could be due to the dissolution of an inclusion near to the pit wall or a localised concentration of the applied current initiating further pits. Clearly, the LCSM would omit data relating to these undercutting parts of the corrosion pit as they are not visible from directly above the pit mouth. This will have an impact on estimating the volume of corrosion pits and also any assumption about the pit geometry that may be used within FE methods.

The volume of each corrosion pit can also be calculated from first principle using Faraday's law and the current and time data from Table 6.1. The theoretical volumes of



FIGURE 6.23: Part of the gauge section of the ground fatigue specimen segmented in Avizo to highlight the location and size of the corrosion pits, each represented in a different colour.



FIGURE 6.24: (A–F) Reconstructed images of each segmented corrosion pit from the ground fatigue specimen captured with macro-XTC system. They correspond to F1–F6 shown in Fig. 6.23 with geometry given in Table 6.1.



FIGURE 6.25: Experimentally measured and theoretical corrosion pit volumes vs applied charge, where the current used was  $20 \,\mu\text{A}$  or  $40 \,\mu\text{A}$ .

each corrosion pit were calculated using Eq. (6.1), where *I* is current, *t* is time, *M* is molar mass, *z* is the number of electrons transferred per ion, *F* is Faraday's constant and  $\rho$  is density.

Volume of oxidised material 
$$=$$
  $\frac{ItM}{zF\rho}$  (6.1)

This yields a linear relationship between applied charge,  $Q(I \times t)$  and volume of oxidised material. However, this calculation does not account for corrosion products formed from the corrosion process or the time taken for the necessary diffusion of ions within the electrolyte system. Furthermore, any corrosion occurring away from the dominant pit will also draw charge without contributing to the calculated volume. Combining a plot of this relationship with the volume of each segmented corrosion pit from macro-XCT, it can be seen that pit volumes are underestimated by the calculated volumes from XCT (Fig. 6.25).

Additionally, the pit volume was calculated from the height maps generated by LCSM. At the lower applied charges (0.006 C and 0.054 C), the calculated pit volume is very similar to the volumes calculated from the XCT data. This is due to the total volume of the corrosion pit being directly beneath the corrosion pit mouth, so the line-of-sight LCSM



FIGURE 6.26: A 2D corrosion pit profile is represented by the red dotted line and the solid black line shows the pit profile measured by LCSM as it is a line-of-sight technique. The shaded red area highlights the pit volume that is missed by LCSM measurements.

is able to capture all this information as it is not obscured. However, when the corrosion pits begin to undercut around the corrosion pit mouth (Figs. 6.24C to 6.24F) these regions cannot be 'seen' by the primary beam from the LCSM so the pit's volume is smaller than its actual volume (Fig. 6.26). As a consequence, the difference in pit volume between macro-XCT and LCSM is lowest at small applied charge ( $\leq 0.054$  C) and greater at higher passed charge ( $\geq 0.216$  C).<sup>6</sup>

While these XCT scans reveal important details about the pit morphology below the surface, no information was obtained relating to the cracks observed during fatigue testing (Figs. 6.16B and 6.17B).

To further reduce the pixel size, improving the resolution of topographical features around the pit and associated cracks, the samples dimensions were downsized from the  $4 \text{ mm} \times 1 \text{ mm}$  gauge section. Cylinders were extracted around each corrosion pit on the gauge section using a microPREP to give a final diameter of 500 µm (Fig. 6.6). These samples were suitable for the Zeiss micro-XCT system and gave a pixel size of 1.144 µm (Settings 'C') or 0.566 µm (Settings 'D') depending on the optical magnification used.

To determine whether the cracks could be seen from these micro-XCT radiographs, a single XY plane was used. The radiograph plane was rotated/manipulated to align with the surface of the material and corrosion pit mouth as shown in Fig. 6.27. By identifying the unique features of each corrosion pit from the optical fatigue micrographs, it was possible to align the images by rotating the data set and pinpoint where cracks should be visible in each radiograph—indicated by red arrows in the figure. Despite the much reduced sample and pixel size. the cracks are still not visible in the raw radiographs of the

<sup>&</sup>lt;sup>6</sup>The applied charge at which undercutting is visible in the 3D reconstructions.



FIGURE 6.27: (A–C) Radiographs from pits F1, F3 and F6 respectively of each corrosion pit mouth with arrows indicating where cracks were visible with the in-situ optical microscope. Geometries given in Table 6.1.

corrosion pits. This is likely due to the effect of the fatigue cracks being closed in the absence of an applied load. As the fatigue samples had been tested in mode I loading, mode II or III deformation takes place due to the inhomogenous and anisotropic microstructure (Fig. 2.19). This results in local displacement and some crack propagation occurring out of the plane from the crack growth direction, varying upon the local microstructure. This asymmetry in deformation of the crack tip leads to a misfit of rough fracture surfaces due to the necessary arrangement of dislocations that would allow for volume rotation [273, 274].

As a comparison to the macro-XCT results, the data was again segmented into metal and pit labels by using the same segmentation routine as previously used. The generated surfaces (Fig. 6.28) show a greater level of detail relating to the microtopography of the corrosion pit profile.<sup>7</sup> The reduced pixel size should also produce a more accurate calculation of the volume of the corrosion pit due to the corrosion pit being represented by a larger number of voxels compared to the macro-XCT scans. These volumes are shown in Fig. 6.25 as '+' symbols and it was noted that in all three of the corrosion pits scanned with the micro-XCT system that the calculated volume is highest. A comparison between the calculated volumes from macro and micro-XCT scans shows that the measured volume can be up to 33.2 % larger, when measured by micro-XCT, in the case of the smallest corrosion pit (F1). This is likely due to the number of voxels that represent the corrosion pit. In the macro-XCT scan, the corrosion pit was represented by just a few hundred larger voxels, whereas in the micro-XCT scan the number was  $1000 \times$  more due to the

<sup>&</sup>lt;sup>7</sup>The reconstructed images from macro-XCT can be seen in Fig. 6.24.



FIGURE 6.28: Reconstructed images, from micro-XCT scans, of pillars containing a corrosion pit segmented in Avizo. (A) Pit F1 (B) Pit F3 (C) Pit F6.

much smaller voxel size giving a much more accurate calculation of the pit volume.

As a further comparison into the differences obtained in the volume of the corrosion pits, a free and open source piece of software, 3D Slicer [275], was also used to segment the XCT data. The software was created for the interactive segmentation and visualisation of medical images. However, the many tools and instruments available can also be applied to the XCT data sets in this project, although 3D Slicer's segmentation tools require a higher level of user decision and input to allocate voxels. The differences in calculated volumes between Avizo and 3D Slicer ranged from 6% to 50% for the 6 pits analysed from the macro-XCT system. This highlights the importance of ensuring a rigorous segmentation routine is followed to be confident in the accuracy of voxel allocation to each defined label.

The use of XCT to analyse crack initiation at corrosion pits clearly has some limitations. A great level of detail of the corrosion pit morphology can be obtained by using a sample with reduced dimensions and an advanced 3D X-ray microscope. However, due to the effect of the crack being closed in the absence of an applied load, it is not possible to capture radiographs containing information pertinent to the location of crack nucleation at corrosion pits even with a voxel size  $<1 \,\mu$ m. It may be possible to image a sample in a reduced field of view [263], however this would result in very limited information about the surrounding pit morphology. In order to achieve an understanding of the correlation between corrosion pits and fatigue crack initiation, further techniques were explored (see below) that provide a much greater level of resolution, although it was necessary to destroy the sample during these measurements.

#### 6.3.4 Plasma Focused Ion Beam

The non-destructive XCT scans provided a great amount of detail relating to the 3D morphology of each corrosion pit, as well as showing where secondary pits had initiated near the base of some pits. However, due to the closure of the fatigue cracks, cracks were not captured in any of the radiographs obtained. The use of PFIB ensures that the cracks will be observed as the resolution can be on the nanometre scale due to the SEM imaging of each sequential slice. PFIB serial sectioning also avoids mechanical damage, which would interfere with cracks that may otherwise be introduced by more traditional sectioning techniques [193].

The serial sectioning of the corrosion pit and associated crack produced a stack of SEM images which were aligned in Avizo using a least squares algorithm in the align slices module. When viewing the aligned slices in sequence, it was relatively simple for the human eye to track the crack path as the angle of any curtains<sup>8</sup> which would alternate in successive slices due to the rocking polish motion. The greyscale value of the crack and curtaining streaks were similar, making the use of an automated segmentation method difficult. Furthermore, applying a filter such as the fast fourier transform (FFT) filter, designed to remove periodic noise from the data, would minimise curtaining but also blur the crack, making it harder to identify. For these reasons, the segmentation was done manually using the brush tool with a greyscale mask to ensure that only voxels corresponding to the bright crack were selected.

First, the largest corrosion pit was examined (F6 in Table 6.1) as this pit had cracks of significant length initiate from the corrosion pit. The pit had an AR<sup>9</sup> of 2.27, meaning it was slightly deeper than it was wide. Due to the overall pit volume, only half of the corrosion pit could be imaged by PFIB within the recommended 400 slices, each being 250 nm apart. The schematic in Fig. 6.29, shows the geometry of the corrosion pit and the location of each PFIB image that was captured during the slice and view process. The letters shown refer to the subfigures in Fig. 6.30.

The sequence of SEM images is shown in Fig. 6.30 with each image being 12 slices

<sup>&</sup>lt;sup>8</sup>Due to the inhomogeneous nature of the material, the milling rate varies locally across the cut face. This creates vertical ripples or striations on the surface of the sample known as the *curtaining effect*.

<sup>&</sup>lt;sup>9</sup>See Section 5.3.1 for the definition.



FIGURE 6.29: Schematic diagram showing the volume of corrosion pit that was milled, from left to right, with PFIB. The dashed red lines and letters, indicate the position of captured SEM images that are shown in Fig. 6.30.

apart corresponding to a separation of  $3 \mu m$ . The slices begin within the pit, at the edge of the pit mouth. The undercut of the corrosion pit can be seen in the lower half of the image. The slices progress through the remainder of the pit and down the length of the crack towards the crack tip. In the SEM images, the rough microtopography of the pit wall is evident and appears to consist of many globular features.

The crack first becomes visible in Fig. 6.30C indicated by the arrow, in the remaining section of material between the surface and the undercutting corrosion pit. Clearly, the undercut feature will have an impact on the localised stress and strain in the remaining material. Previous FE analysis has shown that the strain can be localised to the pit shoulder/mouth [177, 182]. The slices progress through the remainder of the pit undercut, revealing more of the crack path between the surface of the material and the edge of the undercut. The crack path roughly follows the boundaries of the grains suggesting intergranular fracture which may contribute towards the retardation and propagation of crack growth observed during fatigue [109, 124]. In Fig. 6.30N, the very edge of the corrosion pit is captured as well as a short portion of the crack, again between the surface and the pit. However, the crack no longer fully extends between the surface and the wall of the pit undercut. It now is only visible a short distance above the pit, meaning that the crack tip lies somewhere below the surface. In the final two images, only a very small part of



FIGURE 6.30: A sequence of images, 3 µm apart, captured during the PFIB milling process starting close to the edge of the pit mouth. The fatigue crack first becomes visible in (C) at the location of the arrow. In subsequent images, the crack extends from the surface to the edge of the pit until (M). In (N) we reach the edge of the pit at its widest point and in the final two

images only the end of the crack is visible as we reach the crack tip.

the crack is visible, thought to be the crack tip.

From the sequence of images it is possible to deduce information regarding the length of the crack in relation to the amount of pit undercutting. The crack joins with the edge of the pit mouth on the surface, which allows us to use this position as a reference point. The pit undercut is visible in 152 SEM images correlating to a distance of 38  $\mu$ m. Given that the width of the pit was 180  $\mu$ m and assuming the same amount of undercutting around the entire pit mouth, this represents a significant proportion (~40%) of pit that is missed using a line of sight measurement technique such as LCSM. The crack tip can be seen beyond the end of the corrosion pit giving a total crack length of 41.5  $\mu$ m, with the final 6.25  $\mu$ m of crack being below the surface.

By tracing the crack path, visible in each slice, in the segmentation editor of Avizo, it is possible to produce a reconstruction of the crack in 3D. Additionally, the segmented corrosion pit volume from XCT can be overlaid with this data set to show the relationship between corrosion pit and crack path (Fig. 6.31).

