Liquid *In Situ* Analytical TEM:
Technique Development and Applications to Austenitic Stainless Steel

A thesis submitted to the University of Manchester for the degree of

Doctor of Philosophy (Ph.D.)

in the Faculty of Science & Engineering

2017

Sibylle Schilling

School of Materials

Materials Performance Centre
Contents

CONTENTS .......................................................................................................................... 1

LIST OF FIGURES AND TABLES .................................................................................. 5

LIST OF ABBREVIATIONS ............................................................................................... 10

ABSTRACT .......................................................................................................................... 12

DECLARATION .................................................................................................................... 13

COPYRIGHT ......................................................................................................................... 14

ACKNOWLEDGMENT ........................................................................................................... 15

CHAPTER 1: INTRODUCTION ............................................................................................. 16

CHAPTER 2: LITERATURE REVIEW .................................................................................... 19

2.1 Classification of Austenitic stainless steels ................................................................. 19

  2.1.1 Composition ............................................................................................................. 19

  2.1.2 Microstructure ........................................................................................................ 21

    • Inclusions ..................................................................................................................... 22

    • Phase Stability: Martensite ....................................................................................... 23

    • Carbide Precipitation ............................................................................................... 24

2.2 Environmentally-Assisted Cracking and Stress Corrosion Cracking ....................... 26

  2.2.1 Mechanisms of SCC .............................................................................................. 28

    • Slip Dissolution Model (SD) ...................................................................................... 28

    • Hydrogen Embrittlement (HE) .................................................................................. 29

2.3 Overview of Light Water Reactors and EAC/SCC .................................................... 30

  2.3.1 Factors affecting PWSCC (Primary Water Stress Corrosion Cracking) of Cold Worked Material 31

    • Effect of MnS Inclusion Dissolution in Primary Water .............................................. 31

    • Effect of Planar Slip on SCC .................................................................................... 33

    • Effect of Temperature .............................................................................................. 33

    • Effect of Environment ............................................................................................. 34

2.4 Electrochemical Analysis Techniques ........................................................................ 35

  2.4.1 Conventional Potentiodynamic Polarisation Behaviour ....................................... 35

  2.4.2 Factors which influence the electrochemical reaction .......................................... 37
• Influence of the passivity ................................................................. 38
• Influence of pH .................................................................................. 40
• Influence of the temperature .............................................................. 41
• Solution velocity effect ...................................................................... 43

2.4.3 Microcapillary Cell Technique .......................................................... 44

2.5 In situ transmission electron microscopy ................................................ 48
  2.5.1 In situ Heating Studies in the TEM ................................................ 48
  2.5.2 In situ TEM: Gas Reaction Cell .................................................. 50
  2.5.3 In situ TEM: Gas-H$_2$O Cell ......................................................... 51
  2.5.4 Applications of In Situ HVEM: Oxidation, Corrosion and Hydrogen Embrittlement .......... 55
    • Oxidation .................................................................................. 56
    • Corrosion .................................................................................. 56
    • Hydrogen embrittlement .............................................................. 56

2.5.5 Factors which influence the in situ system .......................................... 57
  • Resolution .................................................................................. 57
  • Electron beam heating ................................................................. 59
  • Ionization damage ........................................................................ 60

2.6 Summary of Literature Review .................................................................. 63

CHAPTER 3: EXPERIMENTAL METHODS AND CELL DEVELOPMENTS .......... 64

3.1 Experimental Methods for Investigation of Type 304 SS ............................ 64
  3.1.1 Specimen Preparations ................................................................. 64
    • Grinding and Polishing ............................................................... 64
    • Etching ..................................................................................... 64
    • Electropolishing ....................................................................... 65
    • Transmission Electron Microscopy Preparation ......................... 65
  3.1.2 Microscopy and Analysis techniques ............................................... 65
    • Light Optical Microscopy .......................................................... 65
    • Electron Microscopy ................................................................ 65
    • Scanning Electron Microscope (SEM) ........................................ 66
    • Transmission Electron Microscope (TEM) .................................... 66
  3.1.3 Mechanical Test Conditions ......................................................... 67
3.2 General Electrochemical Test Parameters and Construction of the Microcell ..........68
   3.2.1 Electrochemical Setups .................................................................68
   3.2.2 Construction of the Microcell ..........................................................68

3.3 Liquid in situ TEM cell technique ..................................................................69
   3.3.1 Development of the specimen preparation technique for in situ TEM studies ....71

CHAPTER 4: CONTROL AND SCOPING EXPERIMENTS ........................................73

4.1 Material Characterisations .........................................................................73
   4.1.1 Microstructural Characterisation ..........................................................73
       • Light Optical Microscopy ........................................................................74
       • Scanning Electron Microscopy (SEM) .......................................................74
       • Grain Size analyse ................................................................................77
       • Transmission Electron Microscopy ..........................................................78
   4.1.2 Mechanical Test ..................................................................................80
       • Vickers Hardness Test ............................................................................80
       • Slow strain rate test (SSRT) ..................................................................81

4.2 Microcell Technique Observations .............................................................83
   4.2.1 Microcell tip investigations ..................................................................83
   4.2.2 Comparison of microcell data for Type 304 SS with conventional polarization data .............85

4.3 Develop Experimental Protocols/Techniques to enable validated in situ liquid cell reactions at the nano-scale .................................................................87
   4.3.1 In situ holder and assembly of E-Chip ...................................................87
   4.3.2 Pre-Experimental of liquid in situ TEM: Type 304 SS .................................90
   4.3.3 Electrodes modifications and application of the electrochemical E-chips ..........................92
   4.3.4 Stability tests for reference electrodes ...................................................94

4.4 Summary of Control and Scoping Experiments .............................................96

CHAPTER 5: FIRST PROPOSED MANUSCRIPT ..................................................97

5.1 Introduction: ............................................................................................97
5.2 Manuscript: .............................................................................................97

CHAPTER 6: SECOND PROPOSED MANUSCRIPT ........................................118

6.1 Introduction: ............................................................................................118
6.2 Manuscript: ........................................................................................................... 118

CHAPTER 7: THIRD PROPOSED MANUSCRIPT ......................................................... 142

7.1 Introduction: ....................................................................................................... 142
7.2 Manuscript: ......................................................................................................... 142

CHAPTER 8: FOURTH PROPOSED MANUSCRIPT .................................................... 153

8.1 Introduction: ....................................................................................................... 153
8.2 Manuscript: ......................................................................................................... 153

CHAPTER 9: FURTHER DISCUSSIONS ..................................................................... 178

9.1 Pre- investigations of Type 304 SS ................................................................. 178
9.2 In situ TEM investigations and evaluations .............................................. 179
  • Hybrid specimen preparation technique and E-Cell modifications ............... 179
  • Applications of the liquid in situ Cell and electrochemical in situ Cell .......... 181

CHAPTER 10: FINAL CONCLUSIONS .................................................................. 185

CHAPTER 11: FUTURE WORK .............................................................................. 187

CHAPTER 12: APPENDIX ....................................................................................... 190

Applying Advanced Analytical In Situ TEM to Assess SCC “Precursor” Reactions in Austenitic Stainless Steel in H₂O .................................................................................................................. 190

Liquid In Situ Analytical Electron Microscopy: Examining SCC Precursor Events for Type 304 Stainless Steel in H₂O ......................................................................................................................... 203

Novel Hybrid Sample Preparation Method for In Situ Liquid Cell TEM Analysis .................................................................................................................. 207

BIBLIOGRAPHY ...................................................................................................... 211

Final Word Count: ~48,819
List of Figures and Tables

Figure 1: Schaeffler-Delong diagram with position of some common Grades. [3].............21
Figure 2: Schematic of microstructure of a stainless steel. [10]........................................21
Figure 3: Area distribution for sulphide particles found in 304 SS. [16]...............................23
Figure 4: Schematic illustration of deformation process. [20].............................................24
Figure 5: Schematic Factors Affecting Corrosion and Stress Corrosion Cracking. [26].........26
Figure 6: The stages of development of SCC with time. [28].............................................27
Figure 7: The use of austenitic stainless steel (a) BWR and (b) PWR. [44, 45].....................30
Figure 8: Economy; Scott and Combrade, image reproduced from Steahle. [69]...............34
Figure 9: Schematic representation of passivation. Anodic current density-potential curve of a Cr-passivated steel under acidic conditions. Ordinate axis: $E_O$: equilibrium potentials of O, $E_p$: activation potential; $E_F$: critical passivation potential; $E_{Corr}$: corrosion potential. Abscissa axis: $i_p$: residual current and $i_{crit}$: critical current density. [73]...36
Figure 10: Chloride concentration in neutral water on polarisation curve of 304 SS. [73].....39
Figure 11: Pourbaix diagram for Fe/H$_2$O system with indicated areas of immunity, corrosion and passivation. Dashed lines are (a) hydrogen and (b) oxygen reactions. [82]........40
Figure 12: Schematic illustration (a) of pH vs. temperature effect in H$_2$O [83] and (b) the effect of increasing temperature on polarisation behaviour on steel. [84]..........42
Figure 13: Schematic illustration of the effect of aeration, deaeration and velocity in neutral seawater. [84].........................................................................................................................43
Figure 14: Schematic representation of different Microcell Tips by Suter. [87].................44
Figure 15: (a) Schematic of the Suter microcell system and (b) photograph of microcell. [90]........................................................................................................................................45
Figure 16: Potentiodynamic polarization curves of AISI 304 in 0.1 M Na$_2$SO$_4$ at room temperature, 60, and 90 °C, 70 mm, 0.5 mV/s. [91]..................................................46
Figure 17: (a) Schematic of microcell system developed by Martin and (b) photograph of microcell. [87].........................................................................................................................46
Figure 18: Polarisation curve of different zones of AISI 304SS. [89]..................47
Figure 19: The specimen tip of single tilt hot stage. [99].................................49
Figure 20: Double tilt hot stage with fine hair spring thermocouple. [99]...............49
Figure 21: Schematic of the differentially pumped apertured gas reaction cell located between
(a) upper and lower objective pole pieces with (b) side entry specimen holder
developed by Swann. [108]..................................................................................51
Figure 22: Schematic of the environmental cell with side entry by Allinson. [111]..........51
Figure 23: Schematic illustration of a liquid in situ cell by Williamson and Ross. [118].....52
Figure 24: Resolution vs. Liquid thickness for TEM, STEM and SEM. [122].................53
Figure 25: Cyclic Voltammetry tests of a Pt film on E-Chip in (a) thick liquid and (b) in
thinner liquid........................................................................................................54
Figure 26: Polarisation curve of Al coated chip in 0.01M NaCl with scan rate 0.5 mV/s [127]
.............................................................................................................................55
Figure 27: Egerton’s classification of electron beam-induced effects. [137]....................58
Figure 28: TEM experiment of Fe78Si12B10 specimen to consider the model. TEM images
of (a) amorphous morphology and (b) diffraction pattern. (c) Crystallized
morphology and (d) diffraction pattern after 1h electron irradiation from 200 keV
TEM. [143]..............................................................................................................60
Figure 29: Schematic diagram, indicating the products of radiolysis. [145].................61
Figure 30: Sheet specimen used for SSRT. .................................................................67
Figure 31: Microcell version of the system constructed in this thesis project: (a) schematic of
the cell and (b) photograph of actual microcell. ......................................................69
Figure 32: Schematic of a fully encapsulated liquid in situ TEM cell with 50nm SiNx
windows. The sandwich-like configuration with a top and a bottom chip is shown,
the specimen is placed between these two chips. A specially-designed Be lid
(optimised for XEDS) seals the cell between O-rings in the TEM stage by N.
Zaluzec. ..................................................................................................................70
Figure 33: Schematic diagram of inlet and outlet of in situ TEM holder by Protochip .........70
Figure 34: FIB Cut and paste” approach for removing a thin section of an electropolished
specimen and relocating on top of a SiNx window for E-Cell studies. (a) STEM BF
image in the FIB/SEM, (b) SE image of lift out process with cut outs around the perimeter of the specimen, (c) SE image of specimen placed on the E-chip with SiNx liquid cell window visible, notice the Pt deposits at the four corners attaching the lift out to the Si frame. ................................................................. 72

Figure 35: (a) SE image of wall thickness measurement, (b) lift-out of specimen and (c) placing specimen onto working electrode. Note the tapered slot at the top left of the specimen, which will be used to attach the specimen to the electrode using a Pt FIB deposition. ............................................................................................................ 72

Figure 36: Light optical microscopy of (a) transverse and (b) closer observation of the 304SS. ............................................................................................................................................................................. 74

Figure 37: SEM/BSE image of deformed microstructure in 304 SS. ....................... 75

Figure 38: SEM/BSE Z-contrast images of 304SS transverse orientation. ................. 76

Figure 39: (a) Closer observation of SEM/EBSD z-contrast image of 304 SS. (b) Inverse pole figure map and c) Phase fraction of 304SS transverse orientation. ....................... 76

Figure 40: IPF colouring reference. .................................................................................. 76

Figure 41: (a) Inverse pole figure and (b) Phase volume map of deformed austenitic grains.77

Figure 42: Lower magnification EBSD maps of CW304SS. (a) grain areas and (b) linear intercept method. .......................................................................................................................................................... 78

Figure 43: TEM Images of deformation austenite. ......................................................... 79

Figure 44: (a) TEM image and (b) diffraction pattern obtained from cold worked 304 SS. .. 79

Figure 45: (a) TEM morphology of deformed austenite grain with a “twin-like” structure and (b) diffraction pattern obtained from cold worked 304 SS. ................................. 80

Figure 46: SSRT of rolling direction (red curve) and normal direction (black curve) in autoclave at 300ºC and 95 bar pressure (H₂O with a conductivity of less than 0.1 µS/cm; DO less than 5ppb, and 30 cc/kg H₂). Strain rate of 1x10⁻⁷ 1/s was applied to σ_yield before transitioning to 1x10⁻⁸ 1/s. ...................................................................................... 81

Figure 47: Fracture morphology of CW 304 SS after SSRT: (a) cleavage and mixed mode fracture, (b) intergranular areas, and (c) large ductile dimples. ......................... 82

Figure 48: Schematic illustration of the microcell tip reaction with the surface. .............. 83
Figure 49: Laser scanning confocal microscope images of the pit produced during the microcell experiments. (a) Microcell tip size (inner black circular region), (b) irregular pits produced by a leaky microcell tip (red circle is exposed area) and (c) pit formation after polarisation experiments.................................................................83

Figure 50: (a) Summary of the Pitting Potential Measurements for the 20% CW Type 304 SS and (b) potentiodynamic polarisation curve of 20% CW Type 304 SS in 0.1 mol/l NaCl with a scan rate 1 mV/s and 400 µm tip size. .................................................................84

Figure 51: Potentiodynamic Polarisation curve of 20% CW Type 304 SS in 1mol/l NaCl. Black curve was measured using the microcell (µm²) and red curve was measured using conventional bulk cell (cm²) range. .................................................................86

Figure 52: Laser scanning confocal image of hybrid specimen onto E-chip. .........................88

Figure 53: Laser scanning confocal image of modified hybrid specimen onto modified E-chip. .................................................................................................................................88

Figure 54: Schematic diagram of assembly procedure of electrochemical in situ TEM holder with a modified Be top lid by Protochips. .................................................................89

Figure 55: (a) Schematic of cross-section of an AEM’s objective lens showing a conventional XEDS/eCell geometry and illustrating the shadowing of the line-of-sight path of the detector by the penumbra of the eCell holder. (b) Schematic diagram showing cross-section of eCell holder before (left) and after modifications (right), illustrating the removal of material that blocks the line of sight path to the X-ray detector. Si wafer (green), SiN windows (blue), Si clamping mechanism (gray), tapered slot in Si clamp mechanism (gray), Holder body (orange) by N.J. Zaluzec. [128]..................90

Figure 56: (a) SEM images and (b) EDX analysis of particles on hybrid sample after in situ investigation under the beam conditions. ..............................................................................91

Figure 57: STEM-EDX spectrum images before (a) and after (d) 3h exposure in distilled water. .................................................................................................................................92

Figure 58: Schematic illustration of the two original Protochips electrochemical-chip configurations: (a) Type I - linear configuration of Pt-electrodes, (b) Type II- glassy carbon electrode with a horizontal direction of the SiNx window. ........................................93
Figure 59: (a) Schematic illustration of modified electrochemical (Type III) chip and (b) detail of red dashed region. The WE electrode is ~10 µm outside of the SiNx window edge and RE and CE surrounds the SiNx window. ..............................93

Figure 60: Ex Situ OCP measurement of different electrolyte and E-Chip design..............95

List of Tables

Table 1: Typical composition of austenitic stainless steels. (Note that the balance is Fe) [2]19
Table 2: Volume between bottom and top E-Chips by Protochip. .................................70
Table 3: Chemical Composition of Type 304. .................................................................73
Table 4: Summary of the average grain size analyses. .......................................................78
Table 5: Results of Vickers-Microhardness Tests [HV1] for the CW 304 SS. .................80
### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEM</td>
<td>Analytic electron microscopy</td>
</tr>
<tr>
<td>ASTM</td>
<td>American society for testing and materials</td>
</tr>
<tr>
<td>AP</td>
<td>Active path</td>
</tr>
<tr>
<td>BCC</td>
<td>Body-centered cubic</td>
</tr>
<tr>
<td>BWR</td>
<td>Boiling water reactor</td>
</tr>
<tr>
<td>CE</td>
<td>Counter electrode</td>
</tr>
<tr>
<td>CGR</td>
<td>Crack growth rate</td>
</tr>
<tr>
<td>CT</td>
<td>Compact tension</td>
</tr>
<tr>
<td>CW</td>
<td>Cold work</td>
</tr>
<tr>
<td>EAC/EAF</td>
<td>Environmentally-assisted cracking/ Environmentally-assisted fracture</td>
</tr>
<tr>
<td>EBSD</td>
<td>Electron backscattered diffraction</td>
</tr>
<tr>
<td>EDXS/XEDS</td>
<td>Energy-dispersive X-ray spectroscopy/ X-ray energy dispersive spectroscopy</td>
</tr>
<tr>
<td>EPRI</td>
<td>Electric Power Research Institute</td>
</tr>
<tr>
<td>FCC</td>
<td>Face-centered cubic</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused ion beam</td>
</tr>
<tr>
<td>FIC</td>
<td>Film induced cleavage</td>
</tr>
<tr>
<td>H₂</td>
<td>Dihydrogen</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>Hydrogen peroxide</td>
</tr>
<tr>
<td>HCP</td>
<td>Hexagonal close-packed</td>
</tr>
<tr>
<td>HE</td>
<td>Hydrogen Embrittlement</td>
</tr>
<tr>
<td>HEDE</td>
<td>Hydrogen Enhanced Decohesion</td>
</tr>
<tr>
<td>HELP</td>
<td>Hydrogen Enhanced Localized Plasticity</td>
</tr>
<tr>
<td>HREM</td>
<td>High resolution electron microscopy</td>
</tr>
<tr>
<td>HVEM</td>
<td>High voltage electron microscopy</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------------------------------------------------</td>
</tr>
<tr>
<td>IASCC</td>
<td>Intergranular stress corrosion cracking</td>
</tr>
<tr>
<td>IGSCC</td>
<td>Intergranular stress corrosion cracking</td>
</tr>
<tr>
<td>K</td>
<td>Stress intensity factor</td>
</tr>
<tr>
<td>KIC</td>
<td>Critical Stress Intensity Factor for mode I fracture</td>
</tr>
<tr>
<td>KISCC</td>
<td>Critical stress intensity factor for crack propagation</td>
</tr>
<tr>
<td>LWR</td>
<td>Light water reactor</td>
</tr>
<tr>
<td>MPC</td>
<td>Materials Performance Centre</td>
</tr>
<tr>
<td>O₂</td>
<td>Oxygen</td>
</tr>
<tr>
<td>Ox</td>
<td>Oxidation</td>
</tr>
<tr>
<td>OPS</td>
<td>Oxide polishing suspension</td>
</tr>
<tr>
<td>PEEK</td>
<td>Polyether ether ketone</td>
</tr>
<tr>
<td>PWR</td>
<td>Pressurised water reactor</td>
</tr>
<tr>
<td>PWSCC</td>
<td>Primary water stress corrosion cracking</td>
</tr>
<tr>
<td>RE</td>
<td>Reference electrode</td>
</tr>
<tr>
<td>Red</td>
<td>Reduction</td>
</tr>
<tr>
<td>SAM</td>
<td>Scanning auger microscopy</td>
</tr>
<tr>
<td>SCC</td>
<td>Stress corrosion cracking</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope/microscopy</td>
</tr>
<tr>
<td>SFE</td>
<td>Stacking fault energy</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard hydrogen electrode</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary ion mass spectrometry</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TGSCC</td>
<td>Transgranular stress corrosion cracking</td>
</tr>
<tr>
<td>UoM</td>
<td>The University of Manchester</td>
</tr>
</tbody>
</table>
ABSTRACT

“Liquid In Situ Analytical TEM: Technique Development and Applications to Austenitic Stainless Steel”

Sibylle Schilling,

Doctor of Philosophy (Ph.D.), The University of Manchester, 2017.

Environmentally-assisted cracking (EAC) phenomena affect the in-service behaviour of austenitic stainless steels in nuclear power plants. EAC includes such degradation phenomena as Stress Corrosion Cracking (SCC) and Corrosion Fatigue (CF). Factors affecting EAC include the material type, microstructure, environment, and stress. This is an important degradation issue for both current and Gen III+ light water reactors, particularly as nuclear power plant lifetimes are extended (>60 years). Thus, it is important to understand the behaviour of the alloys used in light water reactors, and phenomena such as SCC to avoid failures. Although there is no agreement on the mechanism(s) of SCC, the importance of localized electrochemical reactions at the material surface is widely recognised. Considerable research has been performed on SCC and CF crack growth, but the initiation phenomena are not fully understood. In this project, novel in situ analytical TEM techniques have been developed and applied to explore localised reactions in Type 304 austenitic stainless steel.

In situ transmission electron microscopy has become an increasingly important and dynamic research area in materials science with the advent of unique microscope platforms and a range of specialized in situ specimen holders. In metals research, the ability to image and perform X-ray energy dispersive spectroscopy (XED) analyses of metals in liquids are particularly important for detailed study of the metal-environment interactions with specific microstructural features. To further facilitate such studies a special hybrid specimen preparation technique involving electropolishing and FIB extraction has been developed in this thesis to enable metal specimens to be examined in the liquid cell TEM specimen holder using both distilled H₂O and H₂SO₄ solutions. Furthermore, a novel electrode configuration has been designed to permit the localized electrochemical measurement of electron-transparent specimens in the TEM.

These novel approaches have been benchmarked by extensive ex situ experiments, including both conventional electrochemical measurements and microcell measurements. The results are discussed in terms of validation of in situ test data as well as the role of the electron beam in the experiments. In situ liquid cell TEM experiments have also explored the localized dissolution of MnS inclusions in H₂O, and correlated the behaviour with ex situ experiments.

Based on the research performed in this thesis, in situ liquid cell and in situ electrochemical cell experiments can be used to study nanoscale reactions pertaining to corrosion and localized dissolution leading to “precursor” events for subsequent EAC phenomena.
Declaration

No portion of the work referred to in the dissertation has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.
Copyright

- Copyright in text of this dissertation rests with the author. Copies (by any process) either in full, or of extracts, may be made only in accordance with instructions given by the author. Details may be obtained from the appropriate Graduate Office. This page must form part of any such copies made. Further copies (by any process) of copies made in accordance with such instructions may not be made without the permission (in writing) of the author.

- The ownership of any intellectual property rights which may be described in this dissertation is vested in the University of Manchester, subject to any prior agreement to the contrary, and may not be made available for use by third parties without the written permission of the University, which will prescribe the terms and conditions of any such agreement.

- Further information on the conditions under which disclosures and exploitation may take place is available from the Head of the School of Materials.
Acknowledgment

I would like to thank all the people whom helped me in the completion of this thesis.

My special thanks goes to Prof. M. Grace Burke for the provision of this scientifically very interesting and challenging project and the patient support during the completion of this thesis. Particularly noteworthy are the many valuable discussions and suggestions as well as the steady interest in the progress of the work and for providing a significant amount of technical expertise in the acquiring and analysis of TEM data. My second supervisor Dr. Dirk Engelberg, who gave me a chance to show my interest and ability in the field of materials by providing me an internship at the University of Manchester. Also, I would like to thank Dr. Nicholas Stevens for his comments and discussions of the electrochemical part of the thesis.

Throughout my PhD I have had to use a wide range of instrumentation, as such I would like to thank all those who have trained me in there use, Dr. Arne Janssen (TEM), Xiang li Zhong (FIB), Michael Faulkner (SEM), Gary Harrison (XRD) and Dr. Jonathan Duff (Autoclaves).

I would like to acknowledge Dr. Nestor J Zaluzec from Electron Microscopy Center, NST Division, Argonne National Laboratory for his support and TEM/STEM/EDX expertise. Financial support for this research was provided by the EPSRC PROMINENT Programme (EP/ 1003290/1). Also gratefully acknowledge support from Dr. M.A. Kulzick of BP.

I am grateful to Freyja Peters and Dr. Jane Deakin for helping with the administrative tasks associated with the PhD and Paul Jordan for all the assistance he provided in the setting up of laboratories and being the first person to contact when anything went wrong.

I would like to acknowledge all the students and post-docs who made my time in Manchester enjoyable, especial Dr. Joanna Walsh for her support and help through my PhD time.

Finally a special mention goes to my family for made this so far with your love, sympathy and a huge patient of support.
Chapter 1: INTRODUCTION

This thesis has dealt with the development of a novel technique to examine localized reactions in liquid environments for conventional metals and alloys using in situ Transmission Electron Microscopy (TEM). It provides details of the development of the hybrid specimen preparation technique and how the chemical, electrochemical and physical properties are influenced by electron beam-induced changes. Specifically, this has been achieved by the in situ investigation and analysis of the microstructure of Type 304 austenitic stainless steel (304 SS), the dissolution of MnS inclusions, and the electrochemical behaviour of Type 304 stainless steel in various solutions. This type of study can assist the development of predictive life models for nuclear power plants components by helping to provide information concerning the initial reactions occurring in the water environment that can be the “precursor events” prior to Stress Corrosion Cracking (SCC) initiation.

Chapter 2 provides a review of environmentally-assisted cracking (EAC) including stress corrosion cracking (SCC) phenomena of austenitic stainless steels in nuclear power systems. This includes a discussion of the mechanisms and factors affecting SCC in pressurised water reactor (PWR) primary water. This is followed by an overview of in situ TEM and its application to materials research over the past ~60 years to provide context for the developments that has occurred over the past ~10 years. The primary emphasis of this thesis is the development of hybrid specimen fabrication and modification of in situ cells for liquid in situ TEM work to study nanoscale reactions on conventional metal microstructures (i.e., non-nano) pertaining to localized corrosion events that may lead to EAC initiation.

Also, in this project utilises numerous microstructural characterisation techniques including analytical electron microscopy (AEM), used to characterise the phase stability. The effect of crack propagation on mechanical properties of the austenite stainless steel will be assessed via slow strain rate tests (SSRT) in simulated PWR operating conditions (autoclave testing) and hardness tests of the produced specimens. This will be complemented by transmission electron microscopy (TEM), specimen preparation, and electron backscatter diffraction (EBSD) characterisation of the initiation sites to investigate the role of microstructure in damage generation. Also, it will be correlative microstructural analysis coupled with site-specific micro-scale electrochemical measurements. This thesis will be involved the development and optimisation of E-chips and electrodes so that valid electrochemical
measurements can be performed on Type 304 austenitic stainless steel \textit{in situ} in liquid environments of interest in Chapter 3.

Chapter 4 provides the control and scoping results of experiments. This presents the microstructural, mechanical and electrochemical results of the cold worked Type 304 austenitic stainless steels. In additional, metrological difficulties associated with developing a large-area measuring method are outlined, followed by a detailed description of various \(\mu\text{-}m\)-scale measurement techniques. The comparison of the advantages and disadvantages of each method allows the classification of their suitability and provides a brief overview of measurement techniques in the sub-micron/nanometer range.

Chapter 5 – Chapter 8 contains 4 manuscripts which reflect the main scientific outcome of the PhD project. The first manuscript describes the hybrid sample preparation for \textit{in situ} TEM. Due to the difficulty in the preparation of suitable specimens, liquid environmental TEM studies have been generally limited to nanoscale materials such as nanoparticles, nanowires, or sputtered thin films. In this paper we present two novel methods which have been developed to facilitate the preparation of electron-transparent samples from conventional metals and alloys for \textit{in situ} liquid cell TEM experiments. These methods take advantage of both electrochemical jet polishing and FIB extraction techniques to create large electron-transparent areas for site-specific observation with minimum contamination. As an example, we illustrate the application of this methodology to the preparation of \textit{in situ} specimens from a cold-rolled Type 304 austenitic stainless steel sample, which was subsequently examined in a H\textsubscript{2}O environment in the TEM. These techniques can be successfully applied as a general procedure for a wide range of metals and alloys and for a range of environmental \textit{in situ} TEM studies in both liquids and gases.

The second manuscript describes the requisite steps in order to make the technique fully analytical, from the modification of the hybrid sample preparation, through electrode investigation in different electrolytes, to electrochemical \textit{in situ} experiments which are compared to conventional bulk cell and microcell configurations. This technique provides an unprecedented opportunity to examine the real-time processes of physical and chemical/electrochemical reactions during the interaction between the metal surface and environment.

The third manuscript explores the effect of the electron beam in \textit{in situ} experiments. Specifically, this paper is focused on the possible localized heating due to the interaction of
the 200 kV incident electron beam with the metal sample. In this particular study, a low melting point alloy has been examined to provide an independent assessment of localized heating. Despite numerous reports in the literature discounting any localized heating effect during in situ TEM experiments, this project has generated evidence of localized sublimation and oxidation obtained during gas and liquid in situ TEM experiments performed on Cerrolow 117.

The final manuscript in chapter 8 reports the real-time investigation of the dissolution process of a MnS inclusion in H₂O at ambient temperature. The effect of H₂O on MnS inclusions and the local electrochemical potential has been examined using a special liquid cell and a liquid electrochemical cell TEM specimen holder in the FEI Talos 200 kV FEG-AEM. The in situ ATEM studies have been compared with bulk ex situ dissolution studies of MnS inclusions in Type 304 stainless steel during room temperature H₂O exposure. Additional ex situ tests were conducted at 80°C to further explore the temperature effect. This novel in situ liquid cell TEM approach can provide information on localized corrosion/oxidation reactions that can be helpful in identifying local microstructural features that can affect the “precursor” events ultimately leading to localized corrosion or environmentally-assisted crack initiation.

Chapter 9 provides the further discussion of the key results of thesis. It will be present the pre-investigations of the CW 304SS, the scoping results of in situ investigation, the role of electron beam effect of in situ cell system and application of in situ TEM investigation of MnS inclusion dissolution in H₂O.
Chapter 2: LITERATURE REVIEW

2.1 Classification of Austenitic stainless steels

2.1.1 Composition

Stainless steels can be classified into four categories: ferritic (body-centered cubic), austenitic (face-centered cubic), martensitic (body-centered tetragonal or cubic), and the combination of ferrite and austenite in roughly equal proportions, called “duplex” stainless steel. [1] The steels predominantly examined in this study are two Type 304 austenitic stainless steels. The standard grades of the steel and chemical compositions (bal. Fe) are given in Table 1.

Table 1: Typical composition of austenitic stainless steels. (Note that the balance is Fe) [2]

<table>
<thead>
<tr>
<th>Grade</th>
<th>Carbon</th>
<th>Nitrogen</th>
<th>Manganese</th>
<th>Silicon</th>
<th>Chromium</th>
<th>Nickel</th>
<th>Molybdenum</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>S20100</td>
<td>0.15</td>
<td>0.25</td>
<td>5.5–7.5</td>
<td>1.0</td>
<td>16.0–18.0</td>
<td>2.5–5.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S30100</td>
<td>0.15</td>
<td></td>
<td>2.0</td>
<td>1.0</td>
<td>16.0–18.0</td>
<td>6.0–8.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S30400</td>
<td>0.08</td>
<td>0.10</td>
<td>2.0</td>
<td>1.0</td>
<td>18.0–20.0</td>
<td>8.0–10.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S31600</td>
<td>0.08</td>
<td>0.10</td>
<td>2.0</td>
<td>1.0</td>
<td>16.0–18.0</td>
<td>10.0–14.0</td>
<td>2.0–3.0</td>
<td></td>
</tr>
<tr>
<td>S17400</td>
<td>0.07</td>
<td></td>
<td>1.0</td>
<td>1.0</td>
<td>15.0–17.5</td>
<td>3.0–5.0</td>
<td></td>
<td>3.0–5.0 Cu,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.15–0.45 (Nb–Ta)</td>
</tr>
<tr>
<td>S17700</td>
<td>0.09</td>
<td></td>
<td>1.0</td>
<td>1.0</td>
<td>16.0–18.0</td>
<td>6.5–7.75</td>
<td></td>
<td>0.75–1.5 Al</td>
</tr>
</tbody>
</table>

The Schaeffler-Delong diagram [3] shows in a simple way what phases are present as a function of composition for stainless steels in the as-solidified condition. It was originally established to estimate the delta ferrite content of welds in austenitic steels. [4] Nickel is an austenite stabilizer and the Cr acts a ferrite stabilizer. Trace elements can act as both an austenite or ferrite stabilizer, the effective amount expressed as the concentration of nickel and chrome can be calculated as outlined by Hammar and Svensson. [5] By evaluating a variety of alloy compositions, they were able to determine a relationship between austenite-stabilising elements and ferrite stabilizing elements and the resultant solidification phases. The equations developed for the Ni equivalent (austenite stabilising elements) and Cr equivalent (ferrite stabilizing elements) are:

\[
\text{Ni equivalent (Ni}_{\text{eq}}) \approx \% \text{Ni} + (0.31) \times \% \text{Mn} + (22) \times \% \text{C} + (14.2) \times \% \text{N} + \% \text{Cu}
\]

\[
\text{Cr equivalent (Cr}_{\text{eq}}) \approx \% \text{Cr} + (1.37) \times \% \text{Mo} + (1.5) \times \% \text{Si} + (2) \times \% \text{Nb} + (3) \times \% \text{Ti}
\]
Sutaala [6] assessed the ratio of $\text{Cr}_{\text{eq}}/\text{Ni}_{\text{eq}}$ of a variety of austenitic/ferritic stainless steel welds to predict the solidification of austenite versus ferrite primary dendrites, and showed that the critical value for the transition from primary austenite solidification to primary ferrite solidification was 1.55; above this value ferrite solidification occurred first whereas below this value, austenite was the primary solidification phase.

The hot-workability of continuously cast austenitic stainless steel is improved by the retention of delta ferrite in the steel. The use of small amounts of delta ferrite, which can be dissolved in the subsequent stages of processing is a method used to improve this feature and requires knowledge of the $\text{Cr}_{\text{eq}}/\text{Ni}_{\text{eq}}$ ratio to predict the volume of delta ferrite retained.

