An Investigation into the Corrosion Fatigue Behaviour of High Strength Carbon Steel Tensile Armour Wires

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

Doctor of Philosophy

in the Faculty of Engineering and Physical Sciences

2014

Peter Barnes

The School of Materials
Table of Contents

List of Tables ........................................................................................................... 3
List of Figures ........................................................................................................... 5
Abbreviations ........................................................................................................... 12
Abstract .................................................................................................................... 14
Declaration ............................................................................................................... 16
Copyright ................................................................................................................ 17
Acknowledgement .................................................................................................. 18
Chapter 1 Introduction ............................................................................................ 19

1. Introduction .......................................................................................................... 20
   1.1 Flexible Risers ................................................................................................ 20
      1.1.1 Flexible Riser Structure ....................................................................... 20
      1.1.2 Failure Modes ...................................................................................... 21
      1.1.3 Testing and Qualification ..................................................................... 23
      1.1.4 Summary .............................................................................................. 26
   1.2 Aims & Objectives ........................................................................................ 26

Chapter 2 Literature Review .................................................................................... 28

2. Literature Review ................................................................................................ 29
   2.1 Cold Drawn Steel Wire ................................................................................. 29
   2.2 Corrosion of Carbon Steel .......................................................................... 32
      2.2.1 Introduction ........................................................................................ 32
      2.2.2 Electrochemistry .................................................................................. 32
      2.2.3 Environment ......................................................................................... 37
      2.2.4 Types of Corrosion .............................................................................. 41
   2.3 Corrosion Fatigue ........................................................................................ 43
      2.3.1 Introduction ........................................................................................ 43
      2.3.2 The Fatigue Process ............................................................................ 45
      2.3.3 Corrosion Fatigue ............................................................................... 48
      2.3.4 Fatigue Crack Initiation in Cold Drawn Carbon Steel Wire ............... 55
   2.4 Residual Stress .............................................................................................. 56
      2.4.1 X-ray Diffraction Stress Measurement .............................................. 58
   2.5 Surface Strain Mapping ................................................................................ 61

Chapter 3 Corrosion Fatigue Cracking .................................................................... 64

3. Corrosion Fatigue Cracking ................................................................................ 65
   3.1 Introduction .................................................................................................. 65
   3.2 Corrosion Fatigue Testing .......................................................................... 65
   3.3 Experimental Methods ................................................................................. 71
      3.3.1 Material Characterisation .................................................................... 71
      3.3.2 Sample Preparation ............................................................................. 72
      3.3.3 Crack & Pit Depth Measurement .......................................................... 72
      3.3.4 Crack & Pit Depth Analysis ................................................................ 73

2
3.3.5 Corrosion Behaviour & Surface Scale Formation ............................................. 76
3.4 Material Characterisation .................................................................................. 81
  3.4.1 Chemical Composition ............................................................................... 81
  3.4.2 Tensile Testing .......................................................................................... 81
  3.4.3 Microstructure .......................................................................................... 82
3.5 Secondary Cracks and Localised Corrosion ...................................................... 84
  3.5.1 12 mm x 4 mm High Strength Steel Wire .................................................. 84
  3.5.2 12 mm x 7 mm High Strength Steel Wire .................................................. 95
  3.5.3 Secondary Crack and Corrosion Pit Population Comparison .................... 107
3.6 Surface Scale Formation .................................................................................. 114
  3.6.1 Aerated Seawater Environment ................................................................ 114
  3.6.2 CO₂ Saturated Seawater Environment ..................................................... 119
  3.6.3 100 mbar absolute H₂S/CO₂ Balance to 1 bar absolute Seawater Environment ................................................................. 122

Chapter 4 Residual Stress .................................................................................... 124
  4. Residual Stress ................................................................................................ 125
    4.1 Introduction ................................................................................................ 125
    4.2 Experimental Methods ............................................................................. 125
      4.2.1 Test Methodology ................................................................................ 125
      4.2.2 Through Thickness Measurements ................................................. 126
      4.2.3 Surface Measurements ..................................................................... 127
    4.3 Through Thickness Residual Stress Measurements ................................... 128
    4.4 Surface Measurements ............................................................................ 135
      4.4.1 Corrosion Fatigue Tested High Strength Steel Wire ......................... 136
      4.4.2 Fatigue in Air ..................................................................................... 143

Chapter 5 Surface Strain Mapping ..................................................................... 146
  5. Surface Strain Mapping .................................................................................. 147
    5.1 Introduction .............................................................................................. 147
    5.2 Experimental Methods ............................................................................. 147
      5.2.1 Slow Strain Rate Test Rig ................................................................. 147
      5.2.2 Artificial Pit Growth ........................................................................... 149
      5.2.3 Stable Surface Oxide ....................................................................... 156
      5.2.4 Surface Strain Mapping ................................................................. 157
    5.3 Results ...................................................................................................... 160
      5.3.1 Initial SSRT Tests ............................................................................. 160
      5.3.2 Localised Strain Analysis ................................................................. 162

Chapter 6 Discussion ......................................................................................... 177
  6. Discussion ...................................................................................................... 178
    6.1 Corrosion Fatigue Cracking ..................................................................... 178
    6.2 Residual Stress ........................................................................................ 186
    6.3 Surface Strain Mapping ........................................................................... 189

Chapter 7 Conclusions ...................................................................................... 192
  7. Conclusions .................................................................................................. 193

Chapter 8 Future Work ...................................................................................... 196
  8. Future Work .................................................................................................. 197
    8.1 The effects of chloride and iron ion concentration on the corrosion fatigue behaviour of high strength steel tensile armour wire .................................................. 197
    8.2 Corrosion fatigue testing at elevated temperatures .................................. 197
    8.3 Corrosion fatigue testing at elevated pressures ........................................ 197
8.4 The use of electrochemical noise techniques for detecting or quantifying/measuring failure points ................................................................. 198
8.5 Exploring the development of plastic strain fields during the fatigue process using etching reagents................................................................. 198

Appendices........................................................................................................ 199
1. Initial Sample Review of 12 mm x 4 mm High Strength Steel Wire .............. 200
2. Chemical Composition Test Certificate .......................................................... 204
3. Preparation of Substitute Ocean Water............................................................ 205
4. General Arrangement and Detail Drawings of Slow Strain Rate Test Rig........ 208
5. Detailed Drawing of Slow Strain Rate Test Sample Grips............................... 211
6. Detailed Drawings of Slow Strain Rate Test Samples.................................... 212

References ........................................................................................................ 213
List of Tables

Table 1-1: Examples of flexible riser failure modes for various oilfields [11].......................... 22
Table 2-1: Composition of ASTM D1141 substitute ocean water [54]............................... 38
Table 3-1: 12 mm x 4 mm high strength steel wire corrosion fatigue test data for an aerated seawater environment ................................................................. 68
Table 3-2: 12 mm x 4 mm high strength steel wire corrosion fatigue test data for a \( \text{CO}_2 \) saturated seawater environment ................................................................. 68
Table 3-3: 12 mm x 7 mm high strength steel wire corrosion fatigue test data for an aerated seawater environment ................................................................. 69
Table 3-4: 12 mm x 7 mm high strength steel wire corrosion fatigue test data for a \( \text{CO}_2 \) saturated seawater environment ................................................................. 69
Table 3-5: 12 mm x 7 mm high strength steel wire corrosion fatigue test data for 100 mbar absolute \( \text{H}_2\text{S} \) with \( \text{CO}_2 \) balance seawater environment ...................................................... 70
Table 3-6: Grinding and polishing stages .............................................................................. 72
Table 3-7: Cross sectional areas of the 3 different high strength carbon steel wires .......... 78
Table 3-8: Chemical composition of high strength steel wire ............................................... 81
Table 3-9: High strength carbon steel wire mechanical properties ...................................... 81
Table 3-10: Manufacturer rating for the high strength steel wires ....................................... 82
Table 3-11: Corrosion fatigue cracking data for the 12 mm x 4 mm high strength steel wire in an aerated seawater environment .................................................... 84
Table 3-12: Corrosion fatigue cracking data for the 12 mm x 4 mm high strength steel wire in a \( \text{CO}_2 \) saturated seawater environment ................................................................. 84
Table 3-13: Localised corrosion pitting data for the 12 mm x 4 mm high strength steel wire in an aerated seawater environment .................................................... 89
Table 3-14: Localised corrosion pitting data for the 12 mm x 4 mm high strength steel wire in a \( \text{CO}_2 \) saturated seawater environment ................................................................. 89
Table 3-15: Corrosion fatigue cracking data for the 12 mm x 7 mm high strength steel wire in an aerated seawater environment .................................................... 95
Table 3-16: Corrosion fatigue cracking data for the 12 mm x 7 mm high strength steel wire in a \( \text{CO}_2 \) saturated seawater environment ................................................................. 95
Table 3-17: Corrosion fatigue cracking data for the 12 mm x 7 mm high strength steel in a 100 mbar absolute \( \text{H}_2\text{S} \) with \( \text{CO}_2 \) balance seawater environment ...................................................... 95
Table 3-18: Localised corrosion pitting data for the 12 mm x 7 mm high strength steel wire in an aerated seawater environment .................................................... 100
Table 3-19: Localised corrosion pitting data for the 12 mm x 7 mm high strength steel wire in a CO₂ saturated seawater environment

Table 3-20: Localised corrosion pitting data for the 12 mm x 7 mm high strength steel wire in a 100 mbar absolute H₂S with CO₂ balance seawater environment

Table 4-1: Recommended X-ray tube and \{hkl\} plane for Ferrite, reproduced from [126]

Table 4-2: 12 mm x 4 mm high strength steel wire corrosion fatigue tested samples chosen for through thickness residual stress measurement

Table 4-3: Example of the surface residual stress measurements and log cycles to failure values for 12 mm x 4 mm high strength steel wire corrosion fatigue tested in an aerated seawater environment

Table 4-4: Fatigue in air applied stress values

Table 5-1: Chemical composition of 0.1 M sodium carbonate-bicarbonate-chloride solution

Table A3-1: Stock Solution No. 1

Table A3-2: Stock Solution No. 2

Table A3-3: Chemical composition of substitute ocean water
List of Figures

Figure 1-1: The internal structure of an unbonded flexible pipe [2] ................................................................. 21
Figure 2-1: Fe-C phase diagram [27] .................................................................................................................. 29
Figure 2-2: Pearlite microstructure example [29] .............................................................................................. 30
Figure 2-3: Three different spatial arrangements of pearlite lamellar [35] ....................................................... 31
Figure 2-4: Typical example of iron corrosion in water ....................................................................................... 33
Figure 2-5: Typical Pourbaix diagram for iron at 25°C, reproduced from [48] .................................................... 34
Figure 2-6: Electrochemical Cell Set Up ........................................................................................................... 35
Figure 2-7: Example of the three-working electrode set up ............................................................................. 35
Figure 2-8: Example of a Tafel plot .................................................................................................................. 36
Figure 2-9: Potential-pH diagram for MnS-H2O-Cl from [69] ........................................................................ 42
Figure 2-10: A schematic of pitting and mesa attack [64] .............................................................................. 43
Figure 2-11: Typical S-N curve for steel in two environments [48] ................................................................. 45
Figure 2-12: Example of the slip systems in bcc structure [27] ...................................................................... 46
Figure 2-13: Fatigue damage accumulation stages (a) persistent slip band formation [79], (b) Intrusion and extrusion formation (Wood 1956) from [84] and (c) Surface profile of intrusions and extrusions [79] .............................................................................................. 47
Figure 2-14: Typical example of a fatigue crack growth rate curve from [81] .................................................. 48
Figure 2-15: Schematic of corrosion fatigue cracking behaviour from [81] ..................................................... 49
Figure 2-16: A schematic of surface film breakdown from slip band protrusion [84] ................................. 50
Figure 2-17: A schematic of corrosion fatigue crack growth curve [88] ....................................................... 53
Figure 2-18: A schematic of the corrosion fatigue crack environment[96] ................................................................ 55
Figure 2-19: Diffraction of X-rays by planes of atoms from [125] ................................................................. 59
Figure 2-20: Typical schematic of a portable stress measuring system from [126] ................................. 59
Figure 2-21: Example of the linear dependence of the d(211) upon sin2ψ .................................................. 61
Figure 2-22: Example of the elliptical fit of the d(211) upon sin2ψ showing the presence of a shear stress .............................................................................................................................. 61
Figure 2-23: Schematic of the stages of digital image correlation [130] .......................................................... 63
Figure 3-1: Corrosion fatigue testing rig ........................................................................................................ 67
Figure 3-2: 12 mm x 4 mm high strength steel wire corrosion fatigue tested S-N curve statistical data points .......................................................................................................................................................... 70
Figure 3-3: 12 mm x 7 mm high strength steel wire corrosion fatigue tested S-N curve statistical data points .................................................. 71

Figure 3-4: Optical microscope image showing a typical example of secondary cracks initiating at the surface of the high strength steel. .......................................................... 73

Figure 3-5: Relationship between distribution function, F(x), and random variable x (pit depth) ......................................................................................................................... 74

Figure 3-6: Relationship between normalised variable, y, and random variable x (pit depth) .......................................................... 75

Figure 3-7: Tensile test curve for the 12 mm x 4 mm high strength steel wire ........................................... 82

Figure 3-8: Optical micrographs of the 12 mm x 4 mm high strength carbon steel wire (a) Normal plane (b) Transverse plane ................................................................................ 83

Figure 3-9: Optical micrographs of the 12 mm x 7 mm high strength carbon steel wire (a) Normal plane (b) Transverse plane ................................................................................ 83

Figure 3-10: Optical micrographs of the 10 mm x 5 mm high strength carbon steel wire (a) Normal plane (b) Transverse plane ................................................................................ 83

Figure 3-11: No. of secondary cracks versus applied stress for the 12 mm x 4 mm high strength steel wire in the two different seawater environments ........................................... 85

Figure 3-12: Probability plot for corrosion fatigue cracking data for the 12 mm x 4 mm high strength steel wire in an aerated seawater environment ........................................... 86

Figure 3-13: Probability plots for corrosion fatigue cracking data for the 12 mm x 4 mm high strength steel wire in a CO2 saturated seawater environment at numerous applied stress; (a) 428 MPa, (b) 367 MPa, (c) 275 MPa, (d) 214 MPa .......................................................... 87

Figure 3-14: Probability plot for corrosion fatigue cracking data for the 12 mm x 4 mm high strength steel wire in a CO2 saturated seawater environment ........................................... 87

Figure 3-15: Geometric mean crack depth versus applied stress versus no. of secondary cracks for the 12 mm x 4 mm high strength steel wire in a CO2 saturated seawater environment .................................................................................. 88

Figure 3-16: No. of localised corrosion pits versus applied stress for the 12 mm x 4 mm high strength steel wire in the two different seawater environments ........................................... 89

Figure 3-17: Probability plots for corrosion fatigue localised pitting data for the 12 mm x 4 mm high strength steel wire in an aerated seawater environment; (a) 428 MPa, (b) 244 MPa, (c) 183 MPa, (d) 153 MPa, (e) 107 MPa .......................................................... 90

Figure 3-18: Geometric mean pit depth versus applied stress versus no. of corrosion pits for the 12 mm x 4 mm high strength steel wire in an aerated seawater environment .......... 91

Figure 3-19: Probability plot for corrosion fatigue localised pitting data for the 12 mm x 4 mm high strength steel wire in an aerated seawater environment ........................................... 92

Figure 3-20: Probability plots for corrosion fatigue localised pitting data for the 12 mm x 4 mm high strength steel wire in a CO2 saturated seawater environment; (a) 428 MPa, (b) 367 MPa, (c) 275 MPa, (d) 214 MPa .......................................................... 93

Figure 3-21: Probability plot for corrosion fatigue localised pitting data for the 12 mm x 4 mm high strength steel wire in a CO2 saturated seawater environment ........................................... 93
Figure 3-22: Geometric mean pit depth versus applied stress versus no. of corrosion pits for the 12 mm x 4 mm high strength steel wire in a CO₂ saturated seawater environment... 94

Figure 3-23: No. of secondary cracks versus applied stress for the 12 mm x 7 mm high strength steel wire in the three different seawater environments............................................. 96

Figure 3-24: Probability plot for corrosion fatigue cracking data for the 12 mm x 7 mm high strength steel wire in an aerated seawater environment............................................. 97

Figure 3-25: Probability plots for corrosion fatigue cracking data for the 12 mm x 7 mm high strength steel wire in a CO₂ saturated seawater environment at numerous applied stress; 
(a) 329 MPa, (b) 201 MPa ........................................................................................................ 98

Figure 3-26: Probability plot for corrosion fatigue cracking data for the 12 mm x 7 mm high strength steel wire in CO₂ saturated seawater environment......................................... 98

Figure 3-27: Probability plot for corrosion fatigue cracking data for the 12 mm x 7 mm high strength steel wire in a 100 mbar absolute H₂S with CO₂ balance seawater environment
.......................................................................................................................... 99

Figure 3-28: No. of localised corrosion pits versus applied stress for the 12 mm x 7 mm high strength steel wire in the two different seawater environments........................................ 101

Figure 3-29: Probability plots for corrosion fatigue localised pitting data for the 12 mm x 7 mm high strength steel wire in an aerated seawater environment; (a) 327 MPa, (b) 257 MPa, (c) 201 MPa, (d) 193 MPa, (e) 127 MPa...................................................................................... 102

Figure 3-30: Probability plot for corrosion fatigue pitting data for the 12 mm x 7 mm high strength steel wire in an aerated seawater environment............................................. 103

Figure 3-31: Probability plot for corrosion fatigue pitting data for the 12 mm x 7 mm high strength steel wire in a CO₂ saturated seawater environment......................................... 103

Figure 3-32: Probability plots for corrosion fatigue localised pitting data for the 12 mm x 7 mm high strength steel wire in a CO₂ saturated environment; (a) 327 MPa, (b) 257 MPa, 
(c) 201 MPa, (d) 193 MPa, (e) 127 MPa ...................................................................................... 104

Figure 3-33: Probability plots for corrosion fatigue pitting data for the 12 mm x 7 mm high strength steel wire in a 100 mbar absolute H₂S with CO₂ balance seawater environment; 
(a) 321 MPa, (b) 256 MPa, (c) 200 MPa ...................................................................................... 105

Figure 3-34: Probability plot for corrosion fatigue pitting data for the 12 mm x 7 mm high strength steel wire in a 100 mbar absolute H₂S with CO₂ balance seawater environment
.......................................................................................................................... 106

Figure 3-35: Applied stress range versus sample test piece number for both the 12 mm x 4 mm and 12 mm x 7 mm high strength steel wire in an aerated seawater environment 107

Figure 3-36: Applied stress range versus sample test piece number for both the 12 mm x 4 mm and 12 mm x 7 mm high strength steel wire in a CO₂ saturated seawater environment
.......................................................................................................................... 108

Figure 3-37: Applied stress range versus sample test piece number for both the 12 mm x 4 mm and 12 mm x 7 mm high strength steel wire in an H₂S test environment............. 108
Figure 3-38: SEM images of 12 mm x 4 mm high strength steel wire corrosion fatigue test sample fracture surfaces for two different seawater environments (a) Aerated, (b) CO\textsubscript{2} Saturated

Figure 3-39: SEM images of 12 mm x 7 mm high strength steel wire corrosion fatigue test sample fracture surfaces for three different seawater environments (a) Aerated, (b) CO\textsubscript{2} Saturated and (c) 100 mbar absolute H\textsubscript{2}S-CO\textsubscript{2} Balance

Figure 3-40: SEM image - Straight crack with crack widening by corrosion

Figure 3-41: SEM image - Straight crack with partial crack widening by corrosion

Figure 3-42: SEM images - Evidence of horizontal grain attack

Figure 3-43: SEM images - Evidence of short crack blunting

Figure 3-44: SEM images - Evidence of subsurface and undercutting corrosion pits

Figure 3-45: SEM images - evidence of crack bifurcation

Figure 3-46: 30 day corrosion rate test for 12 mm x 4 mm and 12 mm x 7 mm high strength steel wire corrosion tested in an aerated seawater environment

Figure 3-47: GIXRD plot for 12 mm x 4 mm high strength steel wire corrosion tested in an aerated seawater environment for (a) 15 Days (b) 30 Days

Figure 3-48: GIXRD plot for 12 mm x 7 mm high strength steel wire corrosion tested in an aerated seawater environment for (a) 15 Days (b) 30 Days

Figure 3-49: SEM image of the surface scale formation on high strength steel wire corrosion tested in aerated seawater

Figure 3-50: SEM images of the left hand side of Figure 3-49 consistent with the formation of iron oxide

Figure 3-51: SEM images of the right hand side of Figure 3-49 consistent with the formation of iron oxyhydroxide

Figure 3-52: Five-day corrosion rate test for 10 mm x 5 mm high strength steel wire corrosion tested in a CO\textsubscript{2} saturated seawater environment

Figure 3-53: Five-day oxygen concentration measurement in an electrochemical cell

Figure 3-54: SEM images of the surface scale formation on high strength steel wire corrosion tested in CO\textsubscript{2} saturated seawater

Figure 3-55: GIXRD plot for 10 mm x 5 mm high strength steel wire corrosion tested in a CO\textsubscript{2} saturated seawater environment

Figure 3-56: GIXRD plot for 12 mm x 7 mm high strength steel wire corrosion fatigue tested in a 100 mbar absolute H\textsubscript{2}S with CO\textsubscript{2} balance seawater environment

Figure 4-1: Example of a two point linear square map

Figure 4-2: Through thickness residual stress measurement of an as received sample of 12 mm x 4 mm high strength steel wire
Figure 4-3: Through thickness residual stress measurement of 12 mm x 4 mm high strength steel wire corrosion fatigue tested in an aerated seawater environment at an applied stress of 244 MPa. ..................................................................................................................130

Figure 4-4: Through thickness residual stress measurement of 12 mm x 4 mm high strength steel wire corrosion fatigue tested in a CO₂ saturated seawater environment at an applied stress of 214 MPa. ..................................................................................................................131

Figure 4-5: Through thickness residual stress measurement of 12 mm x 4 mm high strength steel wire corrosion fatigue tested in corrosion fatigue tested in a CO₂ saturated seawater environment at an applied stress of 275 MPa. ..................................................................................................................132

Figure 4-6: Through thickness residual stress measurement of all 12 mm x 4 mm high strength steel wires .............................................................................................................................133

Figure 4-7: Through thickness residual stress measurement of 10 mm x 5 mm high strength steel wire fatigue tested in air at an applied stress of 428 MPa. ..................................................134

Figure 4-8: Through thickness residual stress measurement of all 12 mm x 4 mm high strength steel wires including the 10 mm x 5 mm results. ..........................................................134

Figure 4-9: Surface residual stress measurements against log cycles to failure for 12 mm x 4 mm high strength steel wire corrosion fatigue tested in an aerated seawater environment ..........................................................................................................................137

Figure 4-10: Surface residual stress measurements against log cycles to failure for 12 mm x 4 mm high strength steel wire corrosion fatigue tested in a CO₂ saturated seawater environment ..........................................................................................................................138

Figure 4-11: Surface residual stress measurements against applied stress for 12 mm x 4 mm high strength steel wire corrosion fatigue tested in two different seawater environments ........................................................................................................................................138

Figure 4-12: Surface residual stress measurements against log cycles to failure for 12 mm x 7 mm high strength steel wire corrosion fatigue tested in an aerated seawater environment ........................................................................................................................................139

Figure 4-13: Surface residual stress measurements against log cycles to failure for 12 mm x 7 mm high strength steel wire corrosion fatigue tested in a CO₂ saturated seawater environment ........................................................................................................................................140

Figure 4-14: Surface residual stress measurements against log cycles to failure for 12 mm x 7 mm high strength steel wire corrosion fatigue tested in a seawater environment containing 100 mbar absolute H₂S/CO₂ Balance to 1 bar absolute ..........................................................................................................................141

Figure 4-15: Surface residual stress measurements against applied stress for 12 mm x 7 mm high strength steel wire corrosion fatigue tested in three different seawater environments ........................................................................................................................................142

Figure 4-16: Surface residual stress measurements along the length of 10 mm x 5 mm high strength steel wire fatigue tested in air at high stress ..................................................................................................................144

Figure 4-17: Surface residual stress measurements along the length of 10 mm x 5 mm high strength steel wire fatigue tested in air at low stress ..................................................................................................................145

Figure 5-1: Pictures of the existing chamber with new liner, sample grips and sample installed. ........................................................................................................................................149
Figure 5-2: Anodic potentiodynamic polarisation curves for high strength carbon steel wire in sodium carbonate bicarbonate solution with and without the addition of sodium chloride

Figure 5-3: Images of chronoamperometry test samples with different solution exposure times (a) 30 s, (b) 60 s & (c) 300 s

Figure 5-4: High magnification images of chronoamperometry test samples with different solution exposure times (a) 30 s, (b) 60 s & (c) 300 s

Figure 5-5: Images of the SSRT samples being prepared for testing with lacomi and sealac (a) small pitted area (b) Large pitted area (c) Sample after pre-corrosion stage

Figure 5-6: Current versus time plots for the chronoamperometry experiments

Figure 5-7: Pictures of the microcell set up

Figure 5-8: Optical microscope images of the single corrosion pits with different solution exposure times (a) 60 s (b) 300 s and (c) 600 s

Figure 5-9: Optical microscope images of the single corrosion pits (a) Small (b) Large

Figure 5-10: DaVis analysis comparison of initial ssrt tests in air

Figure 5-11: The effects of strain rate on the stress-strain response compared to tensile test data for 12 mm x 4 mm high strength steel wire

Figure 5-12: Example of a histogram for each sample extension for high strength steel wire

Figure 5-13: Histogram of the surface strain for high strength steel wire tested in air

Figure 5-14: Surface strain maps (1) and optical microscope images (2) for high strength steel wire tested in air (A) yield, (B) ultimate tensile strength (C) strain at failure

Figure 5-15: Histogram of the surface strain for high strength steel wire polished surface tested in seawater

Figure 5-16: Surface strain maps (1) and optical microscope images (2) for high strength steel wire polished surface tested in seawater (A) yield, (B) UTS (C) strain at failure

Figure 5-17: Histogram of the surface strain for high strength steel wire large pitted area tested in seawater

Figure 5-18: Histogram of the surface strain for high strength steel wire small pitted area tested in seawater

Figure 5-19: Surface strain maps (1) and optical microscope images (2) for high strength steel wire large pitted area tested in seawater (A) yield, (B) UTS (C) strain at failure

Figure 5-20: Surface strain maps (1) and optical microscope images (2) for high strength steel wire small pitted area tested in seawater (A) yield, (B) UTS (C) strain at failure

Figure 5-21: Histogram of the surface strain for high strength steel wire large single pit tested in seawater

Figure 5-22: Histogram of the surface strain for high strength steel wire small single pit tested in seawater
Figure 5-23: Surface strain maps (1) and optical microscope images (2) for high strength steel wire large single pit tested in seawater (A) yield, (B) UTS (C) strain at failure.....175

Figure 5-24: Surface strain maps (1) and optical microscope images (2) for high strength steel wire small single pit tested in seawater (A) yield, (B) UTS (C) strain at failure.....176

Figure A1-1: Run 1A - Mean Stress = 428 MPa; Stress Range = 700 MPa..............................200
Figure A1-2: Run 2A - Mean Stress = 244 MPa; Stress Range = 400 MPa..............................201
Figure A1-3: Run 3A - Mean Stress = 153 MPa; Stress Range = 250 MPa..............................201
Figure A1-4: Run 4A - Mean Stress = 107 MPa; Stress Range = 175 MPa..............................201
Figure A1-5: Run 5A - Mean Stress = 183 MPa; Stress Range = 300 MPa..............................202
Figure A1-6: Run 1C - Mean Stress = 428 MPa; Stress Range = 700 MPa..............................202
Figure A1-7: Run 2C - Mean Stress = 367 MPa; Stress Range = 600 MPa..............................202
Figure A1-8: Run 3C - Mean Stress = 275 MPa; Stress Range = 450 MPa..............................203
Figure A1-9: Run 4C - Mean Stress = 214 MPa; Stress Range = 350 MPa..............................203
Figure A2-1: Chemical composition certificate........................................................................204
Figure A4-1: Slow strain rate test chamber general arrangement drawing.............................208
Figure A4-2: Slow strain rate test chamber detail drawing.......................................................209
Figure A4-3: Slow strain rate test chamber lid detail drawing..................................................210
Figure A5-1: Detailed drawing of slow strain rate test sample grips........................................211
Figure A6-1: Slow strain rate test sample drawings for two different high strength steel wires (a) 12 mm x 4 mm wire, (b) 10 mm x 5 mm wire.................................................................212
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>API</td>
<td>American Petroleum Institute</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>BCC</td>
<td>Body Centre Cubic</td>
</tr>
<tr>
<td>BSI</td>
<td>British Standards Institution</td>
</tr>
<tr>
<td>CDF</td>
<td>Cumulative Distribution Function</td>
</tr>
<tr>
<td>CE</td>
<td>Counter Electrode</td>
</tr>
<tr>
<td>CTOD</td>
<td>Crack Tip Opening Displacement</td>
</tr>
<tr>
<td>CP</td>
<td>Commercially Pure</td>
</tr>
<tr>
<td>DIC</td>
<td>Digital Image Correlation</td>
</tr>
<tr>
<td>EDM</td>
<td>Electric Discharge Machining</td>
</tr>
<tr>
<td>EMF</td>
<td>Electromotive Force</td>
</tr>
<tr>
<td>FCG</td>
<td>Fatigue Crack Growth</td>
</tr>
<tr>
<td>FCGR</td>
<td>Fatigue Crack Growth Rate</td>
</tr>
<tr>
<td>FEA</td>
<td>Finite Element Analysis</td>
</tr>
<tr>
<td>FEM</td>
<td>Finite Element Modelling</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier Transform</td>
</tr>
<tr>
<td>FPSOs</td>
<td>Floating Production Storage and Offloading</td>
</tr>
<tr>
<td>GIXRD</td>
<td>Grazing Incidence X-ray Diffraction</td>
</tr>
<tr>
<td>HCF</td>
<td>High Cycle Fatigue</td>
</tr>
<tr>
<td>HIC</td>
<td>Hydrogen Induced Cracking</td>
</tr>
<tr>
<td>HSE</td>
<td>Health and Safety Executive</td>
</tr>
<tr>
<td>JONSWAP</td>
<td>Joint North Sea Wave Observation Project</td>
</tr>
<tr>
<td>LCF</td>
<td>Low Cycle Fatigue</td>
</tr>
<tr>
<td>LPR</td>
<td>Linear Polarisation Resistance</td>
</tr>
<tr>
<td>OCP</td>
<td>Open Circuit Potential</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>OES</td>
<td>Optical Emission Spectroscopy</td>
</tr>
<tr>
<td>OPS</td>
<td>Oxide Polishing System</td>
</tr>
<tr>
<td>PEEK</td>
<td>Polyether Ether Ketone</td>
</tr>
<tr>
<td>PSBs</td>
<td>Persistent Slip Bands</td>
</tr>
<tr>
<td>PSD</td>
<td>Position Sensitive Detectors</td>
</tr>
<tr>
<td>PSMs</td>
<td>Persistent Slip Markings</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene Fluoride</td>
</tr>
<tr>
<td>RE</td>
<td>Reference Electrode</td>
</tr>
<tr>
<td>SAD</td>
<td>Stress Assisted Dissolution</td>
</tr>
<tr>
<td>SCE</td>
<td>Saturated Calomel Electrode</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard Hydrogen Electrode</td>
</tr>
<tr>
<td>SRB</td>
<td>Sulphate Reducing Bacteria</td>
</tr>
<tr>
<td>SSRT</td>
<td>Slow Strain Rate Testing</td>
</tr>
<tr>
<td>UHCF</td>
<td>Ultra High Cycle Fatigue</td>
</tr>
<tr>
<td>UTS</td>
<td>Ultimate Tensile Strength</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra Violet</td>
</tr>
<tr>
<td>VHCF</td>
<td>Very High Cycle Fatigue</td>
</tr>
<tr>
<td>VIV</td>
<td>Vortex Induced Vibration</td>
</tr>
</tbody>
</table>
Abstract

Peter Barnes, Doctor of Philosophy


The corrosion fatigue behaviour of high strength carbon steel tensile armour wires that are used in flexible risers has been explored.

An investigation of the corrosion fatigue failure mechanisms for two different sets of corrosion fatigue tested high strength steel wires has been carried out. The two different tensile armour wires were 12 mm x 4 mm and 12 mm x 7 mm. The wires had been corrosion fatigue tested in up to three different seawater environments, namely aerated, CO₂ saturated to 1 bar absolute and 100 mbar absolute H₂S-CO₂ balance to 1 bar absolute.

The corrosion fatigue failure investigation included undertaking statistical analysis of fatigue crack and corrosion pit data to establish the effects of environment, applied stress, R-ratio and microstructure due to degree of cold drawing on the corrosion fatigue behaviour. The 12 mm x 4 mm has fine grain martensite-pearlite structure with anisotropic microstructure in the transverse plane. The 12 mm x 7 mm has larger grain martensite-pearlite structure with equiaxed microstructure in the transverse plane. The corrosion fatigue crack path for the two tensile armour wires exhibits transgranular and intergranular cracking due to variations in R-ratio and microstructure.

The analysis identified that a significant amount of localised corrosion pitting was present on the surface of both the 12 mm x 4 mm and 12 mm x 7 mm high strength carbon steel tensile armour wires and that many corrosion fatigue cracks had initiated from these geometric discontinuities.

A method was developed in order to apply an optical image correlation technique to a sample immersed in seawater. The research has shown that digital image correlation may be applied for *in-situ* imaging of a corroding and dynamically deforming surface within a seawater environment. The technique demonstrated the establishment of localised surface strain around the corrosion pits during mechanical loading.

The results of the surface strain mapping show that the interaction between multiple corrosion pits is consistent with a significant increase in surface strain when compared to a single surface pit acting alone. The results also show that a small single stress raiser can exhibit a high surface stress concentration when compared to a larger one as the strain is...
dependent upon the geometry of the pit. The highest strain concentration is at the edge of the pit, parallel to the loading direction.

The results show the interaction that multiple pits have with each other, the effect they have on surface strains and how they and other types of stress raiser lead to premature failure of components.

Further to this the effects of residual stress on crack nucleation were considered. Fatigue cracks initiate at the surface of the high strength carbon steel tensile armour wire therefore surface measurements were carried out to establish the effects of environment and applied load on the development of residual stress fields.

The 12 mm x 4 mm wire shows some correlation between applied stress range and surface residual stress measurements with. For the 12 mm x 4 mm wire corrosion fatigue tested in aerated seawater the surface residual stress becomes increasing compressive with an increase in applied stress. For the 12 mm x 4 mm wire corrosion fatigue tested in CO2 saturated seawater the surface residual stress appears to be independent of applied stress. However for the 12 mm x 7 mm carbon steel tensile armour wire there is no correlation between the applied stress range and the surface residual stress. The differences in surface residual stress may be due to the differences in R-ratio, microstructure and level of cold drawing due to the Bauschinger effect.

Surface residual stress measurements have been used to explore the effects of the shakedown process on the high strength carbon steel tensile armour wires prior to corrosion fatigue testing. They show that at a high applied stress range the shakedown process readily develops a compressive residual stress on the surface of the carbon steel wire. This is mostly the case for the low applied stress range; however care should be taken when considering the effects of shakedown on a lower stress range in so far as it may not completely remove the tensile residual stress.

Through thickness residual stress measurements show a similar distribution of residual stress fields throughout the high strength carbon steel tensile armour wires independent of the applied stress range and environment.
Declaration

I declare that no portion of the work referred to in the thesis 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

i. The author of this thesis (including any appendices and/or schedules to this thesis) owns certain copyright or related rights in it (the “Copyright”) and s/he has given The University of Manchester certain rights to use such Copyright, including for administrative purposes.

ii. Copies of this thesis, either in full or in extracts and whether in hard or electronic copy, may be made only in accordance with the Copyright, Designs and Patents Act 1988 (as amended) and regulations issued under it or, where appropriate, in accordance with licensing agreements which the University has from time to time. This page must form part of any such copies made.

iii. The ownership of certain Copyright, patents, designs, trade marks and other intellectual property (the “Intellectual Property”) and any reproductions of copyright works in the thesis, for example graphs and tables (“Reproductions”), which may be described in this thesis, may not be owned by the author and may be owned by third parties. Such Intellectual Property and Reproductions cannot and must not be made available for use without the prior written permission of the owner(s) of the relevant Intellectual Property and/or Reproductions.

iv. Further information on the conditions under which disclosure, publication and commercialisation of this thesis, the Copyright and any Intellectual Property and/or Reproductions described in it may take place is available in the University IP Policy (see http://documents.manchester.ac.uk/DoculInfo.aspx?DocID=487), in any relevant Thesis restriction declarations deposited in the University Library, The University Library’s regulations (see http://www.manchester.ac.uk/library/aboutus/regulations) and in The University’s policy on Presentation of Theses.
Acknowledgement

First of all, I would like to say a massive thank you to my wife, Vicky, who has supported me throughout this whole process. The day I came home from work and said that I wanted to quit my job to become a student again and do a PhD she thought I was crazy.