From the surface view of the reconstructed corrosion pit and crack, it can clearly be seen that the crack path is tortuous and is deflected around the microtopograhical features of the corrosion pit wall. The location at which the crack has initiated is also easier to visualise compared to the sequence of PFIB-SEM images in Fig. 6.30. The crack is located between the pit mouth/shoulder and the widest part of the corrosion pit undercut, suggesting that it also initiated somewhere within this region. These observations are comparable to those described in [157, 177] for stress corrosion cracking (SCC) in much larger corrosion pits, the shoulder/mouth of the pit was identified as the crack initiation location was attributed to the pit mouth having the highest localised strain for a "bullet-shaped" pit, i.e., an AR > 2.

To establish if the AR of a corrosion pit affects the crack initiation location, a second corrosion pit was chosen with a differing AR. The smallest corrosion pit (F1 in Table 6.1) offered a smaller AR, compared to the previous corrosion pit, of 1.67, meaning this pit was slightly wider than its depth. Additionally, due to the width and depth both being



FIGURE 6.31: Images of the volume of corrosion pit, F6, (red) and crack (green) that were milled using PFIB. The surface view of the corrosion pit was generated from segmented XCT data and overlaid with the surface view of the crack. (A) An angled view of pit and crack. (B) View down the axis of applied load. (C) View down the crack growth direction.



FIGURE 6.32: Reconstructed XCT surface showing a crack growing from the shoulder region of a corrosion pit due to SCC. The image is best considered as being viewed from inside the steel [157].



FIGURE 6.33: Schematic diagram showing the volume of corrosion pit that was milled, from left to right, with PFIB. The dashed lines indicate the position of captured SEM images. The red lines correspond to Fig. 6.34 and the blue lines are Fig. 6.35.

less than 100 µm, the total volume of corrosion pit could be examined in one PFIB measurement using a slice thickness of 200 nm to mill a total Z-distance equal to  $105.2 \,\mu$ m. The prepared PFIB block of the smaller corrosion pit was shown earlier in Fig. 6.13. The front face is perpendicular to the cracks that had initiated from the corrosion pit, meaning that the milling direction was directly down the crack path to maximise the number of slices within which the crack was detected. The schematic diagram in Fig. 6.33, shows the geometry of the corrosion pit and the location of each PFIB image that was captured during the slice and view process. The dashed lines show the locations at which SEM images were captured, with the red group corresponding to Fig. 6.34 and the blue group Fig. 6.35.

Sequences of SE images from the PFIB milling process are given in Figs. 6.34 and 6.35, each sequence focusing on one location of observed fatigue crack initiation on either side of the corrosion pit. The pixel size of the SE images was  $\sim$ 50 nm—one order of magnitude greater than the resolution achieved when using XCT.

The slices from the first sequence begin within the material's metallic microstructure, milling progresses towards the edge of the corrosion pit. After a Z-distance of  $11.8 \,\mu$ m, only the microstructure of the material can be observed (Fig. 6.34A). The edge of the corrosion pit undercut starts to become visible in the very next slice and is more apparent



FIGURE 6.34: A sequence of SE images captured during the PFIB milling process of the smaller corrosion pit. The sequence commences in the metal's microstructure, next to the edge of the undercut of the corrosion pit and progresses down the expected crack growth direction towards to pit mouth. The Z distance from the first slice is indicated within each sub-figure.

after a total milling distance of  $13.8 \,\mu$ m, as shown in (Fig. 6.34B). Further milling into the main volume of the pit reveals its complex morphology which is strongly defined due to the deposited layer of platinum filling the corrosion pit cavity.

At a Z-distance of 18.8  $\mu$ m, a dark rectangular region begins to appear between the undercutting corrosion pit and the surface of the material, at 19.8  $\mu$ m, this is a very distinctive rectangular box (highlighted by the red rectangle in the figure). While this feature does not have the same bright appearance or width as the crack shown from the larger corrosion pit, it is believed that this is the crack on the edge of the pit. This can be justified by comparing the milling distance to the SEM images of the corrosion pit during PFIB. The distance milled from when this dark region appears to the edge of the corrosion pit mouth, is 4  $\mu$ m and is approximately equal to the length of the crack as measured from the optical images captured at  $F_{max}$ . The reason for the lack of contrast within this region is unclear. The dark appearance suggests that the SEs ejected by ionisation arising from the impact of the primary electron beam have not reached the SE detector producing the



FIGURE 6.35: A sequence of SE images captured during the PFIB milling process of the smaller corrosion pit. The sequence commences within the corrosion pit, at the edge of the mouth, with milling progressing in the direction of expected crack growth towards to the tip of the crack. The Z distance from the first slice is indicated within each subfigure.

dark region. Consequently, it was difficult to obtain accurate information about the tortuosity or width of this crack from the SE images. However, it was still possible to use the SE images to infer the position of the crack relative to the corrosion pit and estimate the length of the crack by looking at the number of slices in which this dark region is visible within. As observed in the large corrosion pit, with an AR of 2.27, the crack location is again located between the pit mouth/shoulder and the undercut of the corrosion pit. This suggests that for 'Narrow and deep' corrosion pits, where the AR is > 1, the same crack initiation location might be expected. The milling sequence also shows no evidence that a crack initiated near the base of the corrosion pit, as observed in a previous study of CF crack initiation and propagation in 12Cr SSs [140].

The SEM images of the majority of the corrosion pit ( $Z = 22 \,\mu\text{m}$  to  $86 \,\mu\text{m}$ ) contain no evidence of any crack initiation, so they are not included here. As there were two cracks visible in the optical micrograph of the fatigue sample under load, a second crack was expected to become visible as the milling progressed beyond the mouth of the pit as shown in Fig. 6.35.

These images are noticeably darker than the sequence of images presented from the start of the milling process. This is caused by redeposition of the milled material within close vicinity to the face to be imaged by the SEM, resulting in shadows on the surface. Wider and deeper front and side channels can be milled initially in order to minimise the effect of this. However, it is still possible to distinguish between the lighter region—the corrosion pit (again filled with platinum) and the material's microstructure surrounding it (darker region). In Fig. 6.35A, the edge of the corrosion pit was observed reaching the bright platinum surface towards the top of the image with the majority of the corrosion pit below. In the next three images (up to Fig. 6.35D), the sharpening of a very dark region in the upper left hand side of the image pertaining to be the crack can be observed (highlighted by the red rectangle in the figure). This is consistent with the location visible in the optical image and with a calculated length of 5 µm, it is similar in length to the crack length measured from the optical micrograph and the lack of contrast is the same as the previous sequence of images. Again, no evidence of any further crack initiation at other sites around the pit in the remaining sub figures of Fig. 6.35 is seen. This suggests that only the two cracks that were visible by optical observation, with the sample under load,

initiated between the mouth and undercut of this corrosion pit.

## 6.4 Conclusions

A number of conclusions can be made regarding the corrosion pit morphology, the location of crack initiation at corrosion pits under cyclic fatigue loading and the limitations of XCT and PFIB used to provide this information.

- Surface breaking fatigue cracks were observed optically with the sample under load, at corrosion pits with depths from 50 µm to 225 µm. The number of cycles to initiate these cracks was much larger for the shot peened material due to the effect of the compressive residual stresses on delaying crack initiation.
- CGR behaviour in shot peened material followed conventional observations with an initial period of fast crack growth until the crack arrests at a microstructural boundary. The crack growth then continues at a slower rate than before.
- Macro-XCT scans were used to identify the location of corrosion pits on the gauge section of the fatigue specimens. Additionally, the macro-XCT scans provided improved visual representation of the corrosion pit morphology and a more accurate measurement of pit depth and volume when compared to LCSM.
- The pits analysed in the current work, with depths up to 100 µm, did not display any characteristics of pit undercutting. Undercutting only became more apparent as the pit size increased beyond 100 µm. There was also evidence of secondary pit nucleation at the base of the largest corrosion pits generating a very complex pit morphology. This in turn would produce complex geometries for FE analysis of stress/strain localisation.
- The 3D-Micromac microPREP has been shown to be an essential tool in the preparation of microscale samples needed for XCT analysis. A method has been developed that produces a 500 µm pillar containing a single corrosion pit.
- The micro-XCT scans produced the most accurate measurements of pit volumes due to the pit being represented by a much larger number of voxels within the data

set.

- The cracks observed in the optical micrographs were not captured in the micro-XCT scans despite the sub-micron pixel size in some of the final scans. A JIMA resolution chart was used to show that the actual obtained resolution was between 1 µm and 2 µm when using a 0.566 µm voxel size.
- PFIB measurements were able to identify the location of the cracks from a large and small corrosion pit on fine ground material. The two pits had depths and ARs of 206  $\mu$ m and 52  $\mu$ m and 2.27 and 1.67, respectively, classifying them to have 'Narrow and deep' morphologies. An AR > 2 corresponded to a 'bullet' like profile where the pit depth exceeds to the pit mouth width. For the two ARs examined, the crack nucleation location was between the shoulder region of the pit and the widest point of the corrosion pit undercut.
- Further PFIB analysis needs to be performed in order to ascertain whether the crack initiation location is affected by the compressive residual stress induced by the shot peening procedure.

# Chapter 7

# General Discussion and Final Summary

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# 7.1 Introduction

The development of a methodology for the prediction of corrosion, pitting and fatigue failure of steam turbine blades is a significant challenge, which requires a multidisciplinary approach. As such, this project has involved developing an understanding of how the environment chemistry impacts upon corrosion pit initiation and growth, and fatigue and fracture mechanics concerning the development of cracks from corrosion pits. The research initially focused on two grades of 12Cr martensitic stainless steels (SSs), namely, 403 and FV566, which are widely used to manufacture steam turbine blades in the USA and Europe, respectively. Excursions in steam turbine chemistry pose a major challenge in predicting the overall corrosion response of the component,s which may lead to corrosion pit initiation and growth. The propensity for crack initiation at corrosion pits under fatigue cycling was investigated for the FV566 SS material using a range of characterisation techniques including X-ray computed tomography (XCT) and plasma focused ion beam (PFIB). Additional work was also undertaken that utilised digital image correlation (DIC) to measure the evolution of strain around a corrosion pit; the preliminary results are presented separately in Appendix B.

To develop the understanding of bulk corrosion chemistry, a variety of environments were assessed, see Chapter 4. The simulated steam turbine environments include a range of chloride concentrations, aiming to imitate the carefully controlled power plant water chemistry; as well as higher chloride concentrations expected during an excursion in water chemistry, due to an event such as a leaking seal. Additionally, the effect of two-shifting between off-load and on-load conditions was investigated as the change in oxygen concentration affected both the response of the corrosion potential and passive film composition. In order to study the crack initiation location at such corrosion pits, a method was chosen that allowed accurate recreation of these pits in a desired location, as discussed in Chapter 5. The corrosion pits were subject to fatigue loading, as described in Chapter 6, and a range of characterisation techniques were used to identify the crack initiation location. The main results can be found within each Chapter mentioned previously and this Chapter aims to collate the main findings from each and discuss them in relation to the main objectives and the research gaps identified from the literature review (Chapter 2).

## 7.2 Summary of Main Findings

A summary of the research gaps identified in the literature review and the corresponding outcomes of the research undertaken is presented here. The subsequent following sections, then discuss the main topics of investigation in greater detail.

- 1. The literature review highlighted that the critical chloride concentration [Cl]\* required to induce corrosion pitting in a steam turbine environment was not defined.
  - (a) Measurements of E<sub>corr</sub> and electrochemical noise (EN) analysis showed that [Cl]\* was between 6 ppm and 12 ppm and >100 ppm for 403 and FV566 SSs, respectively.
- 2. The impact of a period of exposure to on-load conditions (environment ageing) was known to reduce the likelihood of corrosion pit growth. There had previously been little effect to measure the changes either through electrochemistry or surface analysis techniques
  - (a) As a result of environmental ageing of 403 SS, the value of [Cl]\* increased from 12 ppm to >100 ppm.
  - (b) Furthermore, the use of X-ray photoelectron spectroscopy (XPS) revealed that this was likely due to the enrichment of chromium containing species within the passive film—providing increased corrosion resistance.
- Various techniques are available for creating artificial corrosion pits but comparison to 'real' corrosion pits is rarely made.
  - (a) Two electrochemical techniques were evaluated for suitability, with the aim of finding a technique that would create corrosion pits akin to those that initiated in the laboratory steam turbine tests. The droplet technique was found to create pits with similar aspect ratio (AR) and with microtopographical features.
- 4. There is a common assumption that cracks with favourably initiate at the base of the pit as the area of highest localised stress. However, XCT has been used previously, to show that cracks initiate at the mouth of 3NiCrMoV steel in stress corrosion cracking (SCC) testing.
  - (a) Crack growth at the pit mouth was observed with an optical microscope during fatigue testing of pitted FV566 SS coupons.