The general chemical composition of austenitic stainless steels is shown in Table 1 (note that Fe is not listed but is the balance). The major elements that affect austenite stability include Cr, Ni and Fe. Other important elements are C, Mn, Mo, N and Si. Carbon is important for several reasons: 1) it (along with Cr) reduces the martensite start temperature so that austenite is stable; and 2) it can promote the formation of carbides during ageing in the temperature range ~600 to 900°C. However, by reducing the carbon content of the steel (such as the L Grade), carbide precipitation at grain boundaries can be suppressed. Carbon stabilises the $\gamma$-Fe. The elements Mo and Mn decreases susceptibility to pitting, this is attributed to their sulphide-forming abilities. Mn combines with sulphur to form MnS inclusion. [7] Nitrogen increases the mechanical properties and stabilizes $\gamma$-Fe. Silicon is added for deoxidation during melt processing. It also promotes ferrite formation, and promotes the martensitic transformation of the austenite during cold deformation. [8-10]
2.1.2 Microstructure

To investigate the microstructure it is important to understand what phases and microstructural features can be present in stainless steel. The schematic diagram from Sedriks [10] shows examples of the various phases that can be present in stainless steels (see Figure 2). Many of these features have an effect on chemical, electrochemical and mechanical properties of stainless steel, as noted in the following discussion

Figure 1: Schaeffler-Delong diagram with position of some common Grades. [3]

Figure 2: Schematic of microstructure of a stainless steel. [10]
Inclusions
In steel production, contaminants (such as S, P, Ca, As, Sb) can be tied up in the form of inclusions. Common inclusions are silicates, various complex oxides, and sulphides, including MnS. The negative impact of inclusions, particularly MnS, on the pitting resistance of steel has been known for several decades. In the 1950’s it was recognized that sulphide inclusions were a possible cause of localized corrosion. Several authors determined the number and chemical composition of inclusions in steels. [11-14] In addition to the optical light microscopy studies, other techniques such as analytical electron microscopy (AEM) with energy dispersive X-ray (EDX) analysis, second ion mass spectrometry (SIMS), electron probe microanalysis (EPMA), and Scanning Auger Microscopy (SAM) have been used to characterise inclusions, particularly in Types 304, 304, Type 316, 316L austenitic stainless steels. The steels with the L Grade contain less the 0.03% C and this makes them resistant to thermal sensitisation and intergranular corrosion due to the limited carbide precipitation in those steels. Typical characterisation results obtained for two Type 304L SS with different S contents revealed that the steel with 0.010% S contained a high proportion of inclusions (1242 inclusions per mm$^2$). Coarse MnCrS inclusions observed in sulfurized steel were found to contain many small calcium aluminium silicate inclusions; some oxide inclusions were occasionally surrounded by a sulphide. [11]

Castle and Ke [12] used high-resolution SAM with EDX to evaluate the surface chemistry of inclusions. Castle discovered two types of inclusions in Type 316 with 0.009% S. The former consisted of individual sulphide inclusions and the second types were inclusions contain oxides. Ke [13] observed three different types of inclusions in Type 304 SS: 1) oxide inclusions of different composition, but mainly Cr$\textsubscript{2}$O$_3$ and MnO with small amounts of Al$_2$O$_3$; 2) MnS inclusions; and 3) mixed oxide / sulphide inclusions. Zheng et al. [14] came to the same conclusion and detected nano-sized octahedral MnCr$_2$O$_4$ crystals in MnS in Type 316F austenite stainless steel. Also, Krawiec et al. [15] found the presence of various sulphide inclusions, such as MnS, CrS, FeS, or a homogeneous MnFeS or MnCrS can impact the local chemical or electrochemical reactions occurring at the inclusion/steel matrix/electrolyte interface. In the following points, however, there is agreement such as the steels contain three types of inclusions: sulphide, oxide and mixed sulphide/oxide inclusions.

In his study of S-containing steels, Jansen [16] showed that the number and size distribution of inclusions is largely determined by the sulphur content of the steel (see Figure 3). The proportion of sulphide inclusions decreased in an approximately linearly with the sulphur
content, with a large number of small inclusions (<1 µm²) and fewer large inclusions (1 µm² to 10 µm²).

![Graph showing area distribution for sulphide particles found in 304 SS.][16]

**Figure 3:** Area distribution for sulphide particles found in 304 SS. [16]

- **Phase Stability: Martensite**

Several papers document the effect of the transformation of a metastable austenite (fcc) to the thermodynamically more stable alpha-prime martensite (bcc) due to either cryogenic cooling or deformation. An excellent review of the physical metallurgy of austenitic stainless steels and martensite formation was published by Gordon. [18]

Breedis [19] observed 5 different types of martensite at the transformation: lath, plate, surface, massive and epsilon martensite. The differences between the 5 types of martensite result from the transformation temperature and the stacking fault energy (SFE). The stacking fault energy is a function of temperature and composition, and governs the dominate deformation mechanism. Breedis reported that a SFE of 80 ergs/cm² and high transformation temperature favour the transformation to lath martensite whereas a lower temperature favours plate; type martensite. A lower SFE (<20 erg/cm²) and low transformation temperature results in the coexistence of bcc lath and epsilon martensite, where epsilon martensite is dominant. Epsilon martensite is a hexagonal close-packed (hcp) structure and is an intermediate phase formed during the transformation by fcc austenite to bcc alpha-prime martensite. Materials with low stacking fault energy (<20 erg/cm²) are susceptible to corrosion and materials with higher stacking fault energy (>80 erg/cm²) are more resistance
to chloride corrosion. Y.Shen et al. [20] represent that during the mechanical deformation of 304 SS shows the microstructure a combination of dislocation slip, mechanical twinning and martensite transformation (see Figure 4).

**Figure 4:** Schematic illustration of deformation process. [20]

On the other hand, Das et al. [21] described the stress- and strain-induced transformation, which could be differentiated because a few studies have shown an affect of both stress and strain during the formation of martensite from austenite. However, Patel and Cohen [22] attempted to separate the roles of stress and strain by examining the shear stress resulting from an applied stress. The cold-working process can have the same effect on the microstructure.

**Carbide Precipitation**

The precipitation of M$_{23}$C$_6$, (where M is predominantly Cr), occurs in the temperature range of ~500 to ~900°C. The carbides preferentially form at austenite grain boundaries (or within the grains on dislocations or slip bands). For precipitation in a specific temperature range (~500 to ~750°C), M$_{23}$C$_6$ formation can result in a decrease in the intergranular corrosion resistance. During ageing, the carbides form mainly on the grain boundaries. The diffusivity of C is significantly greater than that of Cr, and as a result, the C can diffuse rapidly to the grain boundaries. M$_{23}$C$_6$ precipitation requires the diffusion of Cr to the growing carbide, so that the local austenite in the vicinity of the carbide is Cr-depleted. Depending upon the ageing temperature, the Cr diffusion is too low to replenish the Cr-depleted zone, and so very
long ageing times are required for Cr to diffuse and heal this depleted region. If the Cr content within the depleted zone at the grain boundaries fall to ~12 wt. % or below, the austenitic stainless steel cannot passivate locally, and the sample will be sensitive to preferential intergranular corrosion or attack. [23]

In this condition, the material is called “sensitised”. This theory was originally proposed by Bain et al. in 1933. [23] In addition, the change in the local chemical composition (particularly Cr and C contents) results in the region becoming susceptible to a martensitic transformation. [24] This transformation can promote SCC of the steel due to the preferential susceptibility of martensite to hydrogen embrittlement in dilute acidic environments. The way to avoid this problem with metastable austenitic stainless steels was to add Ti and Nb (as in stabilised austenitic stainless steels), so that there is a greater tendency to form TiC and NbC carbides rather than Cr-rich M23C6. The consequence of this is that Cr remains in the matrix, no Cr-depleted zone is formed, and a uniform and stable Cr2O3 layer is formed on the steel.
2.2 Environmentally-Assisted Cracking and Stress Corrosion Cracking

Environmentally-assisted cracking or environmentally-assisted fracture (EAC / EAF) is the premature failure of a susceptible material under load in a specific environment. EAC encompasses a variety of phenomena including stress corrosion cracking (SCC) (see Figure 5). Environmentally-assisted cracking may be considered to be a result of localized oxidation/corrosion effects occurring at the crack tip. For the crack to develop there must be an initial defect. Environmentally-assisted cracking, and more specifically, SCC is generally considered to be comprised of three phases [25-28]: 1) an early incubation phase in which small surface-related defects develop within the general microstructure; 2) a subsequent stage of initiation in which microstructural features develop into localized embryonic sub-critical cracks; and 3) a final crack propagation stage when localized crack propagation occurs along the tips of well-developed crack fronts. Because of the inability to detect when general microstructural features have evolved in the presence of the environment into viable crack nuclei, the initiation and incubation stages of SCC are often grouped together. The inability to discriminate between incubation and initiation makes it difficult to specifically study either phase of the process. Thus, to date studies of EAC precursors have been exacerbated by the difficulty of isolating incubation features and following their development into initiated and propagating cracks. It is therefore difficult to identify how specific microstructural features and their interaction with the environment can affect formation of a SCC crack in practice.

Figure 5: Schematic Factors Affecting Corrosion and Stress Corrosion Cracking. [26]
Literature references over many years illustrate how difficult it can be to study the specific details of these three stages of SCC. [27-28] SCC can appear to progress in a “continuous” manner because it is difficult to isolate the specific stages. Hänninen et al. [27] has reviewed the initiation, propagation and failure for EAC steels. The initiation stage can be promoted by surface-related defects and local pits. Staehle [28] has described the formation of local features that lead to the development of SCC cracks as “precursor” events that are dependent on the initial material condition (see Figure 6). These defects can include any pre-existing surface features, or surface-breaking microstructural features, such as inclusions in the alloy or localized deformation. Such features can play an important role in accelerating the incubation and initiation of SCC cracks. The presence of these features does not, however, imply that incubation and initiation processes do not occur, and that viable cracks develop immediately because of their presence; these features merely serve to accelerate the generally slow processes of crack incubation and initiation. The processes of crack incubation and initiation may still take several decades to develop even under such conditions (e.g. under highly cold-worked surface conditions). [28]

![Figure 6: The stages of development of SCC with time. [28]](image)
2.2.1 Mechanisms of SCC

There are two general categories of proposed mechanisms for SCC. These include mechanisms that are based on the electrochemical behaviour of the material, (Active Path (AP) Mechanisms) or on Hydrogen Embrittlement (HE). Each general category has several specific mechanisms. In particular, Active Path Mechanisms that have been proposed over the years include: Slip-Dissolution/Film Rupture; Film-Induced Cleavage; Corrosion Product Wedging; Stress-Assisted Localized Corrosion; and Solute Segregation Theory. Similarly, there are numerous mechanisms of Hydrogen Embrittlement. These include: Lattice Decohesion/Hydrogen-Enhanced Decohesion (HEDE), Hydrogen-Enhanced Localized Plasticity (HELP), Hydrogen-Induced Transformations; and Pressurisation theory. However, several of these AP and HE mechanisms have been discounted over the years. [27], [29-31]

- Slip Dissolution Model (SD)

The slip dissolution model, originally proposed by Staehle *et al.* [32] based on the film rupture mechanism of Logan [33]. In this case an oxide layer or passive film covers the crack and protects the metal surface. The necessary condition for the occurrence of anodic stress corrosion cracking is a critical combination of a specific aggressive agent and plastic strain in the metal. Typical SCC-generating aggressive agents include chlorides (Cl\(^{-}\)), sulphates (SO\(_{4}\)\(^{2-}\)) and nitrates (NO\(_{3}\)\(^{-1}\)), which are known to be promoters of anodic dissolution-based SCC. The aggressive media, coupled with strain in the metal lead to fracture of the protective oxide film at the crack tip due to the emergence of slip-steps. Then, localized dissolution/oxidation occurs at the “clean” exposed metal, followed by repassivation. [34, 35]. Crack growth occurs by a cyclic process of film rupture, localized dissolution/oxidation, and repassivation. [33] The cracks can grow, depending on the material, intergranularly or transgranularly. The corrosion rate is equivalent to the anodic metal dissolution in the crack tip. This model can be applied to intergranular cracking of ferritic steels in passivating environment (Carbonate-bicarbonate) and to sensitized stainless steels in certain environments. Ford and Andresen [36] presented a slip-dissolution/film rupture model to understand the mechanism of intergranular SCC of Type 304 SS. Crack advance due to slip dissolution can be related to the oxidation reaction that occurs at the crack tip. The oxide film at the crack tip is stable until ruptured by emergent slip steps (increase in strain).
• Hydrogen Embrittlement (HE)

Hydrogen embrittlement is a complete failure mechanism in its own right. Three of the main mechanisms of hydrogen embrittlement are: Hydrogen-Enhanced Localized Plasticity (HELP), Adsorption-Induced Dislocation Emission (AIDE) and Hydrogen-Enhanced Decohesion (HEDE), which was originally known as Lattice Decohesion. HELP is based on the observations that hydrogen in the metal can locally increase plasticity. The increased plasticity allows greater work hardening in the crack tip region. The highly localized increased work hardening results in fracture. [37-41]

Whiteman and Troiano [37] demonstrated that austenitic stainless steel (Type 310 SS) can be embrittled by hydrogen under slow strain rate conditions, and that the embrittlement can be recovered via thermal treatment. Birnbaum and Sofronis [38] reviewed the mechanism of hydrogen-related fracture, and described how hydrogen enhances the mobility of dislocations. They discussed the hydrogen effect on macroscopic deformation, slip localization and elastic shielding of stress centres. Hydrogen-induced slip localization can increases in the measured flow stress under imposed strain rates and as well the solute hydrogen can increase the dislocation mobility. The hydrogen shielding effect can account for the observed hydrogen-enhanced dislocation mobility. Hydrogen shielding effect considers the accumulation of hydrogen in the stress field of the dislocation and consequence the presence of this atmosphere has on dislocation defect interactions. [38]

Robertson and Birnbaum [39] demonstrated the effect of hydrogen on the deformation and fracture of Ni by performing in situ straining stage experiments in a high voltage electron microscope (HVEM) with an environmental gas cell. The presence of H₂ in the environmental cell increased the generation of dislocations, velocity of dislocations in Ni and the ease of cracking during their in situ experiment. They proposed that the advance of transgranular cracks occurred by either the direct emission of dislocations from the crack tip or via entry of hydrogen at the crack tip. Deformation was localized in the vicinity of crack tips as a result of dissolved hydrogen promoting dislocation activity. The interaction between hydrogen at dislocations and obstacles to dislocation motion, which affects dislocation mobility, was suggested by Birnbaum. [40] The dislocation mobility resulted in microvoid formation to occur and are more localized in inert environments. This form needs a high hydrogen diffusivity to move with the dislocations. Lynch et al. [41] reconfigure when interacting with other hydrogen atmospheres and stress fields.
Oriani [42] and Magnin et al. [43] used the decohesion model to suggest the possible mechanism of hydrogen-enhanced decohesion (HEDE). The stress generated by a crack increases the solubility of hydrogen. The decohesion is based on dissolved hydrogen in the metal decreasing the atomic binding forces, therefore lowering the energy to fracture. The combination of these two factors is that the stress build up at a crack tip produces an embrittlement, which will fail and propagate the crack.

2.3 Overview of Light Water Reactors and EAC/SCC

The Pressurized Water Reactor (PWR) and Boiling Water Reactor (BWR) belong to the Light Water Reactor (LWR) group and the difference between the two is the pressuriser in the PWR and oxygen level, which maintains the high temperature water in a liquid state. In both reactor systems water is used as the coolant, but there are slight variations in the additives used. Figure 7 contains a schematic of the PWR and BWR. In the BWR water is circulated through the reactor vessel to pick up heat, which is converted into steam. The steam goes through the main steam line to drive the turbine and then flows through the condensers to be pumped back to the core. The reactor power is controlled through a combination of control rods and variable water flow. Under the reactor vessel is a suppression pool; this removes excess heat produced. BWRs are not as stable as PWRs and require more maintenance, but the thermal efficiency of BWRs is greater.

Figure 7: The use of austenitic stainless steel (a) BWR and (b) PWR. [44, 45]
Austenitic stainless steels and Ni-base alloys are widely used in LWRs for components such as the BWR recirculation piping system and core internals, and PWR core internals and selected piping (as well as cladding).[46] In 1969, SCC was reported in a heat-affected zone in a welded austenitic stainless steel in a BWR system. During the 1970’s, SCC was also observed in stainless steel (SS) welded piping. Between the 1980s and 2000s more instance of SCC were identified in the BWR internals, generally thought to be caused by cold-work and crevice corrosion [47]. Since the 1960s, there have been approximately 137 case of intergranular stress corrosion cracking (IGSCC) in stainless steel components in the primary circuit system.

2.3.1 Factors affecting PWSCC (Primary Water Stress Corrosion Cracking) of Cold Worked Material

Primary Water SCC (PWSCC) is a complex phenomenon controlled by the synergistic interaction of metallurgical/microstructural, electrochemical and mechanical factors. PWSCC occurs in both BWR and PWR components, can be transgranular or intergranular in fracture morphology. According to Scott et al. [48, 49] it is possible that intergranular and transgranular cracks form at the same time in parallel or sequentially. The subsequent sections discuss the factors that affect PWSCC in austenitic stainless steels. [50]

- Effect of MnS Inclusion Dissolution in Primary Water

The dissolution of MnS inclusions in low alloy steel was shown to be responsible for Environmentally-Assisted Cracking (EAC). [51] Recent research has also indicated that MnS inclusions may also be associated with the observed low crack growth rates in high S austenitic stainless steels during certain conditions of corrosion fatigue in high temperature H₂O environments. [52-59]

Mills [52] reported accelerated and retarded corrosion fatigue crack growth rates (CGR) for Type 304 SS in 250°C air and deaerated pressurized H₂O at 288°C. He assumed the hydrogen from the H₂O is absorbed into the crack tip region where it promotes planar slip processes and a crystallographic fracture mechanism. He examined the oxide formation and corrosion products on crystallographic facets of longitudinal sections obtained from compact tension specimens. He proposed that formation of thicker oxide films and oxide penetrations
along slip bands were more effective in restricting reverse slip and contributed to higher CGRs in high temperature H\textsubscript{2}O. He also postulated that the S from dissolved MnS stringers destabilized the oxide film and increased the local corrosion rate.

More recently, Mukahiwa et al. [53] investigated fatigue crack growth for a low and high S solution-annealed Type 316 SS in a simulated PWR environment (250°C and 300°C). They used scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) techniques to characterize the microstructure of the crack path from a cross-section specimen obtained from a tested compact tension (CT) specimen. They observed oxidation of the branched and main crack path and a blunt crack-tip region in the high S steel.

James et al. [54] and Tice et al. [55] noted that the most important inclusions in low alloy steels were the MnS. When present at a crack tip, the MnS inclusions dissolved when exposed to high temperature water (>200°C), thereby promoting local corrosion, which could initiate SCC. Also, Clarke et al. [56] studied a Type 304 stainless steel in stressed and unstressed condition exposed to oxygenated H\textsubscript{2}O at 288 °C. The authors demonstrated a strong effect of precipitates such as chrome carbide and inclusions in crack nucleation. The dissolution process started around the particle and this led to the formation of a crevice region around the particles and changed the H\textsubscript{2}O chemistry, which leads to initiation of intergranular attack. Hence, the nucleation of SCC cracks often extends from pits, which develop near sulphide inclusions. Thus, it is logical to assume that MnS inclusions also affect SCC propagation. Nevertheless, the correlation between S content and EAC susceptibility in low alloy steels is not simply a function of composition as it also depends on the distribution of the sulphides, i.e. the size, geometry, chemical composition, morphology or amount of S present in solid solution. [57-59] SCC is also related to passivity breakdown (caused by either electrochemical or mechanical factors).

Considering this process from the corrosion perspective, several investigations have proposed the chemical and electrochemical mechanisms for the dissolution of MnS inclusions and the initiation of localized corrosion in an aggressive environment at room temperature, such as pit initiation. The influence of temperature and environment on SCC is significant.
- **Effect of Planar Slip on SCC**

According to Swann [60], there is a correlation between the SCC resistance and the stacking fault energy (SFE), which is attributed to unfavourable effects of easy planar slip: he ascribed the low SCC resistance of metastable 18 Cr-8 Ni austenitic stainless steel to the low SFE in this material. This conclusion was supported by the finding that increasing the Ni content caused an increase in SFE, which resulted in a change in dislocation structures from planar arrays to cells and improvements in SCC resistance. Swann found that addition of Cr also increased SFE of α-Fe solid solution and provided SCC resistance. The higher the SFE, the harder it is to form coplanar arrays, instead dislocations form tangles and pile-ups. In another study, Swann et al. [61] showed that preferential dissolution of slip bands is associated with co-planar dislocation motion of Cu-Al and Cu-Zn. They reported that the coplanar dislocations cause a coarse slip-step, which exposes more “clean” metal that can be attacked than non-localized or more uniform deformation.

- **Effect of Temperature**

Several studies have investigated the effect of temperature on PWSCC of austenitic stainless steel. [62-66] The crack growth rate was shown to increase with increasing temperature. SCC tests were generally performed in the temperature range 250°C to 350°C.

Wire et al. [64] performed fatigue tests on Type 304 SS at 243°C and 288°C to investigate the effects of rise time and temperature on corrosion fatigue. They found that at lower rise time (<50 sec) a lower temperature yield formed lower crack growth rate. The retardation was observed only for the 500 sec rise time in tests at 288°C, whereas no change was observed for rise times between 50 and 500 sec for 243°C tests. Wire and Mills [65] suggested that a hydrogen embrittlement mechanism was responsible for the accelerated corrosion fatigue crack growth rates in PWR water at 288°C. The high crack growth rates in 288°C deaerated water were associated with a faceted growth mechanism. They demonstrated that the highly angular, cleavage-like appearance of the facets suggests that a hydrogen embrittlement mechanism was the primary cause of accelerated cracking in this environment.
Effect of Environment

In a PWR, the dissolved oxygen content is ~ 5ppb, and H₂ is added to ~30cc/Kg STP H₂O. The pH is slightly basic at high temperature due to the addition of Boron (B), Lithium (Li) and Hydrogen (H₂). Li is a pH-stabilisator. Nordmann [67] and Economy et al. [68] have shown that Li greater than 3.5 ppm increases the initiation time of PWSCC. The H₂ content has the biggest effect on PWSCC and corrosion products. It controls the availability of O in the system. The excess H₂ in the PWR system reacts with the O₂ in the H₂O to de-oxygenate the H₂O. The H₂ in the system is such that the partial pressure of O₂ is in the region of the Ni/NiO transition point; this is the point at which the stable form of Ni in the system goes from metallic Ni to NiO (see Figure 8). Staehle et al. [69] reviewed the susceptibility relative to the Ni/NiO transition point. Also, Tice et al. [70] investigated the crack growth rate of cold-worked Type 304SS in PWR primary water over a range of temperatures and loading conditions. Tice showed that the growth rate in air and in H₂O increased with decreasing loading frequency.

![Figure 8](image.png)

**Figure 8:** Economy; Scott and Combrade, image reproduced from Steahle. [69]
2.4 Electrochemical Analysis Techniques

There are numerous methods available to investigate local corrosion processes, such as current- and potential-controlled measurement methods where experiments can be static or dynamic. In the following section, two important measuring methods are presented, which were used for macro- and micro-electrochemical studies.

2.4.1 Conventional Potentiodynamic Polarisation Behaviour

When a metal is exposed to a corrosive medium without any external voltage (i.e., under free corrosion conditions), it is possible to determine the free corrosion potential also known as open circuit potential (OCP). Under OCP conditions the sum of anodic and cathodic partial currents is zero. The OCP can be measured by monitoring the potential of the metal over time with respect to a suitable reference electrode such as the standard hydrogen electrode (SHE). By comparing the potential-time data with current-potential data measured by potentiodynamic polarisation curves, one can predict whether the material is passive, transpassive, active, or whether it changes from one to the other during exposure. [71]

A potentiodynamic polarisation curve represents the current density as a function of potential where the current flows through the working electrode. The potential can be changed stepwise or continuously with the help of a potentiostat. For a sufficiently slow rate of change of the potential steady-state conditions may be reached. This type of polarisation curve is called a stationary current-potential curve. Due to the lack of time, it is not always possible to wait for steady state conditions. Furthermore, during polarisation changes in electrolyte composition and pH value occur. Therefore, a compromise between achieving the steady-state and not perturbing the electrolyte conditions is usually sought. This compromise is known as the "quasi-stationary" condition for the current-potential curves. [72] A typical polarization curve is shown in Figure 9.
Figure 9: Schematic representation of passivation. Anodic current density-potential curve of a Cr-passivated steel under acidic conditions. Ordinate axis: $E_O$: equilibrium potentials of O, $E_p$: activation potential; $E_F$: critical passivation potential; $E_{Corr}$: corrosion potential. Abscissa axis: $i_p$: residual current and $i_{crit}$: critical current density. [73]

The relationship between current density and potential for oxidation (Ox) and reduction (Red) of a single redox species is given by the Butler-Volmer equation: where $j$ is the sum of all anodic and cathodic partial current densities, measurable in the external circuit current density and $\eta$ the activation overpotential.

$$j = j_{ox} - j_{Red} = j_0 \left( \exp^\frac{\alpha \cdot z \cdot F}{R \cdot T} \cdot \eta - \exp^{-\frac{(1-\alpha) \cdot z \cdot F}{R \cdot T} \cdot \eta} \right)$$

Equ. 1

where $\alpha$ is charge transfer coefficient, $z$ is number of electrons involved in electron reaction, $F$ is Faraday constant, $R$ is universal gas constant and $T$ is the absolute temperature.

If the activation overpotential ($\eta \gg (R \cdot T)/(n \cdot F)$) is large and negative, the anodic term in Eq.1 can be neglected. Therefore, the reaction rate may be expressed by the following equation:

$$j = j_0 \exp^\left(\frac{(1-\alpha) \cdot z \cdot F}{R \cdot T} \cdot \eta\right)$$

Equ. 2
The equation can be rearranged to:

\[ \eta = \frac{RT}{(1-\alpha)z_F} 2,303 \log j_0 - \frac{RT}{(1-\alpha)z_F} \log |j_0|. \]

Equ. 3

The measurement of current-potential curves is the most commonly used electrochemical technique for the evaluation of the corrosion behaviour of metallic materials. In this measurement method, the potential of the material is scanned over the range of interest continuously or in a stepwise manner. In practice, the potential of a component is determined by the ambient conditions for example, the redox potential of the surrounding medium. [74-76]

For passive materials such as stainless steels, a protective oxide layer on the metal surface begins to form from the critical current density \( i_{crit} \) and is complete by the primary passivation potential (\( E_{pp} \)). This reduces the metal dissolution by several orders of magnitude so that the corrosion in the passive region virtually comes to interruption. In neutral or basic media, most steels spontaneously behave in a passive manner. In this case, they have no active region. In environments without harmful ions, the passive film protects the material up to the trans-passive region. The trans-passive region is the region of an anodic polarisation curve which is a significant increase in current density as the potential becomes more positive. In the presence of some aggressive media e.g. chlorides, corrosion may occur if the passive layer fails locally due to local corrosion attack. [77]

The purpose of current-potential curves is to elucidate the relationships between corrosion reactions and electrochemical factors. This allows a characterization of the corrosion system, in particular the occurrence of specific types of corrosion when exceeding threshold potentials, as e.g. pitting, crevice corrosion or stress corrosion cracking.

Electrochemical measurements are almost always carried out in cells having a three-electrode configuration. The three electrodes are the Working Electrode, Counter Electrode and Reference Electrode.

2.4.2 **Factors which influence the electrochemical reaction**

The following section describes the various factors that affect the electrochemical measurements. It is important to understand the electrochemical reaction of metal with the liquid from the thermodynamic and kinetics perspectives. In addition, it is essential to understand the investigation technique and the resulting factors which affect the system such
as chemical and physical reaction, e.g. surface condition, specimen area, temperature, flow rate, pH.

- **Influence of the passivity**

In the 19th century Faraday and Schönbein made the observation that metals in corrosive media can be stable. In 1836 Faraday introduced his oxide layer hypothesis, in which he argued that the passivity of the Fe proceeded from a very thin, invisible oxide film. This hypothesis is confirmed experimentally today because it has been proven that passive metals have oxide layers. A familiar example of a passive metal is Al that forms an Al$_2$O$_3$ layer with atmospheric oxygen, which protects it from further dissolution. Passivity is deemed to exist when a metal only dissolves slowly in an expectedly corrosive environment because it has a protective oxide layer. [77, 78]

By conducting experiments on Fe in H$_2$SO$_4$, the processes that led to passivation were largely resolved. Anodic metal dissolution occurs in close proximity to the electrode surface, to produce an excess of metal ions. Thus, the solubility of Fe$_2$(SO$_4$)$_3$ is exceeded, and it precipitates out to form a porous coating layer on the metal surface. Due to the precipitate layer blocking further oxidation at the surface, the anodic current density (current per unit area) decreases sharply and moves the electrode potential to passivation. [79] The oxide is formed not as a precipitated product from the solution, but by direct crystallisation and growth on the Fe. The resulting nanometre-thick passivation layer is non-porous and protects the Fe from further dissolution. The growth of this layer causes a sudden decrease in the anodic current. Even with further polarization in the anodic direction, only a small residual current flows, which is limited by the rate of migration of the metal ions through the passive layer that has a low ionic and electrical conductivity. The suppression of ion migration also suppresses the reaction of H$_2$O molecules with the metal ions, as they are prevented from coming together. Thus, both the metal dissolution as well as further layer formation can be suppressed. In contrast, the electronic conductivity of the underlying metal is very high, especially in steels.

Upon further anodic polarization the sample enters the trans-passive state, where metal atoms may again be oxidised and released into solution. A further current increase may occur due to oxygen evolution (H$_2$O electrolysis):

$$2 \text{H}_2\text{O} \leftrightarrow \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \quad (11)$$
However, this is only the case for metals whose oxides form electron-conducting layers, such as Fe, Ni, Co and Zn. The electrons can either diffuse through the layer or the layer may form with semiconductor properties allowing conduction in certain conditions. The quality of the top layer also depends crucially on the electrolyte. Thus, by adding activating substances, such as chloride ions can chemisorb on crack or pores in the passive layer and dissolve passive film. Chloride is a relatively small anion with a high diffusivity, it interferes with passivation, and it is present as a contaminant. This contaminations are depends on chloride ion concentration which effect passive film breakdown (see Figure 10). The local breakdown of passive film is decrease with increase the ion concentration. [80]

![Figure 10: Chloride concentration in neutral water on polarisation curve of 304 SS. [73]](image)

In the passivation of Cr-Ni steels, an approximately 20 to 30 nm thick porous oxide layer forms which consists of a Cr-rich oxide-hydroxide layer. This chromium oxide layer adheres firmly to the surface and, after damage, forms again within a short time except at highly acidic pH. To maintain this layer, however, a sufficient supply of O₂ from the environment of the material is required. This process is called re-passivation. [81]

An example of a material with a stable nonporous passive layer on steel during the measurement in the anodic potential area is given in Figure 9. According to Figure 9 the polarisation curve shows an initially high current density, which is linked to material
dissolution. With increasing potential the current density drops down suddenly; this phenomenon is called passivation. The passive current density value is that obtained for material dissolution within the passive state. In certain solutions containing Cl\(^-\) or Br\(^-\), the increase of current is linked to pitting events. Furthermore, if there are no harmful ions, the passive layer protects the material up to the trans-passive area. [77-80]

- **Influence of pH**

The pH of an aqueous corrosive solution is influenced by cathodic partial reactions. This can be explained by a Pourbaix diagram. In principle, any redox system is regarded as one electrode and the behaviour of this system is considered theoretically. [73-75] A common cathodic reaction is oxygen reduction:

\[
E^0 = 1.226 \, \text{V} \quad O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (12)
\]

and another is the hydrogen reaction

\[
E^0 = 0 \, \text{V} \quad H_2 + 2H_2O \rightarrow 2H_3^+O + 2e^- \quad (13)
\]

Both reactions are present in the Pourbaix diagram (see Figure 11 dash lines).

![Pourbaix diagram for Fe/H\(_2\)O system](image)

**Figure 11:** Pourbaix diagram for Fe/H\(_2\)O system with indicated areas of immunity, corrosion and passivation. Dashed lines are (a) hydrogen and (b) oxygen reactions. [82]

The horizontal lines (1 and 2) represents pure electrons transfer reactions which are dependent on potential, and independent of pH value and the vertical lines (3) represents lines
which are extend across the diagram until the pH is sufficiently high to facilitate the
formation of hydroxides. There by reducing the concentration of Fe$^{2+}$ and Fe$^{3+}$ ions. The
equilibrium involving both electron transfer and pH are given by sloping lines (5). [82]

The electrochemical potential is corresponds to the chemical potential of the underlying
process. Therefore the concentration in the electrolyte is significant - like in the law of mass
action.

\[
E = E^0 + \frac{0.057 \text{(V)}}{z} \log \frac{c_{\text{ox}}}{c_{\text{red}}} \quad \text{at } 20^\circ\text{C} \quad \text{Equ.4}
\]

To determine the concentration dependence consider Red $\leftrightarrow$ Ox + z e$^-$: Using the Nernst
equation the redox potential can now be calculated:

\[
E = E^0 + \frac{RT}{zF} \ln \frac{c_{\text{ox}}}{c_{\text{red}}} \quad \text{Equ.5}
\]

Here only concentrations in the electrolyte are considered, not those of the pure solid phases.
A change in the pH produces a potential difference (at 20°C) of:

\[
\Delta E_{\text{pH}} = -0.057 \left( \text{pH}_{\text{mess}} - \text{pH}_{\text{Ref}} \right) \quad \text{Equ.6}
\]

A change of pH from neutral (pH = 7) to alkaline (pH = 10) would create a difference in the
equilibrium potential for the reaction of approximately 0.2 V.

- **Influence of the temperature**

For a thermodynamic cell, the magnitude of the change in potential with temperature is
determined largely by the temperature coefficient of $E_0$ and, to some extent, by the second
term in the Nernst equation.

An increase in temperature has several effects, which, in turn, affect the corrosion rate
through the variation in oxygen solubility, especially in an aqueous system. With increasing
temperature all diffusion coefficients in the system (solution + material) increase, the
metabolic and corrosion rates also increase. The dissociation of H$_2$O also increases, thereby
reducing the pH. The following diagrams (Figure 12) show the (a) temperature vs. pH and
(b) the effect of temperature on the polarisation curve reported by Hackerman [83] and Jones
[84]. Hackerman showed that H$_2$O is strongly corrosive at 60°C, not only because of the
normal increase in reaction rates at higher temperature, but also due to greater hydrogen ion
activity as reflected by lower pH, and due to changes in potential difference. Jones [84] further described the influence of pH and temperature on the polarisation curve. He demonstrate in a schematic plot, that increasing the temperature increase current densities and corrosion rate at all potential and decrease the passive potential range.

Figure 12: Schematic illustration (a) of pH vs. temperature effect in H₂O [83] and (b) the effect of increasing temperature on polarisation behaviour on steel. [84]

Corrosion reactions are generally controlled by either diffusion rate of the oxidization agent (i.e. diffusion control) or the rate of the oxidization reaction (i.e. kinetic control). Temperature can influence both of them. In terms of the kinetics, the Arrhenius equation is the governing equation:

\[ k = Ae^{\left(-\frac{Q}{RT}\right)} \]  

where \( k \) is the reaction kinetics, \( A \) is a constant, \( Q \) is the apparent activation energy, \( R \) is the ideal gas constant and \( T \) is the absolute temperature.

As we can see from the above equation, as the temperature increases, the theoretical reaction rate increases. Also, numerous experiments have been conducted and have demonstrated that at a higher temperature, the oxidization reaction rate will increase until it becomes diffusion-controlled. For example, according to Gerasimov and Rozenfeld [85], using Ni and Pt as
electrode pair in a 1.0 M NaCl solution, they observed that the overvoltage increased with increasing temperature, which indicated that the cathodic reaction rate increased.

- **Solution velocity effect**

The special significance of the limited mass transfer between the pit and the outer electrolyte solution can also be seen in the dependence of pitting corrosion on flow velocity and the degree of aeration/deaeration of the corrosive medium. Figure 13 shows a subsequent increase in solution velocity increases the limiting diffusion current from 1 progressively up to 6. The current-potential curve shifts to higher currents because with increasing flow velocity and re-passivation is facilitated. If the flow velocity is sufficiently high, subsequent pitting corrosion can be stopped. [84]

![Figure 13](image)

**Figure 13:** Schematic illustration of the effect of aeration, deaeration and velocity in neutral seawater. [84]

- **Influence of oxidizing agents**

It is known from practice that the corrosion susceptibility of stainless steels increases in the presence of oxidants. During measurements of redox potentials, which is the potential of a reversible oxidation reduction electrode measured with respect to a reference electrode, for example in artificial seawater containing various additives to oxidants, an assessment of the oxidizing effect of the additives could be achieved by measuring the size of the potential change. Gräfen and Kuron [86] studied several oxidants, which react slowly when in direct contact with Fe. When they added in the starting solution 0.8 g/l H₂O₂, the redox potential
shifted on the basis of $E = 460 \text{ mV (SHE)}$. For the following starting solutions the redox potential shifts are listed:

- $\text{Na}_2\text{S}_2\text{O}_6 = 605 \text{ mV}$,
- $\text{K}_2\text{Cr}_2\text{O}_7 = 640 \text{ mV}$,
- $\text{Fe}_2(\text{SO}_4)_3 \times \text{H}_2\text{O} = 895 \text{ mV}$,
- $\text{KMnO}_4 = 915 \text{ mV}$,
- $\text{Ce}(\text{SO}_4)_2 \times 4\text{H}_2\text{O} = 1175 \text{ mV}$.

All potentials are SHE.

In these solutions the polarisation curves showed that with the addition of the oxidizing agent only the OCP migrated in anodic direction, but not the pitting corrosion potential. Adding an oxidant can cause the OCP to shift to a more noble value than the pit corrosion-potential and the potential of pit re-passivation, and, thus, more stable pitting occurs.

### 2.4.3 Microcapillary Cell Technique

The development of a smaller system for the analysis of electrochemical reactions of certain areas of a material is necessary because it is better to understand reactions at the surface of the material. The investigations using the microcapillary cell have been described in detail by Böhni et al. [87], Lohrenge [88] and Martin et al. [89]. This has facilitated the study of localized corrosion, e.g. of single grains in welds, or single micron-sized particles in metal.

