Effect of Platinum Group Metal (PGM) additions on the stress corrosion cracking resistance of type 304 stainless steel in pressurised water reactors

A thesis submitted to the University of Manchester for the degree of Doctor of Philosophy (PhD) in the faculty of Engineering and Physical Sciences

2010

Ouarda Sophia Necib
School of Materials
LIST OF CONTENTS

1 Introduction ......................................................................................................................... 34

2 Literature Review ................................................................................................................ 38

2.1 Introduction to light water reactors .................................................................................... 38

2.1.1 Application and generalities of PWRs and BWRs ............................................................ 38

2.1.2 The primary circuit in PWRs and BWRs ........................................................................... 38

2.1.2.1 Introduction .................................................................................................................. 38

2.1.2.2 Materials in the primary circuit of PWRs and BWRs ..................................................... 40

2.1.2.3 Operating conditions in the primary circuit of PWRs and BWRs .................................. 40

2.1.2.3.1 Temperature and pressure ......................................................................................... 40

2.1.2.3.2 Water chemistry in PWRs and BWRs ......................................................................... 40

2.2 Materials: Type 304 stainless steel ..................................................................................... 41

2.2.1 Metallurgy ....................................................................................................................... 41

2.2.1.1 Microstructure ............................................................................................................. 41

2.2.1.2 Composition ............................................................................................................... 43


2.2.2 Tensile properties .............................................................................................................. 44
2.2.3 Heat Treatment of type 304 SS ......................................................................................... 45
2.2.4 Oxide formed on type 304 SS under PWR conditions ................................................... 45

2.3 Stress Corrosion cracking .................................................................................................... 47
2.3.1 What is it? ....................................................................................................................... 47
2.3.2 Factors of SCC ............................................................................................................... 48
  2.3.2.1 Introduction ............................................................................................................. 48
  2.3.2.2 Stress ..................................................................................................................... 48
  2.3.2.3 Materials susceptibility to SCC in PWRs conditions ............................................... 50
    2.3.2.3.1 Grain size and grain orientation ......................................................................... 50
    2.3.2.3.2 Sensitisation .................................................................................................... 51
    2.3.2.3.3 Delta ferrite ..................................................................................................... 53
    2.3.2.3.4 Cold work ....................................................................................................... 54
    2.3.2.3.5 Pitting ............................................................................................................. 54
    2.3.2.3.6 Crevice corrosion ............................................................................................ 56
    2.3.2.3.7 Oxide of type 304 SS in PWRs conditions ....................................................... 56
  2.3.2.4 Environmental factors ............................................................................................. 57
    2.3.2.4.1 Water chemistry in BWRs and PWRs ................................................................. 57
    2.3.2.4.2 Electrochemical corrosion potential (ECP) in hydrogen water chemistry (HWC) ... 58
    2.3.2.4.3 Effect of hydrogen and oxygen concentrations .................................................... 61
    2.3.2.4.4 Effect of radiolytic species on ECP ................................................................. 62
    2.3.2.4.5 Effect of anionic impurities ........................................................................... 63
    2.3.2.4.6 Temperature .................................................................................................... 63
    2.3.2.4.7 Flow rate ........................................................................................................ 66
  2.3.3 Phenomenology of cracking .......................................................................................... 68
  2.3.4 Crack initiation .............................................................................................................. 68
  2.3.5 Crack propagation ......................................................................................................... 68
    2.3.5.1 Dissolution models ............................................................................................... 68
    2.3.5.2 Corrosion Tunnel Model ..................................................................................... 70
    2.3.5.3 Film induced cleavage model ............................................................................... 70
2.3.5.4 Adsorption induced brittle fracture ........................................................... ........................................ 71
2.3.5.5 Hydrogen embrittlement ........................................................................ 71
2.3.5.6 Internal oxidation ............................................................................. 73
2.3.6 SCC of alloy 600 in PWRs ........................................................................ 73
2.3.6.1 Introduction ....................................................................................... 73
2.3.6.2 SCC mechanism of Alloy 600 in PWRs ........................................................ 74
2.3.6.3 Parameters affecting SCC susceptibility of Alloy 600 in PWRs ......................... 74
2.3.7 SCC testing of type 304 SS ........................................................................ 76
2.3.7.1 Environments to simulate intergranular stress corrosion cracking (IGSCC) ....... 76
2.3.7.2 The different mechanical tests ................................................................ 78
  2.3.7.2.1 Tests on statically loaded smooth samples .............................................. 78
  2.3.7.2.2 Tests on statically loaded pre-cracked samples .......................................... 78
  2.3.7.2.3 Tests on strained samples ........................................................................... 82
2.4 Platinum Group Metals (PGM) ........................................................................ 84
  2.4.1 Introduction to PGM additions ................................................................. 84
  2.4.2 Techniques for PGM surface enrichment .................................................. 84
  2.4.3 Introduction to noble metal chemical addition (NMCA) ............................... 85
  2.4.4 Introduction to PGM-doped titanium alloys ............................................... 86
  2.4.5 Effect of PGM in acid media ...................................................................... 87
    2.4.5.1 General corrosion ............................................................................... 87
    2.4.5.2 Effect of PGM on pitting ....................................................................... 93
    2.4.5.3 Hydrogen embrittlement ....................................................................... 94
    2.4.5.4 Effect of PGM on stress corrosion cracking behaviour .............................. 95
    2.4.5.5 Simultaneous effect of PGMs and alloying elements ............................... 96
    2.4.5.6 Film characterisation ......................................................................... 97
  2.4.6 Effect of PGM in high temperature water ................................................... 99
    2.4.6.1 Electrochemistry ............................................................................... 99
    2.4.6.2 Effect of PGMs on the oxide in high temperature water ............................ 103
    2.4.6.3 Effect of PGMs on cracking behaviour ................................................ 104
  2.4.7 Effect on mechanical properties ............................................................... 105
3. Materials characterisation ................................................................................................................................. 107

3.1 Introduction .......................................................................................................................................................... 107

3.2 Experimental procedures ...................................................................................................................................... 107

  3.2.1 Composition .................................................................................................................................................. 107
  3.2.2 Material history ............................................................................................................................................. 107
  3.2.3 Heat treatment .............................................................................................................................................. 108
    3.2.3.1 Solution annealing ................................................................................................................................. 108
    3.2.3.2 Sensitisation .......................................................................................................................................... 108
  3.2.4 Metallographic preparation .......................................................................................................................... 108
    3.2.4.1 Microstructure ..................................................................................................................................... 108
    3.2.4.2 Grain size measurements ..................................................................................................................... 109
  3.2.5 Tensile properties ....................................................................................................................................... 109
  3.2.6 Hardness at room temperature .................................................................................................................... 110

3.3 Results .................................................................................................................................................................. 112

  3.3.1 Composition .................................................................................................................................................. 112
  3.3.2 Microstructures ........................................................................................................................................... 112
  3.3.3 Grain size measurements results ................................................................................................................. 119
  3.3.4 Tensile properties results ........................................................................................................................... 119
  3.3.5 Hardness results ........................................................................................................................................... 121

3.4 Discussion ............................................................................................................................................................ 122

3.5 Summary .............................................................................................................................................................. 125

4 Crack initiation in simulated PWR environments .............................................................................................. 128

4.1 Introduction .......................................................................................................................................................... 128

4.2 Experimental procedures ...................................................................................................................................... 128

  4.2.1 Surface preparation and U-bend samples .................................................................................................... 128
  4.2.2 Operating procedure ................................................................................................................................... 130
4.3 Results............................................................................................................................ 132
   4.3.1 Conditions of cracking.......................................................................................... 133
   4.3.2 Surface analysis .................................................................................................... 134
      4.3.2.1 Macrographs ................................................................................................. 134
      4.3.2.2 Micrographs .................................................................................................. 136
         4.3.2.2.1 Legs ........................................................................................................... 137
         4.3.2.2.2 Surface under high tension ........................................................................ 138
         4.3.2.2.3 Surface under high tension ........................................................................ 139
   4.3.3 Cracking and PGM effects on crack initiation............................................................ 142
   4.3.4 Discussion.............................................................................................................. 146
      4.3.4.1 Cracking conditions ....................................................................................... 146
         4.3.4.1.1 Stress distribution ....................................................................................... 146
         4.3.4.1.2 Environmental conditions for crack initiation ............................................. 147
      4.3.4.2 Cracking features and PGM effect on crack initiation ....................................... 149
         4.3.4.2.1 Oxide on surface ......................................................................................... 149
         4.3.4.2.2 PGM effects on crack initiation .................................................................. 150
   4.3.5 Summary................................................................................................................. 150

5. Fracture mechanics approach to stress corrosion crack propagation: fatigue

precracking ...................................................................................................................... 153

5.1 Introduction ................................................................................................................. 153

5.2 Experimental procedure .............................................................................................. 153
   5.2.1 Material and heat treatment ................................................................................ 153
   5.2.2 Tensile properties and hardness .......................................................................... 154
   5.2.3 Sample design ...................................................................................................... 155
   5.2.4 Fatigue precrack in air ....................................................................................... 156

5.3 Results............................................................................................................................ 158
   5.3.1 Numerical approach of the key mechanical parameters under fatigue rotation ........ 158
   5.3.2 General results of the fatigue precrack study ......................................................... 160
5.3.3 Direct current potential drop (DCPD) method and precrack measurement using fractography ................................................................. 164

5.4 Discussion ...................................................................................................................... 168
   5.4.1 Fractography ........................................................................................................ 168
   5.4.2 Precrack length .................................................................................................. 169
   5.4.3 Precrack monitoring ......................................................................................... 169
   5.4.4 Number of cycles ............................................................................................ 170
   5.4.5 Summary .......................................................................................................... 171

6. Stress corrosion cracking propagation study ................................................. 173

6.1 Introduction ............................................................................................................. 173

6.2 Experimental procedure ......................................................................................... 173
   6.2.1 Material and heat treatment ........................................................................ 173
   6.2.2 SCC propagation experiment in potassium tetrathionate (0.01 M K₂S₂O₇, pH = 1.5) at room temperature .......................................................... 174

6.3 Results ....................................................................................................................... 176
   6.3.1 General results ............................................................................................ 176
   6.3.2 Time to failure ............................................................................................ 181
   6.3.3 Fractography ............................................................................................... 183
      6.3.3.1 Fractography of the standard alloy FP-304MC ........................................ 185
      6.3.3.2 Fractography of the medium carbon Pd doped alloys ........................ 187
      6.3.3.3 Fractography of the medium carbon Ru doped alloys ...................... 189
      6.3.3.4 Fractography of the high carbon Pd doped alloys FP-Pd3HC ............ 191
      6.3.3.5 Fractography of the high carbon Ru doped alloys FP-Ru3HC ............ 192
   6.3.4 Crack growth rate ....................................................................................... 193
   6.3.5 Crack depth ................................................................................................. 194
      6.3.5.1 Micrographs revealing the crack depth of the standard alloy .......... 196
      6.3.5.2 Micrographs revealing the crack depth of medium carbon Pd doped alloys .. 196
      6.3.5.3 Micrographs revealing the crack depth of medium carbon Ru doped alloys 197
6.4 Discussion ...................................................................................................................... 199
  6.4.1 Effect of (PGM) additions on time to failure ................................................................. 199
  6.4.2 Effect of (PGM) on crack depth and crack growth rate ................................................. 201

6.5 Summary ....................................................................................................................... 202

7. Electrochemical experiments in lithiated and borated solution ........................... 205

  7.1 Introduction .................................................................................................................. 205

  7.2 Experimental procedure .............................................................................................. 205
    7.2.1 Materials and heat treatment ..................................................................................... 205
    7.2.2 Electrode preparation ............................................................................................... 205
    7.2.3 Electrolyte preparation ............................................................................................. 206
      7.2.3.1 Mass calculations ................................................................................................. 206
      7.2.3.2 Summary of the electrolyte preparation ............................................................... 206
    7.2.4 Operating conditions ............................................................................................... 206
      7.2.4.1 Temperature ....................................................................................................... 206
      7.2.4.2 Atmosphere ....................................................................................................... 207
      7.2.4.3 Set up of the experiments .................................................................................... 207

  7.3 Results ............................................................................................................................ 208
    7.3.1 Open circuit potential in a solution of (1000 ppm Li + 2 ppm Li) in aerated conditions .... 208
    7.3.2 Open circuit potential in a solution of (1000 ppm B + 2 ppm Li) under deaerated conditions with nitrogen ................................................................................................................................. 211
    7.3.3 Potentiodynamic scan in a solution of (1000 ppm B + 2 ppm Li) under aerated conditions . 214
    7.3.4 Potentiodynamic scan in a solution of (1000 ppm B + 2 ppm Li) under deaerated conditions (with nitrogen) ................................................................................................................................. 216
    7.3.5 Effect of temperature and dissolved oxygen in a solution of (1000 ppm B + 2 ppm Li) ....... 219
      7.3.5.1 Effect of temperature and oxygen on the open circuit potential (OCP) ....................... 219
7.3.5.2 Effect of oxygen and temperature on the electrochemical behaviour in a solution of (1000 ppm B + 2 ppm Li) ........................................................................................................................................ 220

7.3.6 Effect of the Ru content under aerated and deaerated conditions ............................................................................................................................. 221

7.3.6.1 Effect of the Ru content on the OCP under aerated conditions ............................................................................................................................. 221

7.3.6.2 Effect of the Ru content on the electrochemical behaviour under aerated and deaerated (with nitrogen) conditions ...................................................................................................................................... 222

7.3.7 Open circuit potential in a solution of (1000 ppm B + 2 ppm Li) under hydrogenated conditions ............................................................................................................................................... 224

7.3.8 Potentiodynamic scan in a solution of (1000 ppm B + 2 ppm Li) under hydrogenated conditions .................................................................................................................................................. 226

7.3.9 Effect of the Ru content in a solution of (1000 ppm B + 2 ppm Li) under hydrogenated conditions at 25°C ........................................................................................................................................... 227

7.3.9.1 Effect of the Ru content on the OCP of the standard alloy 304MC under hydrogenated conditions at 25°C.................................................................................................................................................... 227

7.3.9.2 Effect of the Ru content on the potentiodynamic scan of 304MC in a solution of (1000 ppm B + 2 ppm Li) under hydrogenated conditions ........................................................................................................................................ 228

7.10 Discussion .................................................................................................................................................................................................................. 229

7.10.1 Effect of PGM additions on the open circuit potential of a sensitised type 304 SS (304MC) .................................................................................................................................................. 230

7.10.2 Effect of PGM on the electrochemical behaviour of the standard alloy 304MC in a solution of (1000 ppm B + 2 ppm Li) ......................................................................................................................................... 234

7.11 Summary of the PGM effect in (1000 ppm B + 2 ppm Li)................................................................................................................................................................. 240

8. Electrochemical experiments simulating IGSCC environment ............................................................................................................................................... 242

8.1 Introduction .................................................................................................................................................................................................................. 242

8.2 Experimental procedure ........................................................................................................................................................................................................ 242

8.2.1 Materials tested ........................................................................................................................................................................................................... 242

8.2.2 Preparation of the electrolyte ........................................................................................................................................................................................................ 243

8.2.3 Temperature ........................................................................................................................................................................................................... 243
8.3 Results .......................................................................................................................... 244
  8.3.1 Open circuit potential (OCP) in aerated and deaerated (with nitrogen) conditions ........ 244
  8.3.2 Potentiodynamic scan in aerated conditions .............................................................. 247
    8.3.2.1 Potentiodynamic scan in aerated conditions at a scan rate of 0.5 mV.s$^{-1}$ ............ 247
    8.3.2.2 Potentiodynamic scan in aerated conditions at 5 mV.s$^{-1}$ ............................... 249
  8.3.3 Potentiodynamic scan in deaerated conditions with nitrogen .................................. 250
    8.3.3.1 Potentiodynamic scan in deaerated conditions at 0.5 mV.s$^{-1}$ ......................... 250
    8.3.3.2 Potentiodynamic scan in deaerated conditions at 5 mV.s$^{-1}$ ............................ 252
  8.3.4 Surface characterisation in potassium tetrathionate ............................................... 253

8.4 Discussions .................................................................................................................. 255
  8.4.1 Effect of the experimental parameters on the electrochemical response ................. 256
  8.4.2 Effect of (PGM) on the open circuit potential of the standard alloy 304MC in the sensitised conditions .......................................................... 258
  8.4.3 Effect of (PGM) on the anodic dissolution current density of the standard alloy 304MC in the sensitised conditions ................................................... 261
  8.4.4 Effect of PGM additions on the potentiodynamic scan of the standard alloy 304MC ........ 262

9 Electrochemistry in high temperature water ................................................................. 266

9.1 Introduction .................................................................................................................. 266

9.2 Experimental procedure .............................................................................................. 266
  9.2.1 Material tested ........................................................................................................ 266
  9.2.2 Sample preparation ................................................................................................ 266
  9.2.3 Operating conditions .............................................................................................. 267
    9.2.3.1 Autoclave ......................................................................................................... 267
    9.2.3.2 Temperature ..................................................................................................... 267
    9.2.3.3 Pressure ........................................................................................................... 267
LIST OF TABLES
Table 1 Composition of type 304 SS [16]................................................................. 44
Table 2 Tensile properties of standard type 304 SS [16]........................................ 44
Table 3 Table of the composition of titanium and titanium alloys [16, 112]......... 87
Table 4 Composition of the alloys........................................................................... 112
Table 5 Grain size measurements of the main alloys investigated...................... 119
Table 6 Mechanical properties of the alloys at 300°C........................................ 121
Table 7 Hardness measurements of the main alloys investigated......................... 121
Table 8 Table presenting the δ-ferrite present in the main alloys in the as-received
    condition (solution annealed) [140]...................................................................... 123
Table 9 Operating conditions in the autoclave....................................................... 132
Table 10 Table presenting the cracking results of the autoclave results ............. 134
Table 11 Composition of the type 304 SS used in this fatigue study [146]............. 154
Table 12 Tensile properties and hardness of the type 304 SS used in the fatigue study
    [146]...................................................................................................................... 155
Table 13 Dimensions of the CCB samples FP ......................................................... 156
Table 14 Table summarising the fatigue precracking results............................... 162
Table 15 Table presenting the total precrack (notch+ fatigue precrack) length for each
    sample.................................................................................................................. 163
Table 16 Circumferential cracked bar (CCB) specimen dimensions..................... 175
Table 17 Table giving the values of the geometric f for a given ratio $a_{tot}/R$ [154]..... 177
Table 18 Table summarising the parameters to calculate $K_I$ at the start of the SCC
    propagation.............................................................................................................. 179
Table 19 Summary of the experimental parameters for the stress corrosion cracking propagation
........................................................................................................................................ 180
Table 20 Table summarising the average SCC crack growth rate ........................................... 194
Table 21 Maximum crack depth measured after cross sectioning the sample in the longitudinal direction ...................................................................................................................... 195
Table 22 Table summarising the OCP values under different environmental conditions
................................................................................................................................................ 260

LIST OF FIGURES

Figure 1 Schematic of a representative PWR nuclear power station; Heat generated in the core (by fission of U$^{235}$) is transferred to the primary circuit (pressurised water). Heat from the primary circuit evaporates water in the secondary circuit. The turbine generator set converts mechanical power provided by steam into electricity. A=reactor core, B=control rods, C=reactor vessel, D=pressuriser, E=steam generator, F=primary pump, G=containment, H=turbine, I=generator, J=condenser, K=extraction and feedwater pump, L=reheater, M=river (or sea) water [14]........ 39
Figure 2 Schematic diagrams of two boiling cycles used in boiling water reactors (BWRs) supplying same turbine requirements : (a) direct boiling cycle; (b) boiling cycle using pressurised water coolant and heat exchanger [15]............... 39
Figure 3 Stainless steel phase diagram at 900°C [30] ................................................................. 42
Figure 4 Schaeffler diagram predicting the structure especially in austenitic welds as a function of the Cr and Ni equivalences [31]................................................................. 43
Figure 5 Pourbaix diagrams calculated using thermodynamics computation code (HSC chemistry). The potential E has been measured using a standard hydrogen electrode (SHE) [33, 34]........................................................................................................... 45
Figure 6 High magnification SEM photographs of 304 SS after exposure to high temperature hydrogenated ammoniated water: (a) after 1000 hours; (b) after 2000 hours; (c) after 5000 hours and (d) after 10000 hours [35].

Figure 7 Diagram illustrating the SCC concept: interaction of three parameters (stress, material and environment) [39].

Figure 8 Schematic representation of log stress versus log time to failure [40].

Figure 9 Schematic representation of the crack growth velocity as a function of the stress intensity factor K [40].

Figure 10 Time temperature precipitation diagram for M_{23}C_{6} in 304 type austenitic stainless steel containing 0.06 wt% C [24].

Figure 11 Schematic of the sensitisation phenomenon [24].

Figure 12 Variations of delta ferrite content versus dissolution time. Rapid dissolution at the early stage and diffusion controlled dissolution at the normal stage [28].

Figure 13 Schematic of the pitting phenomenon.

Figure 14 Schematic diagram showing a potentiodynamic scan with the susceptible regions for SCC indicated [60].

Figure 15 SCC crack growth rate vs. corrosion potential for stainless steel tested at 288°C in high-purity water containing 2000 ppb O₂ and 95-3000 ppb H₂ [18].

Figure 16 Schematic of the crack tip when oxidants are present: 1) Oxidation of metal; 2) Hydrogen evolution; 3) Hydrogen oxidation 4) Oxygen reduction [18].

Figure 17 Corrosion potential versus dissolved oxygen concentration for carbon steel in high temperature water [21].

Figure 18 Effect of dissolved hydrogen concentration on the oxide film thickness of type 316SS. Measurements performed using Auger Electron Spectroscopy (AES) [33].
Figure 19 Stress strain and current density strain from a slow strain rate tensile (SSRT) test of a type 304 SS in a dilute Na$_2$SO$_4$ solution at four temperatures using an initial strain rate of ................................................................. 65

Figure 20 Effect of temperature on total time to fracture (Tf), crack initiation time (Ti) ........................................................................................................................................... 65

Figure 21 Effect of temperature on mean crack propagation rate expressed as Arrhenius relation [19] ........................................................................................................................................... 66

Figure 22 Effect of a change in the stirring rate on the crack opening displacement (COD) vs. time for a sensitised type 304 SS CT specimen in 15 ppm NaCl + 150 ppb O$_2$ solution at 250°C [75] ........................................................................................................................................... 67

Figure 23 Effect of a change in stirring rate on the crack opening displacement (COD) vs. time for a sensitised type 304 SS CT specimen in 25 ppm NaCl + 70 ppb O$_2$ solution at 250°C [75] ........................................................................................................................................... 67

Figure 24 Schematic representation of crack propagation by the film rupture model [41] ........................................................................................................................................... 69

Figure 25 Corrosion tunnel models: (a) schematic of tunnel model showing the initiation of crack by the formation of corrosion tunnel at slip steps and ductile deformation and fracture of the remaining ligaments; (b) Schematic diagram of the tunnel mechanism of SCC and flat slot formation[41] ........................................................................................................................................... 70

Figure 26 Schematic representation of the corrosion enhanced-plasticity mechanism [78] ........................................................................................................................................... 72

Figure 27 Main domains of IGA and IGSCC of Alloy 600 in aqueous solutions at 290°C / 360°C [87] ........................................................................................................................................... 76

Figure 28 Classification of pre-cracked samples for SCC testing [41] ........................................................................................................................................... 81
Figure 29 Fracture surface of a CCB cast iron specimen after fatigue precracking, SCC and ductile failure [99]......................................................................................................................... 82
Figure 30 Schematic of a slow strain rate tensile (SSRT) test apparatus [41]............. 83
Figure 31 Schematic diagram of the principle of cathodic modification; the dashed blue line represents the standard alloy and the red line represents the cathodically modified alloy [111]......................................................................................................................... 88
Figure 32 Potentiodynamic curves for a series of duplex stainless steel in 1mol.dm$^{-3}$ $\text{H}_2\text{SO}_4$ at 25°C: (a) 0% Ru; (b) 0.14% Ru; (c) 0.22% Ru, (d) 0.29% Ru [115] ...... 91
Figure 33 Potentiodynamic curves for a series of duplex stainless steel in 1 mol.dm$^{-3}$ $\text{HCl}$ at 25°C: (a) 0% Ru; (b) 0.14% Ru; (c) 0.22% Ru, (d) 0.29% Ru [115]........ 91
Figure 34 Evans diagram showing how alloying titanium with PGMs achieves passivation in reducing acids via cathodic depolarisation [117]...................... 92
Figure 35 Effect of the palladium content on the titanium corrosion rate in boiling hydrochloric acid solution [112]............................................................... 92
Figure 36 Corrosion rate profile for Ti and Ti-alloys containing 0.1 wt% Pd or 0.1wt% Ru in boiling hydrochloric acid solutions [112].................................................... 93
Figure 37 Effect of chloride concentration on the pitting (Epit) and repassivation potentials (Erp) for standard Ti grade 2 and Pd doped Ti grade 7 in deaerated solution at 95°C [119]........................................................................................................ 94
Figure 38 Summary of the effect of alloying additions on the polarisation characteristics of Fe-Cr stainless steels in sulphuric acid [2].............................................. 97
Figure 39 Schematic diagram showing the electrochemical corrosion potential (ECP) against molar ratio of $\text{H}_2/\text{O}_2$ for type 304 SS, Pd-modified type 304 SS and pure Pt electrodes in 288°C water containing 300ppb $\text{O}_2$ [108].............................................. 101
Figure 40 Schematic Evans diagram showing intersections of O$_2$ and H$_2$ on metal surfaces such as SS and Pt ($i_L$, limiting current)[108] ........................................... 101

Figure 41 ECP of type 304 SS as a function of immersion time: (a) SW-HVOF-coated type 304 SS electrodes in 288°C water containing 200 ppb O$_2$, with and without addition of 35 ppb H$_2$; (b) SW-PS-coated type 304 SS electrodes in 288°C water containing 1 ppm O$_2$, with and without addition of 150 ppb H$_2$[103] ............. 102

Figure 42 Schematic of the dog bone sample used to measure the mechanical properties ................................................................. 110

Figure 43 Vickers hardness test principle (a) and principle of calculation (b) ........... 111

Figure 44 Optical micrographs showing the microstructure of 304MC, etched electrolytically in 10% oxalic acid: (a) as-received and (b) heat-treated at 650°C for 24 h .................................................................................................................. 113

Figure 45 Optical micrographs showing the microstructure of Pd1MC, etched electrolytically in 10% oxalic acid: (a) as-received and (b) heat-treated at 650°C for 24 h .................................................................................................................. 113

Figure 46 Optical micrographs showing the microstructure of Pd2MC, etched electrolytically in 10% oxalic acid: (a) as-received and (b) heat-treated at 650°C for 24 h .................................................................................................................. 114

Figure 47 Optical micrographs showing the microstructure of Pd3MC , etched electrolytically .................................................................................................................. 114

Figure 48 Optical micrographs showing the microstructure of Ru1MC, etched electrolytically .................................................................................................................. 115

Figure 49 Optical micrographs showing the microstructure of Ru2MC, etched electrolytically .................................................................................................................. 115
Figure 50 Optical micrographs showing the microstructure of Ru3MC, etched electrolytically ................................................................. 116

Figure 51 Optical micrographs showing the microstructure of RuPdLC, etched electrolytically in 10% oxalic acid: (a) as-received and (b) heat-treated at 650°C for 72 h ........................................................................................................ 116

Figure 52 Optical micrographs showing the microstructure of RuPdMC, etched electrolytically in 10% oxalic acid: (a) as-received and (b) heat-treated at 650°C for 48 h ........................................................................................................ 117

Figure 53 Optical micrographs showing the microstructure of Ru3HC, etched electrolytically in 10% oxalic acid: (a) as-received and (b) heat-treated at 650°C for 24 h ........................................................................................................ 117

Figure 54 Optical micrographs showing the microstructure of Pd3HC, etched electrolytically in 10% oxalic acid: (a) as-received and (b) heat-treated at 650°C for 24 h ........................................................................................................ 118

Figure 55 Mechanical properties: 304MC at room temperature (grey); Ru1MC at 300°C (red); Ru3MC (blue); Pd3MC at 300°C (green), 304MC at 300°C (pink) ........... 120

Figure 56 Schematic showing how the U-bend samples (represented in green) were cut from the plates (represented in pink) ................................................................. 129

Figure 57 Photography showing a representative disposition of the U-bend samples in the autoclave ........................................................................................................ 130

Figure 58 Photography of a representative U-bend sample (304MC in A7) prior to running the autoclave test: (a) and (b) The two sides of the sample reveal the features of the legs; (c) Surface of the bent-part of the sample showing the region under high tensile stress ............................................................................. 135
Figure 59 Photography of a representative U-bend sample (304MC in A7) after running the autoclave test: (a) and (b) The two sides of the sample reveal the features of the legs; (c) Surface of the bent-part of the sample showing cracking in the region under high tensile stress ............................................................. 136

Figure 60 Scanning electron micrographs showing a representative surface of the leg:
(a) Leg of Ru3MC in A6; (b) oxide on surface of the leg in A6 ......................... 137

Figure 61 Representative scanning electron micrograph revealing the region of high tensile stress and the edge of the U-bend sample after an autoclave experiment under hydrogenated conditions (tests A2, A3, A4 and A5)......................... 138

Figure 62 Representative scanning electron micrograph revealing the oxide on the outer surface: (a) lower magnification of a 304MC under hydrogenated conditions (A4); (b) higher magnification revealing the presence of crystals in white ............... 139

Figure 63 Scanning electron micrographs revealing the “holes” observed on surface after an autoclave test under hydrogenated conditions (A6): (a) sensitised 304MC; (b) sensitised Pd3MC; (c) sensitised Ru3MC................................................................. 141

Figure 64 Scanning electron micrographs revealing the region of cracking: (a) 304MC showing cracking after testing in A7; (b) Pd3MC after testing in A7; (c) Ru3MC after testing in A7................................................................. 143

Figure 65 Scanning electron micrographs showing the region under high tensile stress where no cracks were found. Grinding marks and magnetite crystals were observed: (a) 304MC; (b) Pd3MC; (c) Ru3MC ................................................................. 144

Figure 66 Scanning electron micrographs revealing the cracking morphology observed on 304MC after testing under oxygenated conditions (A7): (a) cracks A and B; (b) high magnification of crack A; (c) High magnification of crack B................. 145
Figure 67 Scanning electron micrographs showing a high magnification inside crack A revealing the oxide morphology .............................................................. 146

Figure 68 The stress condition of a stressed U-bend specimen [144] ...................... 147

Figure 69 Schematic of corrosion oxide film formed on austenitic stainless steels in LWR environments [37].......................................................... 149

Figure 70 Representative etched microstructure of a sample further to solution annealing at 1050 °C for 40 min and sensitisation at 650 °C for 24 hours ........... 154

Figure 71 Schematic showing how the specimens were cut from the plates ............ 155

Figure 72 Schematic of the CCB sample design used in the fatigue precracking study .......................................................... 155

Figure 73 Photography of the R.R Moore machine [148] .................................. 157

Figure 74 Schematic of the rotating bend rig showing the bending moment applied to the specimen .......................................................... 158

Figure 75 Schematic of the fracture surface representing $K_{\text{max}}$ and $K_{\text{min}}$ on the CCB specimen under fatigue rotation ........................................... 160

Figure 76 Representative scanning electron micrograph (SEM) fractography of standard type 304 SS after fatigue rotation for 8682 cycles ( $K_1 = 8.11 \text{ MPa}\sqrt{\text{m}}$ at the start of the fatigue process). Three regions are shown: 1. the notch, 2. the fatigue precrack and 3. the ligament .................................................. 166

Figure 77 Scanning electron micrograph showing the fatigue precrack region........ 167

Figure 78 Scanning electron micrograph showing the ligament region ................... 167

Figure 79 Graph showing the resistance variation versus the precrack length of FP samples type 304 SS while under fatigue rotation .............................. 168

Figure 80 Schematic of the circumferential cracked bar (CCB) sample design ....... 175
Figure 81 Schematic diagram of the SCC experiments showing the CCB specimen under tension in a solution of 0.01 M K$_2$S$_4$O$_6$, pH=1.5, at room temperature .... 175

Figure 82 Non-dimensional stress intensity factor for a circumferential crack in a cylindrical bar under tension [154] ................................................................. 178

Figure 83 Graph determining the relation between ‘f’ and ‘atot/R’: f=exp (0.1167exp(3.4737(atot/R))) .................................................................................. 178

Figure 84 Graph presenting the load against time in a solution of 0.01 M K$_2$S$_4$O$_6$ at pH=1.5 and 25°C .................................................................................................................................. 183

Figure 85 Fractography of FP304MC-1 after fatigue precracking and tensile testing in 0.01 M K$_2$S$_4$O$_6$, pH=1.5: (a) the machined notch, fatigue precrack and ligament are revealed (b) dimples in the ligament region .................................................................................. 185

Figure 86 Fractography of FP304MC-2 after fatigue precracking and tensile testing in 0.01 M K$_2$S$_4$O$_6$, pH=1.5: (a) the machined notch, fatigue precrack and intergranular stress corrosion cracking are revealed; The black arrows present the eight average point that measures the SCC crack length (b) IGSCC .............. 186

Figure 87 Fractography of FP-Pd2MC-2 after fatigue precracking and tensile loading in 0.01 M K$_2$S$_4$O$_6$, pH=1.5: (a) the notch and intergranular stress corrosion cracking are revealed (b) IGSCC ........................................................................................................... 187

Figure 88 Fractography of FP-Pd3MC-2 after fatigue precracking and tensile loading in 0.01 M K$_2$S$_4$O$_6$, pH=1.5: (a) the notch and intergranular stress corrosion cracking are revealed (b) IGSCC ........................................................................................................... 188

Figure 89 Fractography of FP-Ru2MC-1 after fatigue precracking and tensile loading in 0.01 M K$_2$S$_4$O$_6$, pH=1.5: (a) the notch and intergranular stress corrosion cracking are revealed (b) IGSCC ........................................................................................................... 189
Figure 90 Fractography of FP-Ru3MC after fatigue precracking and tensile loading in 0.01 M K$_2$S$_4$O$_6$, pH=1.5: (a) the notch and intergranular stress corrosion cracking are revealed (b) IGSCC failure ................................................................. 190

Figure 91 Fractography of a typical high carbon Pd doped alloy (FP-Pd3HC) after fatigue precracking and tensile loading in 0.01 M K$_2$S$_4$O$_6$, pH=1.5: (a) the notch and intergranular stress corrosion cracking are revealed (b) intergranular stress corrosion cracking on surface ................................................................. 191