- (b) The resolution achievable with XCT setup used meant that the cracks were unresolvable in the radiographs obtained but high resolution 3D pit profiles were obtained that could be used in future finite element analysis (FEA) work.
- (c) Through use of PFIB, cracks were found to initiate at the mouth of the corrosion pit.

#### 7.3 Pitting in Simulated Steam Turbine Environments

One of the initial objectives of this research study was to identify the critical chloride concentration, [Cl]\*, required for corrosion pit initiation for 403 and FV566 SS materials as the value of [Cl]\* was not clearly reported when a review of the literature was conducted.<sup>1</sup> The literature review did highlight that cycling the water chemistry between on-load (deaerated) and off-load (aerated) conditions would impact upon the corrosion potential of steam turbine disk steel [4] and that significant chloride contamination (35 ppm) would induce the initiation and growth of corrosion pits [98]. To further develop the contributions from these pieces of research work, a similar lab setup was constructed to that reported in [98], that allowed the recirculation and monitoring of a simulated steam turbine environment while exposing test coupons to a variety of possible environments. This setup was enhanced by incorporating the ability to make EN measurements, to help with evaluating the performance of the test materials being subjected to different chloride and oxygen concentrations.

#### 7.3.1 Critical Chloride Concentration for Pit Initiation

The off-load steam turbine environment can provide conditions that promote the initiation of a corrosion pit due to the formation of a condensate, concentrated with contaminants, onto the hot surface of the turbine blades. Research published in [4, 98, 100, 151] has shown that the electrochemical parameter  $E_{corr}$ , could be monitored in order to ascertain the performance of a material in a given chloride containing environment. The research highlighted did not declare a simple value of [Cl]\* required for corrosion pit initiation during a water chemistry excursion. By replicating the design of the flow loop in

<sup>&</sup>lt;sup>1</sup>Salzman et al. [98] reported that corrosion pits would form on 403 SS in 35 ppm chloride solution; but it was not declared as a minimum threshold value. No related information for FV566 SS was found.

the given references, it was possible to identify [Cl]\* for both 403 and FV566 SS materials using the same electrochemical monitoring technique, where a reduction in  $E_{corr}$  would be indicative of corrosion pit initiation. It was found that [Cl]\* was 6 ppm to 12 ppm for 403 SS and beyond 100 ppm for FV566 SS. The higher concentration of chloride required to induce passive film breakdown for FV566 SS was attributed to the fact that the composition of this alloy had a higher content of molybdenum than 403 SS. It is well established that molybdenum contributes towards the resistance to pitting and is included in the pitting resistance equivalent number (PREN) calculation (Eq. (2.4)) along with chromium and nitrogen. The addition of molybdenum will also extend  $E_p$  to more noble potentials, in turn expanding the passive potential range of that alloy [30].

The corrosion pits that initiated in the chloride solutions were observed to be akin to those reported in [100], as shown in Figs. 2.17 and 4.12. The active corrosion pit was surrounded by a small etched area and a much larger protected region. The edge of this region was confined by a band of colour that forms due to thin film interference.

The literature review highlighted that EN could be used as a technique to observe the spontaneous transients in potential or current due to corrosion (or cracking) activity stimulated by environment excursions [83–86, 140, 197, 202–204]. Through incorporating a multichannel potentiostat with zero resistance ammeter (ZRA), it was possible to make EN measurements of coupons in simulated environmental conditions akin to the environment in a low pressure steam turbine (LPST), as Zhou and Turnbull [4] and Salzman et al. [98] did. ASTM G119-09 [205] provided guidance on the mathematical and statistical analysis that should be performed on the collected data to interpret the electrochemical current noise (ECN) and electrochemical potential noise (EPN) signals, which appear to be similar to those obtained in [86, 140]. A MATLAB® script was written to automate such analysis; consequently it would be possible to analyse the EN data in *real time*, by running EN data through the script as it was received, providing a definite period at which corrosion pitting occurs. Such a system incorporated into the turbine system may allow for better informed decisions on the inspection intervals required during service. The calculation of pitting index (PI) from the ratio between the standard deviation and the root mean square of the current noise provided results that correlated well with the observed changes in  $E_{corr}$ . This meant that for 403 SS the value of PI was <0.6

initiates within their system using artificial seawater.

until the chloride concentration was increased to 12 ppm. Likewise, for FV566 SS, the PI only reached the threshold value of 0.6 when the chloride concentration was increased to 100 ppm, offering reassurance that measurements of EN support the observations from  $E_{corr}$  monitoring. Cuevas Arteaga et al. [86] shows that for a similar grade SS a system without corrosion has a PI close to 0.1 and the variation of this increases as corrosion

Additionally,  $R_n$  can also be calculated from the ratio between the standard deviations of EPN and ECN, the value of which has been compared with  $R_p$  [200, 203]. When coupons of 403 and FV566 SSs were exposed to the predicted concentrations of chloride contaminants due to standard operation (0.3 ppm chloride), the calculated  $R_n$  was higher for 403 SS than FV566 SS by circa one order of magnitude. The  $R_n$  of 403 SS remained higher than FV566 SS at increasing concentrations of chloride up to 20 ppm, at which point the  $R_n$  of 403 SS was slightly lower than FV566 SS. The indication from  $E_{corr}$ monitoring and calculation of the PI was that FV566 SS would be passive at chloride concentrations in the range 0.3 ppm to 100 ppm so it could be an artefact of the experiment result that  $R_n$  of FV566 SS is lower and further tests should be undertaken to confirm this. It would be inappropriate to calculate a corrosion rate (CR) from the values of  $R_n$  as the Stern-Geary coefficient would need to be estimated. As the anodic reaction is under diffusion control and the electrochemical reactions occur at localised sites, Tafel's law is violated. However, it does not prevent other authors [86, 276] from attempting to calculate CR from EN data for passive materials in sea water and sulphuric acid solutions respectively.

Other explanations for the difference in  $R_n$  between the two grades of SSs investigated are possible—these are discussed in the following sections. Based upon the composition of the alloy the expectation was that FV566 SS would have a lower CR, as FV566 SS contains higher concentrations of both molybdenum and nickel. Only the concentration of nitrogen is higher in 403 SS (0.057 mass % vs. 0.026 mass %), but such a small difference in concentration does not have a significant impact upon the calculated PREN of the two alloys, unless nitrogen has a greater influence than the equation provides for. The materials may exhibit differences in the values of electrochemical parameters such as  $i_{pass}$  and  $E_p$  (shown in Fig. 2.5) that would explain the differences in CR and [Cl]\* for pit initiation. It is likely that the value of  $i_{pass}$  is lower for 403 SS (vs. FV566 SS) resulting in a lower CR, but the passive range is extended for FV566 SS (higher  $E_p$  and [Cl\*]) due to the included molybdenum [30]. Alternatively, the CR could be calculated using a second electrochemical techniques such as electrochemical impedance spectroscopy (EIS), described in ASTM G102 - 89 [211], to see if the CR measurements are consistent with those obtained from EN techniques. However, this would require significant alteration of the testing cells to incorporate a Luggin capillary and salt bridge, which would help to minimise the *IR* drop. This is achieved by positioning the tip close (1 mm to 3 mm) to the surface of the working electrode (WE), as discussed in [277], to minimise the effects of solution resistance.

Alternatively, the different CRs may be an effect of carbides or intermetallic phases that are present in the microstructure of the two alloys.<sup>2</sup> Both have the potential to form during the hardening and tempering stages of the heat treatment process, where temperatures range from 300 °C to 1050 °C [27] or after considerable operating time in the steam turbine environment [6]. Other authors [278-280] have found that intermetallics may form, albeit at long ageing times, consequently it may be more likely that carbides of the form  $Mo_2C$  or  $M_{23}C_6$  precipitate instead; where M may be iron or chromium. These intermetallics and carbides may offer a potential difference from the surrounding bulk material, meaning they either preferentially dissolve (anodic vs. steel matrix) or cause dissolution of the surrounding matrix (cathodic vs. steel matrix). The dissolution provides a defect in the surface which is then prone to localised corrosion. The presence of carbides and intermetallic phases is determined by the alloy composition and the heat treatment used [27]. It is plausible that the higher concentration of molybdenum in FV566 SS allows for the formation of such carbides and intermetallics and coupled with an insufficiently short heat treatment would mean they are still present during current testing. Further detailed examination of the two microstructures with transmission electron microscope (TEM) would be needed to confirm the presence of carbides or intermetallics and determine whether they are sufficient to explain the increased CR.

<sup>&</sup>lt;sup>2</sup>Although not evident in micrographs from literature (Fig. 2.6) or in this study (Fig. 4.1).

#### 7.3.2 Effect of Environmental Ageing on Pit Initiation

Historically, power plants would operate for significant periods without the requirement for shut-down. Such an event would only occur at the point of inspection or maintenance. Recently, to better match consumer demand, the power plants are cycled between on-load and off-load conditions through day and night and weekend cycles, as reported by Zhou and Turnbull [6]. Over time, the blades of the turbines experience an 'ageing' process where it is proposed that the passive film develops due to the exposure to onload deaerated environment usually containing low concentrations of impurities. To further investigate the effects of ageing on the passive film, fine ground test coupons were exposed to a simulated on-load environment for a period of  $\sim$ 30 d before exposure to increasing chloride concentrations in an aerated environment while monitoring  $E_{corr}$  for indication of corrosion pitting.

Similar measurements were made and reported by Salzman et al. [98] and Turnbull [281], who noted that exposure to the deaerated environment resulted in retardation of pit growth and sluggish response of the corrosion potential respectively. Furthermore, Salzman et al. [98] reported a change of a darker appearance to the passive film, thought to be due to the effect of ageing but did not investigate how this impacted on [Cl]\* for pit initiation. The results from the measurement of  $E_{corr}$  and inspection of coupons as they were removed from the test cells showed that [Cl]\* had increased from 12 ppm to >100 ppm due to the period of on-load exposure. As postulated by Salzman et al. [98], a higher concentration of chloride was needed to initiate the corrosion pits after ageing of the turbine blade material, possibly due to an alteration of the passive film as a result of the exposure to simulated on-load environmental conditions.

Explanation for this could come from similar observations made using the alternating voltage passivation technique which is used to improve the corrosion resistance of SS alloys [282, 283]. The imposed alternating potential is often over a range (0.8 V to 2 V), resulting in a thicker passive film enriched with chromium compounds, i.e., improved corrosion resistance. Improved corrosion resistance was observed after exposure to onload (deaerated) and off-load (aerated) conditions within the research of this thesis. Due to the change of oxygen concentration, when switching from aerated to deaerated conditions, there was a shift in potential of 0.6 V, which may induce some similar effects to those observed after use of the alternating voltage passivation technique.

To further investigate the re-initiation or arrest of pit growth due to exposure to simulated on-load environment conditions discussed by Salzman et al. [98], studies were conducted on coupons which had been exposed to 35 ppm chloride solution; consequently this generated some corrosion pits on the surface. The pitted coupons were exposed to the on-load environment for a shorter period of time,  $\sim 5 d$ , and then the value of [Cl]\* was evaluated under aerated environmental conditions. Similar to the findings of the previous test, [Cl]\* increased to >100 ppm and it was apparent that corrosion pits mainly initiated at new sites rather than pre-existing corrosion pits continuing to grow. These results highlight the behaviour of 'dormant' pits that become inactive during exposure to the on-load environment but also demonstrate that a short period of exposure to on-load conditions is sufficient to alter the passive film; as these coupons also appeared darker in colour after testing.

#### X-ray Photoelectron Spectroscopy of Passive Films

As noted by other researchers, a darkening of the passive film was observed after on-load exposure and an effort was made to quantify the changes to the passive film as a result of this process. The sample size required for XPS was smaller than that of those coupons used in exposure testing, so a multi-tool was used to extract smaller sub-regions of the coupon. This offered the possibility of contamination of the passive films, but deionised water and compressed air were used to minimise the temperature excursion during the extraction procedure. If the coupons were contaminated by this process, then the XPS spectra should show identical results, which was not the case in the results presented here (see Figs. 4.32 and 4.33).