![Schematic representation of different Microcell Tips by Suter.](image)

**Figure 14:** Schematic representation of different Microcell Tips by Suter. [87]
The usual large-scale electrochemical tests provide the electrochemical behaviour of the tested materials averaged over a large surface area. The large-scale tests are thus inadequate to investigate local corrosion processes. Due to the enhanced spatial resolution of the micro-electrochemical methods, processes occurring at the micro- and submicron range can readily be studied. The use of the microcell permits local electrochemical investigations of small areas of special interest, such as grain boundaries, second-phase precipitates or inclusions. Therefore, the microcapillary technique is well-suited to study the corrosion behaviour of microsystems. In principal, the setup of the microcell is the same as a standard electrochemical measurement, which includes the necessary reference and counter electrode. The tip is made of a glass capillary with a layer of silicon rubber to protect and seal the tip of microcell. The microcell is an encapsulated system.

Suter et al. [90] used this technique to investigate (Figure 15) the dissolution of MnS inclusions in 1M NaCl. They used a capillary with a tip diameter of 2.5 µm to investigate the different zones such as bulk matrix, interface inclusion/bulk and centre of a single MnS inclusion. Furthermore, they used this technique to investigate dissolution at various temperatures (30°C, 60°C and 90°C) with a tip size of 70 µm in 1M Na₂SO₄. Their results indicated that the potential shifted to the cathodic direction with an increase of the temperature and this accelerated the MnS dissolution (see Figure 16). [91]

![Figure 15: (a) Schematic of the Suter microcell system and (b) photograph of microcell. [90]](image)
Figure 16: Potentiodynamic polarization curves of AISI 304 in 0.1 M Na2SO4 at room temperature, 60, and 90°C, 70 mm, 0.5 mV/s. [91]

Martin et al. [89] developed another type of electrochemical cell for localized corrosion testing, which is shown in Figure 17. They used a tip size of 850 µm in diameter and measured polarisation curves in a scanning method across the surface for Types 304 and 316 stainless steel. Their results show that it is possible to study the intrinsic heterogeneous microstructure in the heat-affected zone of a welded joint, see Figure 18.

Figure 17: (a) Schematic of microcell system developed by Martin and (b) photograph of microcell. [87]
Figure 18: Polarisation curve of different zones of AISI 304SS. [89]
2.5 In situ transmission electron microscopy

Over the past decades there has been great interest to develop and modify the TEM to study in situ the microstructure and behaviour of materials in real-time experiments under controlled environments such as gas or liquid. In situ TEM, specifically, in situ high voltage electron microscopy (HVEM), provided a unique platform for conducting a wide variety of materials science and life science experiments. These experiments aimed to address one of the fundamental challenges of science inside the TEM [92]. The in situ HVEM techniques were developed by introducing various environmental TEM holders for heating, cooling and straining experiments and gas-metal reactions [92 – 96]. More recently, advanced micro-electro-mechanical system (MEMS) -based stages for heating, as well as novel atmospheric pressure gas, liquid, electrochemical cells have been developed [97 -100]. The following sections highlight major accomplishments achieved using in situ TEM and HVEM, particularly via the use of the unique differentially-pumped gas reaction cell designed by Swann [92], hot stages, cold stages and straining stages, the applications of which have provided unique insights into materials science and the behaviour of some modified specimen holders and their application.

2.5.1 In situ Heating Studies in the TEM

The first heating stage was reported in 1960 by Silcox and Whelan. [92] They used a furnace type heating stage to investigate prismatic dislocation loops in thin foils and bulk experiments of aluminum (Al). The heating stage contains a two-pin socket, to isolate the body of the holder and carrying a specimen support such as Pt which is welded to a grid. To measure the temperature, they determined the grid temperature against the heating current curves by calibration of different specimen supports. They estimated that heating rise by ~ 15 µA beam current is less than 15°C-deg at 100 kV.

In situ hot stage experiments in the HVEM conducted by Humphreys [93] provided unique direct evidence of particle-stimulated recrystallisation in Al-Si alloys in 1977. Such in situ experiments were important in developing further understanding of recrystallisation phenomena in metals and alloys. HVEM in situ hot stage experiments were also used to assess precipitation in alloys, an example of which can be seen in the research of Westmacott et al. [94] and colleagues into the precipitation of Fe nitrides. Heating stages were also used
for high resolution TEM studies of nanoparticle catalysts in the 1970’s [95] as well as for solid state phase transformations [95] and solid-liquid transformations. [97-99]

Swann [100] introduced several side entry specimen stages for \textit{in situ} investigations. For example, a single tilt and double tilt heating stage are shown in Figure 19 & 20. Both heating stages are furnace-type holders. The specimen was placed between two overlapping resistance ribbons in the single tilt holder. These early hot stages were not well-insulated; thus it was difficult to ascertain temperatures accurately. To measure the specimen temperature, a calibrated heater ribbon was measured against a known phase transformation temperature.

To solve the main problem of hot stages, which is flexural failure of electrical leads, Swann developed a modified double tilt holder (see Figure 20). The double tilt holder contained a fine hair spring thermocouple to reduce the damage of plastic flexing strains and split the tilt cradle and insulated the connection in the heater area to avoid the electrical leads.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure19.png}
\caption{The specimen tip of single tilt hot stage. [99]}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure20.png}
\caption{Double tilt hot stage with fine hair spring thermocouple. [99]}
\end{figure}

In the 1980s Sinclair and Parker [101] studied crystallisation and defect reaction such as defective silicon crystal amorphous in silicon between 500°C and 800°C to demonstrate the heating effect of the imaging electron beam. They used a single-tilt heating holder (Philips Type PW 6592) at 120 kV. The specimen was placed on to a Pt pad, which was heated
through an electrical feed. They demonstrated that it is possible to image defects and observe phase transformations in Si using high resolution electron microscopy (lattice imaging) (HREM).

Another type of heating stage is a MEMS-based nano-reactor. Creemer et al. [102] and de Jong et al. [103] used this type of heating stage to analyse materials using HREM at specimen temperatures greater than 1000°C. This type of heating stage has been successfully used to investigate catalytic reaction at the nanometer scale and gas-solid interactions in order to understand the various chemical reactions for synthesizing nano-materials. [104, 105]

2.5.2 In situ TEM: Gas Reaction Cell

The first documentation of a closed environmental cell for electron microscopy was by Marton [106] in 1935. He suggested two methods to isolate the cell from the column. The first method was a closed cell produced using two thin Al foils as electron-transparent windows; the second method involved placing a pair of small apertures above and below the specimen between the objective pole pieces of the TEM. In 1944, Abrams and McBain [107] adopted a cell using plastic film instead of Al foil, and sputtered O, SiO₂, Ag, or Au on the window. A modification of this design was SiO sputtered between the environment and plastic materials.

In the 1960s and 1970s, Swann and Tighe [108] developed a differentially-pumped gas reaction cell for the High Voltage Electron Microscope (HVEM). The environmental specimen chamber was located between the upper and lower objective pole pieces of the microscope. The Chamber consisted of four apertures with the upper objective pole piece and side entry specimen stage (see Figure 21). The specimen chamber was surrounded by a second pumped chamber, which reduced the leakage rate of the reaction gas into the microscope column. They used this cell to conduct a variety of redox experiments on the reduction of hematite to magnetite. [109]

Also, Flower and Swann [110] used this cell to investigate the oxidation of α-titanium in gas atmosphere in the HVEM. Based on the in situ observations, they noted that coarsening of the oxide particles occurred during the reaction at temperature as low as 650°C.
Figure 21: Schematic of the differentially pumped apertured gas reaction cell located between (a) upper and lower objective pole pieces with (b) side entry specimen holder developed by Swann. [108]

2.5.3 In situ TEM: Gas-H$_2$O Cell

“Wet” cell microscopy were mostly used for the biological science because it is important to observe cellular process in biological materials in “wet” condition such as H$_2$O or in a hydrated (gas + H$_2$O vapour) stage. In the 1970s Allinson [111] developed a two-side entry environmental cell to observe biological and cement hydration in a gas-H$_2$O vapour environment (see Figure 22). He modified his cell because the specimen could move between the gap in the cell (i.e., the gap was too large so that specimen movement could not be controlled). [112]

Figure 22: Schematic of the environmental cell with side entry by Allinson. [111]
In 1976 Swann [113] developed a miniature differentially-pumped cell for a side entry specimen stage to avoid time-consuming installation and removal of the environmental chamber, see Figure 21. This environmental cell consisted of a specimen chamber with an internal reservoir containing a H$_2$O vapour-saturated He environment. The image quality changed minimally in terms of contrast and resolution as a result of electron scattering through the H$_2$O vapour/He mixture. [114] In contrast to Swann’s results, significant electron scattering promoted H$_2$O droplet formation during investigations by Allinson [115], Heide [116] and Moretz [117]. For example, Heide observed H$_2$O droplet formation leading to condensation on the windows of his environmental cell during an in situ hydration experiment. Moretz noted that care must be taken in the selection of the appropriate environmental cell based on the specific environment to be used and the nature of the windows in order to avoid window failure.

Since 2000s the development and modification of Si chip-based in situ TEM holders have increased the interest in the biological and corrosion fields. The installation and removal of sealed windowed Si chip TEM holders are less time-consuming than the in-column environmental reaction cells. Williamson and Ross [118, 119] developed a customized home-made electrochemical liquid cell using two Si microchips with a 100 x 100 µm Si$_3$N$_4$ window. The window on the top chip was placed between the sealed Cu-reference electrode reservoir and Au-counter electrode reservoir. Ross and co-workers investigated nanoparticle growth, bubble formation and corrosion on sputter Cu and Al films onto the SiNx windows with this liquid in situ cell (see Figure 23).

Figure 23: Schematic illustration of a liquid in situ cell by Williamson and Ross. [118]
A large number of studies have been conducted of Ross’s group [119-121] who investigated nanoparticle growth, bubble formation and corrosion on electrodeposited Cu and Al chips using a modern environmental cell, which is based on a microchip with electron transparent windows. For example, de Jong and Ross [122] described recent applications in life and materials sciences. Their paper includes an overview of the state of in situ TEM with consideration of present experimental limitations which are resolution and electron beam effects including radiation damage. These authors quantified the spatial resolution that can be expected within liquids imaged with different ratios of liquid thickness and resolution of TEM, STEM and SEM, based on both calculated data, and data collected from a variety of experiments, see Figure 24.

![Figure 24: Resolution vs. Liquid thickness for TEM, STEM and SEM. [122]](image)

Other studies exploring in situ TEM/STEM/SEM includes that of Klein et al. [123] who observed gold nanoparticles in H₂O in a liquid flow cell in TEM and STEM mode. They demonstrate that the spatial resolution of conventional TEM bright field imaging is limited by chromatic aberration due to multiple inelastic scattering in the H₂O. They also found a local displacement of the H₂O by electron beam induced gas phase development if the beam intensity is too high. They suggest that H₂O is displaced by vaporisation caused by heating effects of an intensely focused electron beam. However, they mention that under suitable conditions, such as lower beam current (< 7nA) TEM imaging with a liquid flow cell can be used to understand the behaviour of nanoscale structures and a dynamically changing chemical environment.
Woehl et al. [124] also discuss inelastic scattering in H₂O as a cause of physical and chemical changes in the samples, for example crystal growth caused by secondary electron formation. They implicate inelastic scattering in the creation of image artefacts. A low dose imaging (~100 e⁻/ (sÅ²)) technique can be used to reduce the charging and beam damage. These authors also demonstrated several mitigated electron beam induced artefacts such as carbon contamination, electron beam interaction with liquid and particles and particles growth during in situ fluid imaging of gold nanomaterials. Improvements in imaging can be obtained by eliminating contamination or bubbles through plasma cleaning and glow discharge of the SiN windows to make the window surface hydrophilic.

Some in situ electrochemical studies do exist, for example those of Mullers group [125, 126], who investigated battery materials during charge cycles. To demonstrate the beam effect on the system, they performed cyclic voltammetry of a platinum film on E-Chip in the in situ electrochemical cell. They demonstrated in a pre-investigation that no difference in the cyclic voltammetry curve both in beam off/on, but a slanted curve in the thinner liquid (~150 nm) than in a thicker liquid (see Figure 25).

![Figure 25: Cyclic Voltammetry tests of a Pt film on E-Chip in (a) thick liquid and (b) in thinner liquid. [125]](image)

Chee et al. [127] deposited an Al thin layer with gold on an electrochemical SiN window to measure the galvanic corrosion in a 0.01 mol NaCl electrolyte. Scan rate was 0.5mV/s and a scan range of -0.8mV to 0.1V. Their study demonstrated that it was possible to measure the electrochemical behaviour of the interface between sputtered Al and the electrolyte for pit
initiation and galvanic corrosion. They suggest that the fluctuation of the potential curve around zero potential could cause of bubbles formation to the reference electrode (see Figure 26).

![Polarisation curve of Al coated chip in 0.01M NaCl with scan rate 0.5 mV/s.](image)

**Figure 26:** Polarisation curve of Al coated chip in 0.01M NaCl with scan rate 0.5 mV/s. [127]

The development of *in situ* electrochemical cells opened a new pathway in being able to investigate local reactions and to carry out imaging in liquid environments. Furthermore, the ability to image and perform X-ray energy dispersive spectroscopy (XEDS) analyses of metals in liquids are particularly important for studying the localized interaction of the environment with specific microstructural features in the alloy of interest. [128]

### 2.5.4 Applications of In Situ HVEM: Oxidation, Corrosion and Hydrogen Embrittlement

The advent of 1MeV transmission electron microscopes in the 1960’s-1970’s provided new opportunities applying the special *in situ* stages and the differentially-pumped gas reaction cell to real-time studies of metal oxidation and reduction, deformation, precipitation and recrystallization on a variety of alloys. The high voltage electron microscope (HVEM) have several advantages against conventional transmission electron microscope (TEM), which is operate at accelerating voltage of 100-300 keV: (1) thick specimens are easily penetrated by the beam; (2) chromatic aberration caused by energy losses and scattering in the specimen is decreased; and (3) specimen heating and irradiation damage of organic samples are decreased. [130]
- **Oxidation**

The use of the HVEM gas reaction cell and hot-stage provided a unique opportunity to explore oxidation in a variety of alloys. Specifically, researchers were able to observe oxide formation in real time and observed specific microstructural features in the metal and their effect on oxidation. Scamans *et al.* [129] studied the oxidation of Al and Al-Zn-Mg alloys via *in situ* HVEM studies between 400°C to 520°C. They identified the structure and morphology of the oxide by selected diffraction area and stereomicroscopy and demonstrated the oxidation of pure aluminium by nucleation of crystalline γ-Al₂O₃ at the amorphous oxide/metal interface after temperature. Zinc delayed the oxidation process, but magnesium forced the process by rapid nucleation and growth of MgAl₂O₄ or MgO.

Using Ar/H₂O vapour in the HVEM gas reaction cell, Flower and Swann [130] observed the reaction of Si with H₂O vapour, which resulted in the formation of surface blisters and bubbles internally pressurised with hydrogen at a temperature below 250 K (-23 C). Similarly, Scamans and Butler [129], and Christodoulou [131] used the gas reaction cell to examine the formation of H₂ bubbles along grain boundaries in Al-Zn-Mg alloys at room temperature in Ar/H₂O vapour. Complementary *ex situ* studies showed that these features were also observed in hydrogen-embrittled Al-Zn-Mg alloys. [132] A draw-back of these HVEM *in situ* studies was the damage to the specimen caused by the high voltage incident electron beam. However, an important aspect of these studies was the demonstration that the *in situ* behaviour was consistent with bulk oxidation behaviour.

- **Corrosion**

Limited research has been conducted using *in situ* HVEM techniques, as it was not possible to introduce a liquid into the environmental cell. However, specimens exposed to corrosive environments *ex situ* have been further studied and strained in the HVEM. Thus, the ability to actually assess localized corrosion/dissolution reactions in real time was not possible for the HVEM *in situ* capabilities of the 1970’s-80’s.

- **Hydrogen embrittlement**

*In situ* TEM straining experiments in H₂ gas made it possible to observe the effect hydrogen has on the deformation (and fracture) of alloys. These investigations required the ability to
deform a sample in an environmental cell without degrading the imaging resolution. This was achieved by Swann [113] via the modification of the sample holder and/or objective pole piece. Butler and Hale [133] in their review of dynamic experiments in the TEM noted that the identification of the process responsible for the hydrogen embrittlement of metal on the atomic scale is challenging, and most current mechanistic models are based on macroscopic observations with the microscopic mechanisms implied.

Robertson [134] investigated hydrogen embrittlement of numerous materials, including Type 310 austenitic stainless steel, by performing *in situ* straining experiments in a HVEM with an environmental cell containing H$_2$. The presence of H$_2$ increased the generation and velocity of dislocations during straining, and promoted fracture. He observed that for a wide range of materials, hydrogen can cause increase the velocity for edge, screw and mixed dislocation, which may be entirely within foils or intersect the surface and decreases in the spacing of dislocations in pile-ups as well decreases in the extent of cross-slip.

### 2.5.5 Factors which influence the *in situ* system

Besides electrochemical effects, the electron beam of a 200 or 300 keV TEM has sufficient energy to influence the liquid *in situ* system. The extent of this influence and what processes are affected at the beam/electrolyte/specimen interface are not entirely clear. Hence, a detailed study of the electron beam effect is important.

- **Resolution**

*In situ* TEM is a powerful tool for investigating local reactions in order to explore material-environment interactions. However, it is important to understand the effect of the incident electron beam during *in situ* TEM examination. It is well-known that the electron beam can damage the specimen depending on the beam energy, current, diameter and dose rate. Egerton *et al.* [135, 136] has reviewed the various factors related to the elastic and inelastic scattering effects in a dry system, such as electrostatic charging, atomic displacements, sputtering, specimen heating, structural damage, mass loss, hydrocarbon contamination and energy threshold effects (see Figure 27). The beam-induced damage is proportional to the electron dose and is dependent on beam diameter, as well as the amount of energy deposited in the specimen.
A crucial consideration for liquid \textit{in situ} investigations is the resolution of the TEM images. The resolution is first dependent on the thickness of the assembled \textit{in situ} cell. The electrons need to pass through the SiN$_X$ windows and the liquid thickness. It should also be noted that the additional volume introduced by bowing of the windows in vacuum can reduce the resolution. [104, 138, 139] The bowing effect occurs when the SiN$_X$ windows bend outwards away from each other and increase the gap between the top and bottom chip.

The position of the sample between the two chips is also crucial for the image resolution. In 2014, De Jonge and Schuh [138] developed an analytical equation for resolution as a function of the sample thickness and the position of a specimen in the liquid cell. Au nanoparticles in H$_2$O were evaluated with 200keV JEOL ARM200 STEM/TEM microscope with a beam current of 80 pA and a pixel dwell time of 5 µs. Interestingly, it was concluded that the best resolution in STEM mode obtained with nanoparticles on the top chip, whereas the best resolution for TEM mode was with the particles located on the bottom chip. [139] Also, they noted motion of the nanoparticles with a higher magnification (M=1200000x), which they ascribed to the transference of electrons into the particles. However, it is important to recognize that higher magnification imaging will be far more sensitive to detecting nanoparticle movement in liquid. Also, the authors neglected any possible beam heating effect in their analyses.

\textbf{Figure 27:} Egerton’s classification of electron beam-induced effects. [137]
**Electron beam heating**

Several papers dealing with liquid *in situ* experiments claimed that there is a negligible beam heating effect and any associated temperature change is also negligible \[104][140], although they started from the assumption that the transferred energy from the incident electron beam into the specimen would have a significant or measurable effect.

Howe *et al.* [141] demonstrated a heating effect of the incident electron beam on Al-Si alloy particles. They studied the phase transformation of particles induced by the electron beam. The temperature rise and poor thermal conduction away from the particles were responsible for melting (initial melting temperature of 577°C to final melting of 581°C) the Al-Si particles. Another example of electron beam heating in the TEM was reported by J. Liu *et al.* [142] According to J Liu *et al.* [142], the phase transformation of \(\alpha\)-Al\(_2\)O\(_3\) to hexagonal Al\(_2\)O\(_3\) was induced by the incident electron beam, which enhanced this thermally activated transformation. Their experiments were performed in JEM-100CX to investigate melting process of various dose rates (< 10 mA/cm\(^2\)-500 mA/cm\(^2\)) as a function of exposure time.

M. Liu *et al.* [143] developed a model to investigate temperature rise due to electron beam bombardment. Using an amorphous Fe\(_{78}\)Si\(_{12}\)B\(_{10}\) specimen, he experimentally studied the stability of the material under a 200 kV electron beam in a JEOL TEM, and observed that the amorphous specimen crystallized after 1h under the electron beam, see Figure 28. The crystallizing temperature of Fe\(_{78}\)Si\(_{12}\)B\(_{10}\) specimen is 540°C and they calculated the temperature at 557°C.

Klein *et al.*, [123] mention that it is a possibility of a local temperature rise and sample evaporation effects in addition to radiolysis. They observed a local displacement of electrolyte by the gas phase development during their investigation of gold nanoparticles in aqueous solution. Klein *et al.* suggested that a steam mixture including H\(_2\) and O\(_2\) gases had developed during exposure under the 200 keV electron beam.

Schneider *et al.* [120] and Grogan *et al.* [140] believe that the only effect of the incident electron beam is to promote significant radiolysis of the H\(_2\)O. Thus, the report of bubble creation in the liquid after prolonged several hour exposures under the incident electron beam was attributed to formation of H\(_2\). [123, 144] Despite the statements of Schneider and Grogan discounting electron beam effect other than radiolysis, conventional TEM studies
have shown that the electron beam damage, such as melting of metal samples, or crystal structure changes, surface under high electron flux, can result in local temperature increases.

Another suggestion of heating effect is that the top chip of the sandwich configuration heating up and the temperate the whole cell. Currently, it is not possible directly measure the specific temperature in a closed in situ cell, because it is not possible to insert a thermocouple to assess local heating in the in situ TEM holder.

Figure 28: TEM experiment of Fe78Si12B10 specimen to consider the model. TEM images of (a) amorphous morphology and (b) diffraction pattern. (c) Crystallized morphology and (d) diffraction pattern after 1h electron irradiation from 200 keV TEM. [143]

- **Ionization damage**

The decomposition of H₂O into O₂ and H₂ at electrodes, due to an electric current through the H₂O, is referred to as electrolysis. Another method to produce dihydrogen, is by radiolysis of H₂O. Key to the radiolysis of H₂O is the energy introduced into the system, which can vary according to the respective sources, ranging from 30 eV to 1000 keV. Hence, it is crucial to understand the mechanisms underlying radiolysis of H₂O.

H₂O radiolysis is fundamentally the decomposition of H₂O molecules by ionizing radiation. This ionizing radiation results from the decay of radioactive nuclei, beams of accelerated charged particles and X-rays. For a better understanding of which products are developed due
to this ionizing radiation, Caer [145] established a schematic illustration (Figure 29), adapted from Buxton. [146, 147]

![Schematic diagram, indicating the products of radiolysis.](image)

**Figure 29:** Schematic diagram, indicating the products of radiolysis. [145]

Caer explained the mechanism of radiation in three stages, related to the process duration: the physical, physico-chemical and chemical stages. Physical stage occurs after the initiation of the radiation a relaxation process begins and creates ionized H$_2$O molecules, H$_2$O molecules and sub-excitation electrons. The physico-chemical stage is the transition period from unstable products and can cause recombination reactions such as ion-molecule reactions, dissociative relaxations, auto-ionization of excited states, and thermalization of sub-excitation electrons. The chemical stage is a return to a stable state; in this stage species react in tracks and then diffuse in the solution.

Considering only the radiolysis of the H$_2$O without the influence of metal in the system, Pimblott [148] and Garett [149] analysed the hydrolysis of H$_2$O by electrons introduced from different sources. The authors studied low and high energy electrons to demonstrate the electron driven reaction and the resulting decomposition of H$_2$O. Garrett showed that more than one molecule is ionized between 30 and 100 eV, so high concentrations of ionized species can be formed in local areas. Pimblott discussed four reactive species that are
produced during radiolysis of H₂O including hydrated electrons, hydrated protons, hydrogen atoms and hydroxyl radicals. Pimblott suggested that under irradiation with high energy >100 keV electrons, H₃O⁺ and H₂O₂ form in aerated H₂O. In addition, that work used a Monte Carlo track-structure simulation to determine the chemistry of the spatially inhomogeneous distribution of diffusing and reacting particles. It was shown that for decreasing electron energy from 100 keV to 1 keV, there is an increase in rate and amount of reaction leading to increased production of H₂ and H₂O₂. However, with energies greater than 100 keV, a decrease in reaction rate is expected, along with a decrease in production of free radicals due to the fast-electron effect.

Several papers [150, 151] described the effect of the transferred electron in liquid in situ systems, but discussion primarily focused on the significant effects of electron beam /liquid interaction and the generation of H₂ bubbles.

Abellan et al. [150] investigated nucleation and growth-driving processes on silver nanoparticles, including several setups to measure dose rate, beam current, voltage and image mode, for a better understanding of beam influence. They found that nanoparticles grow better at higher voltage (300 keV) in STEM mode than with a lower voltage (80 keV STEM) and in TEM image mode (300 keV). Abellan attributes the slight particle growth in the TEM (300 keV) to the spread electron beam, also noting a bubble formation during the test phase. Verch and de Jonge [151] also note bubble development, in their investigation of slow movement of gold nanoparticles with a dose rate (current per area and time) between 0.2 to 4 e⁻/s Å².

Schneider et al. [120] described an irradiation simulation model of various solutions (aerated and deaerated H₂O) with high and low dose rates. They reported that bubbles were not generated from aerated distilled H₂O at lower dose rate (1.4 x 10⁹ Gy/s) over a 50 minute period when exposed to an electron beam. They present some evidence that high electron dose rates in an aerated solution, which is predominantly used in liquid in situ experiments, can change the steady-state concentration of the radiolysis products depending on the initial pH of the solution and speculated that oxygen molecules in solution reduce the eH⁻ concentration at low dose rates.

Nearly all of the above studies investigated nanoparticles, nanowires or sputtered thin films, assembled between two SiN windows, with a half- or fully filled cell chamber of aqueous
solution. The incident electron beam can change the pH depending on the pre-irradiated solution.

2.6 Summary of Literature Review

This literature overview has highlighted several key points of direct relevance to this thesis project:

- Microstructure features such as MnS inclusions affect the chemical, electrochemical and mechanical properties of stainless steel.
- The SCC behaviour of austenitic stainless steel with respect to a number of important parameters has been reviewed. Two leading mechanisms, slip dissolution, and hydrogen embrittlement mechanisms, have been presented.
- IGSCC and TGSCC can affect stainless steel components in the primary water system of PWRs and BWRs.
- The dissolution of MnS inclusions in low alloy steel was shown to be responsible for Environmentally-Assisted Cracking. Temperature and Environment along with microstructure (including inclusion content and distribution) are factors which can affect corrosion fatigue crack growth rates in high temperature H₂O.
- The review of the in situ TEM technique demonstrate the importance of studying the microstructure and behaviour of materials in real-time experiments under controlled environments such as gas or liquid. While a significant amount of in situ HVEM research was performed in the 1970’s-80’s, serious technical limitations precluded the use of liquid cells for in situ corrosion studies. Developments and modification of the technique have evolved over decades. Recent Si-chip-based designs are revolutionizing and re-invigorating in situ TEM studies in gases and in liquids.
- Corrosion studies remain an important and dynamic research area in materials science. Corrosion investigations typically focus on bulk characterization of a material in terms of the effects of grain boundaries, inclusions or precipitation, it is critical that any in situ experiments must be correlated with bulk ex situ data.
Chapter 3: Experimental Methods and Cell Developments

This chapter outlines utilises numerous microstructural characterisation techniques including analytical electron microscopy (AEM), used to characterise the phase stability. The effect of crack propagation on mechanical properties of the austenite stainless steel will be assessed via slow strain rate tests (SSRT) in simulated PWR operating conditions (autoclave testing) and hardness tests of the produced specimens.

Also, it will be correlative microstructural analysis coupled with site-specific micro-scale electrochemical measurements. The main technique is for the application of TEM in situ liquid cell AEM studies of austenitic stainless steel will be used.

3.1 Experimental Methods for Investigation of Type 304 SS

3.1.1 Specimen Preparations

- **Grinding and Polishing**

   The samples were sectioned using a Stuers Accutom 5 cutting machine. The specimens were subsequently ground with coarse SiC paper to a finish of 4000 grit. Between the different grinding papers the specimens were cleaned with a water-soap mixture and rinsed with water. Finally, the specimens were polished with a 3µm and a 1µm polycrystalline diamond spray produced by MetPrep, a water-based lubricant was used.

- **Etching**

   Specimens were etched for 30sec at 50°C in etchant V2A. The composition of the etching solution V2A is 100ml H₂O, 100ml HCL, 10ml HNO₃ and 3ml Dr. Vogel’s pickle. Dr. Vogel’s pickle is a mixture of organic solvents with Thiourea. It consists of 1-Methoxy-2-2-propanol, Thiourea and Nonylphenol-ethoxylate.

   The mentioned composition, there are also other slightly modified mixtures, one of the most commonly used for stainless steels. It is possible to develop a wide variety of microstructure and phases. Austenite and delta-ferrite are just etched as to carbide precipitation and high alloy annealing structure ferrites. Compensation structure for high alloyed martensitic steels can also be developed. During the etching process it is vital to ensure good movement of the sample in the acid to ensure a uniform etching attack. For etching of the carbide precipitations temperature of the etchant is better to keep the bottom, the grain boundary
development brings an etching at somewhat higher temperatures usually better results. The etching time varies greatly and is dependent on the material and the age of the acid.

- **Electropolishing**
  Bulk specimens were electro polished at 60°C between 15 and 30 min depending on the specimens’ surface area. The electrolyte was a mixture of 25 % sulphuric acid, 65 % phosphoric acid and 10 % distilled water.

- **Transmission Electron Microscopy Preparation**
  The Transmission Electron Microscopy specimens were cut into thin (~0.7 mm thick) sections sliced from the bulk material using a Stuers Accutom-5. The slices were first mechanically thinned to 0.1mm by 600 grit grinding paper. Discs, 3.0 mm diameter were punched from the 0.1mm slices. Finally, thin foils for TEM were prepared by twin-jet electropolishing using a Struers Tenupol 5 unit with an electrolyte of 20% HClO₄ and 80% CH₃OH at the temperature of -35°C. The polishing potential was 25 V at a current of 15 mA. The same samples were used for electrochemical measurements, SEM and EBSD for more detailed microstructural and electrochemical characterization. The EBSD images were analyzed by the software Channel 5.

### 3.1.2 Microscopy and Analysis techniques

- **Light Optical Microscopy**
  The characterisation of the microstructure used the light optical microscope from the company Carl Zeiss with a digital camera, AxioCam ERc5s. Image analyses was used the software Axio Version 6.5.

- **Electron Microscopy**
  Multiple electron microscopy methods were used in the analysis of the samples. The following sections are intended to give an overview of the use, details of the operating procedure is given in the literature review.
**Scanning Electron Microscope (SEM)**

Scanning electron microscopy (SEM) has been performed for two reasons. These are: topographical imaging, microstructural imaging at the surface of polished specimens using electron channelling contrast and for electron backscattered diffraction (EBSD) measurements. The principal instrument which has been used in this project and the detectors they are equipped with were:

- **FEI Quanta 650 field emission gun (FEG):**
  - Secondary Electron Detector
  - Backscatter Electron Detector
  - EBSD
  - Oxford instruments XMax 80 SSD EDX detector

- **FEI Sirion FEG:**
  - Secondary Electron Detector
  - Backscatter Electron Detector
  - EBSD

- **Carl Zeiss EVO 50 and EVO 60:**
  - Secondary Electron Detector
  - Backscatter Electron Detector
  - EDX detector

- **Transmission Electron Microscope (TEM)**

  The TEM experiments outlined herein were performed using FEI Talos F200X STEM and FEI Tecnai T20 analytical transmission electron microscopes and both were operated at 200 kV. FEI Talos F200X STEM equipped with an Super-X EDS system 4 SDD (30 mm²) symmetric design windowless and the FEI Tecnai T20 equipped with an Oxford Instruments X-MaxN 80TLE windowless Silicon Drift Detector (SDD) for XED spectrum imaging and an AZTEC analyser. XED spectrum imaging data were acquired at Process Time 5, with a dwell time of 0.1 sec/pixel, and background subtracted using Oxford Instruments “TruMap” software.
3.1.3 Mechanical Test Conditions

- **Vickers hardness Test**

The hardness of the CW 304 SS was measured by a Struers Duramin microhardness tester to determine whether there was a difference between the orientations of the sheet material (longitudinal/transverse). The hardness measurements were obtained on mounted samples polished to 1 µm using the Vickers Hardness 1.0 (HV 1) setting, 10sec with 1 Kg (9.81 N) loading. The indents were located within the grains, away from the grain boundaries which may produce spurious results due to the potentially different chemistry.

- **Slow Strain rate Test**

The Slow Strain Rate Test specimens were cut from a CNC-machined block (see Figure 30). Samples were prepared from both the transverse and longitudinal orientations for the CW304SS material. The CNC blocks were sliced into 1.5 mm-thick sections using the Struers Accutom-5. The samples were then mechanically thinned to 1.2 mm with 600 grit and finally to 1.0 mm with 4000 grinding paper. Afterwards, the specimens were polished with polycrystalline diamond spray from 3 µm to 1 µm and finished with OPS.

![Figure 30: Sheet specimen used for SSRT.](image)

The SSRT tests were conducted in the Nuclear Manufacturing and Technology Research Laboratory at The University of Manchester. The test apparatus consisted of a 0.9 litre high temperature, high pressure autoclave manufactured by Cormet Oy with sample loading via a pull rod linked to a variable speed motor by a planetary gear allowing minimum displacements of 1 nm/s. A simulated PWR water environment was provided by a recirculation loop, with a 10 litre stainless steel storage tank, a double diaphragm high-
pressure pump, a pre-heater, a back pressure regulator, and an ion exchange resin. The flow loop was also equipped with a Hach-Lange luminescent dissolved oxygen probe.

Strain rate of $1 \times 10^{-7}$ 1/s was applied until the sample reached yield point before transitioning to a strain rate of $1 \times 10^{-8}$ 1/s. All tests were conducted at 300°C and 95 bar pressure, with ultra-pure feed tank water with a conductivity of less than 0.1 µS/cm, a dissolved oxygen content less than 5 ppb, and 30 cc/kg dissolved hydrogen as calculated by the hydrogen overpressure in the feed tank.

3.2 General Electrochemical Test Parameters and Construction of the Microcell

3.2.1 Electrochemical Setups
The current-potential curves were measured with a three-electrode measuring system. The curves were recorded in a potential range of -400 mV to 1000 mV vs. RE and with a scan rate of 1 mV / s. The open circuit corrosion potential (OCP) was measured 10 min before each polarisation curve was obtained. For the measurement, the Reference 600 series potentiostat was used with Gamry software. The measured curves were plotted and the pitting potential was determined.

3.2.2 Construction of the Microcell
The microcell construction used in this thesis was adapted from the Suter et al. [87], Lohrengel [88] and Martin et al. [89] microcells. The microcell was constructed as follows (see Figure 31): The top cell was made of Plexiglas (PMMA) and had three terminals. The first port was for the Pt wire counter electrode. The second port was the reference electrode, which in this case was an Ag / AgCl electrode from the ALS Company. The third port was used to supply the electrolyte via a polypropylene (PP) syringe. The measuring head of the cell had a diameter of about 0.4 cm, and the resulting sample area was approximately 0.2 cm$^2$. For the measuring head were used pipette tips. The original diameter size of the opening pipette tip was 0.4 cm. To create different diameter of the tip, pipette tips were filled with epoxy resin and drilled with 50µm and 100µm diameter drill an opening.
Figure 31: Microcell version of the system constructed in this thesis project: (a) schematic of the cell and (b) photograph of actual microcell.

3.3 Liquid in situ TEM cell technique

The design of the first closed-window cell, subsequent modifications, and the development of various environmental stages for in situ TEM investigations have been discussed in detail in Chapter 2. Since 2000s, the design of Si chip-based cells (Ross [118]) has generated increasing interest in the fields of battery development, corrosion and life sciences. Most of the liquid in situ cells are based on a similar design. A commonly-used TEM holder design for a liquid in situ TEM cell contains a pair of Si chips with a field-of-view defined by electron-transparent (generally 50 nm thick) SiN$_X$ windows and two O-ring seals (see Figure 32). This sandwich-like configuration is located at the tip of the TEM holder. Depending on the specimen thickness it is possible to choose chips with different size spacers (e.g., 50 nm, 150 nm, 500 nm, 1 µm or 5 µm) to accommodate the specimen between the two Si chips. The use of different sized spacers enables the use of the reservoir with different liquid volumes. The total volume of liquid in the reservoir is 1.192 µl without internal PEEK tubing. For example, in a Protochips P210 holder, a spacer thickness of 500 nm has liquid volume of 2 nl between the two chips (see Table 2).
Table 2: Volume between bottom and top E-Chips by Protochip.