Figure 92 Fractography of a typical high carbon Ru doped alloy (FP-Ru3HC) after fatigue precracking and tensile loading in 0.01 M K$_2$S$_4$O$_6$, pH=1.5: (a) the notch, fatigue precrack and intergranular stress corrosion cracking are revealed (b) intergranular stress corrosion cracking on surface and final ductile ligament ..... 192

Figure 93 Cross section of a representative standard type 304 SS (FP-304MC) after fatigue precracking and SCC propagation test in 0.01M K$_2$S$_4$O$_6$ at pH=1.5: (a) IGSCC region; (b) machined notch region......................................................... 196

Figure 94 Cross section of a representative medium carbon Pd (0.23 wt%) doped type 304 SS (FP-Pd2MC) after fatigue precracking and SCC propagation test in 0.01 M K$_2$S$_4$O$_6$ at pH=1.5: (a) SCC region; (b) machined notch region................................. 196

Figure 95 Cross section of a representative medium carbon Pd (0.96 wt%) doped type 304 SS (FP-Pd3MC) after fatigue precracking and SCC propagation test in 0.01M K$_2$S$_4$O$_6$ at pH=1.5: (a) SCC region; (b) machined notch region................................. 197

Figure 96 Cross section of a representative medium carbon Ru (0.26 wt%) doped type 304 SS (FP-Ru2MC) after fatigue precracking and SCC propagation test in 0.01M K$_2$S$_4$O$_6$ at pH=1.5: (a) SCC region; (b) machined notch region................................. 197
Figure 97 Cross section of a representative medium carbon Ru (1.01 wt%) doped type 304 SS (FP-Ru3MC) after fatigue precracking and SCC propagation test in 0.01M $\text{K}_2\text{S}_2\text{O}_6$ at pH=1.5: (a) SCC region; (b) machined notch region.......................... 198

Figure 98 Cross section of a representative high carbon Pd doped type 304 SS after fatigue precracking and SCC propagation test in 0.01M $\text{K}_2\text{S}_2\text{O}_6$ at pH=1.5: (a) SCC region; (b) machined notch region.......................... ........................................... 198

Figure 99 Cross section of a representative high carbon Ru doped type 304 SS after fatigue precracking and SCC propagation test in 0.01M $\text{K}_2\text{S}_2\text{O}_6$ at pH=1.5: (a) SCC region; (b) machined notch region............................................................. 199

Figure 100 Open circuit potential in a solution of (1000 ppm B + 2 ppm Li) at 25°C in aerated environment, at pH~7-8: Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (black solid line)............................................ 208

Figure 101 Schematic diagram showing the influence of PGM additions on the OCP when oxygen reduction is the main cathodic reaction................................................. 210

Figure 102 Open circuit potential in a solution of (1000 ppm B + 2 ppm Li) at 70 °C in aerated environment, at pH~7-8: Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (black solid line)............................................. 210

Figure 103 Open circuit potential in a solution of (1000 ppm B + 2 ppm Li) at 25 °C in deaerated environment with nitrogen, at pH~7-8: Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (solid black line).......................... 212

Figure 104 Open circuit potential in a solution of (1000 ppm B + 2 ppm Li) at 70 °C in deaerated environment with nitrogen, at pH~7-8: Ru3MC (blue solid line), Pd3MC (green solid line), 304MC (red solid line), Pt (black solid line).......................... 213
Figure 105 Polarisation scan in a solution of (1000 ppm B + 2 ppm Li) at 25°C in aerated environment, at pH~7-8 : Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (solid black line)................................. 214

Figure 106 Polarisation scan in a solution of (1000 ppm B + 2 ppm Li) at 70°C in aerated environment, at pH~7-8 : Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (solid black line)................................. 215

Figure 107 Polarisation scan in a solution of (1000 ppm B + 2 ppm Li) at 25°C in deaerated environment, at pH~7-8 : Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (solid black line)................................. 217

Figure 108 Polarisation scan in a solution of (1000 ppm B + 2 ppm Li) at 70°C in deaerated environment with nitrogen, at pH~7-8 : Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (solid black solid).............. 218

Figure 109 Graph presenting the OCP against the PGM concentration in aerated (circles) and deaerated with nitrogen (triangles) environments and at 25°C (white) and 70°C (black) in a solution of (1000 ppm B + 2 ppm Li)................................. 219

Figure 110 Polarisation scan of Ru3MC in a solution of (1000 ppm B + 2 ppm Li) in aerated (dashed lines) and deaerated with nitrogen (solid lines) at 25°C (black) and 70°C (red).................................................................................................................. 220

Figure 111 Open circuit potential in a solution of (1000 ppm B + 2 ppm Li) at 25 °C in aerated environment, at pH~7-8: Ru1MC (green solid line), Ru2MC (red solid line), Ru3MC (blue solid line), 304MC (black solid line)................................. 221

Figure 112 Polarisation scan of Ru doped alloys in a solution of (1000 ppm B + 2 ppm Li) in aerated conditions at 25°C, at pH~7-8: Ru1MC (green solid line), Ru2MC (red solid line), Ru3MC (blue solid line), 304MC (black solid line)................................. 222
Figure 113 Polarisation scan of Ru doped alloys in a solution of (1000 ppm B + 2 ppm Li) in deaerated conditions with nitrogen at 25°C: Ru1MC (green solid line), Ru2MC (red solid line), Ru3MC (blue solid line), 304MC (black solid line)..... 223

Figure 114 Open circuit potential in a solution of (1000 ppm B + 2 ppm Li) at 25 °C in hydrogenated environment, at pH~7-8: Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (solid black line) .......................... 225

Figure 115 Polarisation scan in a solution of (1000 ppm B + 2ppm Li) in hydrogenated conditions at 25°C, at pH~7-8: Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (solid black line).............................................. 226

Figure 116 Open circuit potential in a solution of (1000 ppm B + 2 ppm Li) at 25 °C in hydrogenated environment, at pH~7-8: : Ru1MC (green solid line), Ru2MC (red solid line), Ru3MC (blue solid line), 304MC (black solid line)........................ 228

Figure 117 Polarisation scan of Ru doped alloys in a solution of (1000 ppm B + 2 ppm Li) in hydrogenated conditions at 25°C, at pH~7-8: Ru1MC (green solid line), Ru2MC (red solid line), Ru3MC (blue solid line), 304MC (black solid line).......... 229

Figure 118 Polarisation scan in a solution of (1000 ppm B + 2 ppm Li) at 25°C, at pH~7-8: in hydrogenated conditions (solid lines) and deaerated condition with nitrogen (dashed lines): Ru3MC (blue), Pd3MC (green), 304MC (red), Pt (black ) ............................................................. 238

Figure 119 Open circuit potential in a solution of 0.01 M K₂S₄O₆, pH=1.5 at 25°C in aerated environment: Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (solid black line).............................................. 244

Figure 120 Open circuit potential in a solution of 0.01 M K₂S₄O₆ at 25 °C, at pH=1.5 in deaerated environment with nitrogen: Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (solid black line) ........................... 246
Figure 121 Potentiodynamic scan (0.5 mV.s\(^{-1}\)) in a solution of 0.01 M K\(_2\)S\(_4\)O\(_6\), at 25 °C and pH=1.5 in aerated environment: Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (solid black line).................................................. 247

Figure 122 Potentiodynamic scan (5 mV.s\(^{-1}\)) in a solution of 0.01 M K\(_2\)S\(_4\)O\(_6\) at 25°C and pH=1.5 in aerated environment: Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (solid black line).................................................. 249

Figure 123 Potentiodynamic scan (0.5 mV.s\(^{-1}\)) in a solution of 0.01 M K\(_2\)S\(_4\)O\(_6\) at 25°C, pH=1.5 in deaerated environment with nitrogen: Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (solid black line).......................... 251

Figure 124 Polarisation scan (5 mV.s\(^{-1}\)) in a solution of 0.01 M K\(_2\)S\(_4\)O\(_6\) at 25°C, at pH=1.5, in deaerated environment with nitrogen: Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (solid black line).......................... 252

Figure 125 Optical micrographs showing the surface of the alloys after immersion in 0.01 M K\(_2\)S\(_4\)O\(_6\) at pH=1.5 and 25°C for 1 hour: (a): 304MC; (b): Pd3MC; (c): Ru3MC........................................................................................................................................ 254

Figure 126 Potentiodynamic scan of Ru3MC in 0.01 M K\(_2\)S\(_4\)O\(_6\): Ru3MC in aerated environment at 0.5 mV.s\(^{-1}\) (red solid line), Ru3MC in deaerated environment with nitrogen at 0.5 mV.s\(^{-1}\) (red dashed line), Ru3MC in aerated environment at 5 mV.s\(^{-1}\) (black solid line), Ru3MC in deaerated environment at 5 mV.s\(^{-1}\) (black dashed line) .......................................................................................................................... 257

Figure 127 Graph showing the calibration of the reference electrode at 260°C ............ 270

Figure 128 Polarisation measurements under deaerated conditions with nitrogen at 260°C: Pd3MC (green line), Ru3MC (blue line), Pt (black line)......................... 271
Figure 129 Potential measurements under deaerated conditions with nitrogen at 260°C:
Pd3MC (green line), Ru3MC (blue line), Pt (black line), autoclave body (red line)

Figure 130 Potential measurements from 260°C to room temperature under deaerated conditions with nitrogen: Pd3MC (green line), Ru3MC (blue line), Pt (black line), autoclave body (red line)

Figure 131 Polarisation measurements under deaerated conditions with nitrogen at 260°C: 304MC (red line), Ru3MC (blue line), Pt (black line)

Figure 132 Polarisation measurements under deaerated conditions with nitrogen at 260°C: 304MC (red line), Ru3MC (blue line), Pd3MC (green line)

Figure 133 Polarisation measurements under hydrogenated conditions at 260°C: Pt (black line), Ru3MC (blue line), 304MC (red line)

Figure 134 Polarisation measurements under hydrogenated conditions at 260°C: Pt (black line), Ru3MC (blue line), Pd3MC (green line)

Figure 135 Polarisation measurements under hydrogenated conditions at 260°C: Ru3MC (blue line), Pd3MC (green line), 304MC (red line)
LIST OF ABBREVIATIONS

ATEM Analytical transmission microscopy
BWR Boiling water reactor
ECP Electrochemical corrosion potential
FIB Focused ion beam
HWC Hydrogen water chemistry
IGSCC Intergranular stress corrosion cracking
IGC Intergranular corrosion
IGA Intergranular attack
OCP Open circuit potential
PGMs Platinum group metals
PWR Pressurised water reactor
SEM Scanning electron microscope
SS Stainless steel
SCC Stress corrosion cracking
TEM Transmission electron microscopy
ABSTRACT

In pressurised water reactors (PWRs), hydrogen overpressure is used to keep the corrosion potential below the threshold for onset of intergranular stress corrosion cracking (IGSCC) in type 304 SS. However, some regions may contain higher oxygen levels resulting in an increase in the potential. These “dead space” regions are difficult to access and during refuelling; oxygen may become trapped in these locations. The objective of this study was to investigate the influence of PGM additions on IGSCC susceptibility of type 304 stainless steels (SS) in the sensitised state within PWRs.

The work presented herein investigates several aspects of the IGSCC problem. Virgin and platinum group metal (PGM)-modified (Ru and Pd) 304 SS have been studied. Material characterisation, including microstructural, tensile properties, hardness and grain size measurements, has been conducted. Crack initiation studies using U-bend samples in autoclaves simulating PWR environments have also been performed. In addition, crack propagation studies using circumferential cracked bar (CCB) specimens under constant extension in potassium tetrathionate solutions, a well-known medium to promote IGSCC on sensitised stainless steels, have been conducted in order to evaluate cracking resistance. Electrochemical studies using model solutions for PWR chemistry (containing boric acid and lithium hydroxide) and also potassium tetrathionate were carried out to look at the influence of the PGM on the kinetics of the main electrochemical reactions.

The results revealed that PGM additions appeared to reduce crack initiation on sensitised type 304 SS under oxygenated conditions in high temperature water containing sulphate and chloride. PGM-doped and standard sensitised type 304 stainless steels revealed susceptibility to IGSCC propagation in 0.01 M K₂S₂O₆, at pH=1.5 and 25°C. Electrochemical studies in potassium tetrathionate media showed smaller anodic dissolution peaks with PGM additions and metallography indicated less intergranular attack with PGM additions. In PWR model electrolytes, PGM additions, particularly 1 wt% Ru, were shown to catalyse the oxygen reduction reaction or hydrogen oxidation reaction, depending on the oxygen/hydrogen level.

Overall findings showed that Ru additions can improve the IGSCC resistance of sensitised type 304 SS in PWR, while Pd additions are less effective.
DECLARATION
No portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualifications of this or any other university, or other institute of learning.

COPYRIGHT STATEMENT
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 or 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 Rights and /or Reproductions.

IV. Further information on the conditions under which disclosure, publication and commercialisation of this thesis, the Copyrights and any Intellectual Property and/or Reproductions described in it may take place is available in the University IP policy (see http://www.campus.manchester.ac.uk/medialibrary/policies/intellectual-property.pdf), 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 the presentation of theses.
DEDICATION

I dedicate my PhD thesis to my son Houssine Ammour who gave me the strength and motivation to achieve my PhD.

J’espère que tu grandiras dans de bonnes conditions et que tu seras fier de ta maman qui t’aime beaucoup et qui a tant voulu t’avoir.

Ta naissance a été le plus beau jour de ma vie et je n’oublierai jamais ton regard lorsque la sage femme t’a posé sur mon ventre, tu étais si mignon…
ACKNOWLEDGMENT

I would like to thank my supervisor Professor Stuart Lyon and my co-supervisor Professor Andrew Sherry for their guidance throughout the duration of my PhD. I wish to express my gratitude to MOD for sponsoring this project as well as Johnson Matthey (JM) and the Universities of Birmingham and Oxford for their great collaboration.

I am very thankful to Kuvasani Govender and Fabio Scenini, who helped me with the experimental work and advised me a lot on the PhD. The staff in the Material Performance Centre (MPC), and especially the technicians in the workshop and Stuart Morse, were a great help and contributed to the advancement of my PhD.

I give my best wishes to the staff in the Corrosion and Protection Centre (CPC) for their advice and kindness. I thank my co-workers in the lab for their friendship and finally, I would like to thank my whole family for their support and encouragement during my PhD.
Chapter 1: Introduction

Chapter 2: Literature review

Chapter 3: Materials characterisation

Chapter 4: Crack initiation

Chapter 5: Fracture mechanics approach to stress corrosion crack propagation: fatigue precracking

Chapter 6: SCC propagation study

Chapter 7: Electrochemistry in borated and lithiated water

Chapter 8: Electrochemistry in IGSCC simulated environment

Chapter 9: Electrochemistry in high temperature water

Chapter 10: Discussion

Chapter 11: Conclusions

Chapter 12: Future work
Chapter 1  Introduction

This section presents the objectives of this PhD study and gives a brief introduction on PGM additions and stress corrosion cracking in PWRs.

The objectives of this PhD are to investigate different aspects of the influence of PGMs on the SCC resistance of type 304 SS in PWRs. The main aims of this project are to study the following:

- The influence of PGMs on the material properties of type 304 SS.
- The influence of PGMs on the kinetics of the main electrochemical reactions controlling the OCP in PWRs.
- The influence of PGMs on the crack initiation of type 304 SS in PWRs.
- The influence of PGMs on the crack propagation of type 304 SS in PWRs.

Stress corrosion cracking may be an issue affecting components of pressurised water reactors (PWR) in regions where deoxygenation has been compromised, e.g. “dead space regions”, near stagnant regions of the plant [1]. In PWRs, hydrogen is added to the primary coolant to suppress the formation of oxidising species produced during water radiolysis. In addition, boric acid and lithium hydroxide are added, with boron controlling neutron irradiation and lithium hydroxide for pH control. However, corrosion issues regarding austenitic stainless steel components remain a matter of concern, in particular crevice corrosion and SCC in the “dead space” regions. Sensitisation can increase the risk of IGC and IGSCC of austenitic stainless steels and lead to the failure of materials in certain environments. In PWRs, sensitisation, which results in chromium depletion along the grain boundaries of the material, may occur after a certain time due to irradiation of the materials and long time exposure at high temperature (around 300°C). Over the last 60 years, researchers have demonstrated that
minor additions of platinum group metals (PGMs) to a variety of alloys can result in enhanced corrosion resistance in a range of different chemical environments [2-9]. For example, palladium/ruthenium additions to titanium have improved corrosion resistance in reducing acid media [7], whilst ruthenium and palladium additions (0.2 wt%) to Fe-40%Cr ferritic steels significantly decrease corrosion rates in boiling 10% sulfuric acid (by a factor of $\sim 1-5 \times 10^4$) [10]. However, the effect of PGMs has not always revealed good performance. For instance in boiling magnesium chloride, Pd was detrimental to stainless steel. So the real effect of PGM additions to steels has a distinct but variable effect upon their corrosion resistance. In recent years, the practical application of the Noble Metal Chemical Addition (NMCA) technology to mitigate intergranular stress corrosion cracking (IGSCC) in boiling water reactors (BWRs) has been demonstrated and is now well established [11]. By employing similar protocols to those shown to be effective in BWRs using cathodic modification strategies, it may be possible to use PGM-doped austenitic stainless steels to mitigate these corrosion problems in PWRs. However, metallurgical, chemical and mechanical factors can also affect the SCC susceptibility of materials. The understanding of how these parameters influence the mechanical behaviour of type 304 SS alloys is of great importance to be able to investigate the influence of PGM additions in terms of SCC mechanisms in PWRs environment.

The overall structure of the study takes the form of twelve Chapters, including this introductory Chapter, the literature review. Chapter 3 begins by laying out the material characterisation for the research. The fourth Chapter is concerned with the crack initiation used for this study. The fifth chapter presents the fracture mechanics approach to stress corrosion crack propagation; Chapter 6 presents the stress corrosion crack propagation investigation. Chapter 7, Chapter 8 and Chapter 9 analyse the
electrochemical behaviour of standard and PGM -doped materials in IGSCC simulated environments and PWR simulated environments. Chapter 10 gives a general discussion of all the work conducted. Chapter 11 draws upon the entire thesis. The final Chapter identifies the future work for this research project.
Chapter 1: Introduction

Chapter 2: Literature review

Chapter 3: Materials characterisation

Chapter 4: Crack initiation

Chapter 5: Fracture mechanics approach to stress corrosion crack propagation: fatigue precracking

Chapter 6: SCC propagation study

Chapter 7: Electrochemistry in borated and lithiated water

Chapter 8: Electrochemistry in IGSCC simulated environment

Chapter 9: Electrochemistry in high temperature water

Chapter 10: Discussion

Chapter 11: Conclusions

Chapter 12: Future work
2 Literature Review

2.1 Introduction to light water reactors

This project focuses on the possible susceptibility of type 304 stainless steel to stress corrosion cracking (SCC) in the primary circuit of pressurised water reactors (PWRs). Therefore, a general background is given on PWRs to better understand the key parameters of the involved environment. The PWR is one of the light water reactors (LWRs) and was first used in the nuclear submarine propulsion program. Boiling water reactors (BWRs) are also light water reactors. Significant work has been carried out on BWRs and noble metal additions have been extensively applied to mitigate intergranular stress corrosion cracking (IGSCC) [12, 13]. For this reason, BWRs are also reviewed to better understand the application of noble metal additions to PWRs.

2.1.1 Application and generalities of PWRs and BWRs

Nowadays, most BWRs and PWRs are used to produce electrical power, although naval propulsion reactors are also used. There are civil and military plants. The principle to produce electricity is based on nuclear fission as a primary source for the generation of heat energy. PWRs are composed of several circuits but only the primary circuit is described in the following sections as it is the one of interest for this work. A brief description of BWRs will be given as well as interesting work on noble metal additions that has been undertaken in this type of reactor.

2.1.2 The primary circuit in PWRs and BWRs

2.1.2.1 Introduction

The primary circuit in PWRs is composed, for example of U-shaped tubes (Figure 1). Its main function is to heat water in a secondary circuit that is then used in a turbine to generate electricity (275°C under 7 MPa). The coolant is water of variable composition depending on the application. Figure 1 shows the primary circuit in a representative schematic of a PWR steam supply system.
Figure 1 Schematic of a representative PWR nuclear power station; Heat generated in the core (by fission of U$^{235}$) is transferred to the primary circuit (pressurised water). Heat from the primary circuit evaporates water in the secondary circuit. The turbine generator set converts mechanical power provided by steam into electricity. A=reactor core, B=control rods, C=reactor vessel, D=pressuriser, E=steam generator, F=primary pump, G=containment, H=turbine, I=generator, J=condenser, K=extraction and feedwater pump, L=reheater, M=river (or sea) water [14]

In BWRs, the boiling cycles are presented in Figure 2.

Figure 2 Schematic diagrams of two boiling cycles used in boiling water reactors (BWRs) supplying same turbine requirements: (a) direct boiling cycle; (b) boiling cycle using pressurised water coolant and heat exchanger [15]
2.1.2.2 Materials in the primary circuit of PWRs and BWRs
Type 304 stainless steel is often used for the pipes and tubing in the primary circuit of PWRs and BWRs. For sufficient resistance and suitability, the materials must have good corrosion resistance and mechanical properties at high temperature [16].

2.1.2.3 Operating conditions in the primary circuit of PWRs and BWRs

2.1.2.3.1 Temperature and pressure
The primary side of a recirculating generator in PWRs has a gradient in temperature and pressure. Indeed, the coolant leaves the reactor core at about 315°C under 15 MPa while it enters the secondary circuit at about 275°C [17]. In BWRs, the temperature is lower than that in PWRs; usually the maximum temperature is about 288°C [15].

2.1.2.3.2 Water chemistry in PWRs and BWRs
Hydrogen overpressure is used in PWRs where there is an excess of hydrogen in order to recombine the oxidising species and form water on the surface of the materials. This process improves the corrosion resistance in PWR environments by ensuring a generally reducing potential. The water chemistry in PWRs usually contains lithium hydroxide and boron. The former is used to control the pH and the latter to control neutron moderation. The amounts of lithium and boron vary from one PWR design to another but it is usually about 0.2-20 ppm of Li and 100-13000 ppm B [18-21]. The resultant conductivity is about 2-20 µS/cm. The pH of the water is slightly alkaline but it may be in the acidic range (about 5.6) in the regions where the temperature is higher or when the water is pure. Certain parameters such as the corrosion potential, the temperature and chemistry influence the SCC resistance of type 304 SS under PWRs conditions. The minimum corrosion rate and least likelihood of SCC are given where the potential is close to that of the equilibrium hydrogen electrode. In order to facilitate this, excess hydrogen is added to the water circuit. Hydrogen water chemistry (HWC) is the name
given to this type of treatment where an excess of hydrogen is added to the water in order to combine with residual dissolved oxygen.

In BWRs, the coolant is high purity, neutral pH and contains oxygen, hydrogen peroxide and hydrogen. Previously normal water chemistry (NWC) was used; under these conditions, the oxidants (\(O_2\), \(H_2O_2\)) present in the coolant are in stoichiometric excess and lead to high corrosion potentials (\(>100\) mV vs. SHE). This results in a high risk of IGSCC. In order to suppress IGSCC, hydrogen water chemistry (HWC) was then introduced to lower the corrosion potential below the critical value for IGSCC to happen (\(<230\) mV vs. SHE) [22]. This potential value may vary from one BWR to another as it depends on the water chemistry.

2.2 Materials: Type 304 stainless steel

2.2.1 Metallurgy

2.2.1.1 Microstructure

Type 304 stainless steel is a stable, austenitic (face-centred cubic) solid-solution alloy (see Figure 3). Chromium additions in the range of 16 to 20 percent form a solid solution in alpha iron. However, the addition of sufficient nickel to iron chromium alloy suppresses the ferritic structure, thus the remaining structure is essentially austenitic. Austenitic alloys are non magnetic with a gamma structure [16]. The structure of the alloys depends on the composition and the temperature as temperature affects the solubility of the elements. Austenitic stainless steels contain second phase precipitates which are generally carbides (or intermetallic compounds). At ambient temperature, the intermetallic compounds are of little importance as they are relatively slow to precipitate due to the difficulty in nucleation. However, carbides such as \(M_{23}C_6\) may nucleate in the range of temperature 400-800°C. Unfortunately, these carbides form at the grain boundaries and enhance intergranular corrosion (IGC) and intergranular stress
corrosion cracking (IGSCC). This phenomenon is known as sensitisation and is caused by local chromium depletion. Other phases that are generally present include delta ferrite and sigma phase [23, 24]. Delta ferrite $\delta$ is a body centered cubic (bcc) phase that may be present in austenitic material after hot rolling and it can influence significantly the mechanical properties [25]. In welds, a minimum of delta ferrite is required to ensure good cracking resistance and a maximum amount must not be exceeded to avoid the formation of sigma phase $(\text{Fe, Ni})_3(\text{Cr, Mo})_2$ [26-28]. The amount of delta ferrite is often predicted in welds using the Schaeffler diagram (see Figure 4). This diagram calculates the delta ferrite level as a function of the Ni and Cr equivalences. Delta ferrite formation is dependent on the composition and the temperature of the heat treatment and it has magnetic properties. In type 304 SS, the amount of delta ferrite is usually between 2 and 6% [29].

![Stainless Steel Phase Diagram at 900°C](image)

Figure 3 Stainless steel phase diagram at 900°C [30]
2.2.1.2 Composition

The specifications for most common type of 304 SS alloys are presented in Table 1. The low carbon type 304L is more suitable when sensitisation is possible as the low carbon level limits the formation of carbides. Ni, Cr and Fe form the basic matrix composition. N, S and P are known as tramp elements and derive from the manufacturing process. Mn and Si are usually useful during the melting process and contribute to improve the mechanical properties of the alloy. They increase the resistance to wear, improve the rolling and forging qualities, strength, toughness and stiffness [16]. Mn additionally controls the deleterious effects of S by forming MnS precipitates. Therefore there is less S present in the matrix, which improves the corrosion resistance as S can promote hydrogen embrittlement by acting as a trap site for hydrogen. It can also enhance chromium depletion along the grain boundaries.

Figure 4 Schaeffler diagram predicting the structure especially in austenitic welds as a function of the Cr and Ni equivalences [31]
<table>
<thead>
<tr>
<th>Elements (wt%)</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
<th>N</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>304</strong></td>
<td>0.08 max</td>
<td>2.00 max</td>
<td>0.045 max</td>
<td>0.03 max</td>
<td>0.75 max</td>
<td>18.00-20.00</td>
<td>8.00-10.5</td>
<td>0.1 max</td>
<td>Balance</td>
</tr>
<tr>
<td><strong>304L</strong></td>
<td>0.03 max</td>
<td>2.00 max</td>
<td>0.045 max</td>
<td>0.03 max</td>
<td>0.75 max</td>
<td>18.00-20.00</td>
<td>8.00-10.5</td>
<td>0.1 max</td>
<td>Balance</td>
</tr>
</tbody>
</table>

2.2.2 Tensile properties

The tensile properties of type 304 SS are of great importance to investigate SCC as the stress involved in this corrosion process is tensile. Table 2 gives the typical values for type 304 SS.

<table>
<thead>
<tr>
<th>Tensile properties</th>
<th>Tensile strength (MPa) min</th>
<th>Yield strength (0.2% proof) (MPa) min</th>
<th>Elongation (% in 50 mm) min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room temperature</td>
<td>515</td>
<td>205</td>
<td>40</td>
</tr>
</tbody>
</table>

In order to increase the tensile properties, different methods can be used:

- Strain or work hardening that involves deformation and increase in dislocation density. It can increase the strength up to 100% but it lowers the ductility.

- Grain refinement is also used to strengthen and involves the refinement of grains within the matrix to create a barrier for dislocation movements. Its effect is summarised in Equation 1 [32]. The smaller the grain size the stronger the material is.

\[
\sigma_y = \sigma_i + k_y d^{-0.5}
\]

Where,

- \(\sigma_y\) = Yield strength of the material
- \(\sigma_i\) = Yield strength of a single grain

44
• $k_y =$ Material constant

• $d =$ Average grain size

2.2.3 Heat Treatment of type 304 SS
Type 304 SS is not hardenable by thermal treatment. This alloy is solution annealed between 1010-1120°C for 30-45 minutes and cooled rapidly to avoid the formation of carbides. The purpose is to form a solid solution, recrystallise the grains and dissolve the carbides.

2.2.4 Oxide formed on type 304 SS under PWR conditions
The Pourbaix diagrams displayed in Figure 5 show that type 304 SS forms an oxide under PWR conditions so it is of great importance to identify its microstructure and composition.

![Figure 5 Pourbaix diagrams calculated using thermodynamics computation code (HSC chemistry).](image)
The potential E has been measured using a standard hydrogen electrode (SHE) [33, 34]

The oxide film formed is generally composed of two layers: a iron-rich outer layer $Fe_2O_3$ and a chromium-rich spinel inner layer $FeCr_2O_4$ [33, 35, 36]. Under hydrogenated conditions, the oxide contains crystals such as in Figure 6. The longer the time of exposure, the bigger the crystal size is. Moreover, the effect of Cr content on the oxide
particles has been investigated [33] and higher Cr content (20 wt%) alloys develop a smaller crystal size compared to lower Cr content (5 wt%) alloys. As well as the crystal size, the thickness of the inner layer changes with the chromium level, and seems to be greater with lower chromium. More importantly, the chromium concentration affects the corrosion resistance of the materials. This remark is obviously consistent with the stainless characteristics of the Fe-Ni-Cr that contains a minimum of 13 wt% Cr, making them more corrosion resistant. The oxide morphology has been demonstrated by many workers, also under oxygenated conditions [37]. However, in terms of composition, both layers showed differences as a function of the environment, especially the oxygen level and water chemistry pH. The double layer structure seems to be quite well understood under oxygenated conditions; indeed, since the corrosion potential changes with the dissolved oxygen, it is expected to be the parameter controlling the oxide structure [33]. Under hydrogenated conditions, the corrosion potential is thought to be similar through the film and at the moment, no clear understanding of the structure has been given under these conditions. However, since the general structure of the film is the same under oxygenated and hydrogenated conditions, the corrosion potential may not be the only possible explanation for the oxide structure.
2.3 Stress Corrosion cracking

2.3.1 What is it?

Stress corrosion cracking (SCC) is a corrosion phenomenon that results in cracking from the simultaneous action of tensile stress, susceptible material and corrosive environment [38]. Many alloys are susceptible to SCC in at least one environment but SCC does not occur in all environments nor does an environment that induces SCC in one alloy necessarily induce SCC in another alloy. It can proceed in two modes, which are intergranular (IG) and/or transgranular (TG). In the case of type 304 SS in PWR conditions, the cracking mode is often referred to as being intergranular. SCC can be divided into three main stages: initiation, propagation and failure.

Figure 6 High magnification SEM photographs of 304 SS after exposure to high temperature hydrogenated ammoniated water: (a) after 1000 hours; (b) after 2000 hours; (c) after 5000 hours and (d) after 10000 hours [35]
2.3.2 Factors of SCC

2.3.2.1 Introduction
The concept of SCC is illustrated in Figure 7. SCC can be eliminated by the reduction of one of these parameters below a certain threshold value or by eliminating any of them.

![Figure 7 Diagram illustrating the SCC concept: interaction of three parameters (stress, material and environment) [39]](image)

2.3.2.2 Stress
For SCC to happen, the stress must be tensile with a sufficient magnitude. Some researchers mention the existence of a threshold stress intensity factor $K_{\text{ISC}}$ below which SCC cannot propagate [40]. The stresses are tensile in nature, external, applied, residual or thermal. The crack growth generally propagates perpendicular to the principal tensile stress axis. In the primary circuit of PWRs, the main source of stress is residual from tube manufacture and installation but pressure and thermal stress need to be taken into consideration as well. The most highly strained regions of PWRs (U-bends, expanded regions) have already suffered from SCC in PWRs. Laboratory tests have also shown that plastically deformed (cold-worked) materials may undergo SCC. The threshold stress for SCC has been evaluated near the yield stress of the alloy for
high temperature water [41]. For smooth samples, a plot of stress versus time to failure correlates SCC data and determines the threshold stress corresponding to crack initiation (see Figure 8). For pre-cracked samples, the crack propagation rate (da/dt) can be plotted against the stress intensity factor K to evaluate SCC (see Figure 9). The size of a defect leading to the transition between crack initiation and crack propagation can be obtained from Equation 2 [40].

**Figure 8** Schematic representation of log stress versus log time to failure [40]

**Figure 9** Schematic representation of the crack growth velocity as a function of the stress intensity factor K[40]

**Equation 2**  

\[ K = f \sigma \sqrt{a} \]

Where,
- K, is the stress intensity factor
- \( \sigma \), is the applied stress
- \( a \), is the defect size (crack length)

### 2.3.2.3 Materials susceptibility to SCC in PWRs conditions

Bulk composition can affect passive film stability and phase distributions. Minor alloying elements can also modify the passive film locally. Precipitates like carbides may induce a depletion of chromium and a risk of IGC/IGSCC. Local crack tip chemistry can be changed with the presence of inclusions.

Type 304 SS may suffer from SCC in PWRs after long exposure times. The regions that are more subject to SCC are the welds and occluded areas, where oxygen may be trapped. Welds have a different microstructure from that of the parent material and residual stress may be present in the heat affected zone (HAZ), leading to lower mechanical resistance and a greater risk of SCC. In order to overcome the SCC phenomenon of type 304 SS in PWRs, it is critical to know and understand the main factors that influence the susceptibility. From previous studies, it has been established that the grain size and orientation, sensitisation, delta ferrite, cold work, pitting and crevices, the oxide on surface etc., have a significant effect on the SCC resistance. The following sections review these parameters effects on the SCC susceptibility.

#### 2.3.2.3.1 Grain size and grain orientation

Grain size affects the mechanical properties; therefore it can contribute to SCC susceptibility. On one hand, small grains improve the mechanical properties as the stress of the material increases as the grain size decreases (see Equation 1) and on the other hand they promote sensitisation due to the high density of grain boundaries [42, 43]. Similarly the grain orientation has a critical impact on SCC resistance. Indeed, previous studies [43, 44] have reported that high angle grain boundaries are more susceptible to cracking than low angle grain boundaries and twins. The low angle grain
boundary corresponds to a small misorientation between two grains while a high grain boundary is a greater misorientation between two grains. The latter have an open structure with lots of free volume while the former have little free volume. High angle grain boundaries have highly distorted interatomic bounds compared to low angle grain boundaries that have slightly distorted interatomic bounds.