I would also like to thank my parents and in-laws for all their help and support. Especially for looking after my children whilst I was writing up.

I would like to thank the Advanced Metallic Systems Centre for Doctoral Training for giving me the opportunity and funding to carry out a PhD.

I would like to thank Professor Stuart Lyon and Dr Dirk Engelberg for all their help and advice.
Chapter 1 Introduction
1. Introduction

1.1 Flexible Risers

For more than thirty years [1] flexible pipe work has been used in the oil and gas industry to transport oil based products from the seabed to Floating Production Storage and Offloading systems (FPSOs).

The flexibility and bending radius of these types of pipe work mean that they can withstand a greater wave loading and require shorter lengths of pipe work than a rigid bodied alternative, thus requiring a lower capital expenditure. Flexible risers have the advantage over rigid steel alternatives that they have reduced installation times and are better at adapting to change in field layout, therefore making them a more economical solution. They are commonly used in dynamic and static risers, static flow lines, jumpers and expansion joints [1–4].

The use of high-pressure flexible pipe work has been limited by the availability of only small diameters, up to 3" [1]. The demand for oil remains high and this has driven the exploration into challenging geographical areas, which are now economically viable for oil production. The development of high-pressure reservoirs over many years has increased the requirements for high-pressure large diameter flexible pipes. In turn this has driven the development, verification and qualification of such pipe work [2–9].

The current operating pressure requirements of the flexible pipe work are 15000 psi (~1000 bar) as set out by American Petroleum Institute (API), with research currently taking place to design and qualify a flexible pipe work capable of 20000 psi (~1400 bar). The current operating temperature requirements, process fluid temperature, within the flexible pipe work is 130–170 °C [1].

1.1.1 Flexible Riser Structure

The structure of an unbonded flexible pipe consists of a carcass, an inner liner, pressure armour and tensile armour and an outer sheath.

The carcass prevents collapse of the inner liner due to the high external pressures on the pipework in deep oceans. It also provides protection against maintenance operations such as pigging tools used to inspect pipeline. The carcass is predominantly made from interlocking strips of stainless steel [4], however it can be made from thermoplastics which provide an additional leak proof barrier [1].
The inner liner is made from extruded polymer providing fluid integrity within the riser. The polymers that are commonly used to act as fluid barriers are polyethylene, polyamide 11 and polyvinylidene fluoride (PVDF).

The pressure armour acts to resist radial load from the internal pressure within the pipe. This layer is a carbon steel wire with either a flat or zeta shape profile. The zeta profile wire interlocks providing resistance to lateral movement. The wire is wound at approximately 90° to the axial direction thus maximising the resistance to radial loads.

The tensile armour acts to resist the axial loads on the pipe from self-load, wave loading and pressure. This layer is a carbon steel wire with a flat profile. It is helically counter-wound in pairs with a laying angle between 25° and 55° to provide a torque balance for the pipework [10]. This project investigated these layers of wire.

The outer protective sheath is an extruded polymer layer that protects the pipework from seawater ingress and external mechanical damage. In between the pressure and tensile armour layers, a high strength anti-wear tape is provided to prevent slippage due to movement of the pipework. Figure 1 shows a cross section through a typical unbonded flexible pipe [2].

![Figure 1-1: The internal structure of an unbonded flexible pipe][2]

### 1.1.2 Failure Modes

The environment within the annular space can determine the life of a flexible riser. This can contain corrosive gases, the presence of condensed water and seawater ingress. The corrosion reactions and kinetics associated with this environment and the action of the fatigue process will determine the life of the material. According to the literature [4,10–12] there are two main modes of failure:

- Damage to the outer sheath – caused during installation, by foreign objects either rubbing up against or embedded in the pipe sheath or aging of the thermoplastic
sheath. This leads to ingress of seawater into the annular space thus enabling the corrosion fatigue process to begin. This is why the tensile armour is corrosion fatigue tested in an aerated synthetic seawater environment.

- Permeation of corrosive gases and condensed water through the inner polymer sheath lead to a corrosive environment within the annular space. The water vapour condenses on the surface of the wire armour into which carbon dioxide (CO$_2$), hydrogen sulphide (H$_2$S) and methane (CH$_4$) dissolve, creating an acidic environment in which corrosion will occur.

Both corrosive environments combined with the wave loading from the sea lead to corrosion fatigue failure and ultimately fracture of the tensile armour.

A report by the Health and Safety Executive (HSE) [11], summarised in Table 1-1, details numerous offshore production facilities where flexible risers have experienced the above failure modes.

<table>
<thead>
<tr>
<th>Name of Oilfield &amp; Location</th>
<th>Failure Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Galley Field, North Sea</td>
<td>Gas bubbles emanating from the pipework indicated damage to the outer sheath, caused by a foreign object rubbing against the pipe wall. This combined with a seawater flooded annulus led to the corrosion fatigue failure of the riser.</td>
</tr>
<tr>
<td>Kristin Field, North Sea</td>
<td>Damage to the outer sheath due to wear.</td>
</tr>
<tr>
<td>Banff, North Sea</td>
<td>A bore to annulus leakage of seawater from the high-pressure water injector system. Localised corrosion was observed on the surface of the tensile armour. This is known to significantly reduce the fatigue life of a material, as the formation of corrosion pits will act as stress raisers for fatigue crack initiation.</td>
</tr>
<tr>
<td>Foinaven, North Atlantic, West of Shetland</td>
<td>Damage to the outer sheath during installation leading to seawater ingress into the annular space.</td>
</tr>
<tr>
<td>Varg, North Sea</td>
<td>Along with damage to the outer sheath, there were fatigue cracks observed in all the individual layers that make up a flexible riser. The damage was attributed to manufacturing defects.</td>
</tr>
</tbody>
</table>
1.1.3  Testing and Qualification

A large amount of testing and verification work has been carried out on the flexible pipes in order that they satisfy the design requirements of the numerous international codes and standards, such as the American Petroleum Institute (API) and British Standards Institution (BSI) [1,3,4,13].

The verification and qualification work includes testing the flexible pipe work as a whole unit using a hydrostatic collapse test, internal pressure and burst test, and dynamic fatigue [1,14]. Additionally, the component parts, such as the tensile armour, are subjected to fatigue testing [3,4,15–17]. Testing results are fed into finite element analysis (FEA) fatigue lifetime models developed by flexible riser suppliers and oil companies to provide additional information of pipework behaviour [6,18].

1.1.3.1  Annular Space Environmental Conditions

Initially work was carried out to establish the fatigue life of flexible risers in air. It was originally thought that the annular space was a sealed environment, free from condensed water and permeated gases. Therefore, fatigue life predictions from S-N curves were made by carrying out testing in air, which as expected overestimated the life of the flexible riser wire by up to 50 times [10,19]. This is partly due to the loss of the fatigue endurance limit when testing in a corrosive environment.

The differential pressure across the inner sheath and the operating temperature of the riser result in the permeation of gases and water through the thermoplastic layer thus establishing a corrosive environment. The water vapour condenses on the steel wires and the gases dissolve into the liquid. Much work has been carried out to establish the specific environment within the annular space [2–5,10–12,20,21]. This can be split into two, firstly, establishing the permeability of the thermoplastic layer to water vapour and gases, followed by inputting this data into a computer based model to simulate the annular space conditions.

Corrosive gases permeate through the polymer layers of the flexible risers. Work carried out by Flaconneche et al. [22] and Andersen et al. [23] have established the permeability, diffusivity and solubility of gases in polymers, termed the transport coefficients. Using Fick’s first law, a method is derived that considers the pressure within the pipework, the thickness and cross sectional area of the polymer membrane to establish gas permeability. Flaconnèche et al. [24] then goes on to establish the transport coefficients of various grades of poly ethylene for numerous gases including the corrosive gases, methane (CH₄) and carbon dioxide (CO₂), that are present within the annular space. However, the author does not
provide the transport coefficients for the most corrosive gas within the annular space, hydrogen sulphide (H₂S).

Work carried out by Benjelloun-Dabaghi et al. [10] uses the established solubility and diffusivity of the fluid in the pipe bore at a given pressure and temperature, the absorbed fluid quantity and fluid flow, to establish the annulus composition. It comprises of a computer-based model similar to a Finite Element Model (FEM) that again uses Fick’s Law and Henry’s Law. The geometrical shapes of the individual wire and sheath layers are modelled and given the appropriate properties of solubility, diffusion, thermal conductivity and mechanical properties. Simplification of the helical shape of the wires in the FE modelling is compensated for dividing the actual width of the wire layer by the laying angle, thus generating an increased area. However, it would be interesting if the work had gone further to establish the effects, if any, of the true annular geometry.

Benjelloun-Dabaghi et al. [10] provides details of the pipe bore conditions with respect to gases pressure and temperature but it does not state the exact environmental conditions experienced within the annular space, with respect to salt, water and gas concentrations. It is assumed that this information is sensitive and held by the individual oil companies concerned.

The annular space has a high ratio of steel surface area to free volume, with the free volume being between 5 to 15 % of the total volume [5]. Work by Remita et al. [21] demonstrates that the corrosion rates found for the high strength steel wire in laboratory tests exhibit 2 to 3 orders of magnitude higher corrosion rate than that established within the annular space. A comparison was done between a traditional corrosion rate test using an electrochemical cell with a bulk solution and a relatively small working electrode cross-sectional area, i.e. a large volume to surface area ratio (V/S) and a thin electrolyte film on an exposed steel surface [20], a low V/S ratio. This work demonstrates a level of conservatism in the current testing and qualification regime, with assessment using a low V/S ratio potentially showing a demonstrable increase in fatigue life of the flexible risers. This is due to the lower corrosion rate experienced with low V/S ratio, thought to be due to a homogenous concentration gradient on the steel surface.

As expected in any engineering qualification process, the testing carried out shows a level of conservatism in the results thus allowing for a safety factor in the design of the flexible risers. The design can be and is based upon the worst-case scenario, even if this is not the operating condition that is experienced out in the field. However, a balance has to be struck between
overly conservative design and the possibility of non-conservatism leading to catastrophic failure.

1.1.3.2 Fatigue Conditions

Flexible risers are subjected to fatigue loading by Vortex Induced Vibrations (VIV). These vibrations are caused by wave action, vortex shedding of the pipework, FPSOs vessel motion and pressure changes. The three main components of the applied stress to be considered for fatigue loading are:

- Tensile induced axial stresses from the weight of the flexible riser suspended from a FPSOs.
- Bending stresses. The fatigue process will cause the flexible riser to change shape by bending. Movement of the wire layers, whereby each layer will slide with respect to each other to form the new shape, facilitates this bending.
- Friction induced axial stresses are caused by the sliding of each wire layer. High strength tapes are used between the wire layers to reduce the effects of friction and wear during sliding.

An increase in pressure, required to explore more challenging environments, means that the flexible risers will be subjected to higher stresses and increased fatigue damage. This is due to an increase in friction forces between the wire layers that requires an increased bending moment in order that they are overcome.

The natural cyclic wave loading of the sea is random and defined as stochastic. However, laboratory fatigue testing uses a deterministic analysis to establish fatigue life. Sheehan et al. [12] has carried out research to establish if this is a valid approach to fatigue life assessment.

Stochastic analysis is more representative of the irregular sea based wave that would be experienced. The sea conditions were characterised using the wave spectrum from the Joint North Sea Wave Observation Project (JONSWAP) [25] which began in 1967 as a means to study the generation, propagation and decay of the ocean surface waves.

Deterministic analysis uses a regular waveform fatigue based upon that produced by a fatigue-testing machine in a laboratory. Sheehan et al. [12] shows that corrosion fatigue testing using a deterministic methodology will provide a realistic fatigue life estimate of the tensile armour.

Fatigue testing carried out on the complete flexible riser assembly uses a section of pipework manufactured to the same specifications as the actual riser [1]. Fatigue testing of the
individual components such as the tensile armour [3,4] is carried out at numerous stress ranges. If a flexible riser is found damaged then a residual life study can be carried out to establish the remaining life of the riser, knowing that the annulus is flooded, using the S-N curve established from testing.

1.1.4 Summary
Work has been carried out to establish the environmental conditions within the annular space, followed by a suitable level of fatigue testing. This aids the understanding of flexible risers for industry suppliers and oil companies. However, there is a need to fundamentally understand why the material fails using a materials and corrosion science approach to the problem.

1.2 Aims & Objectives
The aim of this project was to assess and analyse the behaviour of high strength carbon steel used as tensile armour in flexible risers. The assessment was with respect to corrosion fatigue behaviour and residual stress development within the material.

In order to achieve this aim, the objectives of this project were as follows:

1. To explore corrosion fatigue cracking with respect to microstructure, cycles to failure, applied stress and environment.
   a. Intertek carried out corrosion fatigue testing of the high strength carbon steel tensile armour at their test facility in Manchester in accordance with the requirements of their clients. Corrosion fatigue testing was carried out on two different tensile armours in up to three different environments.
      i. The two tensile armour wires considered were 12 mm x 4 mm and 12 mm x 7 mm.
      ii. The three different environments considered were a D1141 synthetic seawater that was either aerated, CO₂ saturated to 1 bar absolute or 100 mbar absolute H₂S-CO₂ balance to 1 bar absolute.
   b. Post-test analysis of the corrosion fatigue tested sample included exploring the mechanisms involved in corrosion fatigue cracking and crack initiation.
2. To measure the residual stresses in the material, and to investigate their role in the propagation of crack nuclei.
   a. Through thickness residual measurements to be carried out to establish a residual stress profile of the tensile armour wires.
   b. Surface measurements
i. Post corrosion fatigue tested samples provided by Intertek.
ii. Samples fatigue tested in air to establish the development of the residual stress field in the carbon steel tensile armour due to the fatigue process.

3. To detect crack initiation using in-situ observation, slow strain rate testing (SSRT) with digital image correlation (DIC).
   a. To determine surface strains and to detect crack nucleation by in situ observation.
   b. To compare the surface strain from SSRT with the strains experienced during fatigue from the applied stress range values.
   c. To explore strain fields around corrosion pits
Chapter 2 Literature Review
2. Literature Review

2.1 Cold Drawn Steel Wire

Steel is the most widely used engineering material due to its formability, mechanical properties and it being relatively inexpensive. Steel wires are used in many applications including suspension bridges, reinforcement in tyres and in reinforced concrete to name but a few. They are utilised due to their high strength, which is related to the steel microstructure. They are formed by a multi-pass drawing process [26] in order to produce high carbon steel wires with a fine pearlite lamellar structure.

Carbon steel is an alloy of iron and carbon. The carbon steel wires used in this project have a carbon content of 0.61 to 0.70 wt% as shown in Table 3-8. Steel with less than 0.8 wt% carbon is known as hypo-eutectoid. Upon cooling from the liquid phase to room temperature the steel will form a ferrite and pearlite microstructure via a eutectoid reaction, shown as point ‘S’ on Figure 2-1. Pearlite nuclei occur on austenite grain boundaries or carbides. Pearlite occurs by nucleation and growth of the α-iron and iron carbide phases and relies on diffusion of carbon.

![Fe-C phase diagram](image)

Figure 2-1: Fe-C phase diagram [27]
Pearlite is a composite of alternate layers of ferrite and cementite in a lamellar structure, see Figure 2-2. Ferrite, α-iron, has a body centred cubic (BCC) crystal structure and the cementite, Fe₃C, has an orthorhombic crystal structure. The volume fraction of cementite within pearlite for cold drawn steel is generally low; however its presence will greatly increase the mechanical properties of the cold drawn wire. The drawing process produces an elongation of the grains, in the drawing direction and a contraction in the perpendicular direction thus creating an anisotropic microstructure. The preferred orientation of the grains, with the <110> more or less parallel with the wire axis, due to the drawing process is called a fibre texture [26,28]. The microstructure and deformation of pearlite has been widely studied in order to understand the effects of the drawing process on the strength and fracture behaviour of a cold drawn steel [28–45].

Toribio et al. [35] demonstrated the effects of cold drawing on three different spatial arrangements of the pearlite lamellar, (see Figure 2-3). It was suggested that lamellar that were inclined to the wire axis would exhibit an increase in angle towards the drawing direction and a reduction in lamellar spacing with increasing amounts of cold drawing. For lamellar parallel to the wire axis increased levels of cold drawing would cause a decrease in the lamellar spacing. For lamellar that were perpendicular to the wire axis increased levels of cold drawing would cause them to start to kink, with the wavy shape being indicative of the level of cold drawing and the orientation of the grain to the drawing direction. The increase in cold drawing of the steel leads to the curling effect of the pearlite lamellar is due to the ferrite microstructure having a BCC crystal structure. The deformation due to cold drawing causes the cementite colonies to become bent, kinked, wavy and wrinkled [30,31,33]. This is thought to be due to the creation of a slip step, created at the cementite-
ferrite interface by dislocations crossing the cementite structure during plastic deformation [30,45].

![Figure 2-3: Three different spatial arrangements of pearlite lamellar [35]](image)

Embry et al. [45] demonstrated that the texture and reduction in interlamellar spacing is due to increased amounts of cold drawing. The decrease in lamellar spacing is due to the anisotropic grain orientation, perpendicular to the drawing direction. The Hall-Petch relationship states that the strength of metal is inversely proportional to the square root of the grain size [26]. However, it was thought that this relationship was not completely satisfactory for a pearlitic microstructure. Langford [29] showed that the 0.2 % proof stress against the inverse of the square root of the wire diameter is a linear function. He consequently established that based on the Hall-Petch relationship the strength of the cementite lamellae is inversely proportional to square root of the lamellar spacing. The interlamellar spacing has been reported to widely vary from 250 nm down to 1 nm depending on the amount of cold drawing. The plastic deformation from the cold drawing process therefore increases the strength of the steel by thinning of the cementite lamellar, the creation of slip steps and an increase in the interfacial free energy of the cementite [30,42,46]. The strengthening of the wire is due to the boundary strengthening, dislocation strengthening and solid-solution hardening due to carbon enrichment of the ferrite phase [32].
2.2 Corrosion of Carbon Steel

2.2.1 Introduction

Corrosion is the breakdown of a metal by means of electrochemical reactions that take place on the metal surface and within the surrounding environment. The corrosion products of iron or steel are mainly iron-based oxides and carbonates depending upon the presence of oxygen and corrosive gases in the environment. Economics and safety are the main drivers for corrosion research. There are wide ranging figures on the financial cost of corrosion but [47] puts this at 1.5 % of revenue, which for the six big oil companies equates to $3-7 billion per year.

Carbon steels are used in the oil and gas industry because of their availability, mechanical properties, ease of fabrication and cost. Even though it is known that they have poor corrosion properties in this type of environment, they provide a cost effective solution.

2.2.2 Electrochemistry

Electrochemistry is a branch of chemistry that studies the chemical reactions that take place in an aqueous solution between a metal electrode, an electron conductor and the electrolyte, an ionic conductor which involves transfer of charge.

An example of an electrochemical reaction is that of iron in aerated seawater. The iron corrodes and dissolves into solution and reacts with the oxygen to form iron oxides. This is schematically shown in Figure 2-4. The anode is defined as the electrode where chemical oxidation occurs and the cathode is defined as the electrode where chemical reduction occurs. In this case the iron acts as both the anode and the cathode. Oxidation reactions produce electrons and reduction reactions consume electrons. These individual reactions are called half-reactions and are detailed in Section 2.2.3. The reactions exhibit charge conservation whereby the sum of the anodic reaction is equal to the sum of the cathodic reactions.

Corrosion is a thermodynamically driven and a kinetically controlled process. Therefore, the probability of a reaction occurring, in this case corrosion of steel, is measured by the change in Gibbs free energy ($\Delta G$). The increase in negative value of $\Delta G$ indicates the increased tendency of the metal to corrode. On the other hand, reactions of metals with a positive value of $\Delta G$ have no tendency to corrode and are said to be noble; examples are Au and Pt. The negative $\Delta G$ value is not an indication of the corrosion rate of the metal, purely an indication of whether the metal will corrode. The corrosion tendency expressed in terms of...
electromotive force (EMF), E, is related to the Free Energy by Equation 2-1, hence the greater the circuit potential, the greater the corrosion tendency.

\[ \Delta G^0 = -nFE^0 \]  \hspace{1cm} \text{Equation 2-1}

\[ E = E^0 - \frac{RT}{nF} \log \left( \frac{[\text{products}]}{[\text{reactants}]} \right) \]  \hspace{1cm} \text{Equation 2-2}

where \( \Delta G^0 \) = Gibb’s free energy, \( n \) = number of electrons taking part in the reaction, \( F \) = Faraday’s Constant, (96,500 C/mol), \( E \) = Potential (V), \( E^0 \) = Standard Potential (V), \( R \) = Gas Constant, \( T \) = Temperature (K)

A potential-pH diagram was developed by Marcel Pourbaix which relates the electrochemical and corrosion behaviour of a metal in water, see Figure 2-5. At the bottom of the diagram Fe is a solid and does not corrode. It is said to be immune and this is the immunity zone. On the right hand side of the diagram is the passive region where various types of iron-based oxide passive films form. The left hand side of the diagram is the active region, where corrosion occurs, either by oxygen reduction or hydrogen evolution. Below line (a) hydrogen evolution occurs and above line (b) is where oxygen reduction takes place. This diagram provides an understanding of how the iron will behave, which half-reactions will occur, in a particular potential-pH solution.

Figure 2-4: Typical example of iron corrosion in water
The electrochemical cell used for this work comprised of a glass cell to hold the electrolyte and three electrodes, namely, the working electrode (WE), a counter electrode (CE) and the reference electrode (RE). The working electrode, where the corrosion reactions take place, was a cross section of the high strength steel wire. The counter electrode, used to carry the current created by the corrosion reactions, was a platinum wire. Platinum is used as it is a noble metal and will not introduce any contaminating ions into the electrolyte. The reference electrode was a Saturated Calomel Electrode (SCE), Hg/HgCl₂ within a solution of saturated potassium chloride KCl. A reference electrode enables the measurement of an absolute potential value for a working electrode in an electrolyte, rather than just the potential difference across two electrodes. This is achieved by establishing the standard electrode or reduction potential, which is +0.2412 V versus Standard Hydrogen Electrode (SHE) for a SCE. The reference electrode is housed in a reservoir and connects to the electrochemical cell by a salt bridge.

A working electrode in an electrolyte will exhibit a free corrosion potential or an open circuit potential that can be defined as the steady-state potential of the metal that occurs when the oxidation and reduction rates are equal. The difference in electrode potential from the potential at equilibrium is known as the polarisation or overvoltage. This is a useful parameter as it can be used to establish corrosion rates.
There are three types of polarisation that can act to lower the efficiency and kinetics of the reaction. These are called activation, concentration and resistance polarisation. Activation polarisation occurs as a consequence of factors that slow down the reaction rate such as the rate of electron transfer from a metal will determine the rate of hydrogen evolution. Concentration polarisation occurs when the reaction rate is faster than the rate at which the species being oxidised or reduced can reach the metal surface such as steel in aerated seawater [49]. The reaction then becomes controlled by the rate of diffusion of reacting species to the surface. Resistance polarisation is a function of the ohmic resistance by electrons or ions to current flow.
Polarisation measurements are important to establish the electrochemical behaviour with respect to corrosion mechanisms and kinetics of a metal-electrolyte system.

The potentiodynamic polarisation curve or Tafel plot enables the understanding of the corrosion behaviour of a metal-electrolyte system over a range of overvoltage. It is established by polarising the working electrode between chosen potentials. The anodic and cathodic parts of the curve can then be analysed to determine the Tafel constants. For each individual corrosion cell system considered a potentiodynamic polarisation scan should be carried out to establish a Tafel plot, from which the associated values of $\beta_a$ and $\beta_c$ can be calculated. This will give a more realistic indication of corrosion rate for a particular metal-electrolyte system. However, the data produced for corrosion rate should be treated with care, especially if it is to be applied to engineering design, as it may underestimate the true effects of the metal-electrolyte system behaviour.

Analysis of the shape of polarisation curves to establish corrosion parameters was proposed by Stern and Geary [50]. The linear polarisation resistance (LPR) technique can be used to establish corrosion rates [51]. The measurements can be carried out iteratively over a period of time. The technique involves polarising the sample by a small overvoltage either side of the open circuit potential and measuring the current. The potential is plotted ($E$, $V$) vs current density ($i$, A/m$^2$), the gradient of the line is called the polarisation resistance ($R_p$), whose inverse is proportional to the corrosion current. Therefore using Equations 3 and 4 the corrosion rate can be calculated.
\[ i_{corr} = \frac{\beta_a \beta_c}{2.3 R_p (\beta_a + \beta_c)} \]  

Equation 2-3

\[ Corrosion \ Rate = \frac{10i_{corr} m_r s_{year}}{\rho n F} \]  

Equation 2-4

where \( i_{corr} \) is the corrosion current, \( \beta_a \) and \( \beta_c \) are the Tafel constants, \( R_p \) = polarisation resistance, \( m_r \) = molar mass of iron, \( s_{year} \) = seconds in a year, \( \rho \) = density of iron, \( n \) = number of electrons, \( F \) = Faraday’s Constant.

2.2.3 Environment

Throughout the world’s oceans and seas there is a variation in the corrosiveness of natural seawater. This is due to variations in salinity, microbial activity such as the presence of Sulphate Reducing Bacteria (SRB), dissolved oxygen concentration and water temperature. Natural seawater is a more aggressive solution than synthetic seawater [49,52,53].

There are many environmental factors that affect the rate of corrosion. These include the solution chemistry, in this case seawater, the partial pressure of the corrosive gases, \( \text{CO}_2 \) and \( \text{H}_2\text{S} \), solution pH and temperature. The solution chemistry and gas partial pressures will determine the solution pH. The half reactions for steel in seawater are shown in Equation 2-5 to Equation 2-8. The chemical composition of seawater is shown in Table 2-1. The pH of seawater is adjusted to pH 8.2, as per the requirements of the American Society for Testing and Materials (ASTM) standard [54] for synthetic seawater, at the start of an experiment using sodium hydroxide solution.

Anodic (Oxidation) Reaction

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \]  

Metal dissolves  

Equation 2-5

\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^- \]  

Ferrous ion is oxidised in solution  

Equation 2-6

Cathodic (Reduction) Reactions

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

Hydrogen Evolution [55]  

Equation 2-7

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \]  

Oxygen Reduction  

Equation 2-8
Table 2-1: Composition of ASTM D1141 substitute ocean water [54]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>24.53</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>5.2</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>4.09</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>1.16</td>
</tr>
<tr>
<td>KCl</td>
<td>0.695</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.201</td>
</tr>
<tr>
<td>KBr</td>
<td>0.101</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>0.027</td>
</tr>
<tr>
<td>SrCl₂</td>
<td>0.025</td>
</tr>
<tr>
<td>NaF</td>
<td>0.003</td>
</tr>
</tbody>
</table>

2.2.3.1 Aerated

In an aerated environment, the rate of iron corrosion is generally controlled by the cathodic reaction and the diffusion of oxygen to the surface. Ferrous ions, produced at the anode, migrate to the cathode where they react with hydroxide ions to form ferrous hydroxide \( \text{Fe(OH)}_2 \), at a pH of around 9.5, which means the iron corroding at the sample surface in an aerated environment is weakly alkaline.

Reaction of the ferrous hydroxide with dissolved oxygen oxidises the species to hydrated ferric oxide or iron oxy-hydroxide, \( \text{FeOOH} \). Iron oxy-hydroxides has three different forms, goethite, \( \alpha\text{-FeOOH} \), akaganeite, \( \beta\text{-FeOOH} \) and lepidocrocite, \( \gamma\text{-FeOOH} \) which is orange in colour and a constituent of scales formed on steel in aqueous chloride environments [56–58]. Ishikawa et al. [59] suggests that dissolved iron reacts further with iron oxy-hydroxide to form magnetite.

The corrosion reactions for steel in an aerated seawater environment are:

\[
\begin{align*}
\text{Fe} & \rightarrow \text{Fe}^{2+} + 2e^- & \text{Formation of ferrous ion} & \text{Equation 2-9} \\
\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2e^- & \rightarrow 2\text{OH}^- & \text{Principal Reduction Reaction} & \text{Equation 2-10} \\
\text{Fe}^{2+} + 2\text{OH}^- & \rightarrow \text{Fe(OH)}_2 + 2e^- & \text{Formation of ferrous hydroxide} & \text{Equation 2-11} \\
\text{Fe(OH)}_2 + \text{OH}^- & \rightarrow \text{FeOOH} + \text{H}_2\text{O} + e^- & \text{Formation of iron oxy-hydroxide} & \text{(oxidation reaction)} & \text{Equation 2-12}
\end{align*}
\]
\[
Fe^{2+} + 2FeOOH \rightarrow Fe_3O_4 + 2H^+ \quad \text{Formation of magnetite [57,59] Equation 2-13}
\]

### 2.2.3.2 Sweet Corrosion

The majority of oilfield failures are said to be due to \( \text{CO}_2 \) corrosion [47]. Carbon dioxide as a dry gas at low temperature is not corrosive, however when it dissolves into an aqueous phase such as water it forms a weak acid, known as carbonic acid. The solution pH range within a \( \text{CO}_2 \) environment is \( 4 < \text{pH} < 6 \) and has been shown to have no effect on the anodic dissolution mechanism of iron [48,60]. In sweet corrosion, the presence of carbonic acid at relatively high concentration increases the rate of the hydrogen evolution reaction. Elbeik et al. [61] has shown that localised surface pH can be between 10.9 to 11.5 due to the formation of calcareous deposits.

The corrosion reactions for steel in sweet or \( \text{CO}_2 \) saturated seawater environment are:

- \( Fe \rightarrow Fe^{2+} + 2e^- \) \quad \text{Formation of ferrous ion Equation 2-14}
- \( \text{CO}_2 + H_2O \rightleftharpoons H_2\text{CO}_3 \) \quad \text{Carbonic Acid Dissociation \text{(Rate Determining Step, RDS)} [55] Equation 2-15}
- \( H_2\text{CO}_3 \rightleftharpoons H^+ + HCO_3^- \) \quad \text{Carbonic Acid Dissociation \text{(Rate Determining Step, RDS)} [55] Equation 2-16}
- \( HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \) \quad \text{Carbonic Acid Dissociation \text{(Rate Determining Step, RDS)} [55] Equation 2-17}
- \( Fe^{2+} + CO_3^{2-} \rightleftharpoons Fe\text{CO}_3 \) \quad \text{Ionic formation of iron carbonate Equation 2-18}
- \( Ca^{2+} + CO_3^{2-} \rightarrow Ca\text{CO}_3 \) \quad \text{Formation of calcium carbonate [49,52,61] Equation 2-19}
- \( Ca^{2+} + HCO_3^- + OH^- \rightarrow Ca\text{CO}_3 + H_2O \) \quad \text{Formation of calcium carbonate [49,52,61] Equation 2-19}
- \( Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \) \quad \text{Formation of magnesium hydroxide [52] Equation 2-20}

Remita et al. suggests that the reduction of the carbonic species at the steel surface is an incorrect assumption to explain the cathodic behaviour of oxygen free solution containing dissolved \( \text{CO}_2 \). The author suggests that the dissociation reactions associated with dissolved \( \text{CO}_2 \) are adequate to explain the detected current enhancement of the hydrogen evolution reaction [55].

The corrosion reactions within a sweet environment assume the formation of iron carbonate on carbon steel in seawater at all temperatures [62,63] as long as the iron supersaturation is high, however at room temperature this has been shown not to be the case [52]. Moller et al. has shown that the presence of additional cations such as \( Ca^{2+} \) and \( Mg^{2+} \) in seawater, as opposed to experiments carried out with simply sodium chloride, show the formation of
calcium carbonate and magnesium carbonate. The formation of OH\(^-\) ions from cathodic reduction reaction suggests that initially Mg(OH)\(_2\) and Ca(OH)\(_2\) form from which the associated carbonate species will form [49]. However, Mg(OH)\(_2\) has lower solubility than Ca(OH)\(_2\) but MgCO\(_3\) has higher solubility than CaCO\(_3\) therefore Elbeik et al. suggests that the precipitation of Ca(OH)\(_2\) is not the appropriate mechanism to consider for the formation of the calcium deposits and proposes the direct reaction of Ca\(^{2+}\) and CO\(_{3}^{2-}\) [61]. Further to this, complexes of magnesium calcite, Mg,Ca(CO\(_3\)) will form as this is proposed to be the most stable form of calcium carbonate to precipitate in seawater [49].

With regards to corrosion rates in 3.5 % NaCl solution, synthetic and natural seawater, it has been reported [52] that steel corrodes faster in 3.5 % NaCl solution due to the lack of Ca\(^{2+}\) and Mg\(^{2+}\) ions and formation of carbonate surface deposits that act as an oxygen diffusion barrier, thus lowering the corrosion rate [61,64]. However, although the film does reduce corrosion by providing an oxygen diffusion barrier it is still a porous film. In seawater, in the presence of chlorides, and the absence of dissolved oxygen, the rate of iron corrosion is controlled by the anodic reaction, which leads to localised corrosion in the form of corrosion pitting.

2.2.3.3 Sour Corrosion

Dissolved H\(_2\)S can increase corrosion rate by sulphide adsorption or reduce corrosion rate by forming a protective sulphide scale will reduce the tendency for hydrogen to diffuse into the sample surface [65]. H\(_2\)S is three times more soluble than CO\(_2\). Also the acid created by the dissolution of H\(_2\)S is three times weaker than carbonic acid.

The corrosion reactions for steel in sour or H\(_2\)S seawater environment are:-

\[
Fe \rightarrow Fe^{2+} + 2e^- \quad \text{Formation of ferrous ion} \quad \text{Equation 2-21}
\]

\[
H_2S(g) \rightleftharpoons H^+ + HS^- \quad \text{Hydrogen Sulphide Dissociation} \quad \text{Equation 2-22}
\]

\[
HS_{(aq)}^- \rightleftharpoons H^+ + S^{2-} \quad \text{Equation 2-23}
\]

\[
Fe + H_2S \rightarrow FeS + H_2(g) \quad \text{Formation of Iron Sulphide} \quad \text{Equation 2-24}
\]

\[
Fe + 2HS^- \rightarrow FeS + H_2S + 2e^- \quad \text{Equation 2-25}
\]

\[
H_2S_{(aq)} + 2e^- \rightarrow H_2 + 2HS^- \quad \text{Enhancement of the cathodic reaction for hydrogen evolution as suggested by [65]} \quad \text{Equation 2-26}
\]

40
2.2.4 Types of Corrosion

The types of corrosion damage that are experienced by the high strength steel used within this project are that of general and localised corrosion. Both types of corrosion can lead to fatigue crack initiation and material failure during the corrosion fatigue process. General corrosion may lead to a reduction in the thickness of the material and consequently a reduction in the load bearing capacity. Localised corrosion will lead to the formation of localised stress concentrations on the metal surface. The breakdown of the surface film and the dissolution of protruding persistent slip bands (PSBs) will lead to geometric discontinuities. The localised breakdown of the surface film exposing bare metal to the aggressive environment will lead to corrosion pitting where the film acts as the cathode and the bare metal is the anode [64,66,67]. Crevice corrosion at the interface between the metal matrix and an inclusion may lead to the formation of corrosion pits, therefore removal of electrochemically active impurities from the metal will improve the corrosion resistance.

2.2.4.1 General Corrosion

General corrosion is when a metal corrodes evenly producing a thin surface film that either fully or partially covers the metal surface. Uniform corrosion can act to prolong the fatigue life if the corrosion rate is higher than the fatigue damage accumulation rate in the early stages of fatigue [68]. As mentioned previously, the corrosion films that form in seawater are oxide, carbonate or sulphide based [67].