<table>
<thead>
<tr>
<th>Spacer thickness</th>
<th>50nm</th>
<th>500nm</th>
<th>2microns</th>
<th>5microns</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume between Chips</td>
<td>0.6nL</td>
<td>2nL</td>
<td>8nL</td>
<td>20nL</td>
</tr>
</tbody>
</table>

The reservoir is filled with the help of a tube through a microfluidic syringe pump (Harvard Apparatus). Two PEEK (polyether ether ketone) tubes are integrated into the shaft of the TEM holder; one PEEK tube can be used as input port connected to the syringe pump. The other tube can be used as an output to drain the solution at the reservoir (see Figure 33). The syringe pump allows for adjusting the flow rate of the solution between 1 - 5µl/min.

Figure 32: Schematic of a fully encapsulated liquid in situ TEM cell with 50nm SiNₓ windows. The sandwich-like configuration with a top and a bottom chip is shown, the specimen is placed between these two chips. A specially-designed Be lid (optimised for XEDS) seals the cell between O-rings in the TEM stage by N. Zaluzec.

Figure 33: Schematic diagram of inlet and outlet of in situ TEM holder by Protochip.
3.3.1 Development of the specimen preparation technique for in situ TEM studies

All liquid in situ TEM studies performed over the past ~ 20 years, with the exception of this thesis research, have been performed on nanoparticles, nanotubes or films sputtered directly on to the SiNx windows. Thus, by definition, no specific preparation has been required for those materials. However, in this research, it has been necessary to develop a process to prepare electron-transparent specimens of “real” conventional alloys, i.e., austenitic stainless steels. This “hybrid” specimen preparation technique utilizing electropolished TEM discs and focused iron beam (FIB) technique is described in detail in Chapter 5.

The FIB section was extracted of a Type 304SS TEM foil, see Figure 34 a. Figure 34 b shows the lift-out of a square specimen. This section was connected with Platinum on the Si-window of the Bottom-Liquid-Chip. The connection points were on each corner of the FIB section to stabilize the specimen for the flow-rate tests in Figure 34c. The modification of the specimen geometry, in which the specimen was keyed in the region to be attached to the working electrode are demonstrated in Figure 35. The specimen was lifted out as a rectangle from the electron transparent region of the TEM disk with a tab placed on the rectangle for connecting the Omni probe, when removing the Omni probe the entire tab was cut to avoid any Pt contamination of the sample (b). A wedge was created by preforming a cleaning cross-section from the centre of the sample to the outer edge; this produced a gradient of milling, in thicker samples this region was first thinned by a regular rectangular milling. This was achieved by first micromachining a rectangle of 12 x 5 µm for a 10 µm wide electrode into the specimen at the edge to be connected to the electrode (the micromachining was performed using a 0.5 nA, 30 keV and milling angle of 90°, the location was just off from the edge, this was to avoid rapid milling of the specimen edge). Secondly, a cleaning cross-section was used to milling from inside the sample out to the edge with a single pass at 0.5 nA, 30 keV to mill as a set of sequential lines. This modification permitted the Pt deposition to connect the sample to the working electrode without the height of the Pt deposit exceeding the thickness of the original specimen (a) to use a smaller gap (< 5 µm) for the examination.
**Figure 34:** FIB Cut and paste” approach for removing a thin section of an electropolished specimen and relocating on top of a SiNx window for E-Cell studies. (a) STEM BF image in the FIB/SEM, (b) SE image of lift out process with cut outs around the perimeter of the specimen, (c) SE image of specimen placed on the E-chip with SiNx liquid cell window visible, notice the Pt deposits at the four corners attaching the lift out to the Si frame.

**Figure 35:** (a) SE image of wall thickness measurement, (b) lift-out of specimen and (c) placing specimen onto working electrode. Note the tapered slot at the top left of the specimen, which will be used to attach the specimen to the electrode using a Pt FIB deposition.
Chapter 4: Control and Scoping Experiments

This chapter outlines the current state-of-knowledge concerning in situ measurement techniques. In order to better understanding of data of this experimental methodology, the Type 304 SS material is pre-investigated, which was used in this thesis. This presents the microstructural, mechanical and electrochemical results for the cold worked austenitic stainless steels.

First, two important and well-used (in this thesis) measurement methods are presented. Metrological difficulties associated with developing a large-area measuring method are outlined, followed by a detailed description of various µm-scale measurement techniques. The comparison of the advantages and disadvantages of each method allows the classification of their suitability and provides a brief overview of measurement techniques in the sub-micron/nanometer range.

This thesis has involved the development and optimisation of E-chips and electrodes so that valid electrochemical measurements can be performed on Type 304 austenitic stainless steel in situ in liquid environments of interest.

4.1 Material Characterisation

The materials used in this study include a 20% cold-worked (by rolling) wrought Type 304 stainless steel provided by AMEC (Steel A). The chemical compositions were independently measured by MIS (a University of Manchester approved subcontractor). The analytical method used for the compositional analysis was inductively coupled plasma optical emission spectrometry (ICP-OES). The results are shown in Table 3 for Type 304 stainless steel.

Table 3: Chemical Composition of Type 304.

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Al</th>
<th>Ti</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold-rolled</td>
<td>0.045</td>
<td>0.48</td>
<td>1.56</td>
<td>0.027</td>
<td>0.008</td>
<td>18.50</td>
<td>0.02</td>
<td>9.91</td>
<td>0.034</td>
<td>&lt;0.01</td>
<td>0.04</td>
</tr>
</tbody>
</table>

4.1.1 Microstructural Characterisation

In the following section the metallographic results investigated with Light Optical Microscope, SEM, and TEM were prepared from cold worked austenitic stainless steel using standard metallographic procedures, followed by etching. Specimens for the Light Optical
Microscopy and Laser Scanning Confocal microscopy have been etched with V2A etchant. For SEM/EBSD specimens were electro-polished with a mixture of 25% Sulphuric Acid, 65% Phosphoric acid and 10% distilled Water and for TEM specimens were prepared by electro-polished with a mixture of 20% HClO₄ and 80% CH₃OH.

- **Light Optical Microscopy**

Light optical images of the cold worked Type 304SS are shown in Figure 36. Both images show deformation austenites. On closer observation (Figure 36b) of a deformed austenite grain can be observed vertical parallel lines next to the annealed twin. This deformation could be apparent “microtwins”, but also it is possible epsilon martensite or alpha prime martensite. The actually discrimination between mircotwins and epsilon martensite is impossible to identify by using light optical microscopy. Therefore it requires further investigations e.g. EBSD, TEM to identify the exact type.

![Figure 36: Light optical microscopy of (a) transverse and (b) closer observation of the 304SS.](image)

- **Scanning Electron Microscopy (SEM)**

Higher magnification Backscatter Electron (BSE) images of cold-worked Type 304SS in the transverse orientation are shown in Figure 37 and Figure 38. In the BSE images the deformation within the grains is shown as a fine lamellae microstructure due to electron channelling contrast. This morphology of the grains could be interpreted as deformed microtwins or transformed martensite, like epsilon or alpha prime martensite; also, twin-like structures and martensite could co-exist in the cold-rolled austenite. This has been
documented in several papers [152,]. The Kurdjomov-Sachs (K-S) orientation relationship describes the martensite transformation in iron alloys in which the \( \{111\}_{\text{fcc}}\parallel\{011\}_{\text{bcc}} \) and \( <111>\text{bcc}/<101>\text{fcc} \) related together and these two differ by only 5.6° rotation in the interface plane which is reported by Nakada [153]. They reported that the amount of epsilon martensite increased with applied strain during tensile straining. Also, it is expected to be next to the mechanical twins and is examined by EBSD, XRD and TEM.

![Figure 37: SEM/BSE image of deformed microstructure in 304 SS.](image)

Closer observation of Figure 38 shows a pronouced deformation structure in the BSE image due to channelling contrast in Figure 39 a. The high resolution inverse pole figure (IPF) map in X orientation was taken with a step size of 0.05µm (Figure 39 b). It shows that the orientations of horizontal lines (purple) are between [001] and [111] and the orientation of the vertical line (orange red) is nearby [001] in. [111]-grain, which is indicated as austenite grain. The orientations of the structures are correlated to colour coding of the IPF reference image (Figure 40). This reference is the same for all IPF maps in X orientation throughout this report. The volume fraction of the phases shows that 98% indexed pixels are FCC-phase (blue phase of austenite), nearly 0.2% indexed pixels are the BCC-phase (red phase for alpha prime martensite). Approximately 1.5% of pixels could not be indexed and those error pixels are black fields in the phase volume fraction image (Figure 39c). The calculated green lines can be linked to sigma 3, \( <111> \) twins grain orientation. Furthermore, those lines can also be interpreted as epsilon martensite.
Figure 38: SEM/BSE Z-contrast images of 304SS transverse orientation.

Figure 39: (a) Closer observation of SEM/EBSD z-contrast image of 304 SS. (b) Inverse pole figure map and c) Phase fraction of 304SS transverse orientation.

Figure 40: IPF colouring reference.
Based on Figure 41, not all deformed grains contain the bcc-martensite phase. In this case just 0.03% indexed bcc and 89% of indexed FCC. One main problem of this analyse of the grains are the high rate of 11% non-indexed pixels. The precise observation of the relative larger grain (G1) reveals red fine lines in diagonal orientation can be determined in the IPF image. The fine lines shown [001] grain orientation. Correlate to volume fraction image shows exactly the same lines sigma 3 <111> twins boundaries. Attention should be paid to section grain (G2) in which the sigma 3 twins boundaries located closed to the grain boundary and shows an irregular lamellae. The same behaviour was observed by M.N.Gussev et al [154] which described that martensite forms dense, irregularly-shaped colonies and the most of the “linear” colonies are located near the grain boundaries with the co-existence of α and ε martensite.

**Figure 41:** (a) Inverse pole figure and (b) Phase volume map of deformed austenitic grains.

- **Grain Size analyse**

Fields-of-view for EBSD analysis was obtained at lower magnifications in order to obtain a statistical analysis of the grain sizes. Two methods were used to calculate the grain size. Figure 42 a) shows a typical image used for measuring the grain areas and Figure 42 b) shows the linear intercept method in which 10 intercept lines are used to measure the distance between the grains. The results of the austenite grain size analyses are summarised in Table 4. Grains on the edge of the fields of view were not included in the grain size calculation. Smaller regions such as fine lines within a grain were also excluded from the measurements.
The average diameter and average grain area were calculated to be 10µm and 229µm², respectively. The diameter of grain sizes are between 3.7 and 145µm and the grain size areas are between 11 and 16424µm².

**Figure 42:** Lower magnification EBSD maps of CW304SS. (a) grain areas and (b) linear intercept method.

**Table 4:** Summary of the average grain size analyses.

<table>
<thead>
<tr>
<th></th>
<th>Diameter [µm]</th>
<th>Area [µm²]</th>
<th>Intercept [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size of data set</td>
<td>1225</td>
<td>1225</td>
<td>376</td>
</tr>
<tr>
<td>Average</td>
<td>10.1</td>
<td>229.0</td>
<td>9.9</td>
</tr>
<tr>
<td>Minimum Value</td>
<td>3.7</td>
<td>10.9</td>
<td>1.1</td>
</tr>
<tr>
<td>Maximum Value</td>
<td>144.6</td>
<td>16424</td>
<td>107.4</td>
</tr>
</tbody>
</table>

- **Transmission Electron Microscopy**

The examination of the 20% cold worked austenitic stainless steel in Figure 43, Figure 44 and Figure 45 show the morphology of an austenite grain with a twin like structure. This microstructure could be interpreted as microtwins, but also could be epsilon martensite. An accurate statement, which kind of microstructure, requires a higher magnification of the specific area and consequent diffraction pattern.
Figure 43 shows a complex microstructure of an austenite grain. The ultra-fine twin like features shown in one direction until the grain boundary, which is marked with a red line. The loop curves could be show a change of the shape (see Figure 43 b).

**Figure 43:** TEM Images of deformation austenite.

Figure 44 a) corresponds to the Selected Area Electron Diffraction (SAED) pattern of Figure 44b). The analysis of the SAED indicates that this area is alpha prime martensite. The calculation was determined using the lattice parameter of austenitic stainless steel as 0.3589nm and martensite as 0.2873nm [15]. The Camera length was 300nm and the ratio of interplanar spacings between two different planes. Afterwards the data indicated above were inserted into the JEMS software and compare the results.

**Figure 44:** (a) TEM image and (b) diffraction pattern obtained from cold worked 304 SS.
Figure 45 shows a deformed austenite microstructure with parallel lines in the grain. The analysis of the SAED results that strong spots represent the formation of micro-twins with the area axis [111] of austenite.

![Image](image.png)

**Figure 45:** (a) TEM morphology of deformed austenite grain with a “twin-like” structure and (b) diffraction pattern obtained from cold worked 304 SS.

### 4.1.2 Mechanical Test

- **Vickers Hardness Test**

Initial mechanical evaluation of these materials included hardness measurements. The hardness is related to yield strength of the material. 20 micro hardness indents were measured for CW 304 SS in both rolling and transverse orientations. The results are presents in Table 5. The average Vickers Hardness calculated for the transverse orientation was 285 ±20 HV1, the longitudinal orientation was 297±21 HV1. The results of the 20% cold-worked Type 304SS are in agreement with other data for cold-worked steel. The literature reviews of 20% cold-worked austenitic stainless steel provide a value range between 200 HV1 up to 300 HV1. [156]

**Table 5:** Results of Vickers-Microhardness Tests [HV1] for the CW 304 SS.

<table>
<thead>
<tr>
<th>Orientation of CW304SS</th>
<th>rolling orientation</th>
<th>transverse orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>HV1.0</td>
<td>297±21HV1</td>
<td>285 ±20 HV1</td>
</tr>
</tbody>
</table>
- **Slow strain rate test (SSRT)**

Slow-strain-rate tensile (SSRT) tests have been performed on cold worked Type 304 austenitic stainless steel in a simulated pressurized water reactor (PWR) environment. Figure 46 shows the stress-strain curves obtained from normal and rolling direction tensile specimen of the CW 304 SS. Both curve shows similar trend with a slightly higher yield point (720 mPa) and elongation (0.0016 m) for the rolling direction specimen than for normal direction specimen with a yield stress of 615 mPa and elongation of 0.0012 m.

After the SSRT tests, the fractured specimens were transferred to a SEM for fractographic examinations. The SEM used in this study is FEI Quanta 650 field emission gun. Secondary electron imaging at 20-kV acceleration voltage with 10- to 15-mm work distance was used for most of the observations. The fracture morphology of Types 304 SS is shown in Figure 47. The principal fracture morphology is ductile dimples among these samples. Intergranular, cleavage, and mixed-mode cracking can also be seen in some areas on the fracture surfaces. High magnification imaging (Figure 47 b) of the fracture surfaces showed that the intergranular fracture was pure and did not transgress from the grain boundary and Figure 47 c) showed ductile fracture surface with dimple pattern.

![SSRT Stress-Strain Curve](image)

**Figure 46:** SSRT of rolling direction (red curve) and normal direction (black curve) in autoclave at 300°C and 95 bar pressure (H₂O with a conductivity of less than 0.1 µS/cm; DO
less than 5 ppb, and 30 cc/kg H₂). Strain rate of 1×10⁻⁷ 1/s was applied to σ_{yield} before transitioning to 1×10⁻⁸ 1/s.

**Figure 47**: Fracture morphology of CW 304 SS after SSRT: (a) cleavage and mixed mode fracture, (b) intergranular areas, and (c) large ductile dimples.
4.2 Microcell Technique Observations

4.2.1 Microcell tip investigation

The pressure at the microcell-tip had to be sufficient so that the solution could not escape to the edges of the microcell-tip - otherwise crevice corrosion could occur on the measurement area around the microcell-tip edge (see Figure 48). The effect of pH-value could dramatically change in the microcell-tip, thus altering the metal oxidation reaction. Figure 49 illustrates a pit formation without those effects after the polarisation experiments. Also, crevice corrosion at the measured area around the microcell-tip edge could change in chemistry locally in the micocell-tip due to pit growth, thereby creating a larger gap between the tip and the surface.

![Schematic illustration of the microcell tip reaction with the surface.](image)

**Figure 48:** Schematic illustration of the microcell tip reaction with the surface.

![Laser scanning confocal microscope images of the pit produced during the microcell experiments.](image)

**Figure 49:** Laser scanning confocal microscope images of the pit produced during the microcell experiments. (a) Microcell tip size (inner black circular region), (b) irregular pits produced by a leaky microcell tip (red circle is exposed area) and (c) pit formation after polarisation experiments.
The effect of different microcell-tip sizes on the pitting potential is given in Figure 50. The specimens were polished to 1µm and exposed for 1 hour in air to make sure to have the same surface condition. The electrochemical polarisation data were measured 5-times for each microcell-tip of 50µm, 100µm and 400µm diameter for 20% CW Type 304 SS in a 0.1M NaCl solution and recorded over a potential range of – 0.4 V to 1.0 V (Ag/AgCl) and with a scan rate of 1 mV/s. The microcell-tip with a diameter of 50 µm shows a larger deviation of results in comparison to the other microcell-tips, namely, 100 µm and 400 µm. Also, a decrease in pitting potential from 880 mV to 647 mV (Ag/AgCl) was observed as the tip diameter was increased from 50µm to 400µm.

According to Suter and Böhni [90], the pitting potential of high S Type 304 SS is a function of the exposure area of the microcell. They noted that the microcell technique increased the pitting potential due to a decrease in the number of “microstructural features” when the exposed area is small.

Figure 50: (a) Summary of the Pitting Potential Measurements for the 20% CW Type 304 SS and (b) potentiodynamic polarisation curve of 20% CW Type 304 SS in 0.1 mol/l NaCl with a scan rate 1 mV/s and 400 µm tip size.
4.2.2 Comparison of microcell data for Type 304 SS with conventional polarization data

In order to demonstrate the validity of the microcell measurements and their relevance to the bulk material, it is essential to correlate these data with those obtained from conventional electrochemical tests. In this study, conventional (bulk) results have been compared to those obtained using a microcell (~400 micron diameter area). These data span areas of cm² (conventional) and µm² (microcell). Figure 51 shows potentiodynamic polarisation curves of two size scales of 20% cold-worked Type 304 SS in a 1 mol/l NaCl solution. The large-area measurements show a pitting potential of approximately ~ 400 mV (Ag/AgCl). Reducing the exposed surface to an area about 400 µm in diameter leads to an increase of the pitting potential to approximately 450 mV (Ag/AgCl) and decrease of the current density about 4.35 x 10⁻⁷ mA/cm².

Compared to the bulk/conventional data in which many grains, grain boundaries and inclusions are sampled, the microcell region have a measurement area of 1-2 grains with a few grain boundaries or a feature like an inclusion. The diameter of grain sizes are between 3.7 and 145µm. The previously described effect of crevice corrosion could occur on the measured area around the microcell-tip edge; during the measurements, bubbles may form in the micocell-tip due to pit growth, thereby creating a gap between the tip and the surface. The pH-value may dramatically change in the microcell-tip, thus changing the metal oxidation reaction.
**Figure 51:** Potentiodynamic Polarisation curve of 20% CW Type 304 SS in 1mol/l NaCl. Black curve was measured using the microcell ($\mu$m$^2$) and red curve was measured using conventional bulk cell (cm$^2$) range.
4.3 Develop Experimental Protocols/Techniques to enable validated *in situ* liquid cell reactions at the nano-scale

This section describes the specific *in-situ* cell and techniques that have been used in this thesis. Background information pertinent to these *in situ* experiments is discussed. This includes: 1) the liquid *in situ* analytical TEM cell; and 2) the liquid *in situ* electrochemical TEM cell. All papers reflecting the main scientific outcomes of *in situ* TEM technique development and applications are described in detail in Chapter 5–Chapter 8.

4.3.1 *In situ* holder and assembly of E-Chip

During assembly of the top and bottom E chips in the *in situ* TEM holder, it is crucial to check the seal since the SiNx window can be damaged by the FIB (see Figure 52) when making the Pt connection or controlling specimen thickness and small cracks can form at or around the window. The first generation of hybrid specimen was too large and Pt-connection points were on corner of the FIB section to stabilize the specimen for the flow-rate tests. Also, Pt covers up the specimen and contaminates the area around Pt-connection. Additionally, through the Pt connection can be damage the fragile window during the Pt deposition process and caused small cracks.

Figure 53 present the modified hybrid specimen onto electrochemical E-chip to void the FIB damage. The modified FIB specimen is welded with Pt outside the SiNx window onto the working electrode. One disadvantage is that the specimen can exerts pressure on the window, thus could causing stress around the specimen. Also, the Pt contamination is around the connection and cover up not the specimen.
Figure 52: Laser scanning confocal image of hybrid specimen onto E-chip.

Figure 53: Laser scanning confocal image of modified hybrid specimen onto modified E-chip.

To test this, the TEM holder with the integrated E-sandwich chip cell must first be tested in dry mode under vacuum using a HiCube Pfeifer vacuum system. If a vacuum has been established to $10^{-7}$ bar after 30 minutes, the system is hermetically sealed and no damage to the integral SiNx window has occurred. Next, the specimen should be examined in the TEM in dry mode (1 atm air) before the electrolyte is added. Then, the specimen should be placed again into the HiCube to make 100% certain that no leaks or window damage has occurred.
Finally, the electrolyte can be introduced with a smallest flow rate of 1 μl / min into the E-cell system without to destroy SiNx window, because with a higher flow rate (>5 μl / min) the SiNx window can blow up and destroy the window.

**Figure 54**: Schematic diagram of assembly procedure of electrochemical in situ TEM holder with a modified Be top lid by Protochips.

The original Protochips P200 liquid E-Cell holder was modified by Zaluzec [128] in cooperation of the University of Manchester, because the as-received liquid E-Cells would not permit XEDS analysis, i.e., the E-Chip geometry and lid geometry blocked the X-ray path to the XEDS detector. The penumbra of the holder blocked most XEDS detectors even when tilted to maximum extent possible, see Figure 55. Zaluzec solved this problem by modification of the TEM holder design to improve the specimen holder-detector geometry by using a special “cut-out” top “lid”. The result of the modifications of the TEM holder is illustrated in Figure 55b. It shows a full butterfly lid made of Be, which permits XEDS data acquisition in the analytical electron microscope.
Figure 55: (a) Schematic of cross-section of an AEM’s objective lens showing a conventional XEDS/eCell geometry and illustrating the shadowing of the line-of-sight path of the detector by the penumbra of the eCell holder. (b) Schematic diagram showing cross-section of eCell holder before (left) and after modifications (right), illustrating the removal of material that blocks the line of sight path to the X-ray detector. Si wafer (green), SiN windows (blue), Si clamping mechanism (gray), tapered slot in Si clamp mechanism (gray), Holder body (orange) by N.J. Zaluzec. [128]

4.3.2 Pre-Experimental of liquid in situ TEM: Type 304 SS

The first liquid in situ OCP experiments in distilled water were conducted on the thinnest part (the edges) of the specimen as this is the most likely region to react. The edge is considered the weakest area due to possible edge effects. In this area the corrosion products formed faster than on the middle part of the sample. SEM examination of the specimen after the first in situ OCP’s showed that over the region in which the electron beam had been, the specimen had reacted, as shown in Figure 56. This reaction had caused particles enriched in Cr and Fe to develop, as shown in the EDX spectrum. The reacted region appeared to have thinned as a result of exposure, implying that dissolution had occurred. This could be the first indication of a beam-induced effect in the in situ system.
Figure 56: (a) SEM images and (b) EDX analysis of particles on hybrid sample after in situ investigation under the beam conditions.

In another experiment Figure 57 shows the EDX in situ observation of BF-STEM and EDX spectrum images of the 304SS before treatment and after 3h exposure time in distilled water at room temperature. For the OCP measurement, the electron beam spot was always in the same region in TEM mode with a spot size 1 and beam dose about 1.3 A/m². Considering just the BF-STEM images a corrosion product can be seen in the beam spotted area. From the EDX analysis it was found that the Ca and O content dominate this region. This suggests that it is a calcium oxide. After further investigation of the distilled water, it was found that the Calcium content was about 0.4mg/l and the conductivity is 6.8μS. The dissolved calcium from the distilled water was precipitated in a circular footprint on the specimen and E-chip. By local heating of the examined point, the water evaporates through the beam and the existing salts are left as residues. Also the BF-STEM Figure 57 (d) shows better resolution of the exposed region after evaporation of the water than BF-STEM Figure 57 (a). This shows that the electron beam has a bigger influence on the system than expected.
Figure 57: STEM -EDX spectrum images before (a) and after (d) 3h exposure in distilled H₂O.

4.3.3 Electrodes modifications and application of the electrochemical E-chips

The Protochips electrochemical chips for the Protochips Poseidon 500/510 electrochemical holder are based on the original E-chip design with the addition of reference (RE), counter (CE) and working (WE) electrodes, see Figure 58. Standard E-chips contain linear Pt WE electrode or a glassy carbon WE, which was used for cyclic voltammetry investigations of battery materials. [125, 126] Therefore, E-chips were not suitable for use with conventional metal/alloy specimens. The glassy carbon working electrode (Figure 58b) was not appropriate for hybrid metal samples and for electrochemical studies, for several reasons. Firstly, electrode size was very large, thereby obscuring a large proportion of the SiNx window. Secondly, the use of Pt deposition in the FIB production of the hybrid specimens caused galvanic corrosion at the connection points (steel/glassy carbon/Pt).
The configuration of the reference and counter electrodes on the modified electrochemical chip had to consider the geometry of the SiNx windows (see Figure 59). Both electrodes circumnavigate the working electrodes to achieve near-uniform current lines. An important modification of the working electrode was to relocate the WE outside of SiNₓ window, as it was recognized that the FIB Ga ion beam would damage the fragile window during the Pt deposition process. Based on these modifications, Protochips redesigned their electrochemistry chips and fabricated E-Cell chips suitable for metal samples.

**Figure 58:** Schematic illustration of the two original Protochips electrochemical-chip configurations: (a) Type I - linear configuration of Pt-electrodes, (b) Type II- glassy carbon electrode with a horizontal direction of the SiNₓ window.

The configuration of the reference and counter electrodes on the modified electrochemical chip had to consider the geometry of the SiNₓ windows (see Figure 59). Both electrodes circumnavigate the working electrodes to achieve near-uniform current lines. An important modification of the working electrode was to relocate the WE outside of SiNₓ window, as it was recognized that the FIB Ga ion beam would damage the fragile window during the Pt deposition process. Based on these modifications, Protochips redesigned their electrochemistry chips and fabricated E-Cell chips suitable for metal samples.

**Figure 59:** (a) Schematic illustration of modified electrochemical (Type III) chip and (b) detail of red dashed region. The WE electrode is ~10 µm outside of the SiNₓ window edge and RE and CE surrounds the SiNₓ window.
4.3.4 Stability tests for reference electrodes

In the present study considerable effort was focused on assessing reference electrode stability and electrode configuration so that this technique can be used for “bulk” (conventional) alloys. Experiments were performed using both distilled H₂O and dilute H₂SO₄, and are described in the following sections. The prerequisite for a reference electrode is stability in the electrolyte. Measurements of reference electrodes were made using conventional electrochemical methods in distilled water at room temperature at pH 6.8. The potential of the Pt electrode was measured against an Ag/AgCl electrode (Eₚₑᵣₙ = 0.220V) over approximately 12h. The following equation for the calculation of Pt potential vs. Ag/AgCl potential was:

\[
E_{Pt} = E_{MPt} - E_{Ag/AgCl}
\] (6)

The potential of the Pt electrode was then calculated by subtracting the known Ag/AgCl potential (Eₚₑᵣₙ = 0.220V) from that experimentally-measured (Eₚₑᵣₙ = 0.364V). The calculated potential of the Pt electrode (Eₚₑᵣₙ = 0.144V) was compared to the free corrosion potential, also known as the Open Circuit Potential (OCP), of the Pt electrodes in H₂O with no specimen present to insure there was nothing within the E-chip to alter the OCP.

Figure 60 shows the ex situ OCP (as measured in the original Protochips linear Pt electrode configuration E-chip) over a 1 hr period to assess the stability of the Pt and glassy carbon reference electrodes in H₂O. The linear Pt electrode configuration was also used to evaluate the stability in a 0.001 M H₂SO₄ electrolyte. All 3 measurements show a nearly constant OCP as a function of time. The calculated potential (red curve) 0.144 V is in close agreement with the linear Pt electrode configuration cell (black curve) 0.163 V after 1 hour. Comparison of the measured potentials for the linear Pt electrode (black curve) and the glassy carbon electrode (blue curve) in distilled H₂O shows a potential difference of about 400 mV. Comparing the linear Pt electrodes in different electrolytes revealed a difference in OCP of approximately 200mV. The reason for the different potential is the conductivity of the electrolytes. Despite the low electrical conductivity of distilled H₂O (6µS/cm), free corrosion potential measurements could be obtained using the Pt electrode.

The glassy carbon working electrode was not suitable for these electrochemical studies, for several reasons. Firstly, electrode size was very large, thereby obscuring a large proportion of the SiNX window. Secondly, the use of Pt deposition in the FIB production of the hybrid specimens caused galvanic corrosion at the connection points (steel/glassy carbon/Pt).
Furthermore, the incident electron beam must not illuminate both electrodes at the same time, as this can cause an electrical short circuit in the electrochemical E-chip system.

**Figure 60:** Ex Situ OCP measurement of different electrolyte and E-Chip design.
4.4 Summary of Control and Scoping Experiments

In summary, the pre-investigation of the CW 304 SS shows an overview of the microstructure of cold worked austenitic stainless steel. For better examination for local phases, such as like micro-twins or epsilon martensite, EBSD and TEM have proved essential. Analysis of the high resolution EBSD maps shown that fine lines in austenite grain are sigma 3 twins, but this could be also epsilon martensite. Based on SAED identification of alpha prime martensite and micro-twins in CW 304SS are co-existing. The results of Micro-Vickers-Hardness test show no significant characteristics and are within the context of a cold rolled austenitic stainless steel and fracture morphology shows intergranular, cleavage, and mixed-mode cracking in some areas on the fracture surfaces. The SCC behaviour of the cold worked 304SS indicates that there is a link between the deformation microstructure which is induced by rolling and the susceptibility during SSRT.

There are several examples of the application of mm and nm scale techniques and the factors which influence such investigations. An initial assessment of the investigation method is possible based on the literature. The advantages and disadvantages of this technique are clearly demonstrated. For example, the microcell method allows measurements, on small areas such as MnS inclusions, but it is impossible to capture images of the dissolution itself. Interpretation of the shift of the polarisation curve gives insight into the factors in play. For example, negative potential shifts of the polarisation curve can be interpreted as the corrosion susceptibility of a material.

The in situ TEM has opened a new pathway for directly imaging and studying complex chemical and electrochemical processes occurring in an environment in line with the increasing interest in the corrosion science platform since the 1970s. However, this current technique presents some challenges in terms of specimen preparation or beam effects. Previous work using this method has predominantly focused on nanoparticles, nanotubes, or nanowires, but the main interest in corrosion science is for bulk metallic samples which are not nanoparticles. Furthermore, it is not entirely clear what effects the introduced beam has on the liquid in situ cell system or electrochemical in situ investigation.
Chapter 5: First Proposed Manuscript

5.1 Introduction:

The first paper described the hybrid specimen preparation technique. The experiments were performed by Xiang Li Zhang and Sibylle Schilling. The manuscript was written by Xiang Li Zhang, with technical and editorial supervision and proofing by M. Grace Burke and Nestor J. Zaluzec.

5.2 Manuscript:

Sample Preparation Methodologies for In Situ Liquid and Gaseous Cell Analytical Transmission Electron Microscopy of Electropolished Specimens

X.L. Zhong1, S. Schilling1, N. J. Zaluzec1,2 and M.G. Burke1

1 Materials Performance Centre and Electron Microscopy Centre, School of Materials, University of Manchester, Manchester, M13 9PL, U.K.

2 Electron Microscopy Center, NanoScience and Technology Division, Argonne National Laboratory, Argonne, IL 60439 USA

ABSTRACT

In recent years, an increasing number of studies utilising in situ liquid and/or gaseous cell scanning/transmission electron microscopy (S/TEM) have been reported. Due to the difficulty in the preparation of suitable specimens, these environmental S/TEM studies have been generally limited to studies of nanoscale structured materials such as nanoparticles, nanowires, or sputtered thin films. In this paper we present two methodologies which have been developed to facilitate the preparation of electron-transparent samples from conventional bulk metals and alloys for in situ liquid/gaseous cell S/TEM experiments. These methods take advantage of combining sequential electrochemical jet polishing with focussed ion beam extraction techniques to create large electron-transparent areas for site-specific observation. As an exemplar, we illustrate the application of this methodology for the preparation of in situ specimens from a cold-rolled Type 304 austenitic stainless steel.
sample, which was subsequently examined in both one atmosphere of air as well as fully immersed in a $\text{H}_2\text{O}$ environment in the S/TEM with hyperspectral imaging. These preparation techniques can be successfully applied as a general procedure for a wide range of metals and alloys and are suitable for a variety of in situ analytical S/TEM studies in both aqueous and gaseous environments.

**Key words:**

*In Situ TEM, Liquid TEM, Analytical Transmission Electron Microscopy, Focus Ion Beam, FIB, Specimen Preparation, Specimen Preparation Technique, X-ray Energy Dispersive Spectroscopy, Austenitic Stainless Steel*

### 1.0 INTRODUCTION

Understanding dynamic processes at nanometer scales during the reaction of materials in liquid and/or gaseous environments can provide opportunities for improved materials design in numerous applications. *In situ* liquid/gas cell S/TEM is a rapidly developing methodology which can provide real-time dynamic micro-to-nanoscale information to study the evolution of the structure, phase distributions, morphology, composition, crystal structure, deformation, corrosion, as well as elemental and interfacial segregation, during the reaction of a material with a controlled environment [Prestat *et al.* 2015, Parent *et al.*, 2014; Chee *et al.*, 2014; Evans *et al.*, 2011; Zheng *et al.*, 2009; Radisic *et al.*, 2006]. Although the concept of a windowed environmental cell for studying specimens in a gaseous or liquid environment using electron-optical instruments has been recognized for some time, it is only relatively recent that the research and publications related to *in situ* liquid/gas cell S/TEM studies have begun to grow exponentially [Parsons 1974; Williamson *et al.*, 2003, Radisic *et al.*, 2006; de Jonge *et al.*, 2009; Proetto *et al.*, 2014; Zaluzec *et al.* 2014, Schilling *et al.* 2015]. Since the first reported the development of a sealed fluid cell and real-time TEM study of Copper precipitation in liquid [Williamson *et al.*, 2003], commercially-available liquid and gaseous cells have accelerated the research activities *in situ* S/TEM studies. Today, these *in-situ* environmental holders are fabricated by juxta positioning a pair of Environmental Chips (E-Chips) having electron-transparent amorphous SiN$_x$ membrane windows supported along their border by a thicker Silicon frame. These “E-Chips”, are carefully sealed along their periphery to contain the desired media within a small volume which then becomes safely
isolated from the vacuum of a conventional electron optical column. When the pathlength in the *in-situ* environment is suitably small, electrons can readily pass through both the SiNx windows as well as the ensuing media which spans a meticulously engineered gap established between the windows and in which the specimen of interest is immersed. Using advanced MEMS fabrication technologies these E-Chips and their associated holders have also been modified to include electrical connections to facilitate heating, electrochemistry, photoactivation as well as modern analytical spectroscopies [Radisic *et al*., 2009, Zaluzec *et al* 2014, Protochips Inc, 2016, Hummingbird Scientific 2016, Dens Solutions 2016]. More recently, an alternative type of liquid cell based on entrapment of a very thin-liquid film between layers of graphene has also been introduced [Yuk *et al*., 2012] and facilitates high resolution imaging, but presently lacks the ability to support flowing/pressurized media.