### 2.3.2.3.2 Sensitisation

In PWRs, sensitisation of type 304 SS may occur between 400°C and 800°C after a long period of time as the carbides require a long range diffusion (see Figure 10) [24]. Usually type 304 SS is solution annealed and cooled rapidly to avoid the formation of carbides. However in PWRs the operating temperature is about 300°C and sensitisation may still happen with time due to radiation segregation [45]. It results in the formation of carbides at the surface of the grain boundaries. Then these regions are depleted in chromium and it makes them anodic with respect to the matrix of the material [46]. Figure 10 displays the precipitation time/temperature diagram for type 304 SS [24]. The major consequence of the presence of these carbides in the grain boundaries is the risk of intergranular corrosion (IGC) and intergranular stress corrosion cracking (IGSCC).

By lowering the carbon content, sensitisation is more likely to be avoided. Some austenitic stainless steels containing Nb or Ti elements (e.g: type 347 SS) have been conceived especially to overcome sensitisation. Indeed, solutes such as Nb and Ti also prevent sensitisation as they have a greater affinity with C, hence the Cr level is not affected. Different techniques exist to detect sensitisation of austenitic stainless steels. Etching using oxalic acid reveals the grain boundaries and emphasises the grain boundary attack present in sensitised materials compared with non-sensitised materials.

The electrochemical potentiokinetic reactivation (EPR) test [23] is a non-destructive method to quantify the degree of sensitisation in stainless steels and nickel-base alloys. The test measures the amount of charge associated with the corrosion of the chromium-
depleted regions surrounding chromium carbide precipitates. As the particles may be intergranular or intragranular, examination of the surface must be conducted after the test to assure that the measurements correspond mostly to intergranular attack.

Figure 10 Time temperature precipitation diagram for $M_{23}C_6$ in 304 type austenitic stainless steel containing 0.06 wt% C [24]

Figure 11 Schematic of the sensitisation phenomenon [24]
2.3.2.3.3 Delta ferrite

Previous work on austenitic stainless steel revealed that an increase in the delta ferrite concentration increased the number and lengths of cracks in the edges of plates after hot rolling [29]. This tendency was attributed to the brittle effect that delta ferrite may have. Indeed, delta ferrite may be present in the matrix, making the alloy type 304 SS less corrosion resistant at high temperature and subject to hydrogen embrittlement. According to Luppo et al [27], delta ferrite could act as a site to trap hydrogen. This can be eliminated by a heat treatment [28]. Figure 12 shows the evolution of the delta ferrite content as a function of the annealing time for different temperatures. According to the results, more delta ferrite content is dissolved at 1200°C than at 1050°C between 50 s and 300 s. The temperature and time are the key parameters to dissolve delta ferrite.

![Figure 12 Variations of delta ferrite content versus dissolution time. Rapid dissolution at the early stage and diffusion controlled dissolution at the normal stage [28]](image)

Numerous works have been performed on the mechanism of the delta ferrite formation [26-29]. Most workers mentioned that chromium carbides M_{23}C_{6} were present at the
ferrite/austenite interface and inside the delta ferrite. M is composed of nickel, chromium and iron, with chromium being a ferrite stabilizer.

**2.3.2.3.4 Cold work**

Cold work causes strain hardening. The microstructure of a cold worked material reveals the presence of slip bands. Different studies have shown the potential effect of cold work on SCC of austenitic stainless steel in PWRs. However, the real effect remains complex and unclear in terms of mechanistic understanding. According to Zheng [47], the effect of cold work on SCC of type 304 SS in lithium hydroxide solution up to 95°C is detrimental. This effect seems to be more pronounced with an increase of the degree of cold work. This was confirmed by Tice [20] who investigated crack growth of cold worked type 304 SS in PWRs. Indeed, the degree of cold work increased the extent of crack growth. This effect was also emphasised with an increase in temperature. However, this work was conducted on pre-cracked samples and did not take into account the impact of cold work on crack initiation. According to Raquet et al.[48], cold worked type 304 SS does not seem to initiate cracking easily in good quality coolant. Current studies show that dynamic loading is necessary for crack propagation of type 304 SS in PWRs even for cold worked materials [49].

**2.3.2.3.5 Pitting**

Pitting can be one of the initiation sites for SCC [50]. Indeed a pit may turn into crack if the crack velocity is higher than that of pitting. Pitting results in the breakdown of the passive film and can initiate at a surface defect of the material. During dissolution, metal cations accumulate resulting in electro migration of anions. If chloride is present even in small amounts, metal ion hydrolysis causes the pH to decrease significantly in the pit and slows the regeneration of the passive film. In the pitting process, chloride reacts with metal cations and prevents the metal cation reduction. The pitting process is illustrated in Figure 13. The main reactions involved in the pitting process are given in
Equation 3 and Equation 4. Pits can act as occluded (diffusion restricted) corrosion cells similar to crevices and cracks. The transition between pits and cracks depends on the electrochemistry inside the pits, the stress, strain and pit geometry.

![Figure 13 Schematic of the pitting phenomenon](image)

**Equation 3**  
\[ M^{+}\text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{MOH} + \text{H}^+ + \text{Cl}^- \]

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

- Where, \( M^+ \) is the metal cation.

As pitting can be an initiation site for SCC, testing can be performed to evaluate the risk for a material in a given environment. Estimating the pitting temperature is performed by monitoring the current density under a constant anodic potential while increasing the temperature at a ramp of 1°C/min. Current density is monitored until a rapid increase is recorded or when it exceeds 100 µA/cm². A standard ASTM G150 (Electrochemical critical pitting temperature testing of stainless steels) gives the details for this test. It provides a prediction of resistance to pitting propagation on stainless steels.

The determination of the pitting potential is another technique to evaluate the susceptibility to pitting. It is performed in chloride containing solutions. The more negative the pitting potential, the more susceptible to pitting the alloy is.
2.3.2.3.6 Crevice corrosion

Crevices may also act as a location for SCC initiation [51]. It is slightly different from pitting and occurs in areas where there is a gradient in oxygen, enhancing anodic and cathodic regions. Crevices result in a gradient of concentrations and initiate by changes in local chemistry within the crevices. It can be due to a depletion of oxygen in the crevice or a shift to acid conditions in the crevice, build up of aggressive ion species such as chloride etc. This localised form of corrosion can be described in four stages as follows:

- Deoxygenation
- Increase of the salt and acid concentrations in the environment
- Depassivation
- Propagation

Different standard tests [52] exist to assess the crevice corrosion susceptibility of a material. Non electrochemical tests [53, 54] using artificial crevices are conducted to assess the crevice corrosion resistance by mass loss and visual examination methods. Electrochemical tests under open circuit condition [55] can detect localised corrosion and measure corrosion rates. Electrochemical tests under controlled potential and current conditions [56-58] evaluate the crevice corrosion resistance.

2.3.2.3.7 Oxide of type 304 SS in PWRs conditions

As type 304 SS forms an oxide in PWR environments, investigation of the oxide characteristics (microstructure, morphology, composition...) is relevant to the understanding of SCC mechanisms. Numerous works [33, 59] have been conducted on the oxide characterisation and it has been demonstrated that in the presence of SCC, the cracks were filled with chromium-rich spinel oxide and the morphology of the oxide at the crack tip was similar to that of the surface of the material. Therefore an investigation
of the surface oxide can be useful to understand the oxidation process at the crack tip and consequently the SCC mechanisms involved.

### 2.3.2.4 Environmental factors

The environment plays a fundamental role in the SCC risk of a material. In PWRs, several environmental factors may contribute to enhance or mitigate this problem. The environment in PWRs may differ from one reactor to another so the environmental factors affecting the corrosion behaviour can be different. In the following section, the indispensable parameters present in PWRs are reviewed but it is important to keep in mind that there may be more parameters associated with specific PWR design or applications.

#### 2.3.2.4.1 Water chemistry in BWRs and PWRs

Water chemistry is a key environmental parameter of SCC in light water reactors. BWR water chemistry is also reviewed as it has been investigated in terms of its effect on SCC susceptibility and similar experimental protocols are applied to study the water chemistry effect on SCC in PWRs.

As presented in 2.1.2.3.2, in PWRs the coolant is water, which is generally under hydrogen overpressure (hydrogen water chemistry is referred to as HWC). Hydrogen addition keeps the potential low so that IGSCC is unlikely to occur. In BWRs, it is added in order to suppress the radiolytic oxidised species and keep the potential sufficiently low to prevent IGSCC from happening. However, dissolved hydrogen has been reported to be also a parameter that could increase the susceptibility to SCC. Indeed, a recent study [33] on the oxide of stainless steels in PWRs has shown that dissolved hydrogen can accelerate SCC of compact tensile (CT). Indeed, the latter is related to the species present in solution so all depends on the final equilibrium. Therefore the corrosion potential would be a more appropriate parameter to consider for SCC susceptibility; the corrosion potential is affected by the hydrogen and oxygen...
concentration, the radiolytic species and the impurities. In the case of PWRs, it is mostly affected by hydrogen and oxygen concentrations while in the case of BWRs, it is affected by hydrogen, oxygen and hydrogen peroxide concentrations.

2.3.2.4.2 Electrochemical corrosion potential (ECP) in hydrogen water chemistry (HWC)

From a general point of view, electrochemical measurements can determine the susceptible regions for SCC. Figure 14 displays a representative diagram of a potentiodynamic scan.

![Potentiodynamic Scan Diagram](image)

Figure 14 Schematic diagram showing a potentiodynamic scan with the susceptible regions for SCC indicated [60]

The corrosion potential (E\text{corr}) is the potential at which the rates of the cathodic and anodic reactions are equal. In PWRs, there are many different species so from one water coolant to another, the electrochemical corrosion potential may vary. It is of great importance to mention the electrochemical corrosion potential in hydrogen water...
chemistry as it is one of the key parameters that controls the susceptibility to SCC in PWRs. Numerous studies on BWRs have demonstrated that below a critical value (-230 mV vs. SHE) IGSCC was mitigated [61, 62]. Itow [63] reported that the crack growth rate of an Inconel alloy 182 was reduced significantly by lowering the ECP from 200 mV down to -100 mV vs. SHE in PWRs conditions. Monitoring the corrosion potential is one of the methods for identifying a risk of SCC. Figure 15 shows the effect of the potential on the crack growth rate of sensitised 304 SS in BWRs.

![Figure 15 SCC crack growth rate vs. corrosion potential for stainless steel tested at 288°C in high-purity water containing 2000 ppb O_2 and 95-3000 ppb H_2][18]

According to the mixed potential theory, in order to lower the ECP, the cathodic reaction rate can be lowered and/or the anodic reaction rate can be increased [64].
In practice, hydrogen oxidation provides the electrons needed in the reduction reactions of oxygen and radiolytically generated hydrogen peroxide. Therefore, with an insufficient hydrogen concentration, the need of electrons in the catalysed reduction reactions could enhance the oxidation of the material, hence promoting the susceptibility to IGSCC. According to Andresen [18], corrosion potential gradients at the crack tip are negligible in BWRs. These gradients in potential can occur if there is a consumption of the oxidants present in solution when they diffuse into cracks. In such cases, a concentration of anions such as chloride or sulfate may accumulate at the crack tip, encouraging metal ion hydrolysis and pH reduction. This phenomenon supports the slip-oxidation model [12] and is illustrated below in Figure 16.

Figure 16 Schematic of the crack tip when oxidants are present: 1) Oxidation of metal; 2) Hydrogen evolution; 3) Hydrogen oxidation 4) Oxygen reduction [18]

In PWRs, a rise in potential can be observed in the regions such as the dead space regions where oxygen may be trapped [1]. These regions are those that may be susceptible to SCC. Figure 17 shows the effect of dissolved oxygen on the electrochemical corrosion potential. From Figure 16 and Figure 17, it is clearly revealed that the dissolved oxygen concentration, the potential and the SCC susceptibility are
related. On the other hand, it has been reported that the critical potential for SCC in austenitic stainless steels corresponds to that of the onset for transpassivity [65].

![Figure 17](image)

**Figure 17** Corrosion potential versus dissolved oxygen concentration for carbon steel in high temperature water [21]

### 2.3.2.4.3 Effect of hydrogen and oxygen concentrations

Hydrogen and oxygen are the main agents affecting the ECP in the primary circuit of PWRs. The principal electrochemical reactions that influence the susceptibility to SCC in PWRs are given by Equations 5 and 6 [18].

**Equation 5** \[H_2 \rightarrow 2H^+ + 2e^- \quad E^\circ = 0 \text{ V vs. SHE} [18]\]

**Equation 6** \[O_2 + H_2O + 4e^- \rightarrow 4OH^- \quad E^\circ = 1.23 \text{ V vs. SHE} [18]\]

In order to keep the corrosion potentials sufficiently low, a satisfactory amount of hydrogen must be added. Indeed the dissolved oxygen concentration is one of the main parameters that raise the corrosion potential in PWRs. Between 80 and 100 ppb of dissolved oxygen, the cathodic reaction to consider is oxygen reduction and the potential is about -200 mV vs. SHE while for a low dissolved oxygen concentration, the
main cathodic reaction is hydrogen ion/water reduction at -600 mV vs. SHE. In most PWRs, the hydrogen level is estimated at 30 cc/kg, which is equivalent to 2.68 ppm. This concentration is enough to suppress the radiolysis [18]. In terms of the impact of dissolved hydrogen on the oxide film, a study has demonstrated that there was no major influence on the oxide structure for concentrations between 1 and 45 cc/kg at 320°C [33]. Figure 18 illustrates the oxide film thickness as a function of the dissolved hydrogen concentration for two different boron concentrations. An increase in the dissolved hydrogen content increases the oxide thickness, however the boron level increase does not influence significantly the oxide thickness for dissolved hydrogen concentrations between 0 and 45 cc/kg H$_2$O.

![Figure 18 Effect of dissolved hydrogen concentration on the oxide film thickness of type 316SS. Measurements performed using Auger Electron Spectroscopy (AES) [33]](image)

### 2.3.2.4.4 Effect of radiolytic species on ECP

The main source of oxidants in light water reactors is the radiolysis of water, which is considerably less than in BWRs [18]. Nevertheless, in PWRs, there is sufficient hydrogen to suppress radiolysis.
The concentration of the radiolytic products and therefore the value of the ECP differ consequently in the reactor water depending on the locations in the core. According to previous work, the radiolysis effect was found to depend on several factors such as the dose rate, the flow rate and the water chemistry [18].

2.3.2.4.5 Effect of anionic impurities

Several anionic impurities such as sulphate and chloride have been reported to accelerate the initiation and propagation of IGSCC in sensitised type 304 SS in high-temperature water [66, 67]. Sulphate may come from contamination due to oils or the atmosphere, anti-friction, de-oxygenated agents or degradation of ion exchange resins [68, 69]. As impurities affect the conductivity of the coolant, some researchers have investigated the conductivity to understand the effect of impurities on SCC. The general trend revealed an increase in the crack growth rate with the conductivity [62]. However this does not provide a clear understanding of the effect of a particular impurity and it is certainly not giving any information on the nature of the impurity. Sulphate and chloride are thought to be the most detrimental impurities for pitting and crevice corrosion of type 304 SS under Pars conditions, with sulphate being worse than chloride [70]. Apparently they accelerate the crack initiation of type 304 SS [19, 71, 72]. When sulphur is present in the alloy, it can be particularly harmful as it can facilitate hydrogen embrittlement.

2.3.2.4.6 Temperature

The temperature seems to have a significant impact on the crack growth rate of sensitised austenitic steels in PWR conditions [73]. Temperature influences the pH of the coolant, formation and stability of the different oxides, transport of ions and also the mechanical properties of the materials. Therefore temperature is obviously an important parameter influencing SCC resistance. A study using slow strain rate tensile (SSRT) test was conducted to investigate crack initiation and propagation in sensitised type 304 SS
in high temperature water. Results revealed that increasing the temperature decreased the time required for the first crack to initiate [19]. This is illustrated in Figure 19. However, the final number of cracks did not increase with temperature but was at its maximum at 150°C. This has not been explained clearly so far. Final time to failure was also influenced by temperature as shorter time to failure was observed with increasing the temperature as represented in Figure 20. This work showed as well that the mean crack propagation rate followed an Arrhenius relationship (see Equation 7) with activation energy of 8.76 kJ/mol. Crack propagation rate as a function of 1/T is presented in Figure 21.

**Equation 7**  
\[ k = A \exp\left(\frac{-Q}{RT}\right) \]

Where,

- \( k \) is the rate constant,
- \( A \) is a constant,
- \( Q \) is the activation energy (J/mol)
- \( R \) is the gas constant (8.314 J.K\(^{-1}\).mol\(^{-1}\)),
- \( T \) is the temperature (K)
Figure 19 Stress strain and current density strain from a slow strain rate tensile (SSRT) test of a type 304 SS in a dilute Na$_2$SO$_4$ solution at four temperatures using an initial strain rate of $8.3 \times 10^{-7}$ s$^{-1}$; triangles denote the strain where the first crack is observed [19].

Figure 20 Effect of temperature on total time to fracture (Tf), crack initiation time (Ti) and crack propagation time (Tp=Tf-Ti)[19].
Figure 21 Effect of temperature on mean crack propagation rate expressed as Arrhenius relation [19]

2.3.2.4.7 Flow rate

Work has been conducted to study the effect of flow rate on crack initiation of type 304 SS [74]. Slow strain rate tensile (SSRT) testing has been carried out in oxygenated water at 250°C on sensitised type 304 SS. The results revealed a longer time to failure for specimens submitted to higher flow velocity. The crack initiation time doubled with a flow velocity of 8 cm/s compared to that under static conditions. This was confirmed by other studies in similar environments and suggests that flow rate has a beneficial effect on crack initiation and propagation. On the other hand, the effect of flow rate on crack propagation has been investigated using compact tensile specimens (CT). According to a study on the effect of the flow rate on sensitised type 304 SS under high temperature conditions [75], an increase in the flow velocity would first increase the crack growth rate and then, lower it below the initial value. This was attributed to the enhanced rate of mass transfer of oxygen to the external surface of the crack; this would consume the current emanating from the crack mouth. This explanation is based on the
crack environment fracture model (CEFM) [76]. The decrease in crack velocity has been related to crack flushing. These observations implied that the crack’s internal and external environments are electrochemically coupled [77]. Figure 22 and Figure 23 display the crack opening displacement (COD) as a function of time. They both demonstrate that at higher stirring rates, which simulate the flow rate, COD rate decreased. This shows the effect of flow velocity and illustrates the fact that there are competitive influences of the stirring on mass transfer of oxygen to the external surface of the specimen and interchange of the solution inside and outside the crack. This effect was emphasised with higher flow rate. Indeed, the faster the flow rate, the shorter the transition between fast and slow crack growth rate.

![Figure 22](image1)

**Figure 22** Effect of a change in the stirring rate on the crack opening displacement (COD) vs. time for a sensitised type 304 SS CT specimen in 15 ppm NaCl + 150 ppb O₂ solution at 250°C [75]

![Figure 23](image2)

**Figure 23** Effect of a change in stirring rate on the crack opening displacement (COD) vs. time for a sensitised type 304 SS CT specimen in 25 ppm NaCl + 70 ppb O₂ solution at 250°C [75]
All in all, the previous investigations showed that higher flow rates reduced the time to failure for crack initiation. However, crack propagation seemed to be accelerated and then lowered with faster flow rates. These observations revealed that there are different stages in the effect of flow rates on crack initiation and crack propagation. From these laboratory results, it is difficult to predict the effect of flow rates after long-time exposure in PWRs. Indeed the crack initiation might be delayed with faster flow rates and the first stage of crack propagation might be high enough to be detrimental.

### 2.3.3 Phenomenology of cracking

Crack initiation and crack propagation are different stages and need to be investigated separately as they do not involve the same mechanism and processes. The propagation depends mostly on the electrochemistry and chemistry at the crack tip, the stress and degree of cold work.

### 2.3.4 Crack initiation

Crack initiation often occurs at physical surface defects, which can be grooves and laps resulting from fabrication process. Highly sensitised re-crystallised areas, pits and crevices can be the site of crack initiation. Cold-worked layers, where slip bands are present can also assist crack initiation.

### 2.3.5 Crack propagation

Different models have been proposed to explain the SCC. Under PWR conditions, it is still complex and unclear. According to Terachi [33], it is more likely to be a mechanism related to the corrosion behaviour as both the material composition and water chemistry are key parameters of the SCC response. The most important suggested models are reviewed as follows.

#### 2.3.5.1 Dissolution models

The anodic dissolution model is also called film rupture model or slip dissolution model. A schematic diagram of this model is displayed in Figure 24. In this mechanism,
the crack initiates and propagates in three stages, which are plastic strain and fracture of the protective film, oxidation/passivation of the crack walls and localised dissolution at the crack tip, and re-passivation of the crack tip. Observations of crack arrest markings and discontinuous cracks are an indication that crack propagation is discontinuous. Transgranular SCC shows fracture surfaces that are crystallographically oriented, flat and match on the opposite sides of the fracture surface and indicate very little dissolution during the crack growth. Therefore anodic dissolution models are attributed mostly to be intergranular stress corrosion cracking. A study on SCC of sensitised type 304 SS in thiosulfate solutions demonstrated that IGSCC was the mode of fracture, mostly enhanced by the sensitised microstructure. The presence of sulphate promoted IGSCC, however the slip dissolution model was not considered to explain the mechanism of cracking in the presence of sulphur although IGSCC was the fracture mode. Indeed, the crack length was of the order of one grain size and continuous. Consequently, these two points suggested another mechanism.

Figure 24 Schematic representation of crack propagation by the film rupture model [41]
2.3.5.2 Corrosion Tunnel Model

Corrosion tunnels occur by active corrosion on emerging slip planes. The metal is removed in the tunnels by growth and the final ligament resulting from the two tunnels undergoes ductile fracture. Figure 25 shows a schematic diagram of the corrosion tunnel model.

![Figure 25 Corrosion tunnel models: (a) schematic of tunnel model showing the initiation of crack by the formation of corrosion tunnel at slip steps and ductile deformation and fracture of the remaining ligaments; (b) Schematic diagram of the tunnel mechanism of SCC and flat slot formation[41]](image)

2.3.5.3 Film induced cleavage model

This model assumes that a thin film of low fracture toughness forms on the surface, a brittle crack crosses the film/matrix interface with little loss in velocity and then the brittle crack propagates and arrests into the ductile matrix, with the process repeating
once the film is re-formed. This model explains the crack arrest markings, the cleavage-like facets on fracture surfaces and the discontinuous nature of crack propagation.

### 2.3.5.4 Adsorption induced brittle fracture

This model assumes that species from the environment are adsorbed and it lowers the interatomic bond strength and the stress required from cleavage fracture. This model predicts continuous crack propagation at a rate determined by the arrival of the embrittling species at the crack tip. The crack grows until it is blunted by plastic deformation.

### 2.3.5.5 Hydrogen embrittlement

Hydrogen embrittlement is a possible mechanism of SCC. It involves absorption of hydrogen into the material, followed by a reduction in the ductility and load-bearing capacity of the metal causing cracking and catastrophic brittle fracture at stresses below the yield stress. Several models can explain hydrogen embrittlement:

The pressure theory attributes hydrogen embrittlement to the diffusion of atomic hydrogen into the metal and its eventual accumulation at voids or other internal surfaces in the alloy. As the concentration of hydrogen increases at these microstructural discontinuities, a high internal pressure is created that initiates void growth or cracking. This model does not explain many factors of hydrogen stress cracking. For instance, the plastic deformation due to void formation is not seen and high hydrogen fugacity is required for localised high pressure conditions.

The surface adsorption theory suggests that hydrogen is adsorbed on the free surfaces created adjacent to the crack tip, decreasing the surface free energy and thus the work for fracture. The problem with this model is that it underestimates the work for fracture and does not account for the discontinuous crack growth observed for hydrogen cracking.
The decohesion model describes the effect of hydrogen on the cohesive forces between atoms of the alloy matrix. Hydrogen can weaken interatomic cohesive forces at, or ahead of, crack tips resulting in tensile separation of atoms.

The enhanced plasticity model is associated with hydrogen dislocation interactions and is primarily based on fractographic observations. Hydrogen is thought to enhance dislocation motion and the creation of dislocations at the surfaces of crack tip, leading to softening of the material on a localised scale.

Figure 26 Schematic representation of the corrosion enhanced-plasticity mechanism [78]

Several researchers have reported increased hydrogen concentrations near stress corrosion cracks in stainless steels in high purity water. According to Young [79], the crack tip of nickel-based alloys and austenitic stainless steels in high purity water is intergranular along the crystallographic grain boundaries. This suggests that the mechanism follows the decohesion model. In addition, the crack tip observed with transmission electron microscopy (TEM) and electron backscattered diffraction (EBSD) did not reveal an increased strain gradient. Other studies showed that hydrogen embrittlement was the most likely mechanism in sensitised type 304 SS in the presence of thiosulfate. This was based on the fact that sulphur catalyses the entry of hydrogen
into the matrix ahead of the crack tip [80, 81]. This suggests that in PWRs, if sufficient amount of sulphur is present (e.g: from contamination or the degradation of ion exchange resin), type 304 SS may suffer from SCC caused by hydrogen-induced cracking (HIC). Further investigation showed that 0.5 M sodium thiosulfate solution could initiate and propagate cracking regardless of the applied load. Unloaded specimens revealed IGSCC as well as loaded specimens; the rate the corrosion was accelerated by the applied load [80].

2.3.5.6 Internal oxidation

Internal oxidation is a model in which oxygen dissolves in the alloy, diffuses into the alloy matrix and causes sub-surface precipitation of oxide particles of one or more alloying elements (Fe, Cr, Ni). According to a study on the oxidation behaviour of the crack tips of type 304L SS in high temperature oxygenated water, oxygen plays a key role in nucleation and propagation of SCC cracks. Oxidation along the slip bands was observed for transgranular stress corrosion cracking [82]. For the intergranular stress corrosion cracks, oxidation took place prior to nucleation and growth of microcracks in the oxide ahead of the crack tip on the grain boundary plane.

2.3.6 SCC of alloy 600 in PWRs

2.3.6.1 Introduction

Stress corrosion cracking in pressurised water reactors has been investigated extensively since the last 30 years. Many studies have been conducted on Alloy 600, therefore it is important to give a brief discussion on the SCC of Alloy 600 in PWRs. Alloy 600 has shown cracks in the tubing used in steam generators of PWRs [83].

Material composition and heat treatment

Alloy 600 is a nickel base alloy composed of 72 wt% Ni minimum, 14 – 16 wt% Cr, 4 - 6 wt% Fe [16].
2.3.6.2 SCC mechanism of Alloy 600 in PWRs

Researchers have worked on the cracking mechanisms involved in PWR conditions. One of the alternatives to Alloy 600 is the alloy 690, which contains a higher chromium level. Therefore it lowers the risk of chromium depletion which enhances intergranular attack (IGA) and intergranular stress corrosion cracking (IGSCC) susceptibility. A study on the SCC mechanism of U-bend samples made of Alloy 600 used in the primary side of PWRs has been conducted using advanced transmission electron microscopy (TEM). It revealed that at 330°C, ultrafine oxide was present inside cracks. The results showed the presence of Cr$_2$O$_3$ oxide and Ni-rich metal zones at the majority of crack tip areas and where intergranular attack occurred. This suggested that chromium oxide growth in the grain boundary is involved in the SCC mechanism; therefore both oxygen and chromium diffusion processes. A proposed mechanism in this study is that oxygen could diffuse through nanocrystalline oxide while chromium diffusion would results from strain in grain boundary beyond crack tip [84].

The cracking mode of Alloy 600 in the primary side of PWRs can be both intergranular and transgranular.

SCC of Alloy 600 is rather complex and there is not defined mechanism that has been established so far. Nevertheless, internal oxidation and environmentally assisted creep are the most likely mechanisms to consider. In the primary side, cracks have been detected at the tube sheet in the expansion transition region, at the support region, in the tightest region of the U-bend region. This suggests that a plastically deformed material is susceptible to SCC in PWRs [83].

2.3.6.3 Parameters affecting SCC susceptibility of Alloy 600 in PWRs

As it was explained for type 304 SS, the corrosion potential is also one of the key parameters controlling the primary water stress corrosion cracking (PWSCC) susceptibility of Alloy 600. The well known domain intergranular attack (IGA) and
intergranular stress corrosion cracking (IGSCC) of Alloy 600 is presented in the Pourbaix diagram below (see Figure 27). Later Totsuka and Smialowska conducted constant extension rate testing (CERT) at different applied potentials and hydrogen pressure in a solution of 0.01 M H$_3$BO$_3$ + 0.001 M LiOH, at 350°C. The results revealed that IGSCC was more pronounced near the corrosion potential, which coincides with the Ni./NiO equilibrium [85].

Cold work is also a key parameter affecting SCC susceptibility. So cold worked materials, where plastic deformation has been induced may be more susceptible to SCC. A study on SCC growth rates in simulated PWR environment has been carried out. The findings reveal that increasing the cold work effect from 8% to 20% increase significantly the crack growth rate and this is even more pronounced when compared to the as-received material. The influence of cold work on the crack growth rate has been investigated by analysing the crack tip mechanics and the change of sub-microstructure after severe cold work and their interaction with the crack tip oxidation kinetics [86].
2.3.7 SCC testing of type 304 SS

In order to investigate SCC, testing can be performed electrochemically or mechanically at room temperature or high temperature. In the following sections, some of the possible tests to assess SCC are described.

2.3.7.1 Environments to simulate intergranular stress corrosion cracking (IGSCC)

As IGSCC may occur for type 304 SS in occluded regions under PWR conditions, investigation is required to overcome this problem. There exist environments that can
simulate IGSCC at room temperature. Sulphur species are now well known to enhance IGSCC in austenitic stainless steels and nickel-base alloys [71, 88-91]. Polythionic solutions have been widely used to enhance IGSCC on sensitised stainless steel [81, 89, 92, 93]. The chemical and electrochemical reactions involved are relatively complex as sulphur may exist in a wide range of oxidation state [94]. During the corrosion process of sensitised type 304 SS in thiosulfate solution at pH=7, the characteristic smell of H\textsubscript{2}S gas was noticeable and the test solution turned to yellow. These observations are thought to result from the disproportionation reaction (see Equation 8-Equation 11).

**Equation 8**

\[ \text{S}_2\text{O}_3^{2-} + \text{H}^+ \rightarrow \text{S} + \text{HSO}_3^{2-} \]  

Or possibly,

**Equation 9**

\[ 5\text{S}_2\text{O}_3^{2-} + 6\text{H}^+ \rightarrow 2\text{S} + 2\text{S}_4\text{O}_6^{2-} + 3\text{H}_2\text{O} \]

**Equation 10**

\[ 3\text{S}_2\text{O}_3^{2-} + 2\text{H}^+ \rightarrow 4\text{S} + 2\text{SO}_4^{2-} + \text{H}_2\text{O} \]

**Equation 11**

\[ \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + \text{SO}_4^{2-} \]

Post examinations of the solution and samples revealed the presence of sulphur deposit in the solution and on surface of the samples. Potassium tetrathionate has been used many times to investigate the effect of sulphur in simulated PWR environments. According to Lee and Kim, potassium tetrathionate is found on the surfaces of tubes of steam generators in PWRs [88]. Investigation of the corrosion behaviour in potassium tetrathionate has been performed at different pH on sensitised type 304 SS. Results showed that the pH played a critical role in the IGSCC susceptibility of the alloys and especially on the anodic dissolution rate. Acidic pH showed greater metal dissolution and severe material damage for pH between 1 and 2 [89]. In addition, one of the detrimental effects of sulphur was associated with the catalysis of the dissolution of Cr-depleted regions in sensitised type 304 SS, thus making sulphur a component of SCC [80].
2.3.7.2 The different mechanical tests

Mechanical testing is widely used to investigate SCC. Whether it is to study crack initiation, crack propagation, transition between crack initiation and crack propagation, the sample design and mechanical tests differ. Therefore, three main tests are commonly conducted:

- Tests on statically loaded smooth samples
- Tests on statically loaded pre-cracked samples
- Tests using slowly strained samples

The three techniques are explained and reviewed below.

2.3.7.2.1 Tests on statically loaded smooth samples

The tests on statically loaded smooth samples are conducted at various fixed stress levels and the time to failure is measured. These experiments can be used to determine the maximum stress intensity factor $K_{IC}$, which is defined as the plane-strain fracture toughness corresponding to the minimum plane strain conditions required for crack propagation to occur. It is critical that the tested samples have the same surface finish and history for an optimal and reliable analysis of the results.

Tests on loaded smooth samples such as U-bend can simulate tensile stress combined with elastic and plastic deformation. These samples are of interest to investigate crack initiation implying plastic deformation [95].

2.3.7.2.2 Tests on statically loaded pre-cracked samples

These tests are usually applied with a constant load or fixed-opening displacement. The actual crack growth rate $da/dt$ is measured. The magnitude of the crack distribution at the crack tip is measured with the stress intensity factor $K$ for the specific crack and loading geometry. The different pre-cracked sample types are presented in Figure 28. These tests are conducted to evaluate crack propagation as it is much easier to detect the mechanical precrack and the stress corrosion crack resulting from crack propagation.
For pre-cracked samples and crack propagation investigations, a notch is machined on the sample as shown in Figure 28. However, in order to investigate crack propagation, a sharp crack must have initiated and the machined notch can facilitate the initiation. To initiate cracking from a notch, fatigue is one of the most widely used techniques as it can generate mechanical cracks easily. The most common samples used are the compact tension (CT) samples. There are also the circumferential cracked bar (CCB) samples. Both types of sample can be fatigued in order to generate fatigue pre-cracks.