2.2.4.2 Localised Corrosion

Pitting corrosion is a form of localised corrosion, whereby dissolution of the metal surface leads to the formation of pits and cavities. Pitting corrosion may occur by dissolution of inclusions or slip band dissolution, which is discussed later. There are many internal factors, such as environmental composition, temperature and electrode potential and external factors, such as alloy composition, heat treatment and surface preparation, which influence the pitting process. The heat generated during the cold drawing process may lead to segregation of elements on the metal surface, which acts as electrochemically preferential sites for corrosion pitting. Elements such as C, N and S combine to form inclusions for instance carbides, nitrides and sulphide, which are common in steels. Carbon steels that contain the elements Mn and S, will form MnS and (Mn,Fe)S inclusions [69–71]. In accordance with Figure 2-9, MnS inclusions are stable between pH4.8 to 13.8 and at potentials less than -100 mV to -670 mV vs SHE respectively. However, localised changes in pH and potential at the inclusion cause dissolution producing H₂S and Mn²⁺ which lead to the formation of a corrosion pit and hydrogen entry into the steel. Tronstad et al. 1933, cited in...
investigated carbon steels with the same amounts of C, Si and Mn and increasing levels of S. They found that sulphide inclusions initiated an anodic reaction, which enhanced localised corrosion. However, not all sulphide inclusions were active and it was mainly the MnS inclusions that were active with the formation of crevice type corrosion between the MnS inclusion and the steel substrate. These inclusions are a favourable site for corrosion pit nucleation and ultimately fatigue crack initiation [72,73], which will be discussed later.

Steels in sour service are susceptible to Hydrogen Induced Cracking (HIC) by diffusion of hydrogen into the steel. Cracks form as a result of the accumulated pressure of the hydrogen [74]. In a hydrogen sulphide environment, the sulphide inclusions dissolve and the anodic and cathodic reactions are accelerated. This is due to the \( \text{H}_2\text{S} \) acting as a catalyst and the anodic reaction being accompanied by the formation of \( \text{Fe(H}_2\text{S)} \text{ads} \).

Pitting corrosion is defined as the localised breakdown of a passive film such as the oxide films formed on stainless steels and aluminium [75]. Carbon steels do not exhibit passivation in a seawater environment as the films formed do not fully cover the surface, however discrete regions of partially protective films have been observed [76]. Localised corrosion pitting may occur where some areas are preferentially corroded while others are localised preferential cathodes. The difference between this case and when a material passivates is that the protective film formed does not fully cover the surface and therefore is not completely protective. The susceptibility of a metal to corrosion pitting is established by measuring the pitting potential, as this shows the point at which the passive film begins to break down [77]. However, as mentioned, carbon steel does not passivate in seawater and therefore will not exhibit a clear pitting potential when polarised.
The morphology of localised corrosion pits on steel can be either isotropic or anisotropic (flat walled). In order to understand the processes happening inside the corrosion pit, an appreciation of the chemistry of the solution within the pit is required. This concerns the pH and chloride concentration [78]. The pH is much lower in the pit than in the bulk solution. The formation of local concentrated solutions leads to the production of hydrogen ions, and decreases the pH in the pit.

The formation of carbonate films on the surface of carbon steel in a sweet environment combined with the fatigue operating regime may lead to mesa attack which is a type of localised corrosion [62,63]. The deformation of the fatigue sample during testing could cause the protective surface film to be broken leading to mesa attack. Also, extrusions and intrusions caused by Persistent Slip Bands (PSB) will cause breakdown of the protective film that will lead to mesa attack. Galvanic coupling between two different regions within the carbon steel may lead to mesa attack in a sweet CO₂ containing environment.

Figure 2-10: A schematic of pitting and mesa attack [64]

Corrosion pitting is one of the most important factors influencing corrosion fatigue life of a metal.

2.3 Corrosion Fatigue

2.3.1 Introduction

Fatigue of a metal occurs when it is subject to repeated cyclic loading and unloading. The metal will operate in a nominal stress range, which is below the Ultimate Tensile Strength (UTS) and generally below the yield point. It can be a slow process, where damage due to cyclic loading of the structure or material accumulates over time resulting in the formation of fatigue cracks which grow to reach a critical length at which sudden failure occurs [79]. The time element is usually referred to as cycles to failure. Fatigue can be classified into three different operating regimes known as Low Cycle Fatigue (LCF), High Cycle Fatigue (HCF) and Very High (VHCF) or Ultra High Cycle Fatigue (UHCF). The difference in the operating regimes may be defined in terms of the elastic strain (εₑ) and plastic strain (εₚ) applied to the
material. LCF is when the applied plastic strain is greater than the applied elastic strain ($\varepsilon_p > \varepsilon_e$). HCF is when the applied plastic strain is lower than the applied elastic strain ($\varepsilon_p < \varepsilon_e$).

For LCF and HCF the cycles to failure are from $10^3$ to $10^7$ cycles. VHCF operates at an applied elastic strain that is below the fatigue limit of the material. The fatigue operating regime considered here is HCF with a fatigue cycle limit of $10^7$, known as the run out point. The fatigue life of a material can be said to be subject to its resistance to the applied stresses, the presence of any defects and the operating environment.

A plot of the stress amplitude versus the number of cycles to failure is called a Wohler curve, after August Wohler in 1870 [80], also known as an S-N curve, Figure 2-11, and is used as a way to predict the fatigue life of a material. For fatigue in air at a given applied cyclic stress the material will exhibit an endurance or fatigue limit, where in theory no failure will occur for an infinite number of cycles. This limit has also been classed as the applied stress below which fatigue cracks may initiate but do not propagate beyond the bounds of microstructural features such as a grain boundary or pearlite colony [81,82]. However, within a corrosive environment, failure will occur at a lower number of cycles and there is no well-defined fatigue limit [72,83].

There are many variables that can affect the fatigue behaviour of a material these can be categorised as mechanical, metallurgical and environmental [68,84–86]. The mechanical variables that can influence the fatigue process include the cyclic frequency, R-ratio, cyclic waveform, residual stress, and crack size, orientation and shape. The R-ratio is the ratio between minimum and maximum applied stress or stress intensity. The metallurgical variables that can influence the fatigue process include the alloy chemical composition, the size and distribution of precipitates, the material microstructure, surface condition, heat treatment, mechanical working such as cold drawing and texture. The environmental variables that can influence the fatigue process in terms of corrosion fatigue behaviour include the solution composition and concentration of aggressive anions such as chloride, the solution temperature, pH and electrochemical potential and the structure of surface scales. The number of variables to be considered demonstrates the complexity of trying to understand the corrosion fatigue behaviour of a material.

It is well known that frequency and R-ratio are independent for fatigue tests carried out in air [87]. Work by Endo as cited in [72] demonstrates the effects of test frequency on the corrosion fatigue strength or life of a steel. It is shown that there is a significant decrease in corrosion fatigue strength as the test frequency is decreased, therefore increasing the time in solution for a set number of fatigue cycles [82,88]. The reduction in fatigue strength in a
corrosive environment is more pronounced at lower frequencies due to the effects of the corrosion process due to the increased time in solution and increase in crack growth rates with decreasing frequency [89,90].

For tests carried out in a corrosive environment the R-ratio will affect the maximum Crack Tip Opening Displacement (CTOD) with a reduction in R-ratio producing a decrease in CTOD hence a slower Fatigue Crack Growth Rate (FCGR) [91].

For the initiation phase and stage I fatigue crack growth stage, a decrease in the grain size will reduce the crack growth rate due to the number of grain boundaries that a crack has to penetrate or negotiate past with PSBs more likely to form in larger grain microstructures [81,92].

![Figure 2-11: Typical S-N curve for steel in two environments [48]](image)

2.3.2 The Fatigue Process

Corrosion fatigue is the occurrence of the fatigue process in an aggressive environment, where corrosion can dramatically reduce the life of the material [68,72,79,93]. The general fatigue process can be broken down into the following stages:

1. Pre-crack fatigue damage accumulation due to cyclic plastic deformation, which includes initial cyclic hardening, or softening that causes changes in the microstructure and cyclic strain localisation that causes a pronounced surface relief that act as stress concentrators for fatigue crack nucleation.
2. Fatigue crack nucleation
3. Fatigue crack propagation
4. Final fracture

For the Stage 1 damage accumulation, surface relief or roughness due to cyclic straining was first observed by Ewing et al. in 1902 [94]. They recognised elevations and depressions in
the surface of the material that were later to be known as extrusions and intrusions and termed PSBs or Persistent Slip Markings (PSMs). They also observed that fatigue cracks had initiated from these markings. Ewing et al. also demonstrated that the mean extrusion height increased with an increase in the number of fatigue cycles. Thompson et al. in 1956 cited in [80] demonstrated that the slip bands were “persistent” because after the sample had been fatigued and the slip markings were removed by polishing, further fatigue cycling showed them to have re-emerged at the identical initiation sites. This demonstrated that Persistent Slip Bands are a bulk phenomenon not merely a surface one.

Dislocations are present within the carbon steel wire due to the cold drawing process. Movement of the existing dislocations and nucleation of new dislocations on the preferred slip systems, {110}, {112} and {123} planes in the <111> direction for α-iron bcc structures, due to cyclic loading results in the formation of Persistent Slip Bands (PSBs) [27].

![Figure 2-12: Example of the slip systems in bcc structure [27]](image)

The increase in dislocation density and dislocation interaction within a slip band due to the cyclic loading causes work hardening, which means that a ladder type structure of dislocations forms in the material. The subsequent diffusion of vacancies results in the formation of intrusions and extrusion or PSMs, Figure 2-13 [84,88]. The accumulated plastic strain causes work hardening/softening of the material and it is at this interface between hard and soft material that fatigue crack initiation will occur. Work by Sangid [92] details the numerous steps for PSM formation and fatigue crack initiation. Fatigue crack initiation from regions of cyclic strain localisation in terms of PSBs and PSMs marking has been observed by many authors [68,76,79,95,96].
2.3.2.1 Fatigue Crack Growth

In order for a fatigue crack to initiate from a region of cyclic strain localisation or a surface defect the stress intensity factor at a particular feature must reach a threshold value $\Delta K_{th}$ or $\Delta K_0$. Figure 2-14 shows a typical Fatigue Crack Growth Rate (FCGR) curve with the three distinct regions or stages of crack growth.

Stage I FCG, known as the short crack growth region, is when a crack has initiated and propagates along the high shear stress planes (PSBs) that are at 45 degrees to the surface of the material. The crack propagates until it reaches a microstructural barrier such as a grain boundary or inclusion. The crack grows to have a micro-structurally short crack length. At this stage the crack growth rate is relatively high. The applied plastic strain amplitude controls the short crack growth region, which is where most components often spend the main proportion of their fatigue life [88].

Stage II, known as the long crack growth region of the FCGR curve, demonstrates an increase in crack growth rate with increasing stress intensity factor range and is known as the Paris regime. In 1963, Paris showed that this stage of fatigue crack growth for many materials complies with a power relationship of the form shown in Equation 2-27. The left hand side of the equation, $da/dN$, is crack growth per cycle in terms of change in crack length divided by change in fatigue cycles. The right hand side of the equation is made up of two materials constants $C$ and $m$, where $m$ has been established to be between 2 to 4 [91,97], and $\Delta K$ is the stress intensity factor range. The stress intensity factor range controls the applied plastic strain at the crack tip and the Crack Tip Opening Displacement. Fatigue crack growth rates for structural steels in a chloride environment have been shown to be in the region of $0.01 \mu m/cycle$ [95].

Figure 2-13: Fatigue damage accumulation stages (a) persistent slip band formation [79], (b) Intrusion and extrusion formation (Wood 1956) from [84] and (c) Surface profile of intrusions and extrusions [79]
\[
\frac{da}{dN} = C\Delta K^m \quad \text{Equation 2-27: Paris' Law}
\]

Stage III is where rapid crack growth leading to fast fracture or final failure of the material takes place. The model for fatigue crack growth (FCG) in Figure 2-14 does not fully take into account the concurrent corrosion process that is taking place in corrosion fatigue.

![Diagram of fatigue crack growth rate curve](image)

**Figure 2-14: Typical example of a fatigue crack growth rate curve from [81]**

### 2.3.3 Corrosion Fatigue

Corrosion fatigue strength is mainly influenced by the corrosion resistance of a metal in the particular test environment [89]. Seawater environments can have a dramatic effect on the initiation and propagation of fatigue cracks. This is demonstrated by the reduction factors established by [72] for carbon and stainless steels in various aqueous environments. The stages of corrosion fatigue crack nucleation and growth are somewhat different from that in air, a schematic of which is shown in Figure 2-15. There are two phases, one time dependent corrosion and the other cycle's dependent fatigue. The time dependent corrosion phase considers the growth of a surface film and subsequent breakdown, which leads to localised corrosion initiation, and growth. The cycles dependent fatigue phase considers the elements of fatigue cracking in an environment where it is considered that for long crack growth the effects of corrosion are minimal [86]. The transition phase between pitting and cracking considers how a corrosion fatigue crack will initiate from a corrosion pit or geometric discontinuity [73,95,98].
It is considered that at high stress ranges the corrosion fatigue failure mechanism is that of a fatigue cycles dependent mechanical process, whereas at lower stresses the mechanism is a time dependent corrosion process.

The synergistic effects of the role of the environment and the fatigue process on corrosion fatigue crack initiation and propagation can be classified into four possible mechanisms as follows [81,84]: -

(a) Surface film breakdown and consequent electrochemical attack at the exposed sites
(b) Strain Assisted Dissolution (SAD) of PSBs/PSMs and at the crack tip [85]
(c) Localised corrosion pit formation which act as surface stress concentrations
(d) Surface adsorption of hydrogen from the surrounding environment

Chloride induced general corrosion will take place on the surface of a carbon steel in seawater. The films that form are generally oxide, carbonate or sulphide based depending on the presence of corrosive gases in solution and are partially protective [96]. The surface films formed during the corrosion of steel in an aqueous environment create a volumetric expansion on the surface of the material [93]. The fatigue process acts to breakdown the protective surface film and expose the bare metal surface to the corrosive environment [72,73,88,89,99]. It has been proposed by Duquette and Uhlig, cited in [3], that the localised breakdown of the surface scale allows PSBs to penetrate the surface layer of the metal thus creating areas of strain localisation and enabling fatigue crack initiation from geometric discontinuities [68,96]. A schematic of the breakdown of the surface film and penetration of the exposed surface layer by PSBs is shown in Figure 2-16.
In order for this mechanism to operate there must be cathodic regions on the surface of the material. Parkins [76] discusses the formation of small discrete black spots of magnetite on the surface of carbon steel in a chloride environment which would facilitate this process. However, it is also said that uniform corrosion can prolong the fatigue life if the corrosion progresses at a faster rate than the fatigue damage occurs [68]. The crack growth rate to some extent is controlled by the combination of the rate of growth of the surface film and the exposure of the bare metal to the corrosive environment [65,100].

![Diagram of surface film breakdown from slip band protrusion](image)

Figure 2-16: A schematic of surface film breakdown from slip band protrusion [84]

SAD is a function of the applied strain on the material from the fatigue loading, the test environment in this case seawater and the type of material, ferritic-pearlitic carbon steel. SAD can assist in the initiation and growth of corrosion pits, and it can affect the FCGR.

PSBs protrude the surface of the material causing PSMs. These slip markings have a higher energy state than the bulk crystal lattice due to the dislocation density. They are therefore preferential sites for localised corrosion attack due to the lower activation energy required in order to dissolve these regions [84,101]. There dissolution causes geometric discontinuities from which fatigue cracks may initiate.

It is also noted that at high applied fatigue loading fatigue cracks will initiate from the PSBs alone as there is insufficient time for localised corrosion attack and pit formation to occur [81]. For the initiation of localised corrosion SAD mainly occurs in acidic solutions and not neutral ones such as seawater, unless suitable changes in the local environment, pH and potential were to develop.
Localised corrosion pits can form at microstructural inclusions which for carbon steels are mainly sulphide based such as MnS and (Fe,Mn)S. Localised crevice type corrosion occurs between the inclusion and the matrix and it is said that for sulphide inclusions the zone in between is sulphur rich thus enhancing the corrosion process [68,99,102]. It has also been observed that during cyclic loading corrosion at the inclusion develops more rapidly [72].

Sulphide inclusions have adequate solubility in order to produce local changes in the environment due to the generation of H$_2$S, Equation 2-28, and HS$^-$ ions, which may act as a path for hydrogen diffusion into the metal matrix. Hydrogen diffusion is temperature dependent and at room temperature and pressure the rate of diffusion will be low [103].

The dissolution of the inclusion creates a chloride rich region at the matrix-inclusion interface due to the diffusion of chloride ions toward this high stress region [102]. The dissolution of the inclusion and the subsequent diffusion of chloride into this region facilitate the initiation of a corrosion pit.

\[ MnS + 2H^+ \rightarrow H_2S + Mn^{2+} \quad \text{Equation 2-28} \quad [88] \]

Plasticity localisation around inclusions, due to surface deformation, may explain why most corrosion fatigue cracks initiate at surface inclusions. The difference in mechanical properties at the boundary between the inclusion and the matrix leads to debonding of the inclusion and subsequent dissolution [73,86,98,99,102,104,105] which will inevitably affect the fatigue resistance of the material. Dickson et al. [68] observed that the preferred location for crack initiation is more likely to be from an inclusion or corrosion pit than a slip plane or other deformation feature unless the sample is polished thus removing surface defects.

Localised corrosion pits are geometric stress raisers. The shape of the corrosion pit can be key to the affect it has on fatigue crack initiation as for example; hemispherical pits have a lower stress concentration intensity factor than narrow sharp long pits. The growth rate of a corrosion pit in the fatigue process is due to SAD, which as mentioned previously is a function of the magnitude of the applied strain, environment and the material. SAD can be termed as the chemical driving force for pit growth [106]. Localised corrosion attack at the ferrite-pearlite grain boundaries, the higher energy regions of the microstructure, within the corrosion pit will result in the formation of micro voids, which will coalesce by SAD facilitating pit growth.

Enhancement of the environment within the pit is possible throughout the whole fatigue cycle as unlike cracks, which exhibit closure for part of the cycle, the geometry of pits does
not completely facilitate this [102]. When a corrosion pit reaches a critical pit depth a fatigue crack will initiate [68,95,107], however it has been shown that not all pits result in the initiation of fatigue cracks [73]. The high stress concentration regions within a corrosion pit may exist at the edges of the pit or at a particular grain boundary and therefore crack initiation will occur at these locations and not exclusively at the base of the pit [72,96,107,108]. The synergistic effects of pitting corrosion and cyclic loading can be life limiting to a material. It has been observed that materials spend the majority of their fatigue life, 60-80 %, in the pit initiation and growth phase before fatigue cracks initiate and propagate from the pit [90,95,98,99].

During the corrosion process hydrogen may be adsorbed onto the surface of the metal. The adsorption of hydrogen produces local embrittlement, which coupled with the enhanced plasticity due to the lowering of surface energy leads to crack initiation. The increase in corrosion fatigue degradation of high strength steels is therefore related to their susceptibility and sensitivity to hydrogen embrittlement [72]. It has been observed that adsorption of hydrogen at the metal surface is the rate determining process for corrosion fatigue crack growth rate [84,109].

Hydrogen is also present in the crack tip environment during crack propagation and can cause localised crack initiation near inclusions that may result in crack deviation and propagation paths that follow the path of the inclusions as this is where hydrogen trapping within the microstructure is likely to occur [68,96]. A reduction in crack growth rate due to crack branching or crack tip blunting can increase the corrosion fatigue life of a material [89]. It is suggested that crack branching and large angle crack deflections would limit the maximum stress intensity; conversely the magnitude of the stress intensity factor may also contribute to crack branching with a lower stress intensity causing the fatigue crack to propagate down the path of least resistance [110,111]. As the length of the fatigue crack increases hydrogen embrittlement becomes a more favoured failure mechanism [73].

The faceted nature of corrosion fatigue cracks may be due to the crack path alternating between different {110} slip planes which is caused by changes in the anodic current throughout the corrosion fatigue test [68,84].

Intergranular cracking has been attributed to the preferential dissolution of accumulated dislocations at grain boundaries or with strain intensity. It is suggested that there is a reduced fatigue life with intergranular cracking than for transgranular slip band cracking because the cracks find it difficult to cross grain boundaries and transition from intergranular
to transgranular [68]. FCGRs for intergranular cracking are an order of magnitude faster than for transgranular cracking [81].

2.3.3.1 Corrosion Fatigue Crack Growth

Fatigue cracks may initiate and grow from surface defects and geometric discontinuities such as slip bands and corrosion pits. The mechanisms involved in understanding and determining corrosion fatigue crack propagation are SAD, hydrogen embrittlement and the corrosion products induced wedge effect which influences the CTOD [89]. The mechanism that takes place depends on the metal-environment combination.

\[ \log (\Delta K) \]

\[ \log (d_a/dN) \]

\[ \text{Aggressive} \]

\[ \text{Inert} \]

Figure 2-17: A schematic of corrosion fatigue crack growth curve [88]

SAD will act to increase the crack width thus decreasing the effective stress intensity factor and if corrosion is the dominant mechanism crack blunting will occur. Figure 2-17 shows an example of a FCGR curve in an aggressive environment where typically the curve is displaced to the left indicating a lower threshold stress intensity factor required for crack initiation. However, the threshold $\Delta K$ in an environment can be higher than in air due to the crack blunting effect or the corrosion product causing crack closure [88]. Crack tip dissolution by SAD can lead to retardation of crack growth due to crack blunting and crack arrest [88,96]. However, it may also increase FCGR because at anodic potentials preferential attack of plastic deformation will occur due to the lower activation energy required for dissolution of these regions. SAD therefore plays a key role in short crack growth rate for environment assisted fatigue conditions. Micro-structurally short cracks grow at a faster rate than long cracks due to the enhanced hydrogen production that occurs. The anodic dissolution of iron at the crack tip and the entry of the produced hydrogen into the crack tip plastic zone, which occur simultaneously during corrosion fatigue crack growth, demonstrates the participation of both SAD and hydrogen embrittlement in the acceleration of crack growth rates [73,85]. However
it has been shown that the corrosion fatigue behaviour of carbon steel in seawater is accredited to hydrogen embrittlement which in aerated solution is because of the cathodic reduction of water [85,89,100,106].

Anodic dissolution at the crack tip may be difficult due to the access of the environment governed by the amount of crack opening displacement [102]. The rate controlling processes in environment induced fatigue that affect crack growth are concerned with the chemistry of the crack tip environment, the crack geometry, ion exchange rates, fluid viscosity and fluid flow, see Figure 2-18 [84]. The localised environment within the corrosion pit and at the crack tip demonstrates a difference in pH compared to the bulk solution [76,85,88,106,112]. The localised pH at a corrosion pit can vary considerably from that of the bulk solution which suggests that the cyclic stress acts to enhance the dissolution process [72]. The limited oxygen diffusion to the crack tip means that there is an acidification of the solution in these areas due to hydrogen evolution [89,96,112].

The solution refreshment is dependent upon the bulk solution flow rate past the mouth of the crack. The refreshment is also dependent upon whether the ejected solution during crack opening is re-ingested during crack closure. Consequently, if the solution within the crack is not refreshed then iron saturation will occur. The dissolution process is controlled by the \( \text{Fe}^{2+} \) diffusion rate which for an iron saturated solution will be reduced consequently lowering the corrosion rate. Additionally, depending on the length of the crack, i.e. at the tip of long cracks it will be more significant; the refreshment of the solution due to fluid flow will reduce along the length of the crack and the solution will become saturated with iron and the corrosion rate will dramatically reduce compared to that in the bulk solution. However, the annular space within a flexible pipe is already saturated with iron so there will be no real effects on the chemistry within the crack.

The effects of iron confinement within a fatigue crack will slow down the dissolution process, therefore the long crack growth rate would only be slightly enhanced by corrosion. However, it may be surmised that the limited solution refreshment offered by the fatigue action is enough to sustain the electrochemical reactions taking place [112]. The stress intensity factor \( \Delta K \) controls the plastic strain amplitude at the crack tip and the CTOD, therefore controlling the crack growth rate.
Corrosion products such as iron oxides and calcareous deposits, will form on the internal walls or faces of the fatigue crack during the high stress opening half of the fatigue cycle. This mechanism considers crack closure during the fatigue cycle and has been termed the corrosion products induced wedge effect. This will lead to crack widening which will increase the crack tip stress intensity factor upon crack closure and ultimately the FCGR [82,84,88,90,91,96,100]. However, it has also been suggested that the wedge effect of corrosion products within the crack will decrease the effective stress intensity range at the crack tip which coupled with crack blunting will decrease the crack growth rate [86,89].

2.3.4 Fatigue Crack Initiation in Cold Drawn Carbon Steel Wire

Fatigue cracks tend to initiate from the surface of the wire from stress concentrations that may be produced by either imperfections in the steel surface from the drawing process or at the interface between the substrate and surface inclusions [28]. The crack initiates at the surface then deviates by approximately 90° to follow the drawing direction and the orientation of the pearlite lamellae which demonstrates the anisotropic behaviour of cold drawn eutectoid steel. A fine lamellar spacing can retard crack initiation on the sample surface. The microstructure determines the mechanical strength of the steel, which in turn will define the fatigue properties. The pearlite interlamellar spacing governs the crack initiation and growth due the fact that dislocation motion is blocked at the ferrite-cementite boundaries [36] and crack surface roughness defined by the pearlite interlamellar spacing [108] may lead to crack closure thus reducing the effective crack propagation driving force.
The cold drawing process improves the fatigue resistance of the steel wire because the fatigue crack growth rate decreases as the level of strain hardening increases [111,113]. The Paris region shifts downwards with an increase in cold drawing thus reducing the fatigue crack growth rate. If there is pearlite at the crack tip it tends to inhibit the development of plastic deformation in the crack tip region, which contributes to improved fatigue resistance. The mixed mode propagation that takes place close to the crack tip during crack bifurcation decreases the driving force and ultimately slows down the crack growth rate [33,36].

Fatigue crack growth paths in cold drawn steel wires tend to exhibit crack branching and bifurcations due to the availability of the different preferential orientations for crack growth or advancement [33,36–41]. The crack path may cross pearlite colonies termed transcolonial and it may break the ferrite-cementite lamellar termed translamellar [36]. Two symmetrical crack branches are referred to as crack twinning [40]. The change in direction of crack propagation due to the anisotropy of the wire is a mode of failure termed as splitting, exfoliation or delamination of the cementite lamellar [37,42]. Crack branching and bifurcation would not occur or would be limited if the pearlite were aligned such that the cementite lamellar were aligned parallel to one another and to the loading axis. However, as discussed earlier the cementite lamellar during the drawing process align themselves parallel to the wire axis.

2.4 Residual Stress

Residual stress can be defined as the stress that remains in a component or body when there are no external forces acting on the component. The summation of applied stress and residual stress, up to the yield strength of the material, will give the total stress applied to a component. The applied stress acting on a component is of a known value but predicting and controlling the residual stress is much more difficult and it can therefore significantly alter the mean stress experienced during fatigue cycling.

Residual stresses originate from misfits between different regions, phases and parts of a component or microstructure. They can be caused by the manner in which a component is manufactured, for example by the Bauschinger effect, loaded or by thermal gradients created during welding or heat treatments, or a combination. The Bauschinger effect in the cold drawn carbon steel wire is related to the dislocation structure within the material. The cold drawing process will produce an accumulation of dislocations which whilst increasing the tensile strength of the material will reduce the compressive strength of the material. The build-up of dislocations caused by the plastic deformation from the cold drawing process will influence the residual stress.
Residual stress fields are created around inclusions due to the misfit with the substrate because of the different mechanical properties such as elastic constant and thermal coefficient of expansion. In general this can be considered as the residual stress arising from the distribution of inelastic strains within a sample and is often termed the Eigen strain distribution and relates to the overall residual stress [114–116].

There are two different groups of residual stress due to plastic deformation at different length scales, namely macro and micro stress. Macro stress, known as Type I, vary continuously over large distances, multiple grains and are due to local differences in yield stress, variations in the applied stress, the existence of stress concentrations, surface treatments such as peening and the cold drawing process. Macro stress is defined as the average stress in an intermediate volume over several or numerous grains [114,116,117]. Micro stress is split into two different types. Type II is called intergranular stress and varies over the grain scale. Type III varies over the atomic scale and is caused by dislocations and point defects [116,118]. Fatigue life assessment of metallic components is often not interested in the type II and type III residual stresses. According to Withers et al. [114] the type II and type III residual stresses are washed out by the plasticity within the crack tip zone, therefore only the type I stresses need to be measured for a fatigue life assessment.

Residual stress can either be detrimental or beneficial to the manner in which a component operates. Tensile residual stresses tend to be detrimental as they modify the stress field at the metal surface, which affects hydrogen entry and diffusion towards the fracture zone thus promoting crack initiation and shortening component life. Compressive residual stresses are beneficial for fatigue resistance as they can delay fatigue crack initiation and propagation [119,120]. The benefit in mitigating fatigue crack initiation is dependent upon the magnitude and depth of the residual stress and distribution with deep residual stress fields decreasing the fatigue crack growth rate [116].

The effects of cold drawing are to improve the mechanical properties of the wire so that it has a very high yield and ultimate tensile strength. However, this process has the unavoidable consequence of producing tensile residual stress fields on the surface of the wire [120–123]. A multi-pass wire drawing process will generate residual stresses in the drawn wire from inhomogeneous deformation through the wire cross section, heat generation from plastic deformation and friction between the wire surface and the die. A temperature gradient is created through the cross section of the wire that can lead to surface shrinkage and ultimately a tensile residual stress on the surface of the wire [124].
Residual stresses have been shown to be compressive at the wire core, becoming increasingly tensile towards the wire surface [124]. The maximum measured residual stress value is in the axial direction. Tensile residual stresses promote crack initiation through surface defects. Fatigue cracks tend to initiate at the free surface therefore surface treatment may be beneficial. It is possible to establish the effects of residual stress on the fatigue life by using the Goodman or Gerber relationships.

Removal of tensile residual stresses from cold drawing by, for example, shot peening can improve fatigue resistance by imparting a compressive residual stress on the component surface [82]. However, it has been shown that compressive surface residual stresses can be relaxed by up to 50% within the first few fatigue cycles [119].

2.4.1 X-ray Diffraction Stress Measurement

The atomic spacing or d-spacing in all polycrystalline metals when deformed elastically will change from the stress free value to a value corresponding to the applied stress. When a metal is plastically deformed, the d-spacing will become distorted and this action will impart a residual stress in the metal. In terms of residual stress measurement, this d-spacing or lattice plane distortion will cause a shift and a broadening of the diffraction peak to a new 2θ position. It is this movement that is measured using X-ray diffraction in order to establish the residual stress in the metal by means of strain measurement.

Using X-ray diffraction to measure residual stress relies on the interaction between the wavelength of the X-ray and the crystal lattice. This phenomenon was established by W.L. Bragg in 1912 and is now known as Bragg’s Law. Consider two planes of atoms A-A’ and B-B’ that have the same Miller indices (hkI) and are separated by interplanar spacing dhkl see Figure 2-19. Now consider an X-ray beam, with wavelength λ, is incident with the two planes at an angle θ. Two rays 1 and 2, from the incident beam, strike the two planes of atoms at P and Q. Constructive interference occurs when they are diffracted through an angle θ. If the path length difference between 1-P-1’ and 2-Q-2’, which is SQ + QT, is equal to a whole number, n, then the condition for diffraction can be expressed as Equation 2-29 to Equation 2-31.

\[ n\lambda = SQ + QT \]  \hspace{1cm} \text{Equation 2-29}

\[ n\lambda = d_{hkI}\sin\theta + d_{hkI}\sin\theta \]  \hspace{1cm} \text{Equation 2-30}

\[ n\lambda = 2d_{hkI}\sin\theta \]  \hspace{1cm} \text{Equation 2-31}
Strain measurement is carried out by placing the sample in the X-ray diffractometer, where the sample is exposed to an X-ray beam that interacts with crystal lattice of the surface of the sample producing a diffraction pattern, which is detected by both of the Position Sensitive Detectors (PSD). The material under examination as part of this project is Body Centre Cubic (BCC) high strength carbon steel with a strain free d-spacing ($d_0$) of 1.17 Å. The diffractometer is tilted at an angle $\psi$, so that the {211} planes are brought into a position where they satisfy Bragg’s Law and a measurement of the d-spacing is taken. Using Equation 2-32 the strain along the sample direction can be calculated.

$$\varepsilon_\psi = \frac{d_\psi - d_0}{d_0}$$  \text{Equation 2-32}

Using Hooke’s Law the residual stress in the surface of the sample can be derived as per Eq. 13. The full derivation of which can be found in [126].
\[ \sigma_\psi = \frac{E}{(1 + v) \sin^2 \psi} \left( \frac{d_\psi - d_n}{d_n} \right) \]  

Equation 2.33

where

\( d_\psi \) is the inter-planar spacing of planes at an angle \( \psi \) to the surface

\( d_n \) is the inter-planar spacing of planes normal to the surface

\( \psi \) is the angle between the sample normal and the diffracting plane normal.

The \( \sin^2 \psi \) method is generally used to measure macroscopic residual stresses by means of X-ray diffraction, where \( \psi \) is the angle between the normal to the sample surface and the reflecting plane [121].

According to Bragg’s Law, at high 2\( \theta \) angles small changes in the d-spacing will result in measureable differences in 2\( \theta \), with a recommended 2\( \theta \) greater than 130° [126]. Therefore, the X-ray tube chosen to give a suitable Bragg reflection for the \{211\} for an iron sample at a sufficiently high 2\( \theta \) angle of 156.1° is the chromium tube. If the 2\( \theta \) angle is too low then changes in the d-spacing will be too small to be measured accurately.

Once the measurements have been made, the inter-planar spacing is plotted against \( \sin^2 \psi \), as shown in Figure 2-19. For the linear fit case, the gradient of the line, \( m \), is solved to establish the residual stress, as given by Eq. 14 reproduced from [126].

\[ \sigma_\psi = \left( \frac{E}{1 + v} \right)^m \]  

Equation 2.34

In the case where shear stresses are observed, \( \psi \)-splitting will occur leading to an elliptical type best fit for the \( d \sqrt{\sin^2 \psi} \) plot. The best-fit elliptical equation can then be used to establish the stress, see Figure 2-22.
Residual stress measurement by X-ray diffraction is made difficult due to the presence of the cementite phase because the orthorhombic lamellar structure can spread the scattering intensity into a large number of Bragg reflections [121]. The progressive cold drawing of steel leads to an anisotropic microstructure due to the alignment of the cementite lamellar in the drawing direction that develops a <110> fibre texture. However, Atienza et al. [120] has shown that the anisotropy of the microstructure does not affect the shape of the residual stress profile. A Gaussian function distribution fit is used as it gives a better fit for the cementite peaks. Also, the non-linearity of the slope for the $d_{hkl}$ vs $\sin^2\psi$ plot is said to be due to the plastic deformation and an anisotropic microstructure that exhibits <110> fibre texture in the material [121]. Also, Withers [116] suggests that the curvature of the $\sin^2\psi$ plot may be due to the gradient in out of plane stress that arises over the penetration depth for two phase materials such as ferrite-pearlite steels.

2.5 Surface Strain Mapping

In-situ studies of the microstructure of a material whilst simultaneously carrying out mechanical testing is often difficult to perform. Therefore the value in being able to develop and use a technique that can quantitatively analyse the surface strain on a material during mechanical loading is limitless. This technique is known as Digital Image Correlation (DIC). Optical correlation is an emergent strain-mapping technique that allows full-field surface strain mapping by comparing the images of the same region before, during and after deformation. Standard use of surface strain gauges to monitor changes in strain will establish the global surface strain and not detect the microstructural strain localisation that is likely to be present due to surface heterogeneity. The DIC technique allows the user to identify regions of strain localisation on a sample surface.
Surface sample analysis by means of imaging such as high speed photography has been around in different forms for quite some time [127,128]. Using a speckle pattern on the surface of a material, double exposure of photographic paper was used to map the local displacements of the speckles and calculate the surface strain [129].

Nowadays the technique utilises high speed digital photography to carry out the image acquisition. The images are stored as a discrete light intensity distribution of the sample surface. The digital images are split into a pixelated format and work has been carried out on images with 512x512 to 2000x2000 pixels [127,129,130]. Yusof et al. carried out work with a pixel resolution of 100 µm [131].

The technique compares the light intensity in the pixels of two different images and tries to link them to each other. Correlation of the pixels will establish the image offset in terms of a surface translation from which the displacement vectors can be established, Figure 2-23. A mathematical relationship between the material surface deformation and the distortion of the pixelated image from the intensity changes is required [127]. Sutton et al. [127] developed the use of a bilinear interpolation technique, which is an extension of linear interpolation, in order to provide a surface fit method that would represent the data in the form of a surface contour. The experimental limitations of this technique were that only considering small areas, especially across a crack, means that the correlation method averages the displacements off opposite magnitude and only displays a linear variation [128]. Nowadays, DIC software DaVis by LaVision uses Fast Fourier Transform (FFT) cross-correlation to compare subregions and calculate the displacement vector. FFT are mainly used due to their ability to interpret large amounts of data in a short space of time. The correlation of two images establishes the differences in the images in order to determine the displacement vectors. Displacement is mapped, with the strain established from the differentiation of the displacement vectors.

For slow strain rate testing successive images taken at known sample extensions may be correlated in order to establish how the surface strain develops [132]. A reference image, for correlation purposes, has to be taken at the minimum load to compare subsequent images to.