The majority of liquid/gas cell S/TEM investigations to-date have concentrated upon imaging studies of nanoparticles, nanowires or sputtered thin films due to the difficulty in preparing suitable specimens of ‘bulk’ materials, particularly from heterogenous macroscopic and/or conventional metallic alloys. The former materials and their study are of great interest to major fractions of the industrial and engineering community, and as such there is a growing demand to perform *in situ* TEM examinations in these systems in order to interrogate and understand their real-time behaviour and microstructural evolution. The main barrier to *in situ* environmental cell studies of conventional/bulk metals and alloys has been the difficulty in extracting and placing suitable macroscopic TEM specimen over the fragile silicon nitride window with the necessary sub-micrometer precision while also forming a hermetic environmental seal in the E-Chips. An added challenge is that the overall thickness of material allowed for insertion between the E-Chips must generally be tailored to fit within a 50 nm to 5 µm gap which delimits the typical media space (i.e. engineered gap) between the SiNx windows. This is extremely restrictive and challenging requiring precise, delicate sample placement as well as careful thickness control.

S/TEM specimen preparation using focused ion beam (FIB) technology has become increasingly popular and is widely used due to its versatile capabilities, in particular, the ability that it provides to extract site-specific electron-transparent lamellar shaped specimens having a relatively flat and uniform thickness profiles. Although the *ex situ* lift out of the FIB-prepared S/TEM lamella has been used in numerous S/TEM investigations, including some *in-situ* heating and electrical property studies, the potential for surface modification and Ga+ ion implantation has been raised as a concern [Dalili , *et al*., 2014]. It has also been
noted that Ga ions can be implanted and mixed into the surface layers of the lamellae [Giannuzzi and Stevie, 1999, Giannuzzi et al., 2005], and in addition redeposition during FIB sample preparation can modify the structure and composition of the material surface (Matteson et al., 2002). Low energy argon ion milling post FIB specimen preparation is frequently used to mitigate implantation artifacts for high resolution electron microscopy [Huang 2004], however, doing so for the preparation of specimens for in-situ environmental cell studies has yet to have been successfully reported. Because of these complications as well as the absence of a practical procedural approach, the exclusive use of FIB for the preparation of the very thin lamella required for in-situ environmental studies has seen limited application. In contrast, conventional twin-jet electropolishing of metallic specimens is a well understood and controlled process and, when carried out properly, can mitigate FIB-related surface modification and Ga+ ion implantation issues unfortunately, preparation of thin uniformly thin and small lamella is not the strength of this preparation methodology. Herein, we report on the development of specimen preparation methods which combine both electropolishing and FIB. This methodology incorporates the advantages of the two disparate techniques and has been used to produce site-specific samples with large electron-transparent areas suitable for both gaseous as well as a fully-hydrated environmental studies in E-Cell systems operating at pressures up of one atmosphere [Zhong et al., 2014].

2.0 EXPERIMENTAL EQUIPMENT

Electron transparent specimens for this work were prepared using a combination of conventional electrochemical jet-polishing and FIB extraction techniques, both of which are described in detail in Section 3. In this work a Struers Tenupol 5 twin-jet electropolishing unit and a Jubalo closed cycle refrigeration system were used for the conventional thin-foil electrochemical preparation, while site-specific sample extraction was performed using an FEI Quanta 3D Dual Beam FIB. Equivalent results, should be reproducible with similar equipment from alternate manufacturers. Microstructural and hyperspectral imaging of the resulting electron-transparent specimens were conducted in an FEI Tecnai T20 Analytical Electron Microscope operated at 200kV and equipped with an Oxford Instruments Xmax 80 TLE windowless Si drift detector (SDD) and an AZTEC analyser for conducting hyperspectral imaging using X-ray energy dispersive spectroscopy (XEDS). The in situ holder used in this study was a Protochips Poseidon P210 liquid environmental cell using ambient air as well as deionized H₂O as the environmental media [Zaluzec et al., 2014].
environmental cell windowed E-Chips (300 µm thick Si frame, having ~ 50 nm thick SiNx windows covering rectangular openings of up to 500 µm by 50 µm) were commercially procured from Protochips Inc. Prior to use, these E-Chips were cleaned according to the manufacturer’s recommendations and in addition, a Hitachi ZONE-SEM was used to remove any residual hydrocarbon contamination from the E-Chip surface prior to attaching the electron-transparent specimens of interest. This last step also serves to make the E-Chips SiNx surface hydrophilic. We note that any low power plasma cleaning system can also be employed to remove residual hydrocarbon layers without damaging the SiNx windows.

3.0 SPECIMEN PREPARATION METHODS

The methodology developed in this study consists of 4 basic steps.

1.) Preparation of conventional electropolished TEM thin-foil specimens
2.) Identification and FIB cut-out of regions-of-interest in electropolished specimens
3.) Attachment of the plan view sections to the E-Cell windows
   a. Pt – Attachment “Cut and Attach” Method
   b. Beam-Hardened “Cut and Glue” Method
4.) Sealing and Mounting of the E-Cell in the Holder

Details for each of these procedures will be presented next.

3.1 Electrochemical Twin-Jet Polishing

Cold-rolled Type 304 stainless steel was used as the test material in this work. Slices approximately 0.7 mm in thickness were cut from the Type 304 bulk steel using a Struers Accutom-5 sectioning system. These slices were next mechanically thinned (using SiC grinding papers) to ~100 µm in thickness prior to punching 3 mm diameter disc samples. Conventional TEM specimens were obtained by electropolishing the 304 SS in 20 vol% HClO₄ - 80% CH₃OH at -33°C and 20 V, with automated cut-off upon reaching electron-transparency as detected using the automatic sensor of the polishing unit. Although this experimental procedure is specific to the preparation of the Type 304 SS material used as part of this methodology, corresponding electropolishing procedures for many metallic materials can be substituted [Kestel 1986].
3.2 Identification of Region-of-Interest and “Plan-View” FIB Extraction

After electropolishing to TEM quality, the thin-foil SS specimens were transferred onto a FIB/SEM/STEM imaging compatible sample holder of the FEI Quanta 3D dual beam FIB used in this work. The location of the electron-transparent area-of-interest for in situ TEM analysis could be readily determined using a moderate energy (20-30 kV) STEM imaging in the FIB/SEM. Typical electron beam bright-field (BF) images of such a thin area-of-interest, which can be acquired at the coincident point of the electron and ion beam, are illustrated in Figure 1a and 1b. In the absence of a STEM detector system in a FIB/SEM, secondary electron imaging can also be used for identifying the electron-transparent area [Young, et al. 2010] since these regions will appear significantly brighter than the thick (non-electron-transparent) regions (Figure 2a). This increased signal results from the fact that at 20-30 kV the electron-transparent areas of “thin” TEM specimens have a second source for secondary electrons, namely those emitted from the exit surface of the thin regions, creating an additional source for emission of secondary electrons, relative to the thicker (non-transparent) area.

After the electron-transparent area-of-interest is identified, careful eucentric point alignment of the holder and specimen relative to the electron/ion beam optical axis is carried out. To accomplish this step in the selected dual beam FIB/SEM, the ion beam is blanked and the sample on the STEM specimen holder is first tilted (typically 52 degrees) towards the ion beam column axis. Following tilting, fine tuning of the FIB coincident point of ion beam and electron beam is carried out on a sacrificial area of the specimen. To achieve this, the specimen is translated a few hundred micrometers away from the region of interest (ROI), along a direction parallel to the stage tilt axis, thus retaining the eucentric axis. Next, a small sacrificial area is milled at low current ( ~ 0.4nA/30 kV) in spot mode for several seconds, then the ion beam reblanked. The FIB/SEM stage is next moved in Z direction until that this milled area is re-centered to the electron imaging screen and nominally defines a coincident electron/ion point. This step is iterated as necessary until convergence is achieved. At this juncture, the original region of interest of the specimen is translated (without height adjustment) back to the optic axis and the ROI is ready to be defined and extracted. This procedure by design results in minimal exposure of the ROI to the adverse effects of ion beam as well as any associated sputtering/damage.
Next, the electron-transparent portion of the electropolished TEM disc containing the region-of-interest is delimited (cut out) using site specific Ga ion beam milling (Figure 2b). The specific cutting procedure employed at this juncture is carefully orchestrated as the milling process plays a key role on the overall success rate of the sample preparation. Ultimately, the area-of-interest of the cut out section must extracted and placed carefully on the interior surface of either the electron entrance (top) SiNₓ window for STEM/XEDS studies, or on the electron exit surface (bottom) window for TEM/EELS studies of the respective E-Chips used in the in-situ holder. The selection of mounting on the entrance or exit window is determined by the experimental measurements planned and should be chosen to mitigate the effects of scattering upon the respective imaging and spectroscopy modes employed.

Minimizing Ga deposition/contamination during the extraction step by using reduced current during and FIB operations on the electropolished TEM sample is recommended; however, it is also important to balance the milling time with the current to optimise the speed and minimise damage to the large electron-transparent area. An ion beam voltage of 30 kV was used throughout this work, with ion beam milling currents typically being 3-5 nA. In addition, to prevent Ga contamination of the pristine electron-transparent, electropolished area, the perimeter of the cut-out edge is intentionally located as far away as is practical from the critical region-of-interest. This criteria together with the dimensions of the SiNx window whose dimensions depend upon the application and manufacturer (ranging from 20-50 µm wide to 200-500 µm long) becomes one of the key controlling factors in an operator’s decision of the cut-out a real dimensions. Generally, it is recommended that one targets to cut out a section having at least one supporting dimension twice as wide as the minimum dimension of the SiNx window. Thus, for a 50 µm wide SiNx slot window, a typically section is nominally ~ 100 µm wide while the perpendicular dimension should be of similar dimension but consistent with the ability of the FIB to mill the specimen within an appropriate time frame. At the center of the cut out should be the region-of-interest to the greatest extent possible. Oversizing the cut out and creating a moderately large and thick electron opaque zone surrounding the thin region of interest is appropriate as it leaves sufficient material on the perimeter for handling and attachment to the Si frame of the E-Chip, as will be illustrated shortly. A larger cut out also provides ready access to 3 corners which are unobstructed and well removed from the ROI, while a 4th corner becomes available for micromanipulator attachment. An example of the results of FIB milling defining a cut out area and illustrating this idea is shown in figure 2b. Visible in figure 2b are the
uncut corners used to support the electron-transparent region, while the dimensions of the area (~150 µm x ~ 75 µm) provide adequate mechanical robustness and stability for micromanipulator attachment and eventual fastening to the E-Chips Si frame. FIB Liftout and attachment to the E-Chip is the next step in the workflow and two different procedures are summarized next.

3.3a FIB Liftout: Pt Deposition/Attachment: “Cut and Attach” Method

FIB Liftout is accomplished using organo-metallic Pt (om-Pt) deposition/attachment of a micromanipulator to the region of interest and is identical in all important metrics to the procedure used in traditional cross-section FIB lift-out specimen preparation [Mayer et al., 2007] with the small exception of the orientation of the section to be retrieved which is dictated by the attachment process and location on the E-Chip. At this phase of the process, a micromanipulator is inserted to the FIB/SEM chamber and is carefully manoeuvred to the one corner/edge of the electron-transparent area, which is still connected to the electropolished TEM disc specimen at corner points around the perimeter (Figure 2b). Skilled FIB operators should be able to approach the sample using only electron imaging without using ion beam imaging, if the previously outlined procedure of local coincident point alignment has been carried out carefully, the major difficulty being associated with the orientation of the cut out relative to the manipulator motion. During this step, adjustment of the electron beam current and contrast/brightness can help enhance the shadow of the probe which can be used to assist the approaching to the sample. Once the tip is successfully touching a corner of the section, om-Pt deposition is used to affix the corner of cut-out area to the tip of the micromanipulator (figure 2c). To accomplish this, we have successfully employed both a 0.05-0.3 nA Ga ion beam at 30 kV or 3 nA-5 nA electron beam at 5 kV to perform the om-Pt deposition. Utilizing the smallest beam diameter with a minimum beam tail is a note worthy consideration at this step. If a large beam tail (or beam skirt) is present then some (residual) measure of nonlocalized om-Pt deposition can occur outside of the desired deposition location (see for example figure 2e). This residual om-Pt (which also contains significant hydrocarbon) can become a source of both Pt and C contamination at a later stage of any in-situ experiments and thus it’s minimization is not without merit. In addition, we note that the om-Pt vapour which is literally sprayed out of the GIS (gas injection system) needle during the deposition step will by its very nature also become dispersed over a relatively large area (hundreds of square micrometres) in the vicinity of
the needle shaped gas jet. The presence of this flowing gaseous \textit{om}-Pt vapour over the specimen can not be avoided, and it is not without concern this vapour can traverse large distances and possibly be absorbed in the immediate surface of the previously pristine electropolished specimen. To minimizing the adherence of surface absorbed \textit{om}-Pt on the specimen, electron beam imaging of the region of interest immediately post \textit{om}-Pt deposition following deposition should be avoided to the greatest extent possible. The experienced FIB/SEM operator will be the best judge of the most effective procedure for such minimization in their respective instrument, however, in the absence of a specific cleaning protocol, waiting for fully vacuum recovery after the \textit{om}-Pt vapour source is isolated is a reasonable procedure prior to renewed electron imaging and is the technique used herein. Once the micromanipulator is attached to the ROI section, the remaining three supporting tabs at the corners of the thick opaque areas can be readily FIB cut free from the electropolished foil as is illustrated in (figure 2c). Normal sample extraction and micromanipulator relocation is ready to be conducted (figure 2d, 2e).

3.3b FIB Liftout: \textit{Adhesive - Attachment: “Cut and Adhere” Method(s)}

As an alternative to the \textit{om}-Pt attachment step outlined above, we have also successfully made use of the adhesion force of an epoxy-coated micromanipulator (OmniProbe, Oxford Instrument) to remove the delineated region of interest. This adhesive procedure was developed to mitigate potential issues associated with the deposition of \textit{om}-Pt-rich compound in the vicinity of the specimen as discussed in section 3.3a. In this approach, a thin epoxy coating is intentionally applied to the micromanipulator’s extraction tip in order to increase the adhesion force of the tip by slightly coating the tip. Prior to the coating, the surface of the micromanipulator tip is first irradiated with the ion beam at $\sim 30$ kV/15 nA for 2 min to clean (remove surface oxide) and also to slightly “roughen” its surface. We have found that a suitable coating can be made using commercial superglue (Loctite, Henkel UK), and can be applied by simply dip-coating the micromanipulator. This coating is applied externally from the FIB/SEM vacuum chamber and is typically allowed to dry for $\sim$2 hours after which the coated needle is simply reinserted into the micromanipulator system. Using the coated, and now mildly insulating micromanipulator tip specimens can be “picked up” from an area and relocated onto the E-Chip window without employing \textit{om}-Pt deposition/attachment. It is not clear if this adherence of the tip to the extracted foil is related to the presence of electrostatic and van der Waals forces or if it is due to the fact that the epoxy is still mildly
“sticky”, the mechanism by which this occurs is not important at this point in time. After liftout and transferral to the SiNx window, the specimen must still, however, be anchored to the Si frame by means of $\text{om-Pt}$ deposition to avoid sample movement/drift during \textit{in situ} TEM observation in any media. The principle of minimalist $\text{om-Pt}$ deposition as described earlier should be applied again here. Fundamentally the use of minimal electron beam or low ion beam current $\text{om-Pt}$ deposition should be used throughout the procedure in order to decrease the potential for $\text{om-Pt}$ contamination.

An alternative approach to coating the micromanipulator tip with “superglue” external to the FIB/SEM is to use an electron-beam hard enable glue as the micromanipulator’s adhesive which can be utilitized within the FIB/SEM instrument. Similar in principle to the preceding method the purpose is also to minimize the use of organometallic $\text{Pt}$ for attachment of the cut out ROI to the SiNx window. As previously, the specimen area of interest is identified using the FIB/SEM (Figure 3a). Next, the micromanipulator tip is touched onto a vacuum compatible glue which is co-located within the specimen chamber (SEM glue from Kleindiek Nanotechnik). The advantage hers is that the process can be readily observed in real time under a low current (<0.1 nA) electron beam (Figure 3b). The micromanipulator tip which is now lightly endowed with a thin layer of “glue” is next manoeuvred to the partially cut-out ROI, and the glue-rich tip is allowed to touch an isolated corner of the ROI section. It is then affixed by electron-beam-hardening under a higher current (0.5 - 1 nA) probe. The cut-out sample, which is now attached to the micromanipulator needle by the hardened glue, can next be cut-free by FIB milling and subsequently lifted out (Figure 3c). To affix the lift-out section to the SiNx window, a corner of the cut-free sample edge can also be manipulated so as to gently brush into the SEM Glue while still within the FIB chamber (Figure 3d). As previously described, the sample can be next relocated to the E-Chip window using the micromanipulator and finally held in place by contacting the glue-rich corner to the bulk silicon support area of E-Chip (figure 3e) and beam hardened. All of which must be done while judiciously avoiding the fragile SiNx window. The advantage of this hardened glue method is the minimization of $\text{om-Pt}$ usage during the entire specimen preparation process. The disadvantage of using hardend glues is the great care needed to touch the extracted ROI to the SEM glue without damaging/bending the very fragile cut-out.

### 3.4 Mounting the FIB Liftout to a SiNx E-Chip
To accommodate the preceding steps of relocating the cutout to the E-Chip window, which we have described in section 3.3, it was necessary to fabricate a custom E-Chip holder. This is readily accomplished by modifying a standard pin-type SEM stub and enables holding and the subsequent mounting of the electropolished section onto the SiNx window E-Chip. Figure 4 shows the photograph of our modified SEM stub (termed the E-Chip holder) used for attaching the electron-transparent specimen to the E-Chip. Prior to transfer of the cut out sections of the electropolished thin films, the appropriately selected E-Chip is slid into the customized/grooved holder. When mounting this holder into the dual beam FIB its pairs of parallel to grooves into which the E-Chips are located are intentionally oriented parallel to the FIB/SEM tilt axis so that the chip will be mechanically stable during any tilting operations. This can be avoided if the E-Chips are affixed to the stub by an appropriate procedure (glue, tape, clamps, etc…) however it was found that simple care in handling is more than sufficient. For the Poseidon system used in this work, two different sizes Silicon frames are employed in the in-situ holder design, a large upper chip (green in figure 4) and a smaller lower chip (yellow in figure 4); the sets of grooves in this E-Chip holder are of dimensions needed to accommodate both sizes of E-Chip. Upon close inspection of figure 4, the reader will be able to discern the long SiNx slot window (grey) on the chips, and in particular should notice the orientation of this slot with respect to the holder tilt axis and the slot (red arrow).

The extracted region-of-interest, which has been attached to the manipulator tip by either om-Pt deposition or adhesion is then transferred on to the selected (top or bottom) E-Chip that is loaded onto the aforementioned E-Chip holder. Here, the selected E-Chip of the in-situ cell pair is first slid into the grooved E-Chip holder, with the groove aligned parallel to the tilting axis of the dual beam FIB stage as indicated in Figure 4. Next, the cut-out region-of-interest, which is attached to the manipulator tip, is carefully relocated/positioned over the appropriate SiNx window, and is aligned carefully over the nominal 50 µm wide slotted window. Recalling that this cut out has an intentionally larger width (~ 100 µm) , its terminal edges extend beyong the complete SiNx window onto the Si support frame (figure 2d). During the final om-Pt attachment processes of the cut out to the Si frame the large overhang minimizes any possible contamination near the ROI and also avoids inadvertent milling and damaging the extremely thin and fragile SiNx window. Once in position, a small rectangular area (~ 3 um by 5 um) of low ion beam om-Pt deposition or adhesion is used to attach the corners of the ‘cut-out’ to the Si support base (om-Pt illustrated in figure 2e and adhesion in figure 3e).
Finally, after the specimen is secured the micromanipulator needle tip is cut free from the sample using the FIB

4.0 E-Cell assembly and Demonstration.

To demonstrate the efficacy of this methodology namely to mount and observe electropolished TEM specimens in both a gaseous as well as a flowing liquid, we have selected an alloy of interest, Type 304 austenitic stainless steel, which is generally resistant to corrosion but will oxidise in appropriate H$_2$O environments [Ziemniak et al., 2002], and for which a detailed in situ study will be reported in a follow-up publication. After a conventional TEM specimen was first prepared by twin-jet electropolishing (section 3.1), and the electron-transparent region was “cut out” using the FIB (section 3.2), the extracted sample was carefully attached to the bottom E-Chip surface (section 3.3). As discussed earlier, since TEM was the primary imaging modality of this exemplar, attachment to the bottom E-Chip was selected. In the in-situ holder system used in this study an integrated pre-fabricated spacer on the lower chip introduced a 500 nm gap between the windows (Figure 5). The selected 500 nm gap is sufficient to hold both the cut-out region-of-interest as well as either ambient air or liquid H$_2$O without rupturing the window of the E-Cell under one atmosphere of pressure. Although narrower E-Cell gaps are both available and advantageous from the viewpoint of imaging and spectroscopy, they also create more difficult preparation conditions, as the total thickness of the extracted electron-transparent specimen plus any “attachment” material (i.e. om-Pt or glue) must not be so thick as to inadvertently rupture either of the SiNx window during assembly. We also note that because the thin-foil section is attached to the Si support, a small space between the specimen and the lower SiNx window nearly always exists for these methods, thereby allowing either gas or liquid to flow across both sides of the electropolished specimen, this is particularly important to insure full gas/liquid/solid reactions occur uniformly. Positioning of the specimen along the length of the slotted window is done at the operator’s discretion, depending upon the experiment being conducted and the amount of tilting required for possible spectroscopy, it can be appropriate to offset the section from being centered on the long slot to mitigate detector shadowing effects.

5.0 Exemplar TEM and AEM Observation
Having successfully described a systematic set of procedures for sectioning, transporting, assembling and sealing an electropolished TEM specimen into a in-situ E-Cell, in this last section we end by demonstrating the methodology as part of the initial stages of a study of localized dissolution in Type 304SS in both air and in pure H$_2$O. In figures 6a and 6b, we first present a series of images of the single tilt in-situ holder loaded with a cut-out specimen in a SiNx E-Cell as examined in the TEM with 1 atmosphere of air surrounding the specimen. The atmospheric pressure surrounding the specimen was simply achieved by opening the tubing normally dedicated to transporting liquid to ambient air and allowing equilibration to occur. This was done to not only verify the integrity of the cell to hold pressure, but also to facilitate preliminary TEM observations with minimum multiple scattering from the media surrounding the specimen. Conventional diffraction contrast experiments can be performed in this mode although they are restricted in nature for two reasons: 1.) the in-situ E-Chip holder itself is a single tilt device, and 2.) measurements are limited due to the multiple scattering in the SiNx windows as well as the presence of ~ 500 nm of 1 atm of air both of which affect the image quality. Figure 6c illustrates the effects of the introduction of H$_2$O carefully into the cell, which gradually displaces the air present. The presence of liquid can be recognized by comparing figures 6b (air) versus 6c (H$_2$O). The reduced contrast and blurring is a direct result of multiple scattering of the electron beam in the liquid media both above and below the thin TEM section. It should be also immediately apparent that the liquid media also virtually obscures any electron diffraction measurements during in situ liquid studies. This could, of course, be partially compensated for by either increasing the electron beam energy and/or decreasing the SiNx window and media thickness. After initial confirmation of the integrity of the E-Cell, the specimen was allowed to remain in flowing H$_2$O (with the electron beam blanked) for ~27 hours at room temperature, this was done to assess any liquid corrosion/oxidation without the complicating influence of electron beam effects. Figure 6d, shows the microstructural changes that ensued after the extended exposure to liquid H$_2$O: specifically, one observes the formation of discrete “blocky” structures, which, in this example, appeared as rectilinear precipitates on the sample after prolonged exposure in H$_2$O, as well as bending/distortions of the thin metal film. Since the specimen was mounted on the lower window in anticipation of TEM imaging experiments, this configuration is not optimum for STEM/XEDS, and unfortunately once the specimen configuration is completed it can not be disassembled and reconfigured on the upper window which is best for X-ray spectroscopy. Nevertheless, although less than optimum, in-situ XEDS measurements in the liquid cell can be conducted, providing a
qualitative identification of these coarse discrete microstructural features [Schilling et al., 2014] as Fe-Ni-enriched Cr-poor oxides. We further note that elemental imaging using electron energy loss spectroscopy was not feasible during this liquid H$_2$O experiment as the relative mean free path $t/\lambda$ ($t \gg 500$ nm) was significantly greater than 4. The presence of liquid was additionally verified by the observation of small items of occasional floating debris, but more readily by measuring magnitude of the SiK$\alpha$/OK$\alpha$ x-ray line ratio whose magnitude varies as the media changes from vacuum, to air, to H$_2$O [Zaluzec et al 2014]. Hyperspectral images (Figure 7), created by simply integrating the full-width at half maximum of the O, Fe, Ni, and Cr K$\alpha$ XEDS peaks confirm that the rectilinear precipitates were enriched in O, Fe, and Ni and depleted in Cr. The nature of the precise oxide formed could not be established using electron diffraction due to the amount of liquid H$_2$O present, which as stated earlier precludes all diffraction studies. As can be observed in the sum-spectrum of Figure 7, a small amount of Pt was detectable in our XEDS data which we attribute to the om-Pt used to attach the specimen onto the Si/SiNx window and is not surprising. Importantly, no Ga was detected in the spectral analyses (Figure 7), which is also consistent with an optimised FIB milling procedure. Although no Ga signal was detected in XEDS spectrum, we cannot assume it is completely absent, just that it is less than the detection limit of the XEDS technique in this experimental configuration. Giannuzzi et al has found that after FIB processing small amounts Ga can be present at millimeters away using TOF SIMS technique [Giannuzzi et al 2005] thus it would not be surprising if small amounts were be present but not detected.

5.0 Summary and Conclusion

In summary, a novel set of hybrid electrochemical-FIB sample preparation procedures for the production of S/TEM samples from bulk metals/alloys has been developed to facilitate environmental S/TEM studies. These methodologies have been successfully applied to in situ environmental S/TEM observations of extracted electropolished specimens immersed both ambient air and in H$_2$O, and can be used to prepare a wide range of samples for other unique in situ environmental S/TEM and in-situ hyperspectral imaging experiments. The procedures outlined herein provide the community with a reproducible method of preparing bulk metallic samples and offers significant promise for the broader application of in situ liquid/gaseous cell S/TEM studies.
Acknowledgements

Dr. A. Janssen and Dr. M. A. Kulzick are acknowledged for their insightful comments. S. Schilling acknowledges the Engineering and Physical Sciences Research Council (EPSRC) UK PROMINENT programme for support. In addition, this work was supported in part by research grants including: Grants # EP/G035954/1 and EP/J021172/1 and Defense Threat Reduction Agency grant HDTRA1-12-1-0013, the BP 2013 DRL Innovation Fund, as well as the Electron Microscopy Center in the Center for Nanoscale Materials, a U.S. Department of Energy Office of Science User Facility under Contract No. DE-AC02-06CH11357.

Reference


Figure 1: Electron beam 30 keV STEM bright-field (BF) image shows the thin area of interest: (a) BF image, (b) higher magnification BF STEM image showing preservation of thin electron transparent area at 30 keV

Figure 2: Electron beam images of ‘Cut-and-Attach’ approach: (a) STEM DF image showing the electron-transparent region, (b) FIB slots cut around the periphery of the region-of-interest, with corner attachments still in place, (c) micromanipulator attached to the area of interest and freed by milling off supporting material, (d) sample positioned above the SiNx window, (e) micromanipulator cut-free by milling away the surrounding material after corner attachment to the E-chip by om-Pt deposition
Figure 3: ‘Cut-and-Glue’ Method: (a) electron beam SE image of the electron-transparent area in the electropolished TEM foil, (b) manipulator positioned to pick up the glue deposit, (c) electron beam-hardened glue attached the sample to the manipulator tip and sample was cut free from the electropolished disc, (d) cut-free sample edge brushed/touched into the glue deposit to pick up a small amount, and (e) released sample affixed using glue onto the SiNx window. Note the two vertical structures visible either side of the glued cut out are electrical feed thru’s for use as part of electrochemical cell experiments.

Figure 4. Photograph of the modified E-Chip holder used for attaching the electron-transparent specimen to the E-Chip. The selected E-Chip is slid into the appropriate sized groove on the holder. The dual beam FIB tilting axis is aligned to be parallel to grooves of the holder. For the Poseidon system used the E-Chip sizes are different for the upper (4.5x6 mm) and lower (2x2 mm) chips.
Figure 5. Schematic drawing of the P-210 liquid cell (Protochips) in which the sample is placed in-between the top and bottom chips that are separated by an engineered spacer creating a nominal 500 nm gap, and isolated from the TEM vacuum environments by means of a pair of small and large O-rings.

Figure 6. (a) Low magnification bright field TEM image of hybrid sample and liquid cell window, (b) TEM image in 1 atmosphere air, (c) TEM image of steel sample immersed in H$_2$O, (d) microstructural changes to 6c occurring after 27 hours of exposure to room temperature H$_2$O.
Figure 7: Hyperspectral images obtained from the Type 304 stainless steel specimen in H₂O showing the presence of FeNi rich phases, (Schilling et al 2014, [17]). Colorized inserts are hyperspectral elemental images from Fe (Blue), Cr (Green), Ni (Yellow), and O (Red) K β Ni(Yellow), ether with a sum spectra calculated from all pixels.
Chapter 6: Second Proposed Manuscript

6.1 Introduction:

The second manuscript described in situ TEM technique development and applications to austenitic stainless steel. As with the previous manuscript, the experiment was designed by M. Grace Burke, as the principal investigator. Experiments were performed by Sibylle Schilling and Arne Janssen. The manuscript was written by Sibylle Schilling, with technical and editorial supervision and proofing by M. Grace Burke and Nestor J. Zaluzec.

6.2 Manuscript:

Practical Aspects of Electrochemical Corrosion Measurements during in situ Analytical TEM of Austenitic Stainless Steel in Aqueous Media

S. Schilling¹, A. Janssen¹, N. J. Zaluzec¹,² and M.G. Burke¹

¹Materials Performance Centre and Electron Microscopy Centre, School of Materials, University of Manchester, Manchester, M13 9PL, U.K.

²Electron Microscopy Centre, Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL 60439 USA

ABSTRACT

The capability to perform liquid in situ TEM experiments provides an unprecedented opportunity to examine the real-time processes of physical and chemical/electrochemical reactions during the interaction between metal surface and environment. This study describes the requisite steps in order to make the technique fully analytical, from the modification of the hybrid sample preparation, through electrodes investigation in different electrolytes, to electrochemical in situ experiments compared to conventional bulk cell and microcell configurations.
Keywords: In situ TEM, TEM electrochemical cell, Sample preparation, Bulk sample, FIB, Electro-polishing

1.0 INTRODUCTION

Conventional “bulk” metallic materials still dominate industrial applications, and common methods to study localized corrosion involve experiments with measurement areas in the cm\(^2\) to mm\(^2\) range. However, in today’s technologically demanding research it is frequently necessary to study the corrosion processes at high spatial resolution (i.e. μm to nm range) in order to understand the mechanisms and interactions between specific microstructural features in or at the metal surface and its local environment. At the same time, it is important not to dismiss the effects of bulk material entities such as grain boundaries, inclusions, fine-scale precipitates and/or defects. Several studies have been conducted to assess the electrochemical behaviour of small regions (μm\(^2\) or nm\(^2\)) in bulk samples. For example, Lohrengel, Böhani and Martin all investigated materials via micro- or nano capillary-cells with an exposed area of several μm\(^2\) or nm\(^2\) (Lohrengel, 2004); (Böhani et al, 2000); (Martin et al, 2008). This facilitated the study of localised corrosion, e.g. of single grains in welds, or single micron-sized particles in metal. Vogel combined a microcell and optical/laser microscope to investigate local reactions on the micrometre scale (Vogel and Schultze, 1999). A considerable disadvantage in those studies is the fact that these measurements could not directly record the response or reaction on the surface as a function of time, such as the time–resolved response of a pit initiation or dissolved inclusion; as the detailed examination of the exposed areas were always performed after the electrochemical measurements.

There is now an increasing desire to perform in situ studies on materials in order to understand the near real-time behaviour of the surface interaction in a range of environments. In situ analytical transmission electron microscopy (TEM) in liquids has become an increasingly important and a dynamic research area allowing the experimentalist achieve this in materials science investigations. This re-emergence has become possible due to the advent of a new range of specialized in situ specimen TEM holders which include: liquid, electrochemical, heating, gaseous and tomography holders (Li et al, 2013); (Hummingbird, 2016); (Protochips, 2016); (DENS, 2016). In addition, the recent ability to not only simply image but also to conduct hyperspectral elemental imaging in liquids is particularly important.
for studying the localised interaction of the environment with specific microstructural features in metals and their alloys (Schilling et al, 2015).

1.1 In Situ Aqueous Studies – Background

To understand the electrochemical reaction of metal from both a thermodynamic and kinetic perspective, it is essential to perform detailed examination of the interaction between a reaction surface and its surrounding liquid media. At the same time, it is also crucial to understand the investigation/characterization technique employed as well as any associated factors which can affect the system during in-situ studies, specifically: the chemical and physical reactions, e.g. surface condition, specimen area, temperature, flow rate, and pH during any in situ experiments together with any detrimental electron beam-induced effects, which may be realized in the aerated aqueous media. To explain this comprehensively is beyond the scope of this work; however, to understand the systematic protocols we have established for in situ electrochemical experiments, we will briefly review a compendium of factors which should be understood and controlled to the greatest extent possible in order to achieve reproducible electrochemical studies of corrosion in this new operating mode during in situ TEM.

1.2 In Situ Aqueous Studies – Corrosion Basics

Aqueous corrosion is an electrochemical process whereby electrons produced via anodic oxidation of a metal are consumed by an oxidant in the environment such as dissolved oxygen, protons or H2O. During dissolution/corrosion, metal atoms leave the bulk material as ions. This process is an anodic oxidation reaction; for the general case of a metal M undergoing oxidation is given by equation 1 and a specific example of iron illustrated by equation 2.

\[
\text{M(s)} \rightarrow \text{M}^{n+} + n\text{e}^- \quad (1)
\]
\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^- \quad (2)
\]

The parallel cathodic reaction, in which electrons are released during metal oxidation event and are then consumed is known as a reduction reaction and occurs at the surface of the cathode. Reduction processes can occur in many media and involve numerous species and these processes in aqueous solutions are illustrated by equations 3-6. In neutral aerated
solutions the reduction of dissolved oxygen (equation 5) is the main cathodic process, while in acidic solutions proton reduction predominates (equation 4). The corrosion of iron in neutral H₂O containing oxygen can be described by a combination of equation (2) and equation (5) which can be combined and yield equation (7)

\[
\begin{align*}
2e^- + 2H_2O & \rightarrow H_2 + 2OH^- \\
2e^- + 2H_3O^+ & \rightarrow H_2 + 2H_2O \\
2e^- + \frac{1}{2} O_2 + H_2O & \rightarrow 2OH^- \\
2e^- + \frac{1}{2} O_2 + 2H_3O^+ & \rightarrow 3H_2O
\end{align*}
\]

The products produced during the dissolution of metals are many and complex. For example, in the case of Fe, further oxidation of iron (II) species to form a variety of secondary corrosion products, such as iron (III) oxide, iron (III) hydroxides or iron (III)-oxide-hydroxide may occur. These reactions are described by reactions 8 through 10:

\[
\begin{align*}
2Fe + O_2 + 2H_2O & \rightarrow 2 Fe(OH)_2 \\
2Fe(OH)_2 + \frac{1}{2} O_2 + H_2O & \rightarrow 2 Fe(OH)_3 \\
Fe(OH)_3 & \rightarrow FeO(OH) + H_2O \\
2FeO(OH) + O_2 & \rightarrow Fe_2O_3 + H_2O
\end{align*}
\]

To maintain electro-neutrality, anodic dissolution must be balanced by the reduction process and the current produced via both oxidation and reduction reactions must be equal. Corrosion is only thermodynamically feasible when the change in free energy \(\Delta G < 0\), i.e. when the thermodynamic reversible potential of the cathodic process is greater than that of the anodic process.

By its nature, corrosion is an interfacial reaction of metal surfaces and liquid electrolyte and this region has been generally modelled as having three interaction layers. The first layer, is electrolyte in contact with the metal surface and is termed the inner Helmholtz plane where the charged metal surface adsorbs dipole H₂O molecules due to chemical interaction and behaves differently than the bulk electrolyte. The second layer is composed of ions attracted to the surface charge via the Coulomb force, electrically screening the first layer; and is called the outer Helmholtz plane. This second layer is loosely associated with the covered metal surface. These inner and outer Helmholtz layers are also called the “electrical double
layer” and behave like a plain charged capacitor, and the potentials developed there in are used in part to characterize the electrochemical processes. Finally, a third or diffusion layer is made of free ions that move in the remaining electrolyte under the influence of electric attraction and thermal motion rather than being firmly anchored. This model describes the reaction of the metal surface in H₂O and importantly the electrical potential here can be influenced by numerous factors especially the presence of any excess electrons which might accelerate the interfacial reaction (Bagotsky, 2006); (Hamann et al., 2007); (Perez, 2004), Wendler-Kalsch et al, 1998). Measuring these potentials and their changes is important in establishing reproducible and interpretable measurements and is key to electrochemical studies.