Ibrahim and Kotousov [96] have studied the circumferential cracked bar (CCB) samples versus compact tensile (CT) samples to determine the fracture toughness. They showed that CT specimens are obviously bigger in size and more difficult to machine, therefore it is more expensive and time consuming. CCB samples in rotating fatigue machines revealed successful results in terms of fatigue precrack generation. Indeed, uniform and circular pre-cracks can be obtained by fatigue of CCB samples [96-99]. They present many advantages and especially to investigate crack propagation as the uniformity of the fatigue precrack generated results with a uniform stress intensity factor on the specimen. Therefore crack propagation study is facilitated. In addition, this specimen can achieve the plane strain conditions, which is one of the conditions to represent bigger structures. Obviously, some requirements are needed to meet this condition. Indeed, the sample dimensions must be such that the average stress across the final ligament must not exceed 2.5 times the yield strength of the material to avoid general yielding of the final ligament. In the case of higher stress, the plane strain condition would not be achieved [97]. Moreover, the radius of the plastic zone ahead of the crack tip must be small enough, at least half of the fatigue crack length [100]. This is a condition explaining the fact that the crack tip zone should not be influenced by the free surface of the CCB sample and by the axis of symmetry that can be considered as a
boundary. The plastic zone diameter also known as the Irwin correction factor for a CCB sample in plane strain conditions is given by Equation 12.

\[
\text{Equation 12} \quad r_0 = \frac{1}{6\pi} \left( \frac{K_{IC}}{\sigma_y} \right)^2 \quad [96, 100]
\]

Where,

- \( r_0 \) (m) is the plastic radius,
- \( K_{IC} \) (MPa√m) is the fracture toughness of the material,
- \( \sigma_y \) (MPa) is the yield strength of the material

Ibrahim and Kotousov [96] also investigated the eccentricity that may be present in the final ligament of the CCB samples that underwent fatigue in a rotating fatigue machine. In this case, the sample rotated under a bending moment and a non-uniform crack may have resulted from the anisotropic mechanical properties of a material as well as a defect in the material. This was also confirmed by Rihan et al. who investigated caustic (in alkaline environments) crack propagation of CCB specimens [99]. Figure 29 displays a photograph of the notch, the fatigue crack, stress corrosion crack propagation and the final mechanical ligament resulting from tensile failure. Fatigue precrack monitoring can be performed by using a direct current potential drop (DCPD) method [101] or a deflection measurement method that evaluates the deflection of the specimen due to the bending moment and relates it to the fatigue precrack length after its measurement under tensile failure. The potential drop technique makes use of an increase in electrical resistance of a conducting material due to crack initiation and growth. A constant current is passed through a specimen and the potential drop between probes on either side of a crack is measured. For direct current, the current distribution is uniform; therefore the potential drop between two points will be proportional to the distance between these two points. The increase in potential drop is due to the reduction of specimen cross-sectional area resulting from crack initiation and propagation.
Although the DCPD technique remains the most common technique to detect crack initiation and propagation, there are some disadvantages. Indeed, this technique has shown better performances for the detection of long cracks in materials that do not require large currents to measure a detectable potential drop. However, there are some difficulties in the detection of small cracks (less than a grain size) in common specimen geometries. Apparently it is necessary that the stability of the applied current is such that the variation in the specimen current is less than 0.01% and this degree of stability is easy to achieve for small currents [101].

Figure 28 Classification of pre-cracked samples for SCC testing [41]
2.3.7.2.3 Tests on strained samples

SCC testing can also be conducted using slow strain rate tensile (SSRT) test. Figure 30 shows a representative schematic of a SSRT apparatus. The principle is based on increasing slowly the load or strain on smooth or pre-cracked samples. There is a continuing plastic strain at the surface of the samples that encourages initiation and growth of SCC. The test is used to compare the relative susceptibility of alloys to cracking in an environment. In order to investigate the effect of cold work, slow strain rate testing is appropriate as it imposes a constant deformation rate in the material that can evaluate the effect of cold work against a test in air [102]. Potentiostatic measurements can be performed during the test by applying the potential of the regions promoting SCC. From a general point of view, these regions are the active-passive transition and the passive-transpassive-transition for type 304 SS (see Figure 14). Fractography can also be performed to measure the number of cracks and analyse the
fracture mode (IG, TG etc). SCC can also be assessed from percentage of reduction area (%RA) and time to failure (tf). On the other hand, (SSRT) tests are not very appropriate to predict the crack propagation rate as crack initiation and crack propagation are confused.

Figure 30 Schematic of a slow strain rate tensile (SSRT) test apparatus [41]
2.4 Platinum Group Metals (PGM)

2.4.1 Introduction to PGM additions

Noble metal enriched surfaces on stainless steels and related corrosion-resistant alloys have shown better corrosion resistance compared to the original metals in many applications. Extensive research has been conducted on the PGM effect on carbon steel, stainless steel and titanium in reducing acid media since the 1960s. More recently investigation has been undertaken on the effect of PGMs on Ni-base alloys and stainless steels used in high temperature water. Different techniques exist to produce surface enriched materials such as electroless plating, vapour deposition of pure or mixed noble metals, thermal spray coating of noble metal alloy powders, weld cladding and direct alloying. These techniques are briefly reviewed in the following sections as well as the advantages and drawbacks that noble metal additions have revealed in acid media and in high temperature water so far.

2.4.2 Techniques for PGM surface enrichment

Surface alloying with a platinum group metal is an economical process that requires relatively little noble metal to improve the surface corrosion resistance in many environments. Surface alloying can be performed in many ways which are described below:

- Thermal spraying: This method produces noble metal doped coating using powder. It can be conducted by high-velocity-oxygen-fuel (HVOF) or plasma spray (PS) techniques. This process has promoted corrosion resistance of stainless steel in sulphuric acid for instance; its efficiency has been confirmed by many authors [13, 103].

- Electroless plating is another method for surface alloying. It is conducted by immersing the alloy in a solution containing a noble metal such as $[\text{Na}_2(\text{PtOH})_6$ [13]. Electroplating may be also used to produce a noble metal coating [104].
• Direct alloying of noble metals may also create a catalytic surface. Work performed on the effect of PGMs on the potential of structural materials used in BWRs revealed that very small amounts of PGM such as 1 wt% and below were necessary to lower the potential below the critical value to mitigate SCC (-230 mV vs. SHE). In addition, it was shown that 1 wt% Pd is as efficient as pure platinum in lowering the potential. This was accomplished under BWR conditions with sufficient amount of hydrogen [105].

2.4.3 Introduction to noble metal chemical addition (NMCA)
This technique was used to overcome the problem of IGSCC in BWRs when hydrogen addition was found to be sometimes detrimental in certain parts of vessels. Indeed, high hydrogen levels led to an increase in the main steam radiation level from volatile $\text{N}_16$ [106]. Noble metal chemical addition (NMCA) has efficiently achieved low potentials in BWRs by catalytically reacting oxidants such as oxygen $\text{O}_2$ and hydrogen peroxide $\text{H}_2\text{O}_2$ with hydrogen. The application of NMCA to structural materials subject to high temperature water has been extensively studied and it is now an accepted method to mitigate SCC in BWRs. The hydrogen level must be in stoichiometric excess to the amount of oxygen in order to form water. Potential measurements have demonstrated values below -230 mV vs. SHE, which is the critical potential below which SCC is mitigated [107-110].

Research has been carried out extensively in acid media. The following section presents the effect of PGM additions in acid media. Even though, it does not represent the environment in PWRs, it is of great interest to understand the influence of PGMs on the kinetics, which drive the corrosion potential.
2.4.4 Introduction to PGM-doped titanium alloys

Many grades of titanium alloys exist to increase mechanical properties and corrosion performances in a wide range of environments. Among them, there are Ti-alloys composed of PGM additions, therefore it is interesting for this PhD study to give a brief outline on the influence of PGMs on the corrosion resistance of titanium.

Titanium has good corrosion resistance in oxidising acids such as nitric acid, chromic acid and perchloric acid over a wide range of concentrations and temperatures. Titanium has been used for handling and producing nitric acid in replacement of stainless steel, which showed uniform and intergranular attack. At high temperature, titanium’s corrosion resistance depends highly on the purity of nitric acid. In addition, in reducing acid media such as hydrochloric acid and sulphuric acid, titanium has also poor corrosion resistance and it is worse with increasing the concentration and temperature of the environment. Therefore the alternative of using titanium alloys containing containing small amount of noble metal has revealed better corrosion performance.

In order to overcome the high cost of palladium doped-Ti, ruthenium doped-Ti-alloys were developed from 1994 [111] and evaluated for industrial service in corrosive environments such as dilute reducing acid media, oil & gas and concentrated brine (MgCl₂ and CaCl₂) environments [112]. This led to new grades of Ti-alloys containing PGM additions. Table 3 presents some of the titanium alloys containing PGM additions commonly used in industry. Sections 2.4.5.1 and 2.4.5.4, discuss respectively the influence of palladium and ruthenium additions to titanium in reducing acid media and on SCC resistance.
Table 3 Table of the composition of titanium and titanium alloys [16, 112]

<table>
<thead>
<tr>
<th>ASTM Grade</th>
<th>Nominal composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Commercially pure (unalloyed) Ti</td>
</tr>
<tr>
<td>2</td>
<td>Commercially pure (unalloyed) Ti</td>
</tr>
<tr>
<td>7</td>
<td>Grade 2 + 0.15 wt% Pd</td>
</tr>
<tr>
<td>11</td>
<td>Grade 1 + 0.15 wt% Pd</td>
</tr>
<tr>
<td>16</td>
<td>Grade 2 + 0.05 wt% Pd</td>
</tr>
<tr>
<td>17</td>
<td>Grade 1 + 0.05 wt% Pd</td>
</tr>
<tr>
<td>26</td>
<td>Grade 1 + 0.1 wt% Ru</td>
</tr>
<tr>
<td>27 (soft grade)</td>
<td>Grade 1 + 0.1 wt% Ru</td>
</tr>
</tbody>
</table>

2.4.5 Effect of PGM in acid media

2.4.5.1 General corrosion

In this part, the effect of PGM on the corrosion behaviour of different structural materials in acid media is reviewed. This has been studied for a long time and relatively good performance of PGM additions are revealed in terms of improving corrosion resistance in non oxidising media such as sulphuric acid [113]. The basic mechanism of cathodic modification is well understood from the late 1960s. Cathodic modification by using PGMs to improve the corrosion behaviour is based on four criteria which are explained as follows and illustrated in Figure 31 [111].

- The alloy must be able to passivate in the environment
- The alloy must be easily passivated, which means that the current density $i_{an}$ corresponding to the anodic peak must be small enough to be exceeded by the cathodic reaction
- The cathodic alloying element must be a favourable surface for hydrogen evolution, which means a high exchange current density for hydrogen evolution
- The passive region of the base alloy must extend over a wide range of potentials and the ECP of the cathodically modified alloy must be between the potential of passivation $E_p$ and the potential of transpassivation $E_t$.

![Cathodic modification diagram](image)

**Figure 31** Schematic diagram of the principle of cathodic modification; the dashed blue line represents the standard alloy and the red line represents the cathodically modified alloy [111]

On ferritic steels, the beneficial effect of PGMs increases with the Cr level. This process is known as cathodic modification and is based on alloying with a metal that has a high exchange current density for hydrogen evolution. Therefore, the alloy exhibits passivity over a wider range of environments. In the early stages, Stern [7] investigated the noble metal additions on stainless steels and they showed that corrosion resistance was significantly improved by using 0.5 wt% PGM. Below this concentration, the corrosion behaviour was still improved but was not optimum while above this level, it remained steady. A comparison between the different noble elements revealed that the greatest result was observed with the elements that presented higher exchange current density for hydrogen evolution. Potgieter [2] investigated different alloys that were cathodically...
modified using noble metal additions. Addition of 0.1 to 0.4 wt% Pd to chromium base alloys enhanced self-passivation in sulphuric acid and an enrichment of palladium was observed during the active dissolution stage. However, the dissolution of a certain volume of the material has presented an adverse consequence when insufficient palladium content was added as it only enhanced corrosion (metal dissolution) and not aestivation [114]. On duplex stainless steel, Ru additions have shown a beneficial effect in terms of anodic dissolution and self-passivation in sulphuric acid at 25°C [115]. Figure 32 displays the electrochemical potentiodynamic behaviour in H2SO4 at 25°C. With no Ru additions (standard alloy), the electrochemical corrosion potential was lower than that of the same alloy containing ruthenium additions and the effect increases as the Ru content is increased. The self passivation of the doped alloy was obvious as compared with the standard alloy. Only a small amount of ruthenium (0.14%) was enough for self passivation. A decrease in the anodic passive current was also observed for the doped alloys. The shift of the ECP towards more positive values for the doped alloys can be explained by the self passivation behaviour resulting from the ruthenium additions. The cathodic electrochemical reaction involved in this process is probably hydrogen evolution (2H⁺ + 2e⁻ → H₂). This reaction is catalysed by ruthenium, which has a high exchange current density for hydrogen evolution; therefore the ECP of the cathodically modified alloy is raised towards more positive values. On the other hand, similar work has been conducted in hydrochloric acid (see Figure 33). The beneficial effect of ruthenium additions to duplex stainless steel was also demonstrated in the sense that the anodic dissolution was less pronounced. However, active corrosion was still observed despite the presence of Ru. This revealed that the corrosion was more severe in hydrochloric acid than in sulphuric acid [116]. This could be explained by the presence of chloride that promotes pitting. More details are given on the effect of PGMs on pitting resistance in section 2.4.5.2. By contrast, self-
passivation of Ti-containing PGMs such as palladium and ruthenium in sulphuric acid is well established. Traditionally grade 7 and grade 11 Ti-alloys are used in reducing acid media. Indeed the palladium has a beneficial effect as it lowers significantly the corrosion rate as shown in Figure 35. Increasing the hydrochloric concentration increases the corrosion rate of Ti-alloys. Nevertheless additions of palladium lower the corrosion rate. It is important to highlight that from 0.05 wt% Pd, increasing the palladium content does not affect the corrosion rate. This suggests that palladium surface enrichment is not improved above 0.05 wt% Pd. Ruthenium additions to Ti-alloy exert the same effect as palladium additions in hydrochloric acid as shown in Figure 36. The beneficial effect of palladium and ruthenium was attributed to the alloy ennoblement. In other words, both palladium and ruthenium exhibit minimal solubility (less than 0.1 wt%) in the bcc titanium phase. This results in a fine and uniform dispersion of Ti-Ru precipitates within the alloy. This surface enrichment results from selective dissolution. The mechanism by which PGM additions enhance corrosion resistance in reducing acid media is called cathodic modification and is displayed in Figure 34 [117].
Figure 32 Potentiodynamic curves for a series of duplex stainless steel in 1 mol.dm$^{-3}$ H$_2$SO$_4$ at 25°C: (a) 0% Ru; (b) 0.14% Ru; (c) 0.22% Ru, (d) 0.29% Ru [115]

Figure 33 Potentiodynamic curves for a series of duplex stainless steel in 1 mol.dm$^{-3}$ HCl at 25°C: (a) 0% Ru; (b) 0.14% Ru; (c) 0.22% Ru, (d) 0.29% Ru [115]
Figure 34 Evans diagram showing how alloying titanium with PGMs achieves passivation in reducing acids via cathodic depolarisation [117]

Figure 35 Effect of the palladium content on the titanium corrosion rate in boiling hydrochloric acid solution [112]
2.4.5.2 Effect of PGM on pitting

Research [106] conducted on surface segregation showed that palladium segregates on the surface of high chromium ferritic stainless steels by forming small nuclei-islands (see 2.4.5.6) [118]. This confirmed previous positive points in terms of pitting resistance and crevice corrosion resistance. However, work performed in hydrochloric acid showed that Pd additions to stainless steels revealed a greater weight loss increasing with the palladium content. As chloride is usually the aggressive agent in pitting corrosion, chloride environments were used to investigate the pitting resistance of doped and standard alloys. Russian workers [114] have found that palladium additions both accelerate pitting as well as broadening the range of concentration and temperature over which the alloys are passive. This suggests that palladium additions could be detrimental to localised corrosion resistance of stainless steel in the presence of chloride but the reasons why these happen remain unclear. Recent work [119] has been conducted on the effect of palladium on localised corrosion of titanium. This was carried out by performing cyclic potentiodynamic polarisation (CPP) in order to determine the pitting potential Epit as well as the repassivation potential Erp for different chloride concentrations in deaerated solutions at 95°C. The measurements
were performed on grade 2 Ti and grade 7 Pd-doped Ti and revealed that the higher the chloride content, the more negative Epit and Erp. In other words, the pitting susceptibility increased with the chloride concentration [119]. These results are consistent and were expected as chloride is an aggressive agent promoting pitting. The Pd-doped alloy showed a more positive Epit and Erp than the standard alloy, so palladium additions revealed a beneficial effect in terms of pitting resistance for Ti-alloys, see Figure 37 (It should be noted that the potentials displayed are certainly too high and there must be an error in the scale or measurements). This was attributed to the catalytic effect of Pd to enhance hydrogen evolution and help passivation.

Figure 37 Effect of chloride concentration on the pitting (Epit) and repassivation potentials (Erp) for standard Ti grade 2 and Pd doped Ti grade 7 in deaerated solution at 95°C [119]

2.4.5.3 Hydrogen embrittlement

PGM additions have been extensively studied and their effect on different types of corrosion has been reported. In the case of hydrogen embrittlement, work demonstrated that palladium addition improved the resistance to a form of hydrogen embrittlement known as “flaking”. This is a form of hairline cracking and it does appear as flakes or round spots on the metal surface. In a study [120], samples containing different palladium concentrations were charged with hydrogen for five hours at 1100°C, and left
at room temperature for ten days prior to annealing at 650°C. The samples were then fractured and the flake density was taken. The results revealed that the flake density decreased with an increase in the palladium content and became zero with 0.3 to 0.5 wt% Pd. Further work on the solubility of hydrogen as well as on the proportion of absorbed hydrogen evolved at 400°C (temperature at which hydrogen evolution was maximum) showed that the solubility of hydrogen was not affected by the palladium amount. However, the proportion of absorbed hydrogen evolved at 400°C was significantly less for the alloys containing 0.3 to 0.5 wt% Pd. One of the explanations suggested that palladium in this range of concentrations could modify the hydrogen trap site within the steels (Russian designation: $34\text{KhN}_3\text{M}$ and $34\text{KhN}_3\text{T}$).

### 2.4.5.4 Effect of PGM on stress corrosion cracking behaviour

Stress corrosion cracking behaviour of PGM-doped alloys has been investigated using MgCl$_2$ media. Hanninen [114, 121] reviewed the effect of noble metals on SCC and the general findings indicated a detrimental effect, which was also confirmed by Chaudron [114, 122] who showed a reduction in the lifetime of 18 Cr-10 Ni austenitic alloys with increasing Pt content in boiling magnesium chloride. By contrast no detrimental effect was observed by Streicher [114] for Fe-28Cr - 4Mo ferritic alloys in sodium chloride. Both test solutions (magnesium chloride and sodium chloride) are often used to evaluate the risk of SCC. The contradicting results obtained in these two solutions suggest that SCC testing should be undertaken with caution and more particularly the material should be investigated in the environment of interest.

Investigations on the high strength Ti-alloy grade 5, which contains 6 wt% Al and 4 wt% V has shown poor resistance to SCC in brine and aqueous halides. To overcome this problem, 0.1 wt% Ru was added resulting in new grades Ti-alloys (grades 9 and 29). The mechanism by which SCC resistance is improved is also cathodic modification. One important point highlighted is that ruthenium additions do not alter
the mechanical properties of the base-alloy. This suggests that the ultimate tensile strength does not change with PGMs, therefore dislocation motion is not affected by PGMs. The metallurgy of a material is clearly important to understand the PGM surface enrichment as the precipitates formed with PGMs vary with the alloy composition, which influence the corrosion resistance.

SCC susceptibility of Ti-alloys has also been observed in nitrogen tetroxide (N$_2$O$_4$), liquid or solid cadmium and anhydrous methanol (azome, keytometal.com). In the late 1960s, pressurised fuel tanks made of titanium alloy grade 5 failed while containing methanol under pressure. The results revealed the presence of SCC. Investigations suggested the use of moisturised methanol to lower the SCC susceptibility [123]. Later on in the late 1990s, the use of Ti-alloys containing PGM additions has demonstrated better SCC resistance as higher concentration of methanol were used with Ti-alloys composed of ruthenium (e.g: grade 29) [16]. A comparative study on the effect of methanol on Ti alloys grade 28 and grade 29 revealed that HCl acidification increased methanolic SCC of both Ti-alloys. However, mixing methanol with crude oil or pure hydrocarbons, H$_2$S gas or increasing temperature lowered SCC susceptibility. The SCC mechanism involved in anhydrous methanol are not fully understood but what is known is that methanol must be moisturised to increase SCC resistance and the concentration of moisture decreases with increasing the PGM content.

**2.4.5.5 Simultaneous effect of PGMs and alloying elements**

The simultaneous addition of PGM with other elements such as Mo has been reported by Tomashov [124] as being adverse. It seemed that the range of concentrations and temperatures in which the high chromium ferritic steel self-passivated was narrower in sulphuric acid although the film was more stable. Biefer investigated stainless steel alloyed with Pd and Mo and he also mentioned that the properties of the film were improved. Ferritic steels containing 3 wt% Mo and 0.5 wt% Pd passivated in sulphuric
acid containing 2 to 3% NaCl. This showed the beneficial effect of molybdenum as in
the absence of molybdenum, palladium additions revealed an adverse effect in chloride
media (see section 2.4.5.2). This is due to the beneficial properties of molybdenum in
terms of localised corrosion resistance. Potgieter [2] [125] suggested that molybdenum
could lower the anodic dissolution current density, increase the passive range and
increase the effectiveness of the cathode process by lowering the hydrogen overvoltage
on molybdenum. These effects are summarised in Figure 38.

![Figure 38 Summary of the effect of alloying additions on the polarisation characteristics of Fe-Cr stainless steels in sulphuric acid [2]

2.4.5.6 Film characterisation

In reducing acid media, the passive film formed on alloys modified with noble metal
additions has been extensively characterised using different techniques. Potgieter [115]
studied the corrosion behaviour of ruthenium modified duplex stainless steel in
sulphuric and hydrochloric acids. He observed that ruthenium segregated on the surface,
giving better corrosion resistance in reducing acid media. According to Van der Lingen
who investigated the corrosion behaviour of Ti-doped with ruthenium in hydrochloric
acid, ruthenium forms a second phase with titanium and iron [111]. Film charac-
terisation of different materials in reducing acid media revealed that PGMs do not surface enrich similarly. Indeed, palladium and ruthenium have shown consequent dissimilarities in terms of passive film composition and characteristics. Palladium seems to form nuclei of islands on the surface while ruthenium is included in the composition of the oxide and hydroxide formed in acid media [126]. These observations suggest that the mechanism by which PGMs cathodically modify an alloy may be different. Numerous studies revealed that the size of palladium particles on surface were very dependent on the temperature at which dissolution takes place, the kind of acid and the palladium concentration [127]. Potgieter [128] mentioned that the accumulation of PGMs on surface was during the period of active dissolution. He also suggested that there were two ways to inhibit the corrosion process. The first one is by increasing the efficiency of the cathodic process such as hydrogen evolution and the second one is by inhibiting the anodic dissolution of the alloy to which they are added. In order to understand how these processes function, Higginson [8] proposed three possible mechanisms to explain the distribution:

- dissolution of the PGMs followed by diffusion through the electrolyte and electrochemical deposition of PGMs on surface;
- volume diffusion of the PGMs atoms;
- surface diffusion of the PGMs atoms.

The first mechanism was not considered to be valid especially at later stages of corrosion. Indeed, Potgieter confirmed the active dissolution of the metal surface while PGMs were accumulating. The models have not been fully understood as the volume diffusion and surface diffusion would not imply any dissolution. Another point to highlight is the low diffusion rate of PGMs at room temperature would not validate the
volume diffusion model. So the more sensible mechanism would be the surface diffusion model.

2.4.6 Effect of PGM in high temperature water

2.4.6.1 Electrochemistry

Previous investigations [107, 108, 129] showed that PGM additions could lower the corrosion potential below the critical value to mitigate SCC in BWRs. Under BWR conditions, from 0.1 wt% PGM additions, the ECP of type 304 SS was significantly reduced as shown in Figure 39. The molar ratio H₂/O₂ affected the ECP response of the materials. From a molar ratio of 2, which corresponds to the stoichiometric conditions to form water, the ECP remained low enough and stable. According to Kim et al [108, 130], the ECP behaviour of standard and doped type 304 SS can be explained by the Evans diagram which displays the potential as a function of the logarithm of the current density (see Figure 40). The corrosion potential is based on the mixed potential theory suggested by Wagner and Traud [64]. In high temperature water, the main cathodic and anodic reactions on metal surfaces are respectively oxygen reduction and hydrogen oxidation; see Equations 13 and 14.

\[
\text{Equation 13} \quad \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \\
\text{Equation 14} \quad \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- 
\]

The Evans diagram shows that when the oxygen level increases, the corrosion potential is shifted towards more positive values. Indeed, the intersection point of hydrogen oxidation and oxygen reduction, which is the corrosion potential, is more positive. A higher oxygen level implies faster transport rates from the bulk to the metal surface and therefore more positive corrosion potential values. Beyond a certain value (represented by E7 on Figure 40), the corrosion potential does not depend on mass transport rates. It should be noted that there is no mass transport limitations on hydrogen as hydrogen gas
diffuses much faster than oxygen gas. PGM additions keep the potential low as the exchange current density for hydrogen oxidation in PGM-doped materials is much higher than that for standard material that does not contain PGM additions. This results in a low corrosion potential as the oxygen limiting current intersects with the reversible \( \text{H}_2/\text{H}_2\text{O} \) oxidation potential. This explains how PGMs affect catalytic efficiency of \( \text{H}_2 \) and \( \text{O}_2 \) recombination in high temperature water (BWRs). This explanation is only valid if hydrogen is present in stoichiometric concentration. Indeed, some research [131] has demonstrated that for high dissolved oxygen concentration, with no hydrogen present, the corrosion potential increased and the SCC susceptibility was greater for Pt-treated type 304 SS.

Work on the recombination efficiency of type 304 SS containing 1 wt% Pd was evaluated in 288°C water containing various oxygen and hydrogen amounts [106]. It was shown that the efficiency increased with increasing hydrogen level up to the stoichiometry excess. Above this value, no more improvement was observed. The works discussed in this section revealed that in order to be beneficial to type 304 SS in high temperature and specifically in BWRs, PGMs should be used with a certain \( \text{H}_2:\text{O}_2 \) ratio. A small ratio would make the PGM inefficient and even detrimental according to Yeh et al [131]. By contrast higher ratios corresponding to the stoichiometric hydrogen level, showed beneficial effects on the IGSCC resistance of type 304 SS. It is important to mention that Pt has also a catalytic effect for the oxygen reduction reaction but less pronounced than that for the hydrogen oxidation reaction.
Figure 39 Schematic diagram showing the electrochemical corrosion potential (ECP) against molar ratio of $H_2/O_2$ for type 304 SS, Pd-modified type 304 SS and pure Pt electrodes in $288^\circ C$ water containing 300ppb $O_2$[108]

Figure 40 Schematic Evans diagram showing intersections of $O_2$ and $H_2$ on metal surfaces such as SS and Pt ($i_l$, limiting current)[108]

The techniques used to add noble metal have been compared. In the case of coating, using high-velocity oxy-fuel (HVOF) and plasma spray (PS), the electrochemical corrosion potential has been measured as a function of immersion time in high temperature conditions for different oxygen and hydrogen concentration. Figure 41 shows that the corrosion potential is significantly lowered by using noble metal coatings and hydrogen. For both techniques, HVOF and PS, the catalytic effect seems to show good performances.
Nevertheless, the durability of the catalytic effect of PGMs seemed to be altered in the case of noble metal deposition. A study [132] investigated the Pd concentration after noble metal deposition on the surface of stainless steel in 288°C water under hydrogen water chemistry (HWC). The level of Pd was measured at 2-3 at% with a depth up to 0.4 mm using Auger electron spectroscopy (AES) and the ECP was monitored. It was found that the ECP was well below the critical value to mitigate IGSCC. Nevertheless, after cleaning the surface for one week in an ultrasonic bath at 60°C and extended exposure at high flow rate at 288°C, loss of noble metal was observed as well as an increase in potential towards more positive directions. It could be thought that this technique is limited in terms of efficiency as long term exposure seems to suppress the catalytic properties of the noble metal. Indeed, for PWR application, there is a need of catalysis efficiency for long-term and this technique is not appropriate. The loss of noble metal can be explained by the fact that the surface enrichment could not occur due to the cleaning process.<br><br>Figure 41 ECP of type 304 SS as a function of immersion time: (a) SW-HVOF-coated type 304 SS electrodes in 288°C water containing 200 ppb O₂, with and without addition of 35 ppb H₂; (b) SW-PS-coated type 304 SS electrodes in 288°C water containing 1 ppm O₂, with and without addition of 150 ppb H₂ [103].
2.4.6.2 Effect of PGMs on the oxide in high temperature water

Investigations [109] of the oxide formed on type 304 SS in high temperature water simulating BWRs conditions, revealed that under noble metal chemical additions (NMCA), Pt and Rh modified slightly the oxide composition. The structure of the oxide remained the same: an inner rich Cr layer and an outer rich Fe layer. However, Pt and Rh promoted the transformation of $\alpha$-Fe$_2$O$_3$ to a spinel Fe$_3$O$_4$ type structure. The Pt and Rh were detected on the outer layer using electron dispersive X-ray (EDX) analysis and transmission electron microscopy (TEM). This study revealed that the oxide changes could be related to the variation of ECP with PGM additions. However no clear evidence of the mechanism that relates the ECP and the oxide has been provided in this work. Further investigation was performed in 2005 by Ishida et al [133] on the effect of noble metal deposition with an oxide film of type 304 SS under hydrogen water chemistry (HWC). The results confirmed the change in the oxide film due to noble metal additions. The solubility of $\alpha$-Fe$_2$O$_3$ was correlated to the decrease in ECP and hydrogen oxidation reaction, which is catalysed by the noble metal. It was explained by the fact that the inner layer (FeCr$_2$O$_4$) solubility could decrease with a decrease in ECP.

In this work, the inner layer of the oxide was also rich in chromium and did not seem to change with PGM additions. Another interesting point outlined in the results was on the difference between the type of noble metals in terms of oxide changes. Indeed, platinum, rhodium and both platinum and rhodium solutions were investigated and they did not seem to have the same effect on the solubility of the outer layer. The rhodium amount was also smaller in the outer layer. This point shows that although PGMs seem to catalyse hydrogen oxidation, there may be important variations in terms of efficiency and effect on the corrosion resistance of the materials.
Studies on surface treatment of the recombination efficiency of oxygen with hydrogen to form water was carried out on 1 wt% Pd type 304 SS under BWR conditions. It was shown that the catalytic efficiency was improved by various pre-treatments such as electropolishing and etching. From Auger spectroscopy results, palladium surface enrichment was observed after the pre-treatment.

### 2.4.6.3 Effect of PGMs on cracking behaviour

Cracking behaviour of structural materials used in light water reactors (LWRs) has shown significant changes by using PGMs. Indeed, according to Andresen [107], under BWR conditions, coatings produced by noble metal chemical additions (NMCA) prevented crack initiation and reduced SCC growth rates in stainless steels and nickel-base alloy 600 even after 20,000 hours exposure under conditions that are more severe than the real conditions. This was obviously related to the corrosion potential and the recombination of oxygen with hydrogen to form water in the presence of noble metal. However a study on IGSCC of platinum treated type 304 SS in high temperature water [131] revealed that a decrease in the corrosion potential towards more negative values was not necessarily a parameter confirming IGSCC susceptibility at dissolved oxygen levels that were comparatively high compared with the dissolved hydrogen level. Pt treated type 304 SS and standard (untreated) type 304 SS were investigated in various dissolved oxygen concentrations in high temperature water. Polarisation scans revealed higher current density for the treated samples even if the corrosion potential was more negative. In this case, it means that the corrosion rate could be higher although the ECP is lower and therefore the corrosion potential cannot be used as a unique indicator of the corrosion susceptibility. On the other hand, the corrosion potential of the Pt-treated material was higher than that of the untreated one for an oxygen concentration equal to 300 ppb and a ratio H:O=0. This revealed that Pt catalysed the oxygen reduction reaction, thus making the ECP more positive. From this
result, it is clear that Pt and maybe PGMs in general can catalyse hydrogen oxidation or oxygen reduction depending on the dissolved oxygen concentration present. From slow strain rate tensile (SSRT) tests, Pt treated type 304 SS exhibited more severe IGSCC under oxygenated conditions (no hydrogen) than the untreated type 304 SS. This was confirmed by crack growth rate evaluation under oxygenated conditions (300 ppb O₂) that showed deeper cracks in the treated sample. According to this study, PGM additions could be detrimental to SCC resistance if the oxygen concentration is too high or the dissolved hydrogen concentration too low. What is more difficult to explain is how noble metals reduce crack initiation and crack propagation. This question remains difficult and is still being investigated. In order to understand this point, it is necessary to also understand the mechanism of crack initiation and crack propagation in the absence of PGMs. Unfortunately; it remains unclear at the moment.

2.4.7 Effect on mechanical properties

From a general point of view, platinum group metals do not seem to alter the mechanical properties when they are added to an alloy. According to Tomashov [134], 0.3 wt% Pd added to stainless steel improved the strength characteristics and the yield point of the base-alloy over a range of temperatures. Similarly, Ru has shown beneficial effect in terms of mechanical properties when added to Fe-40Cr [135]. However, simultaneous addition of Ru and Ti or Ni revealed poorer mechanical resistance; which means that the composition of the material has to be considered carefully for the mechanical properties of PGM additions.
Chapter 1: Introduction

Chapter 2: Literature review

Chapter 3: Materials characterisation

Chapter 4: Crack initiation

Chapter 5: Fracture mechanics approach to stress corrosion crack propagation: fatigue precracking

Chapter 6: SCC propagation study

Chapter 7: Electrochemistry in borated and lithiated water

Chapter 8: Electrochemistry in IGSCC simulated environment

Chapter 9: Electrochemistry in high temperature water

Chapter 10: Discussion

Chapter 11: Conclusions

Chapter 12: Future work
3. Materials characterisation

3.1 Introduction
This chapter is aimed at characterising the range of materials that have been investigated in this project. The main objectives were to provide enough knowledge on the materials chemistry, microstructure and mechanical properties to help understand the results in subsequent corrosion investigations. This section is divided into four subsections which are the experimental procedure, the results, the discussion part and the summary. The experimental and results parts are divided into seven parts: the composition, the material history, the heat treatments, the microstructure, the grain size, the hardness and the tensile properties.

3.2 Experimental procedures

3.2.1 Composition
Material consisted of type 304 stainless steels either of a “standard” composition, or containing different concentrations of noble metals. The compositions are presented in Table 4. Most materials were medium carbon austenitic stainless steels and were identified as MC; two materials were high carbon and referred as HC.