High resolution XPS scans were performed on the O 1 s,  $Cr 2 p_{3/2}$  and  $Fe 2 p_{3/2}$  photoelectron peaks of two coupons (Fig. 4.33). One of which had only been exposed to aerated conditions and the other to both deaerated and aerated conditions. Through analysis of the XPS data, it was possible to model peak shapes that allowed the relative contributions from different oxidation states to be calculated in each case. After this, the percentage contribution from each oxidation state was calculated from the area under each corresponding curve and these percentages used to deduce information about the prevalence of each component in the different passive films. This was reported in terms of the Fe/Cr ratio, that is, the ratio of all iron-containing components to chromium-containing ones. In the passive film produced when the coupon was only exposed to off-load aerated conditions, it was found that the Fe/Cr ratio was 3.7, so there were more iron-based components, than chromium ones, in the passive film. A second coupon was measured with XPS after exposure to simulated on-load conditions for 30 d. The analysis of the photoelectron peaks showed that the Fe/Cr ratio had decreased to 0.5. This suggests that the passive film from the deaerated environment had become impoverished in compounds containing  $Fe^{2+}$  and  $Fe^{3+}$  ions and enriched with  $Cr^{3+}$  oxide and hydroxide compounds. It was determined that the enrichment of Cr<sup>3+</sup> compounds within the film due to on-load exposure, may explain the reason for the observed increase in [Cl]\* required to initiate corrosion pits during a water chemistry excursion and those observations made in [98].

# 7.4 Evaluation of Artificial Pit Techniques to Produce Representative Pits

When a specimen is subjected to a corrosive environment, corrosion pits will initiate at numerous sites. If the specimen is under load, the large number of corrosion pits makes it difficult to predict which pit is likely to dominate and be responsible for crack initiation. Cracks may initiate at numerous pits but may become non-propagating as shown in [157, 216]. Consequently, numerous research groups have reported results where single corrosion pits or notches have been included on a fatigue specimen, as the concentration of stress and strain maximises the likelihood that cracks will initiate at this defect [125, 137, 167, 178, 181, 263]. The benefit of this is that, as the location of the corrosion pit can be controlled, so can the location at which embryonic fatigue cracks initiate. This enables observation of these events through an *in-situ* microscope or direct current potential drop (DCPD) system, as described by Turnbull et al. [142] and ISO 21152:2018 [254].

microscope (Fig. 6.4) was used to observe the largest corrosion pit during fatigue cycling. The fatigue cycling was interrupted once evidence of crack initiation had been observed, in the hope that smaller fatigue cracks would have initiated at the other (smaller) corrosion pits.

A wide range of methods exist for creation of single corrosion pits on a fatigue specimen ranging from drilling, spark erosion and electrochemical techniques [167, 249–253]. The method chosen should be able to produce pits that are representative of pit morphologies identified within the simulated steam turbine environment (Chapter 4) and other authors [98]. From the investigations into the effect of environmental excursions on the propensity for pitting corrosion, it was possible to measure the geometries of the corrosion pits that formed and the pit AR was >1 for pits exceeding 50 µm. This provided guidance on the technique that should be chosen in order to generate corrosion pits that had gave similar ARs to those corrosion pits from environment excursion studies. Mechanical or machining methods were not considered suitable, due to the modification of the material's microstructure near to the corrosion pit site, which may either alleviate or increase the amount of residual stress present. Two possible electrochemical techniques were compared in order to evaluate which would produce corrosion pits representative of those measured in simulated steam turbine environments. The first *micro*electrochemical cell was developed by Evans et al. [178], based upon the work of Suter and Böhni [250] and the second *droplet technique* by Turnbull et al. [142].

#### 7.4.1 Micro-Electrochemical Cell

The micro-electrochemical cell was manufactured by Evans et al. [178] at The University of Manchester and allowed corrosion to occur in a region defined by the diameter of the pipette tip that was in contact with the metal surface. The sodium chloride solution was injected into the tip via a syringe and a potentiostatic method at 1.5 V vs. Ag/3M AgCl allowed corrosion to progress for a desired period to control the depth of the pit.

The corrosion pits generated had an AR < 1, as the diameter of the pit was akin to the orifice of the pipette used, meaning that the width of the corrosion pit exceeded the depths produced. Consequently, it meant that this technique did not produce corrosion pits that were representative of those measured as a result of exposure to a simulated steam turbine environments. The AR of the corrosion pit influences the location of crack initiation, due to the localisation of stress and strain, so it was imperative to use a technique that produced pits with AR > 1. Additionally, the morphology of the corrosion pit was of a smooth profile (Fig. 5.6) and while this was comparable to the profiles used in FE analysis [133, 177, 249], it lacks the microtopographical features that are reported by Wright and Turnbull [182] and others [149, 264]. Such microtopographical features are potential sites for crack initiation, due to the localisation of stress and strain at these features.

#### 7.4.2 Droplet Technique

As an alternative to producing corrosion pits with the micro-electrochemical cell; a droplet technique using a galvanostatic method was also investigated. Application of an anodic current exceeding the passive current ensured that the potential of the specimen surpassed that of  $E_p$ . As a result, the conditions facilitate for the initiation of a corrosion pit on the surface, consequently this quickly reduces the potential back below  $E_p$  ensuring that only a single pit initiates. The duration for which the current is applied ultimately determines the final depth of the corrosion pit obtained [142, 254]. However, the results in this work show that the pit depth follows a  $x = \sqrt{y}$  type trend and it was not possible to produce pits with depths exceeding 250 µm. This is attributed to the fact that a constant current is applied throughout the galvanostatic polarisation, so as the size of the corrosion pit grows, the current density is reduced; up to a point where the pit gradually repassivates and stops growing [58, 59].

The minimum pit size produced was  $50 \,\mu$ m, as corrosion pits smaller than this were likely to be of comparable size to inclusions [147] or grinding defects left after use of a 400 grit abrasive paper [39]. The AR of the pits, for depths  $50 \,\mu$ m to  $250 \,\mu$ m, tended to increase from 1.5 towards 2 with increasing depth (Fig. 5.8B). This AR can be described as a 'narrow and deep' type morphology (Fig. 5.4) and when the AR exceeds 2, the pit is a 'bullet' or U-shaped profile [177]. The range of depths and corresponding AR produced were a good representation of corrosion pits that were measured on coupons that had been exposed to a simulated steam turbine environment. When the concentration of chloride contamination was low (20 ppm), the pit depths did not exceed that of the grinding defects ( $<30 \,\mu$ m) previously reported, see Fig. 4.13. A period of a 6 h exposure to 35 ppm chloride solution produced pits with depth  $>30 \,\mu$ m and the AR was increasing towards 2 with deeper corrosion pits, as was shown in Fig. 4.23.

The difference in pit morphology obtained from potentiostatic and galvanostatic (microelectrochemical cell and droplet technique respectively) programmes has previously been reported by Ghahari et al. [59]. They initiated corrosion pits on the top edge of a 304 SS foil through electrochemical procedures and recorded the growth by synchrotron Xray radiography. The pits grown under potentiostatic control were shallow and smooth in morphology, whereas the galvanostatically grown pits were deeper with a rougher surface—matching the observations of the two techniques used here.

Finally, the droplet method also allowed corrosion pits to be produced that had depths exceeding 200 µm, which would allow the effect of shot peening to be investigated. As was shown in Fig. 6.1, the compressive residual stress induced by the shot peening process was up to 700 MPa and extended to a depth of 250 µm when measured by electropolishing layer removal and X-ray diffraction (XRD) [147, 149]. As the depth of the produced corrosion pits was similar to the depth of the residual stress layer, it was possible to observe if the benefit of shot peening had been maintained. During the fatigue tests of fine ground specimens, cracks were observed to have initiated within just 3600 cycles; whereas the shot peened material sustained 111 600 cycles before similar crack initiation was observed, so the benefit of shot peening was still apparent.

## 7.5 Fatigue Crack Initiation Location at Corrosion Pits

Fatigue tests were performed on specimens of FV566 SS where the length of the gauge section contained several corrosion pits of depths 50 µm to 250 µm that were spaced at least 1 mm to avoid pit-pit interaction [249, 256, 271]. The surface finish of the fatigue specimen was either fine ground or shot peened to allow the relationship between corrosion pit depth and compressive residual stress to be evaluated. The fatigue tests were performed at 85 % of  $\sigma_y$  to ensure that cracks would initiate in the smallest corrosion pits, as this level of applied stress was above the reported fatigue limit of 700 MPa [39] and beyond the boundary depicted in the Kitagawa-Takahashi plot (Fig. 2.26) of Turnbull et al.

[147]. As was reported previously, the largest corrosion pit was observed with an optical microscope that had been attached to the loading frame of the Instron testing machine. With the specimen under maximum load, an image was automatically captured every 3600 cycles, with a LabVIEW program, until there was confidence a crack had initiated at this pit. The surface topography, as a result of shot peening, made it more difficult to determine when this occurred, consequently larger cracks grew from the pit within the shot peened specimen.

To verify the location at which cracks had initiated from within the corrosion pit (base or mouth), a new methodology was developed that allowed cylindrical specimens to be produced for micro-XCT imaging. As the resolution of XCT is closely linked to the specimen size (see Section 3.4.1), it was desirable to reduce the XCT object size from the original 4 mm  $\times$  4 mm gauge cross-section to several cylinders with a diameter of 500 µm, each one with a single corrosion pit on the top surface. Relatively new developments in laser micro machining enabled this kind of unique specimen preparation, through the reduction in the laser pulse lengths from nanosecond to femtosecond range. This reduces the superficial surface heat damage (i.e., heat affected zone (HAZ)) to around 1 µm deep [268], while the high power laser facilitates ablation of material at rates greater than those achieved from focused ion beam (FIB). The possibility of such machining options meant that a small section could initially be manually machined from the fatigue gauge section, before being placed inside the microPREP instrument where a 'pillar' type recipe produced the final desired geometry for XCT (Fig. 6.6).

#### 7.5.1 Evaluation of XCT to Quantify Corrosion Pits and Cracks

In order to determine whether the embryonic cracks from the corrosion pits could be detected with XCT, it was desirable to ensure a small voxel size, as this would allow spatial resolution between smaller features. As discussed in Section 3.4.1, this can be accomplished by reducing the sample size, in order to allow the object-to-detector distance to be minimised to give some geometrical magnification; while avoiding penumbral blurring from the cone-shaped laboratory X-ray beam. From the positioning of the source, object and detector and the optical magnification, it was possible to perform theoretical calculations of the resulting voxel size. The minimum voxel size achieved in this project was 0.566 µm using the Zeiss Versa XRM520. Often this value is the resolution that is reported in the literature [181, 263, 265, 284], however, it is often the case that only features significantly larger than this can be resolved from the radiographs. In order to quantify this, it was necessary to use a JIMA microfocus resolution chart to indicate the *real* spatial resolution. For the Zeiss Versa XRM520, the JIMA chart indicated that the achieved true spatial resolution was in the range 1  $\mu$ m to 2  $\mu$ m, as was shown in Fig. 6.8. Consequently, despite the small voxel size obtained, the cracks that had initiated from the corrosion pits were not visible in the obtained radiographs. This was explained in terms of roughness in*duced asymmetric crack wake plasticity* that would compound crack closure upon removal of the applied stress [273, 274]. The possibility of performing a local tomography scan<sup>3</sup> could be investigated, but this would affect the centre of rotation, geometrical magnification and field of view. To enable the cracks to be detected in an XCT measurement in future, it would be advisable to develop a methodology that would allow the specimen to be held at a constant load during scanning so the length of the crack remains open and contrast is obtained, as shown in [181, 285], albeit these results only allowed cracks with length  $>200 \,\mu\text{m}$  to be imaged. Furthermore, there is no guarantee that the entire crack length will be open, due to the remaining applied load being below  $F_{max}$  for XCT imaging; so the results in [181, 285] may not have measured the true total crack length. Alternatively, it may be possible to apply an exceptionally low viscosity resin, such as Master Bond EP62-1LPSP, to the gauge section of the specimen while it remains loaded in tension to  $F_{max}$ . The low viscosity of such resin may allow the resin to penetrate along the majority of the crack length and prevent crack closure after the resin has cured, once the applied load is removed. This would mean that the micro-machined specimen routine developed here could then be utilised with no need for the specimen to be under load as the resin would wedge the crack open.

The XCT results were able to reveal information about the volume of corrosion pits created using the galvanostatic droplet technique. There are very few reports in the literature pertaining to the exact volume of a corrosion pit, as it is not possible to make an accurate measurement from only the pit mouth diameter and depth, as this would

<sup>&</sup>lt;sup>3</sup>A local tomography scan is defined by He et al. [263] as, "the acquisition mode during which only a selected region of the sample is imaged with the rest of the sample going outside the field of view during the rotation...".

exclude any pit undercutting from the calculated final volume. One example [286], uses white light interferometry to obtain detailed topographic images of pits, with measured depths of 50 µm to 150 µm. A method is then proposed to calculate the pit volumes of each pit, giving a range of  $3 \times 10^{-6}$  cm<sup>3</sup> to  $7 \times 10^{-5}$  cm<sup>3</sup>. However, the author states that "the technique does not work for pits that undercut the surface..." highlighting the limitation of this line of sight technique, as well as others such as optical microscopy (OM) and laser confocal scanning microscopy (LCSM). As XCT is able to reveal the true subsurface morphology of the corrosion pit, it is possible to accurately determine the volume from the segmentation of the XCT volume and the corresponding number of voxels assigned to the corrosion pit grey scale range. The results presented in this work (see Fig. 6.25), show that the optical technique used (LCSM) severely underestimates the pit volume of the corrosion pits produced and that macro- and micro-XCT scans provided a larger calculated volume, thought to be much closer to the actual pit volume.