During all EM-based in situ studies, there is nearly always uncertainty as to the process that drives the reaction at the electrolyte/specimen interface. For in situ electrochemical measurements a potentiostat is used to supply and measure the potential difference of the reaction on metal/environment; under potentiostatic control, it is also possible to measure the resulting electrochemical current generated in the system. Importantly, during a TEM experiment, the incident electron beam will also introduce current at this local interface and in addition may also create damage to the specimen and the media. Egerton has reviewed the different factors of the elastic and inelastic scattering effects of the electron beam in a dry system; these include electrostatic charging, radiolysis, atomic displacement, sputtering, specimen heating, structural damage, mass loss, hydrocarbon contamination and energy threshold effects (Egerton et al, 1993);(Egerton, 2014). Recent studies have also identified alternative factors which may also affect the liquid during in situ aqueous experiments, these studies have primarily concentrated on the electron beam /liquid interaction such as the reported generation of H₂ bubbles (Grogan et al, 2013). In other studies investigators were primarily concerned with nanoparticles, nanowires or sputtered thin films located between two SiNx windows resulting in the creation of partially or fully-filled chamber of aqueous solution (Woehl et al, 2012); (Woehl et al, 2013); (de Jonge et al, 2010); (Chee et al, 2015); (Schilling et al, 2015). In these cases, the volume ratio of nanoparticles and electrolyte is small compared to a conventional bulk electrochemical experimental cell, which is comprised of a larger metal specimen and surrounding electrolyte. Thus, comparison of in situ studies with the corrosion of metal surfaces are fraught with scaling issues. In addition, for the specific case of aqueous corrosion studies, the electron beam that is used as the imaging probe has, in addition, two principle detrimental effects: firstly, it may charge the sample
through direct electron transfer, which could lead to a change in the temperature of the solution and/or sample (Cazaux, 1995); (Zheng et al, 2009); secondly, the beam may stimulate radiolysis in the electrolyte subtly changing its chemistry. These can change the pH and together with temperature can accelerate the electrochemical reaction at the Helmholtz double layer in the system (Schneider et al, 2014).

1.3 In Situ Aqueous Studies – Previous work

Given the importance of electron beam-induced phenomena, we first turn to that area which has had a long history of investigation. Radiolysis of H₂O has been extensively studied over the years, for example, both Garett and Pimblott have analysed the hydrolysis of H₂O by electrons introduced from various sources (Garret et al, 2005); (Pimblott et al 1992, 1998). These authors studied low and high energy electrons demonstrating electron driven reactions and the resulting decomposition of H₂O. Garrett showed that more than one water molecule is ionized by electrons having energies between 30 and 100 eV, so high concentrations of ionized species can be formed in local areas. Pimblott discussed four reactive species that are produced during radiolysis of H₂O including hydrated electrons, hydrated protons, hydrogen atoms and hydroxyl radicals. Pimblott suggested that under irradiation with high energy (>100 keV) electrons, H₃O⁺ and H₂O₂ will form in aerated H₂O. In addition, that work used a Monte Carlo track-structure simulation to determine the chemistry of the spatially inhomogeneous distribution of diffusing and reacting particles. There it was shown that by decreasing electron energy from 100 keV to 1 keV, there is an increase in rate and amount of reaction leading to increased production of H₂ and H₂O₂. However, with energies greater than 100 keV, a decrease in reaction rate is expected, along with a decrease in production of free radicals due to the fast-electron effect.

In contrast, Schneider described an irradiation simulation model of various solutions (aerated and deaerated H₂O) with high and low electron dose rates (Schneider et al, 2014). They reported that bubbles were not generated from aerated distilled H₂O at lower dose rate (1.4 x 10⁹ Gy/s) over a 50 minute period when exposed to an 30 kV electron beam but others which formed quickly in a 300 kV instrument. Evidence was presented that high electron dose rates in an aerated solution, which is predominantly used in liquid in situ experiments, can change the steady-state concentration of the radiolysis products and was dependant on the initial pH.
of the solution. It was further speculated that oxygen molecules in solution reduce the eH\(^-\) (hydrated electron) concentration at low dose rates.

In a related study of nanoparticles in aqueous solution, Grogan examined gold nanorods having a trace amount of the surfactant cetrimonium bromide in an in situ TEM experiment using an accelerating voltage of 300 kV with a beam current of 1-10 nA and a beam radius of approximately 2 \(\mu\)m (Grogan et al., 2013). They observed the formation of nano-bubbles with radii between 20 nm and 200 nm after \(~13\) s. The authors assumed that H\(_2\)O vapour did not form; rather, they stated that the H\(_2\)O molecules disassociated into their constituent elements by breaking of the atomic bonds. They assumed that the nano-bubbles contained O\(_2\) and H\(_2\). The proportion of these bubbles did not exceed the saturation point required to form large bubbles, implying a reversible reaction being present to prevent the build-up of gases in the solution.

The first reported experiments using an in situ electrochemical cell were the investigations of battery materials using cyclic voltammetry performed by both Holtz and Zheng (Holtz et al., 2014); (Holtz et al., 2015); (Zeng et al., 2014). Chee deposited an Al thin layer with gold on an electrochemical SiN\(_x\) window to measure the galvanic corrosion in a 0.01 mol NaCl electrolyte (Chee et al., 2015). Their study demonstrated that it was possible to measure the electrochemical behaviour of the interface between sputtered Al and the electrolyte for pit initiation and galvanic corrosion. They also concluded that radiolysis of electrolyte influenced their electrochemical measurement.

### 2.0 Experimental Protocols and Validation

While the preceding work has been illuminating, the ability to explore localized reactions in electron-transparent steel samples or other alloys under potentiostatic control as well as the ability to study potentiostatic polarization behaviour in situ has not been conducted. The reasons are multi-faceted, and the remainder of this work describes the details and requisite modifications of an electrochemical in situ cell, and the specimen geometry to facilitate controlled conditions as well as describes the results of an investigation of a conventional austenitic stainless steel-liquid system under the influence of the electron beam in an analytical transmission electron microscope. Three main aspects are described next:

1) the electrode design and behaviour in different electrolytes under the incident electron beam;
2) the experimental procedure for sample preparation and optimisation;
3) the experimental results of an in situ electrochemical measurement and its comparison to conventional bulk and microcell data

2.1 Conventional Experimental Equipment

The in situ TEM experiments outlined herein were performed using an FEI Tecnai (FEI Company, Hillsboro, USA) G2 T20 analytical electron microscope operated at 200 kV having a LaB6 cathode and equipped with an Oxford Instruments X-MaxN, 80TLE Silicon Drift Detector (SDD) and AZTEC system (Oxford Instruments plc, Abingdon, UK) for spectrum imaging and analysis. XEDS hyperspectral imaging data were acquired at Process Time 5, with a dwell time of 0.1 sec/pixel, and background subtracted using Oxford Instruments “TruMap” software.

The in situ liquid cell holder used in this work was a Poseidon P510 electrochemical cell (Protochips Inc., Morrisville, USA). Distilled H₂O and 0.001 M H₂SO₄ solution (pH=3) were used as electrolytes. This holder employs a liquid environmental cell (eCell) fabricated by juxtapositioning a pair of environmental chips (E-chips) having electron-transparent amorphous SiNₓ membrane windows supported along their border by a thicker Silicon frame. These “E-chips”, are carefully sealed along their periphery to contain the desired environmental media within a small volume, which then becomes safely isolated from the vacuum of a conventional electron optical column; a meticulously engineered gap is established between the windows by spacers into which the specimen of interest is immersed. In this work 5 μm (20 nl) and 500 nm (2 nl) gaps were used. The field-of-view of the SiNₓ (Silicon Nitride) windows was ~ 150 μm x 50 μm x 50 nm during electrochemical cell studies. Prior to use, all E-chips were cleaned for 2 min in Acetone (C₃H₆O), Isopropyl Alcohol (CH₃OH), H₂O₂ and finally rinsed in distilled H₂O. In addition, a Hitachi ZONE-SEM (Hitachi High Technologies America, Schaumburg, USA) with UV irradiation was used to reactivate the E-chip surface to improve hydrophilic properties of the E-chips.

2.2 Electrochemical Configuration of Electrodes for OCP Measurements

The electrochemical chips used in this work are modifications to Poseidon liquid cell chips and are refashioned from simple liquid cell SiNₓ cells by the addition of reference (RE),
counter (CE) and working (WE) electrodes having appropriate connections to a Gamry 600 series potentiostat (Gamry Instruments, Warminster USA) for current/voltage measurements. Two general configurations of electrochemical chips were available from the manufacturer: Type I in which all three electrodes, reference, counter and working electrode, are made of Platinum (Pt) and parallel to each other and extend over the SiNx window (Figure 1a); and Type II in which the working electrode is made of glassy carbon and the reference and counter electrode are made of Pt with the RE and CE surrounding the WE/SiNx window (see Figure 1b). Only the portions of the WE electrodes between 40 μm and 200 μm of the window are exposed to the environment; an SU8 photo-resist film covers most of the electrodes on the chip to isolate them from the environment.

Although the manufacturer’s standard electrochemical chip designs (Types I & II) are reasonably suited for studies of battery materials and nanoparticles, these configurations are not amenable to quantitative electrochemical studies of conventional alloy samples (i.e., our hybrid TEM specimens). Therefore, several design modifications were implemented to the electrochemical E-Chips. These modifications included:

1) change to the geometry of electrodes;
2) change of the size of the working electrode;
3) elimination of the glassy carbon electrode;
4) modification of the working electrode location; and
5) 90° rotation of the SiNx window,

All of these modifications were undertaken so as to optimise attachment of hybrid specimen to the working electrode without breaking SiNx window, to maximize the working area, and finally to facilitate in situ X-ray spectroscopy.

The configuration of the reference and counter electrodes on the third variation (Type III) of electrochemical chip is shown in Figure 2a. In this configuration both the RE and CE electrodes now circumnavigate the working electrode in the shape of extended ovals, allowing the experiment to achieve near-uniform current lines. An additional modification of the working electrode is that its position is now located outside of thin 50 nm thick SiNX window area. This more readily facilitates the use of a FIB Ga ion beam and organometallic Pt deposition to both secure and electrically attach the hybrid corrosion-test specimens to the electrode by displacing this attachment point from direct contact with the SiNx window to the
more robust Si chip. This change was implemented to avoid damage to the SiN\textsubscript{x} window. In addition, the glassy carbon WE has been replaced by a Pt WE. This was done due to the fact that the glassy carbon introduces an additional material with a different potential complicating both measurements as well as data interpretation. Furthermore, the glassy carbon also promotes galvanic and crevice corrosion of the hybrid specimen. Finally, in order to use the optimized XEDS acquisition efficiency of the modified Beryllium butterfly lid (Zaluzec et al, 2014), the window of the EChips was 90° rotated to minimize the shadowing effect.

### 2.3 OCP Measurements

During the electrochemical studies in situ measurements of the Open Circuit Potential (OCP) and potentiodynamic polarization behaviour are used to monitor critical corrosion variables. The OCP, also known as the free corrosion potential, is the potential difference measured between the Working Electrode (WE) and Reference Electrode (RE). The OCP is a function of many system variables; these include material (and prior thermomechanical processing that can affect material microstructure), solution composition, temperature, and solution flow (Hamann and Vielstich, 2007). For this work, in situ potentiodynamic polarization curves were measured using the following conditions: 2 min cathodic cleaning at -500 mV, 10 min delay at the OCP, after which a potentiodynamic polarization scan from -400 mV\textsubscript{RE} to 400 mV\textsubscript{RE} was conducted. The potential scan rate was 1 mV/s. All the measurements were carried out using a Gamry 600 series potentiostat and analysed using the Gamry software.

### 2.4 Specimen preparation

TEM specimens for electrochemical studies of metals are by their nature complex because of the need to control both the geometry and connectivity via previously described electrode configurations. To facilitate this, a hybrid preparation protocol was developed which employs a combination of both electrochemical polishing and Focused Ion Beam (FIB) extraction, the details of this hybrid technique are described elsewhere (Zhong et al, 2016). The base material for this work was cold-rolled Type 304 stainless steel specimens (Table 1), which was mechanically thinned to ~100 \( \mu \text{m} \) in thickness prior to punching of 3 mm diameter discs. The disc specimens were then electropolished in 20% HClO\textsubscript{4} - 80% CH\textsubscript{3}OH at -33\textdegree C and 20 V as is typical for conventional plan-view TEM studies. From the plan-view
specimens, site specific extraction of an electron-transparent thin area was accomplished using an FEI Quanta 3D Dual Beam FIB (FEI Company, Hillsboro, USA) (Zhong et al, 2016). Hybrid specimens are then transferred to the appropriate E-Chip and affixed to the peripheral Silicon surrounding SiNx window using organometallic Pt deposition. Figure 2b is an SEM micrograph showing an example configuration and the position of a hybrid specimen over the SiNx window, the electrical connection on a Type III electrochemical E-chip.

3.0 Validation Experiments

3.1 In Situ Electrode Validation

To validate electrochemical measurements for this work, the stability of the reference electrode and the suitability of electrode configuration were extensively assessed so that this technique could also be used for “bulk” (conventional) alloys. This included experiments using both distilled H₂O and dilute H₂SO₄ (Schilling, 2016). The prerequisite for a reference electrode is its stability in the electrolyte. Common reference electrodes such as Hg₂Cl₂ (saturated calomel) or Ag/AgCl electrodes have a stable potential over time (Inzelt et al, 2013). However, it is also possible to use a pure metal (i.e. the existing Pt electrodes) as a “pseudo-electrode” reference, as has been shown by both Ives and Kasem (Ives and Janz, 1961); (Kasem, 2008). Figure 3 shows the ex situ OCP over a 1 h period to assess the stability of the linear Pt (Type I) and glassy carbon (Type II) reference electrodes in H₂O and 0.001 M H₂SO₄ electrolytes. Once equilibrium is established, all measurements showed a nearly constant OCP as a function of time and the calculated potential (red curve) 0.144 V is in close agreement with the linear Pt electrode configuration cell (black curve) 0.163 V after 1hour. Thus, despite the low electrical conductivity of distilled H₂O (6 μS/cm), free corrosion potential measurements are obtainable using Pt electrodes. The glassy carbon working electrode (Type II) although stable, is not suitable for these electrochemical studies for other reasons. Firstly, electrode size is very large, thereby obscuring a large proportion of the SiNX window. Secondly, the use of Pt deposition in the FIB production of the hybrid specimens causes galvanic corrosion at the connection points (steel/glassy carbon/Pt). Lastly, the incident electron beam should not illuminate both electrodes at the same time, as this can cause an electrical short circuit in the electrochemical E-chip system, a problem with the glassy-carbon configuration because of the limited space.
3.2 *In Situ* OCP Measurements in H₂O

Having carefully assessed the electrodes configuration and stability, we next turn to an assessment of the presence of the incident electron beam during OCP measurements. Figure 4 plots the variation in the OCP in aerated distilled H₂O using a 5 μm E-Chip gap with the electron beam ON and OFF as well as under conditions of both static and flowing electrolyte. The results shows a potential difference change between beam ON/OFF of about 500 mV in static (zero flow) mode (black curve) and 350 mV for 5 μl/min flow (red curve). The temporal response in both curves indicates a charging and discharging of the 304SS specimen resulting from the incident electron beam: an increase when the beam is on, and decaying back to the non-beam OCP levels when the beam is “blanked”. Similar behaviour of the potential curves was observed for a 500 nm gap cell configuration. The explanation for this electrochemical response is simply that this system configuration behaves like a plate capacitor. Between two parallel plates is an electrically conductive electrolyte which enables the exchange of charges: anions migrate to the cathode, and the cations to the anode. In this case, the electrolyte resistance is large due to the marginal conductivity (6μs) of distilled H₂O. If an electric field is now supplied to the system, the metal atoms become polarised, and the metal surface and the electrolyte behave as a dielectric. The supplied energy will be stored in the electric field between the Helmholtz planes and a charge builds up (Hamann and Vielstich, 1997). When the applied electrical field is turned off, the additional energy is no longer supplied and the stored energy decays over time as the system “discharges”. The existing ions migrate slowly to the electrodes until the interaction between surface and electrolyte reaches equilibrium, when the planes are fully discharged. The dose rate during these measurements was approximately 4.46 A/m² without a specimen and 1.28 A/m² with the specimen in the field-of-view. This result shows that the specimen absorbs about 3 A/m². This electrical energy may be converted into heat, which could also locally generate temperature increases in the system.

3.3 *In Situ* OCP Measurements in 0.001 M H₂SO₄

Figure 5 plots experiment OCP as a function of electron beam exposure on a Type 304SS specimen in the 0.001M H₂SO₄ (pH 3) electrolyte and shows (after equilibrium is established) the absence of electron beam effects in the OCP values with electron beam. This should be contrasted with similar experiments in distilled H₂O (Figure 4). Here, the
conductivity of low concentrate acid is 147 μS/cm and the obtained potential curve is reasonably behaved over time, reaching about -500 mV for the 1 μl/min flow rate and -300 mV for the 5 μl/min flow rate. The more cathodic potential measured for the 1 μl/min flow rate can be understood in terms of an electron beam effect as the electrons generated by the incident beam will be absorbed by the ions in the H₂SO₄ electrolyte, which has a resistance that is much lower than that of H₂O. This result indicates that the electron beam effect is dependent on the conductivity of the electrolyte and specimen. Hence, for quantitative studies, it will be necessary to measure OCP in the absence of the incident beam, which clearly disturbs the electrochemical behaviour irrespective of the test condition. Fortunately, equilibrium is reached relatively rapidly and can be accelerated by increasing liquid flow. However, the use of a higher flow rate, thereby refreshing the electrolyte through the cell, is not without consequence. In figure 6, we show the effects of flow rate and E-Chip gap thickness on image resolution, which degrades as either parameter is increased.

3.4  *In Situ* Potentiodynamic Polarisation in 0.001 M H₂SO₄

In order to confirm the validity of the in situ electrochemical measurements on electron transparent Type 304 austenitic stainless steel (Type 304 SS) specimens and their relevance to the bulk material, it is essential to correlate these data with those obtained from conventional electrochemical tests. To accomplish this, conventional (bulk) results have been compared to those obtained using a microcell (~300 micron diameter area) and the results from the electrochemical E-chip. These data span measurement areas of several cm² (conventional), mm² (microcell) and μm² (*in situ*).

The potentiodynamic polarisation curves of the all three regimes for Type 304 SS in a low concentration H₂SO₄ (0.001 mol/l) are presented in Figure 7. All three curves show a similar trend with an open circuit potential of approximately -100 mV (SHE). Thus, to a good approximation, measurements of OCP are achievable, especially when the artifacts associated with the electron beam as previously discussed have been properly addressed. However, there is a noticeable difference is the variation in the current density in the comparison of the three polarisation curves. Decreasing the measurement area decreases the measured current density and thus, one would expect that the current density for the in situ experiments, which are the smallest, to be lower than both the bulk and microcell current density. Contrary to this logic the values obtained exceed the ex situ measurements in both cathodic or anodic...
conditions, however, at the extreme’s microcell data and in situ TEM begin to converge. In these measurements, the increased current density may be attributed to charge accumulation due to the presence of the incident electron beam, which in the mildly acidic electrolyte does not affect the OCP values (Figure 7). Having confirmed the validity of OCP measurement with traditional bulk measurements, it is now possible to create and identify cathodic, neutral, and anodic conditions with an in situ cell and thus control the corrosion environment.

4.0 Application to Austenitic Stainless Steels

As an exemplar of this validated experimental procedure, Figure 8, presents a series of hyperspectral images from a 0.03 wt.% S Type 304 SS containing MnS inclusions prepared using all of the previously described protocols. The initial state of the region of interest is shown in the top row by BF-STEM imaging as well as base-line Fe, Mn, and S elemental distributions. These initial state images were taken in the E-Chip liquid holder, in 1 bar air (i.e., no liquid). Next deionized H₂O was introduced to the E-Chip cell, the OCP conditions allowed to stabilize and the region of interest was then exposed to flowing liquid at room temperature with the electron beam blanked. The lower row documents the dissolution of the MnS inclusion, which was detected after 24 hours in H₂O. MnS inclusions in low alloy steels and in austenitic stainless steels are associated with both localized corrosion/pitting, environmentally-assisted cracking, and corrosion fatigue. Thus, this in situ result shows that even at room temperature, the dissolution process occurs. The ability to microchemically assess and measure such ultrafine-scale localized reactions associated with the initial stages of localised dissolution/corrosion is important in developing an understanding of the precursor events for environmentally-assisted degradation phenomena in engineering alloys, and, ultimately to aid in the development of predictive models for such materials degradation.

5.0 CONCLUSIONS

Using a modified E-chip electrode design, careful control of instrument parameters, the electron beam, as well as employing hybrid specimen preparation procedure we have validated a meticulous procedure for electrochemical studies of traditional metals and alloys during in situ TEM studies. Instances of contact corrosion due to non-optimized electrodes can be avoided as long as the cathode surfaces (more noble metal of the contact pair) are very
small in relation to the anode surfaces (less noble metal of the contact pair). The evaluation of electron beam effects in distilled H₂O and 0.001 M H₂SO₄ has shown that the conductivity of electrolyte and the electrolyte resistance depend on the charge transfer of the electrons in the incident beam and can be mitigated when carefully monitored. The first in situ liquid cell potentiodynamic polarisation curve of Type 304SS in 0.001M H₂SO₄ has been successfully measured in the TEM and comparison of conventional, microcell and in situ open circuit potential data confirmed that the data generated using the hybrid specimen in the electrochemical E-Chip cell were consistent with bulk behaviour, although issues still remain in the measurement of current densities. Electrochemical behaviour was also conclusively shown to be electron beam dependent and studies can be conducted in situ but only after while carefully monitoring and controlling conditions. Increasing the flow rate can reduce side effects such as pH, temperature differences and corrosion products, albeit with concomitant affects on image quality and resolution. When careful attention is paid to details, both meaningful and accurate studies can be conducted.

ACKNOWLEDGMENTS

The authors acknowledge the technical assistance of Dr. J. Lindsay and X.L. Zhong of the Materials Performance Centre for assistance with FIB specimen preparation. The support from EPSRC PROMINENT programme (EP/ 1003290/1), Dr. M.A. Kulzick and BP, is greatly appreciated. N.J. Zaluzec also acknowledges partial support from the U.S. DOE, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357 at the Electron Microscopy Center, in the Center for Nanoscale Materials, Nanoscience and Technology Division of ANL.
REFERENCES


of Electropolished Specimens’, Microscopy and Microanalysis, pp. 1–10. doi: 10.1017/S1431927616011855
Table 1: Chemical Composition (wt.%) of Type 304SS

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Al</th>
<th>Ti</th>
<th>N</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>304SS</td>
<td>0.045</td>
<td>0.48</td>
<td>1.56</td>
<td>0.027</td>
<td>0.008</td>
<td>18.50</td>
<td>0.02</td>
<td>9.91</td>
<td>0.034</td>
<td>&lt;0.01</td>
<td>0.04</td>
<td>69.37</td>
</tr>
</tbody>
</table>

Figure 1: Schematic illustration of the two original Protochips electrochemical-chip configurations: (a) Type 1- linear configuration, (b) Type 2 glassy carbon electrode.

Figure 2: a) Schematic illustration of Type 3 electrochemical chip and electrodes. The WE electrode is ~10μm outside of the SiNx window while the RE and CE electrodes circumscribe the SiNx window. b.) Hybrid prepared specimen connected to the Type 3 WE by an organometallic (om) Pt deposition, with the thin FIB-extracted foil extending over the electron transparent 50 nm thick SiNx window (RE and CE not visible in this image).
Figure 3: *Ex Situ* OCP measurement of different electrolyte and E-Chip electrodes.
Figure 4: *In Situ* OCP in distilled H₂O with 5 µm gap between E-Chips for the static (black curve) and 5 µl/min flow mode (red curve). Note the large effect of the incident electron beam on OCP.
Figure 5: *In Situ* OCP measurement in 0.001M H$_2$SO$_4$, Black curve show a flow rate of 1 and the red curve a flow rate of 5μl/min. Notice, that once equilibrium is established the significantly reduced electron beam effects to OCP measurements in mildly acidic conditions.

Figure 6: BF-TEM images showing the effect of flow rate on image quality. This specimen configuration (electrochemical E-chip assembly) is shown in Figure 2.
**Figure 7:** Potentiodynamic Polarization curve of Type 304 SS in 0.001M H$_2$SO$_4$. The black curve was measured using the *in situ* electrochemical cell with a 500 nm gap, blue curve was measured using the microcell, and the red curve was measured using the conventional bulk sample technique. a) BF-TEM image shows the area imaged during the *in situ* electrochemical test.

**Figure 8:** STEM and STEM-XED spectrum images obtained from a hybrid specimen of 0.03 wt% S in 304 SS containing an MnS inclusion in electrochemical E-cell. (a)-(d) Initial state prior to introduction of H$_2$O. (e)-(h) After 24 hours in flowing deionized H$_2$O, illustrating the RT dissolution of the MnS inclusion.
Chapter 7: Third Proposed Manuscript

7.1 Introduction:

The third manuscript described the beam interactions between incident beam, material and environment. The experiments were performed by Sibylle Schilling and provided support with the TEM by Arne Janssen. The Manuscript was written by Sibylle Schilling with technical and editorial supervision and proofing by M. Grace Burke.

7.2 Manuscript:

An Exploration of the Electron-Beam Heating Effect for In Situ TEM Studies in Gas and Liquid

S. Schilling¹, A. Janssen¹, N. J. Zaluzec¹,² and M.G. Burke¹

¹Materials Performance Centre and Electron Microscopy Centre, School of Materials, University of Manchester, Manchester, M13 9PL, U.K.
²Electron Microscopy Center, NanoScience and Technology Division, Argonne National Laboratory, Argonne, IL 60439 USA

ABSTRACT

The localized heating due to the interaction of the incident electron beam with a low melting point alloy was studied at 200 keV. Evidence of localized sublimation and oxidation was obtained during gas and liquid in situ TEM experiments performed on a low melting point eutectic alloy, Cerrelow 117. Such detailed studies of electron beam/environment/specimen interactions are critical to understand the behaviour of the specimen during liquid in situ TEM experiments.

Keywords: In Situ TEM, Beam-heating, Cerrolow 117

1.0 INTRODUCTION
*In situ* TEM is a powerful tool for investigating local reactions in order to explore material-environment interactions. However, it is important to understand the effect of the incident electron beam during *in situ* TEM examination. It is well-known that the electron beam can damage the specimen depending on the beam energy, current, diameter and dose rate. Egerton *et al.* [1][2] have reviewed the various factors related to the elastic and inelastic scattering effects in a dry system, such as electrostatic charging, atomic displacements, sputtering, specimen heating, structural damage, mass loss, hydrocarbon contamination and energy threshold effects. The beam-induced damage is proportional to the electron dose and is dependent on beam diameter, as well as the amount of energy deposited in the specimen. However, it is still not entirely clear what process(es) are occurring at the beam/electrolyte/specimen interface during liquid *in situ* TEM experiments.

Beam heating effect of the incident electron beam on Al-Si alloy particles were demonstrated by Howe *et al.* [3]. They studied the phase transformation of particles induced by the electron beam. The temperature rise and poor thermal conduction away from the particles were responsible for melting the Al-Si particles. Another example of electron beam heating in the TEM was reported by Liu *et al.* [4]. Phase transformation of α- Al₂O₃ to hexagonal Al₂O₃ was induced by the incident electron beam, which enhanced this thermally activated transformation. Their experiments were performed in JEM-100CX to investigate melting process of various dose rates (< 10 mA/cm²-500 mA/cm²) as a function of exposure time. Liu *et al.* [5] investigated the effect of the incident electron beam on the temperature of an electron-transparent specimen of amorphous Fe78Si12B10 at 200 kV. He reported that the amorphous specimen crystallized after 1h under the electron beam. This suggests that there is a local heating effect for metallic materials under the incident electron beam.

This present study examines the effect of the electron beam on a pseudo-eutectic alloy, Cerrolow 117, which has a melting point of ~47°C. The experiments were performed in three different environments: 1) vacuum; 2) air; and 3) H₂O (between SiNₓ-chips) to assess whether a local heating effect is possible during *in situ* TEM experiments.

### 2.0 EXPERIMENTAL PROCEDURE

To explore the potential electron beam heating effect, a low melting point alloy was identified as a candidate test material. Cerrolow 117, is a pseudo-eutectic alloy with the
composition 44.7 % Bi; -22.6% Pb, - 19.1% In - 8.3% Sn and 5.3% Cd, and has a melting point of 47.2°C. In the molten state, this alloy contracts into a spheroidal shape.

2.1 Specimen Preparation and General Characterisation
Two methods were used to prepare Cerrolow 117 specimens for the electron beam-heating experiments. For the microstructure analysis, a small piece of Cerrolow 117 was mechanically ground with SiC paper to 4000 grit, and polished with a 1 µm H$_2$O-based diamond suspension. The second preparation method involved crushing the Cerrolow metal in a liquid nitrogen-cooled mortar/pestle and suspending the fine metal particles in distilled H$_2$O.

General microstructural analysis was performed using a Zeiss Merlin field emission gun scanning electron microscope (FEG-SEM) equipped with two Oxford Instruments X-Max 150 SDD’s and an AZTEC analysis system.

2.2 In situ TEM experiments
To assess the effect of the electron beam on the stability of Cerrolow 117, experiments were performed on specimens prepared using the previously described techniques in three (3) environments: 1) in vacuo (TEM vacuum); 2) in 1 bar air in the Protochips P210 specimen holder; and 3) in H$_2$O in the P210 liquid cell TEM specimen holder.

A drop of the metal/H$_2$O suspension was deposited on to a bottom Si/SiNx E-Chip that is used for in situ TEM. This E-Chip was subsequently used to form a sealed liquid cell with a 5 µm gap using a “bottom” E-Chip for use in the Protochips P210 liquid analytical TEM holder. For in situ examination, deposited bottom chip was assembled after the drop of metal/H$_2$Osuspension was dried and for H$_2$O investigation, the assembled sandwich chip was filled with a flow of 1 µl/min.

All specimens were examined in an FEI Tecnai T20 analytical electron microscope operated at 200 kV in the TEM mode using spot size 1 and dose rate 1.28 A/m$^2$. This analytical electron microscope was equipped with an Oxford Instruments X-Max 80TLE Silicon Drift Detector (SDD) for X-ray energy dispersive spectroscopy (XEDS) with an AZTEC analysis system.
3.0 RESULTS and DISCUSSION

The general microstructure of Cerrolow 117 is shown in the secondary electron (SE) image of Figure 1. This low melting point alloy was characterised by a lamellar pseudo-eutectic microstructure. FEG-SEM XED analysis confirmed that multiple phases were present, as evidenced by the background-subtracted images in Figures 2 (b)-(f). The XED spectrum images obtained from the Cerrolow 117 specimen containing Pb, Bi and In, and non-uniform distributions of Sn and Cd.

3.1 Cerrolow 117: In situ TEM Examination in Vacuum

TEM examination of a Cerrolow 117 particle on an amorphous SiNx film revealed an irregular particle that was not fully electron-transparent. BF-TEM images of Cerrolow 117 obtained within seconds of examination and after 20 min under the condensed electron beam are shown in Figure 3. After 20 minute under the electron beam a clear difference in particle morphology was observed: a significant region of the specimen had changed. Closer examination of the region under the condensed electron beam revealed the presence of a “lacey” structure with considerable porosity. However, the convergent beam electron diffraction (CBED) patterns from this area showed no loss of crystallinity after 5 min, as diffracted beams were still observed in the pattern (Figure 4).

3.2 Cerrolow 117: In situ TEM Examination in 1 Bar Air

Sub-micron Cerrolow 117 particles were sealed between SiNx E-chips in air and examined using the P210 in situ TEM specimen holder. In contrast to the observed response of the Cerrolow particle in 1 bar air, a dramatic change in the specimen occurred quickly under the electron beam. This is clearly evident in the TEM images of Figure 5 & 6. The reaction in the sample under the electron beam initiated in the outer portion of the particle and progress to the central portion with time. Numerous fine (< 100 nm) diameter “particles” were observed where the original particle had originally been located.

In addition, a complementary sequence of selected area electron diffraction patterns (SADPs) of obtained from the metal sample during exposure 200 keV, spot size 3 and dose rate $4.18 \times 10^4 \text{A/m}^2$ at different time at room temperature are shown in Figure 7. The electron diffraction pattern revealed a change from a crystalline patterns to complete amorphization.
after 4.8 minutes, as shown in Figure 6, in which only diffuse halos in the diffraction pattern were observed. The microstructure exhibited a skeleton-like appearance with extensive porosity.

3.4 **Cerrolow 117: In situ TEM Examination in H₂O**

In contrast to the behaviour observed for the “dry” state, Figure 8 contains images of a Cerrolow 117 particle in an H₂O-filled 5 micron gap E-chip. Note that the presence of the H₂O in the 5 micron gap made it difficult to resolve the specimen in the BF-TEM images. However, during exposure under the electron beam, the H₂O appeared to slowly evaporate. Furthermore, the particle morphology was observed to change after 32 seconds under the incident electron beam. As the area under the incident electron beam was greater than that shown in the image, it was likely that the reaction also occurred on other portions of the particulate sample that were exposed to the beam. At the bottom left of the image taken after 30 seconds, metal appeared to move (flow) diagonally across the field-of-view. After 130 seconds the H₂O was not visible within the imaging region, but fine particles, which had appeared to form in the H₂O began to grow, as shown in the image taken after 300 seconds.

These observations of the beam interaction with the metal suggest that the electron beam heating effect is greater than reported in other studies because the melting point for this sample is ~47°C. Previous studies and calculations maintain that the electron beam has a negligible effect on the temperature of this system. Zheng *et al.* [6] found a negligible heating effect from a small current and good thermal conductance of H₂O. Creemer [7], calculated the beam heating and showed that the electron beam causes a negligible temperature difference in a heating stage. However, in agreement with our findings, Woehl *et al.* [8] concluded that a temperature increase is very possible in addition to radiolysis. Beam heating and evaporation effects similar to those observed in our experiments have been shown by Klein and co-workers.[9] Those authors described a local displacement of electrolyte by the gas phase (assumed to be steam) developed through electron beam, if intensity is too high. They suggest the H₂O displaced by vaporisation of H₂O caused by heating effects of intense focused electron beam.

4.0 **CONCLUSION**
The TEM experiments conducted using Cerrolow 117 have demonstrated that the 200 kV electron beam has a significant effect at an assembled chips. The results from the air and H₂O strongly suggest that the specimen has melted under the electron beam, as indicated by the pronounced change in specimen morphology – including the formation of small “droplets” - and has lost crystallinity as evidenced by the SADPs. Thus, the role of the electron beam in affecting the local temperature during in situ liquid cell and gas cell reactions must be considered.

REFERENCE


**Figure 1:** SEM image of general microstructure of Cerrolow 117

**Figure 2:** SEM-XED "TruMap" Spectrum Images showing the eutectic microstructure of Cerrolow 117 (a) Secondary electron (SE) image of the eutectic microstructure and complementary “TruMap” (background-subtracted) XED spectrum images for (b) Pb), (c) Bi, (d) In, (e) Sn and (f) Cd.
**Figure 3:** BF-TEM images of Cerrolow 117 particle in vacuum examined at 200 kV with spot size 3 and screen current 0.052nA showing the change in particle morphology as a function of time.

**Figure 4:** A sequence of convergent beam electron diffraction (CBED) patterns obtained at times of 0 min, 3 min and 5 min from region of the particle shown in Figure 3.
Figure 5: Closer up BF-TEM images recording of the transformation of surface during penetration of the electron beam at 200 keV.

Figure 6: BF-TEM images tracing of the in situ melting process. The time interval is listed after the first image a). b) After 14 min and c) after 21 min under the 200 kV electron beam.

Figure 7: A sequence of SADPs tracing the progression electron-beam induced changes in the crystalline Cerrolow 117 particle in 1bar air.
Figure 8: BF-TEM video frames of low melting point metal between 5 µm gap in H₂O
Chapter 8: Fourth Proposed Manuscript

8.1 Introduction:

The experiment was designed by M. Grace Burke, with input from Nestor J. Zaluzec and described the dissolution of MnS inclusions in H₂O using analytical in situ TEM. The experiment was performed by Sibylle Schilling and provided support with the TEM by Arne Janssen. The Manuscript was written by Sibylle Schilling with technical and editorial supervision and proofing by M. Grace Burke and Nestor J. Zaluzec.