3.2.2 Material history
The material was supplied as fabricated by Johnson Matthey. They were all subjected to the same fabrication process; however there were slight changes (a few mm) in the dimensions from an alloy to another. The alloys were hot rolled after two hours at 1150°C in a furnace under an exothermic atmosphere. The materials were about 20 mm high, 70 mm wide, 266 mm long before hot rolling and 12 mm high, 75 mm wide, 565-590 mm long after hot rolling. Then they were cold rolled to obtain plates of approximately 10 mm high, 75 mm wide and 800 mm long. After hot and cold rolling, the plates were solution annealed at 1060°C in a muffle furnace under nitrogen. Three samples of approximately 10 mm high, 75 mm wide and 300 mm long were heat treated
for each cycle at 1060°C to dissolve all carbides and residual delta ferrite for 45 minutes, then water quenched before labelling.

3.2.3 Heat treatment

3.2.3.1 Solution annealing

The PGM-doped 304 alloys were supplied in the solution annealed condition as explained in the previous section.

3.2.3.2 Sensitisation

Sensitisation occurs in austenitic alloys at temperatures between 400°C and 800°C. In PWRs, it is also one of the consequences of neutron irradiation. Therefore, investigation of sensitised materials is of great importance for PWR applications. Several attempts were conducted to determine the conditions (temperature and time) under which sensitisation of standard and doped materials occurs. The results presented in this section only display the microstructures of the samples heat-treated at 650°C for 24 hours or 72 hours as they revealed fully sensitised microstructures. The PGM-doped and standard 304 alloys were sensitised in an argon atmosphere at 650°C for 24 h.

3.2.4 Metallographic preparation

3.2.4.1 Microstructure

As-received (solution annealed) and sensitised samples (approximately 5-6 mm high, 71 mm wide and 10 mm long) were cut to obtain smaller specimens 1 cm$^2$ specimen using a Struers Accutom 5 precision cut-off machine. Sensitised and as-received specimens were then embedded in resin, ground (P240, P400, P800, P1200 SiC) and mechanically polished (3 μm, 1 μm, 0.25 μm diamond paste; 60nm colloidal SiO$_2$). All the samples were examined in the plane parallel to the rolling direction. The specimens were then electro-etched in oxalic acid (20 V, 20 s). Optical microscopy was carried out using an Olympus Optical BH2 Microscope interfaced with a Leica DC200 camera. Scanning
electron microscopy was also performed using a high resolution scanning electron microscope (Philips Excel 30 FEG-SEM), equipped with a CCD camera (NORDIF).

### 3.2.4.2 Grain size measurements

The average grain size was determined using the Mean Linear Intercept method [136]. This method is known to determine quite accurately the grain size of alloys. The length of a single test line and the magnification should be such that 50 intersections can be counted. The grain size was determined by counting the number of intersections after drawing ten test lines on a micrograph (x 20). An intersection is where the line cuts a grain boundary; a half intersection is when a test line ends on a grain boundary or when it occurs at a triple point.

The average of the number of grain boundaries that intercepted the line was recorded. Knowing the length of the test line and the number of intersections, the grain size was determined. The standard deviation was also calculated in order to determine an accurate value of the grain size of each alloy.

### 3.2.5 Tensile properties

The measurements have been taken at 300°C, which is a representative temperature in the primary circuit of PWRs. The tensile properties of the alloys were measured by running a tensile test in an Instron machine model 5885H connected to a computer. An environmental chamber was attached to the machine in order to control the temperature. The samples used were dog bone samples as shown in Figure 42. Prior to performing the measurements, the diameter of each sample was measured using a micrometer “Mitutoyo” (precision: 0.001 mm). An extensometer was calibrated prior to being placed in the gauge length. Further to this, the sample was preloaded and the environmental chamber was set to 300°C. After the temperature was stable, the load was adjusted to zero because while heating the environmental chamber, the load decreased due to the thermal expansion. The extension rate was chosen to be 2 mm/min.
The tensile properties were measured only on two samples for each alloy due to the limited number of samples.

Figure 42 Schematic of the dog bone sample used to measure the mechanical properties

3.2.6 Hardness at room temperature

Hardness measurements were performed using a 10 kg UK Calibration Ltd testing machine. Three indentations were carried out in the plane parallel to the rolling direction and the mean and standard deviation were calculated [137]. This test method consists of indenting the test material with a diamond indenter, in the form of a right pyramid with a square base and an angle of 136° between opposite faces, subjected to a load of 1 to 100 kg. The full load is normally applied for 10 to 15 seconds. The two diagonals of the resulting indentation on the surface of the material after removal of the load are measured using a microscope and their average is calculated. The area of the surface of the indentation is calculated. The Vickers hardness is the quotient obtained by dividing the kg load by the square mm area of indentation, see Figure 43.
Figure 43 Vickers hardness test principle (a) and principle of calculation (b)

\[ HV = \frac{2F \sin 136°}{d^2} \]  \[ [137] \]

**Equation 15**

Where,

- HV is the hardness;
- F is the force (N);
- \( d = (D_1 + D_2)/2 \).

When the mean diagonal of the indentation (d) has been determined, the Vickers hardness is calculated from Equation 15. A conversion table is then used to determine the hardness of the alloys in this project.
3.3 Results

3.3.1 Composition

The composition of the materials is presented in Table 4.

Table 4 Composition of the alloys

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Si</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
<th>C</th>
<th>S</th>
<th>Pd</th>
<th>Ru</th>
<th>Co</th>
<th>Cu</th>
<th>Mo</th>
<th>V</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>304MC</td>
<td>0.74</td>
<td>19.01</td>
<td>1.52</td>
<td>68.64</td>
<td>9.4</td>
<td>0.056</td>
<td>0.006</td>
<td>0.13</td>
<td>0.13</td>
<td>&lt;0.05</td>
<td>0.44</td>
<td>0.26</td>
<td>&lt;0.05</td>
<td>0.006</td>
</tr>
<tr>
<td>PD1MC</td>
<td>0.55</td>
<td>18.25</td>
<td>1.35</td>
<td>69.58</td>
<td>9.44</td>
<td>0.056</td>
<td>0.001</td>
<td>0.23</td>
<td>0.26</td>
<td>0.10</td>
<td>0.55</td>
<td>0.25</td>
<td>0.11</td>
<td>0.022</td>
</tr>
<tr>
<td>PD2MC</td>
<td>0.56</td>
<td>18.26</td>
<td>1.36</td>
<td>67.53</td>
<td>9.41</td>
<td>0.04</td>
<td>0.001</td>
<td>0.96</td>
<td>1.01</td>
<td>0.09</td>
<td>0.58</td>
<td>0.26</td>
<td>0.11</td>
<td>0.021</td>
</tr>
<tr>
<td>PD3MC</td>
<td>0.60</td>
<td>18.29</td>
<td>1.80</td>
<td>68.74</td>
<td>9.39</td>
<td>0.05</td>
<td>0.025</td>
<td>0.60</td>
<td>0.99</td>
<td>0.11</td>
<td>0.51</td>
<td>0.30</td>
<td>0.08</td>
<td>0.03</td>
</tr>
<tr>
<td>PD3HC</td>
<td>0.97</td>
<td>18.95</td>
<td>1.72</td>
<td>67.98</td>
<td>9.54</td>
<td>0.075</td>
<td>0.001</td>
<td>0.96</td>
<td>0.14</td>
<td>0.11</td>
<td>0.51</td>
<td>0.24</td>
<td>0.06</td>
<td>0.02</td>
</tr>
<tr>
<td>Ru1MC</td>
<td>0.57</td>
<td>18.68</td>
<td>1.55</td>
<td>67.14</td>
<td>9.57</td>
<td>0.041</td>
<td>0.025</td>
<td>0.78</td>
<td>0.14</td>
<td>0.11</td>
<td>0.51</td>
<td>0.33</td>
<td>0.10</td>
<td>0.02</td>
</tr>
<tr>
<td>Ru2MC</td>
<td>0.51</td>
<td>18.39</td>
<td>1.97</td>
<td>68.32</td>
<td>9.41</td>
<td>0.035</td>
<td>0.001</td>
<td>0.78</td>
<td>0.12</td>
<td>0.11</td>
<td>0.51</td>
<td>0.31</td>
<td>0.09</td>
<td>0.02</td>
</tr>
<tr>
<td>Ru3MC</td>
<td>0.53</td>
<td>17.95</td>
<td>1.67</td>
<td>68.51</td>
<td>9.22</td>
<td>0.047</td>
<td>0.001</td>
<td>0.78</td>
<td>0.12</td>
<td>0.11</td>
<td>0.51</td>
<td>0.31</td>
<td>0.09</td>
<td>0.02</td>
</tr>
<tr>
<td>Ru3HC</td>
<td>0.54</td>
<td>18.74</td>
<td>1.48</td>
<td>68.34</td>
<td>9.52</td>
<td>0.096</td>
<td>0.001</td>
<td>0.78</td>
<td>0.12</td>
<td>0.11</td>
<td>0.51</td>
<td>0.31</td>
<td>0.09</td>
<td>0.02</td>
</tr>
<tr>
<td>RuPdLC</td>
<td>0.46</td>
<td>18.49</td>
<td>1.87</td>
<td>69.06</td>
<td>9.52</td>
<td>0.037</td>
<td>0.001</td>
<td>0.78</td>
<td>0.12</td>
<td>0.11</td>
<td>0.51</td>
<td>0.31</td>
<td>0.09</td>
<td>0.02</td>
</tr>
<tr>
<td>RuPdMC</td>
<td>0.46</td>
<td>18.49</td>
<td>1.39</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- high carbon alloys

Some of these alloys (Pd3HC and Ru3HC) do not meet the specifications given on Table 1.

3.3.2 Microstructures

The microstructures of the materials are presented in Figure 44-Figure 54. As the materials have been investigated in the as received (solution annealed) and sensitised conditions, the following micrographs illustrate both conditions. All the materials were etched electrolytically in oxalic acid in order to observe the grain boundaries.
Figure 44 Optical micrographs showing the microstructure of 304MC, etched electrolytically in 10% oxalic acid: (a) as-received and (b) heat-treated at 650°C for 24 h

The as-received 304MC revealed an austenitic microstructure. The steps at grain boundaries were clearly observed. After 24 h heat treatment at 650°C, the alloy was fully sensitised (ditch microstructure). δ-ferrite was present in both microstructures.

Figure 45 Optical micrographs showing the microstructure of Pd1MC, etched electrolytically in 10% oxalic acid: (a) as-received and (b) heat-treated at 650°C for 24 h

Pd1MC showed an austenitic microstructure that was more difficult to etch. Pits were revealed after etching the as-received and heat-treated samples. A fully sensitised microstructure was obtained after 24 h at 650°C [see (b)]. Fewer pits were revealed after sensitisation.
Figure 46 Optical micrographs showing the microstructure of Pd2MC, etched electrolytically in 10% oxalic acid: (a) as-received and (b) heat-treated at 650°C for 24 h

Pd2MC presented an austenitic microstructure. Pits were revealed after etching in both conditions. A fully sensitised microstructure was obtained after 24h at 650°C [see (b)]. The as-received sample [Figure 46 (a)] was also hard to etch.

Figure 47 Optical micrographs showing the microstructure of Pd3MC, etched electrolytically in 10% oxalic acid: (a) as-received and (b) heat-treated at 650°C for 24 h

Many pits were revealed within grains. A fully sensitised microstructure was obtained after 24 h at 650°C. Equiaxed grains were observed in the sensitised microstructure [see Figure (b)]. However the grain morphology was not clearly visible in the as-received conditions due to difficulties of etching.
Figure 48 Optical micrographs showing the microstructure of Ru1MC, etched electrolytically in 10% oxalic acid: (a) as-received and (b) heat-treated at 650°C for 24 h

Austenitic microstructures were revealed for both micrographs with pits within grains. The ditch microstructure confirmed the specimens are fully sensitised after 24 hours at 650°C.

Figure 49 Optical micrographs showing the microstructure of Ru2MC, etched electrolytically in 10% oxalic acid: (a) as-received and (b) heat-treated at 650°C for 24 h

Austenitic microstructure was observed in both conditions. A fully sensitised microstructure was obtained after 24 h at 650°C as shown by the presence of ditches. The as-received sample [Figure 49 (a)] seems to be hard to etch.
Figure 50 Optical micrographs showing the microstructure of Ru3MC, etched electrolytically in 10% oxalic acid: (a) as-received and (b) heat-treated at 650°C for 24 h

Austenitic microstructures were observed. Pits were revealed in the as-received sample [see (a)] within the grains. A fully sensitised microstructure was observed after 24 h heat treatment for 650°C. The sensitised microstructure highlighted the morphology of the grains as being equiaxed. The as-received sample [Figure 50 (a)] seems to be hard to etch as it was observed for Ru2MC in the as-received condition.

Figure 51 Optical micrographs showing the microstructure of RuPdLC, etched electrolytically in 10% oxalic acid: (a) as-received and (b) heat-treated at 650°C for 72 h

Numerous pits were revealed in the as-received microstructure. Fully sensitised microstructure
was obtained after 72 h heat treatment at 650°C. The sensitised microstructure revealed the presence of δ-ferrite, especially in the grain boundaries. The as-received sample [(Figure 51 (a)] seems to be hard to etch.

![Figure 52 Optical micrographs showing the microstructure of RuPdMC, etched electrolytically in 10% oxalic acid: (a) as-received and (b) heat-treated at 650°C for 48 h](image)

As–received and heat treated microstructures revealed the presence of pits. A fully sensitised microstructure was obtained after 48 h heat treatment at 650°C. Grains boundaries were not clearly visible in the as-received conditions. The as-received sample [Figure 52(a)] seems to be hard to etch.

![Figure 53 Optical micrographs showing the microstructure of Ru3HC, etched electrolytically in 10% oxalic acid: (a) as-received and (b) heat-treated at 650°C for 24 h](image)

The as-received conditions revealed the presence of a second phase. Pits were also
observed. Ru3HC presented a fully sensitised microstructure.

![Figure 54 Optical micrographs showing the microstructure of Pd3HC, etched electrolytically in 10% oxalic acid: (a) as-received and (b) heat-treated at 650°C for 24 h](image)

The as-received microstructure presented an austenitic microstructure; however, the grain boundaries were not clearly visible in the as-received condition. Numerous pits were evident in the as-received condition. Full sensitisation was obtained after 24 hours at 650°C.

The as-received doped alloys revealed a microstructure that was difficult to etch in oxalic acid, therefore the grain boundaries were hardly visible in the as-received condition of the doped materials. The possible reason to explain this is that platinum group metal additions enhance passivation of stainless steels in acid solutions [3, 138]. This means that in oxalic acid solution, the doped alloys are probably passive and the etching process of the grain boundaries does not happen. By contrast, etching is much easier in the sensitised condition as this phenomenon implies chromium depletion along the grain boundaries, making the alloys more susceptible to intergranular attack.
3.3.3 Grain size measurements results

Table 5 presents the results of the grain size measurements. The measurements were performed on the sensitised samples using the linear intercept method.

Table 5 Grain size measurements of the main alloys investigated

<table>
<thead>
<tr>
<th>Alloys ID</th>
<th>Grain size (µm)</th>
<th>Scatter (±µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>304MC</td>
<td>55</td>
<td>2</td>
</tr>
<tr>
<td>Pd1MC</td>
<td>51</td>
<td>5</td>
</tr>
<tr>
<td>Pd2MC</td>
<td>52</td>
<td>1</td>
</tr>
<tr>
<td>Pd3MC</td>
<td>47</td>
<td>3</td>
</tr>
<tr>
<td>Ru1MC</td>
<td>70</td>
<td>7</td>
</tr>
<tr>
<td>Ru2MC</td>
<td>62</td>
<td>5</td>
</tr>
<tr>
<td>Ru3MC</td>
<td>54</td>
<td>1</td>
</tr>
<tr>
<td>PdRuMC</td>
<td>50</td>
<td>3</td>
</tr>
<tr>
<td>PdRuLC</td>
<td>52</td>
<td>7</td>
</tr>
</tbody>
</table>

The average grain size calculated seemed to be between 47 µm (Pd3MC) and 70 µm (Ru1MC). The addition of palladium to the standard 304 SS did not affect the grain size. However the addition of ruthenium increased the grain size; especially 0.11 and 0.25 wt% Ru additions. According to the results in Table 5, the additions of both palladium and ruthenium lowered slightly the grain size of the standard alloy. However, by considering the experimental variation, the grain size of 304MC, PdRuMC and PdRuLC are within the same range of values.

3.3.4 Tensile properties results

Figure 55 presents the stress-strain curve and Table 6 gives the values of the yield stress and maximum stress in the as-received condition.

The tensile properties of 304MC have been measured at room temperature and at 300°C. Figure 55 shows that at room temperature the yield stress and maximum stress are higher.

The trend showed that Ru3MC was more ductile than 304MC, Ru1MC and Pd3MC. The results showed that Ru additions seemed to increase the ductility and elasticity as
higher strains have been measured. This effect was more pronounced when the Ru content increased. Indeed, by comparing Ru1MC that contained 0.11 wt% Ru with Ru3MC that contained 1 wt% Ru, it can be noticed that the main difference is the strain at the failure, 32% and 36% with respect to Ru1MC and Ru3MC. Pd addition seemed to lower the yield stress and ultimate tensile stress with respect to 304MC. However it seemed to increase the strain of the standard material by 5%.

One point to highlight is that the measurements were only taken on two or three samples of each type of alloy due to the restriction in the number of samples available for this project. Therefore the average is not very precise. More samples need to be investigated in order to have a more accurate knowledge of the effect of PGM additions on the tensile properties of the standard alloys. The actual results only give a general idea.

Figure 55 Mechanical properties: 304MC at room temperature (grey); Ru1MC at 300°C (red); Ru3MC (blue); Pd3MC at 300°C (green), 304MC at 300°C (pink)
Table 6 Mechanical properties of the alloys at 300°C

<table>
<thead>
<tr>
<th>Alloy ID</th>
<th>PGM content (wt%)</th>
<th>Yield stress (MPa)</th>
<th>Maximum stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>304MC</td>
<td>0</td>
<td>Test 1: 146 Test 2: 148 (147)</td>
<td>395 (391 (393)</td>
</tr>
<tr>
<td>Mean value</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru1MC</td>
<td>0.13</td>
<td>Test 1: 166 Test 2: 155 (160)</td>
<td>421 (423 (422)</td>
</tr>
<tr>
<td>Mean value</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru3MC</td>
<td>1.01</td>
<td>Test 1: 177 Test 2: 169 (173)</td>
<td>437 (421 (428)</td>
</tr>
<tr>
<td>Mean value</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd3MC</td>
<td>0.96</td>
<td>Test 1: 166</td>
<td>363</td>
</tr>
</tbody>
</table>

3.3.5 Hardness results

Hardness results are displayed as follows. The average means are displayed followed by the errors calculated using the standard deviation method after taking the measurements three times.

Table 7 Hardness measurements of the main alloys investigated

<table>
<thead>
<tr>
<th>Alloy ID</th>
<th>PGM content (wt%)</th>
<th>Hardness (HV10) (As-received)</th>
<th>Hardness (HV10) (Sensitised)</th>
</tr>
</thead>
<tbody>
<tr>
<td>304MC</td>
<td>0</td>
<td>150 ± 3</td>
<td>152 ± 3</td>
</tr>
<tr>
<td>Pd1MC</td>
<td>0.13</td>
<td>150 ± 13</td>
<td>152 ± 10</td>
</tr>
<tr>
<td>Pd2MC</td>
<td>0.23</td>
<td>153 ± 7</td>
<td>159 ± 3</td>
</tr>
<tr>
<td>Pd3MC</td>
<td>0.96</td>
<td>165 ± 4</td>
<td>164 ± 11</td>
</tr>
<tr>
<td>Ru1MC</td>
<td>0.13</td>
<td>151 ± 0</td>
<td>164 ± 15</td>
</tr>
<tr>
<td>Ru2MC</td>
<td>0.26</td>
<td>145 ± 2</td>
<td>146 ± 2</td>
</tr>
<tr>
<td>Ru3MC</td>
<td>1.01</td>
<td>167 ± 9</td>
<td>163 ± 6</td>
</tr>
<tr>
<td>PdRuMC</td>
<td>0.27</td>
<td>157 ± 5</td>
<td>163 ± 10</td>
</tr>
<tr>
<td>PdRuLC</td>
<td>0.27</td>
<td>171 ± 3</td>
<td>165 ± 2</td>
</tr>
</tbody>
</table>

The hardness values varied between 145 HV (Ru2MC) and 171 HV (PdRuLC). The alloy Ru2MC showed the lowest hardness value while the alloy PdRuMC presented the highest value. No significant difference in terms of hardness between the different
alloys was established from the measurements. Sensitisation did not seem to affect the hardness as the results were very similar in both conditions (as-received and sensitised).

3.4 Discussion
The material characterisation presented the composition, material history, microstructure, grain size, tensile properties and hardness of the main alloys in this study. In terms of chemistry, most materials were medium carbon austenitic stainless steels with a carbon level varying between 0.035 and 0.056 except for Pd3HC and Ru3HC which contained much higher level of carbon, respectively 0.075 and 0.096wt%. Full material characterisation was only presented for the materials of interest (medium carbon) as the high carbon content of Pd3HC and Ru3HC made these alloys not suitable for PWR application. Indeed, the high carbon content promotes sensitisation and therefore IGC/IGSCC. Nevertheless it was still interesting to see the difference in terms of microstructure. Those two alloys have also been investigated in terms of crack propagation resistance (see Chapter 6).

The micrographs revealed an austenitic microstructure for the standard and doped 304 SS. Solution annealing was aimed at dissolving the carbides and residual delta ferrite and forming a supersaturated solid solution. From the micrographs presented in Figure 44–Figure 54, solution annealing was successful for most alloys as the microstructures of the as-received (solution annealed samples) were deprived of carbides. Full sensitisation was observed after 24 hours at 650°C as a ditch microstructure, highlighting the grain boundaries, was present. Therefore these conditions of heat-treatment were applied to sensitise the standard and PGM -doped alloys, except PdRuMC and PdRuLC, which needed about 72 hours to sensitise. Indeed, PdRuLC has a low carbon level (0.037 wt%) compared to PdRuMC (0.047 wt%) and in general, low carbon type 304 SS alloys require more time to sensitise as less carbon is present in the
However, PdRuLC has still a higher carbon level than Ru2MC (0.035 wt%), which revealed a sensitised microstructure after 24 hours at 650°C [see Figure 49 (b)]. So the longer time required to sensitise the alloys containing both Pd and Ru additions is more likely to be due to the additions of these two PGM elements rather than the carbon level.

The standard alloy revealed the presence of delta ferrite after heat-treatment, one of the ways to reduce the delta ferrite content is to solution anneal for longer. Delta ferrite is known to reduce the general corrosion properties in austenitic stainless steels as it lowers the chromium content in the matrix. However, it can improve resistance to SCC crack propagation. In order to determine the delta ferrite present in the alloys, it was measured and the results are presented in Table 8.

Table 8 Table presenting the $\delta$-ferrite present in the main alloys in the as-received condition (solution annealed) [140]

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$\delta$-ferrite (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>304MC</td>
<td>3.7</td>
</tr>
<tr>
<td>Pd1MC</td>
<td>2.51</td>
</tr>
<tr>
<td>Pd2MC</td>
<td>2.15</td>
</tr>
<tr>
<td>Pd3MC</td>
<td>2.12</td>
</tr>
<tr>
<td>Ru1MC</td>
<td>2.74</td>
</tr>
<tr>
<td>Ru2MC</td>
<td>2.47</td>
</tr>
<tr>
<td>Ru3MC</td>
<td>2.38</td>
</tr>
</tbody>
</table>

According to Table 8 delta ferrite seemed to be more prevalent in 304MC. Only the sensitised microstructure revealed the presence of delta ferrite. For most doped-alloys, it was quite difficult to distinguish the grain boundaries in the as-received condition. Indeed, PGM -doped materials showed numerous pits. Etching seemed to be affected by the presence of platinum group metals, making the observation of the grain boundaries almost impossible in the solution annealed conditions. Usually, pits are a sign of very
strong etching as the surface layer becomes covered with small regular faceted pits [141]. The sensitised conditions did not reveal any pits for the Pd-doped alloys. Pd3HC and Ru3HC revealed pitting in the as-received conditions; however, the sensitised conditions presented only a ditch microstructure. Pd3HC showed both carbides in the as-received condition, due to the high level of carbon.

Both Pd and Ru additions seemed to increase the time required for full sensitisation to happen. Indeed PdRuLC and PdRuMC needed 72 hours to sensitise. In the as-received conditions, both palladium and ruthenium additions, showed the presence of pits as well. This suggested that the additions of palladium or ruthenium improved the general corrosion as the etching process took more time and did not reveal the grain boundaries. This suggests that another etchant should be used for the PGM-doped alloys. For sensitised stainless steels, a solution of 4% picral plus hydrochloric acid can be used to reveal the grain and twin boundaries [142]. Oxalic acid is widely used for stainless steels in order to reveal sigma phase, cold worked layers, carbides and austenite grain boundaries. On the other hand pitting was promoted in oxalic acid, in which PGM additions seem to self passivate type 304 SS. This can be explained by the fact that localised corrosion such as pitting happens when there is a localised breakdown of the passive film of the alloy and in the presence of an aggressive anion.

In terms of grain size, the doped and standard alloys did not show significant differences. Generally, the grain size relates to the mechanical resistance of the materials. The smaller it is, the more resistant the material is. However, the tensile properties showed that 1 wt% Ru addition increased the maximum stress of the standard alloy, while 1 wt% Pd seemed to lower the maximum stress and the stress in the plastic region. Ru1MC (0.11 wt% Ru) and Ru3MC (1 wt% Ru) additions modified the mechanical behaviour of the standard alloy similarly. Indeed the elastic and plastic regions were similar, although the elongation seemed to increase by 5% from 0.11 to
1wt% Ru. The results showed that at 300°C, Ru-doped alloys would be more ductile in terms of tensile resistance. As previously mentioned, the measurements have been undertaken on two samples of each type of alloy, hence there may be an experimental error to consider to be sure about the performance of the Ru-doped alloys compared to the standard material.

According to the electron backscattered diffraction (EBSD) measurements performed by K. Govender [143], over 90% of the grain boundaries were characterised as high angle, which means that there is a misorientation between adjacent grains of more than 15°. High angle grain boundaries make the material more susceptible to cracking [43, 44].

In terms of hardness, the alloys were investigated in the as-received and sensitised condition. The sensitisation did not seem to affect the hardness for any of the alloys.

Palladium and ruthenium additions had similar effects on the hardness. The hardness was only performed at room temperature but it is expected to be lower at 300°C, as was the case for the tensile properties.

3.5 Summary
From metallographic analysis using optical microscopy, it was found that most alloys showed an equiaxed grain structure and no significant variation in the microstructure in the different samples. The alloys were sensitised after 24 hours at 650°C, except the mixed Pd/Ru alloys that needed 72 hours. From general observations of optical micrographs following the oxalic acid etch, it appeared that 304MC had high concentrations of delta-ferrite due to the material history. It was supplied in the solution-annealed condition and the delta ferrite measurements have been conducted in this condition so the precision of the heat treatment could not be verified. For further investigation, especially cracking investigation, this point has been considered. Abundant pitting was observed on the as-received PGM-doped alloys, suggesting a
difficulty to etch these alloys properly. This was attributed to the aestivation enhancement in oxalic acid due to the presence of PGM additions. The tensile and hardness measurements demonstrated that Ru-doped materials seemed to be more ductile with higher maximum stress than 304MC, whilst Pd-doped alloys showed poorer strength. The mean grain size of the alloys examined was in the range of 47 to 70 µm, with Pd3MC having the smallest grain size and Ru1MC having the biggest grain size. The work presented in Chapter 3 evaluated the material properties and highlighted the principal differences between the standard and PGM-doped alloys that influence the SCC resistance.
Chapter 4: Crack initiation

Chapter 5: Fracture mechanics approach to stress corrosion crack propagation: fatigue precracking

Chapter 6: SCC propagation study

Chapter 7: Electrochemistry in borated and lithiated water

Chapter 8: Electrochemistry in IGSCC simulated environment

Chapter 9: Electrochemistry in high temperature water

Chapter 10: Discussion

Chapter 11: Conclusions

Chapter 12: Future work
Chapter 4 Crack initiation

4 Crack initiation in simulated PWR environments

4.1 Introduction
This chapter aims at giving a qualitative investigation on crack initiation of standard and PGM -doped type 304 SS in simulated PWR environments. Reverse U-bend (RUB) samples of standard and PGM -doped 304 SS have been used in high pressure/high temperature environments that simulated PWRs in order to promote crack initiation. This section is divided into four parts: the experimental procedures describing the materials preparation and the different operating conditions; the results and discussion that relate the factors influencing crack initiation in PWR environments and the effects of 1wt % Ru and 1wt% Pd on crack initiation of type 304 SS; and eventually a brief summary that gives the key messages of this investigation.

4.2 Experimental procedures

4.2.1 Surface preparation and U-bend samples
The preparation of the U-bend samples was based on the ASTM standard G30-97.[95] The material compositions are given in Chapter 3. The samples \( L=10\) mm, \( W=70\) mm, \( l=10\) mm \) were cut from plates of dimensions \( L=300\) mm, \( W=75\) mm, \( l=10\) mm \); see Figure 56. They were kept in the as-received conditions (solution annealed) or sensitised for 24 hours or 72 hours at 650°C. The heat treatments performed on the investigated samples are indicated in Table 8. For the as received samples, the sample ID contains “AR” and for the sensitised samples, it contains the duration of sensitisation (e.g 24h or 72h). After cutting, the samples were ground to a P800 surface finish with SiC paper. The grinding was performed in the longitudinal and lateral directions on all the faces. Further to that, M4 holes were drilled at 5mm from each end of the plates. Following this, the plates were U-bent at their centre after measuring them with a calliper. The samples were approximately bent 180 degrees into a U shape with a 4 mm radius. They were loaded on a vice using washers, bolts and nuts made of stainless steel. The exposed surface was under tension. No additional heat-treatment was performed.
after the bending of the samples. The samples were labelled at the bottom of the leg region using an etchant and cleaned in an ultrasonic bath containing acetone for fifteen minutes. Further to that, the general features were recorded using a digital camera after which the samples were kept in a desiccator prior to running the experiments. The samples were placed in the autoclave as shown in Figure 57. Following the autoclave experiments, the samples were examined visually. The legs and the surface under high tensile stress were analysed under a scanning electron microscope (SEM) to identify the surface features with precision and detect any cracks. The samples were also cross sectioned if cracks were found on surface. The test ID is given by Ax, with A referring to the autoclave test and x being the test number.

![Figure 56 Schematic showing how the U-bend samples (represented in green) were cut from the plates (represented in pink)](image-url)
4.2.2 Operating procedure

Six tests were conducted in static and refreshed autoclaves. The environmental conditions were not chosen specifically to investigate the influence of PGMs in mixed hydrogenated and oxygenated water as the series of tests was set up to study crack initiation resistance in PWRs and the autoclave contained other samples for other projects made of type 304 SS. The experimental conditions are presented in Table 9. For each experiment, the time of exposure, the tested alloy ID, the type of autoclave (static or refreshed), the temperature, the chemical species concentrations, oxygen level, hydrogen level, and pressure are reported. Tests A2 and A3 were mostly conducted on all the samples presented in Chapter 3 for 500 hours at 260°C under hydrogenated conditions. Tests A4, A5, A6 and A7 were run on the main alloys of interests which are 304MC, Ru3MC and Pd3MC. The operating temperatures were either 260°C or 360°C.
respectively corresponding to a pressure of 5.8 MPa and 19 MPa considering that operating conditions in the real environment are about 315°C and 15 MPa. This is because the autoclave contained many samples investigated for different projects, therefore the operating temperatures could not be set at the exact temperature of interest. The alloys were in the sensitised condition except in tests A2 and A3 where both solution annealed (AR) and sensitised conditions were investigated. The environment contained either hydrogen or oxygen. Either hydrogen overpressure was added to simulate PWR environments or oxygen was added in order to accelerate the IGSCC initiation process. The hydrogen level was based on the hydrogen overpressure used in most PWRs [20]. The hydrogen level was constant for the test A2, A3, A4 and A5 as the autoclave was refreshed with new solution. However, in the test A6 no solution refreshing occurred (it was static) so the hydrogen level was only known at the beginning of the test. The last two tests (A6 and A7) contained some small sulphate and chloride additions; also lithium hydroxide was added in A6. Sulphate and chloride were present due to contamination.
Table 9 Operating conditions in the autoclave

<table>
<thead>
<tr>
<th>Tests</th>
<th>Time (hrs)</th>
<th>Alloys Tested</th>
<th>Temperature (°C)</th>
<th>Chemical species</th>
<th>Dissolved Hydrogen (cc/kg) at 25°C</th>
<th>Dissolved Oxygen</th>
<th>Pressure (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2</td>
<td>500</td>
<td>304LC AR, 304LC 72h, Ru1MC24h, Ru2MC 24h, Ru3MC AR, Ru3MC 24h, Pd1MC 24h, Pd3MC AR, PdRuLC AR, PdRuMC 72h</td>
<td>260</td>
<td>-</td>
<td>33</td>
<td>&lt;10 ppb</td>
<td>5.8</td>
</tr>
<tr>
<td>A3</td>
<td>500</td>
<td>Pd2MC AR, Pd2MC 24h, PdRuLC AR, PdRuLC 72h</td>
<td>260</td>
<td>-</td>
<td>33</td>
<td>&lt;10 ppb</td>
<td>5.8</td>
</tr>
<tr>
<td>A4</td>
<td>800</td>
<td>304MCTrans*: 2, 304MCLong*: 2</td>
<td>260</td>
<td>-</td>
<td>30</td>
<td>&lt;10 ppb</td>
<td>5.8</td>
</tr>
<tr>
<td>A5</td>
<td>500</td>
<td>304MCTrans: 2, 304MCLong: 2</td>
<td>360</td>
<td>-</td>
<td>20-30</td>
<td>&lt;10 ppb</td>
<td>19</td>
</tr>
<tr>
<td>A6</td>
<td>Static</td>
<td>304MC, Ru3MC, Pd3MC</td>
<td>360</td>
<td>750ppb SO₄²⁻, 1000ppb Cl⁻, 3.1 ppm Li</td>
<td>50 ppm at the start of the test</td>
<td>40 ppm</td>
<td>19</td>
</tr>
<tr>
<td>A7</td>
<td>Static</td>
<td>304MC, Ru3MC, Pd3MC</td>
<td>360</td>
<td>82.5 ppb SO₄²⁻, 531 ppb Cl⁻</td>
<td>40 ppm at the start of the test</td>
<td>19</td>
<td></td>
</tr>
</tbody>
</table>

*304MCLong: cut parallel to the rolling direction; 304MCTrans: perpendicular to the rolling direction

4.3 Results
Different aspects were studied to investigate the crack initiation of the standard and doped alloys and also the effects of PGM additions on the crack initiation of the standard type 304 SS. First of all, the determination of the conditions for crack initiation
itself; second, surface analysis by visual examination, third, surface characteristics under hydrogenated and oxygenated conditions, and eventually crack morphology and the effects of PGM additions using analytical electron microscopy. The different parts of this investigation presenting the results are as follows.