#### 7.5.2 Analysis of Corrosion Pits and Cracks with PFIB

As the cracks were not resolvable from the XCT radiographs, alternative characterisation techniques were evaluated. One option was a serial sectioning procedure, as demonstrated by Guo et al. [149] and He et al. [263], but the drawback to this was the *large* step size between polishing layers (16  $\mu$ m and  $\sim$ 5  $\mu$ m respectively), which may be large enough that small embryonic cracks are destroyed during a polishing step. To achieve a minimal step size, FIB milling has previously been exploited [192] to remove small sequential layers of material with the narrow ion beam. However, the low material removal rate with a Ga<sup>+</sup> beam limits the volume and depth of material that can be probed to tens of microns. Consequently, this would mean that only a small volume of the pit could be serial sectioned at a time, which would be time consuming and also result in potential loss of crack information if the whole pit is not sectioned and only assumed cracking areas are investigated. The recently emerging technology of plasma Xe<sup>+</sup> PFIB-SEM offers material removal rates that are  $60 \times$  greater than Ga<sup>+</sup> FIB systems, meaning that volumes of hundreds of microns can be examined within a realistic period [195]. This size volume roughly equates to the volume of the corrosion pits that were produced on the fatigue specimens, so PFIB serial sectioning appeared the ideal tool to reveal the relation between crack initiation location and pit morphology as a slice thickness 200 nm to 250 nm could be used.

Slice and view PFIB-SEM routines were performed on two corrosion pits with the milling direction parallel to the direction of crack growth. In both cases, segmentation of the image stack to highlight the crack path indicated that the crack had initiated in the region between the pit mouth/shoulder and the widest part of the undercutting pit which agrees with observations from other authors [115, 157, 177, 178]. This suggests that the assumption of cracks initiating at the base of the corrosion pit, where the stress is highest, is not true in all cases. Additionally, the assumption that the crack size is equal to the pit depth at pit-crack transition was not supported here, as the crack initially formed on either side of the pit and only extended between the pit mouth and the widest part of the pit undercut. No examples of cracks extending from the surface to the base of the pit were found, which raises concern over models entirely based upon the assumptions of Kondo [169]. To confirm the crack location in relation to the pit, the segmented volume of the crack from PFIB-scanning electron microscope (SEM) can be overlaid with the volume of corrosion pit from earlier XCT scans to show the relation between crack and corrosion pit as was shown in Fig. 6.31. From the tortuosity of the crack, it can be inferred that the initial growth of the short crack (Stage I crack propagation) is heavily influenced by the microstructural boundaries present in the material and crack deflection is evident as a result of interaction with such features.

#### 7.5.3 Impact of Excursion on Pit-to-Crack Transition

Although the research undertaken in this project didn't specifically address the environmental effects on crack nucleation, some areas of thought can be discussed. Environment excursions have an impact upon the likelihood of corrosion pit nucleation and growth. Consequently, similar correlation should be expected for environment excursions on crack growth rate. Certain environments may facilitate higher crack growth rate, if the solution is able to breakdown the passive film or form atomic hydrogen that may enter and embrittle the material. In the steam turbine, the continued competition between the pit and crack growth rate ultimately determines the dominant process in the pit-to-crack transition. For the crack to become dominant, its growth rate must exceed that of the pit, otherwise the crack growth may be consumed during the anodic dissolution of the material. The results in this work have shown that pit growth rate is retarded or very low in simulated on-load conditions. Consequently, this offers an environment when the crack growth rate is capable of exceeding the pit growth rate—further encouraged by the complex loading during on-load operation.

# **Chapter 8**

# **Future Work**

#### Contents

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### 8.1 Introduction

The investigations conducted within this PhD research project have provided information that will contribute towards predicting the damage evolution of low pressure steam turbine (LPST) blades during their in-service lifetime. Critical information about the impact of chloride contamination and two-shifting on the propensity for the initiation of corrosion pits in a simulated steam turbine environment has been presented. Additionally, interrupted fatigue tests and state of the art measurement tools were used to determine the behaviour and location of embryonic fatigue cracks at corrosion pits. In order to completely model the rate of damage evolution due to corrosion fatigue (CF) in the steam turbine, the following sections present areas of work which could be further investigated.

# 8.2 Evaluation of Corrosion Pits from In-Service Turbine Blade

If an industrial partner was to offer a used steam turbine blade, then it would be possible to use characterisation tools such as laser confocal scanning microscopy (LCSM) and
X-ray computed tomography (XCT) to quantify and measure the range of corrosion pit morphologies produced due to service conditions. This would better inform the choice of electrochemical technique chosen to represent these corrosion pits through comparative analysis. Furthermore, the flow loop used to simulate environment conditions could be evaluated in terms of its ability to produce corrosion pits akin to those from service. Following the quantification of the size and geometry of each pit on the blade from service, it would be possible to perform a structural integrity assessment and identify the geometries and orientations of corrosion pits that are likely to be responsible for CF failure, as reported by Larrosa et al. [287].

#### 8.3 Evolution of Cracks from Pits with In-situ XCT

The use of XCT was able to reveal the complete sub-surface morphology of the corrosion pits produced, but, in the absence of an applied load, it was difficult to detect the location of crack initiation. One possible solution to this problem would be to conduct fatigue tests with in-situ XCT measurements, using a synchrotron source, at defined time periods. The recent development of the laser micro machining tool could enable the manufacture of fatigue specimens that are small enough to permit a high enough resolution to spatially resolve the crack features near a corrosion pit. It is envisaged that such an experiment would highlight the initiation, growth and coalescence of cracks due to fatigue cycling and help provide essential information for lifetime modelling.

### 8.4 Use of High Resolution Digital Image Correlation

Much recently published research has highlighted that cracks are likely to initiate at the mouth of the corrosion pit where strain is maximised. This enables surface displacement techniques such as digital image correlation (DIC) to be utilised in order to quantify the evolution of localised surface strain and measure a threshold strain ( $\epsilon_{th}$ ) required for crack initiation. Recently, high resolution DIC has been established as a technique that can quantify strain localisation down to the magnitude of individual persistent slip bands (PSBs) [288, 289]. The use of this technique would provide information about stage I short

crack initiation and growth on planes of maximum shear stress and the transition to stage II cracks, which could better inform on the behaviour of short cracks from corrosion pits.

Additionally, once a value of  $\epsilon_{th}$  has been measured for specific materials, it would be possible to introduce hydrogen into the metal lattice through hydrogen charging, to determine the propensity for hydrogen embrittlement (HE). It is envisaged that the introduction of hydrogen will either cause a reduction in the value of  $\epsilon_{th}$  or reduce the number of cycles required to reach the same value of  $\epsilon_{th}$ .

## 8.5 Measurement of Crack Growth Rate in Simulated Steam Environments

The fatigue testing in this study was carried out in air, as a well-controlled power plant should contain low concentrations of impurities during regular operation, Nevertheless, the effect of temperature and the presence of the steam will have some impact upon the growth rate of cracks from corrosion pits. The steam environment may assist crack growth by maintaining the sharpness of the crack tip during fatigue cycling, which will promote an increased crack growth rate (CGR) compared with in air testing. Therefore, it is recommended that fatigue tests could be carried out with an environment chamber to allow circulation of a simulated steam environment and variable concentrations of contaminants can be introduced. Furthermore, the fatigue loading pattern and simulated steam environment could be controlled to match the expected loading and environment conditions in a start-up or shut-down procedure, to see how these impact upon the accumulation of damage over time. It may be possible to use in-situ or periodic XCT measurements or direct current potential drop (DCPD) [141, 142] to observe and calculate the effects of the environment on overall CGR.

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### Appendix A

# **Analysis of Electrochemical Noise**

The mathematical and statistical analysis of electrochemical noise (EN) data was performed within MATLAB<sup>®</sup>. The script provided below was used to detrend the raw, potential and current data and subsequently calculate the EN parameters described in ASTM G199-09—Standard Guide for Electrochemical Noise Measurement [205]. Additionally, figures of the raw and detrended potential and current noise will be generated and saved—followed by figures showing the trends of pitting index *PI*, coefficient of variation *CV*, electrochemical noise resistance  $R_n$  and corrosion rate (CR). The script requires that the EN data has been exported into .txt files, with the data in four tab delimited columns in the order Potential (V), Current (A), Elapsed Time (s) and Segment as shown in Fig. A.1. From the figure, it can also be noted that the filename is of the structure Cell\_1\_EN\_0X, where X indicates the day from which the EN data was collected.

|      | Cell_1_ | EN_03 - N | lotepad |      |          |          |          |         |         |
|------|---------|-----------|---------|------|----------|----------|----------|---------|---------|
| File | e Edit  | Format    | View    | Help |          |          |          |         |         |
| Pot  | tentia  | al (V)    | Cur     | rent | (A)      | Elapsed  | Time (s) | )       | Segment |
| 0.0  | 000919  | 9944373   | 89075   | 8    | -6.4408  | 33288934 | 3E-08    | 90537.4 | 25      |
| 0.0  | 000919  | 9944373   | 89075   | 8    | -6.5021  | 73732769 | 73E-08   | 90537.6 | 25      |
| 0.0  | 000919  | 9944373   | 89075   | 8    | -6.7475  | 39771367 | 88E-08   | 90537.8 | 25      |
| 0.0  | 000919  | 9944373   | 89075   | 8    | -6.5021  | 73732769 | 73E-08   | 90538   | 25      |
| 0.0  | 000919  | 9944373   | 89075   | 8    | -6.5021  | 73732769 | 73E-08   | 90538.2 | 25      |
| 0.0  | 000613  | 3238022   | 19703   | 8    | -6.80888 | 80925746 | 05E-08   | 90538.4 | 25      |
| 0.0  | 000919  | 9944373   | 89075   | 8    | -7.05424 | 46253801 | 47E-08   | 90538.6 | 25      |
| 0.0  | 000919  | 9944373   | 89075   | 8    | -6.93156 | 63234502 | 39E-08   | 90538.8 | 25      |
| 0.0  | 000919  | 9944373   | 89075   | 8    | -6.2568  | 09115257 | 06E-08   | 90539   | 25      |
| 0.0  | 000919  | 9944373   | 89075   | 8    | -6.37949 | 92134556 | 13E-08   | 90539.2 | 25      |
| 0.0  | 000919  | 9944373   | 89075   | 8    | -7.3609  | 52025692 | 31E-08   | 90539.4 | 25      |
| 0.0  | 000919  | 9944373   | 89075   | 8    | -7.5449  | 76199369 | 56E-08   | 90539.6 | 25      |
| 0.0  | 000613  | 3238022   | 19703   | 8    | -6.87022 | 22080124 | 22E-08   | 90539.8 | 25      |
| 0.0  | 000919  | 9944373   | 89075   | 8    | -6.3181  | 50269635 | 23E-08   | 90540   | 25      |

FIGURE A.1: Example of .txt file structure needed to allow successful import into MATLAB<sup>®</sup> script.