In order to map surface displacements a suitable pattern is required on the sample surface. This may be in the form of a speckle pattern using spray paint or gold film coatings [129,133]. However, etched microstructures have a natural pattern of features which makes them suitable for image correlation [130].
During slow strain rate testing the sample will become out of focus with increasing load due to the Poisson contraction, which can bring about pseudo-displacements as out of focus features appear to change in size [130]. Another source of error is the distortion of surface features at high strain due to changes in surface texture which will affect the image quality.

Figure 2-23: Schematic of the stages of digital image correlation [130]
Chapter 3 Corrosion Fatigue Cracking
3. **Corrosion Fatigue Cracking**

3.1 **Introduction**

Corrosion fatigue cracking in high strength carbon steel wire that has undergone fatigue testing at different stress ranges in three different seawater environments (Aerated, CO\(_2\) saturated to 1 bar absolute and 100 mbar absolute H\(_2\)S-CO\(_2\) balance to 1 bar absolute) was investigated to gain an understanding of the mechanisms involved. The seawater environments were specified by Intertek's clients.

Firstly, material characterisation of the high strength carbon steel wires was carried out to establish the chemical composition and mechanical properties of the materials.

Statistical analysis of corrosion fatigue cracking and localised corrosion pitting data was carried out to explore trends with respect to environment, cycles to failure and applied stress. Consequently, investigations were carried out to explore the surface scale formation. Establishing corrosion rates, immersion tests and grazing incidence X-ray diffraction (GIXRD) to determine surface scale compound structure achieved this.

3.2 **Corrosion Fatigue Testing**

The industrial collaborator for this project, Intertek, carried out corrosion fatigue testing at their test facility on two different types of high strength carbon steel that are used as tensile armour in flexible risers.

The fatigue test rig comprised of a stainless steel chamber to provide corrosion resistance to the corrosive environment. A four-point bend displacement controlled test set up was used as shown in Figure 3-1. The distance between the outer contact points is 150 mm and between inner contact points 50 mm. Both sets of contact rods are made from medium carbon steel, are set into polyether ether ketone (PEEK) backing strips and coated with Lacomit to isolate them from the stainless steel chamber, thus eliminating any possible galvanic effects from dissimilar metal contact.

In order to monitor the applied stress of each test piece a strain gauge was attached to the compression side of the sample. The strain gauges were protected from the environment by rubber sealant and bitumised tape. The tests were displacement controlled therefore the samples were cycled between set displacements in order to achieve the required applied stress range.
The fatigue test specimens were subjected to a 20,000 cycle shakedown in air prior to corrosion fatigue testing as required by the client fatigue testing procedure. This is thought to remove or reduce the effects of residual stress that are in the wires due to cold drawing process [134–137]. The effects of the shakedown were investigated and are discussed in Chapter 4.

For the aerated tests the chamber lid remained open to the atmosphere. For the CO$_2$ saturated and H$_2$S tests the chamber was sealed with the lid and continuously purged with high purity commercially pure (CP) grade (99.995 %) carbon dioxide.

Initially the synthetic seawater test solution was purged overnight until the oxygen concentration, measured by Orbisphere equipment, was consistently less than the required 5 ppb in solution. The solution was then introduced into the chamber ensuring that the oxygen concentration remained below the required level and continuous purge with CO$_2$ was maintained throughout the experiment. Daily checks were carried out to measure the oxygen concentration and the pH of the solution.

The make-up pH of the seawater was adjusted to 8.2 using 0.1 M NaOH as stated in the ASTM standard [54]. The solution is unbuffered and therefore final pH at the end of the fatigue test cycle varies for each environment. For the aerated environment the pH is from 6.0 to 8.2. For the CO$_2$ saturated environment the pH is from 5.2 to 5.8 and for the H$_2$S environment the pH is from 4.96 to 5.21.

The corrosion fatigue testing produced data in order to generate the S-N curves shown in Figure 3-2 and Figure 3-3.

The 12 mm x 4 mm steel wires had been corrosion fatigue tested in two modified (5 % NaCl) ASTM D1141 synthetic seawater environments, namely aerated and CO$_2$ saturated to 1 bar absolute. The seawater did not include the addition of stock solution No.3, which contains the heavy metal salts. For the aerated environment there were five nominal stress ranges, from 170 to 700 MPa. For the CO$_2$ saturated environment there were four nominal stress ranges, from 350 to 700 MPa. The mean applied stress for the aerated seawater test environment ranged from 107 to 428 MPa, and for the CO$_2$ saturated environment it ranged from 214 to 428 MPa. A stress ratio of R = 0.1 and a test frequency of 2 Hz was used. The test temperature was 20 °C for both environments.
The 12 mm x 7 mm steel wires had been corrosion fatigue tested in three modified (5 % NaCl) ASTM D1141 synthetic seawater environments, namely aerated, CO$_2$ saturated to 1 bar absolute and 100 mbar absolute H$_2$S with CO$_2$ balance to 1 bar absolute. Again the seawater was without the addition of the heavy metal salts. For this set of samples the applied stresses were somewhat different because the mean applied stress was constant throughout the tests and fixed at 550 MPa. For the aerated and CO$_2$ saturated environments there were five nominal stress ranges, from 125 to 325 MPa. For the H$_2$S test environment there were three nominal stress ranges, from 200 to 325 MPa. The stress ratio, R was between 0.5 and 0.7 and a test frequency of 2 Hz was used. The test temperature, specified by the client, was up to 23 °C for both environments.
### Table 3-1: 12 mm x 4 mm high strength steel wire corrosion fatigue test data for an aerated seawater environment

<table>
<thead>
<tr>
<th>Mean Stress (MPa)</th>
<th>Stress Range (MPa)</th>
<th>Maximum Stress (MPa)</th>
<th>Minimum Stress (MPa)</th>
<th>R ratio</th>
<th>Run Number</th>
<th>Test Piece Number</th>
<th>Cycles to Failure</th>
<th>Time to Failure (Days) [based on 2Hz]</th>
<th>Log Cycles to Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>681</td>
<td>768.5</td>
<td>87.5</td>
<td></td>
<td></td>
<td>1A</td>
<td>0</td>
<td>200000</td>
<td>1.16</td>
<td>5.30</td>
</tr>
<tr>
<td>701</td>
<td>778.5</td>
<td>77.5</td>
<td></td>
<td></td>
<td>1A</td>
<td>1</td>
<td>275950</td>
<td>1.60</td>
<td>5.44</td>
</tr>
<tr>
<td>711</td>
<td>783.5</td>
<td>72.5</td>
<td></td>
<td></td>
<td>1A</td>
<td>2</td>
<td>175950</td>
<td>1.02</td>
<td>5.25</td>
</tr>
<tr>
<td>699</td>
<td>777.5</td>
<td>78.5</td>
<td></td>
<td></td>
<td>1A</td>
<td>3</td>
<td>182280</td>
<td>1.05</td>
<td>5.26</td>
</tr>
<tr>
<td>393</td>
<td>440.5</td>
<td>47.5</td>
<td></td>
<td>0.1</td>
<td>2A</td>
<td>0</td>
<td>689590</td>
<td>3.99</td>
<td>5.84</td>
</tr>
<tr>
<td>394</td>
<td>441</td>
<td>47</td>
<td></td>
<td></td>
<td>2A</td>
<td>1</td>
<td>510530</td>
<td>2.95</td>
<td>5.71</td>
</tr>
<tr>
<td>402</td>
<td>445</td>
<td>43</td>
<td></td>
<td></td>
<td>2A</td>
<td>2</td>
<td>830490</td>
<td>4.81</td>
<td>5.92</td>
</tr>
<tr>
<td>397</td>
<td>442.5</td>
<td>45.5</td>
<td></td>
<td></td>
<td>2A</td>
<td>3</td>
<td>822710</td>
<td>4.76</td>
<td>5.92</td>
</tr>
<tr>
<td>246</td>
<td>276</td>
<td>30</td>
<td></td>
<td></td>
<td>3A</td>
<td>0</td>
<td>3100000</td>
<td>17.94</td>
<td>6.49</td>
</tr>
<tr>
<td>241</td>
<td>273.5</td>
<td>32.5</td>
<td></td>
<td></td>
<td>3A</td>
<td>1</td>
<td>3261540</td>
<td>18.87</td>
<td>6.51</td>
</tr>
<tr>
<td>237</td>
<td>271.5</td>
<td>34.5</td>
<td></td>
<td></td>
<td>3A</td>
<td>2</td>
<td>3423080</td>
<td>19.81</td>
<td>6.53</td>
</tr>
<tr>
<td>242</td>
<td>274</td>
<td>32</td>
<td></td>
<td></td>
<td>3A</td>
<td>3</td>
<td>3569230</td>
<td>20.66</td>
<td>6.55</td>
</tr>
<tr>
<td>172</td>
<td>193</td>
<td>21</td>
<td></td>
<td></td>
<td>4A</td>
<td>0</td>
<td>10000000</td>
<td>57.87</td>
<td>7.00</td>
</tr>
<tr>
<td>170</td>
<td>192</td>
<td>22</td>
<td></td>
<td></td>
<td>4A</td>
<td>1</td>
<td>10000000</td>
<td>57.87</td>
<td>7.00</td>
</tr>
<tr>
<td>163</td>
<td>188.5</td>
<td>25.5</td>
<td></td>
<td></td>
<td>4A</td>
<td>2</td>
<td>10000000</td>
<td>57.87</td>
<td>7.00</td>
</tr>
<tr>
<td>168</td>
<td>191</td>
<td>23</td>
<td></td>
<td></td>
<td>4A</td>
<td>3</td>
<td>10000000</td>
<td>57.87</td>
<td>7.00</td>
</tr>
<tr>
<td>283</td>
<td>324.5</td>
<td>41.5</td>
<td></td>
<td></td>
<td>5A</td>
<td>0</td>
<td>2585030</td>
<td>14.96</td>
<td>6.41</td>
</tr>
<tr>
<td>284</td>
<td>325</td>
<td>41</td>
<td></td>
<td></td>
<td>5A</td>
<td>1</td>
<td>2108840</td>
<td>12.20</td>
<td>6.32</td>
</tr>
<tr>
<td>292</td>
<td>329</td>
<td>37</td>
<td></td>
<td></td>
<td>5A</td>
<td>2</td>
<td>1938780</td>
<td>11.22</td>
<td>6.29</td>
</tr>
<tr>
<td>298</td>
<td>332</td>
<td>34</td>
<td></td>
<td></td>
<td>5A</td>
<td>3</td>
<td>1662590</td>
<td>9.62</td>
<td>6.22</td>
</tr>
</tbody>
</table>

### Table 3-2: 12 mm x 4 mm high strength steel wire corrosion fatigue test data for a CO₂ saturated seawater environment

<table>
<thead>
<tr>
<th>Mean Stress (MPa)</th>
<th>Stress Range (MPa)</th>
<th>Maximum Stress (MPa)</th>
<th>Minimum Stress (MPa)</th>
<th>R ratio</th>
<th>Run Number</th>
<th>Test Piece Number</th>
<th>Cycles to Failure</th>
<th>Time to Failure (Days) [based on 2Hz]</th>
<th>Log Cycles to Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>778</td>
<td>78</td>
<td></td>
<td></td>
<td>1C</td>
<td>0</td>
<td>124300</td>
<td>0.72</td>
<td>5.09</td>
</tr>
<tr>
<td>725</td>
<td>790.5</td>
<td>65.5</td>
<td></td>
<td></td>
<td>1C</td>
<td>1</td>
<td>103950</td>
<td>0.60</td>
<td>5.02</td>
</tr>
<tr>
<td>717</td>
<td>786.5</td>
<td>69.5</td>
<td></td>
<td></td>
<td>1C</td>
<td>2</td>
<td>97175</td>
<td>0.56</td>
<td>4.99</td>
</tr>
<tr>
<td>712</td>
<td>784</td>
<td>72</td>
<td></td>
<td></td>
<td>1C</td>
<td>3</td>
<td>97175</td>
<td>0.56</td>
<td>4.99</td>
</tr>
<tr>
<td>585</td>
<td>659.5</td>
<td>74.5</td>
<td></td>
<td>0.1</td>
<td>2C</td>
<td>0</td>
<td>201590</td>
<td>1.17</td>
<td>5.30</td>
</tr>
<tr>
<td>595</td>
<td>664.5</td>
<td>69.5</td>
<td></td>
<td></td>
<td>2C</td>
<td>1</td>
<td>200000</td>
<td>1.16</td>
<td>5.30</td>
</tr>
<tr>
<td>577</td>
<td>655.5</td>
<td>78.5</td>
<td></td>
<td></td>
<td>2C</td>
<td>2</td>
<td>212700</td>
<td>1.23</td>
<td>5.33</td>
</tr>
<tr>
<td>598</td>
<td>666</td>
<td>68</td>
<td></td>
<td></td>
<td>2C</td>
<td>3</td>
<td>238100</td>
<td>1.38</td>
<td>5.38</td>
</tr>
<tr>
<td>416</td>
<td>483</td>
<td>67</td>
<td></td>
<td></td>
<td>3C</td>
<td>0</td>
<td>317310</td>
<td>1.84</td>
<td>5.50</td>
</tr>
<tr>
<td>423</td>
<td>486.5</td>
<td>63.5</td>
<td></td>
<td></td>
<td>3C</td>
<td>1</td>
<td>281480</td>
<td>1.63</td>
<td>5.45</td>
</tr>
<tr>
<td>424</td>
<td>487</td>
<td>63</td>
<td></td>
<td></td>
<td>3C</td>
<td>2</td>
<td>292590</td>
<td>1.69</td>
<td>5.47</td>
</tr>
<tr>
<td>424</td>
<td>487</td>
<td>63</td>
<td></td>
<td></td>
<td>3C</td>
<td>3</td>
<td>237037</td>
<td>1.37</td>
<td>5.37</td>
</tr>
<tr>
<td>333</td>
<td>380.5</td>
<td>47.5</td>
<td></td>
<td></td>
<td>4C</td>
<td>0</td>
<td>687000</td>
<td>3.98</td>
<td>5.84</td>
</tr>
<tr>
<td>346</td>
<td>387</td>
<td>41</td>
<td></td>
<td></td>
<td>4C</td>
<td>1</td>
<td>649620</td>
<td>3.76</td>
<td>5.81</td>
</tr>
<tr>
<td>337</td>
<td>382.5</td>
<td>45.5</td>
<td></td>
<td></td>
<td>4C</td>
<td>2</td>
<td>736360</td>
<td>4.26</td>
<td>5.87</td>
</tr>
<tr>
<td>342</td>
<td>385</td>
<td>43</td>
<td></td>
<td></td>
<td>4C</td>
<td>3</td>
<td>872730</td>
<td>5.05</td>
<td>5.94</td>
</tr>
<tr>
<td>Mean Stress (MPa)</td>
<td>Stress Range (MPa)</td>
<td>Maximum Stress (MPa)</td>
<td>Minimum Stress (MPa)</td>
<td>R ratio</td>
<td>Run Number</td>
<td>Test Piece Number</td>
<td>Cycles to Failure</td>
<td>Time to Failure (Days) [based on 2 Hz]</td>
<td>Log Cycles to Failure</td>
</tr>
<tr>
<td>------------------</td>
<td>-------------------</td>
<td>---------------------</td>
<td>---------------------</td>
<td>---------</td>
<td>------------</td>
<td>-------------------</td>
<td>-----------------</td>
<td>--------------------------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>328</td>
<td>714</td>
<td>386</td>
<td></td>
<td>0.5</td>
<td>1A</td>
<td>0</td>
<td>770000</td>
<td>4.46</td>
<td>5.89</td>
</tr>
<tr>
<td>324</td>
<td>712</td>
<td>388</td>
<td></td>
<td>1</td>
<td>1A</td>
<td>1</td>
<td>710000</td>
<td>4.11</td>
<td>5.85</td>
</tr>
<tr>
<td>327</td>
<td>713.5</td>
<td>386.5</td>
<td></td>
<td>2</td>
<td>2A</td>
<td>2</td>
<td>645000</td>
<td>3.73</td>
<td>5.81</td>
</tr>
<tr>
<td>329</td>
<td>714.5</td>
<td>385.5</td>
<td></td>
<td>3</td>
<td>3A</td>
<td>3</td>
<td>550000</td>
<td>3.18</td>
<td>5.74</td>
</tr>
<tr>
<td>201</td>
<td>650.5</td>
<td>449.5</td>
<td></td>
<td>0.7</td>
<td>2A</td>
<td>0</td>
<td>4500000</td>
<td>26.04</td>
<td>6.65</td>
</tr>
<tr>
<td>198</td>
<td>649</td>
<td>451</td>
<td></td>
<td>1</td>
<td>3A</td>
<td>1</td>
<td>4500000</td>
<td>26.04</td>
<td>6.65</td>
</tr>
<tr>
<td>201</td>
<td>650.5</td>
<td>449.5</td>
<td></td>
<td>2</td>
<td>4A</td>
<td>2</td>
<td>4905400</td>
<td>28.39</td>
<td>6.69</td>
</tr>
<tr>
<td>203</td>
<td>651.5</td>
<td>448.5</td>
<td></td>
<td>3</td>
<td>5A</td>
<td>3</td>
<td>4905400</td>
<td>28.39</td>
<td>6.69</td>
</tr>
<tr>
<td>123</td>
<td>611.5</td>
<td>488.5</td>
<td></td>
<td>0.8</td>
<td>3A</td>
<td>0</td>
<td>100000000</td>
<td>57.87</td>
<td>7.00</td>
</tr>
<tr>
<td>123</td>
<td>611.5</td>
<td>488.5</td>
<td></td>
<td>1</td>
<td>3A</td>
<td>1</td>
<td>100000000</td>
<td>57.87</td>
<td>7.00</td>
</tr>
<tr>
<td>127</td>
<td>613.5</td>
<td>486.5</td>
<td></td>
<td>2</td>
<td>4A</td>
<td>2</td>
<td>100000000</td>
<td>57.87</td>
<td>7.00</td>
</tr>
<tr>
<td>120</td>
<td>610</td>
<td>490</td>
<td></td>
<td>3</td>
<td>5A</td>
<td>3</td>
<td>100000000</td>
<td>57.87</td>
<td>7.00</td>
</tr>
<tr>
<td>181</td>
<td>640.5</td>
<td>459.5</td>
<td></td>
<td>0.7</td>
<td>4A</td>
<td>0</td>
<td>200000000</td>
<td>11.57</td>
<td>6.30</td>
</tr>
<tr>
<td>193</td>
<td>646.5</td>
<td>453.5</td>
<td></td>
<td>1</td>
<td>5A</td>
<td>1</td>
<td>300000000</td>
<td>17.36</td>
<td>6.48</td>
</tr>
<tr>
<td>196</td>
<td>648</td>
<td>452</td>
<td></td>
<td>2</td>
<td>5A</td>
<td>2</td>
<td>340000000</td>
<td>19.68</td>
<td>6.53</td>
</tr>
<tr>
<td>175</td>
<td>637.5</td>
<td>462.5</td>
<td></td>
<td>3</td>
<td>5A</td>
<td>3</td>
<td>310000000</td>
<td>17.94</td>
<td>6.49</td>
</tr>
<tr>
<td>257</td>
<td>678.5</td>
<td>421.5</td>
<td></td>
<td>0.6</td>
<td>5A</td>
<td>0</td>
<td>129000000</td>
<td>7.47</td>
<td>6.11</td>
</tr>
<tr>
<td>262</td>
<td>681</td>
<td>419</td>
<td></td>
<td>1</td>
<td>5A</td>
<td>1</td>
<td>106000000</td>
<td>6.13</td>
<td>6.03</td>
</tr>
<tr>
<td>261</td>
<td>680.5</td>
<td>419.5</td>
<td></td>
<td>2</td>
<td>5A</td>
<td>2</td>
<td>131000000</td>
<td>7.58</td>
<td>6.12</td>
</tr>
<tr>
<td>265</td>
<td>682.5</td>
<td>417.5</td>
<td></td>
<td>3</td>
<td>5A</td>
<td>3</td>
<td>124000000</td>
<td>7.18</td>
<td>6.09</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mean Stress (MPa)</th>
<th>Stress Range (MPa)</th>
<th>Maximum Stress (MPa)</th>
<th>Minimum Stress (MPa)</th>
<th>R ratio</th>
<th>Run Number</th>
<th>Test Piece Number</th>
<th>Cycles to Failure</th>
<th>Time to Failure (Days) [based on 2 Hz]</th>
<th>Log Cycles to Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>329</td>
<td>714.5</td>
<td>385.5</td>
<td></td>
<td>0.5</td>
<td>1C</td>
<td>0</td>
<td>590000</td>
<td>3.41</td>
<td>5.77</td>
</tr>
<tr>
<td>317</td>
<td>708.5</td>
<td>391.5</td>
<td></td>
<td>1</td>
<td>1C</td>
<td>1</td>
<td>490000</td>
<td>2.84</td>
<td>5.69</td>
</tr>
<tr>
<td>324</td>
<td>712</td>
<td>388</td>
<td></td>
<td>2</td>
<td>1C</td>
<td>2</td>
<td>540000</td>
<td>3.13</td>
<td>5.73</td>
</tr>
<tr>
<td>323</td>
<td>711.5</td>
<td>388.5</td>
<td></td>
<td>3</td>
<td>1C</td>
<td>3</td>
<td>510000</td>
<td>2.95</td>
<td>5.71</td>
</tr>
<tr>
<td>201</td>
<td>650.5</td>
<td>449.5</td>
<td></td>
<td>0.7</td>
<td>2C</td>
<td>0</td>
<td>21000000</td>
<td>12.15</td>
<td>6.32</td>
</tr>
<tr>
<td>202</td>
<td>651</td>
<td>449</td>
<td></td>
<td>1</td>
<td>2C</td>
<td>1</td>
<td>18500000</td>
<td>10.71</td>
<td>6.27</td>
</tr>
<tr>
<td>197</td>
<td>648.5</td>
<td>451.5</td>
<td></td>
<td>2</td>
<td>2C</td>
<td>2</td>
<td>18500000</td>
<td>10.71</td>
<td>6.27</td>
</tr>
<tr>
<td>193</td>
<td>646.5</td>
<td>453.5</td>
<td></td>
<td>3</td>
<td>2C</td>
<td>3</td>
<td>20000000</td>
<td>11.57</td>
<td>6.30</td>
</tr>
<tr>
<td>127</td>
<td>613.5</td>
<td>486.5</td>
<td></td>
<td>0.8</td>
<td>3C</td>
<td>0</td>
<td>96320000</td>
<td>55.74</td>
<td>6.98</td>
</tr>
<tr>
<td>116</td>
<td>608</td>
<td>492</td>
<td></td>
<td>1</td>
<td>3C</td>
<td>1</td>
<td>60000000</td>
<td>34.72</td>
<td>6.78</td>
</tr>
<tr>
<td>128</td>
<td>614</td>
<td>486</td>
<td></td>
<td>2</td>
<td>3C</td>
<td>2</td>
<td>97410000</td>
<td>56.37</td>
<td>6.99</td>
</tr>
<tr>
<td>127</td>
<td>613.5</td>
<td>486.5</td>
<td></td>
<td>3</td>
<td>3C</td>
<td>3</td>
<td>73750000</td>
<td>42.68</td>
<td>6.87</td>
</tr>
<tr>
<td>188</td>
<td>644</td>
<td>456</td>
<td></td>
<td>0.7</td>
<td>4C</td>
<td>0</td>
<td>23000000</td>
<td>13.31</td>
<td>6.36</td>
</tr>
<tr>
<td>188</td>
<td>644</td>
<td>456</td>
<td></td>
<td>1</td>
<td>4C</td>
<td>1</td>
<td>22000000</td>
<td>12.73</td>
<td>6.34</td>
</tr>
<tr>
<td>188</td>
<td>644</td>
<td>456</td>
<td></td>
<td>2</td>
<td>4C</td>
<td>2</td>
<td>27000000</td>
<td>15.63</td>
<td>6.43</td>
</tr>
<tr>
<td>189</td>
<td>644.5</td>
<td>455.5</td>
<td></td>
<td>3</td>
<td>4C</td>
<td>3</td>
<td>28000000</td>
<td>16.20</td>
<td>6.45</td>
</tr>
<tr>
<td>258</td>
<td>679</td>
<td>421</td>
<td></td>
<td>0.6</td>
<td>5C</td>
<td>0</td>
<td>15500000</td>
<td>8.97</td>
<td>6.19</td>
</tr>
<tr>
<td>256</td>
<td>678</td>
<td>422</td>
<td></td>
<td>1</td>
<td>5C</td>
<td>1</td>
<td>14800000</td>
<td>8.56</td>
<td>6.17</td>
</tr>
<tr>
<td>252</td>
<td>676</td>
<td>424</td>
<td></td>
<td>2</td>
<td>5C</td>
<td>2</td>
<td>13500000</td>
<td>7.81</td>
<td>6.13</td>
</tr>
<tr>
<td>249</td>
<td>674.5</td>
<td>425.5</td>
<td></td>
<td>3</td>
<td>5C</td>
<td>3</td>
<td>12600000</td>
<td>7.29</td>
<td>6.10</td>
</tr>
</tbody>
</table>
Table 3-5: 12 mm x 7 mm high strength steel wire corrosion fatigue test data for 100 mbar absolute H₂S with CO₂ balance seawater environment

<table>
<thead>
<tr>
<th>Mean Stress (MPa)</th>
<th>Stress Range (MPa)</th>
<th>Maximum Stress (MPa)</th>
<th>Minimum Stress (MPa)</th>
<th>R ratio</th>
<th>Run Number</th>
<th>Test Piece Number</th>
<th>Cycles to Failure</th>
<th>Time to Failure (Days) [based on 2 Hz]</th>
<th>Log Cycles to Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td></td>
<td></td>
<td></td>
<td>1H</td>
<td>0</td>
<td>1</td>
<td>646100</td>
<td>3.74</td>
<td>5.81</td>
</tr>
<tr>
<td></td>
<td>321</td>
<td>710.5</td>
<td>389.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>331</td>
<td>715.5</td>
<td>384.5</td>
<td>1</td>
<td>1</td>
<td>204710</td>
<td>1.18</td>
<td>5.31</td>
<td></td>
</tr>
<tr>
<td></td>
<td>322</td>
<td>711</td>
<td>389</td>
<td>2</td>
<td>2</td>
<td>50000</td>
<td>0.29</td>
<td>4.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>326</td>
<td>713</td>
<td>387</td>
<td>3</td>
<td>3</td>
<td>530000</td>
<td>3.07</td>
<td>5.72</td>
<td></td>
</tr>
<tr>
<td></td>
<td>201</td>
<td>650.5</td>
<td>449.5</td>
<td>0.7</td>
<td>0</td>
<td>1</td>
<td>10000000</td>
<td>57.87</td>
<td>7.00</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>650</td>
<td>450</td>
<td></td>
<td>1</td>
<td>10000000</td>
<td>57.87</td>
<td>7.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>195</td>
<td>647.5</td>
<td>452.5</td>
<td></td>
<td>2</td>
<td>10000000</td>
<td>57.87</td>
<td>7.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>650</td>
<td>450</td>
<td></td>
<td>3</td>
<td>10000000</td>
<td>57.87</td>
<td>7.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>685</td>
<td>415</td>
<td>0.6</td>
<td>0</td>
<td>1</td>
<td>10000000</td>
<td>57.87</td>
<td>7.00</td>
</tr>
<tr>
<td></td>
<td>263</td>
<td>681.5</td>
<td>418.5</td>
<td></td>
<td>1</td>
<td>10000000</td>
<td>57.87</td>
<td>7.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>266</td>
<td>683</td>
<td>417</td>
<td></td>
<td>2</td>
<td>250000</td>
<td>14.76</td>
<td>6.41</td>
<td></td>
</tr>
<tr>
<td></td>
<td>256</td>
<td>678</td>
<td>422</td>
<td></td>
<td>3</td>
<td>8200000</td>
<td>47.45</td>
<td>6.91</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3-2: 12 mm x 4 mm high strength steel wire corrosion fatigue tested S-N curve statistical data points
3.3 Experimental Methods

The corrosion fatigued samples for both the 12 mm x 4 mm and 12 mm x 7 mm high strength steel wires supplied by Intertek were studied as part of this project to establish the presence of secondary cracks. The cracks were investigated to determine their crack path with respect to microstructure, population, size and location of the cracks. This was in order to determine the relationship between cracking, microstructure, environment and the effects of cyclic stress on the corrosion fatigue process. The test pieces were sectioned and investigated using an optical microscope and a Scanning Electron Microscope (SEM).

3.3.1 Material Characterisation

The information available about the tensile armour at the start of the project was limited with only the manufacturer’s tensile rating accessible. Therefore material characterisation work was carried out to establish further properties of the carbon steel material. The three materials characterised were all tensile armour wires with dimensions of 12 mm x 4 mm, 12 mm x 7 mm and 10 mm x 5 mm.

The chemical composition of the three materials used in this project was established using optical emission spectroscopy (OES).

Tensile testing of the 12 mm x 4 mm was carried out in accordance with BS EN ISO 6892-1:2009 Metallic Materials - Tensile Testing - Part 1: Method of Test at Ambient Temperature [138]. An extensometer was used in the tensile tests to establish sample displacement and
determine the strain. Insufficient as-received material was available for the 12 mm x 7 mm and 10 mm x 5 mm in order to carry out tensile testing and therefore the manufacturers rating was used.

A Keyence VHX2000 optical microscope was used to establish the microstructure of the three different tensile armour wires in the normal plane and transverse plane.

### 3.3.2 Sample Preparation

#### 3.3.2.1 Sample Cleaning

The fatigue-tested samples were received with their strain gauges, protective coating of rubber sealant and bitumised tape still attached. The bitumised tape was removed using petroleum spirit. The rubber sealant was removed using acetone, which enabled the strain gauge to be removed.

In between grinding and polishing stages the samples were cleaned with soap and water, rinsed with ethanol and dried thoroughly.

#### 3.3.2.2 Sectioning and Polishing

The initial sample review Appendix 1 established the approximate locations of the secondary cracks. This information was used to section the test pieces in the appropriate planes and directions. The secondary fatigue cracks were observed to be in the normal plane, therefore the test pieces were cut along the transverse plane in order to expose the crack path. The samples were then mounted in Bakelite and underwent various stages of grinding and polishing, as shown in Table 3-6. The samples were etched in 2% nital (2% nitric acid, 98% ethanol) to expose the microstructure.

<table>
<thead>
<tr>
<th>Media</th>
<th>Lubricant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grinding</td>
<td></td>
</tr>
<tr>
<td>Coarse</td>
<td>Silicon Carbide (SiC)</td>
</tr>
<tr>
<td>Medium</td>
<td>P120, P240, P400</td>
</tr>
<tr>
<td>Fine</td>
<td>P800</td>
</tr>
<tr>
<td></td>
<td>Water</td>
</tr>
<tr>
<td>Polishing</td>
<td></td>
</tr>
<tr>
<td>Coarse</td>
<td>Diamond Paste</td>
</tr>
<tr>
<td>Medium</td>
<td>6 μm</td>
</tr>
<tr>
<td>Fine</td>
<td>1 μm</td>
</tr>
<tr>
<td>Very Fine</td>
<td>Oxide Polishing Solution (OPS) Alumina Oxide</td>
</tr>
</tbody>
</table>

#### 3.3.3 Crack & Pit Depth Measurement

An optical microscope was used to ascertain the population and size of any secondary cracks and localised corrosion pits within the fatigue samples. Using the optical microscope image acquisition software, Axiovision, images of the cracks and pits were captured along the
surface, the transverse plane, of each sample. The 20x objective was used as this gave an appropriate level of magnification for the secondary cracks and localised corrosion pits. Using the scale settings and length measurement tools within the software package individual crack depth and localised corrosion pit depth measurements for each secondary crack and corrosion pit were made.

Crack depth was measured to be the vertical distance from the edge of the sample to the crack tip. Likewise, pit depth was measured to be the vertical distance from the edge of the sample to the base of the pit. The results of which are shown in Section 3.4. Sample length was maintained at a constant 20 mm long therefore enabling a comparison to be made between sets of results. Figure 3-4 shows an example of a long and shorter secondary fatigue crack and evidence of localised corrosion in the form of a corrosion pit.

Figure 3-4: Optical microscope image showing a typical example of secondary cracks initiating at the surface of the high strength steel.

3.3.4 Crack & Pit Depth Analysis

Statistical analysis of the crack depth and pit depth data was carried out taking guidance from [139]. First of all the data was input into a spreadsheet. The cumulative probability function, F(x), is used to represent data that would increase monotonically with increasing values of x. The relationship between F(x) and x is plotted on probability plotting paper. Depending upon the type of probability distribution plotting paper used, the plot should yield a linear relationship, i.e. a straight line. Once a straight-line relationship has been determined the
parameter values for that particular probability distribution can be established. These are the mean, μ, standard deviation, σ and shape factor, λ. Various cumulative distribution functions were used to establish the best-fit curve for the crack and pit statistical data.

The average rank method was used to plot the cumulative probability distribution for either the crack depth or pit depth data. This involves plotting the crack or pit depth on the x-axis and the cumulative probability on the y-axis. First of all the data, x, is sorted into increasing numerical order. Each number is then given a rank number, i. The cumulative probability distribution function, F(x), is then calculated using Equation 3-1. An example of this type of plot is shown in Figure 3-5

\[
F(x) = \frac{i}{n} + 1 \quad \text{Equation 3-1}
\]

Plotting of this type of function enables the establishment of the shape of the distribution. From the shape the associated probability plot can be established and subsequently the distribution parameters, such as mean, standard deviation and shape factor. The scaling of the x and y axes of the probability plotting paper changes in accordance with the type of distribution utilised. The analysis and probability plotting was carried out in Excel and Matlab. Figure 3-6 shows an example of a probability plot.
3.3.4.1 Probability Distributions

Various fundamental and extreme value probability distributions were used to provide an appropriate fit to the crack and pit data. The two types of fundamental distributions used were the Normal and Log-normal distribution. The type of extreme value distribution used was the Generalised Extreme Value distribution.

3.3.4.1.1 Normal Distribution

The normal distribution cumulative distribution function, the arithmetic mean and standard deviation were calculated using Equation 3-2 to Equation 3-4.

\[ F(x) = \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{x - \mu}{\sqrt{2\sigma^2}} \right) \right] \equiv \Phi \]  
\text{Equation 3-2: Normal distribution cumulative distribution function}

\[ \bar{x}_a = \frac{1}{n} \sum_{i=1}^{n} x_i \]  
\text{Equation 3-3: Arithmetic mean}

\[ \sigma_x^2 = \frac{1}{n} \sum_{i=1}^{n} (x_i - \bar{x})^2 \]  
\text{Equation 3-4: Standard deviation}
3.3.4.1.2 Lognormal Distribution

The log-normal distribution cumulative distribution function, the geometric mean and geometric standard deviation were calculated using Equation 5-7.

\[ F(x) = \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{\ln x - \mu}{\sigma \sqrt{2}} \right) \right] \]

**Equation 3-5: Log-normal distribution cumulative distribution function**

\[ \bar{x}_g = \exp \left( \frac{\sum_{i=1}^{n} \ln x_i}{n} \right) \]

**Equation 3-6: Geometric mean [140]**

\[ \sigma_g = \exp \left( \frac{\sqrt{\sum_{i=1}^{n} \left( \ln \frac{A_i}{\mu_g} \right)^2}}{n} \right) \]

**Equation 3-7: Geometric standard deviation**

3.3.4.1.3 Generalised Extreme Value Distribution

The generalised extreme value distribution cumulative distribution function and mean were calculated using Equation 8-9.

\[ F(x, \mu, \sigma, \xi) = \exp \left\{ - \left[ 1 + \xi \left( \frac{x - \mu}{\sigma} \right) \right]^{1/\xi} \right\} \]

**Equation 3-8: Generalised extreme value cumulative distribution function**

\[ \bar{x}_{gev} = \mu + \sigma \gamma \]

**Equation 3-9: GEV mean**

3.3.5 Corrosion Behaviour & Surface Scale Formation

The corrosion fatigue testing undertaken was carried out in substitute ocean water under various environmental conditions, specifically, aerated, CO$_2$ saturated and H$_2$S conditions. Two of these environments, aerated and CO$_2$ saturated, are readily reproducible in the laboratory enabling corrosion parameters for the material be established.

The corrosion behaviour of the various wires in aerated and CO$_2$ saturated synthetic seawater was investigated to gain an understanding of the mechanisms involved. This could potentially be correlated with the corrosion fatigue behaviour of the high strength carbon steel thus establishing the interaction between the corrosion and fatigue processes.