4.3.1 Conditions of cracking

Observations on the various samples after testing revealed cracking in 304MC in test A7. Tests A3 and A4 were run under hydrogenated conditions on samples containing Pd, both Pd and Ru or no PGM additions. In the test A4, 304MC was investigated in different orientations (parallel and perpendicular to the rolling directions) but this did not affect cracking. Tests A5, A6 and A7 were run at 360°C, so the temperature and pressure were increased in order to initiate cracking more quickly. The test A5 was only run on the standard material for a preliminary study while tests A6 and A7 were run on the key samples of this project; e.g., 304MC, Pd3MC and Ru3MC containing respectively 0 wt%, 0.96 wt% and 1.01 wt% PGM additions. From all the tests conducted, only A7 revealed obvious cracking on 304MC in the region under high tensile stress. This test was run for 1456 hours so for longer than the other tests. Impurities such as sulphate were added and the pressure and temperature were also above those of the real conditions. One of the important environmental differences in A7 was the oxygenated conditions that increased the potential, therefore the susceptibility to IGSCC. Table 10 presents the general results after visual inspection and scanning electron microscopy analyses. In summary, no cracking was evident in hydrogenated conditions whatever the sample type or exposure conditions up to the limit of exposure time used.
4.3.2 Surface analysis

4.3.2.1 Macrographs

Optical macrographs were taken before and after testing in the autoclave. For each sample tested, the general features were recorded and the images are displayed in Figure 58 and Figure 59. Figure 58 shows the U-bend sample made from 304MC before testing under oxygenated water in test A7 (see Table 9). No particular defects were detected prior to running the autoclave test. Figure 59 shows the U-bend sample made of 304MC after testing under oxygenated conditions in the test A7 (see Table 9). The region under tensile stress revealed cracking near the edge after testing.

Table 10 Table presenting the cracking results of the autoclave results

<table>
<thead>
<tr>
<th>Tests</th>
<th>A2</th>
<th>A3</th>
<th>A4</th>
<th>A5</th>
<th>A6</th>
<th>A7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cracking Before testing</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Cracking After testing</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>Yes (304MC)</td>
</tr>
</tbody>
</table>
Figure 58 Photography of a representative U-bend sample (304MC in A7) prior to running the autoclave test: (a) and (b) The two sides of the sample reveal the features of the legs; (c) Surface of the bent-part of the sample showing the region under high tensile stress.
Figure 59 Photography of a representative U-bend sample (304MC in A7) after running the autoclave test: (a) and (b) The two sides of the sample reveal the features of the legs; (c) Surface of the bent-part of the sample showing cracking in the region under high tensile stress

4.3.2.2 Micrographs

Further to examining and recording the general characteristics of the autoclave samples, more investigation was performed using a scanning electron microscope (SEM). The samples were analysed on their outer surface in order to detect any cracks and also to investigate the oxide on surface and the PGM effects on the oxide. The two regions analysed were obviously the legs in order to examine the oxide as no stress was applied.
in this region and the bent part, which contains the area under high tensile stress. The micrographs showing the exposed surface characteristics are presented below. Due to the consequent number of tested samples, only the micrographs of representative or relevant samples are displayed.

4.3.2.2.1 Legs

The legs of the samples were not under stress, therefore less likely to stress corrosion crack in the autoclave. They were analysed visually and under a SEM to determine any crack initiation. It is important to observe the oxidation process as internal oxidation is one of the possible mechanisms to consider for stress corrosion cracking [41].

Figure 60 Scanning electron micrographs showing a representative surface of the leg: (a) Leg of Ru3MC in A6; (b) oxide on surface of the leg in A6
4.3.2.2.2 Surface under high tension

Figure 61 Representative scanning electron micrograph revealing the region of high tensile stress and the edge of the U-bend sample after an autoclave experiment under hydrogenated conditions (tests A2, A3, A4 and A5)
Cracking is expected to be perpendicular to the stress direction.

Figure 62 Representative scanning electron micrograph revealing the oxide on the outer surface: (a) lower magnification of a 304MC under hydrogenated conditions (A4); (b) higher magnification revealing the presence of crystals in white.

4.3.2.2.3 Surface under high tension

In most autoclave experiments, small holes that look like tiny cracks or defects on the oxide film were observed on the outer surface. Cross sections of the samples in the regions, where these features were located were performed but due to their small size as compared to that of the cutting wheel, they could not be located. Techniques such as focused ion beam (FIB) would be more appropriate to cross section these features. However, not enough time in this research was left to perform this. Figure 63 presents the details of the features observed on 304MC, Pd3MC and Ru3MC. The holes seemed
to be located randomly on the oxide surface, while longitudinal features seemed to be deep grinding marks. The PGM additions did not affect the features in terms of size. It was not possible to determine the number of holes or deep grinding marks present as they were a great number. They are likely to be cracks/defects in the oxide film that form during exposure. The crystals observed were likely to be magnetite crystals according to the literature [35].
Figure 63 Scanning electron micrographs revealing the “holes” observed on surface after an autoclave test under hydrogenated conditions (A6): (a) sensitised 304MC; (b) sensitised Pd3MC; (c) sensitised Ru3MC
4.3.3 Cracking and PGM effects on crack initiation

Cracking initiated on 304MC under oxygenated conditions during 1460 hours of exposure (test A7 see Table 9). Figure 64-Figure 67 display the micrographs of the region that revealed cracking. Cracks of a length going up to about 900 µm were observed on the surface. Figure 67 revealed cracking that was covered by an oxide. The longest cracks were perpendicular to the stress direction.
Figure 64 Scanning electron micrographs revealing the region of cracking: (a) 304MC showing cracking after testing in A7; (b) Pd3MC after testing in A7; (c) Ru3MC after testing in A7
Figure 65 Scanning electron micrographs showing the region under high tensile stress where no cracks were found. Grinding marks and magnetite crystals were observed: (a) 304MC; (b) Pd3MC; (c) Ru3MC
Figure 66 Scanning electron micrographs revealing the cracking morphology observed on 304MC after testing under oxygenated conditions (A7): (a) cracks A and B; (b) high magnification of crack A; (c) High magnification of crack B
Figure 67 Scanning electron micrographs showing a high magnification inside crack A revealing the oxide morphology

4.3.4 Discussion

4.3.4.1 Cracking conditions

4.3.4.1.1 Stress distribution

Stress distribution is of great importance in understanding which regions of a “U-bend” specimen are more susceptible to cracking. Figure 68 presents a diagram of the stress distribution in a U-bend sample. According to the schematic diagram, the bent region is under high tensile stress. The way of loading the sample while bending has a fundamental impact on the stress distribution. Indeed, by holding the sample under tension while tightening with the nuts and bolts, the stress will remain relatively high and above the yield stress in the bent area. However, if the sample is not held, the stress applied will be released and the sample will not be at the expected optimum stress distribution. The U-bend samples can only give a qualitative analysis of the crack initiation as the residual stress was not measured. In this work, one sensitised sample (304MC) tested under oxygenated conditions in A7 initiated cracking. In this alloy cracking was observed at 1mm from the edge, in the region under high tensile stress. According to Figure 68, the stress is higher at the edge than at the half width. This is in
agreement with the observations. Three main cracks were found: two located near each other and one situated at about 100µm from the widest crack.

![Figure 68 The stress condition of a stressed U-bend specimen [144]](image)

Previous researchers [19] investigated crack initiation of sensitised type 304 SS in high temperature water. They used slow strain rate tensile (SSRT) apparatus to conduct the experiments and monitor crack initiation in situ. They found that for an initial strain rate of $8.3 \times 10^{-7} \text{ s}^{-1}$, cracks initiated at a strain of 10% and a stress of 300 MPa, under a pressure of 8.8 MPa, in an environment containing a concentration of dissolved oxygen (DO) less than 10 ppb and $10 \times 10^{-4} \text{ kmol/m}^3 \text{ Na}_2\text{SO}_4$ at 250°C. These conditions are obviously well above the yield stress of type 304 SS at 300°C (see Chapter 3 for tensile properties at 300°C). These determined values varied with temperature; the higher the temperature, the lower the required stress/strain for crack initiation.

4.3.4.1.2 Environmental conditions for crack initiation

Cracking did not initiate under hydrogenated conditions either at 260°C (see A2, A3, A4), or at 360°C (see A5 and A6). Under hydrogenated conditions, the time of exposure was increased in tests A4 and A6 and still no crack initiation was observed. However under oxygenated conditions (A7), cracking was observed for 304MC. This test was also run for longer (1460 hours in A7 against 1000 hours and 500 hours in the other tests). A6 and A7 were run at the same temperature (360°C) but the chemistry was
different as higher chloride and sulphate levels and Li were present in A6 (see Table 9).

The various autoclave experiments revealed that crack initiation of sensitised 304MC was enhanced under severe conditions (360°C, 19 MPa, oxygen, sulphate and chloride) that are not those of the real PWR environment. According to the mixed potential theory and the Pourbaix diagram, increasing the oxygen level increases the electrochemical corrosion potential in PWR conditions. Therefore the susceptibility for IGSCC to initiate increased with increasing the oxygen level. Previous work by David Tice at SERCO was carried out on type 304 SS under similar conditions in terms of material composition and chemistry of the environment [20]. However the study focussed on cold worked materials and looked into crack propagation using compact tensile (CT) specimens rather than crack initiation using U-bend samples. The key message to highlight from David Tice is that a cyclic loading is apparently necessary for crack initiation under PWR conditions. Nevertheless, in this project only static loading was applied, therefore it could explain the difficulty to initiate cracking, especially under hydrogenated conditions. Fatigue tests have previously been conducted on type 304 SS to study crack initiation in PWR conditions, in water and in air for comparison [145]. It was found that in water, the crack lengths were longer than in air and in PWR conditions. This highlighted the effect of the environment on crack initiation. It confirmed that cracks can initiate on type 304 SS in PWR with cyclic loading. The whole set of experiments in this work and in the literature showed the difficulty to initiate cracking in PWR conditions. However this does not mean that it is not possible to investigate SCC initiation, but it helps understand that to achieve this, severe conditions of stress, long time of exposure and oxygenated environment need to be considered to enhance this process.
4.3.4.2 Cracking features and PGM effect on crack initiation

4.3.4.2.1 Oxide on surface

The nature of the surface oxide is known to influence SCC resistance in PWR environments [33, 59]. In the current study, different environments have been investigated but no clear macroscopic oxide differences have been observed except in the size of the outer layer particles. Indeed, according to the literature, the oxide of austenitic stainless steels has different layers and the structure is summarised in Figure 69. There is a fine-grained inner layer and an outer layer made of intermediate and large size particles. The inner layer is rich in chromium while the outer layer is rich in nickel [33]. According to previous studies [37], the inner layer is a non stoichiometric spinel (Ni$_x$Cr$_y$Fe$_{3-y}$O$_4$). The exact composition depends on the environment including water chemistry and oxygen level. The outer layer has also been characterised before and the intermediate particles seem to be Ni$_{0.75}$Fe$_{2.25}$O$_4$ + Fe$_3$O$_4$ while the large particles seem to be Ni$_{0.75}$Fe$_{2.25}$O$_4$ [37].

Figure 69 Schematic of corrosion oxide film formed on austenitic stainless steels in LWR environments [37]

Oxide was found inside the cracks observed in 304MC after exposure in oxygenated water at 360°C for 1460 hours (see A7). This could be an indication to determine the
mechanism for cracking in these conditions. More work involving focused ion beam (FIB) would need to be performed on the crack tip to determine the oxide composition and structure in more detail. The small holes/cracks observed in both hydrogenated and oxygenated environments (see Figure 63), were only a few micrometers long so there was no clear evidence of crack initiation and these were probably related to minor cracking of the oxide only.

### 4.3.4.2.2 PGM effects on crack initiation

Under the exposure conditions, none of the PGM-doped type 304 SS initiated cracking in hydrogenated and oxygenated conditions. There could therefore be a possible beneficial effect of PGM additions in terms of crack initiation but this would need complementary work to be confirmed. Only one sample made of type 304 SS (sensitised 304MC) revealed cracking under oxygenated conditions, which is not sufficient to clearly establish the environmental conditions for cracking of type 304 SS under high pressure/high temperature. This result gives an optimistic effect of PGM additions in PWR conditions. As no work has been done previously to assess mechanically PGM-doped type 304 SS in terms of crack initiation, this result cannot be discussed and compared with former studies. Nevertheless, PGM additions have shown beneficial effects on the IGSCC resistance of type 304 SS in BWRs as they maintain a potential low enough to avoid or mitigate IGSCC [107]. In this study, electrochemical studies have been carried out on PGM-doped and standard type 304 SS and are presented in Chapters 7, 8 and 9. The work presented in these chapters explains in more detail the effects of PGM additions on the electrochemical corrosion potential under PWRs conditions.

### 4.3.5 Summary

This work showed that crack initiation is not easy on sensitised type 304 SS after less than 1500 hours (about nine weeks). More severe operating conditions such as an
increase in temperature, pressure and/or time of exposure can accelerate the initiation of cracking in type 304 SS. Sulphate and chloride could also accelerate the crack initiation process under oxygenated conditions. According to previous studies [20], cold work and preliminary cyclic loading seem to be some of the key parameters that enhance crack initiation in PWR environments.

More tests were not carried out due to the lack of time and access to the autoclave.
Chapter 1: Introduction

Chapter 2: Literature review

Chapter 3: Materials characterisation

Chapter 4: Crack initiation

Chapter 5: Fracture mechanics approach to stress corrosion crack propagation: fatigue precracking

Chapter 6: SCC propagation study

Chapter 7: Electrochemistry in borated and lithiated water

Chapter 8: Electrochemistry in IGSCC simulated environment

Chapter 9: Electrochemistry in high temperature water

Chapter 10: Discussion

Chapter 11: Conclusions

Chapter 12: Future work
5. Fracture mechanics approach to stress corrosion crack propagation: fatigue precracking

5.1 Introduction
Fatigue precracking using circumferential cracked bar (CCB) samples in a rotating bend rig is an effective method to generate circular and uniform precracks [97]. It produces good quality finish of the precrack and one of its main advantages is that it is quick and gives a known and relatively constant stress intensity factor due to the uniformity of the precrack [96-99]. By contrast, the use of compact tension (CT) specimens for fatigue precracking investigation requires bigger samples and it is more expensive. As little research has been carried out on crack propagation using pre-cracked CCB samples, this study focusses on CCB samples under fatigue rotation to generate fatigue precracks. This preliminary study prepares the investigation of stress corrosion crack propagation (see Chapter 6).

There are four primary aims of this study: 1. To investigate a fatigue precracking method for stress corrosion cracking propagation (refer to Chapter 6) 2. To monitor the fatigue precrack length using a direct current potential drop (DCPD) method. 3. To ascertain a relationship between the precrack length and the ohmic resistance of the material. 4. To determine the parameters to generate a 2.2-2.5 mm fatigue precrack.

5.2 Experimental procedure
5.2.1 Material and heat treatment
The precracking study was investigated on sixteen specimens made of type 304 SS.

The composition of the material is presented in Table 11. The specimens were cut from plates of dimensions 13mm x 2000 mm x 4000 mm. First, the samples were solution annealed at 1050 °C for 40 min, then they were machined and sensitised at 650 °C for 24 hours. The heat-treatments were conducted in tubular furnaces under an argon atmosphere. Figure 70 presents the typical microstructure of the investigated samples after heat treatments.
Table 11 Composition of the type 304 SS used in this fatigue study [146]

<table>
<thead>
<tr>
<th>Elements</th>
<th>C</th>
<th>Ni</th>
<th>Cr</th>
<th>Si</th>
<th>P</th>
<th>Mn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Wt %)</td>
<td>0.053</td>
<td>8.61</td>
<td>18.18</td>
<td>0.44</td>
<td>0.030</td>
<td>1.37</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Figure 70  Representative etched microstructure of a sample further to solution annealing at 1050 °C for 40 min and sensitisation at 650 °C for 24 hours

Sensitisation was confirmed by the ditch structure evident in Figure 70. Indeed, sensitisation is a phenomenon resulting in chromium depletion along the grain boundaries [24, 42]. It makes the grain boundaries anodic to the matrix and the presence of ditches is evidence that the microstructure is sensitised.

5.2.2 Tensile properties and hardness

Table 12 presents the tensile properties and hardness of the material at room temperature.
Table 12 Tensile properties and hardness of the type 304 SS used in the fatigue study [146]

<table>
<thead>
<tr>
<th>Hardness HV10</th>
<th>Yield stress (MPa)</th>
<th>UTS (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>170</td>
<td>214</td>
<td>658</td>
</tr>
</tbody>
</table>

5.2.3 Sample design

The samples consisted of circumferentially cracked bar (CCB) specimens machined in the rolling direction as shown in Figure 71. The design of the samples is presented in Figure 72 and the dimensions are presented in Table 13. The samples were referred to as ‘FP’ for ‘fatigue pre-cracked’. All specimens were machined after solution annealing and before sensitisation.

Figure 71 Schematic showing how the specimens were cut from the plates

Figure 72 Schematic of the CCB sample design used in the fatigue precracking study
Table 13 Dimensions of the CCB samples FP

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>2L, mm</th>
<th>2R, mm</th>
<th>a₀, mm</th>
<th>θ°</th>
</tr>
</thead>
<tbody>
<tr>
<td>FP</td>
<td>87</td>
<td>9.4</td>
<td>2</td>
<td>55</td>
</tr>
</tbody>
</table>

5.2.4 Fatigue precrack in air

This technique has been used previously in several studies and revealed good performance in generating circular and uniform fatigue precracks [96-99, 147]. Further to fatigue precracking, the sample can be fractured under tension and examined using a scanning electron microscope (SEM) to measure the machined notch and fatigue precrack length. Hence, the initial stress intensity factor characteristics can be determined [96, 97]. In this study, the samples were fatigue pre-cracked in a machine shown in Figure 73 with the bending stress applied to the specimen by means of dead weights. A digital indicator provided the number of completed cycles with automatic shut-off upon specimen failure and provided an indication of the operating speed (rotations per minute or RPM.). Each specimen was rotated at 30 Hz, under various bending moments (see Figure 74) and for various numbers of rotations. The fatigue precracking was monitored using a direct current potential drop (DCPD) technique. The initial potential was recorded for each specimen prior to fatiguing. Because it was not possible to measure the potential drop while the specimen was rotating, the fatigue precracking process was interrupted periodically to monitor the potential drop and establish the progress of the precrack. The specimens were loaded symmetrically at two points. At any given point in a cycle the upper portion of the crack tip was under tension whilst the lower portion was under compression. The fatigue precrack was generated from the V-notch and propagated relatively uniformly around the specimen growing a circular ligament (see Figure 75). The measurement of the actual precrack length was determined after fracturing the specimens under tension. Fractography was then
performed to analyse precracking features, and the average precrack length was calculated from eight measurements (see Figure 72) around the circumference of the precrack.

Figure 73 Photography of the R.R Moore machine [148]
5.3 Results

5.3.1 Numerical approach of the key mechanical parameters under fatigue rotation

The rate of the precracking growth was controlled by the stress intensity factor range and hence the bending moment applied to the specimen while rotating. The bending stress and the bending moment are respectively expressed in Equation 16 and Equation 17 [149]. All equations below are taken from reference [149].

**Equation 16** \[
\sigma_b = \frac{4M}{\pi R^3}
\]

- \( \sigma_b \) = Bending stress
- \( M \) = Bending moment
- \( R \) = Radius of the specimen

**Equation 17** \[
M = \frac{PL}{4}
\]

- \( P \) = load applied

Figure 74 Schematic of the rotating bend rig showing the bending moment applied to the specimen
• \( L = \text{half length of the specimen, see Figure 72} \)

The stress intensity factor is given by Equation 18.

**Equation 18** \( K_I = f.K_o \)

Where, \( f \) is the geometric factor (see Equation 19) and \( K_o \) is expressed in Equation 20.

**Equation 19**

\[
f = \frac{K_I}{K_o} = \left( \frac{b}{R} \right)^{5/2} [0.375(1 + 0.5 \frac{b}{R}) + 0.375 \left( \frac{b}{R} \right)^2 + 0.3 \left( \frac{b}{R} \right)^3 + 0.273 \left( \frac{b}{R} \right)^4 + 0.537 \left( \frac{b}{R} \right)^5]
\]

Where,

• \( b = \text{half length of the ligament, see Figure 72} \)
• \( R = \text{radius of the specimen, see Figure 72} \)

**Equation 20** \( K_o = \sigma \sqrt{\frac{\pi a_{\text{tot}}}{3}} \)

Where \( a_{\text{tot}} \) is given by \( a_{\text{tot}} = a_0 + a_{fp} \) (notch + fatigue precrack)

Fatigue precrack growth rate is dependant on \( \Delta K \) through the Paris law (see Equation 21),

**Equation 21** \[ \frac{da}{dN} = A \Delta K^B \]

A and B are material parameters

In this study, \( \Delta K = K_{\text{max}} - K_{\text{min}} = K_{\text{max}} \) as \( K_{\text{min}} \) was equal to zero (see Figure 75).
5.3.2 General results of the fatigue precrack study

The main parameters that have been investigated are the total precrack (notch + fatigue precrack) length atot, the resistance variation ΔR of the CCB specimens, the number of cycles and the load applied to the CCB specimens. From these parameters, the final stress intensity factor during the fatigue process has been determined. For each sample, different cyclic loading conditions have been applied in order to determine the relationship between the total precrack length and the number of cycles at a given load, or between the total precrack length and the DC resistance variation. Table 14 presents the results of interest for this investigation. Only the results of four representative samples are displayed: sample FP-A that failed under fatigue rotation, sample FP-B that grew the longest total precrack (3.1 mm) that did not lead to failure in this study, sample FP-C and FP-D that grew the precracks with length of interest for this study (between 2.2 and 2.5 mm long). Table 15 displays the total precrack length for each of the four samples presented in Table 14. From the table results, a total precrack length of 3.1 mm (sample FP-A) led to failure under a load of 20 kg. However, the sample failed after a relatively high number of cycles (about 32000) as significantly lower loads were applied, which were increased gradually to enhance the fatigue precrack. When the
applied load was fairly high (17 kg) from the start of the experiment, the number of cycles needed to obtain an approximate 2.5 mm total precrack length was much less (about 3000).

The resistance variation was in the order of 0-20 $\mu\Omega$ and increased with the precrack length. The initial resistance of the specimens varied between 85 $\mu\Omega$ (sample FP-A) and 95.752 $\mu\Omega$ (sample FP-D).
<table>
<thead>
<tr>
<th>Specimen ID</th>
<th>V (mV)</th>
<th>I (A)</th>
<th>R (µΩ)</th>
<th>∆R (µΩ)</th>
<th>F (kg)</th>
<th>N (cycles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FP-A</td>
<td>0.31</td>
<td>0.3</td>
<td>3.45</td>
<td>85.2</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>0.335</td>
<td>0.376</td>
<td>3.69</td>
<td>89.1784</td>
<td>0.65</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>0.305</td>
<td>0.333</td>
<td>3.33</td>
<td>91.2532</td>
<td>2.733</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>0.296</td>
<td>0.324</td>
<td>3.29</td>
<td>92.0261</td>
<td>3.5061</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.304</td>
<td>0.322</td>
<td>3.23</td>
<td>92.4405</td>
<td>3.92</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>0.332</td>
<td>0.332</td>
<td>3.3</td>
<td>94.665</td>
<td>6.134</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>0.33</td>
<td>0.316</td>
<td>3.31</td>
<td>102.671</td>
<td>14.15</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>0.35</td>
<td>0.34</td>
<td>3.19</td>
<td>108.232</td>
<td>19.71</td>
<td>18</td>
</tr>
</tbody>
</table>

Failure under fatigue rotation  20  32242
### Table 14 to continue.../

<table>
<thead>
<tr>
<th>Specimen ID</th>
<th>V (mV)</th>
<th>I (A)</th>
<th>R (µΩ)</th>
<th>ΔR (µΩ)</th>
<th>F (kg)</th>
<th>N (cycles)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>FP-B</strong></td>
<td>0.359</td>
<td>3.56</td>
<td>93.3725</td>
<td>0</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0.319</td>
<td>3.58</td>
<td>3.57</td>
<td>0.321</td>
<td>3.56</td>
<td>0.356</td>
</tr>
<tr>
<td></td>
<td>0.356</td>
<td>3.82</td>
<td>94.0562</td>
<td>0.368</td>
<td>3.89</td>
<td>0.6837</td>
</tr>
<tr>
<td></td>
<td>0.369</td>
<td>3.89</td>
<td>3.91</td>
<td>3.56</td>
<td>3.91</td>
<td>3.91</td>
</tr>
<tr>
<td></td>
<td>0.412</td>
<td>3.87</td>
<td>108.006</td>
<td>0.420</td>
<td>3.84</td>
<td>14.6339</td>
</tr>
<tr>
<td></td>
<td>0.423</td>
<td>3.91</td>
<td>3.91</td>
<td>3.56</td>
<td>3.91</td>
<td>3.91</td>
</tr>
<tr>
<td><strong>FP-C</strong></td>
<td>0.333</td>
<td>3.53</td>
<td>95.1267</td>
<td>0.337</td>
<td>3.57</td>
<td>0.346</td>
</tr>
<tr>
<td></td>
<td>0.346</td>
<td>3.56</td>
<td>3.58</td>
<td>3.53</td>
<td>3.56</td>
<td>3.56</td>
</tr>
<tr>
<td></td>
<td>0.358</td>
<td>3.57</td>
<td>3.58</td>
<td>3.53</td>
<td>3.56</td>
<td>3.56</td>
</tr>
<tr>
<td></td>
<td>0.343</td>
<td>3.56</td>
<td>98.3066</td>
<td>0.346</td>
<td>3.57</td>
<td>3.17996</td>
</tr>
<tr>
<td></td>
<td>0.358</td>
<td>3.56</td>
<td>3.56</td>
<td>3.53</td>
<td>3.56</td>
<td>3.56</td>
</tr>
<tr>
<td><strong>FP-D</strong></td>
<td>0.369</td>
<td>4.04</td>
<td>94.9588</td>
<td>0.398</td>
<td>4.04</td>
<td>0.382</td>
</tr>
<tr>
<td></td>
<td>0.382</td>
<td>4.02</td>
<td>0.793251</td>
<td>3.2</td>
<td>4.02</td>
<td>3.52</td>
</tr>
<tr>
<td></td>
<td>0.292</td>
<td>3.2</td>
<td>95.752</td>
<td>0.34</td>
<td>3.42</td>
<td>3.52</td>
</tr>
<tr>
<td></td>
<td>0.34</td>
<td>3.52</td>
<td>3.52</td>
<td>3.2</td>
<td>3.52</td>
<td>3.52</td>
</tr>
</tbody>
</table>

### Table 15 Table presenting the total precrack (notch+ fatigue precrack) length for each sample

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>FP-A (mm)</th>
<th>FP-B (mm)</th>
<th>FP-C (mm)</th>
<th>FP-D (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final fatigue precrack length (mm)</td>
<td>3.325</td>
<td>3.098</td>
<td>2.485</td>
<td>2.215</td>
</tr>
</tbody>
</table>
5.3.3 Direct current potential drop (DCPD) method and precrack measurement using fractography

The direct current potential drop (DCPD) method was used to monitor the precrack length as accurately as possible. The principle of the (DCPD) is based on Ohm’s law (see Equation 22). The resistance of the specimen increases while the precrack grows, therefore by applying a current, it was possible to determine the potential drop and the resulting specimen ohmic resistance. Each potential and current measurement were taken three times and the average values were considered to determine the resistance variation.

**Equation 22** \[ V = R_sI \]

Where,

- \( V \) = Potential
- \( R_s \) = Resistance of the specimen
- \( I \) = Applied current

A current of about 3 to 4 A (see Table 14) was applied to the specimen using two probes placed at 5 mm from the notch and the voltage was measured using a voltmeter. The resistance variation was then related to the precrack length determined after fracturing under tension. Other experiments were performed at a lower current but insufficient precision was obtained to measure a significant potential drop while the precrack was growing. After fatigue precracking and measurement of the final values of potential drop, they were fractured using an Instron tensile machine to measure the precrack length and relate the measured resistance variations to the actual precrack length. The features of the fracture surface were recorded using a scanning electron microscope (SEM) model ZEISS Evo 60 and the mean average precrack length was calculated after
taking measurements in eight different directions \( \langle a \rangle = \frac{1}{8} \sum_{i=1}^{8} a_i \) as represented in Figure 76. A representative fracture surface of a type 304 SS sample further to fatigue precracking and fracturing under tension is also illustrated in Figure 72. Three regions are revealed: the notch, the fatigue precrack and the ligament, where further stress corrosion cracks will grow (see Chapter 6). More details of the fatigue region and ligament are displayed in Figure 77 and Figure 78. The former shows the fatigue marks and the latter reveals the region that failed under tension, representative of a ductile failure (final ligament).

Figure 79 presents the resistance variation against the total precrack length. As the precrack length increased, the resistance also increased. It seemed to be more difficult to detect a sensible resistance variation when the total precrack length was close to the notch length (2 mm). For a total precrack (notch + fatigue precrack) of about 2.5 mm long, the variation was not significant. Indeed, sixteen specimens were monitored but only ten could be investigated as six failed under fatigue rotation. Indeed, above 3 mm, corresponding to a stress intensity factor \( K_I \sim 25.8 \text{ MPa}\sqrt{\text{m}} \), failure was more likely to occur; therefore it was difficult to obtain many values in this range of precrack lengths.
Figure 76 Representative scanning electron micrograph (SEM) fractography of standard type 304 SS after fatigue rotation for 8682 cycles ($K_I = 8.11$ MPa√m at the start of the fatigue process). Three regions are shown: 1. the notch, 2. the fatigue precrack and 3. the ligament
Figure 77 Scanning electron micrograph showing the fatigue precrack region.

Figure 78 Scanning electron micrograph showing the ligament region.
5.4 Discussion

5.4.1 Fractography

Fatigue rotation on CCB specimens has already shown that it was possible to determine $K_{\text{ISC}}$ of stainless steel, mild steel etc. [96-98, 150]. In this study, the fracture surface has revealed relatively uniform and circular fatigue precrack confirming the results found previously by Ibrahim et al. [96-98, 150]. The fatigue striations were observed in the fatigue precrack as expected. The ligament was ductile as the specimens were quickly fractured under tension. The eccentricity in the ligament was negligible for most samples, which implies that the material was relatively isotropic in the fatigue characteristics [99].
Another parameter to consider in terms of fracture susceptibility is the plastic zone. It was shown that the sharper the fatigue crack, the bigger the plastic zone and the higher the fracture toughness [97].

Previously, Irwin worked on the plastic zone and showed that the minimum precrack length should be more than twice the plastic zone in order to be in the plane strain conditions. Practically, it is necessary that the plastic zone be small compared to the distance from the crack tip to any boundary [151].

5.4.2 Precrack length
The precrack length varied with the bending moment applied. In this study, it was not possible to monitor the evolution of the stress intensity factor while fatiguing so it was only calculated initially and after fracturing under tension.

The minimum stress intensity factor, corresponding to the load of the rotating bend rig itself was calculated from Equation 19 (K_{max} = 2.38 \text{ MPa}\sqrt{\text{m}}). The bending moment when no load was applied was equal to M = 1.066 \text{ N.m}. For the CCB samples, the maximum load used was 17 kg, corresponding to a moment M = 3.62 \text{ N.m} and a stress intensity factor between 8.11 \text{ MPa}\sqrt{\text{m}} and 28.8 \text{ MPa}\sqrt{\text{m}} with a maximum total precrack (notch + fatigue precrack) length a_{tot} = 3 \text{ mm}.

5.4.3 Precrack monitoring
Precrack monitoring using the direct current potential drop (DCPD) method showed that it was possible to detect the precrack propagation. However the scatter in the resistance variation was important for a total precrack length of about 2 mm (notch length) or above 3 mm. During the fatigue precrack initiation, the resistance variation was too small to be detected while above 3 mm, the stress intensity factor was possibly too high, which often led to the specimen failure. One of the purposes of this work was to be able to measure the precrack length accurately in order to further investigate SCC propagation under known stress intensity factor K_{I} (see Chapter 6). The DCPD results
seemed to show that it was not possible to be precise in determining the precrack length and therefore the stress intensity factor $K_I$. This can be explained with the experimental errors induced while taking the measurements. Indeed, using the probes to take the voltage is not a reproducible method as the potential difference strongly depends on the location of the probes and therefore, even taking four measurements to calculate one resistance variation was not sufficient to obtain a representative value of the resistance variation. One possibility would be to take hundreds of measurements and average them using software but this is time consuming and not really practical. In addition, there is the thermal effect to take into consideration as it also affects the potential measurements and therefore the resistance variation. For further stress corrosion crack propagation investigation (see Chapter 6), a precrack length between 2.2 and 2.5 mm corresponding to a resistance change between 0.18 and 2 $\mu\Omega$ was chosen. Samples FP-C and FP-D (see Table 14 and Table 15) revealed total precrack between 2.2 and 2.5 mm long so the experimental conditions used to fatigue precrack these two samples have been considered for the study presented in Chapter 6.

5.4.4 Number of cycles

The maximum number of cycles above which fatigue failure occurred varied widely; by increasing the bending moment, the number of cycles leading to failure was reduced significantly, see Table 14. Other parameters such as defects in the materials could also affect the material susceptibility. The lower the load, the higher number of cycles could be conducted. Nevertheless, in this study, the important point was to be able to control the initiation of fatigue precracking and generate a precrack of the order 2.2 to 2.5 mm long. This work showed that it was possible to achieve this in different ways; either by applying a low load for a high number of cycles or by applying a higher load for fewer cycles. From the results presented in Table 14, a load of 17 kg for 3000 cycles was used
Chapter 5 Fracture mechanics approach to SCC propagation: fatigue precracking

to generate a total precrack of about 2.2 to 2.5 mm for the SCC propagation study presented in Chapter 6.