| LISTING A.1: | MATLAB® | script | to | perform | mathematical | and | statistical |
|--------------|---------|--------|----|---------|--------------|-----|-------------|
|--------------|---------|--------|----|---------|--------------|-----|-------------|

```
analysis of EN data.
   clear variables
1
2
   close all
3
   %%
4
   tic
5
6
   set(0, 'defaultAxesFontSize',14);
7
   Markers = {'^','o','x','s','+','d','v','*','>','<'}; % Ensures different markers
8
       are used if image is printed B&W
9
10
   % The parameters below should be checked for the experimental setup
11
12
   freq = 5; % frequency of EN acquisition
13
    stern_geary = 26; % used later to calculate corrosion rate
14
15
   Material = 403;
   Specimen_area = 4*5; % used for Rn. Units are cm
16
17
   Density = 7.8; %g/cm^3
18
19
   %Chemical composition of alloy for elements which are >1%
20
   Cr = 11.8; Mo = 0; Ni = 0; Fe = 100-(Cr+Mo+Ni); % atomic percent
   Cr_val = 3; Mo_val = 3; Ni_val = 2; Fe_val = 2; % valence of ion produced
21
22
   Cr_weight = 51.9961; Mo_weight = 95.94; Ni_weight = 58.6934; Fe_weight = 55.845;
23
   % Equivalent weight
24
   EW = 100/(((Cr_val*Cr)/Cr_weight)+((Mo_val*Mo)/Mo_weight)+((Ni_val*Ni)/Ni_weight)
       +((Fe_val*Fe)/Fe_weight));
25
26
   a = dir('*.txt'); % counts the number of txt files. NB folder should only contain
       txt files containing EN data
27
   n = numel(a);
28
29
   numArrays = n;
30
   PbV_store = cell(numArrays,1);
   PbI_store = cell(numArrays,1);
31
32 fIburg_store = cell(numArrays,1);
33 fVburg_store = cell(numArrays,1);
```

```
34
   PI_store = cell(numArrays,1);
35
   R_n_store = cell(numArrays,1);
   R_n_detrend_store = cell(numArrays,1);
36
37
   CV_store = cell(numArrays,1);
38
   I_corr_store = cell(numArrays,1);
39
   corrosion_rate_store = cell(numArrays,1);
40
41
   % Want to calculate the standard deviation for different window sizes.
   \% Recommended sizes are 2^n where n is 8 - 12. This allows conversion to remove DC
42
        trend
43
44
   window_range = 2.^(8:12);
45
   window = window_range(1); % choose the smallest window size for highest accuracy
46
   %%
47
    for d = 1:n %
48
        disp (['Processing day ',num2str(d)])
49
50
        PI = [];
51
        R_n = [];
52
        R_n_detrend = [];
53
        CV = [];
54
        I_corr = [];
55
        corrosion_rate = [];
56
        base_file_name = 'Cell_1_EN_0'; % NB file name may need to be altered to match
            this command.
58
        filename = [base_file_name,num2str(d),'.txt'];
59
        delimiterIn = '\t';
60
61
        headerlinesIn = 1;
62
        A = importdata(filename,delimiterIn,headerlinesIn);
63
        A.data = [A.data(:,(1:3)),(A.data(:,4)+1)]; % have to add one as segment 1 in
            versastudio is actually segment 0 and matlab cant index 0
64
        M = max(A.data(:,4));
65
        ind = cell(1,M);
66
        V = cell(1,M);
67
        I = cell(1,M);
        Time = cell(1,M);
68
```

```
69
 70
         % This section takes each segment of data (1 hr) and detrends the data with a
             polynomial with order two using the window size determined earlier.
 71
         for seg = 1:M
 72
             ind{seg} = (A.data(:,4)) == seg;
 73
 74
             V{seg} = A.data(ind{seg},1);
 75
             V_detrend{seg} = detrend(V{seg},2,0:window:size(V{seg}));
 76
 77
             I{seg} = A.data(ind{seg},2);
 78
             I_detrend{seg} = detrend(I{seg},2,0:window:size(I{seg}));
 79
 80
             Time{seg} = A.data(ind{seg},3);
 81
         end
 82
 83
         % Need to remove the empty cells from data
 84
         index = cellfun(@isempty, V) == 0;
 85
         V = V(index);
 86
 87
         index = cellfun(@isempty, V_detrend) == 0;
 88
         V_detrend = V_detrend(index);
 89
 90
         index = cellfun(@isempty, I) == 0;
 91
         I = I(index);
 92
 93
         index = cellfun(@isempty, I_detrend) == 0;
 94
         I_detrend = I_detrend(index);
 95
 96
         %%
 97
         % Cell array has been reduced in size so redfine M
 98
         M = numel(V);
99
100
         % Now we want to calculate some of the mathematical/statistical parameters used
              within the EN standards.
101
         for p = 1:M
102
             rms_I(p) = rms(I\{1,p\});
103
             std_I(p) = std(I\{1,p\});
104
             std_I_detrend(p) = std(I_detrend{1,p});
```

```
105
             mean_I(p) = mean(I\{1,p\});
106
             mean_I_detrend(p) = mean(I_detrend{1,p});
107
108
             std_V(p) = std(V{1,p});
109
             std_V_detrend(p) = std(V_detrend{1,p});
110
111
             PI(p) = std_I_detrend(p)/rms_I(p);
112
             PI_store{d,1} = PI;
113
             PI_store{d} = rmmissing(PI_store{d});
114
             PI_avg(d) = mean(PI_store{d});
115
             PI_std(d) = std(PI_store{d});
116
117
             R_n(p) = (std_V(p)*Specimen_area)/std_I(p);
118
             R_n_store\{d,1\} = R_n;
119
             R_n_avg(d) = mean(R_n_store{d});
120
121
             R_n_detrend(p) = (std_V_detrend(p)*Specimen_area)/std_I_detrend(p);
122
             R_n_detrend_store{d,1} = R_n_detrend;
123
             R_n_detrend_store{d} = rmmissing(R_n_detrend_store{d});
124
             R_n_detrend_avg(d) = mean(R_n_detrend_store{d});
             R_n_detrend_std(d) = std(R_n_detrend_store{d});
125
126
127
             I_corr(p) = stern_geary/R_n_detrend(p);
128
             I_corr_store{d,1} = I_corr;
129
             I_corr_store{d} = rmmissing(I_corr_store{d});
130
131
             corrosion_rate(p) = (3272*I_corr(p)*EW)/Density; % Calculation of CR based
                 on equation from ASTM standard
132
    %
               corrosion_rate(p) = (I_corr(p)*10*31536000*55.85)/(2*96485*7.8); %
         alternative way to calculate CR
133
             corrosion_rate_store{d,1} = corrosion_rate;
134
             corrosion_rate_avg(d) = mean(corrosion_rate_store{d});
135
             corrosion_rate_std(d) = std(corrosion_rate_store{d});
136
137
             CV(p) = std_I_detrend(p)/(abs(mean_I(p)));
138
             CV_store{d,1} = CV;
139
             CV_store{d} = rmmissing(CV_store{d});
140
             CV_avg(d) = mean(CV_store{d});
```

```
141
             CV_std(d) = std(CV_store{d});
142
143
             %%
144
             % This section will plot the original and detrended data of ECN and EPN for
                  each hour of each day. It takes a long time so can be skipped (comment
                  out) once it has been plotted.
145
             close all
146
147
             figure('Name','Original and detrended E&I')
148
             movegui('northwest')
149
150
             subplot(2,1,1);
151
             plot(V{p})
152
             hold on
153
             plot(V_detrend{p})
154
             plot(V{p}-V_detrend{p})
155
156
             subplot(2,1,2);
157
             plot(I{p})
158
             hold on
159
             plot(I_detrend{p})
160
             plot(I{p}-I_detrend{p})
161
162
             if ~exist ('Detrended\E_I','dir') % this will create subdirectories in the
                 current folder to store the data.
163
                 mkdir('Detrended\E_I')
164
             end
             print('-dpng','-r300',[pwd '\Detrended\E_I\',[num2str(Material)],'
165
                 _Voltage_Current','_detrend_day_',[num2str(d)],'_hour_',[num2str(p)]]);
166
167
             if ~exist ('Detrended\E','dir')
168
                 mkdir('Detrended\E')
169
             end
170
             figure('Name','Original and detrended voltage')
171
             movegui('north')
172
             subplot(2,1,1)
173
             plot(V{p}, 'DisplayName', 'Raw')
174
             hold on
```

```
175
             plot(V{p}-V_detrend{p}, 'linewidth', 1, 'color', [0.9290, 0.6940, 0.1250],'
                 DisplayName', 'Trend')
176
             axis ([0 numel(V{p}) -inf inf])
             ylabel('Potential vs. SCE (V)')
177
             legend('show', 'location', 'best')
178
179
180
             subplot(2,1,2)
181
             plot(V_detrend{p}, 'color', [0.8500, 0.3250, 0.0980])
182
             plot(V_detrend{p}, 'color', [0.8500, 0.3250, 0.0980], 'DisplayName','
                 Detrended')
183
             axis ([0 numel(V{p}) -inf inf])
184
             xlabel('Time (s)')
185
             ylabel('EPN (V)')
186
             legend('show', 'location', 'best')
187
             print('-dpng','-r300',[pwd '\Detrended\E\',[num2str(Material)],'_Voltage','
                 _detrend_day_',[num2str(d)],'_hour_',[num2str(p)]]);
188
189
             if ~exist ('Detrended\I','dir')
190
                 mkdir('Detrended\I')
191
             end
             figure('Name','Original and detrended current')
192
193
             movegui('northeast')
194
             subplot(2,1,1)
195
             plot(I{p}, 'DisplayName', 'Raw')
             hold on
196
197
             plot(I{p}-I_detrend{p}, 'linewidth', 1, 'color', [0.9290, 0.6940, 0.1250],'
                 DisplayName', 'Trend')
198
             axis ([0 numel(I{p}) -inf inf])
199
             ylabel('Current (A)')
200
             legend('show', 'location', 'best')
201
202
             subplot(2,1,2)
203
             plot(I_detrend{p}, 'color', [0.8500, 0.3250, 0.0980])
204
             plot(I_detrend{p}, 'color', [0.8500, 0.3250, 0.0980], 'DisplayName','
                 Detrended')
205
             axis ([0 numel(I{p}) -inf inf])
206
             xlabel('Time (s)')
207
             ylabel('ECN (A)')
```

```
208
             legend('show', 'location', 'best')
209
             print('-dpng','-r300',[pwd '\Detrended\I\',[num2str(Material)],'_Current','
                 _detrend_day_',[num2str(d)],'_hour_',[num2str(p)]]);
210
211
         end
212
         %%
213
         % now we can make a plot of the statistical parameters for each day by indexing
              from the stored variable
214
         figure('Name','Daily Pitting Index')
215
216
         movegui('northwest')
217
         PI = PI_store{d};
218
         plot(PI)
219
220
         xlabel('Time (h)')
221
         ylabel('Pitting index')
222
         axis ([-inf inf 0 1])
223
224
         if ~exist ('Pitting_index','dir')
225
             mkdir('Pitting_index')
226
         end
227
         print('-dpng', '-r300', [pwd '\Pitting_index\', [num2str(Material)], '_PI_Day_', [
             num2str(d)]]);
228
229
         figure('Name', 'Daily Electrochemical Noise Resistance')
230
         movegui('north')
231
         R_n = R_n_store\{d\};
232
         plot(R_n)
233
234
         xlabel('Time (h)')
235
         ylabel('R_n (\Omega cm^2)')
236
237
         if ~exist ('Electrochemical_noise_resistance','dir')
238
             mkdir('Electrochemical_noise_resistance')
239
         end
240
         print('-dpng', '-r300', [pwd '\Electrochemical_noise_resistance\', [num2str(
             Material)], '_Rn_Day_', [num2str(d)]]);
241
```

```
242
243
         figure('Name', 'Daily Electrochemical Noise Resistance of Detrended')
244
         movequi('northeast')
245
         R_n_detrend = R_n_detrend_store{d};
246
         plot(R_n_detrend)
247
248
         xlabel('Time (h)')
         ylabel('R_n (\Omega cm^2)')
249
250
251
         print('-dpng', '-r300', [pwd '\Electrochemical_noise_resistance\', [num2str(
             Material)],'_Rn_Day_',[num2str(d)],'_Detrend']);
252
253
         toc
254
    end
255
256
    %%
257
    % Here we plot each of the data sets overlapping with each other to show the change
          in data.
258
259
    close all
260
    figure('Name','Total Pitting Index')
261
    movegui('northwest')
262
     for k = 1:d \% Plot days 1 - 7
263
         if k == 1% Exlude day 1
264
             continue
265
         end
         if k == 6
266
267
             PI_store{k} = [NaN(1,8) PI_store{k}]; % fudge factor as day 6 had 8 hours
                 of missing data
268
         end
269
270
         PI = PI_store{k};
271
         text = ['Day ', num2str(k)];
272
         plot(PI,strcat('-',Markers{k}), 'DisplayName', text, 'linewidth', 1);
273
         hold on
274
    end
275
    yline (0.6,'-k','Threshold', 'linewidth', 1,'HandleVisibility','off');
276
    hold off
```

```
277
    xlabel('Time (h)')
278
    ylabel('Pitting index')
279
    axis([0 inf 0 1])
280
    legend ('show','Location', 'best', 'NumColumns', 2)
281
    h = legend;
    set(h, 'fontsize', 9);
282
283
    set(gca, 'XTick', (0:6:24))
284
    % legend('boxoff')
    print('-dpng','-r300',[pwd '\Pitting_index\',[num2str(Material)],'_PI_all']);
285
286
287
    %%
288
    figure('Name','Total Coefficient of Variation')
289
    movegui('southwest')
290
    % movegui([1, 50])
291
    for k = 1:d
292
         if k == 1
293
             continue
294
         end
295
         if k == 6
296
             CV_store\{k\} = [NaN(1,8) CV_store\{k\}];
297
         end
298
         CV = CV_store{k};
299
         text = ['Day ', num2str(k)];
300
         plot(CV, strcat('-',Markers{k}),'DisplayName', text, 'linewidth', 1);
301
         hold on
302
    end
303
    hold off
304
    xlabel('Time (h)')
305
    ylabel('Coefficient of variation')
306
    axis([0 26 0 inf])
307
    set(gca,'XTick',(0:6:24))
308
    legend ('show', 'Location', 'northwest', 'NumColumns', 2)
309
    h = legend;
    set(h, 'fontsize', 9);
310
311
312
    if ~exist ('Coefficient_of_variation','dir')
313
         mkdir('Coefficient_of_variation')
314
    end
```

```
315
    print('-dpng','-r300',[pwd '\Coefficient_of_variation\',[num2str(Material)],'
        _CV_all']);
316
    %%
317
    figure('Name', 'Total Electrochemical Noise Resistance')
318
319
    movegui('north')
320
    % movegui([675, 50])
321
    for k = 1:d \% Plot days 1 - 7
322
         if k == 1
323
             continue
324
         end
325
         if k == 6
326
             R_n_store\{k\} = [NaN(1,8) R_n_store\{k\}];
327
         end
328
         R_n = R_n_store\{k\};
329
         text = ['Day ', num2str(k)];
330
         plot(R_n,strcat('-',Markers{k}),'DisplayName', text, 'linewidth', 1);
331
         hold on
332
    end
333
    hold off
334
    xlabel('Time (h)')
335
    ylabel('R_n (\Omega cm^2)')
    set(gca, 'YScale', 'log')
336
337
    axis([0 26 10^5 10^9])
338
    set(gca,'XTick',(0:6:24))
339
    legend ('show', 'Position', [0.55 0.5 0.2 0.2], 'NumColumns', 3, 'Orientation', '
         horizontal')
    % legend('boxoff')'Location','best',
340
341
    h = legend;
    set(h, 'fontsize', 9);
342
343
    print('-dpng','-r300',[pwd '\Electrochemical_noise_resistance\',[num2str(Material)
         ],'_Rn_all']);
344
    %%
345
346
    figure('Name', 'Total Electrochemical Noise Resistance Detrended')
347
    movegui('south')
348
    % movegui([675, 50])
349 | for k = 1:d % Plot days 1 - 7
```

```
350
         if k == 1
351
             continue
352
         end
353
         if k == 6
354
             R_n_detrend_store{k} = [NaN(1,8) R_n_detrend_store{k}];
355
         end
356
         R_n_detrend = R_n_detrend_store{k};
357
         text = ['Day ', num2str(k)];
358
         plot(R_n_detrend,strcat('-',Markers{k}),'DisplayName', text, 'linewidth', 1);
359
         hold on
360
    end
    hold off
361
362
    xlabel('Time (h)')
    ylabel('R_n (\Omega cm^2)')
363
364
    set(gca, 'YScale', 'log')
    axis([0 26 10^5 10^8])
365
366
    set(gca,'XTick',(0:6:24))
367
    legend ('show', 'Position', [0.55 0.48 0.2 0.2], 'NumColumns', 3, 'Orientation', '
        horizontal')
368
    % legend('boxoff')'Location','best',
369
    h = legend;
370
    set(h, 'fontsize', 9);
     print('-dpng', '-r300', [pwd '\Electrochemical_noise_resistance\', [num2str(Material)
371
         ],'_Rn_all_detrend']);
372
373
    %%
374
375
    figure('Name','Total Corrosion Current Density')
376
    movegui('northeast')
377
    % movegui([1345, 50])
378
    for k = 1:d \% Plot days 1 - 7
379
         if k == 1
380
             continue
381
         end
         if k == 6
382
383
             I_corr_store{k} = [NaN(1,8) I_corr_store{k}];
384
         end
385
         I_corr = I_corr_store{k};
```

```
386
         text = ['Day ', num2str(k)];
387
         plot(I_corr,strcat('-',Markers{k}),'DisplayName', text, 'linewidth', 1);
388
         hold on
389
    end
390
    hold off
391
    xlabel('Time (h)')
392
    ylabel({'i_{corr} (?A)'})
393
    set(gca, 'YScale', 'log')
394
    axis([0 26 —inf inf])
395
    set(gca,'XTick',(0:6:24))
    % legend ('show','Location','best')
396
    legend ('show', 'Position', [0.53 0.38 0.2 0.2], 'NumColumns', 3, 'Orientation', '
397
         horizontal')
398
    h = legend;
399
    set(h, 'fontsize', 9);
400
    print('-dpng','-r300',[[num2str(Material)],'_corrosion_current_density']);
401
    %%
402
    figure('Name','Total Corrosion Rate')
403
    movegui('southeast')
404
    for k = 1:d \% Plot days 1 - 7
405
         if k == 1% Exlude day 1
406
             continue
407
         end
408
         if k == 6
409
             corrosion_rate_store{k} = [NaN(1,8) corrosion_rate_store{k}];
410
         end
411
         corrosion_rate = corrosion_rate_store{k};
         text = ['Day ', num2str(k)];
412
         plot(corrosion_rate,strcat('-',Markers{k}), 'DisplayName', text, 'linewidth',
413
             1);
414
         hold on
415
    end
    set(gca, 'YScale', 'log')
416
417
    xlabel('Time (h)')
418
    ylabel('Corrosion rate (mm year^{-1})')
419
    axis([0 24 0 10^1])
420 set(gca, 'XTick', (0:6:24))
421 |legend ('show', 'Location', 'best', 'NumColumns', 2)
```

```
422 h = legend;
423 set(h, 'fontsize', 9);
424
    print('-dpng','-r300',[[num2str(Material)],'_corrosion_rate']);
425
    200
426 % close all
427
    save ('Pitting_index\403_PI_avg.txt', 'PI_avg', '—ascii')
    save ('Pitting_index\403_PI_std.txt', 'PI_std', '—ascii')
428
    save ('Coefficient_of_variation\403_CV_avg.txt', 'CV_avg', '-ascii')
429
430
    save ('Coefficient_of_variation\403_CV_std.txt', 'CV_std', '_ascii')
    save ('Electrochemical_noise_resistance\403_Rn_avg.txt', 'R_n_avg', '—ascii')
431
432
    save ('Electrochemical_noise_resistance\403_Rn_detrend_avg.txt', 'R_n_detrend_avg',
          '—ascii')
433
    save ('Electrochemical_noise_resistance\403_CR.txt','corrosion_rate_avg','
        corrosion_rate_std', '—ascii')
434
    toc
```