This involved establishing the corrosion rate, over a period of time, of the different wires in the two different synthetic seawater environments. The linear polarisation resistance was
used to establish the corrosion rate. Subsequently the corroded sample surfaces were analysed using GIXRD to establish the composition of the surface scale.

### 3.3.5.1 Electrochemical Cell Setup

The electrochemical cell set up consisted of a three electrode system with working, reference and counter electrodes. A glass electrochemical cell, complete with a five-port flange was used. Three of the ports were used for the electrodes and the other two for gas inlet and outlet, in particularly during CO₂ saturated experiments. A 3 mm rubber gasket was used to improve the seal between the two flanges, and the two faces were clamped together with a proprietary metal clamp. All the glass-to-glass push fit connections were wrapped with PTFE tape to provide an additional seal.

For aerated test conditions, the cell was operated with the two gas inlet/outlet ports open to the atmosphere.

For the CO₂ saturated test conditions, experiments were carried out in a N₂ purged glove box, the cell solution was mechanically purged with CO₂, CP-grade (99.995 %) for 24 hours. Carbon dioxide was passed through a gas bubbler in order to obtain maximum coverage of the solution. During purging the sample was not present in the cell and the sample port was sealed with a stopper. After purging the sample stopper was then removed and the sample inserted into the cell so that it was contained within the upper flange section. After 1 hour of further mechanical purging, the gas bubbler was withdrawn from solution in order that the CO₂ pass over the surface of the solution. At this point the sample was immersed in the solution and the experiment could begin.

In order to establish the O₂ concentration during a CO₂ saturated experiment and due to insufficient ports in the cell to carry out this test with an experiment running, a test was carried out offline. The equipment used was a Hach Lange Orbisphere with an A1100 Electrochemical Sensor, a Type 410 Oxygen Meter and a Cole Parmer Masterflex 7554-95 Peristaltic pump with 77200-62 pump head. This involved purging the solution in the cell in the same manner as for an actual experiment and measuring the O₂ concentration throughout mechanical purging and pass over for a 5 day period, i.e. the same period as the CO₂ saturated corrosion rate experiments. The results are shown in Figure 3-53.
Table 3-7: Cross sectional areas of the 3 different high strength carbon steel wires

<table>
<thead>
<tr>
<th>Size of Wire (mm)</th>
<th>Cross Sectional Area of Drawing Plane (mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 x 5</td>
<td>47.83</td>
</tr>
<tr>
<td>12 x 4</td>
<td>47.10</td>
</tr>
<tr>
<td>12 x 7</td>
<td>78.80</td>
</tr>
</tbody>
</table>

The Reference Electrode (RE) used was a Saturated Calomel Electrode (SCE), which was housed in a reservoir containing saturated 3 M saturated potassium chloride. A salt bridge, passed through a 6 mm plastic tube, was used to provide a connection for the flow of ions between the reservoir and the electrochemical cell. This was established to be the most stable and consistent set up for electrochemical measurement. The Counter Electrode (CE) was a platinum wire. The Working Electrode (WE) was, depending on the particular experiment, one of the high strength steel wires as listed in Table 3-7.

3.3.5.2 Working Electrode Sample Preparation

Working electrodes were made out the three different sizes of wire, namely 10 mm x 5 mm, 12 mm x 4 mm and 12 mm x 7 mm. First of all, 10 mm long sections were cut out from a length of the high strength carbon steel wire. A 300 mm length of single core sheathed copper wire was then spot welded to the drawing plane of the carbon steel wire. The copper wire was then passed through a length of 6 mm diameter plastic tube. The carbon steel wire along with the end of the plastic tube was placed into a reusable sample mould and two-part epoxy resin cement was used to bond everything together. After 24 hours of curing the sample was removed from the mould ready for grinding. The samples were initially ground using a coarse grade, P120 SiC grinding paper to quickly reveal the steel through the resin. The samples were then ground in stages down to P4000 SiC grinding paper.

3.3.5.3 Linear Polarisation Resistance

From the corrosion fatigue test data provided it was shown that for the 12 x 4 mm wire all the samples tested in a CO₂ saturated environment failed after 5 days and all the tests in an aerated seawater environment were complete after 58 days. Therefore it was decided that a 5 day corrosion rate test in a CO₂ saturated seawater environment would be carried out to understand how it varies over this time period. It was decided that a 30 day corrosion rate test be carried out in the aerated seawater environment, this was in order to reduce the testing time and it was shown, from the localised corrosion pit analysis, that pits were present after 30 days or less.
Linear polarisation resistance experiments were carried out to establish the corrosion rates of the material in the two different environments.

Two different potentiostat's were used, depending upon availability, to carry out the linear polarisation measurements, a Solartron Analytical Modulab, Model 2100A with Modulab ECS software and an Ivium CompactStat with IviumSoft. The Solartron potentiostat was used for the CO₂ saturated experiments, as this was part of the laboratory glove box experimental set up. The Ivium CompactStat was used for the aerated seawater experiments.

For the CO₂ saturated experiments, a loop was set up using the Solartron Modulab software. The loop consisted of measuring the Open Circuit Potential (OCP) for 1 hour followed by three cycles of LPR, scanning -10 mV to +10 mV either side of the OCP. The OCP was measured and recorded at a period of 1 s. The test temperature was ambient room temperature. The LPR scan rate was 1 mV/s. The loop was then set to run once every hour for a total of five days.

For the aerated seawater experiments, the same type of loop was set up using the Ivium software. However, the experimental duration was much longer therefore the loop was executed once a day for 30 days rather than every hour.

The polarisation resistance is the gradient of the E v log(i) plot with the average value of the three cycles being used for corrosion rate analysis.

3.3.5.4 Grazing Incidence X-ray Diffraction

Once the corrosion tests were complete the samples were removed from the electrochemical cell and cleaned with deionised water to remove the salt solution on the surface. Analysis was carried out without prior cleaning and a large sodium chloride peak was evident within the results, therefore cleaning with deionised water was deemed the best approach for removing the salt solution. Once cleaned the samples were placed in a vacuum desiccator to allow them to dry and for storage purposes.

The equipment used to carry out GIXRD was a Phillips XPert X-ray diffractometers. The angle of incidence used was 3°. The samples were scanned through a 2θ of 20 - 85°.

Analysis of the experiment data was carried out using the proprietary software. First of all, the background noise of the data was determined, then a peak search was carried out and diffraction peaks were assigned to the spectrum in appropriate places. The next step is to select the appropriate chemical elements from the periodic table and carry out a search for compounds that match the numerous diffraction peaks. The suggested compounds can then
be analysed to check that they ties-n-up with the diffraction peaks. Care has to be taken when choosing the appropriate compounds as the software can predict the presence of unexpected or erroneous compounds. For a suggested compound to be a valid choice it has to match up with a least three/five of the diffraction peaks.
3.4 Material Characterisation

3.4.1 Chemical Composition

The results of the chemical composition for the three different high strength carbon steel wires are shown in Table 3-8. All three of the high strength carbon steel tensile armour wires are hypo-eutectoid steels with a carbon content range from 0.61 to 0.70 wt% carbon. They have comparable elemental compositions with similar levels of manganese but varying amounts of sulphur. The varying level of sulphur may indicate a variation in the number of inclusions in the steels. The inclusions can act as electrochemically active sites for corrosion leading to pitting corrosion which act as stress raisers for crack initiation and therefore are an important consideration when investigating the corrosion fatigue behaviour of the material.

Table 3-8: Chemical composition of high strength steel wire

<table>
<thead>
<tr>
<th>Element (wt%)</th>
<th>Fe</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>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mm x 5 mm Wire</td>
<td>Bal.</td>
<td>0.68</td>
<td>0.21</td>
<td>0.64</td>
<td>&lt;0.01</td>
<td>0.013</td>
<td>0.01</td>
<td>&lt;0.01</td>
<td>0.03</td>
<td>0.0058</td>
</tr>
<tr>
<td>12 mm x 4 mm Wire</td>
<td>Bal.</td>
<td>0.70</td>
<td>0.25</td>
<td>0.64</td>
<td>&lt;0.01</td>
<td>0.008</td>
<td>0.03</td>
<td>&lt;0.01</td>
<td>0.02</td>
<td>0.003</td>
</tr>
<tr>
<td>12 mm x 7 mm Wire</td>
<td>Bal.</td>
<td>0.61</td>
<td>0.20</td>
<td>0.69</td>
<td>&lt;0.01</td>
<td>0.003</td>
<td>0.01</td>
<td>&lt;0.01</td>
<td>0.01</td>
<td>0.0048</td>
</tr>
</tbody>
</table>

3.4.2 Tensile Testing

The results for the tensile testing for the 12 mm x 4 mm tensile armour wire are shown in Figure 3-7. From the stress-strain curve the mechanical properties of the 12 mm x 4 mm wire have been established, see Table 3-9.

Table 3-9: High strength carbon steel wire mechanical properties

<table>
<thead>
<tr>
<th>Material</th>
<th>Ultimate Tensile Strength (MPa)</th>
<th>0.2 % Proof Stress (MPa)</th>
<th>Estimated Yield Stress (MPa)</th>
<th>Strain at Failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 mm x 4 mm</td>
<td>1450</td>
<td>1000</td>
<td>800</td>
<td>24.0</td>
</tr>
</tbody>
</table>
Insufficient as-received material for the 12 mm x 7 mm and 10 mm x 5 mm high strength carbon steel wires was available to carry out tensile testing. The manufacturer rating of the three different tensile armour wires is shown in Table 3-10. The yield stress was estimated to be $0.7\sigma_{uts}$ [141].

3.4.3 Microstructure

Optical micrographs for the normal plane and transverse plane of the three different carbon steel tensile armour wires is shown in Figure 3-8, Figure 3-9 and Figure 3-10.

The microstructure of the 12 mm x 4 mm carbon steel tensile armour consists of a martensitic-pearlitic grain structure in the normal plane and an anisotropic grain structure in the transverse plane. The microstructure of the 12 mm x 7 mm carbon steel tensile armour consists of larger grain martensitic-pearlitic grain structure in the normal plane and an equiaxed microstructure in the transverse plane with no visible signs of anisotropy. The
The microstructure of the 10 mm x 5 mm carbon steel tensile armour consists of a martensitic-pearlitic grain structure in the normal plane with an anisotropic grain structure in the transverse plane.

Figure 3-8: Optical micrographs of the 12 mm x 4 mm high strength carbon steel wire (a) Normal plane (b) Transverse plane

Figure 3-9: Optical micrographs of the 12 mm x 7 mm high strength carbon steel wire (a) Normal plane (b) Transverse plane

Figure 3-10: Optical micrographs of the 10 mm x 5 mm high strength carbon steel wire (a) Normal plane (b) Transverse plane
3.5 Secondary Cracks and Localised Corrosion

3.5.1 12 mm x 4 mm High Strength Steel Wire

3.5.1.1 Corrosion Fatigue Cracking

The data collected from the secondary crack analysis of the 12 mm x 4 mm high strength steel wire for the two different seawater environments is shown in Table 3-11 and Table 3-12. The tables show the number of secondary cracks and cycles to failure along with the minimum, maximum and mean crack depth for each mean stress and nominal stress range. The cycles to failure and applied stress data is taken from the corrosion fatigue test report [134].

For the aerated environment the average crack depth is the arithmetic mean and for the CO$_2$ saturated environment it is the geometric mean for each data set. This is because the aerated secondary crack data is consistent with a normal cumulative distribution function (CDF) and the CO$_2$ saturated crack data is consistent with a lognormal CDF.

Table 3-11: Corrosion fatigue cracking data for the 12 mm x 4 mm high strength steel wire in an aerated seawater environment

<table>
<thead>
<tr>
<th>Mean Stress (MPa)</th>
<th>Nominal Stress Range (MPa)</th>
<th>Sample ID</th>
<th>Number of Cracks</th>
<th>Log Cycles to Failure</th>
<th>Crack Depth (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Maximum</td>
</tr>
<tr>
<td>428</td>
<td>681</td>
<td>R1A0</td>
<td>2</td>
<td>5.301</td>
<td>1511</td>
</tr>
<tr>
<td>244</td>
<td>397</td>
<td>R2A3</td>
<td>5</td>
<td>5.915</td>
<td>1765</td>
</tr>
<tr>
<td>153</td>
<td>246</td>
<td>R3A0</td>
<td>4</td>
<td>6.491</td>
<td>974</td>
</tr>
<tr>
<td>107</td>
<td>172</td>
<td>R4A0</td>
<td>0</td>
<td>7</td>
<td>N/A</td>
</tr>
<tr>
<td>183</td>
<td>298</td>
<td>R5A3</td>
<td>5</td>
<td>6.221</td>
<td>1596</td>
</tr>
</tbody>
</table>

Table 3-12: Corrosion fatigue cracking data for the 12 mm x 4 mm high strength steel wire in a CO$_2$ saturated seawater environment

<table>
<thead>
<tr>
<th>Mean Stress (MPa)</th>
<th>Nominal Stress Range (MPa)</th>
<th>Sample ID</th>
<th>Number of Cracks</th>
<th>Log Cycles to Failure</th>
<th>Crack Depth (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Maximum</td>
</tr>
<tr>
<td>428</td>
<td>700</td>
<td>R1C0</td>
<td>104</td>
<td>5.094</td>
<td>1297</td>
</tr>
<tr>
<td>367</td>
<td>585</td>
<td>R2C0</td>
<td>95</td>
<td>5.304</td>
<td>1709</td>
</tr>
<tr>
<td>275</td>
<td>424</td>
<td>R3C3</td>
<td>16</td>
<td>5.375</td>
<td>1191</td>
</tr>
<tr>
<td>214</td>
<td>337</td>
<td>R4C2</td>
<td>19</td>
<td>5.867</td>
<td>2428</td>
</tr>
</tbody>
</table>

The crack population data against mean stress values for both environments has been plotted in Figure 3-11. This graph shows that for the aerated seawater environment the number of secondary cracks within the high strength steel wire is independent of applied stress. However, for the CO$_2$ saturated environment the graph shows that the secondary crack population increases with increasing applied stress. Analysis of corrosion fatigue secondary
cracking for each applied stress in the CO₂ saturated seawater environment have been explored in 3.5.1.1.2.

![Diagram showing the number of secondary cracks versus applied stress for the 12 mm x 4 mm high strength steel wire in the two different seawater environments.](image)

**Figure 3-11:** No. of secondary cracks versus applied stress for the 12 mm x 4 mm high strength steel wire in the two different seawater environments

3.5.1.1.1 Aerated Seawater

There is insufficient data for this environment in order to perform any meaningful statistical analysis for each nominal stress range. However, the crack depth data has been grouped, plotted in Figure 3-12 and statistical analysis carried out for the environment.

The arithmetic mean and standard deviation have been calculated using Equation 3-3 and Equation 3-4 and found to be 986 μm and 658 μm respectively. As suggested by Kowaka et al. [139] the range of the data is within ±2σ of the mean.
As shown in Figure 3-11 and Table 3-12, the secondary crack population in the CO₂ saturated environment is far higher than for the aerated environment. There is sufficient data in order to carry out statistical analysis for each mean stress value or nominal stress range. First of all, this data was plotted on probability plotting paper, as shown in Figure 3-13, in order to establish a straight-line fit. The most appropriate CDF to use was the lognormal distribution. Therefore the geometric mean crack depth values were established using Equation 3-6 and are also shown in Table 3-12.

Examining the data in more detail and plotting the geometric mean crack depth and number of secondary cracks against mean applied stress as shown in Figure 3-15, it is shown that as the applied stress increases the number of secondary cracks increase linearly whereas the mean crack depth decreases linearly. This demonstrates that, for the 12 mm x 4 mm high strength steel wire in a CO₂ saturated seawater environment, at low applied stress the samples exhibit few long cracks whereas for the higher applied stress there are many short cracks. This implies that as the applied stress increases there are more crack nucleation sites.
Figure 3-13: Probability plots for corrosion fatigue cracking data for the 12 mm x 4 mm high strength steel wire in a CO$_2$ saturated seawater environment at numerous applied stress; (a) 428 MPa, (b) 367 MPa, (c) 275 MPa, (d) 214 MPa

Figure 3-14: Probability plot for corrosion fatigue cracking data for the 12 mm x 4 mm high strength steel wire in a CO$_2$ saturated seawater environment

The crack depth data for the CO$_2$ saturated environment has also been grouped in order to compare the effects of environment on corrosion fatigue cracking of high strength steel wire. The data has been plotted in Figure 3-14 and again statistical analysis carried out for the
environment. The geometric mean and geometric standard deviation have been calculated using Equation 3-6 and Equation 3-7 and found to be 138 μm and 3.2 μm respectively. The mean crack depth for the CO₂ saturated environment is approximately an order of magnitude lower than for the aerated environment.

![Geometric mean crack depth versus applied stress versus no. of secondary cracks for the 12 mm x 4 mm high strength steel wire in a CO₂ saturated seawater environment](image)

**Figure 3-15: Geometric mean crack depth versus applied stress versus no. of secondary cracks for the 12 mm x 4 mm high strength steel wire in a CO₂ saturated seawater environment**

### 3.5.1.2 Localised Corrosion Pitting

Subsequent analysis of the secondary cracks demonstrated that a significant amount of localised corrosion pitting was present on the sample surfaces. Therefore a further investigation of the samples was carried out exploring pitting population and size thus establishing a relationship between crack and pit population and cyclic stress.

The data collected from the localised corrosion pit analysis of the 12 mm x 4 mm high strength steel wire for the two different seawater environments is shown in Table 3-13 and Table 3-14. The tables show the number of corrosion pits and cycles to failure along with the minimum, maximum and mean pit depth for each mean stress and nominal stress range. Both sets of pit depth data for the aerated and CO₂ saturated test environments are consistent with a lognormal cumulative distribution function (CDF). Therefore the average pit depth for both environments is the geometric mean.
Table 3-13: Localised corrosion pitting data for the 12 mm x 4 mm high strength steel wire in an aerated seawater environment

<table>
<thead>
<tr>
<th>Mean Stress (MPa)</th>
<th>Nominal Stress Range (MPa)</th>
<th>Sample ID</th>
<th>No. of Pits</th>
<th>Log Cycles to Failure</th>
<th>Pit Depth (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Maximum</td>
</tr>
<tr>
<td>428</td>
<td>681</td>
<td>R1A0</td>
<td>50</td>
<td>5.301</td>
<td>11</td>
</tr>
<tr>
<td>244</td>
<td>397</td>
<td>R2A3</td>
<td>179</td>
<td>5.915</td>
<td>54</td>
</tr>
<tr>
<td>153</td>
<td>246</td>
<td>R3A0</td>
<td>139</td>
<td>6.491</td>
<td>104</td>
</tr>
<tr>
<td>107</td>
<td>172</td>
<td>R4A0</td>
<td>145</td>
<td>4.621</td>
<td>14</td>
</tr>
<tr>
<td>183</td>
<td>298</td>
<td>R5A3</td>
<td>157</td>
<td>6.221</td>
<td>62</td>
</tr>
</tbody>
</table>

Table 3-14: Localised corrosion pitting data for the 12 mm x 4 mm high strength steel wire in a CO2 saturated seawater environment

<table>
<thead>
<tr>
<th>Mean Stress (MPa)</th>
<th>Nominal Stress Range (MPa)</th>
<th>Sample ID</th>
<th>No. of Pits</th>
<th>Log Cycles to Failure</th>
<th>Pit Depth (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Maximum</td>
</tr>
<tr>
<td>428</td>
<td>700</td>
<td>R1C0</td>
<td>518</td>
<td>5.094</td>
<td>49</td>
</tr>
<tr>
<td>367</td>
<td>585</td>
<td>R2C0</td>
<td>325</td>
<td>5.304</td>
<td>62</td>
</tr>
<tr>
<td>275</td>
<td>424</td>
<td>R3C3</td>
<td>236</td>
<td>5.375</td>
<td>59</td>
</tr>
<tr>
<td>214</td>
<td>337</td>
<td>R4C2</td>
<td>174</td>
<td>5.867</td>
<td>224</td>
</tr>
</tbody>
</table>

Figure 3-16: No. of localised corrosion pits versus applied stress for the 12 mm x 4 mm high strength steel wire in the two different seawater environments

The corrosion pit population data against mean stress values for both environments has been plotted in Figure 3-16. This graph shows that, as for the crack depth population data in Figure 3-11, for the aerated seawater environment the number of localised corrosion pits within the high strength steel wire is independent of applied stress. However, for the CO2
saturated environment the graph shows that the localised corrosion pit population increases with increasing applied stress.

3.5.1.2.1 Aerated Seawater

There is sufficient data in order to carry out statistical analysis for each mean stress value or nominal stress range. Again this data was plotted on probability plotting paper, as shown in Figure 3-17, in order to establish a straight-line fit. The most appropriate CDF to use was the lognormal distribution. Therefore the geometric mean crack depth values were established using Equation 3-6 and are also shown in Table 3-13.

Figure 3-17: Probability plots for corrosion fatigue localised pitting data for the 12 mm x 4 mm high strength steel wire in an aerated seawater environment; (a) 428 MPa, (b) 244 MPa, (c) 183 MPa, (d) 153 MPa, (e) 107 MPa
Examining the data in more detail and plotting the geometric mean pit depth and number of localised corrosion pits against mean applied stress as shown in Figure 3-18, it is shown that, when plotted on its own, as the applied stress increases the number of corrosion pits increases linearly along with the mean pit depth except for the highest applied stress range value of 428 MPa.

![Figure 3-18: Geometric mean pit depth versus applied stress versus no. of corrosion pits for the 12 mm x 4 mm high strength steel wire in an aerated seawater environment](image)

Again, as per the crack depth analysis, the pit depth data has been grouped in order to compare the effects of environment on localised corrosion pitting of high strength steel wire. The data has been plotted in Figure 3-19 and again statistical analysis carried out for the environment. The geometric mean and geometric standard deviation have been calculated using Equation 3-6 and Equation 3-7 and found to be 7.9 μm and 1.7 μm respectively.
3.5.1.2.2 CO₂ Saturated – 1 bar absolute CO₂ (CP grade) Seawater

Statistical analysis of the localised corrosion pit data for the 12 mm x 4 mm high strength steel wire has been carried out as shown in Figure 3-20 for each stress range and for the environment as a whole in Figure 3-21. Again the data was plotted on probability plotting paper, as shown in Figure 3-20, in order to establish a straight-line fit.

The most appropriate CDF to use was the lognormal distribution. Therefore the geometric mean pit depth values were established using Equation 3-6 and are shown in Table 3-14 and found to be 10.2 μm and 1.8 μm respectively.

Examining the data in more detail and plotting the geometric mean pit depth and pit population against mean applied stress as shown in Figure 3-22, it is shown that as the applied stress increases the number of localised corrosion pits and the geometric mean pit depth increase linearly.

Comparing Figure 3-11 and Figure 3-22, it is shown that for the 12 mm x 4 mm high strength steel wire in a CO₂ saturated seawater environment there is a correlation between crack and pit population. As the applied stress increases the number of secondary cracks increases because the number of crack initiation sites in the form of localised corrosion pits also increases. The formation of a surface scale and the initiation of localised corrosion pits has been explored further in Section 3.6.
Figure 3-20: Probability plots for corrosion fatigue localised pitting data for the 12 mm x 4 mm high strength steel wire in a CO₂ saturated seawater environment; (a) 428 MPa, (b) 367 MPa, (c) 275 MPa, (d) 214 MPa

Figure 3-21: Probability plot for corrosion fatigue localised pitting data for the 12 mm x 4 mm high strength steel wire in a CO₂ saturated seawater environment
Figure 3-22: Geometric mean pit depth versus applied stress versus no. of corrosion pits for the 12 mm x 4 mm high strength steel wire in a CO₂ saturated seawater environment.
3.5.2 12 mm x 7 mm High Strength Steel Wire

3.5.2.1 Corrosion Fatigue Cracking

The data collected from the secondary crack analysis of the 12 mm x 7 mm high strength steel wire for the three different seawater environments is shown in Table 3-15, Table 3-16 and Table 3-17. The tables show the number of secondary cracks and cycles to failure along with the minimum, maximum and mean crack depth for each mean stress and nominal stress range. The cycles to failure and applied stress data is taken from the corrosion fatigue test reports [135–137].

Table 3-15: Corrosion fatigue cracking data for the 12 mm x 7 mm high strength steel wire in an aerated seawater environment

<table>
<thead>
<tr>
<th>Mean Stress (MPa)</th>
<th>Nominal Stress Range (MPa)</th>
<th>Sample ID</th>
<th>Number of Cracks</th>
<th>Log Cycles to Failure</th>
<th>Crack Depth (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Maximum</td>
</tr>
<tr>
<td>550</td>
<td>327</td>
<td>R1A2</td>
<td>3</td>
<td>5.810</td>
<td>35</td>
</tr>
<tr>
<td>550</td>
<td>201</td>
<td>R2A2</td>
<td>8</td>
<td>6.691</td>
<td>67</td>
</tr>
<tr>
<td>550</td>
<td>127</td>
<td>R3A2</td>
<td>1</td>
<td>7.000</td>
<td>24</td>
</tr>
<tr>
<td>550</td>
<td>193</td>
<td>R4A1</td>
<td>6</td>
<td>6.477</td>
<td>3239</td>
</tr>
<tr>
<td>550</td>
<td>257</td>
<td>R5A0</td>
<td>10</td>
<td>6.111</td>
<td>541</td>
</tr>
</tbody>
</table>

Table 3-16: Corrosion fatigue cracking data for the 12 mm x 7 mm high strength steel wire in a CO₂ saturated seawater environment

<table>
<thead>
<tr>
<th>Mean Stress (MPa)</th>
<th>Nominal Stress Range (MPa)</th>
<th>Sample ID</th>
<th>Number of Cracks</th>
<th>Log Cycles to Failure</th>
<th>Crack Depth (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Maximum</td>
</tr>
<tr>
<td>550</td>
<td>329</td>
<td>R1C0</td>
<td>133</td>
<td>5.771</td>
<td>213</td>
</tr>
<tr>
<td>550</td>
<td>201</td>
<td>R2C0</td>
<td>30</td>
<td>6.322</td>
<td>3293</td>
</tr>
<tr>
<td>550</td>
<td>127</td>
<td>R3C0</td>
<td>0</td>
<td>6.984</td>
<td>0</td>
</tr>
<tr>
<td>550</td>
<td>189</td>
<td>R4C3</td>
<td>1</td>
<td>6.447</td>
<td>905</td>
</tr>
<tr>
<td>550</td>
<td>258</td>
<td>R5C0</td>
<td>1</td>
<td>6.190</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 3-17: Corrosion fatigue cracking data for the 12 mm x 7 mm high strength steel in a 100 mbar absolute H₂S with CO₂ balance seawater environment

<table>
<thead>
<tr>
<th>Mean Stress (MPa)</th>
<th>Nominal Stress Range (MPa)</th>
<th>Sample ID</th>
<th>Number of Cracks</th>
<th>Log Cycles to Failure</th>
<th>Crack Depth (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Maximum</td>
</tr>
<tr>
<td>550</td>
<td>321</td>
<td>R1H0</td>
<td>0</td>
<td>5.810</td>
<td>0</td>
</tr>
<tr>
<td>550</td>
<td>200</td>
<td>R2H0</td>
<td>21</td>
<td>7.000</td>
<td>69</td>
</tr>
<tr>
<td>550</td>
<td>256</td>
<td>R3H0</td>
<td>0</td>
<td>6.914</td>
<td>0</td>
</tr>
</tbody>
</table>

The 12 mm x 7 mm crack population for the aerated environment is of a similar magnitude to the 12 mm x 4 mm data; however, the mean crack depth is up to several orders of magnitude lower. For the CO₂ saturated environment the samples tested at the higher nominal stress
ranges generally exhibit equivalent secondary crack population except for the 258 MPa nominal stress range. However, again they exhibit a lower mean crack depth range throughout the samples.

For all three seawater environments the average crack depth is the geometric mean because all sets of data are consistent with a lognormal CDF.

The crack population data against mean stress values for all three environments has been plotted in Figure 3-23. Like the 12 mm x 4 mm high strength steel wire, this graph shows that for the aerated seawater environment the number of secondary cracks is independent of applied stress. However, for the other two environments the picture is less clear. For the CO₂ saturated environment there are signs that the number of secondary cracks increases with increasing applied stress, which is further supported by the fact that the localised corrosion pit analysis of the 12 mm x 7 mm steel wire shows that the number of corrosion pits also increases with increasing applied stress.

![Figure 3-23: No. of secondary cracks versus applied stress for the 12 mm x 7 mm high strength steel wire in the three different seawater environments](image)

3.5.2.1.1 Aerated Seawater

Again like the 12 mm x 4 mm steel wire, there is insufficient data for this environment in order to perform any meaningful statistical analysis for each nominal stress range. However, the crack depth data has been grouped, plotted in Figure 3-24 and statistical analysis carried out for the environment.
The geometric mean and standard deviation have been calculated using Equation 3-6 and Equation 3-7 and found to be 70 μm and 3.5 μm respectively.

3.5.2.1.2 CO₂ Saturated – 1 bar absolute CO₂ (CP grade) Seawater

As shown in Figure 3-23 and Table 3-16 the secondary crack population in the CO₂ saturated environment is quite different from that for the 12 mm x 4 mm steel wire. The lower nominal stress range exhibit very few, if any, corrosion fatigue cracks. For the higher stressed samples the amount of corrosion fatigue cracking is generally of a similar magnitude to that for the 12 mm x 4 mm wire.

There is sufficient data in order to carry out statistical analysis for the nominal stress ranges of 329 MPa and 201 MPa. This data was plotted on probability plotting paper, as shown in Figure 3-25, in order to establish a straight-line fit. The most appropriate CDF to use was the lognormal distribution. Therefore the geometric mean crack depth values were established using Equation 3-6 and are shown in Table 3-16. The straight line fit for the 329 MPa nominal stress range shows excellent correlation with the test data, however, the straight line fit for the 201 MPa nominal stress range does not correlate as well with the test data and is thought to be due to the higher range of the data points. The test data for the 201 MPa nominal stress range was plotted on probability paper for other cumulative distribution functions in order to establish the best fit and it was shown that lognormal was the best fit for this data.
The data for the 329 MPa and 201 MPa nominal stress ranges shows that, comparable to the 12 mm x 4 mm steel wire, as the applied stress increases the number of secondary cracks increase linearly whereas the mean crack depth decreases. This also emphasises the trend for few long cracks at low applied stress and many short cracks at high applied stress. Again, this indicates that as the applied stress increases there are more crack nucleation sites.

The crack depth data for the CO₂ saturated environment has also been grouped in order to compare the effects of environment on corrosion fatigue cracking of high strength steel wire. The data has been plotted in Figure 3-26 and again statistical analysis carried out for the environment. The geometric mean and geometric standard deviation have been calculated using Equation 3-6 and Equation 3-7 and found to be 65 μm and 2.1 μm respectively. The mean crack depth for the 12 mm x 7 mm high strength steel wire tested in a CO₂ saturated and an aerated environment is almost identical.

Figure 3-25: Probability plots for corrosion fatigue cracking data for the 12 mm x 7 mm high strength steel wire in a CO₂ saturated seawater environment at numerous applied stress; (a) 329 MPa, (b) 201 MPa

Figure 3-26: Probability plot for corrosion fatigue cracking data for the 12 mm x 7 mm high strength steel wire in CO₂ saturated seawater environment
3.5.2.1.3 100 mbar absolute H₂S/ CO₂ Balance to 1 bar absolute Seawater

The only nominal stress range to exhibit corrosion fatigue cracking is 200 MPa. Therefore this dataset represents both the applicable nominal stress range and the environment. There is sufficient data in order to carry out statistical analysis for this nominal stress range. This data was plotted on probability plotting paper, as shown in Figure 3-27, in order to establish a straight-line fit. The most appropriate CDF to use was the lognormal distribution. The geometric mean crack depth and geometric standard deviation have been calculated using Equation 3-6 and Equation 3-7 and found to be 36 μm and 1.5 μm respectively. The mean crack depth for the 12 mm x 7 mm high strength steel wire tested in a H₂S test environment is approximately half that for the CO₂ saturated and aerated environments.

Figure 3-27: Probability plot for corrosion fatigue cracking data for the 12 mm x 7 mm high strength steel wire in a 100 mbar absolute H₂S with CO₂ balance seawater environment

3.5.2.2 Localised Corrosion Pitting

Analysis of the corrosion fatigue test samples, for all of the test environments, demonstrated that a significant amount of localised corrosion pitting was present on the sample surfaces. Therefore, as for the 12 mm x 4 mm high strength steel wire, a further investigation of the samples was carried out exploring pitting population and size thus establishing a relationship between crack and pit population and cyclic stress.

The data collected from the localised corrosion pit analysis of the 12 mm x 7 mm high strength steel wire for the three different seawater environments is shown in Table 3-18, Table 3-19 and Table 3-20. The tables show the number of corrosion pits and cycles to failure along with the minimum, maximum and mean pit depth for each mean stress and nominal stress range.
For the aerated and CO$_2$ saturated test environments the average pit depth is the geometric mean because the pit data from both of these environments is consistent with a lognormal CDF. The H$_2$S test environment is slightly different as the pit depth data is best fit by a generalised extreme value distribution as shown in Figure 3-34. The mean for this type of cumulative distribution function is calculated using Equation 3-9.

The corrosion pit population data against mean stress values for all three environments has been plotted in Figure 3-28. The correlation between number of corrosion pits and nominal stress range for the 12 mm x 7 mm high strength steel wire tested in an aerated and H$_2$S containing seawater environment is indistinct. However, for the CO$_2$ saturated environment there are clear signs that the number of corrosion pits increases with an increase in nominal stress range.
3.5.2.2.1 Aerated Seawater

Individual probability plots for each nominal stress range are shown in Figure 3-29. Using Equation 3-6 the geometric mean for each stress range has been calculated and can be found in Table 3-18.

The pit depth data for the 12 mm x 7 mm steel wire in an aerated environment has also been grouped in order to compare the effects of environment on localised corrosion pitting of high strength steel wire. The data has been plotted in Figure 3-30 and again statistical analysis carried out for the environment. The geometric mean and geometric standard deviation have been calculated using Equation 3-6 and Equation 3-7 and found to be 8.7 μm and 1.9 μm respectively.
Figure 3-29: Probability plots for corrosion fatigue localised pitting data for the 12 mm x 7 mm high strength steel wire in an aerated seawater environment; (a) 327 MPa, (b) 257 MPa, (c) 201 MPa, (d) 193 MPa, (e) 127 MPa
3.5.2.2 CO₂ Saturated – 1 bar absolute CO₂ (CP grade) Seawater

Individual probability plots for each nominal stress range are shown in Figure 3-32. Using Equation 3-6 the geometric mean for each stress range has been calculated and can be found in Table 3-19.

The pit depth data for the 12 mm x 7 mm steel wire in a CO₂ saturated environment has also been grouped in order to compare the effects of environment on localised corrosion pitting of high strength steel wire. The data has been plotted in Figure 3-31 and again statistical
analysis carried out for the environment. The geometric mean and geometric standard deviation have been calculated using Equation 3-6 and Equation 3-7 and found to be 8.7 μm and 2.1 μm respectively. The mean pit depth for the CO₂ saturated environment is identical to that for the aerated environment.

Figure 3-32: Probability plots for corrosion fatigue localised pitting data for the 12 mm x 7 mm high strength steel wire in a CO₂ saturated environment; (a) 327 MPa, (b) 257 MPa, (c) 201 MPa, (d) 193 MPa, (e) 127 MPa

3.5.2.2.3 100 mbar absolute H₂S/ CO₂ Balance to 1 bar absolute Seawater

Individual probability plots for each nominal stress range are shown in Figure 3-33. Using Equation 3-6 the geometric mean for each stress range has been calculated and can be found in Table 3-20.

The pit depth data for the 12 mm x 7 mm steel wire an H₂S test environment has also been grouped in order to compare the effects of environment on localised corrosion pitting of high
strength steel wire. The data has been plotted in Figure 3-34 and again statistical analysis carried out for the environment. The mean and standard deviation have been calculated using Equation 3-6 and Equation 3-7 and found to be 31.4 μm and 17.7 μm respectively. The mean pit depth for the H₂S test environment is significantly higher than that for the other two environments.