5.4.5 Summary

This study confirmed that fatigue precracking was suitable to initiate mechanical precracking relatively quickly in a circumferential cracked bar (CCB) specimen. It showed that it was possible to detect the precrack growth using a DCPD method. Nevertheless, this technique is not very accurate and only gives a general range of precrack lengths rather than a precise value. In Chapter 6, stress corrosion cracking propagation is investigated on samples made of type 304 SS that have been fatigue pre-cracked for 3000 cycles under a load of 17 kg as these conditions generated the total fatigue precrack length of interest (about 2 to 2.5 mm).
Chapter 1: Introduction

Chapter 2: Literature review

Chapter 3: Materials characterisation

Chapter 4: Crack initiation

Chapter 5: Fracture mechanics approach to stress corrosion crack propagation: fatigue precracking

Chapter 6: SCC propagation study

Chapter 7: Electrochemistry in borated and lithiated water

Chapter 8: Electrochemistry in IGSCC simulated environment

Chapter 9: Electrochemistry in high temperature water

Chapter 10: Discussion

Chapter 11: Conclusions

Chapter 12: Future work
6. Stress corrosion cracking propagation study

6.1 Introduction
Previously, stress corrosion crack propagation was examined by using expensive specimens such as compact tension (CT) or double cantilever beam (DCB) specimens, requiring expensive testing infrastructure, especially at high temperature or high pressure. Recently, the use of circumferential cracked bar (CCB) specimens also called circumferential notched tensile (CNT) specimens has provided reliable results in terms of SCC propagation study. A fracture mechanics technique has been employed for the determination of the critical stress intensity factor $K_{ISC}$ by correlating the crack growth rate and the stress intensity factor $K_I$ [147]. This novel method provided accurate, quick and cost-effective testing.

In this study the crack growth rate, stress intensity factor, crack length, crack depth and time to failure are being considered and the main goals are to investigate the effect of PGM additions on these parameters in a solution of potassium tetrathionate, that promotes intergranular stress corrosion cracking (IGSCC) [71, 89, 152]. Testing was performed on CCB samples with a 9.4 mm diameter. Ahead of the notch, a fatigue precrack was grown using a rotating bend rig machine (see Chapter 5 for the experimental details).

This section is divided into five parts which are this introduction, the experimental procedure, the result part, the discussion and the summary.

6.2 Experimental procedure

6.2.1 Material and heat treatment
The tested materials were 304MC, Pd2MC (0.23 wt% Pd), Pd3MC (0.96 wt% Pd), Ru2MC (0.26 wt% Ru), Ru3MC (1.01 wt% Ru), Pd3HC (1 wt% Pd) and Ru3HC (1 wt% Ru), see Chapter 2 for material compositions and microstructures. The samples were in the sensitised condition (heat treated at 650°C for 24 hours) and fatigue pre-cracked for 3000 cycles under a 17 kg load as explained in Chapter 5. Due to the limited
number of samples available for this study, only a maximum of two samples of each material were investigated.

6.2.2 SCC propagation experiment in potassium tetrathionate (0.01 M \(\text{K}_2\text{S}_4\text{O}_6\), pH = 1.5) at room temperature

The samples were loaded up to a given load at a constant rate of 0.01 mm/min and the extension was kept fixed to measure the load variation against time. A load decrease was used as an indication of the crack propagation. The pre-cracked area was exposed to a solution of potassium tetrathionate (0.01 M \(\text{K}_2\text{S}_4\text{O}_6\), pH=1.5) and the rest of the specimen was masked off with Lacomite lacquer prior to loading up in order to promote IGSCC at the root of the fatigue precrack by isolating the rest of the specimen from solution. First, the standard alloy type 304 SS (304MC) was investigated at different loads (17 kN and 7 kN) in order to determine the range of appropriate stresses to apply in order to enhance IGSCC and to analyse the variations in terms of fracture surface features. Then, PGM -doped type 304 SS samples were tested and compared to the standard alloy. An Instron tensile machine model 5569 was used to run the experiments. The surface was then characterised using a SEM ZEISS model Evo60 and one half of the sample was cross sectioned in the longitudinal direction using a Struers cutting machine, to measure the crack depth. Figure 80 and Table 16 show the sample design and dimensions also presented in Chapter 5. Figure 81 displays a schematic diagram of the SCC propagation experiment device.
Gauge length, 2L

Figure 80 Schematic of the circumferential cracked bar (CCB) sample design

Table 16 Circumferential cracked bar (CCB) specimen dimensions

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>2L, mm</th>
<th>2R, mm</th>
<th>a₀, mm</th>
<th>0°</th>
</tr>
</thead>
<tbody>
<tr>
<td>FP</td>
<td>87</td>
<td>9.4</td>
<td>2</td>
<td>55</td>
</tr>
</tbody>
</table>

Figure 81 Schematic diagram of the SCC experiments showing the CCB specimen under tension in a solution of 0.01 M K₂S₄O₆, pH=1.5, at room temperature
6.3 Results

6.3.1 General results

Particular attention should be given to the time to failure and stress intensity factor under tension as they are the key factors representative of the stress corrosion cracking susceptibility of the investigated materials in terms of crack propagation in potassium tetrathionate. The initial stress intensity factor $K_I$ is given by Equation 23. Table 17, Figure 82 and Figure 83 present the geometric factor ‘$f$’ for the investigated circumferential cracked bar (CCB) samples. In order to determine the relation between ‘$f$’ and ‘a/R’, ln($f$) was plotted as a function of $a_{tot}/R$ and the equation of the curve was determined (see Figure 83).

\[ K_I = f \sigma \sqrt{\pi a_{tot}} \]  

Equation 23

Where,

- $f$, is the geometric factor
- $\sigma$, is the stress
- $a_{tot}$, is the total crack length (notch + fatigue precrack + stress corrosion crack)

For the samples examined, the geometric factor ‘$f$’ was calculated according to the handbook of mechanics [153] and estimated as a function of the ratio $a_{tot}/R$, which represents the total crack length over the radius $R$ of the specimen (see Figure 80). The $K_I$ values given in Table 17 correspond to the stress intensity at the start of the experiment in potassium tetrathionate, which means that the resultant total crack length was equivalent to the machined notch length added to the fatigue precrack length. The measurements of the fatigue precrack length and SCC crack lengths were conducted after fractography under a scanning electron micrograph (SEM). The average of the crack lengths were performed using an eight point average method as described in Chapter 5, and reported in Table 17. An example of the calculations of the geometric
factor ‘f’ and the stress intensity factor ‘$K_I$’ using the equation presented in Figure 83, is given for a sample type 304 SS (FP304MC-1) as follows:

- $a_{tot} = 2.302$ mm
- $a_{tot}/R = 2.302/4.7 = 0.44$
- $f = e^{0.1167 e^{3.4737(a/R)}} = 1.71$ for $a_{tot}/R = 0.44$
- $\sigma = \frac{F}{\pi R^2}$

Where $F$ is the tensile load applied (see Table 17)

\[ \sigma = 244 \text{ MPa} \]

- $K_I = f \sigma \sqrt{\pi a_{tot}} = 1.71 \times 244 \sqrt{\pi \times 2.302 \times 10^{-3}} = 37.4 \text{ MPa} \sqrt{\text{m}}$

The general results of interest, which are the time to failure, type of failure, estimated stress corrosion crack propagation growth rate, crack length, crack depth and initial $K_I$ are presented in Table 18.

**Table 17** Table giving the values of the geometric $f$ for a given ratio $a_{tot}/R$ [154]

<table>
<thead>
<tr>
<th>$a_{tot}/R$</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>1.133</td>
</tr>
<tr>
<td>0.03</td>
<td>1.139</td>
</tr>
<tr>
<td>0.05</td>
<td>1.150</td>
</tr>
<tr>
<td>0.1</td>
<td>1.180</td>
</tr>
<tr>
<td>0.2</td>
<td>1.261</td>
</tr>
<tr>
<td>0.3</td>
<td>1.393</td>
</tr>
<tr>
<td>0.33</td>
<td>1.452</td>
</tr>
<tr>
<td>0.4</td>
<td>1.602</td>
</tr>
<tr>
<td>0.5</td>
<td>1.940</td>
</tr>
<tr>
<td>0.6</td>
<td>2.516</td>
</tr>
<tr>
<td>2/3</td>
<td>3.158</td>
</tr>
<tr>
<td>0.7</td>
<td>3.618</td>
</tr>
<tr>
<td>0.8</td>
<td>6.243</td>
</tr>
<tr>
<td>0.9</td>
<td>16.67</td>
</tr>
</tbody>
</table>
Figure 82 Non-dimensional stress intensity factor for a circumferential crack in a cylindrical bar under tension [154]

Figure 83 Graph determining the relation between ‘f’ and ‘atot/R’: \[ f = \exp(0.1167 \exp(3.4737(atot/R))) \]
### Table 18 Table summarising the parameters to calculate $K_I$ at the start of the SCC propagation

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$a_{tot}$, m (at the start of the tensile test)</th>
<th>$a_{tot}/R$</th>
<th>Geometric factor $f$</th>
<th>Surface area $A$, m²</th>
<th>$2R$, m</th>
<th>Tensile load $F$, kN</th>
<th>Tensile stress $\sigma$, MPa</th>
<th>Initial $K_{I_0}$, MPa/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>FP-304MC-1</td>
<td>0.002302</td>
<td>0.48</td>
<td>1.8</td>
<td>6.9E-05</td>
<td>0.0094</td>
<td>17</td>
<td>244.9</td>
<td>37.4</td>
</tr>
<tr>
<td>FP-304MC-2</td>
<td>0.002304</td>
<td>0.49</td>
<td>1.8</td>
<td>6.9E-05</td>
<td>0.0094</td>
<td>7</td>
<td>100.8</td>
<td>15.4</td>
</tr>
<tr>
<td>FP-Pd2MC-1</td>
<td>0.002035</td>
<td>0.432</td>
<td>1.68</td>
<td>6.9E-05</td>
<td>0.0094</td>
<td>9</td>
<td>129.6</td>
<td>17.4</td>
</tr>
<tr>
<td>FP-Pd2MC-2</td>
<td>0.00204</td>
<td>0.434</td>
<td>1.68</td>
<td>6.9E-05</td>
<td>0.0094</td>
<td>9</td>
<td>129.6</td>
<td>17.4</td>
</tr>
<tr>
<td>FPRu2MC-1</td>
<td>0.0022</td>
<td>0.47</td>
<td>1.75</td>
<td>6.9E-05</td>
<td>0.0094</td>
<td>9</td>
<td>129.6</td>
<td>18.8</td>
</tr>
<tr>
<td>FP-Ru2MC-2</td>
<td>0.0022</td>
<td>0.47</td>
<td>1.75</td>
<td>6.9E-05</td>
<td>0.0094</td>
<td>9</td>
<td>129.6</td>
<td>18.8</td>
</tr>
<tr>
<td>FP-Pd3MC-1</td>
<td>0.0022</td>
<td>0.46</td>
<td>1.7</td>
<td>6.9E-05</td>
<td>0.0094</td>
<td>8</td>
<td>115.2</td>
<td>16.2</td>
</tr>
<tr>
<td>FP-Pd3MC-2</td>
<td>0.00249</td>
<td>0.52</td>
<td>2.1</td>
<td>6.9E-05</td>
<td>0.0094</td>
<td>8</td>
<td>115.2</td>
<td>21.4</td>
</tr>
<tr>
<td>FP-Ru3MC-1</td>
<td>0.002294</td>
<td>0.047</td>
<td>1.88</td>
<td>6.9E-05</td>
<td>0.0094</td>
<td>8</td>
<td>115.9</td>
<td>18.5</td>
</tr>
<tr>
<td>FP-Pd3HC-1</td>
<td>0.002</td>
<td>0.42</td>
<td>1.65</td>
<td>6.9E-05</td>
<td>0.0094</td>
<td>5</td>
<td>72</td>
<td>9.4</td>
</tr>
<tr>
<td>FP-Pd3HC-2</td>
<td>0.002</td>
<td>0.44</td>
<td>1.675</td>
<td>6.9E-05</td>
<td>0.0094</td>
<td>5</td>
<td>72</td>
<td>9.4</td>
</tr>
<tr>
<td>FPRu3HC-1</td>
<td>0.002</td>
<td>0.44</td>
<td>1.675</td>
<td>6.9E-05</td>
<td>0.0094</td>
<td>5</td>
<td>72</td>
<td>9.4</td>
</tr>
<tr>
<td>FPRu3HC-2</td>
<td>0.002</td>
<td>0.45</td>
<td>1.72</td>
<td>6.9E-05</td>
<td>0.0094</td>
<td>5</td>
<td>72</td>
<td>9.4</td>
</tr>
</tbody>
</table>
Table 19 Summary of the experimental parameters for the stress corrosion cracking propagation

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>PGM (wt%)</th>
<th>C (wt%)</th>
<th>Type of failure</th>
<th>$K_I$ (MPa$\sqrt{m}$)</th>
<th>Time to failure (hours)</th>
<th>Estimated average SCC Crack growth rate (mm/hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FP-304MC-1</td>
<td>0</td>
<td>0.056</td>
<td>Ductile</td>
<td>37.4</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>FP-304MC-2</td>
<td>0</td>
<td>0.056</td>
<td>IGSCC</td>
<td>15.4</td>
<td>240</td>
<td>0.0069</td>
</tr>
<tr>
<td>FP-Pd2MC-1</td>
<td>0.23</td>
<td>0.04</td>
<td>IGSCC</td>
<td>17.4</td>
<td>30</td>
<td>0.067</td>
</tr>
<tr>
<td>FP-Pd2MC-2</td>
<td>0.23</td>
<td>0.04</td>
<td>IGSCC</td>
<td>17.4</td>
<td>35</td>
<td>0.057</td>
</tr>
<tr>
<td>FP-Ru2MC-1</td>
<td>0.26</td>
<td>0.035</td>
<td>IGSCC</td>
<td>18.8</td>
<td>15</td>
<td>0.015</td>
</tr>
<tr>
<td>FP-Ru2MC-2</td>
<td>0.26</td>
<td>0.035</td>
<td>IGSCC</td>
<td>18.8</td>
<td>15</td>
<td>0.015</td>
</tr>
<tr>
<td>FP-Pd3MC-1</td>
<td>0.96</td>
<td>0.05</td>
<td>IGSCC</td>
<td>16.2</td>
<td>26</td>
<td>0.065</td>
</tr>
<tr>
<td>FP-Pd3MC-2</td>
<td>0.96</td>
<td>0.05</td>
<td>IGSCC</td>
<td>21.4</td>
<td>21</td>
<td>0.076</td>
</tr>
<tr>
<td>FP-Ru3MC-1</td>
<td>1.01</td>
<td>0.047</td>
<td>IGSCC</td>
<td>18.8</td>
<td>24</td>
<td>0.084</td>
</tr>
<tr>
<td>FP-Pd3HC-1</td>
<td>1</td>
<td>0.075</td>
<td>IGSCC</td>
<td>9.4</td>
<td>11</td>
<td>0.23</td>
</tr>
<tr>
<td>FP-Ru3HC-1</td>
<td>0.99</td>
<td>0.096</td>
<td>IGSCC</td>
<td>9.8</td>
<td>11</td>
<td>0.23</td>
</tr>
</tbody>
</table>
6.3.2 Time to failure

The time to failure in 0.01 M K$_2$S$_4$O$_6$ has been taken into consideration as one of the key parameters to investigate the SCC susceptibility of the standard and doped materials in this study. Figure 84 shows the load against time for most investigated samples. The graph displayed in Figure 84 does not present the stress intensity factor values so the time to failure must be considered as an indication of the average crack propagation rate and not as a unique parameter to investigate the IGSCC susceptibility of the materials. Both, the stress intensity factor values presented in Table 18 as well as the time to failure are more representative of the material resistance to IGSCC propagation.

The shortest time to failure seemed to be for the high carbon PGM-doped alloys. Indeed, FP-Pd3HC and FP-Ru3HC that contain respectively 0.075 wt% C and 0.095 wt% C, failed after 11 hours while the medium carbon PGM-doped alloys (Pd3MC and Ru3MC) failed after 26 hours and 24 hours, see Table 19. Pd3HC and Ru3HC failed after 11 hours under an initial K$_I$ of about 9 MPa$\sqrt{m}$, see Table 19. This stress intensity factor value is relatively low compared to those applied to the other materials. This shows that the IGSCC resistance of high carbon PGM-doped is quite poor despite the PGM additions.

The results of FP304MC-1 showed that for a load of 17 kN, the failure was ductile and not IGSCC. This led to lower the load in order to slow down the crack propagation rate as well as promoting IGSCC for the other tested samples. FP-304MC-2 was loaded twice. The first time up to 6kN but no significant reduction of the load was observed even after 120 hours (5 days) so it was loaded a second time up to 7 kN and a decrease in the load was observed after 2 days, indicating possible crack propagation, see Figure 84.

Only the second loading of FP-304MC-2 is displayed as the first loading (6 kN) did not reveal a significant variation in load after 120 hours.
For a load of 7 kN, the decrease was in three stages. The first stage was a slow decrease and lasted about 60 hours while the second and third stages were much faster. The ratio load over time has been calculated for the second and third stages to estimate the time to failure. A decrease of 105 N/hr was estimated, which corresponded to an approximate time to failure of 105.5 hours if it is assumed that the failure occurred for a load equal to zero.

By contrast, medium carbon Pd and Ru doped alloys containing about 0.25 and 1 wt% PGM failed quickly with a more rapid crack growth rate (see Figure 84). Pd doped alloys containing 0.23 wt% Pd (FP-Pd2MC-1 and FP-Pd2MC-2) were both loaded up to 9 kN. For similar $K_I$ at the start of the tensile test (about 17 MPa√m, see Table 19), they revealed a time to failure of about 30 hours and 35 hours. With 0.96 wt% Pd (FP-Pd3MC), the failure was also relatively quick as the specimen failed after about 26 hours. The stress intensity factors applied to the medium carbon Pd doped alloys containing 0.23 wt% and 0.96 wt% Pd were respectively 17 MPa√m and 21 MPa√m so the time to failure of these two alloys cannot be compared but it shows that increasing the Pd content does not, in this experiment, improve the stress corrosion cracking propagation resistance. Similarly, 0.26 wt% Ru doped alloys (FP-Ru2MC-1 and FP-Ru2MC-2) and 1.01 wt% Ru doped alloy (FP-Ru3MC-1) failed quickly (respectively after about 15 hours and after 24 hours, see Table 18 and Figure 84). The stress intensity factors applied to these alloys (FP-Ru2MC and FP-Ru3MC) were very similar (about 18 MPa√m), see Table 17. So, increasing the Ru content from 0.26 wt% to 1.01 wt% seemed to have a beneficial effect in terms of stress corrosion cracking propagation resistance.
Figure 84 Graph presenting the load against time in a solution of 0.01 M K$_2$S$_4$O$_6$ at pH=1.5 and 25°C

6.3.3 Fractography

This section presents typical fractography obtained for the standard and PGM-doped alloys after SCC propagation experiments in 0.01 M K$_2$S$_4$O$_6$, pH=1.5 at room temperature. Fractographies are displayed in Figure 85-Figure 92. For most samples, the fractography showed four areas: the machined notch, fatigue precrack, IGSCC crack and final ductile ligament. Figure 86 and Figure 88 highlight the four areas and the eccentricity of the ligament. Most samples failed intergranularly in 0.01 M K$_2$S$_4$O$_6$, except FP304MC-1, which showed ductile failure, probably because the initial stress conditions applied were too high (about 37 MPa$\sqrt{m}$, see Table 17).

However, IGSCC was still observed with Pd and Ru additions. Medium carbon Pd doped alloys revealed also four regions and IGSCC was present on surface, see Figure 87 and Figure 88. Increasing the Pd content from 0.23 to 0.96 wt% did not affect the surface features. Indeed IGSCC was promoted similarly in potassium tetrathionate (see Chapter 8). Medium carbon Ru doped alloys revealed IGSCC on surface and the Ru
content did not affect the fracture surface in terms of IGSCC, see Figure 89 and Figure 90.

High carbon level (above 0.075 wt %) PGM (Pd or Ru) doped samples did not reveal an obvious fatigue precrack, see Figure 91 and Figure 92. It suggested that the fatigue behaviour could be different from that of the medium carbon samples.

From a general point of view, the fractography revealed that under similar fatigue precracking conditions in terms of number of cycles and applied load, the materials did not show identical fatigue precrack lengths. Obviously, this reveals that the fatigue behaviour varies with the PGM content and also with the carbon content. This point makes the investigation more difficult as the crack length at the start of the tensile loading in potassium tetrathionate and therefore the applied stress intensity factor are not similar even for an equivalent applied load.

Ideally, it would have been better to investigate the fatigue properties of the PGM-doped alloys as well. However, this would have taken too much time. In addition, there were not a sufficient number of samples available for this study.

An alternative to investigate IGSCC propagation resistance is slow strain rate testing but this technique combines crack initiation and crack propagation.
6.3.3.1 Fractography of the standard alloy FP-304MC

Figure 85 Fractography of FP304MC-1 after fatigue precracking and tensile testing in 0.01 M $K_2S_2O_8$, pH=1.5: (a) the machined notch, fatigue precrack and ligament are revealed (b) dimples in the ligament region
Figure 86 Fractography of FP304MC-2 after fatigue precracking and tensile testing in 0.01 M $\text{K}_2\text{S}_2\text{O}_8$, pH=1.5: (a) the machined notch, fatigue precrack and intergranular stress corrosion cracking are revealed; The black arrows present the eight average point that measures the SCC crack length (b) IGSCC
6.3.3.2 Fractography of the medium carbon Pd doped alloys

Figure 87 Fractography of FP-Pd2MC-2 after fatigue precracking and tensile loading in 0.01 M K$_2$S$_4$O$_6$, pH=1.5: (a) the notch and intergranular stress corrosion cracking are revealed (b) IGSCC
Figure 88 Fractography of FP-Pd3MC-2 after fatigue precracking and tensile loading in 0.01 M $\text{K}_2\text{S}_2\text{O}_8$, pH=1.5: (a) the notch and intergranular stress corrosion cracking are revealed (b) IGSCC
6.3.3.3 Fractography of the medium carbon Ru doped alloys

Figure 89 Fractography of FP-Ru2MC-1 after fatigue precracking and tensile loading in 0.01 M K$_2$SiO$_4$, pH=1.5: (a) the notch and intergranular stress corrosion cracking are revealed (b) IGSCC
Figure 90 Fractography of FP-Ru3MC after fatigue precracking and tensile loading in 0.01 M $\text{K}_2\text{S}_2\text{O}_8$, pH=1.5: (a) the notch and intergranular stress corrosion cracking are revealed (b) IGSCC failure.
6.3.3.4 Fractography of the high carbon Pd doped alloys FP-Pd3HC

(a) Notch IGSCC

(b) FP-Pd3HC-1

Figure 91 Fractography of a typical high carbon Pd doped alloy (FP-Pd3HC) after fatigue precracking and tensile loading in 0.01 M K$_2$S$_2$O$_4$, pH=1.5: (a) the notch and intergranular stress corrosion cracking are revealed (b) intergranular stress corrosion cracking on surface
6.3.3.5 Fractography of the high carbon Ru doped alloys FP-Ru3HC

Figure 92 Fractography of a typical high carbon Ru doped alloy (FP-Ru3HC) after fatigue precracking and tensile loading in 0.01 M K$_2$S$_2$O$_6$, pH=1.5: (a) the notch, fatigue precrack and intergranular stress corrosion cracking are revealed (b) intergranular stress corrosion cracking on surface and final ductile ligament
6.3.4 Crack growth rate

The crack growth rate was estimated from the graph presented in Figure 84. However, as it is not constant and present different stages, only a qualitative investigation was performed. The measurements took into account the ratio ‘average stress corrosion crack length over time to failure’. The resulting SCC crack length was obtained by using the eight average point method as shown in Figure 86. Table 20 gives the value for the crack growth rate.

FP-304MC-2 revealed IGSCC from the root of the fatigue precrack and the fractography highlighted the presence of a ductile ligament (radius 0.9 mm) at the centre of the specimen, see Figure 86. So the crack growth rate was calculated from these measurements. The initial crack length (notch + fatigue precrack) was 2.303 mm see Table 17) and the final crack length (notch + fatigue precrack + SCC) was 3.8 mm; so the average crack growth rate for this sample was evaluated at 0.0069 mm/hour. However, it is important to consider that the crack growth rate is not constant and may vary from the initiation stage to the final stage. So the calculated values give only an indication but cannot be used as a precise key parameter describing the crack propagation behaviour.

Medium carbon Pd doped alloys (FP-Pd2MC-1, FP-Pd2MC-2, FP-Pd3MC-1 and FP-Pd3MC-2) presented a fast crack growth rate as shown in Figure 84. They all failed after less than two days. Crack propagation seemed to happen quickly as a significant load decrease was observed in the first thirty hours for all the medium carbon PGM (Pd or Ru) doped alloys. The specimen failures were nearly sudden after a load decrease of about 10%. For the medium carbon samples, the crack growth rate of FP-Pd3MC-1 was estimated at 0.08 mm/hour as the SCC length was about 2.1 mm for a time to failure of 26 hours.
High carbon Pd and Ru doped alloys did not show a clear fatigue precrack and the final ductile ligament was difficult to measure as it was relatively small. Therefore, the SCC length was considered to be about 2.7 mm (specimen radius (4.7 mm) - notch length (2 mm)= 2.7 mm). The estimated crack growth rates for the high carbon PGM (Pd or Ru) doped alloys were much faster than those of the medium carbon PGM (Pd or Ru) doped alloys. Indeed, they were estimated at about 0.23 mm/hour against 0.08 mm/hour for FP-Pd3MC for instance.

Table 20 Table summarising the average SCC crack growth rate

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Average SCC crack growth rate mm/hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>FP-304MC-2</td>
<td>0.006*</td>
</tr>
<tr>
<td>FP-Pd2MC-2</td>
<td>0.057</td>
</tr>
<tr>
<td>FP-Ru2MC-1</td>
<td>0.015</td>
</tr>
<tr>
<td>FP-Pd3MC-1</td>
<td>0.076</td>
</tr>
<tr>
<td>FP-Ru3MC-1</td>
<td>0.084</td>
</tr>
<tr>
<td>FP-Pd3HC-1</td>
<td>0.236</td>
</tr>
<tr>
<td>FP-Ru3HC-1</td>
<td>0.236</td>
</tr>
</tbody>
</table>

*FP-304MC-2 has much more delta ferrite, which will slow the cracking

6.3.5 Crack depth

The crack depth was measured further to cross sectioning the upper half of the samples in the longitudinal direction. Figure 93-Figure 99 show the cracking and corrosion features in the different areas: machined notch, fatigue precrack, IGSCC area and final ligament. Table 21 displays the crack depth values for the samples that underwent IGSCC while immersed in the solution of 0.01 M K₂S₂O₆ at pH=1.5 under tension. Standard type 304 SS revealed IGSCC under 7 kN. Figure 93 reveals that cracking propagated in the longitudinal direction and was intergranular as expected for austenitic stainless steels in potassium tetrathionate [91].
Pd additions in medium carbon alloy (FP-Pd2MC and FP-Pd3MC) enhanced deep IGSCC with respect to the standard alloy (304MC), see Figure 94 and Figure 95. Medium carbon Pd doped alloys revealed IGSCC with a maximum crack depth of about 300 µm. The cracks were relatively wide (10 to 20 µm) at the beginning and then sharper.

Medium carbon Ru doped alloy (FP-Ru2MC and FP-Ru3MC) revealed mostly grain dropouts in the longitudinal direction as shown in Figure 96 and Figure 97. For high carbon alloys (FP-Pd3HC and FP-Ru3HC), the crack depth was negligible with Pd addition under a load of 5 kN. However, IGC was observed as seen in Figure 98, where the grains dropped off the surface. By contrast, high carbon Ru doped alloy (1 wt%) revealed a maximum crack depth of about 300 µm (see Figure 99), which is comparable to that observed in the medium carbon Pd doped alloy (FP-Pd2MC).

Table 21 Maximum crack depth measured after cross sectioning the sample in the longitudinal direction

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Maximum crack depth, µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>FP-304MC-2</td>
<td>50</td>
</tr>
<tr>
<td>FP-Pd2MC-1</td>
<td>300</td>
</tr>
<tr>
<td>FP-Ru2MC-1</td>
<td>Mostly grain dropout</td>
</tr>
<tr>
<td>FP-Pd3MC-1</td>
<td>300</td>
</tr>
<tr>
<td>FP-Ru3MC</td>
<td>Mostly grain dropout</td>
</tr>
<tr>
<td>FP-Pd3HC-1</td>
<td>negligible</td>
</tr>
<tr>
<td>FP-Ru3HC-1</td>
<td>300</td>
</tr>
</tbody>
</table>
6.3.5.1 Micrographs revealing the crack depth of the standard alloy

Figure 93 Cross section of a representative standard type 304 SS (FP-304MC) after fatigue precracking and SCC propagation test in 0.01M $\text{K}_2\text{S}_2\text{O}_8$ at pH = 1.5: (a) IGSCC region; (b) machined notch region

6.3.5.2 Micrographs revealing the crack depth of medium-carbon Pd-doped alloys

Figure 94 Cross-section of a representative medium carbon Pd (0.23 wt%) doped type 304 SS (FP-Pd2MC) after fatigue pre-cracking and SCC propagation test in 0.01 M $\text{K}_2\text{S}_2\text{O}_8$ at pH = 1.5: (a) SCC region; (b) machined notch region
6.3.5.3 Micrographs revealing the crack depth of medium-carbon Ru-doped alloys

Figure 95 Cross-section of a representative medium-carbon Pd (0.96 wt%) doped type 304 SS (FP-Pd3MC) after fatigue pre-cracking and SCC propagation test in 0.01 M K$_2$S$_3$O$_6$ at pH = 1.5: (a) SCC region; (b) machined notch region

Figure 96 Cross-section of a representative medium-carbon Ru (0.26 wt%) doped type 304 SS (FP-Ru2MC) after fatigue pre-cracking and SCC propagation test in 0.01 M K$_2$S$_3$O$_6$ at pH = 1.5: (a) SCC region; (b) machined notch region
Figure 97 Cross-section of a representative medium carbon Ru (1.01 wt%) doped type 304 SS (FP-Ru3MC) after fatigue pre-cracking and SCC propagation test in 0.01 M \( \text{K}_2\text{S}_2\text{O}_8 \) at \( pH = 1.5 \): (a) SCC region; (b) machined notch region

6.3.5.4 Micrographs revealing the crack depth of high-carbon Pd-doped alloy

Figure 98 Cross-section of a representative high-carbon Pd-doped type 304 SS after fatigue pre-cracking and SCC propagation test in 0.01 M \( \text{K}_2\text{S}_2\text{O}_8 \) at \( pH = 1.5 \): (a) SCC region; (b) machined notch region
6.3.5.2 Micrographs revealing the crack depth of medium-carbon Ru-doped alloy

Figure 99 Cross-section of a representative high-carbon Ru-doped type 304 SS after fatigue pre-cracking and SCC propagation test in 0.01 M K$_2$S$_2$O$_6$ at pH = 1.5: (a) SCC region; (b) machined notch region

6.4 Discussion
6.4.1 Effect of (PGM) additions on time to failure

Different PGM additions have been investigated and it seemed that increasing Pd additions from 0.23 wt% (FP-Pd2MC) to 0.96 wt% (FP-Pd3MC) lower the IGSCC resistance as shorter time to failure were observed (see Table 19). It should be noted however that subsequent analysis (see Chapter 3) of the 304MC base alloy showed a significantly greater volume fraction of delta ferrite than the other alloys. This factor is probably why the base alloy was seen to be rather resistant to IGSCC. There is also to consider the experimental error as under similar conditions, slightly different times to failure (30 and 35 hours) have been determined for FP-Pd2MC. Nevertheless, it seemed that increasing the Pd content of the medium carbon alloys did not show a real beneficial effect in terms of IGSCC propagation resistance. On the other hand, increasing the Ru additions from 0.26 wt% (FP-Ru2MC) to 1.01 wt% (FP-Ru3MC) seemed to be beneficial as a longer time to failure was observed even under higher stress intensity factors (see Table 18). FP-Ru2MC has shown repeatable results in terms
of crack propagation rate and time to failure (see Figure 84) under equivalent initial stress intensity factors. At the highest carbon level (>0.075%) Pd and Ru additions did not reveal any good performances in terms of IGSCC and/or IGC resistance. Indeed the time to failure was very short (11 hours) for FP-Pd3HC and FP-Ru3HC although the initial stress intensity factors applied were quite low (9 MPa√m). Despite the fact that fatigue cracks did not grow on those alloys with high carbon level, IGSCC propagated from the root of the notch. This means that a sharp precrack was not required for IGSCC propagation to occur in the high carbon alloys.

Pd additions may affect the time to failure with respect to the standard alloy. Indeed, for medium carbon alloys, Pd additions (0.23 wt%) seemed to reduce the time to failure by a factor of 10 (see FP-Pd3MC-1 and FP-304MC-2 in Table 18). FP-Pd3MC-1 and FP-304MC-2 can be compared as the initial stress intensity factors applied were equivalent (respectively 16.2 MPa√m and 15.4 MPa√m). Increasing the initial stress intensity factor applied to 0.23 wt% Pd doped alloy (FP-Pd3MC) from 16.2 MPa√m (FP-Pd3MC-1) to 21 MPa√m (FP-Pd3MC-2) reduced the time to failure from 26 hours to 21 hours. This showed that the initial stress intensity factor applied has an important effect on the time to failure. Therefore it is critical to compare the time to failure of two samples that have been under very similar stress conditions. However, in these experiments, the environment (potassium tetrathionate) has to be taken into consideration as well as the tensile resistance. Further investigation on the electrochemical behaviour of the PGM -doped and standard alloys in potassium tetrathionate has been carried out and is presented in Chapter 7.

FP-Ru3MC-1 failed after about 24 hours under an initial stress intensity factor $K_I=18.8$ MPa√m. The time to failure cannot be compared to that of the standard alloy (FP-304MC-2) which was under a lower initial stress intensity factor $K_I$ (15.4 MPa√m). However, when compared to FP-Pd3MC-1 and FP-Pd3MC-2, it seems that FP-
Ru3MC–1 had a similar behaviour in terms of time to failure and crack propagation rate.