8.2 Manuscript:

Direct Observation of the Dissolution of MnS inclusions in H₂O using Advanced Analytical In Situ TEM

S. Schilling¹, A. Janssen¹, Y. Yao¹, N.J. Zaluzec¹,², and M. G. Burke¹

¹Materials Performance Centre and Electron Microscopy Centre, School of Materials, University of Manchester, Manchester, M13 9PL, U.K.

²Electron Microscopy Center, NanoScience and Technology Division, Argonne National Laboratory, Argonne, IL 60439 USA

ABSTRACT

In situ transmission electron microscopy (TEM) is one of the preferred techniques to obtain nano-scale information about the morphological, structural and chemical changes in materials caused by the environment. In this study, the effect of H₂O on MnS inclusions and the local electrochemical potential has been examined using a special in situ liquid cell TEM specimen holder in the Analytical Electron Microscope. The in situ TEM results have been compared with bulk studies of the dissolution MnS inclusions in Type 304 stainless steel during room temperature H₂O exposure. These results are discussed in relation to the reported behaviour of MnS on environmentally-assisted fracture behaviour austenitic stainless steels. The use of novel in situ liquid cell TEM approach can provide information on localized
corrosion/oxidation reactions that can be helpful in identifying local microstructural features that can affect the “Precursor” events ultimately leading to crack initiation.

1.0 INTRODUCTION

Environmentally-assisted cracking (EAC) is the premature failure of a susceptible material under load in a specific environment. EAC encompasses a variety of phenomena including stress corrosion cracking (SCC). Environmentally-assisted cracking may be considered to be a result of localized electrochemical effects occurring at the crack tip. For the crack to develop there must be an initial defect. Environmentally-assisted cracking is generally considered to be comprised of three phases: 1) an early incubation phase in which small surface-related defects develop within the generalized microstructure; 2) a subsequent stage of initiation in which microstructural features develop into localized embryonic cracks; and 3) a final crack propagation stage when localized crack propagation occurs along the tips of well-developed crack fronts. Because of the inability to detect when general microstructural features have evolved in the presence of the environment into viable crack nuclei, the initiation and incubation stages of SCC are often grouped together. The inability to discriminate between incubation and initiation makes it difficult to specifically study either phase of the process. Thus, to date studies of EAC precursors have been exacerbated by the difficulty of isolating incubation features and following their development into initiated and propagating cracks. It is therefore difficult to identify how specific microstructural features and their interaction with the environment can affect formation of a SCC crack in practice.

Literature references illustrate how difficult it can be to study the specific stages of separate these three stages of SCC [1-5]. SCC can appear to progress in a “continuous” manner because it is difficult to isolate the specific stages. Hänninen et al. [2] has reviewed the initiation, propagation and failure for EAC steels. The initiation stage can be promoted by surface-related defects and local pits. Staehle [3] has described the formation local features that lead to the development of SCC cracks as “precursor” events that are dependent on the initial material condition. These defects can include any pre-existing surface features, or surface-breaking microstructural features, such as inclusions in the alloy or localized deformation. Such features can play an important role in accelerating the incubation and initiation of SCC cracks. The presence of these features does not, however, imply that incubation and initiation processes do not occur, and that viable cracks develop immediately
because of their presence; these features merely serve to accelerate the generally slow processes of crack incubation and initiation. The processes of crack incubation and initiation may still take several decades to develop even under such conditions (e.g. under highly cold-worked surface conditions).

The dissolution of MnS inclusions in low alloy steel has been shown to be responsible for EAC in certain environments. James [4] and Tice [5] noted that the most important microstructural features for EAC in low alloy steels were sulfide inclusions. When these inclusions were present at a crack tip they were found to dissolve when exposed to high temperature H$_2$O (>200°C). Furthermore, dissolution of surface-breaking particles in the microstructure were found to be preferred sites for the initiation of SCC cracks.

In contrast to the effect of MnS on EAC in low alloy steels, recent research has indicated that MnS inclusions can be associated with low crack growth rates in austenitic stainless steels during certain conditions of corrosion fatigue in high temperature H$_2$O environments[6, 7]. Corrosion fatigue crack-tips associated with such crack “retardation” effects are generally oxide-filled and significantly coarser than corresponding low S specimens, which are characterized by very narrow, sharp crack tips. [8]

To address the mechanism by which second phases could affect SCC in stainless steels Clarke et al. [9] studied a Type 304 stainless steel that had been exposed to oxygenated H$_2$O at 288 °C. The authors demonstrated a strong effect of second phase precipitates and inclusions in crack nucleation in stressed specimens. In both unstressed and stressed specimens, a dissolution process was observed to start around and within the second phase particles. In the stresses specimens this led to the initiation of intergranular attack and this caused a crevice region around individual particles. While the removal of material by chemical dissolution may, on its own, have caused the development of cracks it is also possible that the dissolution products affected the crack tip chemistry and enhances the potential for acceleration of crack formation in that way also.

A manifestation of this mechanism of crack formation is the observed nucleation of environmentally-assisted cracks from pits, which may themselves form by the dissolution of sulphide inclusions. While there appears to be a well-established dependence of the EAC susceptibility of low alloy steels in H$_2$O and the S content of the alloy, this correlation is not straight forward since it appears to be affected by the form and distribution of the sulphide
particles [10-12]. Furthermore, the development of the initial defects that may lead to SCC may also be related to passivity breakdown enhanced by chemical, electrochemical or mechanical effects.

With regard to the possibility of dissolution of MnS particles being responsible for the acceleration of the early stages of SCC in steels in H$_2$O environments, several researchers have proposed the chemical and electrochemical mechanisms for the dissolution of sulphide inclusions and the initiation of localized corrosion in aggressive medium at room temperature, such as pit initiation. These researchers have demonstrated the significant influence of temperature and environment on the extent of the SCC. Eklund [13] suggested that pitting starts almost exclusively at non-metallic inclusions in stainless steels and that sulphide inclusions, notably MnS, are the most detrimental. He calculated that in a pH range between 4.8 and 13.8 in chloride environments, the MnS sulphides are not stable at potentials higher than -100 mV vs. standard hydrogen electrode (SHE). Under such conditions the MnS particles should tend to dissolve above this level. This finding is significant since this electro-potential regime is in the region where the steel would be expected to be passivated.

Wranglen [14], has further explained that dissolution of MnS could further enhance SCC initiation due to the preferential adsorption of chloride ions on to the surface of the inclusions, further facilitating anodic dissolution. Wranglen explained that the preferential adsorption caused by the higher electron conductivity of the inclusions compared to the surrounding oxide film of the stainless steel. He proposed electrochemical dissolution of MnS inclusions in neutral chloride solution to the following reactions.

\[
\text{MnS + 4 H}_2\text{O} = \text{Mn}^{2+} + \text{SO}_4^{2-} + 8\text{H}^+ + 8\text{e}^- \quad (1)
\]

\[
2\text{O}_2 + 8\text{H}^+ + 8\text{e}^- = 4\text{H}_2\text{O} \quad (2)
\]

In previous studies to assess MnS dissolution microcell techniques have been employed to develop controlled potential chemical interactions between H$_2$O-based environments and individual MnS particles using micro- or nano-capillary electrochemical cells with subsequent evaluation of the resulting particle microstructure using SEM. [15-20]. In these studies the analysed areas were on the order of $\mu$m$^2$ or nm$^2$. However, these methods do not generally allow one to observe real-time imaging of particle dissolution and other related microstructural features (such as grain boundaries) while controlled potential dissolution is
occurring. However, Sudesh et al. [21] did investigate real-time pit initiation events by using \textit{in situ} atomic force microscopy (AFM) in combination with a conventional electrochemical technique. With this approach, they did observe pit initiation occurring close to the dissolving MnS inclusions.

The need to image and analyze such localized reactions in real time is driving the development of \textit{in situ} studies that allow the specimen to be imaged during exposure in the environment. \textit{In situ} transmission electron microscopy (TEM), coupled with X-ray energy dispersive spectroscopy (XEDS) analyses of metals in liquids is particularly important for detailed study of the interaction of the environment with specific microstructural features in the metal sample. These capabilities now make it feasible to explore what has been termed “precursor phenomena” – that is, those sub-micron-scale reactions between an alloy of interest and the environment. The examination of local metal-liquid reactions \textit{in situ} can provide a novel perspective on EAC and SCC precursor events that can lead to initiation.

In this study, we have used an \textit{in situ} liquid cell TEM combined with XEDS to explore the dissolution of MnS inclusions as a “precursor phenomena” that can promote the development of defect initiation in Type 304 austenitic stainless steel. For this work, the focused ion beam (FIB) lift-out technique was used to fabricate specimens with the required microstructures for study in the liquid cell TEM specimen holder.

\section{Material and Experimental Procedure}

A high S Type 304 austenitic stainless steel was used in this investigation. The chemical composition of the high S (0.03 wt. \%) Type 304 stainless steel used for these experiments is listed in Table 1. This steel was supplied in the annealed condition.

\subsection{Ex situ Specimen Preparation}

For the \textit{ex situ} investigation, the bulk specimen was mechanically ground with SiC paper to 4000 grit, and polished with a 1 µm H₂O-based diamond suspension. In order to simulate the FIB-prepared specimen configuration for the \textit{in situ} experiments, 50 µm Platinum (Pt)-lines close to selected MnS inclusions were sputtered with the FIB on the as as-polished surface. The bulk specimen was subsequently exposed in distilled H₂O for 8 days. A Keyence Laser Scanning Confocal Microscope VK-X210 was used to assess the depth of inclusion dissolution for the bulk specimens after exposure in distilled H₂O.
2.2 Microstructural Characterisation

The general microstructural analysis of the bulk specimens was performed using a Zeiss Merlin field emission gun scanning electron microscope (FEG-SEM) equipped with two Oxford Instruments X-Max^N 150 Silicon drift detectors (SDD) for X-ray energy dispersive (XED) microanalysis.

All general TEM characterisation and the liquid in situ analytical TEM experiments were performed using an FEI Tecnai T20 200 kV LaB$_6$ cathode equipped with an Oxford Instruments X-max 80TLE Windowless SDD X-ray energy dispersive (XED) spectrometer and in an FEI Talos 200 kV FEG analytical electron microscope with Super X (4 SDDs) XED analysis system.

2.3 In Situ Environmental Cell

The in situ experiments were performed using the Protochips Poseidon P210 liquid cell and the P510 electrochemical cell TEM specimen holders. The liquid cell windows are made from 50 nm thick amorphous SiN$_X$ membranes deposited onto 300 µm-thick Si wafers, which are fabricated into E-Chips. The specimen of interest is attached to the E-Chip (described in 2.3). Electrons can pass through the sealed thin layer of liquid and specimen that are “sandwiched” between the two SiN$_X$ membranes. A modified Be butterfly lid was used for optimized XEDS microanalysis [22].

2.4 Liquid Cell Analytical In Situ TEM – FIB Specimen Preparation and Data Acquisition

The conventional FIB “lift-out” technique using an FEI Quanta 3D field emission gun (FEG) FIB-SEM was used to prepare electron-transparent specimens containing MnS inclusions. The FIB-prepared MnS/304SS sample was placed on a Protochips Environmental Chip (E-Chip) and “attached” using Pt. The specimen between the top and bottom chip was sealed from the environment with a 500 nm gap like a sandwich configuration.

The XED spectrum image data acquisition live time was 600 s with a 100 ms pixel dwell time for each frame with a STEM spot size of 6 (3.65e$^{-1}$ A/m$^2$).
A Gamry 600 Potentiostat was used to measure the open circuit potential (OCP) over 10 min after 0 h, 2 h and 24 h in distilled H₂O.

3.0 RESULTS

3.1 General Microstructure

The Type 304 stainless steel used in this investigation was characterised by an equiaxed uniform grain structure, with an average grain size of approximately 50 µm. Delta ferrite was also detected in this austenitic stainless steel. Due to the 0.03 wt. % S content, this steel contained numerous MnS inclusions. The laser scanning confocal optical image in Figure 1 shows a region with a distribution of inclusions in this high S Type 304 SS. The MnS inclusions ranged in size from ~1 to ~10 µm.

3.2 In situ Observations

Regions of the Type 304 SS polished sample that contained MnS inclusions were identified using the SEM, and selected for FIB-TEM specimen preparation. Several FIB “lift-out” TEM specimens containing several MnS inclusions were attached onto Omniprobe Cu grids, and further thinned using the Ga ion beam to obtain electron-transparent specimens. These thinned specimens were subsequently transferred onto the working electrode of the top E-chip, so that the MnS inclusions were located between the top and bottom SiNx window (Figure 2).

Before the liquid was inserted in the sealed in situ cell, the pristine samples were characterized in 1 atm air using STEM-XEDS microanalysis (an example is shown in Figures 3 & 4). The FIB specimen in Figure 3 contained a small inclusion on the top and a large inclusion on the right side; the large inclusion contained several internal boundaries and discrete particles. XEDS spot analyses obtained from the darkly-imaging discrete particles within the MnS inclusion confirmed that they were Cr-rich oxides. Figure 4 shows an XEDS spectrum from a small particle in the MnS inclusion that contained Cr and O. The high Si peak in the spectrum comes from the SiNx window (Figure 3).

XEDS semi-quantitative composition analyses were conducted from the austenite into the MnS inclusion to determine any compositional variations in the vicinity of the matrix –
inclusion interface (Figure 5). The composition profile revealed that there was no depletion or segregation of Cr and Ni to the matrix/inclusion interface; the composition of the austenite was uniform and consistent with the nominal alloy content. STEM-XEDS analysis of the inclusion revealed an elevated Mn and S contents and a reduced levels of Fe, Cr and Ni in the inclusion phase.

The STEM-HAADF and XED spectrum images of the MnS inclusion in 1 atm air are presented in Figure 6. The XED spectrum images revealed that Cr and O-enriched particles were present in the MnS inclusion (Figure 6 b & f), consistent with the XED spectra obtained from the particles. Figure 7(d)-(e) shows the extent of dissolution the MnS inclusion after 2 h exposure in aerated H$_2$O. The dissolution of the MnS was non-uniform, and initiated near the austenite/inclusion interface rather than at the Pt/MnS interface in this FIB-prepared specimen, consistent with the anodic behaviour of inclusion. The MnS inclusion fully dissolved within 24 h at room temperature in Figure 7(h)-(n).

3.3 In Situ Electrochemical Measurements

The OCP was measured for this FIB-prepared in situ TEM specimen in order to assess the effect of the MnS dissolution on the OCP of the H$_2$O. The initial OCP measured prior to MnS dissolution is shown in Figure 8, and was approximately -250 mV (SHE). After 2 h exposure in aerated H$_2$O, the OCP was approximately -230 mV. The black curve in Figure 7 shows a slow increase of the OCP with time until electrochemical equilibrium has stabilized in the system, as shown by the red curve. This electrochemical equilibrium depends on the time and pH changes [23]

An open circuit potential of -340 mV was measured after 24 h in distilled H$_2$O, which is approximately 100 mV, as illustrated by the green curve in Figure 8. The potential is most negative after 24 hours because the MnS inclusion has completely dissolved; the inclusion was no longer visible (see Figure 7 h) and only the steel matrix in the Mn and S-containing H$_2$O remained.

3.4 Ex situ Observations

The relevance of the in situ observations was confirmed by ex situ exposure of a bulk sample containing a sputtered Pt line close the MnS inclusions to most closely simulate the
configuration of the Pt layer on the FIB specimen. The FEG-SEM XED spectrum images obtained from the bulk Type 304 stainless steel specimen containing MnS inclusions are shown in Figure 9(a)-(f); and after 8 days in distilled H₂O (Figure 9(g)-(l)). The XEDS analysis revealed that the coarser inclusions had dissolved. Some finer inclusions were still present. Some inclusions had partially dissolved and closer examination by XED analysis revealed the presence of Cr, Mn and S. It was observed that the MnS inclusions dissolved in H₂O whereas the oxides did not dissolve, as shown in Figure 10. The XED spectrum images also confirmed the presence of Cr and S-enriched oxide covering the remnant MnS inclusions after 8 days exposure in distilled H₂O.

Further FEG-SEM evaluation of the ex situ specimen revealed such partial dissolution of shallow inclusions after the H₂O exposure, as shown in the secondary electron images in Figure 11. Phase is attacked in an inhomogeneous inclusion (image 11a) and the cathodic inclusion behaves nobler than the steel matrix. The dissolution process took place at the interfacial and created a micro-crevice (image 10b). However, both images Figure 11a) and Figure 11b) shows an underneath attack, which has the consequence of a pH change below the inclusions and thus accelerating the dissolution process. [13, 15]

Laser scanning confocal microscope images were obtained from selected MnS inclusions on a mirror finished specimen prior to exposure and after 7 day exposure in distilled H₂O. The topography line scan across the MnS inclusion indicates a total height change (peak to peak) of ~0.30 µm, as a result of the exposure. This value is calculated from a single inclusion, not averaged from multiple sites. The detailed dissolution profiles are presented in Figure 12. The highest and the lowest point of the entire scan are associated with the dissolved inclusion. The baseline height was the flat steel matrix and this value was subtracted from the profile scan over the inclusion to obtain the absolute inclusion height. Figure 12 also shows that the steel matrix has a surface roughness (average variation of surface height) of 2.03 µm and the inclusion of 2.09 µm. The calculated height of the inclusion is 0.06 µm (± 0.03 µm). After dissolution of the inclusion in distilled H₂O, the profile scan shows a hole of 2.47 µm depth against the steel matrix height of 2.71 µm. The calculated depth of the inclusion is 0.24µm (±0.11µm). Hence, the maximum total height of inclusion before dissolution was 0.30µm and the average total height was 0.14 µm. The measurement also shows that both the steel matrix and the inclusion are altered and became rougher due to the dissolution process.
3.5 **Ex Situ** Electrochemical Measurements

Electrochemical measurements were also performed on bulk specimens to evaluate the influence of environment on the MnS dissolution at room temperature and 80°C. According to the present understanding of localized corrosion processes such as pit initiation, the pitting potential represents a critical threshold value, which will affect the cracking potential. With respect to SCC susceptibility, the curve permits the identification of the range of critical potentials where the alloy is usually active, passive and transpassive to quantitatively indicate the SCC cracking risk [1, 2].

The OCP curve of a conventional bulk specimen (*ex situ*) at room temperature was –380 mV (SHE), and approximately –315 mV (SHE) at 80°C. The sharp rise in OCP (red curve) 80°C with time compared to the more shallow increase in OCP at room temperature (black curve) indicates that at room temperature a passive layer was slowly formed on the metal surface (Figure 13). The polarization curves determined in austenite regions (with no inclusions) after a 10 min hold at the OCP are shown in Figure 14. The red polarisation curve showed a potential shift of approximately -70 mV to the anodic side and a higher current density at 80°C, which accelerated the anodic dissolution of the MnS inclusions.

4.0 **DISCUSSION**

*Analysis of the MnS inclusions*

The results of this investigation showed that the dissolution of the inclusion initiated at the steel matrix/inclusion interface in distilled H₂O at room temperature and had dissolved completely within 24 h. It should be noted that the specimen was very thin (< 100 nm) and that it was surrounded by H₂O, so that the dissolution reaction was readily observed.

An important factor of the dissolution process is the chemical composition of the inclusion. Zheng *et al.* [24] detected nano-sized octahedral MnCr₂O₄ crystals within MnS inclusions, and that the dissolution process occurred around these particles because of the potential difference between the MnCr₂O₄ and MnS. Also, Krawiec *et al.* [25] noted that the presence of various sulphide inclusions, such as MnS, CrS, FeS, or a homogeneous MnFeS or MnCrS can impact the local chemical or electrochemical reactions occurring at the inclusion/steel matrix/electrolyte interface.
The large MnS inclusion in Figure 3 had an elongated and oval morphology. The geometry and the orientation of the MnS inclusions are important parameters in the initiation of pitting. Webb et al. [15] described that inclusions ~ 2 to 3µm in thickness only cause metastable pitting. However, thin stringered inclusions dissolved around the edges of the inclusion and created deep micro-crevices between the inclusion and steel matrix, which caused pitting. The dissolution process also depends on the inclusion size. MnS inclusions or MnS/O inclusions smaller than <0.7 -0.8 µm were shown to be more resistant to pit initiation before repassivating. [25, 26] Ke et al. [27] had previously shown that the dissolution of sulphide inclusions can also depend on their chemical composition.

**Factors affecting in situ dissolution of MnS inclusions**

The observed dissolution of the MnS inclusions could be related to the effect of the electron beam on the surface in H$_2$O during the *in situ* STEM-XED spectrum imaging. The incident electron beam could accelerate the reduction of the MnS inclusion via a local heating effect. Howe et al. [28] demonstrated a heating effect of the incident electron beam on Al-Si alloy particles. They studied the phase transformation of particles induced by the electron beam. The temperature rise and poor thermal conduction away from the particles were responsible for melting the Al-Si particles. Another example of electron beam heating in the TEM was reported by Liu et al. [29] According to Liu et al. [30], the phase transformation of α-Al$_2$O$_3$ to hexagonal Al$_2$O$_3$ was induced by the incident electron beam, which enhanced this thermally activated transformation. Their experiments were performed in JEM-100CX to investigate melting process of various dose rates (< 10 mA/cm$^2$-500 mA/cm$^2$) as a function of exposure time. Liu et al. [30] developed a model to investigate the temperature increase due to electron beam bombardment, which was subsequently evaluated experimentally. An amorphous Fe$_78$Si$_{12}$B$_{10}$ alloy was analysed in a 200keV JEOL TEM. After 1 h under the incident electron beam, the amorphous specimen crystallized. Thus, the MnS dissolution observed during *in situ* analysis could also have a thermally-enhanced component. It should be noted, however, that experiments were performed such that the specimen was not under the electron beam for prolonged periods.

Several reports concerning the local austenite composition in the vicinity of the sulphide inclusions have been published. Any variation in local composition of the austenite may affect the inclusion dissolution. Ryan et al. [31] suggested that a Cr-depleted zone formed in
the austenite around the sulfide inclusions during steel fabrication. They observed that pit initiation began in the austenite at the inclusion boundary rather than the dissolution of the inclusion. However, Meng et al. [32] investigated the same material (Type 316F), which had been investigated by Ryan et al. The authors found no evidence of Cr-depleted zones around the inclusions. In this study only Mn, S, Cr and O were detected in the MnS inclusion. Our results agree with Meng et al. investigation that there was no Cr-depletion at the interface of austenite and inclusion, as shown in the composition profile of Figure 5.

**Electrochemical Analysis of Ex Situ MnS Dissolution**

After 8 days in distilled H$_2$O, it is clearly evident in the SEM image (Figure 12) that the inclusion had not completely dissolved. Partial dissolution had occurred resulting in the formation of a protective layer on the inclusion surface.

The OCP measured during the in situ experiments initially increased slowly, and stabilised after 2 h. This suggests that it is possible that the inclusion had completely dissolved and formed a protective layer over the steel matrix, which resulted in a negative potential. The potential was most negative after 24 hours because the MnS inclusion had completely dissolved; the inclusion was no longer visible (see Figure 6 h) and only the steel matrix in the Mn and S-containing H$_2$O remained.

The OCP of the ex situ test revealed a similar stabilized potential behaviour. The ex situ data also showed that temperature accelerated the dissolution reaction. Krawiec et al. [25], investigated surface changes induced by the chemical dissolution of MnS inclusions under OCP for 50 and 204 min in 1M NaClO$_4$. The authors observed that all MnS inclusions formed large holes after 50 min and completely dissolved after 204 min OCP. Schmucki et al. [33] reported that the oxide film formed on inclusions shows more defects at the inclusion/bulk interface due to the change of the crystallographic structure. The presence of various sulphide inclusions, such as MnS, FeS, or a homogeneous MnFeS can impact the local chemical or electrochemical reactions occurring at the inclusion/steel matrix/electrolyte interface [26].

The ex situ polarisation curve measured at 80°C exhibited an increased current density and shift of OCP to the anodic side. If the temperature of the H$_2$O is increased, MnS dissolution and metal oxidation will be enhanced, which was observed for the ex situ experiment. This
suggests that electron beam may affect the system, consistent with the beam-induced heating that Howe [28] and Liu [29] demonstrated in their phase transformation studies.

Our *ex situ* observations support previous work of MnS inclusion dissolution in high temperature H$_2$O environment in low alloy steels. In particular, these capabilities now make it feasible to explore what has been termed “SCC precursor phenomena” – that is, those sub-micron scale reactions between an alloy of interest and the environment.

5.0 CONCLUSIONS

This work represents the first demonstration of *in situ* liquid cell TEM imaging and STEM-XED microanalysis/spectrum imaging documenting MnS dissolution in distilled H$_2$O at room temperature. *In situ* and *ex situ* experiments showed that dissolution of MnS inclusions can readily occur in distilled H$_2$O at room temperature in stainless steel. The excellent agreement between the *in situ* and *ex situ* results demonstrates that the liquid cell observations are valid. The enhanced corrosion behaviour under high temperature can be explained by the MnS dissolution, higher reaction kinetics and a possible beam heating effect. In addition, the higher potential measured for the *in situ* OCP compared to that measured *ex situ* could be evidence of thermal activation of the system induced through the electron beam.

The recent advances in microanalytical and microstructural techniques such as the development of unique *in situ* platforms enables previously “impossible” environments (such as liquids) to be used for the study of localized reactions in materials. The combination of electrochemistry and electron microscopy can provide unique future opportunities for the study of nanoscale electrochemical reactions occurring in engineering alloys and lead to new insights for corrosion and environmental reactions.

5.0 ACKNOWLEDGEMENTS

The authors acknowledge the technical assistance of Dr. J. Lindsay and X. L. Zhong of the Materials Performance Centre for assistance with FIB specimen preparation. The support from EPSRC PROMINENT programmes (EP/ 1003290/1) Dr. M.A. Kulzick and BP, and is greatly appreciated. N.J. Zaluzec also acknowledges partial support from the U.S. DOE, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357 at the Center for Nanoscale Materials Science, NST Division of ANL.
REFERENCES

Integrity”, I.M. Editors-in-Chief: R.O. Ritchie, and B. Karihaloo, Editors. (2003),
Pergamon: Oxford. p. 1-29

Dissolution on Environmentally Assisted Cracking in Low-Alloy and Carbon Steels,”

Fe-Cr-Ni Alloys – Initiation of SCC”, Proceedings of Workshop Held at Sun Valley
Resort, Idaho (USA), (2011).

the Initiation and Propagation of Fatigue Cracks in Low-Alloy Steels,” in Corrosion

assisted crack growth of cold-worked type 304 stainless steel in PWR environments”,
In Proc. of the 12th International Symposium on Environmental Degradation of
Materials in Nuclear Power Systems–Water Reactors, (2005), Salt Lake City, UT,
USA, pp. 1037-1048.

Engineering and Design 119, no. 2–3 (1990): 399–413, doi:10.1016/0029-
5493(90)90180-6.

temperature on corrosion fatigue crack growth of reactor pressure vessel steels”, In
6th International Symposium on Environmental Degradation of Materials in Nuclear

Stairmann., “Microstructural Characterisation of Type 316 Austenitic Stainless Steels:
Implications for Corrosion Fatigue Behaviour in PWR Primary Coolant” in 17th
International Conference on Environmental Degradation of Materials in Nuclear
Power Systems- Water Reactors, 2015


Table 1: Chemical Composition (wt. %) of High S Type 304SS

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>P</th>
<th>Mo</th>
<th>S</th>
<th>Fe</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.029</td>
<td>0.20</td>
<td>1.25</td>
<td>18.34</td>
<td>8.00</td>
<td>0.032</td>
<td>0.38</td>
<td>0.031</td>
<td>71.64</td>
<td>0.39</td>
</tr>
</tbody>
</table>

Figure 1: Laser Scanning Confocal Microscopy image of different inclusion sizes of high S type 304SS.

Figure 2: SEM-SE image of the FIB-prepared specimen containing two MnS inclusions attached to the E-Chip.
Figure 3: STEM overview image of MnS inclusions a) BF and b) HAADF between a SiN\textsubscript{X} windows.

Figure 4: XED-Spectrum from particle in MnS inclusion in 1 atm air.
Figure 5: XED semi-quantitative composition profile across metal/inclusion interface. Distance between points is 0.04 µm.
Figure 6: In situ analytical TEM experiment: (a)-(g) Bright-field STEM and corresponding XED spectrum images for Cr, Fe, Mn, S, O and Pt respectively obtained from a MnS inclusion (FIB-prepared specimen) in 1 atm air.

Figure 7: In situ analytical TEM experiment: (a)-(g) Bright-field STEM and corresponding XED spectrum images for Cr, Fe, Mn, S, O and Pt respectively obtained from a MnS inclusion (FIB-prepared specimen) after 2 h exposure, and (h)-(n) after 24 h exposure in distilled aerated H₂O.
**Figure 8:** OCP curves of *in situ* experiments after 0 h (black), 2 h (red) and 24 h (green) exposure in aerated H$_2$O.

**Figure 9:** Pre- and post-exposure analysis of MnS dissolution in distilled H$_2$O. (a) SE image and (b)-(f) corresponding XED spectrum images for Cr, Fe, Mn, S, respectively showing MnS inclusions present in a bulk sample prior to exposure in distilled . (g) SE image and (h)-(l) corresponding XED spectrum images for Cr, Fe, Mn, and S after 8 days exposure in distilled H$_2$O.
**Figure 10:** *Ex situ* MnS dissolution after 8 days exposure in distilled H$_2$O: (a) SE image and corresponding XED spectrum images for Cr, Fe, Mn, S, and O.

**Figure 11:** SE images of different MnS inclusions morphologies after 8 days exposure in distilled H2O. (a) Inhomogeneous dissolution of inclusion and (b) a micro-crevice formation between inclusion and steel matrix.
Figure 12: Laser Scanning Confocal images and topographic profile measurements of the inclusion before and after exposure in distilled H$_2$O.
Figure 13: The variation of OCP as a function of time for bulk *ex situ* samples of the high S Type 304SS in H$_2$O at room temperature and 80°C.

Figure 14: Polarisation data for high S Type 304 SS in H$_2$O at room temperature and 80°C using conventional bulk with scan rate 2mV/s.
Chapter 9: Further Discussions

This Chapter describes an overall discussion of the key results of thesis. It describes the development and modification of a new experimental method in the nanoscale, which presents TEM in situ examinations. In order to better understand the results of this experimental methodology, the material was pre-investigated, which was used in this thesis. Subsequently, the individual steps of the new methodology were investigated and tested with cold worked 304 austenitic steel. These were compared with the previous data in order to exclude errors from the material.

9.1 Pre-investigations of Type 304 SS

Characterisation of cold-worked 304 SS based on Light Optical Microscopy, TEM and EBSD provide a precise identification of the phases present in the alloy. The EBSD method is a powerful tool to measure local residual plastic strains and localisation of deformation. The method can, and should, be utilised to characterise typical nuclear components or mock-ups, such as specimens from welding procedure tests, from parts removed from operation and from failed sections. The analysis of complex phases in these materials requires high resolution EBSD with fine step sizes of 0.05µm. Grains smaller than <10µm can be very challenging for assessing the phase fraction in the analysed images. However, it readily provides crystallographic orientation data for texture analysis. TEM observations clearly showed the microstructural features that characterised the cold worked. The microstructures of the cold worked 304 SS are complex, making it difficult to distinguish between microtwins and epsilon martensite simply based on morphology. Vickers Hardness Test measurements have been successfully used to assess the plastic deformation of the material, but show no signification characterise and are within the context of a cold work austenitic stainless steel. The SCC behaviour of the cold worked 304SS indicates that there is a link between the deformation microstructure which is induced by rolling and the susceptibility during SSRT. Localized electrochemical method and Pit analysis via Laser Scanning Microscopy allowed the precise location of the measurement to be identified and related to the phases/local microstructure of the alloy. Compared to the bulk/conventional data in which many grains, grain boundaries and inclusions are sampled, the microcell region has a measurement area of 1-2 grains with a few grain boundaries. The diameter of grain sizes are between 3.7 and 145µm. The previously described effect of crevice corrosion could occur on the measured
area around the microcell-tip edge; during the measurements. The pH value may accelerate the metal oxidation reaction and form in the micocell-tip due to pit growth, thereby creating a gap between the tip and the surface.

The main point was to develop and modified in situ cells and specimen fabrication for in situ TEM investigations to study nanoscale reactions on conventional metal microstructures (i.e., non nano) pertaining to localized corrosion events.

9.2 In situ TEM investigations and evaluations

- Hybrid specimen preparation technique and E-Cell modifications
First steps were to development a new specimen preparation technique procedures for the production of TEM samples from bulk metals/alloys have been developed to facilitate environmental TEM studies. This technique combines the conventional electropolished TEM thin-foil specimens and identification and FIB cut-out of regions-of-interest in electropolished specimens. The attachment of the plan view sections to the E-Cell windows were performed with the Pt attachment “Cut and Attach” method and sealing and mounting of the E-Cell in the TEM holder. An issue with this configuration/specimen shape is that during the electrochemical measurement localized corrosion will also occur outside of the experimental field-of-view and in the non-electron transparent regions that are not located over the thin SiNX window. In addition, the use of FIB Pt deposition to electrically connect the specimen to the electrodes can produces a marginally thicker region on the E-chip. This increase in overall thickness of the total system (E-chip + specimen + Pt) which without due care can become too great for the smaller 500 nm gap E-Cell configuration. In this configuration a 5 μm gap eCell must be used; unfortunately, a 5 μm gap results in a larger volume of liquid in the cell, causes greater beam attenuation as well as correspondingly reduced imaging resolution due to multiple scattering. As an alternative, with care a significantly smaller section can be FIB cut from an electropolished steel specimen. The smaller specimen (~ 25 μm x 50 μm) fits completely within the field-of-view of the electrochemical eCell SiNX window, except for a small tab used to connect the specimen to the electrodes of the E-chip. In this type of E-chip, the reference and working electrode terminate over the SiNX window. Because the use of Pt deposition increases the total thickness of the experimental “sandwich”, a modified attachment procedure was developed to avoid this problem. Prior to FIB lift out, a slot or trench is milled in the thicker bulk region.
of the electropolished specimen at the location that will be eventually used for connection to the working electrode. The trench is allowed to taper in thickness from inner/central portion of the sample to the outer edge. This modification permitted the Pt deposition to connect the sample to the working electrode without the height of the Pt deposit exceeding the thickness of the original specimen, thereby facilitating the use of a smaller cell gap (< 5 μm) for the in situ experiments.

The modified hybrid specimen configuration and modified E-chip electrode design have enabled electrochemical analyses of conventional metals and alloys to be performed in situ in the TEM. Three different types of E-chips have been tested before modification. The difference between Type I, II (original), and III (modified) E-Chips are:

- Type I all three electrodes, reference, counter and working electrode, are made of Platinum (Pt) and parallel to each other.
- Type II the working electrode is made of glassy carbon and the reference and counter electrode are made of Pt. RE and CE surround the working electrode/SiN\(_X\) window.
- Type III: the modified E-chip window configuration.

While these original electrochemical chip designs are reasonably well-suited for studies of battery materials and nanoparticles, these configurations are not amenable to electrochemical studies of more conventional alloy samples (i.e., our hybrid TEM specimens). Therefore, several design modifications were made to the electrochemical E-Chips. These modifications included: the geometry of electrodes, the size of the working electrode, elimination of the glassy carbon electrode, modification of the working electrode location; and 90° rotation of the SiN\(_X\) window, to optimise attachment of hybrid specimen to the working electrode without breaking SiN\(_X\) window.

The configuration of the reference and counter electrodes on the modified electrochemical chip (Type III) was dependant on the geometry of the SiNx windows. Both electrodes circumnavigate the working electrodes to achieve near-uniform current lines. An important modification of the electrode is that the WE is located outside of SiN\(_X\) window.

Initial measurements of the reference electrodes were made using conventional electrochemical methods in distilled H\(_2\)O at room temperature and pH 6.8. The potential of the Pt electrode was measured against an Ag/AgCl electrode (ERE\(F\)= 0.220V) over about 12h. The measured Pt potential (EM= 0.364V) was then calculated by subtracting the known Ag/AgCl potential from that experimentally measured. This Pt potential (E=0.144V) was
compared to the Open Circuit Potential/free corrosion potential (OCP) of both E-chips in electrolytes, with no specimen present to insure none of the components within the E-chip altered the OCP. All 3 measurements show a nearly constant OCP as a function of time. The calculated potential is most closely matched by the E-chip Type I cell with Pt-potentials of 0.144V and 0.163V, respectively after 1 hour. Comparing the E-Chips Type I and Type II glassy carbon in distilled H₂O shows a potential difference of about 400 mV. Comparing Type I in different electrolytes, a free potential difference of approx. 200mV exists. The reason for the different potential is the conductivity of the electrolytes. Despite the low electrical conductivity of distilled H₂O (6µS/cm), free corrosion potential curves could be obtained with Pt electrode.