**Figure 3-33**: Probability plots for corrosion fatigue pitting data for the 12 mm x 7 mm high strength steel wire in a 100 mbar absolute H₂S with CO₂ balance seawater environment; (a) 321 MPa, (b) 256 MPa, (c) 200 MPa
Figure 3-34: Probability plot for corrosion fatigue pitting data for the 12 mm x 7 mm high strength steel wire in a 100 mbar absolute H₂S with CO₂ balance seawater environment.
3.5.3 Secondary Crack and Corrosion Pit Population Comparison

The difference in crack population between the 12 mm x 4 mm wire and the 12 mm x 7 mm wire may be explained by the effects of the degree of cold drawing and the R-ratio. The CTOD will increase with a reduction in R-ratio, therefore the longer the crack is open the increase likelihood for corrosion to occur down the crack and corrosion product to form on the faces or walls of the crack, thus causing crack widening [96]. An example of crack widening due to corrosion is shown in Figure 3-40. The R-ratio for the 12 mm x 4 mm wire is 0.1 compared to a range of 0.5-0.7 for the 12 mm x 7 mm wire. This means that for the same frequency, 2 Hz, the crack generated in the 12 mm x 4 mm wire is open for a longer period of time than in the 12 mm x 7 mm which means that it is more prone to the effects of corrosion on crack closure. However, it should be noted that the range of applied stress is higher in the 12 mm x 7 mm wire than in the 12 mm x 4 mm wire, see Figure 3-35, Figure 3-36 and Figure 3-37.

With regards to the degree of cold drawing affecting the crack population with the two high strength carbon steel wires, it has been shown that a materials ductility increases as the level of cold drawing increases, with a consequent increase in the number of secondary cracks. [33].

![Figure 3-35: Applied stress range versus sample test piece number for both the 12 mm x 4 mm and 12 mm x 7 mm high strength steel wire in an aerated seawater environment](image-url)
Figure 3-36: Applied stress range versus sample test piece number for both the 12 mm x 4 mm and 12 mm x 7 mm high strength steel wire in a CO₂ saturated seawater environment.

Figure 3-37: Applied stress range versus sample test piece number for both the 12 mm x 4 mm and 12 mm x 7 mm high strength steel wire in an H₂S test environment.

Many images of the corrosion fatigue cracks in the both sets, 12 mm x 4 mm and 12 mm x 7 mm, of the high strength steel wires were taken in order to carry out statistical population analysis. The following figures, Figure 3-38 to Figure 3-45, pertain to the important parts of the corrosion fatigue fracture surfaces and secondary cracks.
Figure 3-38 shows an example of the typical fracture surface for the two different seawater environments (a) aerated and (b) CO₂ saturated for the 12 mm x 4 mm wire. The fracture surfaces exhibit a ductile type failure with evidence of micro-cracks, with secondary cracks propagating perpendicular to the loading direction into the drawing plane and cleavage facets. Figure 3-39 shows typical examples of the fracture surface for the three different seawater environments (a) aerated and (b) CO₂ saturated for the 12 mm x 7 mm wire. The fracture surfaces exhibit a more brittle type failure with smooth dimpled fracture surfaces with evidence of some micro cracking the aerated test environment sample. Both sets of fracture surface show an amount of corrosion product on the surface.

The 12 mm x 7 mm high strength steel wires exhibit isotropic fracture surfaces, whereas the 12 mm x 4 mm wires are anisotropic with deflections and bifurcations in the crack path, which is suggested to be due to the increase level of cold drawing that has been experienced by the 12 mm x 4 mm wire. This demonstrates that the increase in cold drawing has increased the transverse ductility of the wire which is important in establishing the fatigue and fracture resistance of the high strength steel [33,46] and may explain the smaller mean crack length in the 12 mm x 7 mm samples being due to the brittle nature of the material. The failure mechanism becomes more ductile as the level of cold drawing increases [34].

There are no signs of fatigue striations on the fracture surface and it has been suggested that this is due to the FCGR being too slow for a cycle by cycle progression [91].
Various types of crack have been shown to exist with the corrosion fatigue tested high strength steel wire. Figure 3-40 shows evidence of a crack that has initiated from a localised corrosion pit, propagated to a particular length whilst being corroded by the environmental conditions and then arresting because the stress intensity factor has reduced due to the effects of crack widening. Figure 3-41 again shows a crack initiating from a localised corrosion pit, however this time the stress intensity is such that the crack is able to propagate and crack widening and corrosion of the crack faces is only partial. The progressive reduction in corrosion down the crack path would indicate the lack of solution refreshment within the crack which will lead to iron saturation and a dramatic reduction in corrosion rate. Figure 3-42 shows evidence of severe crack widening and horizontal grain attack. Figure 3-43 shows the effects of corrosion on the short crack growth. A crack has initiated from a corrosion pit, however the localised corrosion dissolution reactions are faster than the FCGR, therefore consuming the crack causing crack arrest. Figure 3-44 shows evidence of subsurface and undercutting type corrosion pits that are present in the high strength steel wire. Figure 3-45 shows evidence of crack bifurcation and coalescence. Once two cracks have converged the mixed mode stress condition is likely to enhance crack closure and therefore reduce the crack driving force due to the large plastic zone ahead of the crack tip.
from the mode II stress component which also explains the change in crack path direction to perpendicular of the loading direction [110]. The crack coalesce in Figure 3-45 shows that a new single crack may then be initiated.

![Figure 3-40: SEM image - Straight crack with crack widening by corrosion](image1.png)

![Figure 3-41: SEM image - Straight crack with partial crack widening by corrosion](image2.png)
Figure 3-42: SEM images – Evidence of horizontal grain attack

Figure 3-43: SEM images – Evidence of short crack blunting

Figure 3-44: SEM images – Evidence of subsurface and undercutting corrosion pits
Figure 3-45: SEM images – evidence of crack bifurcation
3.6 Surface Scale Formation

The post-test analysis of the corrosion fatigue tested samples, to explore the secondary cracks and localised corrosion pits, established that the surface of the material plays a key part in the initiation of cracks in both sets of high strength steel wires examined. Therefore, experiments to simulate the surface conditions expected in an aerated and CO₂ saturated seawater environment were carried out. The samples were immersed in solution for a set period of time over which LPR measurements were taken.

\[
i_{corr} = \frac{\beta_a \beta_c}{2.3 R_p (\beta_a + \beta_c)} \quad \text{Equation 3-10}
\]

\[
i_{corr} = \frac{1}{R_p} x \text{Stern Geary Coefficient}
\]

\[
\text{Corrosion Rate} = \frac{i_{corr} m_r S_{\text{year}}}{\rho n F} x 10 \quad \text{Equation 3-11}
\]

The Stern-Geary coefficient that is widely used to establish corrosion rate from polarisation resistance measurements is 26 mV. However, this coefficient assumes that the corrosion process takes place by activation polarisation only, and not a combination of activation, concentration and resistance polarisation as is more likely to be the case. Equation 3-10 and Equation 3-11 demonstrate that the corrosion rate is proportional to the reciprocal of the polarisation resistance which has been plotted in order to avoid erroneous interpretation of the results.

3.6.1 Aerated Seawater Environment

Two samples of each of the 12 mm x 4 mm and 12 mm x 7 mm high strength steel wire were submerged in seawater in individual electrochemical cells. One set of the samples was immersed for 15 days and did not undergo any polarisation and the second set was immersed for 30 days and underwent daily linear polarisation resistance measurements.

The results for the polarisation resistance measurements for the 12 mm x 4 mm and 12 mm x 7 mm high strength steel wires carried out in aerated seawater are shown in Figure 3-46. The trend for both sets of results is the same in that they show an increasing corrosion rate over the 30 day period.
GIXRD was carried out on the surface of each sample after the immersion tests were complete. This was to establish the differences in film formation on samples immersed for 15 days and 30 days.

The GIXRD results for the 12 mm x 4 mm and 12 mm x 7 mm high strength steel wire are shown in Figure 3-47 and Figure 3-48 respectively. Figure 3-47(a) shows the formation of iron oxyhydroxide (FeOOH) on the surface of the 12 mm x 4 mm steel wire after 15 days immersion. Figure 3-47(b), for 30 days immersion, shows much more distinct diffraction peaks. However, the scale that has formed on the surface of the high strength steel wire is calcium carbonate (CaCO₃) with some indications of the presence of magnesium hydroxide (Mg(OH)₂) and iron oxyhydroxide. These salt films form a non-protective layer on the surface of the carbon steel.

For the 12 mm x 7 mm high strength steel wire Figure 3-48(a) for 15 days immersion, shows the presence of calcium carbonate. After 30 days immersion in seawater the XRD pattern, Figure 3-48(b), is similar to that for the 12 mm x 4 mm carbon steel wire and demonstrates the formation of calcium carbonate and magnesium hydroxide.

Examining the surface of the sample using an SEM, Figure 3-49, shows the presence of distinct regions of different corrosion scale formation. The region on the right hand side of Figure 3-49 is thought to be calcium carbonate. Upon closer inspection of the left hand side of Figure 3-49, as highlighted in Figure 3-50(a), there are regions which demonstrate the
formation of a localised scale on the sample surface. This partial coverage of the surface by a protective film has been suggested by [76]. A closer inspection of the right hand side of Figure 3-49, as shown in Figure 3-51, is consistent with calcium carbonate formation that was detected by GIXRD analysis.

![GIXRD plot](image)

**Figure 3-47:** GIXRD plot for 12 mm x 4 mm high strength steel wire corrosion tested in an aerated seawater environment for (a) 15 Days (b) 30 Days
Figure 3-48: GIXRD plot for 12 mm x 7 mm high strength steel wire corrosion tested in an aerated seawater environment for (a) 15 Days (b) 30 Days

- C - Calcium Carbonate - CaCO₃
- S - Sodium Chloride - NaCl
- M - Magnesium Hydroxide - Mg(OH)₂
- I - Leperidocrite - γ-FeOOH
- S - Sodium Chloride - NaCl
Figure 3-49: SEM image of the surface scale formation on high strength steel wire corrosion tested in aerated seawater

Figure 3-50: SEM images of the left hand side of Figure 3-49 consistent with the formation of iron oxide
3.6.2 CO$_2$ Saturated Seawater Environment

A sample of 10 mm x 5 mm high strength steel wire was used to carry out corrosion rate and scale formation tests in a CO$_2$ saturated seawater environment. This was due to material availability. The chemical composition has been shown to be similar, see Table 3-8, to that of the 12 mm x 4 mm and 12 mm x 7 mm high strength steel wires.

The sample underwent hourly linear polarisation resistance measurements for a five-day period. The results for the polarisation resistance measurements for the 10 mm x 5 mm high strength steel wire carried out in CO$_2$ saturated seawater are shown in Figure 3-52.
The results show a general increase in the corrosion rate over the five day period. The peaks and troughs in the corrosion rate results may be explained by a combination of two occurrences, one being the formation of a scale which then reaches a critical thickness after which it flakes off and the second being the dissolution of the carbonate film back into solution given the high solubility of calcium carbonate. The results of the oxygen concentration experiment to establish how it varies throughout the duration of the corrosion rate test are shown in Figure 3-53. They show that once the mechanical purge is removed from solution and passed over the liquid surface at zero hours the oxygen concentration for the first 24 hours is approximately 10 ppb. It then starts to rise sharply to around 200 ppb after 54 hours where it plateaus and remains for the duration of the test. This would therefore provide a third explanation as to why the CO₂ corrosion rate increases throughout the experiments; it is due to an increase in oxygen concentration.

![Figure 3-52: Five-day corrosion rate test for 10 mm x 5 mm high strength steel wire corrosion tested in a CO₂ saturated seawater environment](image)

GIXRD was carried out on the surface of the sample tested in a CO₂ saturated seawater environment. This was to establish which compounds are present within the film formed on the sample surface.

The GIXRD results for the 10 mm x 5 mm high strength steel wire are shown in Figure 3-55. It shows the formation of calcium carbonate with some detection of magnesium carbonate. This is supported by work carried out by [49,52,61] that demonstrates the precipitation of calcium carbonate and magnesium hydroxide on the surface of carbon steel alloys in a seawater environment.

120
Figure 3-53: Five-day oxygen concentration measurement in an electrochemical cell

Figure 3-54: SEM images of the surface scale formation on high strength steel wire corrosion tested in CO$_2$ saturated seawater

Examining the surface of the sample using an SEM, Figure 3-54, shows a uniformly corroded surface whereby the whole surface exhibits areas of localised corrosion. Upon closer inspection of the sample surface around the localised corrosion regions, as highlighted on Figure 3-54(b) and using EDX analysis, the surface film exhibited calcium rich regions around the edges of the localised corrosion pits. Therefore it is suggested that localised breakdown of the protective surface film in this case calcium carbonate will create areas of localised corrosion and ultimately corrosion pits.
3.6.3 100 mbar absolute H₂S/CO₂ Balance to 1 bar absolute Seawater Environment

It was not possible to carry out any experimental work within the laboratory using hydrogen sulphide as the test gas. However, corrosion fatigue tests had been carried out on the 12 mm x 7 mm high strength steel wire in a 100 mbar absolute H₂S with CO₂ balance seawater environment. Therefore, for completeness, analysis of the sample surface was carried out using GIXRD to establish the surface scale formation.

The GIXRD results for the 12 mm x 7 mm high strength steel wire are shown in Figure 3-56. The analysis only detected iron that is consistent with the indication that the samples were cleaned prior to them being acquired. Visible inspection of the samples did not find evidence of any black deposits which would have indicated the presence of iron sulphide, as has been shown to be the case by [65] or the surface scale may have been too thin to be analysed with 3° angle of incidence.
Figure 3-56: GIXRD plot for 12 mm x 7 mm high strength steel wire corrosion fatigue tested in a 100 mbar absolute H₂S with CO₂ balance seawater environment
Chapter 4 Residual Stress
4. Residual Stress

4.1 Introduction

Residual stresses have been investigated for high strength carbon steel wires in three
different conditions, namely as received, corrosion fatigue tested in seawater and fatigue
tested in air. All fatigue testing was carried out using a four-point bend methodology as
described in Chapter 3. The residual stresses in the material were measured in order to
investigate their role in fatigue crack propagation.

4.2 Experimental Methods

All residual stress measurements were carried out using a ProtoiXRD residual stress
measurement system. Data extraction was carried out using the proprietary software
interface, XrdWin 2.0.

The ProtoiXRD is a portable type device, which uses the most common method for stress
determination, the sin²ψ method. The X-ray tube chosen to give a suitable Bragg reflection at
a sufficiently high 2θ angle of 156.1° is the chromium tube, the properties of which are shown
in Table 4-1. A circular 2 mm diameter collimator was used throughout the experiments.

<table>
<thead>
<tr>
<th>Material</th>
<th>Bravais Lattice</th>
<th>X-ray Tube</th>
<th>K-β filter</th>
<th>Wavelength Å (All K-α1)</th>
<th>2θ Angle (Approx.)</th>
<th>(hkl)</th>
<th>Multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrite α-iron</td>
<td>BCC</td>
<td>Cr K-α</td>
<td>V</td>
<td>2.2897</td>
<td>156.1</td>
<td>{211}</td>
<td>24</td>
</tr>
</tbody>
</table>

4.2.1 Test Methodology

First of all, the machine required setting up in order to ensure that the residual stress
measurements were valid. This was achieved using a stress free iron powder reference
standard and establishing the measurement gain.

In order to carry out a residual stress measurement, the high strength steel wire sample is
placed on the sample stage and levelled in the x and y-directions. A pointer is attached to the
goniometer head, which is used to focus the machine on the sample surface and retract a
certain distance, in this case 20 mm. The pointer is then removed and the sample is in focus.
The X-rays are then switched on and a measurement is taken. A square map was used to take
measurements at multiple points, in this case in a straight line along the centre of the normal
plane of the sample. Once the measurements have been made XrdWin 2.0 was used to
establish the stress values. Residual stress measurement theory in order to establish the stress values, applicable to XRD, can be found in Section 2.4.

![Image](image_url)

**Figure 4-1: Example of a two point linear square map**

### 4.2.2 Through Thickness Measurements

Through thickness residual stress measurements of the corrosion fatigue tested samples was established using an iterative process of successive material removal by electro polishing followed by stress analyses using a ProtoiXRD.

The mean value from a two point linear square map was used to establish the residual stress of each layer. The two points were 5 mm apart in the x-direction with y=0. Successive measurements for each layer were then correlated and plotted to give a through thickness profile, as shown in Figure 4-2.

#### 4.2.2.1 Layer Removal Methodology

Material removal was carried out by electro polishing the sample in perchloric acid 60 % (8 % by volume) glacial acetic acid (92 % by volume) at room temperature and pressure. Both reagents were laboratory grade and purchased from Fisher Scientific. The temperature of the solution was monitored to ensure the applied current did not exceed 1 A and so that the solution itself did not exceed 40 °C as the two chemicals can form an explosive mixture if the temperature is too high. Two different methods of electro polishing were utilised, depending upon equipment availability. In both cases, the thickness of material removed was accurately measured using a calibrated micrometer.

The first method was to use a proprietary electro polishing system, namely a Struers Lectropol 5 with a 2 cm² mask. The area requiring electro polishing was placed over the aperture of the mask. Using the equipment interface the electrolyte was pumped over the sample area, during which time 40 V was applied to the sample and the current was measured. Whilst stress analyses were being carried out the electrolyte container was removed from the equipment and placed in an ice bath. This lowering of the electrolyte temperature was found to make it last longer, i.e. for additional electro polishing iterations. The material removal rate was found to be 10 μm/min.

The second method consisted of immersing the whole sample in a beaker containing the electrolyte. The areas of the sample that were not to be electro polished were coated with...
Lacomit varnish. The beaker containing the electro polishing solution was placed in an ice bath in order to control the temperature and a magnetic stirrer was used to induce a flow over the sample surface. The sample was the anode, another metallic strip was used as the cathode and 40V was passed through the circuit.

4.2.3 Surface Measurements

Surface residual stress measurements were carried out for two different types of sample, firstly, for the corrosion fatigue tested samples and secondly for fatigue tests carried out in air. The test methodology for both sets of samples is as described in Section 4.2.1; the only parameter that varies is the size of the square map.

For the corrosion fatigue tested samples, as per the through thickness measurements, the mean value from a two point linear square map was used to establish the residual stress on the sample surface. The two points were 5 mm apart in the x-direction with y=0. Given the number of tested samples, this was the most expedient way to establish correlation between environment, applied stress and residual stress. The samples were cleaned with ethanol prior to carrying out the XRD measurements. This was to remove any loose surface oxides or scales that may hinder the diffraction path.

For the fatigue tests in air, measurements were taken along the entire length of the normal plane of the sample in the drawing direction. Again the points were 5 mm apart in the x-direction with y=0. This was in order to establish the full variation of residual stress across the sample.
Through thickness residual stress measurements were carried out to establish the baseline profile through the 12 mm x 4 mm high strength steel wire. The overall shape of the curve is very much like a Gaussian type distribution or a bell curve. This showed a compressive residual stress of -107 MPa at the free surface, rising to a stress free state at a sample depth of ~400 μm, and a maximum residual tensile stress of +159 MPa at a sample depth of ~1200 μm. The profile falls to a second stress free state at a sample depth of ~1600 μm. There is a compressive residual stress at the centre of the sample, 2000 μm, of -186 MPa.

The results of the corrosion fatigue cracking analysis have shown that corrosion fatigue cracks for this material initiate at the free surface, therefore the compressive residual stress at the free surface would indicate a prolonged fatigue life for the material as the net or total applied stress would be lower.

\[ \text{Residual Stress} + \text{Applied Stress} = \text{Total Applied Stress} \]

The residual stress profiles for the samples are for a sample depth of half the wire thickness. The thinner the sample becomes there is less constraint in the stress due to the size and geometry of the sample which will cause more stress relaxation leading to an increased error in the results.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Environment</th>
<th>Mean Stress (MPa)</th>
<th>Nominal Stress Range (MPa)</th>
<th>Max Stress (MPa)</th>
<th>Min Stress (MPa)</th>
<th>Cycles to Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>R2A0</td>
<td>Aerated</td>
<td>244</td>
<td>393</td>
<td>440.5</td>
<td>47.5</td>
<td>689590</td>
</tr>
<tr>
<td>R4C0</td>
<td>CO₂ Saturated</td>
<td>214</td>
<td>333</td>
<td>380.5</td>
<td>47.5</td>
<td>687000</td>
</tr>
<tr>
<td>R3C0</td>
<td>Saturated</td>
<td>275</td>
<td>416</td>
<td>483</td>
<td>67</td>
<td>317310</td>
</tr>
</tbody>
</table>

It was then decided to compare the results for the as-received sample with test pieces that have been corrosion fatigue tested in aerated and CO₂ saturated seawater. This was in order to establish a correlation between the factors of residual stress, applied stress, cycles to failure and environment. The samples that were chosen for comparison are shown in Table 4-2. When taking into account the aforementioned factors, there were no direct comparisons...
in the available test pieces. Therefore two samples were chosen for the CO\textsubscript{2} saturated environment as they sat either side of the chosen aerated sample.

\textbf{Figure 4-2: Through thickness residual stress measurement of an as received sample of 12 mm x 4 mm high strength steel wire}

Through thickness residual stress measurement of the sample corrosion fatigue tested in an aerated environment is shown in Figure 4-3. Again, the overall shape of the curve demonstrates a Gaussian type distribution. When compared to the as-received profile, this showed a lower compressive residual stress of -140 MPa at the free surface. However the profile rises to a stress free state at the same sample depth of ~400 μm. The maximum residual tensile stress of +165 MPa is, within error, the same as for the as-received profile but at a slightly lower sample depth of ~1000 μm. Again, the profile falls to a second stress free state at the same sample depth of ~1500 μm. There is a lower compressive residual stress at the centre of the sample, 2000 μm, of -243 MPa. Overall and within the error values the profiles are very similar, showing that the testing has had minor effect on the through thickness residual stress profile. This is further demonstrated in Figure 4-6, which shows the complete set of through thickness residual stress measurement profiles carried out on the 12 mm x 4 mm high strength carbon steel wire
The next sample chosen was a CO$_2$ saturated corrosion fatigue test piece that had experienced almost the same number of cycles to failure as the aerated test piece but at a slightly lower mean stress of 214 MPa. Through thickness residual stress measurement of this sample is shown in Figure 4-4. Again, the overall shape of the curve demonstrates a Gaussian type distribution. When compared to the aerated profile, this showed the same compressive residual stress of -140 MPa at the free surface, which as stated previously, is lower than that of the as-received material. The profile rises to a stress free state at the same sample depth of ~215 μm which is almost half of that for the as-received and aerated profiles. The maximum residual tensile stress of +122 MPa at a sample depth of ~880 μm are both slightly lower than for the as-received and aerated profile. The second stress free state is at a sample depth of ~1400 μm. The compressive residual stress at the centre of the sample, 2000 μm, is -280 MPa, which is lower than both the as-received and aerated profiles. Overall the profile for the CO$_2$ saturated test piece at an applied stress of 214 MPa is shifted slightly in both the x and y direction. However, within error, the profiles are relatively similar.
The final profile carried out was for a CO$_2$ saturated corrosion fatigue test piece that had experienced a higher mean stress of 275 MPa but with an almost identical nominal stress range. Through thickness residual stress measurement of this sample is shown in Figure 4-5. Again, as per all the through thickness measurements carried out, the overall shape of the curve demonstrates a Gaussian type distribution. When compared to the aerated profile, this showed a lower compressive residual stress of -183 MPa at the free surface, which is the lowest of all the profiles. The profile rises to a stress free state at the same sample depth of ~760 μm which is almost twice that of the as-received and aerated profiles. The maximum residual tensile stress of +103 MPa is at a sample depth of ~1300 μm and is the lowest maximum value of all the profiles. The second stress free state is at a sample depth of ~1500 μm. The compressive residual stress at the centre of the sample, 2000 μm, is -248 MPa, which is lower than the as-received profile. Overall the profile for the CO$_2$ saturated test piece at an applied stress of 275 MPa is shifted in both the x and y direction for the first half of the through thickness measurement but exhibits the same profile shape for the second half of the profile. This means that the sample has a higher sustained amount of compressive residual stress for the initial 1000 μm than the other three test pieces.
Overall, Figure 4-6, it is shown that all the samples, whether they are in the as-received condition or corrosion fatigue tested, exhibit a Gaussian type distribution of through thickness residual stress. Therefore, it is evident that if through thickness residual stress measurements were carried out for all available samples, based on the two different environments, numerous stress ranges and the variation in cycles to failure, a spectrum of Gaussian type distributions would be created. These distributions would have some natural variation from one another but overall would be of a similar magnitude. Given the potential lack of any further information that would truly be established from carrying out such tests, it did not seem timely to do so. However, the surface residual stress, based on these results, is shown to always be compressive. Therefore with corrosion fatigue cracks always initiating from this surface, it would seem appropriate to explore this further.

Upon exploration of surface residual stresses, the development of these stresses with fatigue cycling was carried out in air as shown in 4.4.2. Therefore a further through thickness residual stress profile was established, as shown in Figure 4-7, to compare the effects of environment and to provide a more complete picture.

Again, the overall shape of the curve demonstrates a Gaussian type distribution. It shows a compressive residual stress of -110 MPa at the free surface, rising to a stress free state at a sample depth of ~400 μm, and a maximum residual tensile stress of +100 MPa at a sample
depth of ~1400 μm. The profile then falls to a second stress free state at a sample depth of ~2000 μm. There is a compressive residual stress at the centre of the sample, 2500 μm, of -172 MPa.

The wire used in the fatigue in air experiments had a thickness of 5 mm rather than 4 mm, therefore when compared with the previous results in Figure 4-8 the profile appears elongated. This is to be expected given the increased sample thickness. However, much like the previous results, the profile exhibits a Gaussian type distribution, which is of a similar magnitude to the other profiles.

Figure 4-6: Through thickness residual stress measurement of all 12 mm x 4 mm high strength steel wires
Figure 4-7: Through thickness residual stress measurement of 10 mm x 5 mm high strength steel wire fatigue tested in air at an applied stress of 428 MPa

Figure 4-8: Through thickness residual stress measurement of all 12 mm x 4 mm high strength steel wires including the 10 mm x 5 mm results
4.4 Surface Measurements

The key point to be indicated from the through thickness residual stress measurement profiles is that the surface residual stress, based on these results, is always of a compressive nature. It is apparent from Chapter 3 that corrosion fatigue cracks initiate at the free surface of the high strength steel wire, therefore it was deemed that surface measurements may be of benefit to understanding the initiation process. The two sets of corrosion fatigue tested high strength steel wires, 12 mm x 4 mm and 12 mm x 7 mm, were used to carry out surface residual stress measurements.

The 12 mm x 4 mm steel wires had been corrosion fatigue tested in two seawater environments, namely aerated and CO\textsubscript{2} saturated to 1 bar absolute. For the aerated environment there were five nominal stress ranges, from 170 to 700 MPa. For the CO\textsubscript{2} saturated environment there were four nominal stress ranges, from 350 to 700 MPa. The mean applied stress for the aerated seawater test environment ranged from 107 to 428 MPa, and for the CO\textsubscript{2} saturated environment it ranged from 214 to 428 MPa.

The 12 mm x 7 mm steel wires had been corrosion fatigue tested in three seawater environments, namely aerated, CO\textsubscript{2} saturated to 1 bar absolute and 100 mbar absolute H\textsubscript{2}S with CO\textsubscript{2} balance to 1 bar absolute. For the aerated and CO\textsubscript{2} saturated environments there were five nominal stress ranges, from 125 to 325 MPa. For the H\textsubscript{2}S test environment there were three nominal stress ranges, from 200 to 325 MPa. The mean applied stress for all the 12 mm x 7 mm corrosion fatigue testing was 550 MPa.

For both sets of wires and the different environments, each nominal stress range had four test pieces. For the 12 mm x 4 mm steel wire, this meant there were 36 test pieces, 20 for the aerated environment and 16 for the CO\textsubscript{2} saturated environment. For the 12 mm x 7 mm steel wires, there were 52 test pieces, 20 for each of the aerated and CO\textsubscript{2} saturated environments and 12 for the H\textsubscript{2}S test environment.

A two point square map was carried out on each test piece in the centre of the sample, the most highly stressed region, on the side that was in tension during the four-point bend fatigue test. This side was identified by the fact that the strain gauge was mounted on the reverse side, the side in compression. The average residual stress value for the two points was taken to be the residual stress for that test piece.

Surface residual stress measurements for each nominal stress range produced four data points, based on four test pieces. To represent this data graphically, in a clear manner, it was decided that the average value be taken and error bars used to denote the boundaries of the
result. Table 4-3 shows an example of the data used to represent a single point on a graph and corresponds to the data point for 700 MPa on Figure 4-9. The cycles to failure are known from the test data, an average of which is taken and used as the x-axis value. The minimum and maximum values of cycles to failure represent the size of the error bar in the x-direction. The same procedure is carried out for the residual stress data, whereby the average value represents the y-axis value and the minimum and maximum values are used to establish the size of the error bar in the y-direction. This procedure was then repeated for each nominal stress range and plotted as a scatter graph.

Table 4-3: Example of the surface residual stress measurements and log cycles to failure values for 12 mm x 4 mm high strength steel wire corrosion fatigue tested in an aerated seawater environment

<table>
<thead>
<tr>
<th>Test Piece Number</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>Average</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Log Cycles to Failure</td>
<td>5.301</td>
<td>5.441</td>
<td>5.245</td>
<td>5.261</td>
<td>5.319</td>
<td>5.245</td>
<td>5.441</td>
</tr>
<tr>
<td>Residual Stress (MPa)</td>
<td>-275.6</td>
<td>-192.3</td>
<td>-137.2</td>
<td>-168.0</td>
<td>-193</td>
<td>-275.6</td>
<td>-137.2</td>
</tr>
<tr>
<td>Applied Stress (MPa)</td>
<td>681</td>
<td>701</td>
<td>711</td>
<td>699</td>
<td>698</td>
<td>681</td>
<td>711</td>
</tr>
</tbody>
</table>

4.4.1 Corrosion Fatigue Tested High Strength Steel Wire

4.4.1.1 12 mm x 4 mm High Strength Steel Wire

4.4.1.1.1 Aerated Seawater

The results for the 12 mm x 4 mm steel wire corrosion fatigue tested in an aerated seawater environment, Figure 4-9, show that as the nominal stress range and therefore the applied stress increases the surface residual stress becomes more compressive. It shows that the applied stress rather than the number of cycles to failure dominates the mechanism for the development of residual stress at the surface. This would imply that, as expected, the increase in applied stress is causing more plastic deformation at the sample surface. This is demonstrated by the fact that for the nominal stress range of 170 MPa the residual stress is half that of the samples tested at 700 MPa stress range, even though the sample at the lower applied stress has experienced approximately 50 times more fatigue cycles. This also shows that the damage accumulation of the microstructure is not a product of cycles to failure and applied stress. The damage accumulated at a lower stress with higher cycles to failure is not equivalent to that at a high stress with lower cycles to failure. The results would also indicate that the fatigue process and not the corrosion of the steel govern the residual stress at the surface for the 12 mm x 4 mm high strength steel wire.
Figure 4-9: Surface residual stress measurements against log cycles to failure for 12 mm x 4 mm high strength steel wire corrosion fatigue tested in an aerated seawater environment

4.4.1.1.2 CO₂ Saturated Seawater – 1 bar absolute CO₂ (CP grade) Seawater

The results for the 12 mm x 4 mm steel wire corrosion fatigue tested in a CO₂ saturated seawater environment, Figure 4-10, show that as the nominal stress range increases the surface residual stress, within error, is of the same magnitude. It shows that the applied stress and the number of cycles to failure have little effect on the surface residual stress values. This would imply that the amount of plastic deformation at the sample surface is the same irrespective of applied stress. For this case it could be thought of that the damage accumulation of the microstructure is a product of cycles to failure and applied stress. It is also thought that the steel corrosion process in a CO₂ saturated environment is affecting the surface residual stress. As shown in Section 3.5.1, the corrosion fatigue crack population and localised corrosion pit population in this environment are significantly higher than that in the aerated environment. The corrosion fatigue cracks initiate at the sample surface and it is this initiation and interaction with the surface microstructure that could cause this shift in residual stress.

The two sets of results for the different environments together were plotted, Figure 4-11, and it is shown that there is a demonstrable difference in trend in the results. As stated previously, for the aerated seawater test environment as the applied stress increases the surface residual stress becomes more compressive, whereas for the CO₂ saturated test environment the residual stress appears to be independent of applied stress.
Figure 4-10: Surface residual stress measurements against log cycles to failure for 12 mm x 4 mm high strength steel wire corrosion fatigue tested in a CO₂ saturated seawater environment.

Figure 4-11: Surface residual stress measurements against applied stress for 12 mm x 4 mm high strength steel wire corrosion fatigue tested in two different seawater environments.
4.4.1.2 12 mm x 7 mm High Strength Steel Wire

4.4.1.2.1 Aerated Seawater

The results for the 12 mm x 7 mm steel wire corrosion fatigue tested in an aerated seawater environment, Figure 4-12, show some correlation with the results for the 12 mm x 4 mm steel wires. Overall the surface residual stress does become more compressive as the applied stress increases. However, they also show some distinct differences. Firstly, the overall magnitude of the residual stresses is lower. This is expected to be due to the lower applied stress ranges than for the 12 mm x 4 mm steel wires. Secondly, the surface residual stress at the lowest applied stress of 125 MPa is tensile. A section of the 12 mm x 7 mm steel wire in the as received condition was not available for testing therefore it is not known whether the nature of the residual stress, i.e. tensile, is due to the wire drawing process [120,123] or an artefact of the corrosion fatigue testing. Again the results show some tendency for the applied stress to govern the development of residual stress by plastic deformation at the sample surface. Again the results, when compared to the corrosion fatigue crack population for this material, would also indicate that the fatigue process and not the corrosion of the steel govern the residual stress at the surface for this high strength steel wire.

![Figure 4-12: Surface residual stress measurements against log cycles to failure for 12 mm x 7 mm high strength steel wire corrosion fatigue tested in an aerated seawater environment](image-url)
4.4.1.2.2 CO₂ Saturated Seawater – 1 bar absolute CO₂ (CP grade) Seawater

The results for the 12 mm x 7 mm steel wire corrosion fatigue tested in a CO₂ saturated seawater environment, Figure 4-13, show little correlation with the results for the 12 mm x 4 mm steel wires and in fact are quite scattered. The surface residual stress for two of the stress ranges, 325 MPa and 200 MPa, is tensile. These two stress ranges are in fact the ones that exhibit the greatest amount of corrosion fatigue cracking. Again the results do suggest that the surface initiation and interaction of the corrosion fatigue cracks with the surface microstructure could cause this shift in residual stress. Although for this material the shift is towards the tensile residual stress region rather than compressive which is demonstrated by the 12 mm x 4 mm steel wires.

![Figure 4-13: Surface residual stress measurements against log cycles to failure for 12 mm x 7 mm high strength steel wire corrosion fatigue tested in a co₂ saturated seawater environment](image)

4.4.1.2.3 100 mbar absolute H₂S/ CO₂ Balance to 1 bar absolute Seawater

For the 12 mm x 7 mm high strength steel wires the surface residual stress can be explored for a third set of environmental conditions, namely a H₂S containing seawater test environment. This will potentially provide further information as to the effects of residual stress on the corrosion fatigue crack initiation process. The results for the 12 mm x 7 mm steel wire corrosion fatigue tested in a 100 mbar absolute H₂S with CO₂ balance to 1 bar absolute total pressure seawater environment, Figure 4-14, are reasonably scattered with large error bars, and therefore significant conclusions may not be drawn.
The mean stress and nominal stress range for the 12 mm x 7 mm steel wires are the same for each test environment. Therefore, it should be possible to comment on the effects of environment on the development of residual stress. However, as Figure 4-15 shows, the scatter in the results makes any significant conclusions difficult.

**Figure 4-14**: Surface residual stress measurements against log cycles to failure for 12 mm x 7 mm high strength steel wire corrosion fatigue tested in a seawater environment containing 100 mbar absolute H₂S/CO₂ Balance to 1 bar absolute
Figure 4-15: Surface residual stress measurements against applied stress for 12 mm x 7 mm high strength steel wire corrosion fatigue tested in three different seawater environments.
4.4.2 Fatigue in Air

Surface residual stress measurements for corrosion fatigue tested samples have been carried out. As discussed there is uncertainty in the results with regards to corrosion fatigue cracking and the effect this has to produce either tensile or compressive residual stresses at the surface. The 12 mm x 4 mm wire showed compressive stresses at the surface for a high amount of fatigue cracking, whereas, for the 12 mm x 7 mm wire tensile stresses were shown at the surface for comparable amounts of cracking.

This post-test analysis did not demonstrate how the surface residual stress develops with cyclic fatigue. Therefore two sets of test samples were subjected to cyclic fatigue, one at a high stress and the other at low stress see Table 4-4, with surface residual stress measurements being taken at specified points. These points were in the as received condition, prior to any cyclic loading, after 20,000 cycles shakedown and at sample failure or test run out. The midpoint, 20,000 cycles, is specified in the corrosion fatigue testing reports [134-137] as it is thought to remove or reduce the effects of residual stress on the samples prior to environmental testing. Test run out was set at 10million cycles or $10^7$ as per the original regime of corrosion fatigue testing.