### Appendix **B**

# Strain Evolution at Pits during Fatigue Loading

### **B.1** Introduction

The presence of a stress concentration in a surface, be it a notch or corrosion pit, is known to reduce the number of fatigue cycles required to initiate cracks; leading to specimen failure. Many of the studies reported within this thesis have investigated the effects of corrosion pits on the fatigue life of engineering alloys such as stainless steel (SS) [39, 98, 114, 115, 140].

The prescence of a corrosion pit results in a stress concentration that depends upon the shape and geometry of the pit in relation to the direction of applied load. Despite some authors reporting the initiation of cracks at the base of corrosion pits [133, 140, 179– 181], it appears that most cracks initiate near to the pit mouth. This was initially shown, with X-ray computed tomography (XCT), by Horner et al. [157] and has been supported by publications from Schönbauer et al. [115] and Turnbull [150] who report that at high applied stresses, the plastic strain is concentrated around the pit mouth, facilitating crack initiation at this location.

As the cracks are likely to initiate at the mouth of the corrosion pit, it allows surface observation techniques to be utilised in order to study the initiation and growth of cracks. Previously, techniques such as in-situ optical microscopy (OM) have been used to measure the surface crack length [142]. Whilst this technique is useful for measuring the short crack growth it gives little information about the material changes occurring prior to crack initiation. As such, digital image correlation (DIC) offers itself as a method for monitoring the evolution of surface strain during loading and has previously been used to calculate a threshold strain ( $\epsilon_{th}$ ) value for crack initiation by Evans et al. [178] and Hashim [285] in X-65 carbon steel and 316L SS respectively. A  $\epsilon_{th}$  value of 0.24 ± 0.06 % strain was measured for X-65 material and a higher average  $\epsilon_{th}$  value of 15 ± 2 % was measured in 316L. These results suggest that the value of  $\epsilon_{th}$  is an intrinsic material property, that is unaffected by mechanical factors such as the stress concentration factor (SCF) of the corrosion pit. Such material property could subsequently be used in corrosion fatigue models as the criteria for switching between a corrosion dominated pit growth model to a mechanics based crack growth model.

This initial investigation uses a 12Cr FV566 martensitic SS, used for the low pressure steam turbine (LPST) blades in power plants. Artificial pits were generated on the surface of the specimen, prior to fatigue cycling and images of the surface were captured, that were subsequently used for DIC to provide values of  $\epsilon_{th}$  for this material.

### **B.2** Principles of Operation

In order to calculate the surface displacement between two comparable images, the digital image needs to contain sufficient detail within the greyscale pixel intensities. Usually, a surface speckle pattern is used to generate intensities ranging from 0, representing white, up to a maximum value representing black. Conventionally, a byte image is used with an 8-bit range from 0 to 255 or a 16-bit range that extends up to 65 535. When the speckle pattern surface is imaged with a digital camera it will create a pixel array, where unique features of the speckle pattern will result in different intensities being recorded, creating contrast in the image. Upon the application of load to a specimen, the displacement can be calculated by comparing the *before* (reference image) and *after* images within specialist software that tracks the features of the speckle pattern.

As the specimen and surface speckle pattern usually undergo translation, deformation and rotation during loading, it is required to define subsets within the digital image to make algorithm correlation possible with smaller errors [290]. The LaVision DaVis software used within this research, makes displacement vector calculations, between images, with a least squares matching algorithm. The process starts from a seed point in the reference image, which is a single subset (e.g.  $16 \times 16$  pixels), containing at least three features which are distinguishable due to different greyscale intensity values. Consequently, the speckle pattern chosen determines the minimum size of the subset that can be chosen i.e. if features in the speckle pattern are  $\sim 15 \times 15$  pixels in size then a subset of  $16 \times 16$  pixels would only contain one feature; not three. The algorithm will then attempt to identify the seed point in each subsequent deformed image and calculate the displacement between them. The rest of the image is analysed in iterations from the original seed point, which increases the total analysed region until the whole digital image is mapped.

As previously mentioned, consideration must be taken when choosing the subset size so that it contains an adequate number of features. A large subset size can offer a higher level of precision (due to the increased number of features within a subset), but this limits the spatial resolution on the analysed map as the displacement of all the pixels within a subset is assumed equal. There is clearly benefit in minimising the size of features in the surface speckle pattern as this allows a smaller subset size, increasing the spatial resolution, whilst maintaining high precision. Previous DIC work has used paint droplets to generate a random speckle pattern as the use of white and black paint creates good contrast, however the droplets can be hundreds of microns in size (suitable for horizontal field width (HFW) = 40 mm) and may not deform in the same manner as the surface beneath introducing systematic errors [291]. Consequently, the intrinsic material microstructure can be used to provide an adequate pattern as grain features can measure tens of microns. The system can also be improved by allowing some overlap between subsets in order to locate surface discontinuities (such as cracks) but will increase the processing time. Therefore, LaVision recommend an overlap equal to 25% to 33% of the subset size. Once the displacement vector field has been calculated by the algorithm, various components of strain can be calculated from the change lengths relative to the original length.
| Specimen | Depth (µm) | Width (µm) | Aspect ratio |
|----------|------------|------------|--------------|
| 1        | 67         | 222.00     | 0.61         |
| 2        | 130        | 204.75     | 1.27         |

TABLE B.1: Pit geometries on DIC specimens.

# **B.3** Experimental

Fatigue specimens of FV566 SS were the same as those shown in Fig. 6.2, with a fine ground finish, corresponding to an average surface roughness of 0.1 µm. The droplet method (Section 5.2.2) was used to create a single artificial corrosion pit on the gauge section of the fatigue specimen and the time of polarisation allowed pits of variable depths to be produced. After production and cleaning the corrosion pit geometry was measured with a Keyence VK-X200K 3D laser confocal scanning microscopy (LCSM); the geometries are reported in Table B.1.