- **Applications of the liquid in situ Cell and electrochemical in situ Cell**

The first liquid in situ and electrochemical experiments have been successfully applied to in situ environmental TEM observations of extracted electropolished specimens immersed in H₂O and in dilute H₂SO₄ and can be used to prepare a wide range of samples for other unique in situ environmental TEM experiments. The first in situ electrochemical measurement in aerated distilled H₂O in the TEM over time with a 5 µm gap between bottom and top chip. Additional influence of the beam has been tested on the environmental system with no flow (static) and 5µl/min flow rate. The time interval between beam off/on was 10 min. The plot shows a potential difference of about 500 mV in static mode and for 5 µl/min flow the difference is approx. 350 mV. Both curves show charging and discharging of the 304 SS specimen, when the beam is turned on there is a jump in the potential, but when the irradiation is turned off the potential decays until the OCP level is stable. In contrast to experiment in H₂O shows no drastic difference in potential with beam off/on, because in this case a low-concentration sulphuric acid (0.001M H₂SO₄) was used as the electrolyte. Compared to distilled water, the conductivity of low-concentrate acid is approx. 147 µS/cm, because the weak acid has only a small number of ions present in electrolyte. Also, the potential curve is constant over time, at about -500 mV at 1 µl/min flow rate and -300 mV at 5 µl/min flow rate. It shows that a slower flow rate has a higher potential than with a higher flow rate. SEM examination of the specimen after the first in-situ OCP’s showed that over the region in which the electron beam had been, the specimen had reacted. This reaction had caused particles rich in chromium and iron to develop, as shown in the EDX spectrum. The reacted region appeared to have thinned as a result of exposure, implying that dissolution had
occurred. In another experiments corrosion product can be seen in the beam spotted area. From the EDX analysis it was found that the Ca and O content dominate this region. This suggests that it is a calcium oxide. After further investigation of the distilled water, it was found that the Calcium content was about 0.4mg/l and the conductivity is 6.8µS. The dissolved calcium from the distilled water was precipitated in a circular footprint on the specimen and E-chip.

Those were the first indications of a beam induced effect in the in situ system. To explore the electron beam heating effect of electron beam/environment/specimen interactions, a liquid in situ TEM experiments was performed on a low melting point eutectic alloy, Cerrelow 117. The results from the air (particles were sealed between SiNx E-chips in air ) and H2O (particle in an H2O-filled 5 micron gap E-chip ) strongly suggest that the specimen has melted under the electron beam, as indicated by the pronounced change in specimen morphology – including the formation of small “droplets” - and has lost crystallinity as evidenced by the SADPs. During exposure under the electron beam, the H2O appeared to slowly evaporate. Furthermore, the particle morphology was observed to change after 32 seconds under the incident electron beam. As the area under the incident electron beam was greater than that shown in the image, it was likely that the reaction also occurred on other portions of the particulate sample that were exposed to the beam. The observations of the beam interaction with the metal suggest that the electron beam heating effect is greater than reported in other studies because the melting point for this sample is ~47°C.

Previous studies and calculations maintain that the electron beam has a negligible effect on the temperature of this system. Zheng et al. [14] found a negligible heating effect from a small current and good thermal conductance of H2O. Creemer [102], calculated the beam heating and showed that the electron beam causes a negligible temperature difference in a heating stage. However, in agreement with our findings, Woehl et al. [124] concluded that a temperature increase is very possible in addition to radiolysis. Beam heating and evaporation effects similar to those observed in our experiments have been shown by Klein and co-workers.[123] Those authors described a local displacement of electrolyte by the gas phase (assumed to be steam) developed through electron beam, if intensity is too high. They suggest the H2O displaced by vaporisation of H2O caused by heating effects of intense focused electron beam.

The first electrochemical in situ cell potentiodynamic polarisation curve of Type 304 SS in 0.001M H2SO4 has been successfully measured in the TEM. To validate the in situ
electrochemical measurements, conventional (bulk) results have been compared to those obtained using a microcell (~300 micron diameter area) and the results from the electrochemical E-chip. All three curves show a similar trend with a potential of around -100mV. The only difference is the shift in the current density; the current density is much higher for the in situ case. The increased current density measured for the in situ polarization measurements was conclusively shown to be electron beam dependent, indicating that the thermal contribution may also be important. Increasing the flow rate can reduce side effects such as pH, temperature differences and corrosion products. In addition, the measured current density is much higher than for conventional measurements.

Finally, first demonstration of in situ liquid cell TEM imaging and STEM-XED microanalysis/spectrum imaging documenting MnS dissolution in distilled H$_2$O at room temperature. In situ and ex situ experiments showed that dissolution of MnS inclusions can readily occur in distilled H$_2$O at room temperature in stainless steel. The results of in situ experiments showed that the dissolution of the inclusion initiated at the steel matrix/inclusion interface in distilled H$_2$O at room temperature and had dissolved completely within 24 h. It should be noted that the specimen was very thin (< 100 nm) and that it was surrounded by H$_2$O, so that the dissolution reaction was readily observed. The SEM images of ex situ experiments showed partial dissolution had occurred resulting in the formation of a protective layer on the inclusion surface after 8 days in distilled H$_2$O. The OCP of the in situ and ex situ tests revealed a similar stabilized potential behaviour at room temperature. The ex situ data also showed that temperature accelerated the dissolution reaction. Krawiec et al. [15], investigated surface changes induced by the chemical dissolution of MnS inclusions under OCP for 50 and 204 min in 1M NaClO$_4$. The authors observed that all MnS inclusions formed large holes after 50 min and completely dissolved after 204 min OCP. Schmucki et al. [157] reported that the oxide film formed on inclusions shows more defects at the inclusion/bulk interface due to the change of the crystallographic structure. The presence of various sulphide inclusions, such as MnS, FeS, or a homogeneous MnFeS can impact the local chemical or electrochemical reactions occurring at the inclusion/steel matrix/electrolyte interface [87]. The excellent agreement between the in situ and ex situ results demonstrates that the liquid cell observations are valid. The enhanced corrosion behaviour under high temperature can be explained by the MnS dissolution, higher reaction kinetics and a possible beam heating effect. In addition, the higher potential measured for the in situ OCP compared
to that measured *ex situ* could be evidence of thermal activation of the system induced through the electron beam.
Chapter 10: Final Conclusions

The present work is concerned with the micro- and nano scale development and application of analytical methods to study microstructural features that can affect the initiation and propagation of cracks in austenitic stainless steels. In this context, the in situ analytical TEM technique may provide a valuable contribution in terms of various aspects of localized dissolution, oxidation, and electrochemical effects that can provide a new perspective on those “precursor events” that can lead to environmentally-assisted cracking.

In summary, a novel set of two hybrid electrochemical-FIB sample preparation procedures for the production of TEM samples from bulk metals/alloys have been developed to facilitate environmental TEM studies. These methodologies have been successfully applied to in situ environmental TEM observations of extracted electropolished specimens immersed in H₂O and in dilute H₂SO₄ and can be used to prepare a wide range of samples for other unique in situ environmental TEM experiments. The procedures outlined herein provide the scientific community with a reproducible method of preparing bulk metallic samples and offers significant promise for the broader application of in situ liquid cell TEM studies. We also note that this method is currently being employed for the preparation of bulk metal specimens for elevated temperature studies using in situ gas reaction cell.

The modified hybrid specimen configuration and modified E-chip electrode design have enabled electrochemical analyses of conventional metals and alloys to be performed in situ in the TEM. Any contact corrosion can be neglected as long as the cathode surfaces (more noble metal of the contact pair) are very small in relation to the anode surfaces (less noble metal of the contact pair). Under these conditions no influence on the corrosion behaviour is observed. The evaluation of the electron beam effect in distilled H₂O and 0.001 M H₂SO₄ showed that the conductivity of electrolyte and the electrolyte resistance depend on the charge transfer of the electrons in the incident beam.

The first in situ liquid cell potentiodynamic polarisation curve of Type 304SS in 0.001M H₂SO₄ has been successfully measured in the TEM. Comparison of conventional, microcell and in situ open circuit potential data confirmed that the data generated using the hybrid specimen in the electrochemical E-Chip cell were consistent with bulk behaviour. The increased current density measured for the in situ polarization measurements was conclusively shown to be electron beam dependent, indicating that the thermal contribution may also be important. Increasing the flow rate can reduce side effects such as pH,
temperature differences and corrosion products. In addition, the measured current density is much higher than for conventional measurements.

The TEM experiments conducted using Cerrolow 117 have demonstrated that the 200 kV electron beam has a significant effect at assembled chips. The results from the air and H$_2$O strongly suggest that the specimen has melted under the electron beam, as indicated by the pronounced change in specimen morphology—including the formation of small “droplets” - and has lost crystallinity as evidenced by the SADPs. Thus, the role of the electron beam in affecting the local temperature during *in situ* liquid cell and gas cell reactions must be considered.

The final work represents the first demonstration of *in situ* liquid cell TEM imaging and STEM-XED microanalysis/spectrum imaging documenting MnS dissolution in distilled H$_2$O at room temperature. *In situ* and *ex situ* experiments showed that dissolution of MnS inclusions can readily occur in distilled H$_2$O at room temperature in stainless steel. The excellent agreement between the *in situ* and *ex situ* results demonstrates that the liquid cell observations are valid. The enhanced corrosion behaviour under high temperature can be explained by the MnS dissolution, higher reaction kinetics and a possible beam heating effect. In addition, the higher potential measured for the *in situ* OCP compared to that measured *ex situ* could be evidence of thermal activation of the system induced through the electron beam.

The recent advances in microanalytical and microstructural techniques such as the development of unique *in situ* platforms enables previously “impossible” environments (such as liquids) to be used for the study of localized reactions in materials. The combination of electrochemistry and electron microscopy can provide unique future opportunities for the study of nanoscale electrochemical reactions occurring in engineering alloys and lead to new insights for corrosion and environmental reactions.
Chapter 11: FUTURE WORK

The development of liquid *in situ* measurement technology represents a novel, sensitive measurement method for research and practical purposes. Given that this PhD project focused on the development and early use of this technique, it is inevitable that ideas have been generated that are beyond the remit of the current work; these would provide useful areas of studies for future work, which are outlined as follows.

- **Modification of the *in situ* holder**

  In order to gauge temperature inside the electrochemical cell, thermocouples could be built in at the tip of the TEM holder. The downside of this technique is that it would be expensive to develop, as well as the combination of TEM holder between heating stage and electrochemical stage to investigate materials in solution with higher Temperature (> 25°C).

  It is well-known that increased temperature will accelerate the corrosion reaction at the metal surface. Investigation of elevated temperature effect in aqueous corrosion can be evaluated; specifically, the temperature at which localized corrosion will begin or a passive oxide film will form. This enables new analysis methods to investigate stress corrosion cracking at higher temperature. Also, the possibility of studying the dissolution of MnS inclusion in a temperature range between room temperature and ~90°C.

- **Modification of reference electrode into E-chip**

  The prerequisite for a reference electrode is stability in the electrolyte over time. In particular, the ability to create an Ag/AgCl electrode into an E-chip would open up new regimes for elevated temperature experiments. The idea is to replace the Pt-reference electrode through an Ag/AgCl, by sputtering Ag into a micro-machined “gap” in the Si-chip and filling it with *Agar-Agar gel* inspired by miniature Ag/AgCl reference electrode by the company *ALS Japan*.

- **Work with low-melting point metals**

  Another idea, which has the benefit of being compatible with existing, unmodified holder, is to use various low-melting point metals. For example, a Cerrelow 117 (47.5°C melting
point) could be mounted between two E-chips and sealed, and this could be used to “bracket” the temperature inside the cell. Ga may also be utilised in this way, as it has a very low melting point (~30°C). However, there are increased health and safety concerns associated with the use Ga, to work around this, a “completed” cell could contain a very small amount of Ga alongside a small amount of the Bi-alloy. These chips could be used as a standard calibration for melting points between 30°C to 80°C. These “sealed” chips would mean the user subsequently only needed to load the “cell” into the TEM of interest to determine the temperature. Particularly, if it is possible to generate some heat when the beam remains in an area for an hour.

- **Further experimentation with different solutions**

In the current work, the *in situ* technique has been tested with non-aggressive solution such as distilled H₂O and low-concentration acid, with the purpose of proving the concept, and to gain practice with the procedure of using E-Chips. The worst case is if SiNx windows of the E-chips rupturing inside the microscope during the experiments. The solution would be able access in the microscope and leading to the degradation of the electron column and source vacuum. However, for a better understanding of the complexity of a corrosion reaction, it would be necessary to use an aggressive solution, such as concentrated acid or alkaline chlorides.

- **Characterization of 304 Stainless Steel**

Further examination of the microstructure of CW304 SS would be desirable, in order to improve understanding of the material’s performance. A disadvantage with this is the considerable effort to manufacture a hybrid specimen, so future work would need to be clearly planned in advance, to determined what tests are required, and for what purpose. For example, the material’s dissolution reaction of inclusion was examined by XED over a 24 hour period, but electrochemical measurements could not be performed at the same time; to do this requires a second hybrid specimen.

To use the *in situ* electrochemical cell to examine galvanic corrosion of deformed 304 SS in H₂O to see if the martensite or deformation bands in austenite corrode preferentially to the
austenite grains. Does deformation-induced martensite oxidize preferentially to austenite under galvanic corrosion conditions (i.e., Pt mounting material for specimen).

Also conceivable to use the *in situ* technique to investigate the different zone such as base zone (BZ), heat affected zone (HAZ) and weld zone (WZ) of a weld joint. Conventional electrochemical investigation do not allowed the examination of single heterogeneities such as precipitation of second phase, formation of unmixed zone or recrystallization associated with weld joints. A hybrid specimen of HAZ could be prepared to investigate the critical corrosion behavior in different solution and correlate the *in situ* results with a microcell technique.
Chapter 12: APPENDIX

Applying Advanced Analytical In Situ TEM to Assess SCC “Precursor” Reactions in Austenitic Stainless Steel in H₂O

S. Schilling¹, M. G. Burke¹, X.L. Zhong¹, N.J. Zaluzec¹,²

¹Materials Performance Centre and Electron Microscopy Centre, School of Materials, University of Manchester, Manchester, M13 9PL, U.K.
²Electron Microscopy Center, NanoScience and Technology Division, Argonne National Laboratory, Argonne, IL 60439 USA

ABSTRACT

In Situ transmission electron microscopy has become an increasingly important and dynamic research area in materials science with the advent of unique microscope platforms and a range of specialized in situ specimen holders. In metals research the ability to image and perform X-ray energy dispersive spectroscopy (XEDS) analyses of metals in liquids are particularly important for studying the localized interaction of the environment with specific microstructural features in the alloy of interest.

In order to explore the reaction of MnS inclusions in H₂O, a technique to prepare electron-transparent specimens of austenitic stainless steel for use in a special liquid cell TEM specimen holder has been developed, and used to study the dissolution behaviour of MnS inclusions in austenitic stainless steel in an FEI Tecnai T20 Analytical Electron Microscope. The in situ TEM studies have been performed in parallel with bulk ex situ dissolution studies of MnS inclusions in Type 304 stainless steel during room temperature H₂O exposure. These results are interpreted in view of previous data concerning the effect of MnS on environmentally-assisted cracking behaviour of low alloy steels as well as recent results on the corrosion fatigue behaviour of austenitic stainless steels. The use of novel in situ liquid cell TEM approach can provide information on localized corrosion/oxidation reactions that can be helpful in identifying local microstructural features that can affect the “SCC Precursor” events ultimately leading to SCC initiation.
Keywords: In Situ TEM, Liquid Cell, Type 304SS, MnS inclusions, dissolution, microanalysis

1.0 INTRODUCTION

Stress Corrosion Cracking (SCC) is the premature failure resulting from the simultaneous actions of a stress (normally static and tensile) and a reactive environment on a susceptible metal/alloy. It is also well-known that SCC susceptibility of a material is affected by microstructure. For an active path mechanism cracking is caused by localized corrosion at the crack tip and processed along a path which is electrochemically active with respect to the surrounding metal. Hanninen et al. [1] reviewed three stages of SCC. The first stage, crack initiation, is followed by steady-state crack growth (propagation), and final failure. It can be difficult to separate these three stages because the SCC process appears to progress in a “continuous” manner. Staehle [2] has further described those events comprising SCC initiation: “precursor events”, SCC incubation that is generally not detectable, and formation of SCC “proto-cracks”. The initial material condition will also be important as there can be pre-existing surface features, such as inclusions in the alloy or localized deformation that can promote the development of “precursor events”. Nevertheless, it can be up to several decades until a crack actually forms. In particular, dissolution of MnS inclusions in low alloy steel was shown to be responsible for Environmentally-Assisted Cracking (EAC) in those steels. Recent research has also indicated that MnS inclusions may also be associated with low crack growth rates in austenitic stainless steels during certain conditions of corrosion fatigue in high temperature H2O environments [3], [4], [5].

James [5] and Tice [6] noted that the most important impurities within the low alloy steels are metallurgical sulphide inclusions, which dissolve in contact with high temperature water in case of environmental crack growth. Nevertheless, the correlations between S content and EAC susceptibility in low alloy steels are not simply a function of composition. Sulphide inclusion parameters such as the size, chemical composition, morphology or distribution are important factors in assessing the material susceptibility to EAC [7].

Considering this process from the corrosion perspective, several researchers have proposed the chemical and electrochemical mechanisms for the dissolution of sulphide inclusions and the initiation of localized corrosion. The mechanism of dissolution in aqueous medium has been described by Eklund [8]:

---

191 | P a g e
\[
\text{MnS} + 4\text{H}_2\text{O} = \text{Mn}^{2+} + \text{SO}_4^{2-} + 8\text{H}^+ + 8\text{e}^- \tag{1}
\]

\[
\text{MnS} + 2\text{H}^+ = \text{Mn}^{2+} + \text{H}_2\text{S} \tag{2}
\]

\[
\text{H}_2\text{S} = \text{S} + 2\text{H}^+ + 2\text{e}^- \tag{3}
\]

According to Wranglen [9], the anodic dissolution of MnS inclusion results in exposure of bare steel to the environment, where the preferential attack is between inclusion and active steel and based on the higher current density of the inclusion edge. The following mean dissolution reaction was proposed:

\[
\text{MnS} = \text{S} + \text{Mn}^{2+} + 2\text{e}^- \tag{4}
\]

Common methods to study localized corrosion are based on large-scale experiments with test surface areas in the mm\(^2\)–cm\(^2\) range. It is also important to study the corrosion processes at the micro- and nanometer range to understand the mechanisms of interaction between specific microstructural features and steel matrix in the environment of interest. Using the novel liquid \textit{in situ} TEM method, it is possible to develop an improved understanding of localized reactions in order to investigate processes such as the initiation of a pit through the dissolution of inclusions and the localized corrosion that could lead to proto-crack formation.

### 2.0 EXPERIMENTAL PROCEDURE

The composition of the high S (0.03 wt. %) Type 304 stainless steel used for these experiments is listed in Table 1. The experimental techniques for \textit{in situ} and \textit{ex situ} experiments are described in the following sections.

#### 2.1 Liquid Cell Analytical \textit{In Situ} TEM – FIB specimen preparation

The TEM specimen preparation was performed by a conventional focused ion beam (FIB) “lift-out” technique using an FEI Quanta 3D field emission gun (FEG) FIB - scanning electron microscope (SEM). The MnS inclusions were then “cut out” from Type 304 stainless steel plate with 0.03 wt.% S, using the Ga ion beam and placed on a Cu grid for subsequent FIB “thinning” to produce an electron-transparent sample. The electron-transparent FIB specimen was then placed on a Protochips Environmental Chip (E-Chip) and “attached” using Pt. The specimen in between the top and bottom chip was then sealed from the environment with a 500 nm gap like a sandwich configuration.
The Protochips liquid cell windows are made from 50 nm thick amorphous SiN$_X$ membranes deposited onto 300 micron-thick Si wafers, which are fabricated into E-Chips. Electrons can pass through the sealed thin layer of liquid sandwiched like configuration between these two ultra-thin SiN$_X$ membranes in which the specimen is immersed in the liquid. A modified specimen holder was used for optimized XEDS microanalysis.

The *in situ* experiments were performed using the special Protochips Poseidon P210 liquid cell TEM specimen holder and an FEI Tecnai T20 analytical transmission electron microscope operated at 200 kV and equipped with an Oxford Instruments X-Max$^N$ 80TLE windowless Silicon Drift Detector (SDD) for XED spectrum imaging and an AZTEC analyser.

2.2 *Ex situ* specimen preparation

For the *ex situ* - bulk specimen investigation, the specimen was mechanically ground with SiC paper to 4000 grit, and polished with a 1µm water-based diamond suspension. In order to simulate the FIB-prepared specimen configuration for the *in situ* experiments, which had used a Pt-deposited surface layer as the “cap” over the extracted (and thinned) FIB “lift-out” specimen, a 100µm Platinum (Pt)-line was sputtered with an FEI Quanta 3D FEG FIB-SEM next to MnS inclusions on the as-polished surface. This bulk specimen was subsequently exposed in distilled H$_2$O for 8 days.

A Zeiss Merlin FEG-SEM equipped with two Oxford Instruments X-Max$^N$ 150 SDDs was used for the characterisation of the bulk specimen prior to and after exposure of the sample in H$_2$O. The Keyence Laser Scanning Confocal Microscope VHX 210 was used to assess the depth of inclusion dissolution for the bulk specimens after exposure in distilled H$_2$O.

The potentiodynamic polarisation measurements were performed on bulk specimens using a Gamry 600 potentiostat. The specimen surface was polished with a water-based 1µm diamond suspension prior to measurements. The tests were performed in distilled H$_2$O with pH=5.5 at 20±1°C. A silver-silver chloride electrode (Ag/AgCl) reference electrode and a platinum wire counter electrode were used.
3.0 RESULTS AND DISCUSSION

3.1 In situ Observations

A region of the Type 304 SS bulk metallographically-polished sample that contained MnS inclusions was identified using secondary electron imaging, and selected for FIB cross-section specimen preparation. After extracting a “lamella” containing MnS inclusions, the sample was “welded” on to a Cu grid, and further thinned using the Ga ion beam to obtain an electron-transparent specimen. This thinned specimen was subsequently positioned on to the E-chip, so that the MnS inclusions were located between the top and bottom SiNx windows. Figure 2 shows the in situ observation of BF-STEM and XED spectrum images of the MnS inclusion before treatment and after 24h exposure time in distilled H$_2$O at room temperature. From the XED analysis it was found that the Mn and S content are totally dissolved. Also it shows that the single inclusion is a pure MnS inclusion due to the missing Fe content at the XED spectra.

3.2 Ex situ Observations

The relevance of the in situ observations were confirmed by ex situ exposure of a bulk sample containing a Pt line sputtered next to MnS inclusions (to simulate the Pt-coated FIB section). Due to the noble potential of Pt compared to the MnS inclusion, to accelerate the reaction of dissolution, consequently Pt acts as a support of galvanic corrosion. The FEG-SEM XED spectrum images obtained from a bulk specimen containing MnS inclusions are shown in Fig. 3a; the same area after 8 days in deionised H$_2$O is shown in Fig. 3b.

At the same position of the dissolved MnS inclusions, Oxygen is detected because the resulting pitting oxidizes the surface of the pit.

Figure 4 shows the Laser Scanning Confocal microscope images obtained before and after 8 days exposure in distilled water and it shows also the height different measurements of the MnS inclusion and steel matrix. The inclusions outside of the Pt-sputtered area have totally dissolved, but the MnS inclusions adjacent to the deposited Pt-line are covered with a thin layer of Pt due to the nature of the electron-beam sputter deposition process. This has the consequence that MnS inclusions are insulated from the environment. This can be observed in Figure 3 (e)-(h), which clearly shows that the “protected” inclusions have not been exposed to H$_2$O. XED analysis of those regions demonstrated the presence of Pt. The height difference between pit and matrix was approximately 1µm after 8 days exposure. It has
previously been shown that the dissolution of sulphide inclusions can depend on their chemical composition. The presence of various sulphide inclusions, such as MnS, FeS, or a homogeneous MnFeS can impact the local chemical or electrochemical reactions occurring at the inclusion/steel matrix/electrolyte interface [3], [10]. Further FEG-SEM evaluation of the *ex situ* specimen revealed such partial dissolution of shallow inclusions after the H$_2$O exposure, as shown in the secondary electron image in Figure 5 (a). Note the pronounced dissolution at the inclusion-metal interface in Figure 5.

Electrochemical measurements were also performed on bulk specimens to evaluate the influence of environment on the MnS dissolution and subsequent pit initiation, which will affect the cracking potential. Figure 6 shows the free corrosion potential curve of a conventional bulk specimen (*ex situ*). The OCP value was approx. -110mV versus Ag/AgCl. Despite the low electrical conductivity of distilled H$_2$O (20 dS/m), a potentiodynamic polarization curve could be measured on a high sulphur 304SS plate (see Figure 7). With respect to SCC susceptibility, the curve permits the identification of the range of critical potentials where the alloy is usually active, passive and transpassive to quantitatively indicate the SCC cracking risk [1]. The electrochemical dissolution of MnS inclusions and steel matrix occurs between 600 and 800mV (Ag/AgCl).

**4.0 CONCLUSIONS**

This work represents the first demonstration of *in situ* liquid cell TEM imaging and STEM-XED microanalysis/spectrum imaging documenting MnS dissolution in distilled H$_2$O at room temperature. *In situ* and *ex situ* experiments showed that dissolution of MnS inclusions can readily occur in distilled H$_2$O at room temperature in stainless steel. The agreement between the *ex situ* and *in situ* results demonstrate that the liquid cell observations are valid, and not affected by the electron beam.

Also the present *ex situ* observations support previous work demonstrating that MnS inclusion dissolution in high temperature H$_2$O in low alloy steels is associated with Environmentally-Assisted Cracking [3]. Furthermore, recent research has also indicated that MnS inclusions may also be associated with SCC as well as reduced crack growth rates in austenitic stainless steels during certain conditions of corrosion fatigue in primary water environments.
The recent advances in microanalytical and microstructural techniques such as the development of unique in situ platforms enables previously “impossible” environments (such as liquids) to be used for the study of localized reactions in materials. The combination of electrochemistry and electron microscopy can provide unique future opportunities for the study of SCC “precursor” phenomena.

5.0 ACKNOWLEDGEMENTS

Financial support for this research was provided by the EPSRC PROMINENT Programme. The authors also gratefully acknowledge support from Dr. M.A. Kulzick of BP.
REFERENCES


Table 1: Chemical Composition (wt.%) of High Sulphur Type 304SS

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>P</th>
<th>Mo</th>
<th>S</th>
<th>Fe</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.029</td>
<td>0.20</td>
<td>1.25</td>
<td>18.34</td>
<td>8.00</td>
<td>0.032</td>
<td>0.38</td>
<td>0.031</td>
<td>71.64</td>
<td>0.39</td>
</tr>
</tbody>
</table>

Figure 1: FEG-SEM image of the FIB-prepared specimen containing two MnS inclusions attached to the E-Chip.
**Figure 2**: In situ analytical TEM experiment: (a)-(d) Bright-field STEM and corresponding XED spectrum images for Fe, Mn, and S, respectively obtained from a MnS inclusion (FIB-prepared specimen) in 1 atm air, and (e)-(h) after 24h exposure in distilled H$_2$O.

**Figure 3**: Secondary electron and corresponding XED spectrum images for Mn, S, and O, respectively, of MnS inclusions in the bulk 304 SS specimen (a)-(d) before, and (e)-(h) after the *ex situ* 8 day exposure in distilled H$_2$O. Note: the only MnS inclusions still observed were those covered with a thin layer of Pt (associated with the Pt-deposited marker).
**Figure 4**: Laser Scanning Confocal Microscope images of MnS inclusions (a) before and (b) after 8 days exposure in $\text{H}_2\text{O}$.

**Figure 5**: Secondary electron images of MnS inclusions after 8 days exposure in distilled $\text{H}_2\text{O}$.
Figure 6: The variation of OCP as a function of time for bulk *ex situ* samples of the high S Type 304 SS in distilled H$_2$O.

Figure 7: *Ex Situ* - Potentiodynamic polarisation curve of high S Type 304SS in distilled H$_2$O (vs. Ag/AgCl reference).
In situ transmission electron microscopy (TEM) has become an increasingly important research area in materials science with the advent of unique microscope platforms and a range of specialized in situ specimen holders. The ability to image and perform X-ray energy dispersive spectroscopy (XEDS) analyses of metals in liquids are particularly important for detailed study of the metal-environment interactions with specific microstructural features. In particular, these capabilities now make it feasible to explore what has been termed “SCC precursor phenomena” – that is, those sub-micron scale reactions between an alloy of interest and the environment. This topic is especially timely for this Swann Memorial Symposium, as Peter Swann’s activities in this area, particularly in the 1970’s concerning the initiation and early stages of transgranular SCC in austenitic stainless steels, were clearly prescient. In this study, we have used liquid cell TEM with XEDS to explore the “precursor phenomena” that can promote the development of defect initiation in Type 304 austenitic stainless steel. For this work, the FIB lift-out technique was used to extract specimens to be studied in the liquid cell TEM specimen holder. This technique has been applied to examine the localized dissolution of MnS inclusions, which can lead to pit initiation.

FIB sections containing MnS inclusions were prepared from a 0.3 wt.% S Type 304 stainless steel for study in a Protochips Poseidon P210 liquid cell and P510 electrochemical cell in situ specimen holders with a 500 nm gap between the amorphous SiNx windows. Based on initial tests, the electrochemical Echip configuration was modified to optimize it for electrochemical measurements. The in situ experiments were performed in an FEI Tecnai T20 analytical
electron microscope operated at 200 kV and equipped with an Oxford Instruments X-MaxN 80TLE Silicon Drift Detector (SDD) for spectrum imaging and analysis. A Zeiss Merlin FEG-SEM equipped with two Oxford Instruments X-MaxN 150 SDDs was used to analyse the bulk samples from the ex situ tests. MnS XED spectrum images in 1 bar air and after 24 h in deionised H₂O in the P210 are shown in Fig. 1, and the XED sum spectrum obtained after dissolution is presented in Fig. 2. The relevance of the in situ observations were confirmed by ex situ exposure of a bulk sample containing a Pt line sputtered next to MnS inclusions (to simulate the Pt coated FIB section) since Pt would support galvanic corrosion, and possibly accelerate the dissolution rate [1]. XED spectrum images obtained from a bulk specimen containing MnS inclusions are shown in Fig. 3a; the same area after 8 days in deionised H₂O is shown in Fig. 3b. Both ex situ (Fig. 4) and in situ electrochemical polarisation data will be discussed with respect to localized corrosion.

Dissolution of MnS inclusions in low alloy steels is associated with Environmentally-Assisted Cracking [2]. Recent research has also indicated that MnS inclusions may also be associated with SCC as well as low crack growth rates in austenitic stainless steels during certain conditions of corrosion fatigue in primary H₂O environments in light water reactors.

References:


[3] The authors acknowledge the support of Dr. M.A. Kulzick and BP, and EPSRC PROMINENT programmes (EP/ 1003290/1), also supported in part by the U.S. DoE, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357 at the Electron Microscopy Center, NST Division of ANL..
Fig. 1: BF-STEM and XED spectrum images of MnS Inclusion in E-cell: a) 1 bar air; b) after 24 h in H₂O showing dissolution of MnS during *in situ* exposure in H₂O.

Fig. 2: XED Sum Spectrum from region containing the dissolved MnS inclusion after exposure in H₂O.
Fig. 3: Ex situ observations: SE and XEDS spectrum images of MnS inclusions: a) 0 days; b) 8 days in H$_2$O. Note the dissolution of the large MnS inclusions above the Pt strip whereas the inclusions covered by sputtered Pt remain intact.

Fig. 4: Polarisation data for Type 304 stainless steel in H$_2$O using conventional bulk samples.
Novel Hybrid Sample Preparation Method for In Situ Liquid Cell TEM Analysis

X. Zhong¹, M. G. Burke¹, S. Schilling¹, S. J. Haigh¹, M. A. Kulzick² and N. J. Zaluzec¹,³

¹Materials Performance Centre, University of Manchester, Manchester M13 9PL, UK
²BP Research Center, Naperville, IL 60563 USA
³Electron Microscopy Center, Argonne National Laboratory, Argonne, IL 60439 USA

In situ environmental transmission electron microscopy (TEM) research has increased dramatically in recent years [1-3]. However, due to the difficulty in sample preparation, liquid environmental TEM studies have been limited to materials such as nanoparticles or nanowires [3-5]. To date, no work has been reported on conventional metals/alloys in liquid environment. This is due to the significant difficulty in preparation of suitable “bulk” metal specimens that are compatible with the requirements of the liquid cell in situ specimen holders. We demonstrate a new sample preparation method for the in situ liquid cell TEM study of cold-rolled Type 304 austenitic stainless steel. The proposed new procedure takes advantage of electropolishing and focused ion beam (FIB) sample preparation techniques to extract large electron-transparent site-specific areas with minimum contamination. The liquid cell TEM holder used in these experiments was a Protochips Poseidon 200 liquid cell system, but this novel method can be extended as a general procedure applicable to other types of in situ environmental (E)-TEM studies.

The initial specimens were 3 mm diameter discs that had been mechanically thinned to ~150 μm prior to conventional twin-jet electropolishing using Struers TenuPol-5 with an electrolyte of 20% HClO₄ - 80% CH₃OH at 20 V and -30±2°C. The thin-foil samples were subsequently examined in an FEI Tecnai F30 field emission gun (FEG) analytical electron microscope (AEM) operated at 300 kV to identify suitable electron-transparent areas. The specimens were then mounted on to a STEM sample holder for imaging in a FEI Quanta 3D
dual beam FIB. The thin area-of-interest suitable for *in situ* TEM was located using the STEM image. After confirming the suitable area-of-interest, the sample was tilted to 52 degrees towards ion column and the area was “cut out” using the Ga ion beam at 30 kV and 3-30 nA. The “cut out” area was relatively large (~100 μm x 100 μm) to ensure that the central electron-transparent area was not damaged by the Ga ion beam during cutting.

Two methods of placing the FIB “cut” sample onto the TEM window cell were developed. The first method utilises the electrostatic attraction between the epoxy-coated OmniProbe tip inside the FIB (Fig. 1). Prior to coating, the OmniProbe tip was cleaned using the ion beam (3 nA probe current for 5 min). The epoxy coating was applied externally (outside of the FIB) by dipping the tip into a commercial “superglue”. The coated OmniProbe tip had a greater attraction to the sample and provided an effective tool by which the sample could be picked up from the “cut” area and placed on to the liquid E-cell window without the need for attachment using Pt welding/deposition.

The second approach is termed ‘cut-and-place’. The thin area of interest was again “cut out” from the electropolished thin-foil specimen in the FIB (3-30 nA 30 kV ion beam) and then welded on to the OmniProbe tip. The “extracted” electron-transparent section was then welded onto the wall of the liquid cell window using a small area of Pt (~1μm x 3μm) and the tip cut free, (Fig. 2). The sample is slightly offset with respect to the window in order to avoid possible redeposition, overcutting, and damage to the cell window.

*In situ* liquid cell environmental TEM observation of the extracted electropolished specimen immersed in H₂O revealed the formation crystalline deposits and oxides in water with time (Fig. 3). These experimental results demonstrate the successful development of a new hybrid electrochemical-FIB sample preparation method for the environmental TEM dynamic observation of metal in a liquid water environment. The principle of this hybrid TEM sample preparation procedure can be used to prepare samples for other unique *in situ* environmental TEM experiments including *in situ* spectroscopy [6].

**References:**


Figure 1. Epoxy-coated manipulator approach: (a) manipulator tip surface prepared for epoxy coating with 3nA ion beam, (b) area of interest is cut free and lifted by electrostatic force (DF-STEM image), (c) sample placed on TEM liquid cell window, (d) BF-STEM image of “cut” area of interest.

Figure 2. ‘Cut-and-Paste’ approach. FIB images: (a) DF-STEM image of electropolished foil, (b) BF-STEM image of “cut” sample, (c) “cut” sample placed on TEM liquid cell window.
Figure 3. Liquid environment TEM demonstration: (a) low magnification TEM image of hybrid prepared sample on liquid cell window (400 μm x 50 μm), (b) TEM image of sample (no water), (c) sample in liquid H2O with crystalline deposit formed during exposure under the electron beam.
BIBLIOGRAPHY


---

215 | Page


D. Tice, N. Platts, K. Rigby and J. Stairmand, “Influence of temperature and flow rate on the corrosion fatigue crack growth of austenitic stainless steel in a PWR primary coolant environment”, *in Proc. of the 13th International conference on environmental corrosion*
degradation of materials in nuclear power systems; Whistler, BC (Canada); (2007), p.16.