<table>
<thead>
<tr>
<th></th>
<th>Mean Stress (MPa)</th>
<th>Stress Range (MPa)</th>
<th>Minimum Stress (MPa)</th>
<th>Maximum Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>High Stress Samples</strong></td>
<td>428</td>
<td>700</td>
<td>78</td>
<td>778</td>
</tr>
<tr>
<td><strong>Low Stress Samples</strong></td>
<td>244</td>
<td>400</td>
<td>44</td>
<td>444</td>
</tr>
</tbody>
</table>

The material used was 10 mm x 5 mm high strength carbon steel wire with similar chemical composition and mechanical properties to the 12 mm x 4 mm and 12 mm x 7 mm steel wires. The samples were 170 mm long. They were fatigue tested using a four-point bend fatigue rig similar to the one used for the corrosion fatigue testing that is described in Section 3.2. The fatigue test rig has four channels; therefore four tests pieces were used. This was in order to capture any variation in residual stress across numerous samples rather than relying on a single set of results. However, due to material availability four test samples were used for the high stress test and three test samples were used for the low stress test.

The surface residual stress results for each stage of testing are shown on one graph, with a graph for each test piece. The figures show the central most highly stressed region along the
sample length, as this is where it has been shown in Chapter 3 that most of the corrosion fatigue cracking occurs.

Overall, for the high stress samples, Figure 4-16, the surface residual stress measurements after 20,000 cycles and run out/sample failure are compressive. This is advantageous, as it will increase the time for crack initiation to occur and slow down crack growth just below the surface of the material.

![Sample 1](image1)

![Sample 2](image2)

![Sample 3](image3)

![Sample 4](image4)

**Figure 4-16:** Surface residual stress measurements along the length of 10 mm x 5 mm high strength steel wire fatigue tested in air at high stress

Overall, for the low stress samples, Figure 4-17, the majority of the surface residual stress after 20,000 cycles is compressive. Sample 1 shows some minor signs of tensile residual stress after the shakedown but it is thought to be due to the lower applied stress and that this would be removed within a short period of time during fatigue testing. Due to equipment availability the run out test for the low stress samples was unable to be achieved, however, it is thought that this testing will be completed at a future date.
Figure 4-17: Surface residual stress measurements along the length of 10 mm x 5 mm high strength steel wire fatigue tested in air at low stress

The results for the through thickness residual stress measurements for the as received 12 mm x 4 mm steel wire demonstrated that the surface residual stress is compressive for this sample. However, this investigation has shown that there can be quite some variation in residual stress along the surface of a sample. Many of the samples tested show tensile residual stresses along the surface in the as received condition, which are later removed by fatigue cycling. Therefore caution needs to be taken when assessing results of the analysis from only a few data points. These variations in surface residual stress along the entire sample surface may somewhat explain the scatter in results shown for the surface analysis of the corrosion fatigue tested samples.
Chapter 5 Surface Strain Mapping
5. Surface Strain Mapping

5.1 Introduction

Corrosion fatigue cracks have been shown to initiate from localised corrosion pits. These pits act as stress raisers whereby the surface strain is concentrated around the surface defects thus promoting crack initiation.

A technique, called Digital Image Correlation (DIC), has been used to explore the development of surface strains around corrosion pits due to an applied load [130]. This technique has not been used before to map surface strains in a seawater environment and therefore required developing for this application.

5.2 Experimental Methods

This part of the project required that the establishment of numerous experimental aspects be created before surface strain mapping could be carried out. These included establishing a suitable test rig in which to carry out the experiments, the growth of a stable surface oxide on the high strength steel wire for imaging and development and use of a technique for growing artificial pits.

5.2.1 Slow Strain Rate Test Rig

The existing environmental tensile testing rig comprised of an Instron 5567 tensile testing machine, a stainless steel chamber that provides the sample environment and an Olympus UIS series optical microscope and a LaVision Digital Image Correlation (DIC) system using DaVis 7.4 acquisition and processing software to provide the imaging capability.

The tensile testing machine had a 10 kN load cell. The sample chamber consists of a 316 stainless steel chamber complete with sample grips and thermocouple. There was also a chamber lid complete with a borosilicate glass window that provides an optical view of the sample for use by the microscope and DIC system.

The equipment was originally purchased and installed to carry out stress corrosion cracking tests using deionised hydrogenated water. Therefore, due to the potential risk of contamination of the chamber from using substitute ocean water in the experiments, it was decided that a new liner be made to fit inside the chamber in which this type of experiment could be carried out. The liner was made from acrylic so as not to degrade, due to corrosion, during the experiments. It is also cheap and easy to manufacture products with.
Figure 5-1 shows the details of the existing chamber with the new liner fitted in. Oil seals have been provided where the existing sample grip holders penetrate the new liner. The new liner has been designed with a flange with hole-centres that tie up with the existing stainless steel chamber. In turn, a new chamber lid was provided complete with an ultra-violet (UV) light filter, which provided the optical microscope with a suitable view port for the DIC system. The new chamber lid was bolted onto the existing chamber, using the existing setscrews, with a 3 mm rubber gasket providing a gas seal.

The chamber was then to be used with the standard optical microscope lens provided with the microscope, however, there were issues of condensation forming on the inside of the UV filter which hindered image acquisition. Therefore experiments were carried out with the lid removed; however, this also encountered its own set of problems. Due to vibration and movement of the equipment slight fluctuations in the water level made imaging the sample surface difficult, therefore an immersible optical microscope lens was used.

The existing sample grips consisted of an M14 female screw thread was designed to hold samples with screwed ends. Due to the restricted dimensions of the high strength carbon steel wires, 12 mm x 4 mm and 10 mm x 5 mm; it was not possible to manufacture samples with the appropriate screwed ends. Also the existing sample grips were made from stainless steel that would lead to galvanic corrosion if the two materials were to come into contact with one another. Therefore, new sample grips were made to hold the test specimen. The sample grips were designed to fit the existing test machine grip holders. They consisted of a conversion grip made to fit in the existing holes and provide a flat grip with a shear pin to hold the sample during loading.

The new sample grips were made from stainless steel and were coated in Sealac varnish in order to protect them from the seawater environment and to provide a dissimilar metals barrier between the stainless steel grips and the carbon steel test sample, so as to prevent galvanic corrosion.

Full general arrangement and detailed drawings of the new chamber liner, lid and sample grips can be found in Appendix 4.

5.2.1.1 Slow Strain Rate Test Sample Design

The tensile test rig was an Instron 5567 with a 10 kN load cell. The sample high strength steel wires, 12 mm x 4 mm and 10 mm x 5 mm have a strength rating of 190 ksi (1310 MPa) and 110 ksi (760 MPa) respectively. Therefore the cross sectional areas had to be such that
the sample failed within the 10 kN limit. The chemical composition of the high strength steel wires used in the surface strain mapping experiment is shown in Table 3-8.

The samples used for slow strain rate testing (SSRT) had a cross sectional area $S_0$ of 6 mm$^2$. The samples used complied with the British Standard for Stress Corrosion Testing [142], which states that uniaxially loaded tension specimens shall comply with the British Standard for tensile testing of metallic materials [138]. See Appendix 6 for detailed drawings of the samples used.

The SSRT samples were machined using Electric Discharge Machining (EDM). The EDM residual surface finish was not ideal for carrying out DIC experiments. The machined surface therefore required grinding to a P4000 finish and etching in 2 % nital to reveal the microstructure.

![Figure 5-1: Pictures of the existing chamber with new liner, sample grips and sample installed.](image)

### 5.2.2 Artificial Pit Growth

Corrosion fatigue cracking analysis confirmed what is already known in the literature, that cracks initiate from stress raisers such as corrosion pits [84,99,107]. Consequently it was decided to grow artificial corrosion pits on the surface of the high strength carbon steel so that strain mapping around the pits could be undertaken using Digital Image Correlation.
The effects of pit size and population on the development of surface strain fields were explored by comparing different size pitted areas and different size single pits.

The localised corrosion process has a characteristic feature, in that, below a certain threshold value of the anodic potential, within a given metal-electrolyte system, pitting does not occur; inversely above this value pitting will occur. The sudden increase in the current is due to the breakdown of the passive film and is known as the trans-passive region. In this case the metal-electrolyte system is carbon steel and seawater. It is also known that carbon steel does not passivate, and therefore readily exhibit a pitting potential, in seawater. However, there has been work carried out on the passivation of carbon steel in sodium carbonate (Na\textsubscript{2}CO\textsubscript{3}) bicarbonate (NaHCO\textsubscript{3}) buffer solutions [143–146]. These works have shown that carbon steel will exhibit a passive and transpassive region in sodium carbonate bicarbonate buffer solutions which has a pH of 10 to 11.

An initial set of experiments to confirm this characteristic feature for the carbon steel high strength wire and to establish the pitting potential was carried out. This entailed carrying out potentiodynamic polarisation scans for the high strength steel wire in a 0.1 M Bicarbonate-Carbonate solution with and without the addition of 0.1 M sodium chloride. The results of which are shown in Figure 5-2.

The sample tested in the solution with the addition of sodium chloride was scanned between -600 mV to +250 mV v open circuit potential (OCP). The sample tested in the solution without the addition of sodium chloride was scanned between -600 mV to +1200 mV v OCP. Both sets of results had a scan rate of 1 mV/s. The OCP values for the solution with and without the addition of sodium chloride were -320 mV and -330 mV respectively which are comparable to work by Videm et al. [144]. The working electrodes were made from high strength carbon steel as described in Section 3.3.5.2.

These experiments and analysis established that the pitting potential for the high strength carbon steel wire in a bicarbonate-carbonate solution with the addition of sodium chloride was ~−500 mV above OCP.

Consequently, the establishment of the pitting potential in bicarbonate-carbonate solution meant that artificial pits could be grown in order to carry out localised surface strain measurements using DIC. The techniques used to grow artificial pits in the high strength carbon steel wire were chronoamperometry and chronopotentiometry.
Chronoamperometry was used to grow multiple pits in a specified area within a standard three-electrode electrochemical cell set up. Chronopotentiometry was used to grow single pits using a microcell with various sizes of tips.

![Anodic potentiodynamic polarisation curves for high strength carbon steel wire in sodium carbonate bicarbonate solution with and without the addition of sodium chloride](image)

**Figure 5-2:** Anodic potentiodynamic polarisation curves for high strength carbon steel wire in sodium carbonate bicarbonate solution with and without the addition of sodium chloride

### 5.2.2.1 Preparation of 0.1 M Sodium Carbonate (Na<sub>2</sub>CO<sub>3</sub>) Bicarbonate (NaHCO<sub>3</sub>) Solutions

The chronoamperometry and chronopotentiometry experiments were carried out in a 0.1 M solution of sodium carbonate-bicarbonate-chloride.

In order to prepare 10 litres of solution, first of all, the salts are weighed out on a set of electronic scales, which had accuracy to 2 decimal places. The amount of the different salts required is listed in Table 5-1. These were then dissolved in sufficient deionised water to get them to dissolve. The solution is then made up to 10 l total volume. The pH of the solution was measured and found to be 10.5.
Table 5-1: Chemical composition of 0.1 M sodium carbonate-bicarbonate-chloride solution

<table>
<thead>
<tr>
<th>Compound</th>
<th>Amount Required for 0.1 M Solution (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Carbonate (Na$_2$CO$_3$)</td>
<td>5.84</td>
</tr>
<tr>
<td>Sodium Bicarbonate (NaHCO$_3$)</td>
<td>8.40</td>
</tr>
<tr>
<td>Sodium Chloride (NaCl)</td>
<td>10.6</td>
</tr>
</tbody>
</table>

5.2.2.2 Chronoamperometry

Chronoamperometry was used to grow corrosion pits in two different areas, namely small and large, on the surface of the high strength carbon steel SSRT samples. Isolating the surface area of the sample from the solution using Lacomit varnish created the areas. The small area was 2 mm$^2$ and the large area was 60 mm$^2$ as shown in Figure 5-5. A three electrode system was used in an electrochemical cell as described in Section 2.2.2.

The pitting potential of 500 mV above OCP was applied for a set period of time in order to grow corrosion pits. The measured current versus time plots is shown in Figure 5-6.

The first step was to establish a suitable exposure time in order to obtain the appropriate size and quantity of localised corrosion pits. This was established by exposing numerous samples at different time intervals, namely 30, 60 and 300 s, to the solution and imaging them to establish size and population see Figure 5-3 and Figure 5-4. It is shown that as the exposure time increases the size of the pit increases. For each exposure time a close up image of the sample surface was taken see Figure 5-4. Using a Keyence VHX2000 optical microscope, which is capable of providing a 3D image of the surface, the surface profile and pit depth were established.

For the 30, 60 and 300 s exposures on average the pit depth was 3 μm, 15 μm and 40 μm respectively. Based on the results of the corrosion fatigue cracking and pit depth analysis in Chapter 3 it was decided that an exposure time of 60 s would give a representative set of corrosion pits for use in the DIC surface strain experiments.

Samples (a) and (b) shown in Figure 5-5 were then immersed in aerated seawater in order to grow a suitably stable surface oxide for DIC imaging.
Figure 5-3: Images of chronoamperometry test samples with different solution exposure times
(a) 30 s, (b) 60 s & (c) 300 s
Figure 5-4: High magnification images of chronoamperometry test samples with different solution exposure times (a) 30 s, (b) 60 s & (c) 300 s

Figure 5-5: Images of the SSRT samples being prepared for testing with lacomit and sealac (a) small pitted area (b) Large pitted area (c) Sample after pre-corrosion stage
5.2.2.3 Chronopotentiometry

Chronopotentiometry was used to grow single corrosion pits using a microcell set up as shown in Figure 5-7. The microcell consisted of a small chamber that held the electrolyte solution in this case 0.1 M sodium carbonate-bicarbonate-chloride. The chamber also housed the counter and reference electrodes. A syringe was used to fill the chamber with solution and to pass it through a micro-pipette tip that was in contact with the working electrode i.e. the sample surface. Two different size tips were used. Their diameter was measured using an optical microscope and found to be 400 and 700 μm.

The results from the chronoamperometry experiments show that the measured current for each exposure time consistently plateaued out at 4.126 mA, see Figure 5-6, which is in line with the current values on potentiodynamic polarisation curve at the pitting potential see Figure 5-2. This current was therefore applied to the system using an Ivium Compactstat for various periods of time in order to grow single corrosion pits. Again, a suitable exposure time was established in order to obtain the appropriate depth of localised corrosion pit. Exposing numerous samples at different time intervals, namely 60 s, 300 s and 600 s, to the solution and imaging them to establish pit depth established this. Images of the corrosion pits grown from the initial chronopotentiometry experiments are shown in Figure 5-8. Again using a Keyence VHX2000 optical microscope the pit depth was established for the 60 s, 300 s and 600 s to be 12 μm, 25 μm and 65 μm. After 60 s exposure, as is shown in Figure 5-8 (a), the outline of the localised corrosion pit is evident however the pit was not fully formed.
After 300 s the pit is fully formed with signs of crevice corrosion around the edges of the contact point between the tip of the microcell and the sample surface. After 600 s again the pit is fully formed however the crevice corrosion is much worse. Therefore based on these initial results an exposure time of 300 s was used to grow the single corrosion pits for the SSRT samples, after which they were again immersed in aerated seawater for three days, images of the samples are shown in Figure 5-9.

The microcell was designed and developed by Sybille Schilling as part of her PhD project. I would like to acknowledge her help and for allowing me to use the microcell set up.

5.2.3 Stable Surface Oxide

Corrosion rate measurements were carried out in an aerated seawater environment as shown in Chapter 3. The results of these measurements show that after three days immersed in aerated seawater the corrosion rate had flattened out and reached a steady rate. Therefore based on these results, once the localised corrosion pits had been grown in the high strength steel wire slow strain rate samples, the test pieces were immersed in aerated seawater for three days.

After three days immersion the samples were removed from solution the loose oxide formed on the surface was removed with a soft bristled brush, they were rinsed and dried. An
example of the slow strain rate test sample after this pre-corrosion stage is shown in Figure 5-5 Part (c). An example of the oxide film grown on the SSRT samples is shown in Figure 5-9.

Figure 5-8: Optical microscope images of the single corrosion pits with different solution exposure times (a) 60 s (b) 300 s and (c) 600 s

Figure 5-9: Optical microscope images of the single corrosion pits (a) Small (b) Large

5.2.4 Surface Strain Mapping

5.2.4.1 Slow Strain Rate Testing and Image Capture

For the initial tests carried out in air the samples, as stated previously, the samples were etched in nital to reveal the microstructure. For the tests carried out in seawater, it was thought that, due to the scale that had been grown on the surface, etching was not necessary,
however, trials showed that superior images were gained by etching prior to surface scale growth.

The test is split into two sections, the SSRT part and the image capture part. For the SSRT part, the samples were inserted into the grips and held in place with the shear pins, ensuring that the samples were as flat as possible in order to obtain consistently in focus images. The manual displacement control on the test rig was used to remove the slack in the system. The load at this starting point was recorded and the overall displacement zeroed. The Instron Bluehill proprietary software and program parameters were used to set the required strain rate and displacement step. Displacement steps varying from 25 to 500µm were tried. Initially three different strain rates of $10^{-4}$, $10^{-5}$ and $10^{-6}$ strain/second were used see Figure 5-11. Thereafter, it was decided that a strain rate of $10^{-5}$ be used as this meant that all further experiments could be completed within an 8-12 hour time period.

After each displacement step the applied load and extension were recorded which allowed for the load-extension curve to be plotted. The applied load and original cross sectional area were used to establish the applied stress. No compensation was made for the reduction in cross sectional area due to the applied load.

For the image capture part, first of all the sample surface was brought into focus using the optical microscope. A 10x magnification immersible optical microscope lens was used (Olympus UMPLFLN10W Objective). In order to use the shift correction function, which is explained in 5.2.4.2, a particular feature on the sample surface had to remain in the same place within the image throughout the duration of the slow strain rate test. In order to maintain the position of the surface feature the optical microscope was moved in the x and y planes using the stage controls. The next step was to remove any loose oxide on the sample surface as this would create an error in the result by implying that there are higher levels of strain than the sample is actually experiencing. This was carried out using a soft bristled brush.

The process of sample displacement and image capture was repeated iteratively until the sample failed. Finally all images were correlated using DaVis 7.4 to establish the surface strain. The applied stress and the global surface strain measurement meant that the stress-strain curve could be plotted see Figure 5-11.
5.2.4.2 Image Correlation Procedure

The image correlation procedure was generally as follows.

1. The images were organised into chronological order.
2. The images were then grouped from 1 to n number of images.
3. The shift correction function was then used. This corrected for shift in the x and y directions and for rotation. Without this step in the procedure the results would have been erroneous. To perform shift correction, a specific feature was selected as the origin within the first image around which shift correction was performed. This origin acted as a zero point with all image displacements, and ultimately strains measurements, being relative to this point.
4. The next step was to perform 2D deformation routine. This established the displacement vectors that were in turn differentiated within the software to ascertain the strain vectors. There were numerous parameters within the software that could be changed to enhance the strain analysis. The different parameters and their effects on strain measurement were discussed in the results section.
5. The next step was to establish the strain contour maps in the x and y direction. The global strain for each load increment was also established so that a stress-strain curve may be plotted and statistical analysis carried out.
6. The strain contour maps were exported as an image and in spreadsheet format for statistical analysis purposes. It was also possible to export the images in a video format to show how the strain develops around microstructural features during a loading sequence.
5.3 Results

5.3.1 Initial SSRT Tests

5.3.1.1 SSRT Test in Air

Slow strain rate testing is a form of tensile testing but with a much smaller strain rate, therefore the results of the tensile testing were used to establish the required parameters to be used within DaVis in order to achieve comparable results. Initial SSRT tests were carried out in air within the elastic region of the high strength steel wire and numerous sets of DaVis analyses were carried out see Figure 5-10. As stated previously the strain determined from the tensile testing was established using an extensometer.

The parameters that were investigated were as follows:

1. Correlation mode – Integral or Differential
2. Interrogation window size
3. With and without image pre-processing

There are two different types of correlation mode that were used on the same set of data in order to establish their differences. Integral is the correlation of a set of images relative to the first image. Differential is the correlation between two successive images. Figure 5-10 shows that analysis of a set of images using the integral mode gives the best correlation with the tensile test data; therefore this was used for future analyses.

The interrogation window size can be varied from 1000x1000 pixels to 4x4 pixels. Numerous iterations using different window sizes were carried out, some of which are shown in Figure 5-10. It was established that the best results for the high strength steel wire were obtained using a start window size of 1000x1000 pixels and carrying out a multi pass iteration down to a window size of 32x32 pixels. Variations in window size were found to have very minor effects in the order of the fourth decimal place.

Figure 5-10 also shows that image pre-processing was required by DaVis in order to obtain the best results.
5.3.1.2 Strain Rate Dependency Tests

The results of the tensile testing along with some tests to examine the strain rate dependency of the material are shown in Figure 5-11. Figure 5-11 show that the results obtained using SSRT and the DaVis analysis technique display close correlation with the tensile testing results, which in turn provided validation for future test results.
5.3.2 Localised Strain Analysis

Once the sample preparation stages had taken place, slow strain rate testing could be carried out. The SSRT tests undertaken were in air and in aerated seawater. The sample tested in air was an as received sample with the surface etched in 2% nital.

The samples tested in aerated seawater were as received, a large pitted area and a small-pitted area, as defined previously and a large single pit and a small single pit.

The displacement steps decreased throughout the duration of the experiment in order to capture any large increases in strain. At the start of the test they were 500 μm reducing down in stages to 50 μm towards to failure point, where it is thought that there would be large increases in strain for small amounts of sample extension.

In order to compare the results of each experiment, three points on the stress strain curve that are common to each test were taken, namely the yield point, ultimate tensile strength and strain at failure. The results of which are compared and contrasted below with the figures showing the strain contour maps on the left hand side and the image of the sample surface on the right hand side. When looking at the images the loading direction is left to right.

Within DaVis it is possible to view each strain contour map image as a spreadsheet in which each cell is a pixel from the image with a strain value. The spreadsheet view from DaVis was exported to Excel. The data was then sorted into bins. Given the size and range of the data set numerous numbers of bins were tried however 200 bins were chosen as this gave the optimal spread. The frequency was then calculated for each bin by dividing the quantity in the bin by the total number of data points. This process was then repeated for each contour map and a histogram of the data was plotted. A histogram for each extension was plotted see Figure 5-12; however for comparison purposes the three common points of yield, ultimate tensile strength and strain at failure were used. The histograms are a direct use of the established strain data and were analysed in order to quantitatively compare each set of results.

Figure 5-12 shows the progressive spread of surface strain with an increase in sample extension and ultimately load. At the lower extension 0.5 mm to 2.0 mm, the histogram is narrow, that is to say there is a low range of strain and a high frequency which is indicative of a uniform global strain over the surface of the material. As the extension increases, 2.25 mm to 2.5 mm, there is an observed shift in the average surface strain and the histogram widens meaning there is an increase in the range of strain. The increase in range of strain would
indicate that there is some strain localisation on the surface of the material. At an extension of 2.75 mm to 3.1 mm the histograms have become wide ranging in terms of strain and low frequency which would indicate that there is wide ranging strain on the surface of the material i.e. strain localisation.

A rigid body displacement of the samples in air and in seawater was carried out, with 20 images taken for each test, and the average errors were found to be 0.05 % and 0.01 % respectively, which is in line with that established by Fonseca et al [130].

Figure 5-12: Example of a histogram for each sample extension for high strength steel wire
5.3.2.1 Air

The results for the test carried out in air are shown in Figure 5-14. The results of the strain contour map show that at the yield point there is very little strain evident and that it increases, as expected, with increasing applied load. As stated previously, this test was carried out to establish the viability of this technique on the high strength steel wire. Figure 5-13 shows the results of the statistical analysis that demonstrates that the surface strain is relatively uniform. This is indicated by the fact that the histograms bars are narrowly spread with a high percentage frequency mean strain.

![Histogram of the surface strain for high strength steel wire tested in air](image)

Figure 5-13: Histogram of the surface strain for high strength steel wire tested in air
Figure 5-14: Surface strain maps (1) and optical microscope images (2) for high strength steel wire tested in air (A) yield, (B) ultimate tensile strength (C) strain at failure.
5.3.2.2 Seawater

5.3.2.2.1 As Received Surface

The results for the first test carried out in an aerated seawater environment with an as received sample are shown in Figure 5-16. The results of the strain contour maps show that at the yield point the strain is uniform where as at the ultimate tensile strength and failure points there are signs of localised strain. This is further supported by the results of the statistical analysis in Figure 5-15 that again shows a narrow histogram bar with a high frequency mean strain at the yield point.

Furthermore, the histogram bars at the ultimate tensile strength and failure points have a lower frequency mean stress and are more diffuse or spread out, which would indicate a more localised strain scenario.

The microstructural or surface features that the localised strain points refer to is not clear from the images. It is also unexpected on a supposedly plain surface to see strain localisation, however it is thought that it may be due to the nature of the corroded surface.

![Histogram of the surface strain for high strength steel wire polished surface tested in seawater](image-url)

**Figure 5-15**: Histogram of the surface strain for high strength steel wire polished surface tested in seawater
Figure 5-16: Surface strain maps (1) and optical microscope images (2) for high strength steel wire polished surface tested in seawater (A) yield, (B) UTS (C) strain at failure
5.3.2.2 Large Pitted Area

The next test carried out in an aerated seawater environment was that of the large pitted area, the results for which are shown in Figure 5-19.

At the yield point the results show clear indications of localised surface strain fields around the corrosion pits of around 10-20 % strain. As the load increases it is clear to see the localised strain fields intensify from yield to ultimate tensile strength to around 25 % strain and exhibit clear high strain regions at the failure point. Again, this is further supported by the results of the statistical analysis in Figure 5-17. Although there are clear indications of localised strain fields at the yield point the overall surface strain shown by the high frequency narrow histogram bar demonstrates a low uniform global strain on the sample surface. The histogram bar for the ultimate tensile strength portrays a similar situation to that for the yield point, although there is a slight increase in spread of the result with a lower frequency mean stress. However, the result for the failure point shows a much more diffuse strain field with a low frequency mean stress that is representative of a localised surface strain field. The red region in the contour maps that indicates a localised strain of 120 % whilst the bulk is 20-30 % further supports this.

5.3.2.2.3 Small Pitted Area

The next test carried out in an aerated seawater environment was that of the small pitted area, the results for which are shown in Figure 5-20. Unlike the image of the large pitted area, the shape and size of the corrosion pits from the DaVis image capture appear to be less well defined, therefore they have been circled for clarity.

At the yield point the results show some indications of localised surface strain fields around the corrosion pits of around 10-20 % strain, which have been circled.

Again as the load increases it is clear to see the localised strain fields intensify from yield to ultimate tensile strength. However, for this test there is more of a uniform global strain of 10-15 % over the surface of the sample with obscured regions of localised strain around the pits. At the failure point there appear to be much more areas of localised surface strain with the corrosion pits and areas to the right of the image showing well defined regions. Figure 5-18, shows that when compared to the large pitted area there is approximately the same average strain but with a lower frequency that would indicate a more diffuse result. Unlike the result for the ultimate tensile strength for the large pitted area there is a clear shift in the histogram bar for the small pitted area. There is a slight increase in spread of the result with a lower frequency higher mean stress. This is augmented by the strain contour map that as stated above shows an increase in global strain with a small increase in localised strain.
The result for the failure point, like the large pitted area, shows widespread scatter of surface strain values demonstrating much more localised strain. However, the scatter and mean strain for the large pitted area are greater, which is attuned to the fact that an increase in the number of stress raisers will increase the surface strain.

Figure 5-17: Histogram of the surface strain for high strength steel wire large pitted area tested in seawater

Figure 5-18: Histogram of the surface strain for high strength steel wire small pitted area tested in seawater
Figure 5-19: Surface strain maps (1) and optical microscope images (2) for high strength steel wire large pitted area tested in seawater (A) yield, (B) UTS (C) strain at failure
Figure 5-20: Surface strain maps (1) and optical microscope images (2) for high strength steel wire small pitted area tested in seawater (A) yield, (B) UTS (C) strain at failure
5.3.2.2.4 Large Single Pit

The next test carried out in an aerated seawater environment was that of the large single pit with a diameter of approximately 700 μm, the results for which are shown in Figure 5-23.

At the yield point the results show clear indications of some localised surface strain fields within the corrosion pit of around 30-40 % strain with the remaining area outside of the pit being at a lower strain of less than 5 %.

As the load increases it is clear to see the localised strain fields intensify from yield to ultimate tensile strength within the corrosion pit and the surrounding area. The strain within the pit has at some small circumferential regions reached 60 % with the surrounding area at 5-10 %. At the failure point the localised strain is still approximately 60 %, however there are an increase in the number of localised regions. It should be noted that most of the localised strain is within the pit with the surrounding area exhibiting mainly uniform strain.

Again, this is further supported by the results of the statistical analysis in Figure 5-21. As per the other results thus far, although there are clear indications of localised strain fields at the yield point within the corrosion pit, the overall surface strain shown by the high frequency narrow histogram bar demonstrates a low uniform global strain on the sample surface. The histogram bar for the ultimate tensile strength reveals that there is a slight increase in spread of the result with a lower frequency mean stress. This is demonstrated by the increase in localised strain field within the pit with only a small increase in surface strain outside of the pit.

The histogram results for the failure point show a percentage decrease in mean stress that would concur with an increase in localised strain, which is also demonstrated by the length of the histogram tail.

5.3.2.2.5 Small Single Pit

The final test carried out in an aerated seawater environment was that of the small single pit with a diameter of approximately 400 μm, the results for which are shown in Figure 5-24.

Again, similarly to the large pit, the results show at the yield point clear indications of some localised surface strain fields within the corrosion pit of up to 25 % strain with the remaining area outside of the pit being at a lower strain of less than 5 %.

It is clear to see that as the load increases the localised strain fields intensify from yield to ultimate tensile strength within the corrosion pit and the surrounding area showing clear definition between the two different areas.
The left hand side of the pit around the circumference is beginning to show a region of localised strain of up to 55 % strain with the surrounding area being at 5-10 %.

At the failure point the localised strain field on the left hand side of the pit is now clearly defined with the development of another strain field on the opposite right hand side of the pit. The localised strain on the left hand side of the pit is now up to 90 % strain which when compared to the measured average global strain of around 7.3 % shows a notable difference. The location of this localised strain region is indicative of the fact that the loading direction is left to right.

Again, as with the other results this is demonstrated graphically by the results of the statistical analysis in Figure 5-22. As per the other results thus far, although there are clear indications of localised strain fields at the yield point within the corrosion pit, the overall surface strain shown by the high frequency narrow histogram bar demonstrates a low uniform global strain on the sample surface. The shape of histogram bar for the ultimate tensile strength and failure point are similar to that for the large single pit except for the fact there is a slight increase in mean stress at each stage.
Figure 5-21: Histogram of the surface strain for high strength steel wire large single pit tested in seawater

Figure 5-22: Histogram of the surface strain for high strength steel wire small single pit tested in seawater
Figure 5-23: Surface strain maps (1) and optical microscope images (2) for high strength steel wire large single pit tested in seawater (A) yield, (B) UTS (C) strain at failure
Figure 5-24: Surface strain maps (1) and optical microscope images (2) for high strength steel wire small single pit tested in seawater (A) yield, (B) UTS (C) strain at failure
Chapter 6 Discussion
6. Discussion

The corrosion fatigue behaviour of the high strength carbon steel wires that are used as tensile armour in flexible risers has been investigated. The first stage was to investigate the corrosion fatigue failure mechanisms in terms of crack initiation and crack propagation with respect to environment, applied stress, frequency and R-ratio. The second stage was to quantify the residual stresses within the material and establish their effects on the crack initiation process. The third stage was to investigate the effects of localised corrosion pitting on crack initiation using a surface strain mapping technique called Digital Image Correlation (DIC).

6.1 Corrosion Fatigue Cracking

Corrosion fatigue testing was carried out by Intertek using a four-point bend displacement controlled test methodology. Tests were carried out on two different types of high strength carbon steel tensile armour wires, with comparable chemical compositions Table 3-8 and up to three different environments. Corrosion fatigue tests were carried out on 12 mm x 4 mm high strength carbon steel tensile armour in an aerated and CO₂ saturated to 1 bar absolute ASTM D1141 synthetic seawater. Corrosion fatigue tests for the 12 mm x 7 mm high strength carbon steel tensile armour were carried out in aerated, CO₂ saturated to 1 bar absolute and 100 mbar absolute H₂S with CO₂ balance to 1 bar absolute ASTM D1141 synthetic seawater.

The post-fatigue tested samples were sectioned, mounted, ground and polished and then etched in 2% nital. As stated previously, the cracks were investigated to determine their crack path with respect to microstructure, population, size and location of the cracks. This was in order to determine the relationship between cracking, microstructure, environment and the effects of cyclic stress on the corrosion fatigue process. It was found that many cracks initiate from localised corrosion pits as it is well known in the literature [72,76,88,102,104,107] that these geometric discontinuities act as stress raisers for crack initiation.

For the 12 mm x 4 mm high strength steel wire in an aerated seawater environment the number of secondary cracks is independent of applied stress. There is insufficient data to carry out statistical analysis for each stress range; however analysis of the dataset for the environment as a whole shows a mean crack depth of 986 µm.
For the CO$_2$ saturated seawater environment the number of secondary cracks increased with increasing applied stress. Statistical analysis of the datasets for each stress range was carried out which showed that the mean crack depth decreased and the crack population increased as applied stress increased, see Figure 3-15. This demonstrates that at lower applied stresses there are few long cracks and at higher applied stresses there are many short cracks. The reasoning behind this was further investigated by looking at the crack initiation sites. Analysis of the secondary crack dataset for the environment as a whole shows a mean crack depth of 138µm. There is approximately an order of magnitude difference in crack depth between the aerated seawater and CO$_2$ saturated seawater environments.

Further analysis of the sample surface for the two different environments demonstrated a significant amount of localised corrosion. A comparison of the corrosion pit data for the two environments shows that for the aerated environment the pit population is independent of applied stress, see Figure 3-16. However, the isolated data for the aerated environment see Figure 3-18, interpreted separately shows that the number of corrosion pits and geometric mean pit depth increases with applied stress with an overall geometric mean pit depth for the environment of 10.2 µm. For the CO$_2$ saturated environment, Figure 3-22 shows a clear increase in the pit population and mean pit depth with an increase in applied stress with an overall mean pit depth of 7.9 µm. A comparison of this to the number of secondary cracks shows that there is a clear linear relationship between the number of secondary cracks and the number of localised corrosion pits for the CO$_2$ saturated environment.

The increase in the pit population and mean pit depth with an increase in applied stress would indicate that strain assisted or strain enhanced dissolution is occurring as discussed in the literature by [73,76,81,85,86,89,95,98,101,102,105,106], where the pit growth rate can be a function of the magnitude of the applied stress. For both the aerated and CO$_2$ saturated environments this would suggest a mechanism of surface film breakdown and strain assisted dissolution leading to the formation of many surface geometrical discontinuities.

The overall pit depth for each environment is approximately the same with a similar range, but the pit population for the CO$_2$ saturated test is far higher i.e. more sites for crack initiation equates to a higher probability of more cracking which is demonstrated by the results.

The reason for fewer corrosion pits and fatigue cracks in the corrosion fatigue samples tested in aerated seawater may be due to a combination of factors such as the type of scale formed, a lower corrosion rate and the lower applied stress compared to the CO$_2$ saturated samples.
For the 12 mm x 7 mm high strength steel wire the conclusions on the secondary cracking behaviour are less clear, see Figure 3-19. In an aerated seawater environment the number of secondary cracks is independent of applied stress. Again, there is insufficient data to carry out statistical analysis for each stress range; however analysis of the dataset for the environment as a whole shows a mean crack depth of 70 µm which is an order of magnitude lower than that for the 12 mm x 4 mm wire.

For the CO$_2$ saturated seawater environment there is no demonstrable relationship between the number of secondary cracks and the applied stress. The mean crack depth for the environment is 65 µm which is approximately half the crack depth for the 12 mm x 4 mm wire. There is sufficient crack population data for the high nominal stress range in order to carry out a statistical analysis, however there is insufficient data to make a comparison between secondary cracking and applied stress.

For the H$_2$S environment, only the lowest stress range exhibited any signs of fatigue cracking with a mean crack depth of 36 µm. The sample exhibited a large amount of pitting and the lack of secondary cracks may be due to crack blunting caused by the localised corrosion pitting.

For the 12 mm x 7 mm wire the scatter in the corrosion pitting results for each environment and individual applied stress range is quite high, Figure 3-28, except for the CO$_2$ saturated environment. For the CO$_2$ saturated environment, the localised corrosion pit population increases with an increase in applied stress which is comparable to the trend for the 12 mm x 4 mm wire, with a mean of 8.7 µm.