Following pit generation, the specimen was ground with successive SiC papers up to P4000, then polished with 3 µm and 1 µm diamond paste and finally etched for 90 s with Villela's reagent (1 g picric acid, 5 ml HCl and 100 ml ethanol) to create the over etched speckle pattern required to create contrast for DIC. In order to carry out fatigue tests under strain control, as per ASTM E606-12 [112], a pre-wired Omega KFH-1.5-120-C1-11L1M2R strain gauge with 1.5 mm<sup>2</sup> grid was attached directly behind the corrosion pit using a Loctite<sup>®</sup> cyanoacrylate adhesive.

The micrographs required for DIC analysis were captured with the optical microscope setup described in Section 6.2.3 but images were captured at the same, initially measured, value of maximum strain  $\epsilon_{max}$ , rather than  $F_{max}$ , to ensure changes in strain due to machine compliance were not introduced. A Mitutoyo long WD objective lens with  $10 \times$  magnification was employed and images were captured on a Sony Alpha A77 II in .ARW format with pixel arrays of  $6000 \times 3376$  pixels. The LabVIEW programme was modified so that it included a loop that would process the images using *ImageMagick*, with the command

cmd /k mogrify -format TIF \*.ARW && mogrify -type grayscale \*.TIF && move \*.ARW RAW && move \*.TIF TIF



FIGURE B.1: (A) Etched speckle pattern captured using the optical microscope system showing the corrosion pit and direction of applied load. (B) A histogram of the pixel intensities from the optical image.

to convert the .ARW files into 16-bit greyscale .TIF files, with gray-scale intensity values from 0 to 65 535 and move the files to the relevant sub folders. The result was a sequence of greyscale TIF files with 1000 cycles between images that measured  $6024 \times 4024$  pixels, corresponding to pixel size of 0.23 µm. The reference image captured, prior to fatigue, is shown in Fig. B.1A, where the resultant microstructure from the Vilella etch is visible. The corrosion pit is located in the centre of the image and the direction load will be applied is indicated. From this image a histogram was computed (Fig. B.1B) that shows the average pixel intensity was 42784; approximately two thirds of the maximum possible pixel intensity.

Fatigue cycling was performed on an Instron ElectroPuls E10000 with a stress range  $(\Delta \sigma)$  of 600 MPa i.e.  $\sigma_{max} = 80 \% \sigma_y$  at a stress ratio of R = 0.1 and cyclic frequency 15 Hz. An initial reference image was captured at  $F_{max}$  and the corresponding  $\epsilon_{max}$  was then used within the automated loop where the specimen was cycled for 999 cycles in load control and then the machine loaded the sample to  $\epsilon_{max}$  where the next image was captured after a short period to allow the image to stabilise. This automated loop was continued until sufficient crack initiation and growth occurred that the test was terminated.

2D DIC was performed using LaVision DaVis 8.4 software. A virtual mask was generated within the software to cover the geometry of the pit so that only strain in the remaining bulk material was calculated and to reduce errors from reflections at the edge of the pit. An initial investigation was performed to determine the optimum subset size and overlap to be used within the software as this determines the resolution and precision that are measurable from the results. Once the subset size was chosen, a rigid body translation strain measurement was calculated by analysing the strain map from two images separated by a 25.4 µm shift in the y-axis. A perfect system would calculate a change in strain that was very close to 0% as only translation movement has occurred between the images rather than a deformation or displacement.

### **B.4** Results and Discussion

#### **B.4.1** Calculation of System Error

When undertaking quantitative measurements with DIC, it is important to understand the errors that are introduced. The quoted precision of displacement can be as small as 0.01 pixels but for a larger subset size. In order to accurately resolve the shape of a defect such as a corrosion pit or crack a smaller subset size is required at the cost of reduced precision, so a compromise must be made. A rigid body translation measurement was conducted in order to determine the precision error due to a translation of the pattern and magnification chosen. The root mean square value of the calculated displacement values represents the deviation in subset values across the image array. A smaller measured root mean square would represent a more precise measurement.

The etched microstructure of the martensitic FV566 SS was used as the speckle pattern. Through a rigid body translation measurement, the effect of choosing a different subset size and overlap between subsets is shown in Fig. B.2. As would be expected a smaller subset size creates more deviation in the subset displacement measured resulting in a higher root mean square strain error ( $\epsilon_{yy}$ ).

A small subset size was desired to allow greater resolution of the corrosion pit and provide spatial resolution for detection of crack initiation so a subset size of 29 pixels  $\times$  29 pixels and the recommended 28 % overlap was identified suitable, corresponding to a strain error of 0.32 %.



FIGURE B.2: A plot of precision error (RMS) in  $\epsilon_{yy}$  strain vs. the chosen subset size for different values of subset overlap.

TABLE B.2: The cycle number at which a crack initiated from the left or right hand side of the corrosion pit on each specimen.

| Specimen | Cycle number |        |  |
|----------|--------------|--------|--|
| opeennen | Left         | Right  |  |
| 1        | 11 000       | 55 000 |  |
| 2        | 4000         | 1000   |  |

#### **B.4.2** Crack Initiation at Corrosion Pits

The sequence of captured images was used to identify the region of crack initiation on each side of the corrosion pit. From these, it was also possible to deduce the corresponding fatigue cycle number at which the cracks first became visible—the pit-crack transition. For each specimen, the results are shown in Table B.2, where the cycle number corresponding to the pit-crack transition is reported.

From these results, it is clear that the number of cycles required for crack initiation decreases as the depth of corrosion pit increases (depth<sub>spec. 1</sub> < depth<sub>spec. 2</sub>). For a measured pit depth of 67 µm (spec. 1) a crack initiated on the left hand side after  $1.1 \times 10^4$  cycles and on the right hand side after a further  $4.4 \times 10^4$  cycles. The difference in the number of



FIGURE B.3: Optical micrographs of the corrosion pits on (A) Spec. 1 after 75 000 cycles and (B) Spec. 2 after 20 000 cycles. The black arrow indicates the direction of cyclic load and the white arrows highlight the locations of crack growth.

cycles required for crack initiation on either side of the pit is likely due to the variable microtopography of the corrosion pit generating variation on the local SCF. For a pit depth of 130  $\mu$ m (spec. 2), a crack initiated within the first 1000 cycles and the crack initiated on the opposite side 3000 cycles later.

As can be seen in Fig. B.3, the fatigue cracks grew perpendicular to the direction of applied cyclic load and initiated on both the left and right hand side of the corrosion pit present on the fatigue sample.

The captured micrographs were used to measure the surface length of the crack as it extended from the corrosion pit. From these surface crack length measurements it was possible to calculate a crack growth rate,  $\frac{da}{dN}$ , following the relationship

$$\frac{da}{dN} = \frac{a_2 - a_1}{N_2 - N_1} \tag{B.1}$$

where *a* is the crack length, *N* is the number of cycles and the subscripts 2 and 1 denote measurements at the current and previous interval respectively. The measured surface crack length vs. number of cycles is shown in Figs. B.4A and B.4C for specimen one and two respectively. From these plots the crack growth rate can be calculated and plotted against the measured surface crack length, as shown in Figs. B.4B and B.4D. It can be observed that the crack growth rate oscillates in velocity due to interactions of the crack with microstructrual features such as grain boundaries. The growth rate is of the order



FIGURE B.4: Plots of surface crack length vs. cycle number and crack growth rate vs. surface crack length respectively for (A) and (B) specimen 1 and (C) and (D) specimen 2.

 $1 \times 10^{-8}$  m cycle<sup>-1</sup> to  $3 \times 10^{-8}$  m cycle<sup>-1</sup>, which is of similar magnitude to that measured in [142] using the same material. By performing DIC on the sequences of greyscale images, it was also possible to calculate the change in surface strain due to displacements in the speckle surface pattern.

# **B.4.3** Threshold Strain for Crack Initiation

The generation of plastic strain due to the localisation of stress concentration, at defects such as corrosion pits, suggests that it may be possible to measure a threshold strain  $\epsilon_{th}$  that is required for a crack to initiate. DIC offers a method for analysing images of the surface, during mechanical testing, from which strain maps of the pit area over time can be produced, as shown in Fig. B.5.

The first image in the sequence, shows the  $\epsilon_{yy}$  strain map after  $1.0 \times 10^4$  cycles i.e



FIGURE B.5: A sequence of calculated  $\epsilon_{yy}$  strain maps showing the evolution of strain resulting in crack initiation, highlighted by the white circle on the left hand side of the pit. Strain calculated after (A)  $1.0 \times 10^4$ , (B)  $1.5 \times 10^4$ , (C)  $2.0 \times 10^4$ , (D)  $2.5 \times 10^4$ , (E)  $3.0 \times 10^4$  and (F)  $3.5 \times 10^4$  cycles.



FIGURE B.6: Effect of window size, used for moving average smoothing, in relation to the sum of absolute difference between raw and mean values.

before visible crack initiation. The subsequent images show the localisation of plastic strain, on the left hand side of the pit due to crack initiation. The complete sequence of images was used to identify the region of crack initiation on the left and right hand sides of the two specimens and the evolution of  $\epsilon_{yy}$  strain at these precise locations could be plotted allowing  $\epsilon_{th}$  to be extracted.

The results of strain vs. cycle number showed some noise in the data, so the results were smoothed using a moving average function. To determine the size of the window used for the moving average calculation, window sizes from three to twenty were assessed for suitability and the sum of the absolute difference between the *raw* and *mean* value can be plotted for each window size, as shown in Fig. B.6. A larger window would produce a smoother fitted curve, whereas a smaller window produces noisier data that should be closer to the raw data. From the plot of variable window size, it can be observed there is little benefit in increasing the average window size beyond a value of seven, so this value was chosen as the window size used to smooth the DIC strain data.

The plot of extracted  $\epsilon_{yy}$  strain value for the cracks initiating from the left and right hand sides of the corrosion pit on spec. 1 are shown in Figs. B.7A and B.7B. The cycle number at which crack initiation was observed to occur in the micrographs is indicated in the plots and the value of  $\epsilon_{th}$  reported, was taken as the mean value of  $\epsilon_{yy}$  at this position. The values of  $\epsilon_{th}$  for each specimen are given in Table B.3. For specimen 1, with

| Specimen | $\epsilon_{th}$ (%) |       |
|----------|---------------------|-------|
| opeennen | Left                | Right |
| 1        | 0.80                | 1.48  |
| 2        | 4.28                | 2.39  |

TABLE B.3: The mean value of  $\epsilon_{yy}$  at crack initiation from each pit.

a measured pit depth of 67 µm and AR 0.61, the  $\epsilon_{th}$  was around 1% at each side of the pit; values slightly higher than those measured by Evans et al. [178] (0.24%) but a lot lower than Hashim [285] (15%). Specimen 2 was larger, with a pit depth of 130 µm and AR of 1.27. The measured value of  $\epsilon_{th}$  was larger—around 3%. It would be unjust to draw scientific conclusions from the limited set of preliminary tests. Nevertheless, they may suggest that the value of  $\epsilon_{th}$  may be dependable upon the pit geometry, as presented here a larger pit depth resulted in a higher value of  $\epsilon_{th}$ . However, there is concern that due to the high applied  $\Delta \sigma$ , at 80%  $\sigma_y$ , the reported values of  $\epsilon_{th}$ , for the larger pit, may be higher than the true value, as the cracks were found to initiate in very few cycles. Consequently, it is possible that plastic strain had already developed to the the real value of  $\epsilon_{th}$  within the first 1000 cycles so further studies should be conducted using a lower applied  $\Delta \sigma$ .



FIGURE B.7: Plots of the localised  $\epsilon_{yy}$  strain vs. cycle number from the pit on spec. 1 (A) Crack that initiated on the left hand side of the pit. (B) Crack that initiated on the right hand side of the pit.

# **B.5** Conclusions

- 1. As reported by other authors, cracks were observed to initiate at the mouth of the corrosion pits produced, rather than the pit base.
- 2. The number of cycles required to initiate a crack was found to decrease with increasing pit depth. A crack initiated after  $1.1 \times 10^4$  cycles for a 67 µm deep pit but within  $4 \times 10^3$  cycles for a 130 µm pit.
- 3. These preliminary results suggest that a higher  $\epsilon_{th}$  is reached when the corrosion pit is deeper.
- 4. It is possible that the difference in measured  $\epsilon_{th}$  is an artefact of cracks initiating within the first hundreds of cycles and the true value of  $\epsilon_{th}$  was missed.