The increase in pit population with applied stress may again be attributed to strain enhanced or assisted dissolution of the carbon steel wire, however the lack of cracking would suggest that crack blunting had occurred or that the pits had not reached the threshold or critical pit depth for crack initiation. The mean pit depths for the aerated and H$_2$S environments are 8.7 µm and 31.4 µm respectively. The equivalent environment pit depths are comparable which is to be expected given the comparable corrosion rates, Figure 3-46, and chemical compositions of the two high strength carbon steels. The manganese and sulphur contents for the 12 x 4 mm and 12 x 7 mm high strength carbon steel tensile armour wires are comparable and therefore it may be suggested that the MnS inclusion population are similar but this requires further investigation.
The range and distribution of localised corrosion pit depth for both sets of high strength steel wire is indicative of the statistical nature of pits nucleating at different times throughout the corrosion fatigue test [96].

The observed corrosion mechanism for both the aerated and CO₂ saturated environments are general and localised corrosion. In hindsight, the analysis could have been repeated by applying a threshold pit depth below which depth it could be said that the observed corrosion mechanism is general corrosion and the change in surface depth from the original is due to surface roughness and not localised corrosion pitting.

The mechanisms by which localised corrosion occurs on the material are surface film rupture or breakdown and strain enhanced dissolution. The pitting in the CO₂ saturated environment is attributed to mesa type attack [62]. Carbon steel does not readily form a passive film in pH neutral seawater. Therefore work was carried out in order to establish the composition of the surface scales that will form on the carbon steel wires during corrosion fatigue testing.

LPR was used to establish the corrosion rate of the high strength carbon steel wires in two different environments and the post-test samples were used for GIXRD to establish the surface scale formation. As stated previously, the corrosion rate for the 12 mm x 4 mm and 12 mm x 7 mm high strength carbon steel wires in an aerated seawater environment are comparable, which is expected given the similar chemical composition, materials processing route and identical test environments. The corrosion rate for the CO₂ saturated seawater environment is an order of magnitude greater than for the aerated seawater environment. The higher corrosion rate and lower pH in the CO₂ saturated environment is demonstrated by the increase number of corrosion pits.

GIXRD was used to establish the composition of the surface scales formed on the steel wire in an aerated and CO₂ saturated seawater environment. For the 12 mm x 4 mm wire in the aerated seawater test, after 15 days immersion the sample exhibits an iron oxyhydroxide surface scale in the form of lepidocrocite. After 30 days immersion calcium carbonate has formed on the steel surface with some indications of magnesium hydroxide and the prior lepidocrocite. For the 12 mm x 7 mm wire in the aerated seawater test, after 15 days immersion calcium carbonate had formed on the steel surface. After 30 days immersion additional and more intense calcium carbonate peaks were observed in the GIXRD peak along with indications of the presence of magnesium hydroxide and iron oxyhydroxide.

The rate of scale formation may be indicated by the increase in peak intensities from the 15 day immersion test to the 30 day test.
Due to material availability GI XRD analysis was carried out on a 10 mm x 5 mm high strength carbon steel with a chemical composition as shown in Table 3-8. Calcium carbonate was observed on the surface of the steel wire in a CO₂ saturated environment. The presence of sodium chloride in the GI XRD results is from the seawater and is due to the minimal sample cleaning that was performed in order to conserve the integrity of the film.

The formation of calcium carbonate, magnesium hydroxide and iron oxyhydroxide has been discussed in the literature by [49,52,61,90]. The formation of calcium carbonate can be due to the cathodic reduction of oxygen that produces localised alkaline surface conditions [52] or the reduction of the carbonic species which reacts with calcium ions to produce calcium carbonate [49]. The literature [62,63,67] suggests the formation of iron carbonate in a CO₂ saturated environment, however these tend to be at higher temperatures, in deionised water with iron (Fe²⁺) ion saturation.

GIXRD was carried out for the corrosion fatigue test samples exposed to the H₂S/CO₂ seawater environment. It is well known that mackinawite will predominantly form in an aqueous environment containing H₂S [147–151]; however the GIXRD results show only the presence of iron. It is therefore thought and has been shown previously [150] that the film has either been removed post-test or that it is too thin for analysis.

There are various ways in which surface film break down may occur. These include localised surface film breakdown or rupture caused by changes in the interfacial forces acting on the film produced by the presence of Cl⁻ ions and breakdown whereby the formed scale reaches a critical thickness at which mechanical stresses due to the fatigue process will breakdown the surface film exposing bare metal to the aggressive solution [64,66,67,72,75,88,99].

The localised breakdown or rupture of the surface scale will expose the bare metal to the electrolyte. The corrosion scale acts as a large cathode and the bare metal a small anode thus generating localised corrosion. Localised corrosion preferentially occurs at inclusions, pearlitic regions and grain boundaries [102]. This is demonstrated by the ‘etched’ type surface shown in Figure 3-49 and Figure 3-50. High interfacial strains between the substrate and the inclusion causes the initiation of corrosion pits [73,99] and cracks at the base of the inclusion [108]. Surface film breakdown has been shown to slow down fatigue crack growth rates [100].

It is well known that corrosion pits can act as stress raisers and fatigue crack initiation sites [72,76,88,102,104,107]. It is said that materials spend most of their corrosion fatigue life in the time dependent corrosion stages of surface film breakdown, pit initiation, pit growth and
pit to crack transition [95,98,99]. This is true when we compare low applied stress ranges to high applied stress ranges as for a constant frequency they will be exposed to the corrosive environment for an increased period of time and are therefore more susceptible to the time dependent corrosion processes. The reduction in fatigue strength in a corrosive environment is more pronounced at lower stress. This is very much dependent upon the material-solution combination but holds true for the high strength carbon steel-seawater combination considered here. For high applied stress ranges a material will generally have a shorter fatigue life, therefore the effects of corrosion, because it is a time dependent process, may be minimal. This is due to the fact that the time the material spends in solution will be less and the process then becomes cycle dependent mechanical fatigue [81,86,105]. The synergistic effects of mechanical damage and corrosion will have an effect on crack length for the various stress ranges [82].

Pit growth rate can depend on factors such as the magnitude of applied stress and the localised solution chemistry within the pit [76,85,88,102]. This can lead to localised lowering of the pH within the corrosion pit due to hydrogen evolution [106,112].

Crack initiation from localised corrosion pits can depend upon the geometry of the pit and its interaction with the surrounding surface defects. Both of these will have an influence on the strain field around the pit and ultimately whether a fatigue crack will initiate from it. Corrosion pits can be many different shapes and sizes such as shallow, deep, sharp, blunt and it is this geometry that is key to whether a crack will initiate or not. Many different types of corrosion pit have been observed in the high strength steel wire such as hemispherical, elliptical, undercutting [99] and horizontal grain attack see Figure 3-41 to Figure 3-44.

In order for crack initiation to occur from localised corrosion pits, a critical depth must be reached whereby the strain field within and around the pit are favourable for initiation, they give the highest stress concentration [68,95,107]. The geometry of the pit required for crack initiation may vary depending on the localised strain field.

Once a crack initiates it will propagate, assuming the threshold stress intensity factor has been met or exceeded, through the microstructure along slip planes within the grains and along grain boundaries, which are termed trans-granular and inter-granular cracking respectively. Crack growth rates are said to be an order of magnitude faster down grain boundaries and slip planes than from grain to grain i.e. intergranular crack growth rates are faster than transgranular [81].
The cracks in the 12 mm x 4 mm carbon steel wire exhibit both transgranular and intergranular cracking, whereas the 12 mm x 7 mm carbon steel wire only exhibits transgranular cracking. Figure 3-36 shows an example of a straight transgranular crack and Figure 3-41 shows an example of intergranular cracking causing crack branching, bifurcation and coalescence of two cracks [68,72,76,110,111].

The cracks initiate on the surface of the normal plane of the tensile armour wire and propagate along the transverse plane. The microstructure of the 12 mm x 4 mm wire, Figure 3-8, in the transverse plane is anisotropic which is consistent with the crack path being intergranular and propagation along the martensite-pearlite grain boundaries. The degree of cold drawing influences the pearlite lamellar orientation with respect to alignment with the wire axis which is consistent with the bifurcated crack paths that have been observed. The microstructure of the 12 mm x 7 mm wire, Figure 3-9, in the transverse plane demonstrates an equiaxed grain structure which is consistent with the observed straight less tortuous crack path.

Work by Toribio et al. [33] has demonstrated that effects of cold drawing on the ductility of a high strength carbon steel wire. His work showed that as the degree of cold drawing increased so did the ductility of the material. It is thought that the two different wires are essentially manufactured from the same feed stock but with different degrees of cold drawing; the 12 mm x 4 mm wire having undergone a higher degree of cold drawing than the 12 mm x 7 mm wire. The degree of cold drawing and the microstructure of the cold drawn carbon steel wires would explain the ductile cracking and fracture behaviour demonstrated by the 12 mm x 4 mm wire as opposed to the more brittle fracture and transgranular cracking shown by the 12 mm x 7 mm wire [123]. The fracture surfaces for the 12 mm x 4 mm wire demonstrate a more ductile failure mechanism with evidence of micro cracking and cleavage facets compared to the 12 mm x 7 mm wire which shows a brittle type failure with a dimpled surface.

Corrosion fatigue testing of the 12 mm x 4 mm and 12 mm x 7 mm high strength carbon steel tensile armour wires was carried out at varying R-ratio between the two materials.

The 12 mm x 4 mm wire had constant R-ratio of 0.1 whereas the 12 mm x 7 mm wire had an R-ratio of 0.5 to 0.7 depending on the applied stress range. The R-ratio will determine the crack opening displacement and opening duration, both of which are important as they govern the amount of solution that may enter the crack and the solution refreshment [96]. The lower the R-ratio the longer the crack is open during a single fatigue cycle. This may explain the corrosion product down the crack faces and the degree of crack widening...
exhibited by the 12 mm x 4 mm wire and the lack of corrosion along the crack walls in the 12 mm x 7 mm wire.

The 12 mm x 4 mm wire has a higher nominal stress range but overall a lower mean stress, see Figure 3-35 and Figure 3-36. The 12 mm x 7 mm wire has a constant higher mean stress than the 12 mm x 4 mm wire with a lower nominal stress range but with a higher overall applied stress, see Figure 3-35, Figure 3-36 and Figure 3-37. The R-ratio and microstructure of the carbon steel wire influence the fatigue crack growth rate and crack path.

The overall crack path for both materials is parallel to the direction of the applied stress as reported by Dickson et al. [68]. The change in crack path direction due to branching and bifurcation may be explained by the principles of mixed mode fracture mechanics [110]. The high strength steel wire exhibits both Modes I and II corrosion fatigue characteristics. A reduction in crack growth rate due to crack branching or crack tip blunting can increase the corrosion fatigue life of a material [89].

The high strength wire is a cold drawn ferritic-pearlitic carbon steel which has a highly anisotropic microstructure with the pearlite lamellar preferentially orientated parallel to the wire axis. The orientation of pearlite causes intense crack branching and retardation of the fatigue crack. The two different microstructural phases with different stiffness affect the fatigue crack propagation path. The harder pearlite phase plays an important role in retarding crack growth rate by deflecting the crack path causing crack branching [111].

A crack may initiate and grow from a corrosion pit but because the crack grow rate is slow the crack walls are corroded and the crack is blunted and crack growth is arrested as shown in Figure 3-39 [88,100]. Crack widening may also occur, see Figure 3-38, due to solution within the crack causing dissolution of the crack walls creating corrosion product in the crack [82,84,88,89]. Again hydrogen evolution at the crack tip will cause localised changes in the pH within the crack.

For a multiple cracked sample, as considered here for the high strength carbon steel wires, there will be several different crack growth rates because in order for a crack to grow and propagate it will choose an energetically favourable microstructural route and therefore one crack may grow faster and in preference to another. The crack path will choose what may be termed as the path of least resistance for propagation.

Parkins [76] discusses the reduction in crack tip strain rate due to the increase in the number of cracks. This suggests that a crack initiates, propagates and then arrests because the stress intensity lowers and is below the threshold for crack growth. Angelova et al. [95] discusses
that the number of cracks varies depending on the loading conditions which is consistent with variation in R-ratio and microstructure observed for the high strength carbon steel tensile armour wires analysed in this project.

6.2 Residual Stress

Fatigue cracks initiate at the surface of the high strength steel wire, therefore consideration of surface residual stresses are important to the fatigue process. The cold drawing process used to manufacture wires will generate tensile surface residual stresses. During the cold drawing process the heat generated will cause an expansion of the surface of the wire with the subsequent cooling causing a contraction or shrinkage of the surface thus generating a tensile residual stress field [117,121,122,124]. It is well known that tensile residual stresses promote crack initiation and propagation due to their additive effects on the applied stress [114–116,120,123,124]. However, compressive surface residual stresses can be beneficial for fatigue resistance. The benefit in mitigating fatigue crack initiation is dependent upon the magnitude and depth of the residual stress and distribution. Deep compressive residual stresses will decrease fatigue crack growth rates [116,119,120,152].

The residual stress field development within the post-fatigue tested samples for the 12 mm x 4 mm and 12 mm x 7 mm wire was investigated with respect to the effects of applied stress and environment. Although residual stress is an artefact of a mechanical process, the different environments were compared to check if there were any effects from corrosion on the development of residual stress field, particularly at the surface. Through thickness measurements [122], using an established layer removal methodology for carbon steel [108,114], of the 12 mm x 4 mm wire were carried out. Surface residual stress measurements of all the stress ranges for the 12 mm x 4 mm and 12 mm x 7 mm samples were carried out. A two point square map was used and the average of the two points was taken to establish the residual stress. The fatigue samples had been tested using a four point bend displacement controlled method as discussed previously. The fatigue cracks have been shown to initiate on the side of the sample that is in tension during the test, therefore X-ray diffraction measurements were taken on this side of the sample. The centre of the sample between the two central four point bend loading points is the high stress region for the sample; therefore measurements were taken in this region.

The results for the 12 mm x 4 mm high strength carbon steel wire in the aerated environment, Figure 4-9, show that there is a dependency between the measured surface residual stress and the applied stress, with an increase in compressive surface residual stress with increasing applied stress. This is consistent with the fact that at low applied stresses the
surface condition including residual stress field plays an important role in crack initiation and propagation whereas at high stresses it has little influence on the fatigue life and initiation [108]. It should however be noted that all the surface measurements for the aerated environment exhibit a compressive residual stress field and are therefore not necessarily detrimental to the fatigue process and crack initiation. However, these results are post-fatigue testing and further work looking at the effects of residual stress on the fatigue process pre and post-test are discussed later. It is also known that in bending, the side of the sample that is in compression will have a tensile residual strain and the side that is in tension will exhibit a compressive residual stress [152].

The results for the 12 mm x 4 mm wire in the CO$_2$ saturated environment, Figure 4-10, demonstrate that the measured surface residual stress is independent of the applied stress. This may be due to the increase amount of localised surface corrosion which will act to remove residual stress fields by dissolution. Congleton et al. discuss the provision of a compressive residual stress surface layer is a good preventative measure for corrosion fatigue as long as the protective layer does not corrode away [88].

The results for the 12 mm x 7 mm high strength carbon steel wire are less clear. The results for the 12 mm x 7 mm wire in the aerated environment, Figure 4-12, show that for the lowest applied stress range there are tensile residual stresses on the sample surface. The other stress ranges on average exhibit compressive surface residual stresses. The results for the 12 mm x 7 mm wire in the CO$_2$ saturated environment, Figure 4-13, show scatter in the results with the measured surface residual stress being inconsistent with the increase in applied stress range. At the highest applied stress range the surface residual stress is tensile compared to a compressive residual stress at the lowest applied stress range. The results for the 12 mm x 7 mm wire in the 10 % H$_2$S/CO$_2$ balance environment, Figure 4-14, again demonstrate some scatter in the results but with an almost linear relationship between applied stress and residual stress.

Through thickness residual stress measurements have been carried out to establish how the residual stress field varies through the thickness of the high strength steel wire. The layer removal methodology involved electro polishing the high stress region between the four point bend loading points. Again measurements were carried out on the post-fatigue tested samples provided by Intertek. When carrying out through thickness residual stress measurements using a layer removal technique the redistribution or relaxation of surface residual stresses need to be considered, therefore the results have been corrected accordingly [126].
Through thickness residual stress measurements three different corrosion fatigue tested 12 mm x 4 mm wire samples were carried out. Also a thickness residual stress profile for the as received wire was carried out in order to establish a reference or baseline results that may be used for comparison purposes. The three test pieces that were analysed are an aerated sample fatigued at a stress range of 393 MPa and two CO$_2$ saturated samples fatigued at 333 MPa and 416 MPa stress ranges. There was no direct comparison of stress ranges between the two environments therefore two CO$_2$ samples were chosen as they span either side of the aerated stress range.

All of the profiles exhibited a Gaussian type distribution of residual stress with a compressive residual stress at the sample surface, a peak tensile strength at approximately one quarter of the sample thickness and a compressive stress at the centre of the sample. Lee et al. [124] demonstrated that residual stresses are compressive at the wire core, becoming increasingly tensile towards the wire surface. For the results of the both the surface and through thickness residual stress measurements this suggests that the fatigue process is only effecting the surface and just below the surface volumes of the material.

The third set of results explores the effect of the shakedown process on the development of surface residual stress fields due to the fatigue process. This work was carried out on a 10 mm x 5 mm high strength carbon steel wire with a similar chemical composition as shown in Table 3-8. Intertek, at the request of their clients, carry out a shakedown process which is deemed to remove the tensile surface residual stress fields prior to corrosion fatigue testing. The shakedown consists of carrying out 20,000 fatigue cycles in air, at the same applied stress as for the test, prior to the commencement of corrosion fatigue testing.

Surface residual stress measurements were taken prior to cyclic loading in the as received condition, after the 20,000 cycle shakedown and at sample failure. Fatigue tests were carried in air with two different stress ranges considered 400 MPa and 700 MPa with an R-ratio of 0.1. Residual stress measurements were taken at 5 mm spacing in the high stress region between the four point bend loading points.

For the samples tested at the high stress range, see Figure 4-16 to Figure 4-19, any tensile residual stresses are removed by the shakedown. Further fatigue cycling to sample failure has minimal effect in the overall development of the surface residual stress field. For the samples tested at the low stress range, see Figure 4-20 to Figure 4-22, the majority of the tensile residual stresses have been removed by the shakedown, however there is still a small amount of tensile residual stress in sample 1. Overall, due to the lower applied stress range, the magnitude of the stress reduction is has been reduced which would explain the existence
of the tensile residual stress in sample 1 after shakedown. However, it is thought that these would be removed within a short period of time during fatigue testing. Unfortunately due to equipment availability the samples could not be fatigued to failure and therefore these measurements could not be carried out.

The results demonstrate that the shakedown readily develops a compressive residual stress on the surface of the carbon steel wire at the high applied stress range of 700 MPa. This is mostly the case for the 400 MPa applied stress range; however care should be taken when considering the effects of shakedown on lower stress ranges in so far as it may not completely remove the tensile residual stress.

6.3 Surface Strain Mapping

The investigation of high strength carbon steel wire corrosion fatigue tested in various seawater environments demonstrated that fatigue cracks initiate from localised corrosion pits. A technique called digital image correlation has been used to explore the development of surface strains around corrosion pits due to an applied load. This work has established a novel approach to imaging a carbon steel surface in a corrosive environment.

A methodology for carrying out surface strain mapping of high strength carbon steel in a seawater environment has been established. A significant amount of sample preparation work was required in order to carry out the slow strain rate testing in aerated seawater using samples that exhibited localised corrosion pits. Dog-bone type tensile test samples machined from the high strength carbon steel wire have been used. The samples were cut using Electric Discharge Machining (EDM) in order to reduce the effect of surface residual stress as this technique induces a lower compressive surface residual stress. They were then ground and polished to a 1μm finish.

The next step involved growing artificial corrosion pits on the surface of the steel wire using chronoamperometry for the multiple pitted areas and chronopotentiometry with a microcell set up as developed by [70] for the single pits. As mentioned earlier carbon steel does not readily form a passive film in pH neutral seawater, therefore a solution in which carbon does passivate had to be used to grow artificial corrosion pits. A 0.1 M sodium carbonate-bicarbonate-chloride solution was used with a pH of 10.5. A potentiodynamic polarisation scan was carried out to establish the pitting potential, see Figure 5-2, which also demonstrates the effect the chloride ion has on shifting the pitting potential to a more negative value [56,77]. The pitting potential was then applied to three different samples for 30, 60 and 600 s, see Figure 5-3. The exposure time was important in order to strike a balance between pit population and size as the current density tends to stabilise with
corrosion pitting continually forming [56]. The optimum exposure time was 60 s as this gave pit sizes and population densities that were equivalent to those seen in the corrosion fatigue tested high strength steel wire. Work by Otero et al. [145] demonstrates the use of chronoamperometry for pit growth with images of similar pit morphology as the ones used in this project.

The samples were then immersed in seawater to grow an oxide corrosion scale on the surface. The features of this surface scale were then used for image correlation purposes. Using slow strain rate testing the development of surface strain around single pits was investigated along with the interaction between multiple pits. Two different diameters of single pit were tested, 400µm and 700µm. For the multiple pit arrangement, two different areas were used to grow artificial pits on, 2 mm$^2$ and 60 mm$^2$, which are named the small area and large area with pits respectively.

Once a sample was ready for testing it was placed in the SSRT DIC rig, see Figure 5-1, and testing commenced. The samples were progressively extended until failure with an image of the surface taken at each extension point. The complete set of images for a given test sample were then correlated using DaVis proprietary DIC software [91,92]. The applied stress on the sample will cause microstructural strain localisation that can be observed by the DaVis software. The black regions in my images are due to the fact that the subregion matching of successive images is not possible. This is due to the surface texture of the samples when they reach the higher strained region [130].

In order to establish the error in the imaging technique a rigid body displacement of the samples in air and in seawater was carried out, with 20 images taken for each test, and the average errors were found to be 0.05% and 0.01% respectively which is in line with previous work by Fonseca et al. [130].

The technique showed clear signs of localised surface strain around the corrosion pits. For the multiple pitted areas, as expected, the large pitted area demonstrated a greater range of surface strain than the small pitted area, which will be due to the increased number of stress raisers or corrosion pits. For the single pit the results show that there is a greater stress concentration around the small pit compared to the large one. This will be due to the geometry of the two pits; both have the same depth, but the difference in ratio of diameter to depth for a fixed sample thickness means that the 400 µm pit acts as a sharper stress raiser. The highest strain concentration was at the edge of the pit, parallel to the loading direction. Unlike the results for the pitted areas there is no sharp shift in localised strain with increasing load for the single pits. This would indicate the level of interaction that multiple
pits have with each other and the effect they have on surface strains and how they and other
types of stress raiser lead to premature failure of components.

This work has demonstrated that this technique can be applied to a material within a
seawater environment and that imaging of an unstable surface is possible. More realistic
corrosion fatigue tests should be carried out to explore the effects of surface film breakdown
and strain assisted dissolution, with particular focus on the geometry of the geometric
discontinuities.
Chapter 7 Conclusions
7. Conclusions

The microstructure, R-ratio, applied stress and environment affect the fatigue life and fracture behaviour of the high strength carbon steel tensile armour wire. The level of cold drawing influences the microstructure. The 12 mm x 4 mm has fine grain martensite-pearlite structure with anisotropic microstructure in the transverse plane. The 12 mm x 7 mm has larger grain martensite-pearlite structure with equiaxed microstructure in the transverse plane.

The 12 mm x 4 mm wire exhibits more ductile fracture behaviour with many secondary fatigue cracks compared to the 12 mm x 7 mm wire. The 12 mm x 4 mm wire exhibits transgranular and intergranular crack paths with branching, bifurcations and crack coalescence, whereas the 12 mm x 7 mm wire only exhibits transgranular crack paths. This is thought to be due to the differences in R-ratio and the increased level of cold drawing carried out on the 12 mm x 4 mm wire which has an anisotropic microstructure in the transverse plane compared to the 12 mm x 7 mm wire that has an equiaxed grain structure in the transverse plane.

Many of the corrosion fatigue cracks initiate from localised corrosion pits. The localised corrosion pits are thought to be initiated by the breakdown of the surface scale due to the fatigue process and are subsequently propagated by strain assisted dissolution of the localised area. A linear relationship has been shown between the increase in applied stress range and an increase the number of localised corrosion pits. Localised corrosion has also been shown to cause crack blunting.

The amount of localised corrosion pits in the CO$_2$ saturated environment, when compared to the aerated environment, is higher which may be explained by the higher corrosion rate, the lower pH and the morphology of the scale that forms. The pitting in the CO$_2$ saturated environment has been attributed to mesa type attack.

The surface scales formed on the high strength carbon steel wires in both an aerated and CO$_2$ saturated seawater environment contain calcium carbonate, magnesium hydroxide and iron oxyhydroxide.

Surface residual stress is an important consideration for fatigue crack initiation. The 12 mm x 4 mm wire shows some correlation between applied stress range and surface residual stress measurements. For the 12 mm x 4 mm wire corrosion fatigue tested in aerated seawater the surface residual stress becomes increasing compressive with an increase in
applied stress. For the 12 mm x 4 mm wire corrosion fatigue tested in CO$_2$ saturated seawater the surface residual stress appears to be independent of applied stress. However for the 12 mm x 7 mm carbon steel tensile armour wire there is no correlation between the applied stress range and the surface residual stress.

The differences in surface residual stress may be due to the differences in R-ratio, microstructure and level of cold drawing due to the Bauschinger effect.

Surface residual stress measurements have been used to explore the effects of the shakedown process on the high strength carbon steel tensile armour wires prior to corrosion fatigue testing. They show that at a high applied stress range the shakedown process readily develops a compressive residual stress on the surface of the carbon steel wire. This is mostly the case for the low applied stress range; however care should be taken when considering the effects of shakedown on a lower stress range in so far as it may not completely remove the tensile residual stress.

Through thickness residual stress profiles show a Gaussian type distribution of residual stress through the high strength carbon steel tensile armour wire. The results show a similar distribution of residual stress fields throughout the material independent of the applied stress range and environment.

The effect of corrosion pits on the development of localised strain fields using a surface strain mapping technique has been investigated. The research has shown that DIC may be applied for in-situ imaging of a corroding and dynamically deforming surface within a seawater environment. The technique demonstrated the establishment of localised surface strain around the corrosion pits during mechanical loading.

For the multiple pitted areas, the large pitted area demonstrated a greater range of surface strain than the small pitted area, which will be due to the increased number of stress raisers or corrosion pits. This was evident by the increase in localised strain from the contour maps and the statistical analysis.

For the single pits the results show that there is a greater stress concentration around the small pit compared to the large one. The highest strain concentration is at the edge of the pit, parallel to the loading direction. Unlike the results for the pitted areas there is no sharp shift in localised strain with increasing load for the single pits.
The shape and range of the histogram would indicate the level of interaction that multiple pits have with each other, the effect they have on surface strains and how they and other types of stress raiser lead to premature failure of components.
Chapter 8 Future Work
8. Future Work

The following section details some potential future work that would provide further insight into the corrosion fatigue behaviour of carbon steel tensile armour in the flexible riser annular space.

8.1 The effects of chloride and iron ion concentration on the corrosion fatigue behaviour of high strength steel tensile armour wire

Corrosion fatigue testing of high strength carbon steel wire in seawater and deionised water in order to simulate the annular space environment could be undertaken.

The effects of various gas mixtures including CO$_2$, H$_2$S/CO$_2$ and H$_2$S/N$_2$ could be explored. The annular space has a very low V/S ratio, therefore the effects of V/S ratio on the corrosion fatigue behaviour of the high strength carbon steel tensile armour could be explored.

A threshold V/S for corrosion fatigue testing could be established, below which value the iron confinement has no effect on the corrosion fatigue behaviour of the tensile armour wires. This would be a useful characteristic to establish for industrial testing purposes.

Post-test analysis would look at the effects of environment, in terms of solution, gas mixture and V/S ratio, on the corrosion fatigue cracking and pitting behaviour of the material.

Corrosion rate testing in simulated annular space environments would augment these findings.

8.2 Corrosion fatigue testing at elevated temperatures

As far as the author is aware there are very few, if any, publications on the corrosion fatigue behaviour of flexible riser tensile armour wires in simulated annular space environment at elevated temperatures.

Corrosion fatigue testing of the tensile armour in line with the parameters outlined in Section 8.1 above could be carried out in order to compare and contrast the differences in corrosion fatigue behaviour.

8.3 Corrosion fatigue testing at elevated pressures

A further variable to explore would be the effects of pressure on the corrosion fatigue failure mechanism for tensile armour wires in a simulated annular space environment. Similar to tests carried out in Section 8.1 but at elevated pressures. Again this is in order to compare and contrast results.
8.4 The use of electrochemical noise techniques for detecting or quantifying/measuring failure points

The use of electrochemical noise techniques could be explored in order to:

(a) Establish time to pit initiation
(b) Establish pit to crack transition
(c) Establish fatigue crack growth rates
(d) Establish corrosion fatigue failure points

The ability to establish FCGRs for high strength carbon steel tensile armour wires in a simulated annular space environment would be beneficial to the integrity management of flexible risers.

8.5 Exploring the development of plastic strain fields during the fatigue process using etching reagents

There are numerous etching reagents that can be used to explore plastic deformation within a material. These reagents could be used and developed to explore the effects the fatigue process has on the development of plastic deformation.
Appendices
1. Initial Sample Review of 12 mm x 4 mm High Strength Steel Wire

An initial review of the corrosion fatigue tested BZW 12 mm x 4 mm 190 ksi wires, provided by Intertek, was carried out to establish the secondary crack population density for each test run and individual test piece. An optical microscope was used to identify the location and size of the secondary crack within the individual test pieces.

The review was to enable the identification of the appropriate samples that were to be studied in further detail using optical microscopy and SEM.

In Figures 3-1 to 3-9, the fracture crack and the secondary cracks have been identified for each test piece. They can be distinguished as follows:

- Fracture
- Secondary Cracks / Arrested Cracks

![Figure A1-1: Run 1A - Mean Stress = 428 MPa; Stress Range = 700 MPa](image)
Figure A1-2: Run 2A - Mean Stress = 244 MPa; Stress Range = 400 MPa

Figure A1-3: Run 3A - Mean Stress = 153 MPa; Stress Range = 250 MPa

Figure A1-4: Run 4A - Mean Stress = 107 MPa; Stress Range = 175 MPa
Figure A1-5: Run 5A - Mean Stress = 183 MPa; Stress Range = 300 MPa

Figure A1-6: Run 1C - Mean Stress = 428 MPa; Stress Range = 700 MPa

Figure A1-7: Run 2C - Mean Stress = 367 MPa; Stress Range = 600 MPa
Figure A1-8: Run 3C - Mean Stress = 275 MPa; Stress Range = 450 MPa

Figure A1-9: Run 4C - Mean Stress = 214 MPa; Stress Range = 350 MPa

The above figures demonstrate an increase in the number of secondary cracks as the applied stress decreases. This is more marked for the CO₂ saturated seawater environment, which has a far higher secondary crack population density as the applied stress decreases.
2. Chemical Composition Test Certificate

![Chemical Composition Test Certificate Image]

**Figure A2-1: Chemical composition certificate**
3. Preparation of Substitute Ocean Water

The synthetic seawater or substitute ocean water used in the experiments was prepared generally inline with the American Society for Testing and Materials standard D1141-98 (Reapproved 2003) entitled Standard Practice for the Preparation of Substitute Ocean Water [54].

First of all, the standard requires the preparation of three stock solutions. Stock solution No. 3 was not used in the experiments. This is because Intertek, in their standard testing practice as set out in their reports [135], [136], [137], [134], state that they use synthetic seawater without the heavy metal salts.

Each stock solution requires the dilution of a prescribed amount of salts to a total volume, for each stock solution, of 7.0 L. However, this volume is far in excess of the requirements of the experiments, therefore, 1.0 L of each stock solution was prepared. Table A3-1 and Table A3-2 show the salts and quantities dissolved into each stock solution.

Table A3-1: Stock Solution No. 1

<table>
<thead>
<tr>
<th>Salt</th>
<th>Quantity (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium Chloride MgCl\textsubscript{2}.6H\textsubscript{2}O</td>
<td>555.6</td>
</tr>
<tr>
<td>Calcium Chloride CaCl\textsubscript{2} anhydrous</td>
<td>57.9 (76.75)</td>
</tr>
<tr>
<td>Strontium Chloride SrCl\textsubscript{2}.6H\textsubscript{2}O</td>
<td>2.1</td>
</tr>
</tbody>
</table>

The calcium chloride available from stores was not anhydrous and was in fact calcium chloride dihydrate (CaCl\textsubscript{2}.2H\textsubscript{2}O). Therefore the amount of salt required was increased to reflect this and is shown in brackets in Table A3-1.

To make each stock solution, first of all, the salts are weighed out on a set of electronic scales, which has accuracy to 2 decimal places. The total amount of salt, for that particular stock solution is poured into a 2 L beaker. Using a volumetric flask, 1 L of deionised water is measured out. This is then poured into the 2 L beaker. The beaker is placed on a magnetic stirrer hotplate and the solution is heated and stirred until all the salt is dissolved. The stock solution is then poured into a volumetric flask, labelled and stored.

Once the stock solutions have been prepared the substitute ocean water solution can be prepared. To prepare 10.0 L of substitute ocean water measure out 1 L of deionised water using a volumetric flask and pour into a 2L beaker. Place the beaker on a magnetic stirrer
hotplate. Weigh out 245.34 g of sodium chloride (NaCl) and 40.94 g of anhydrous sodium sulfate (Na₂SO₄). Pour both of these salts into the 2 L beaker. Stir and heat until dissolved and then pour into a suitable container that will hold 10 L of solution. Measure out sufficient deionised water to dilute this solution up to 9 L in total, making a note of each addition in order to keep track of where you are. To this add 200 mL of stock solution No. 1 and then 100 mL of stock solution No. 2. Both of which should be measured out accurately using a volumetric flask. The solution will then require 700 mL of deionised water to make up 10 L of substitute ocean water. The 10 L container is then labelled and stored.

**Table A3-2: Stock Solution No. 2**

<table>
<thead>
<tr>
<th>Salt</th>
<th>Quantity (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium Chloride</td>
<td>69.5</td>
</tr>
<tr>
<td>KCl</td>
<td></td>
</tr>
<tr>
<td>Sodium Hydrogen</td>
<td>20.1</td>
</tr>
<tr>
<td>Carbonate NaHCO₃</td>
<td></td>
</tr>
<tr>
<td>Potassium Bromide</td>
<td>10.0</td>
</tr>
<tr>
<td>KBr</td>
<td></td>
</tr>
<tr>
<td>Boric Acid H₃BO₃</td>
<td>2.7</td>
</tr>
<tr>
<td>Sodium Flouride</td>
<td>0.3</td>
</tr>
<tr>
<td>NaF</td>
<td></td>
</tr>
</tbody>
</table>

**Table A3-3: Chemical composition of substitute ocean water**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>24.53</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>5.20</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>4.09</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>1.16</td>
</tr>
<tr>
<td>KCl</td>
<td>0.695</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.201</td>
</tr>
<tr>
<td>KBr</td>
<td>0.101</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>0.027</td>
</tr>
<tr>
<td>SrCl₂</td>
<td>0.025</td>
</tr>
<tr>
<td>NaF</td>
<td>0.003</td>
</tr>
</tbody>
</table>

The chemical composition of substitute ocean water is as per Table A3-3, reproduced from [54]. The standard requires that the pH of the solution be adjusted to 8.2 using 0.1 N sodium hydroxide (NaOH) solution immediately prior to use. In this case, normality and molarity are equivalent. Therefore to make 200 mL of 0.1N NaOH, weigh out 0.8 g of NaOH and dissolve in 200 mL of deionised water. Pour into a volumetric
flask, label and store. When an amount of the solution is required for an experiment, the pH is adjusted using a few millilitres of the NaOH solution.
4. **General Arrangement and Detail Drawings of Slow Strain Rate Test Rig**

![Diagram of Slow Strain Rate Test Rig](image)

**Figure A4-1**: Slow strain rate test chamber general arrangement drawing
Figure A4-2: Slow strain rate test chamber detail drawing
Figure A4-3: Slow strain rate test chamber lid detail drawing
5. Detailed Drawing of Slow Strain Rate Test Sample Grips

Figure A5-1: Detailed drawing of slow strain rate test sample grips
6. Detailed Drawings of Slow Strain Rate Test Samples

Figure A6-1: Slow strain rate test sample drawings for two different high strength steel wires
(a) 12 mm x 4 mm wire, (b) 10 mm x 5 mm wire
References


[58] Waanders FB, Vorster SW, Olivier GJ. 2002;239.