It is difficult to compare all the results obtained in this study because the fatigue precracking results were not identical for the different alloys under similar conditions. Defects, microstructure, notch geometry and fatigue behaviour may affect the fatigue precracking results. Consequently, the initial stress intensity factors further to fatigue precracking were different and thus the initial conditions for the stress corrosion cracking propagation investigation were different even under similar tensile loading. Further, as noted, variation in levels of delta ferrite will have a marked effect on the crack propagation rate and time to failure.

6.4.2 Effect of (PGM) on crack depth and crack growth rate

Cross sections have been performed in the longitudinal direction of the CCB samples and they revealed the presence of IGSCC, IGC or even grain dropouts, see Figure 93-Figure 99. Medium carbon Pd doped alloys seemed to reveal deeper cracks (about 300 µm). By contrast medium carbon Ru doped alloys seemed to show grain dropout. As expected the mode of cracking was intergranular in potassium tetrathionate [152]. The standard alloy (FP-304MC-2) showed IGSCC and material loss but the cracks were less deep, see Figure 93. The flanks did not reveal either IGSCC or IGC as the samples were masked off with Lacomite in order to promote IGSCC propagation from the root of the fatigue precrack. Nevertheless, the micrographs of the cross sections revealed that IGSCC was also in the bulk of the samples. In terms of crack propagation rate, PGM -doped alloys have revealed faster average crack propagation rates, see Table 20. However, this table presents the average values which do not indicate the crack propagation behaviour. It only gives an indication on the time to failure rather than being an accurate key parameter evaluating the cracking propagation behaviour. According to Figure 84, all the alloys revealed a slight load decrease after reaching the
maximum load. PGM-doped alloys seemed to fail in two stages: first the load decreased slowly with time until it lost about 10% of its initial value and then, the load decreased rapidly until failure. The second stage seemed to take one hour or less for most medium carbon PGM-doped alloys except FP-Pd3MC-2 for which it took about five hours. On the other hand, FP-304MC-2 did not fail but revealed a different behaviour in terms of load variation. Indeed, three main stages could be determined: first, a slow load decrease, except after about three hours, a slight increase from 6437 N to 6532 N was observed, see Figure 84. This was not expected as the load should have remained constant or lower. The second stage was a faster load decrease after fifty hours and the third stage was from 60 hours with a more important load variation with time, indicating faster crack propagation rate. The results with the standard alloy are not really exploitable as only one sample (FP-304MC-2) revealed IGSCC. Unfortunately FP-304MC-1 was loaded to 17 kN, which enhanced ductile failure and not IGSCC. Consequently the effects of PGM additions on standard type 304 SS cannot be investigated but the effect of different PGM content could be compared and seemed to show similarities in terms crack propagation behaviours. The main problem is the higher delta ferrite level in the standard alloys that makes them more resistant to cracking.

6.5 Summary
Stress corrosion cracking propagation in 0.01 M K$_2$S$_4$O$_6$, pH=1.5 at room temperature on fatigue pre-cracked circumferential cracked bar (CCB) samples revealed that it was possible to determine interesting factors such as the time to failure, mode of failure, crack depth, crack length and initial stress intensity factors. IGSCC was revealed for the medium and high carbon PGM and standard alloys under initial stress intensity factors going up to 22 MPa√m. The uniformity of the fatigue precrack made it easy to calculate
the fatigue precrack length and therefore the initial stress intensity factor. The experiments were easy to perform. However, to compare the results obtained for different alloys, this technique might not be the best as the fatigue behaviour of two different materials may vary and results in different fatigue precrack lengths and initial stress intensity factors for the SCC propagation experiment. This has made the comparative study more difficult than expected and the exploitation of the results sometimes not possible. For a set of similar materials, it would be appropriate but for different materials, it would be time consuming although the results are interesting. In this study, the effects of different PGM levels has been investigated and increasing the Ru content seemed to increase the time to failure, by contrast increasing the Pd content seemed to decrease the time to failure. In addition, for a high carbon level (above 0.075 wt%), PGM -doped alloys seemed to have poor resistance in terms of IGSCC in potassium tetrathionate. Further investigation on the electrochemical behaviour of the PGM -doped and standard alloys has been performed and is presented in Chapter 8 to complete this investigation.
Chapter 1: Introduction

Chapter 2: Literature review

Chapter 3: Materials characterisation

Chapter 4: Crack initiation

Chapter 5: Fracture mechanics approach to stress corrosion crack propagation: fatigue precracking

Chapter 6: SCC propagation study

**Chapter 7: Electrochemistry in borated and lithiated water**

Chapter 8: Electrochemistry in IGSCC simulated environment

Chapter 9: Electrochemistry in high temperature water

Chapter 10: Discussion

Chapter 11: Conclusions

Chapter 12: Future work
7. Electrochemical experiments in lithiated and borated solution

7.1 Introduction
The objective is to investigate the influence of PGM additions on the electrochemical response of the standard type 304 SS (304MC) in PWR chemistry. The effect of PGM additions on the kinetics of the main electrochemical reactions in PWR chemistry: metal dissolution, oxygen reduction, water reduction and hydrogen oxidation have been investigated.

This section is structured as follows: this introduction, the experimental procedure, the results, the discussion and summary.

7.2 Experimental procedure

7.2.1 Materials and heat treatment
The tested materials were 304MC (a standard type 304 SS), Ru3MC (1 wt% Ru), Ru2MC (0.25 wt% Ru), Ru1MC (0.11 wt% Ru), Pd3MC (1 wt% Pd) and pure Pt (see chapter 2 for material composition and microstructure). They were all in the sensitised condition (heat treated at 650°C for 24 hours under an argon atmosphere).

7.2.2 Electrode preparation
All electrodes had dimensions 1 x 1 cm (1 cm²). The samples were spot welded to a copper wire. A plastic tube 30 cm long was then used to protect the copper wire and the samples were embedded in epoxy resin. The exposed surfaces were polished to a 1200 grade SiC finish, and cleaned with distilled water and acetone before the start of each electrochemical experiment.

The electrodes were ground in two perpendicular directions to obtain a good quality of surface finish. The interface between the sample edges and the mounting material was masked using a commercial lacquer (Lacomite) to prevent the initiation of crevice corrosion while running the experiments.
Two electrodes of each material were prepared and all the experiments were repeated three times to verify the consistency of the results. The results section presents only one representative graph of the materials in each investigated environmental condition.

### 7.2.3 Electrolyte preparation

A solution of 1000 ppm boron (B) containing 2 ppm of lithium (Li) was prepared to simulate PWR chemistry. Lithium was used as lithium hydroxide (LiOH) and boron was used as boric acid (H$_3$BO$_3$). The chemicals were supplied by Sigma-Aldrich.

#### 7.2.3.1 Mass calculations

The mass calculation is explained as follows:

- **M$_w$ of LiOH** is $6.94 + 16 + 1 = 23.94$ g.mol$^{-1}$
- **Mass fraction of lithium in LiOH** is $6.94/23.94 = 0.29$
- For 2 ppm of Li = 2 mg.dm$^{-3}$,
  - The mass of LiOH needed is equal to $2/0.29 = 6.9$ mg.dm$^{-3}$.
- For 2ppm Li, there is 0.0069 g (6.9 mg) LiOH for 1L solution.

- **M$_w$ of boric acid (H$_3$BO$_3$)** is 61.83 g.mol$^{-1}$
- **Mass fraction of boron in H$_3$BO$_3$** is $10.81/61.83 = 0.175$
- For 1000 ppm of boron = 1000 mg dm$^{-3}$, so the mass of boric acid needed is equal to $1000/0.175 = 5714$ mg dm$^{-3}$ or 5.714 g.dm$^{-3}$.

#### 7.2.3.2 Summary of the electrolyte preparation

A two litre flask was used to prepare the solution. First, the amounts of Li and B were weighed accurately to ± 0.1 mg. The chemicals were then placed in the flask, which was filled up to the mark with deionised water.

### 7.2.4 Operating conditions

#### 7.2.4.1 Temperature

The operating temperatures were 25°C and 70°C. A water bath (GD 100 grant) was used to control the temperature of the solution to ± 1°C. Both temperatures were
chosen to investigate the influence of PGMs as well as the effect of temperature. So 25°C and 70°C; the former is commonly used as it is close to the room temperature and the latter to avoid being too close to the boiling temperature (100°C) under standard conditions.

7.2.4.2 Atmosphere

The experiments were conducted in three different atmospheres: aerated, deaerated with nitrogen and hydrogenated. The purpose was to investigate the influence of PGM additions on the kinetics of oxygen reduction, water reduction and hydrogen reduction of the standard alloy 304MC in the sensitised conditions. Indeed the PWR environment has an overpressure of hydrogen and intergranular stress corrosion cracking (IGSCC) may happen where there is a residual amount of oxygen in the “dead-space” regions. The deaeration was performed by purging nitrogen in the solution and the hydrogenation was performed by purging hydrogen in the solution at atmospheric pressure. The solution was purged with gas for one hour prior to running the experiments.

7.2.4.3 Set up of the experiments

Electrochemical experiments were conducted in a standard three-electrode cell consisting of the specimen or working electrode, a platinum counter electrode and a saturated calomel reference electrode (SCE) and employing a Solartron Model 1286 potentiostat and CorrWare software. The reference electrode was connected to a 500 ml cell using a gel bridge. A capillary probe was placed very close to the sample in order to measure the potential more efficiently and avoid the IR drop problem, due to the resistance of the electrolyte.
7.3 Results
For an easier understanding of the PGM effects, the graphs present the results of 304MC, Ru3MC, Pd3MC and Pt together or only the Ru doped alloys (Ru1MC, Ru2MC, and Ru3MC) with 304MC.

7.3.1 Open circuit potential in a solution of (1000 ppm Li + 2 ppm Li) in aerated conditions
The open circuit potential (OCP) in aerated environment at 25°C and 70°C was measured against a saturated calomel electrode (SCE) for thirty minutes. The influence of PGM additions on the kinetics of the cathodic and anodic reaction has been investigated as well the effect of temperature. The results are presented in Figure 100 and Figure 102.

![Graph](image)

Figure 100 Open circuit potential in a solution of (1000 ppm B + 2 ppm Li) at 25°C in aerated environment, at pH~7-8: Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (black solid line)

The OCP measured for 30 minutes was constant for all the alloys, indicating that the surface of the alloys had reached equilibrium in borated and lithiated solution under
aerated conditions at 25°C. Pt had the most noble open circuit potential (+0.17 V vs. SCE). 1 wt% Ru additions shifted the OCP of the standard alloy 304MC towards more positive values (+0.015 V). 1 wt% Pd additions seemed to increase slightly the OCP of the standard alloy by about 0.05 V. These changes in OCP with PGM additions indicated catalysis of the oxygen reduction reaction. Indeed, using the Nernst equation (see Equation 24) at pH~7-8, the redox potential for the oxygen reduction reaction was calculated (+0.509→0.569V vs. SCE), see Equation 25 and Equation 26.

Equation 24
\[ E = E^\circ - \frac{R T}{n F} \ln \frac{[a \text{Re}]}{[a \text{Re}^\circ]} \]

Equation 25
\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \]

At pH~7-8, and 25°C, the potential is given by Equation 26.

Equation 26
\[ E = E^\circ - 0.06 \text{ pH} \]

E^\circ=1.23 V at 25°C for the oxygen reduction reaction
E=1.23-0.06x7=0.81 V vs SHE at pH=7
E=0.569 V vs SCE at pH=7 and E=0.509 V vs. SCE at pH=8

Figure 101 illustrates the influence of PGM additions on the OCP of stainless steels in aerated environment.
Figure 101 Schematic diagram showing the influence of PGM additions on the OCP when oxygen reduction is the main cathodic reaction.

Figure 102 Open circuit potential in a solution of (1000 ppm B + 2 ppm Li) at 70 °C in aerated environment, at pH~7-8: Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (black solid line)
The OCP was measured in aerated solution of (1000 ppm B + 2 ppm Li) at 70°C. The OCP values reached a steady state for all the alloys although a slight decrease (from +0.32 V to +0.29 V vs. SCE) was observed for Pt and an increase from -0.3 V to -0.2 V vs. SCE was observed for 304MC. The alloys were stable in these environmental conditions. Pt had the most noble potential (+0.3 V vs. SCE). 1 wt% Ru additions shifted the OCP of the standard alloy 304MC towards more positive values (+0.15 V). 1 wt% Pd additions seemed to increase slightly the OCP of the standard alloy by about +0.05 V. In these environmental conditions, PGM additions (1 wt% Ru and 1 wt% Pd) seemed to have a similar effect on the OCP as that observed under similar conditions at 25°C (see Figure 100).

7.3.2 Open circuit potential in a solution of (1000 ppm B + 2 ppm Li) under deaerated conditions with nitrogen

The open circuit potential in deaerated (with nitrogen) conditions at 25°C and 70°C was measured against a saturated calomel electrode (SCE) for thirty minutes. The results are presented in Figure 103 and Figure 104.
From Figure 103, the OCP measured for 30 minutes was stable for all the alloys. Under deaerated conditions with nitrogen, Pt revealed the most noble OCP (+0.12 V vs. SCE). Similarly, 1 wt% Ru additions shifted the OCP of the standard alloy 304MC towards more positive values (+0.2 V). 1 wt% Pd additions increased the OCP of the standard alloy towards more positive values (from -0.8 to -0.6 V vs. SCE respectively for 304MC and Pd3MC).
Figure 104 Open circuit potential in a solution of (1000 ppm B + 2 ppm Li) at 70 °C in deaerated environment with nitrogen, at pH~7-8: Ru3MC (blue solid line), Pd3MC (green solid line), 304MC (red solid line), Pt (black solid line)

From Figure 104, the OCP measured in nitrogen purged conditions for 30 minutes was quite constant for all the alloys. Pt revealed an OCP of about +0.2 V vs. SCE. 1 wt% Ru additions shifted the OCP of the standard alloy 304MC towards more positive values (+0.4 V). 1 wt% Pd additions seemed to increase slightly the OCP of the standard alloy by about +0.2 V. PGM additions (1 wt% Ru and 1 wt% Pd) seemed to increase the OCP of the standard alloy 304MC towards more positive values. This trend is the same as that observed under similar experimental conditions (solution, deaeration) at 25°C (see Figure 103).
7.3.3 Potentiodynamic scan in a solution of (1000 ppm B + 2 ppm Li) under aerated conditions

The potentiodynamic scan in aerated conditions at 25°C and 70°C was measured against a saturated calomel electrode (SCE) from -0.3 V below the OCP to +1 V above the OCP at a scan rate of 1 mV/s. The results are presented in Figure 105 and Figure 106.

Figure 105 Polarisation scan in a solution of (1000 ppm B + 2 ppm Li) at 25°C in aerated environment, at pH~7-8: Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (solid black line)

The order of $E_{\text{corr}}$ under aerated conditions at 25°C in borated and lithiated solution was as follows: Pt>Ru3MC>Pd3MC>304MC. Significantly 1 wt% Ru additions reduced the anodic and passive current density of the standard alloy 304MC by a decade while 1 wt% Pd additions lowered the anodic current density of the standard alloy less significantly (only by half a decade). Indeed, the current density in the anodic region
was about $1 \times 10^{-7}$, $5 \times 10^{-7}$ and $1 \times 10^{-6}$ A/cm$^2$, respectively for Ru3MC, Pd3MC and 304MC. At potentials above 0.4 V vs. SCE, the current density increased for the PGM-doped and standard alloy. This increase is consistent with the transpassive region, which is where the passive film dissolves. For pure platinum, there is an increase in the current density around +0.6 V vs. SCE. This is probably the oxygen evolution reaction. Indeed, the redox potential for oxygen reduction/oxygen evolution is around +0.5-0.569 V vs. SCE at pH~7-8 (see Equation 26). Pt shows also an increased exchange current density for the hydrogen evolution reaction.

Figure 106 Polarisation scan in a solution of (1000 ppm B + 2 ppm Li) at 70°C in aerated environment, at pH~7-8 : Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (solid black line)

From Figure 106, at 70°C Pt had also a more noble corrosion potential (about +0.25 V vs. SCE) than Ru3MC, Pd3MC and 304MC, which revealed respectively an OCP of -0.15V, -0.18V and -0.22 V vs. SCE. These observations confirmed the noble order
(Pt>Ru3MC>Pd3MC>304MC) observed in Figure 102. The same trend as that in aerated conditions at 25°C (see Figure 105) was observed. 1 wt% Ru additions lowered the current density in the anodic region (~5x10^{-7} A/cm^2) of the standard alloy 304MC (1x10^{-6} A/cm^2). 1 wt% Pd additions did not lower significantly the current density of the standard alloy 304MC in the anodic region. Around 0 V vs. SCE, the current density of the PGM-doped and standard alloys increased. However, in this case, it was almost certainly due to crevice corrosion of the sample. An increase in the current density for pure Pt was observed at +0.6 V vs. SCE, revealing the oxygen evolution reaction.

7.3.4 Potentiodynamic scan in a solution of (1000 ppm B + 2 ppm Li) under deaerated conditions (with nitrogen)

The potentiodynamic scan in deaerated conditions at 25°C and 70°C was measured against a saturated calomel electrode (SCE) from -0.3V below the OCP to +1 V above the OCP. Deaeration with nitrogen was performed by purging nitrogen one hour prior to running the experiments. The oxygen level was not measured further to deaeration; however, it is assumed that 95% of the oxygen level was removed. This means that the dissolved oxygen in the solution was probably less than 0.4 ppm. This oxygen level is obviously well above that under PWR conditions, even in the ‘dead space’ regions. The results are presented in Figure 107 and Figure 108.
Figure 107 Polarisation scan in a solution of (1000 ppm B + 2 ppm Li) at 25°C in deaerated environment, at pH~7-8 : Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (solid black line)

Under deaerated conditions (with nitrogen), at 25°C in a solution of (1000 ppm B + 2 ppm Li), the noble order was follows: Pt>Ru3MC>Pd3MC>304MC, respectively +0.2 V, -0.58 V, -0.6 and -0.7 V vs. SCE. These results confirmed the OCP measurements obtained in the same experimental conditions (see Figure 103). In terms of current density in the anodic region, Ru3MC revealed the lowest value with about 1x10^{-7} A/cm^2. 1 wt% Ru additions lowered the anodic and passive current density of the standard alloy 304MC by one decade (respectively 1x10^{-7} against 1x10^{-6} A/cm^2). 1 wt% Pd additions lowered the anodic current density of the standard alloy but less significantly than 1 wt% Ru additions. Evidence of increased hydrogen evolution exchange current density with the PGM containing alloys can be pointed out. For the Ru containing alloy, the current density rise at about 0.4 V indicates the transpassive dissolution, however the other alloys show signs of crevice corrosion below transpassive dissolution.
Figure 108 Polarisation scan in a solution of (1000 ppm B + 2 ppm Li) at 70°C in deaerated environment with nitrogen, at pH~7-8 : Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (solid black solid)

Under deaerated conditions with nitrogen, at 70°C, in a solution of (1000 ppm B + 2 ppm Li), the OCP followed the noble order: Pt>Ru3MC>Pd3MC>304MC. The OCP values were respectively 0.2 V, -0.22 V, -0.45 V and -0.7 V vs. SCE. 1 wt% Ru and 1 wt% Pd shifted the OCP of the standard alloy 304MC towards more positive values, confirming the observations presented in Figure 104. 1 wt% Ru additions lowered the current density of the standard alloy in the anodic region (2x10^{-6} to 5x10^{-7}A/cm^2 respectively for 304MC and Ru3MC). In the cathodic region, Pd3MC revealed a transition in the kinetics of the cathodic region around -0.65 V vs. SCE, indicating a residual level of dissolved oxygen in the solution.
7.3.5 Effect of temperature and dissolved oxygen in a solution of (1000 ppm B + 2 ppm Li)

7.3.5.1 Effect of temperature and oxygen on the open circuit potential (OCP)

The OCP of Ru3MC, Pd3MC, 304MC and pure platinum in (1000 ppm B + 2 ppm Li) is presented versus the PGM content in Figure 109.

Figure 109 Graph presenting the OCP against the PGM concentration in aerated (circles) and deaerated with nitrogen (triangles) environments and at 25°C (white) and 70°C (black) in a solution of (1000 ppm B + 2 ppm Li)

Figure 109 displays the OCP as a function of the PGM content in order to highlight the influence of PGM additions on the OCP response of the standard alloy 304MC in different environmental conditions (temperature and dissolved oxygen level). Temperature seemed to affect the OCP as the OCP values were more positive when the temperature was increased from 25°C to 70°C. This is due to the fact that the kinetics of metal dissolution are faster and the dissolved oxygen level is lower when the
temperature increases. Consequently, the OCP is shifted towards more positive values. The effect of temperature was more pronounced in deaerated conditions. Indeed, the oxygen effect is negligible in deaerated condition, which emphasises the effect of metal dissolution on the OCP. Therefore it is sensible to observe a more pronounced effect of temperature in deaerated conditions as the main parameter affecting the OCP is the metal dissolution kinetics.

**7.3.5.2 Effect of oxygen and temperature on the electrochemical behaviour in a solution of (1000 ppm B + 2 ppm Li)**

The potentiodynamic scan in aerated and deaerated conditions with nitrogen at 25°C and 70°C, was measured against a saturated calomel electrode (SCE) from -0.3 V below the OCP to +1 V above the OCP. In this section, the effect of temperature and oxygen level is presented for Ru3MC but it is representative for 304MC and Pd3MC as the same trend was demonstrated. The results are presented in Figure 110.

![Figure 110 Polarisation scan of Ru3MC in a solution of (1000 ppm B + 2 ppm Li) in aerated (dashed lines) and deaerated with nitrogen (solid lines) at 25°C (black) and 70°C (red)](image-url)
From Figure 110, at a given temperature (25°C or 70°C), increasing the oxygen level (from deaeration with nitrogen to aeration) increased the OCP. This confirmed what was presented in Figure 109 (see explanation). At 25°C, the effect of the oxygen level on the OCP was more pronounced than at 70°C.

Increasing the temperature from 25°C to 70°C increased the current density in the anodic and cathodic regions. Thus, temperature affected the diffusion of the species and the kinetics of metal dissolution.

### 7.3.6 Effect of the Ru content under aerated and deaerated conditions

#### 7.3.6.1 Effect of the Ru content on the OCP under aerated conditions

The OCP of the standard and Ru doped alloys (Ru1MC, Ru2MC and Ru3MC) in aerated conditions at 25°C was measured against a saturated calomel electrode (SCE) for thirty minutes. The results are presented in Figure 108.

![Figure 111](image)

**Figure 111** Open circuit potential in a solution of (1000 ppm B + 2 ppm Li) at 25 °C in aerated environment, at pH~7-8: Ru1MC (green solid line), Ru2MC (red solid line), Ru3MC (blue solid line), 304MC (black solid line)
Figure 111 shows that the OCP measured for 30 minutes was relatively stable for all the Ru doped alloys (Ru1MC, Ru2MC and Ru3MC). Ru additions seemed to shift the OCP of the standard alloy 304MC towards more positive values. Indeed, 304MC revealed an OCP of about -0.15 V vs. SCE while Ru1MC, Ru2MC and Ru3MC revealed an OCP, slightly more positive, respectively -0.1, -0.05 and -0.1 V vs. SCE. From these measurements, there was no evidence that Ru2MC was more noble than Ru1MC and Ru3MC as the repeat of the experiments showed that the differences in OCP values between Ru1MC, Ru2MC and Ru3MC remain in the experimental variations.

**7.3.6.2 Effect of the Ru content on the electrochemical behaviour under aerated and deaerated (with nitrogen) conditions**

The potentiodynamic scan in aerated and deaerated conditions at 25°C was measured against a saturated calomel electrode (SCE) from -0.3V below the OCP to +1V above the OCP. The results for Ru1MC, Ru2MC, Ru3MC and the standard alloy 304MC are presented in Figure 112 and Figure 113.

![Polarisation scan of Ru doped alloys in a solution of (1000 ppm B + 2 ppm Li) in aerated conditions at 25°C, at pH-7-8: Ru1MC (green solid line), Ru2MC (red solid line), Ru3MC (blue solid line), 304MC (black solid line)](image)

Figure 112 Polarisation scan of Ru doped alloys in a solution of (1000 ppm B + 2 ppm Li) in aerated conditions at 25°C, at pH-7-8: Ru1MC (green solid line), Ru2MC (red solid line), Ru3MC (blue solid line), 304MC (black solid line)
Figure 112 showed that Ru additions seemed to shift the OCP of the standard 304MC towards more positive values as observed for the OCP measurements under similar environmental conditions (see Figure 108). Importantly the anodic dissolution and transpassive current are decreased by Ru additions. Indeed, Ru additions lowered the anodic dissolution peak of the standard alloy 304MC and they lowered the current density in the anodic region by about half a decade. So the main effect of Ru additions at 25°C under aerated conditions in a solution of (1000 ppm B + 2 ppm Li) was on the anodic dissolution peak, passive current density, and the OCP. Increasing the Ru content (from 0.11 to 1 wt%) did not influence significantly the electrochemical behaviour of the Ru doped alloys. Transpassive dissolution occurred at about 0.4 V vs. SCE with 0 wt% Ru (304MC) and 0.11 wt% Ru (Ru1MC); at 0.4 V vs. SCE for Ru3MC (1 wt% Ru) and 0.5 V vs. SCE for Ru2MC (0.25 wt% Ru).

![Figure 113 Polarisation scan of Ru doped alloys in a solution of (1000 ppm B + 2 ppm Li) in deaerated conditions with nitrogen at 25°C: Ru1MC (green solid line), Ru2MC (red solid line), Ru3MC (blue solid line), 304MC (black solid line)](image)
Figure 113 showed that 1 wt% Ru additions seemed to shift the OCP of the standard alloy 304MC towards more positive values by +0.1 V in deaerated conditions with nitrogen. However, 0.11 wt% Ru and 0.25 wt% did not affect the OCP of the standard alloy 304MC under deaerated conditions with nitrogen. 0.11 wt% Ru (Ru1MC) and 0.25 wt% (Ru2MC) behaved similarly in the anodic region as they both presented an anodic dissolution peak around $10^{-6}$ A/cm$^2$ followed by the passive region. On the other hand, Ru3MC had an anodic current density about one decade lower than that of 304MC. So, under deaerated conditions with nitrogen, 1 wt% Ru seemed to be more efficient than 0.11 wt% and 0.25 wt% to lower the anodic dissolution peak of the standard alloy 304MC.

The following sections present the work performed under hydrogenated conditions in (1000 ppm B + 2 ppm Li). The study simulated the electrochemical behaviour of the doped and standard alloys in PWR chemistry. It focused more on the effect of hydrogen, a parameter that is of great importance in BWRs and PWRs to keep the potential sufficiently low to mitigate IGSCC.

**7.3.7 Open circuit potential in a solution of (1000 ppm B + 2 ppm Li) under hydrogenated conditions**

The open circuit potential (OCP) in borated and lithiated solution under hydrogenated conditions at 25°C was measured against a saturated calomel electrode (SCE) for thirty minutes. The OCP measurements were conducted to investigate the influence of PGM additions on the OCP response of the standard alloy 304MC in terms of catalysis of the hydrogen oxidation reaction. The results for the PGM-doped and standard alloys are presented in Figure 114.
Figure 114 Open circuit potential in a solution of (1000 ppm B + 2 ppm Li) at 25 °C in hydrogenated environment, at pH~7-8: Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (solid black line)

Figure 114 displays the OCP values of pure Pt, Ru3MC (1 wt% Ru), Pd3MC (1 wt% Pd) and 304MC (0 wt% PGM). During the thirty minutes of the measurements, the OCP reached a steady state constant, indicating a stability of the materials in the investigated environment. Under hydrogenated conditions, the noble order was as follows: Pt<Ru3MC<Pd3MC<304MC. It suggested that PGM additions catalysed the hydrogen oxidation reaction by shifting the OCP of the standard alloy 304MC towards more negative values, close to the redox potential of hydrogen oxidation/proton reduction.

Indeed, according to the Nernst equation, at pH~7-8, the redox potential for hydrogen oxidation/proton reduction is between -0.65 and -0.71 V vs. SCE (see Equation 27).

\[ \text{Equation 27} \quad \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \]

\[ E^\circ = 0 \text{ V at 25°C for the hydrogen oxidation reaction} \]

\[ E = 0 - 0.06 \times 7 = -0.42 \text{ V vs SHE at pH=7} \]
E=−0.66 V vs SCE at pH=7 and E=−0.71 V vs. SCE at pH=8

As observed in Figure 114, the OCP of pure Pt set at the redox potential for hydrogen oxidation, suggesting that pure Pt behaved like a hydrogen electrode under the investigated conditions. Pure Pt showed the highest catalytic power for hydrogen oxidation, because it has a higher exchange current density for this reaction. On the other hand, 1 wt% Ru revealed a higher catalytic power than 1 wt% Pd for hydrogen oxidation. Indeed, the OCP of the standard alloy 304MC was shifted from -0.1 V vs. SCE to -0.3 V vs. SCE and -0.15 V vs. SCE respectively with 1 wt% Ru and 1 wt% Pd.

7.3.8 Potentiodynamic scan in a solution of (1000 ppm B + 2 ppm Li) under hydrogenated conditions

The potentiodynamic scan in hydrogenated conditions at 25°C was measured against a saturated calomel electrode (SCE) from -0.3 V below the OCP to +1 V above the OCP. The results for the PGM-doped and standard alloys are presented in Figure 115.

Figure 115 Polarisation scan in a solution of (1000 ppm B + 2 ppm Li) in hydrogenated conditions at 25°C, at pH~7-8: Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (solid black line)
Figure 115 displays the electrochemical behaviours of pure Pt, Ru3MC (1 wt% Ru), Pd3MC (1 wt% Pd) and 304MC (0wt% PGM). The OCP values followed the noble order: Pure Pt<Ru3MC<Pd3MC<304MC. This order confirmed the observations in Figure 114 that indicated the catalytic effect of the 1 wt% Ru, 1 wt% Pd and Pt for hydrogen oxidation. The current density in the anodic region increased with PGM additions. Indeed, the standard alloy 304MC revealed a current density of about $1 \times 10^{-7}$ A/cm$^2$ at the start of the anodic region while Pd3MC and Ru3MC showed respectively a current density of about $3 \times 10^{-7}$ and $6 \times 10^{-7}$ A/cm$^2$ at the start of the anodic region. The shifts in the anodic current density with PGM additions can be explained by the catalysis of hydrogen oxidation. Indeed, hydrogen oxidation contributes to the anodic current density as it is an anodic electrochemical reaction, hence, its catalysis increases the current density in the anodic region, which is what happened according to Figure 115. Metal dissolution is also one of the anodic reactions but it is negligible according to the electrochemical responses presented in the previous Figures (see Figures 104-107). The transpassive region of the PGM-doped alloys Ru3MC and Pd3MC was around 0.3 V vs. SCE as the current density increased more significantly.

The effect of the Ru content has been investigated in more details as Ru3MC seemed to catalyse more efficiently the hydrogen oxidation reaction. The results are presented in the following section.

**7.3.9 Effect of the Ru content in a solution of (1000 ppm B + 2 ppm Li) under hydrogenated conditions at 25°C**

**7.3.9.1 Effect of the Ru content on the OCP of the standard alloy 304MC under hydrogenated conditions at 25°C**

The open circuit potential in (1000 ppm B + 2 ppm Li) under hydrogenated conditions at 25°C was measured for thirty minutes. The results for the Ru doped alloys are presented in Figure 116.
Figure 116 Open circuit potential in a solution of (1000 ppm B + 2 ppm Li) at 25 °C in hydrogenated environment, at pH~7-8: Ru1MC (green solid line), Ru2MC (red solid line), Ru3MC (blue solid line), 304MC (black solid line)

Figure 116 displays the OCP measurements of Ru1MC, Ru2MC, Ru3MC and 304MC. The OCP values followed the noble order: Ru1MC<Ru2MC<Ru3MC<304MC. Ru additions shifted the OCP of the standard alloy 304MC towards more negative values, revealing a catalytic effect for the hydrogen oxidation reaction as explained previously for Figure 114. This effect was more pronounced while decreasing the Ru content (from 1 to 0.11 wt%). Indeed, Ru1MC lowered the OCP of 304MC (-0.6 V against -0.1 V vs. SCE). Similarly, Ru2MC and Ru3MC revealed an OCP of -0.4 and -0.2 V vs. SCE. In these environmental conditions, the OCP seemed to be stable.

7.3.9.2 Effect of the Ru content on the potentiodynamic scan of 304MC in a solution of (1000 ppm B + 2 ppm Li) under hydrogenated conditions

The potentiodynamic scan in hydrogenated conditions at 25°C was measured against a saturated calomel electrode (SCE) from -0.3 V below the OCP to +1 V above the OCP. The results for the Ru doped alloys are presented in Figure 117.
Figure 117 Polarisation scan of Ru doped alloys in a solution of (1000 ppm B + 2 ppm Li) in hydrogenated conditions at 25°C, at pH~7-8: Ru1MC (green solid line), Ru2MC (red solid line), Ru3MC (blue solid line), 304MC (black solid line)

From Figure 117, the results showed that Ru additions lowered the OCP of the standard alloy 304MC. They revealed a catalytic power for the hydrogen oxidation reaction as observed in Figure 116. The OCP of the different Ru doped alloys was similar despite a different Ru content. However, looking at the current density in the anodic region suggested that Ru2MC may be more catalytic as it revealed a higher anodic current density than Ru1MC and Ru3MC. Indeed, 0.11 wt%, 0.25 wt% and 1 wt% Ru additions increased the current density of the standard alloy 304MC in the anodic region. Indeed, the anodic current was $6 \times 10^{-6}$, $2 \times 10^{-6}$, $7 \times 10^{-7}$ and $1 \times 10^{-7}$ A/cm$^2$ respectively for Ru2MC, Ru1MC, Ru3MC and 304MC.

7.10 Discussion
The solution of (1000 ppm B + 2 ppm Li) simulated PWR chemistry as it contained boron and lithium, which are used in PWRs to respectively control neutron irradiation and the pH [20]. The discussion below will highlight several key points to better
understand the influence of PGM (Ru and Pd) additions on the electrochemical behaviour of a sensitised type 304 SS (304MC) in PWR environment. Particular attention has been given to the effect of PGM additions on the kinetics of the main electrochemical reactions in the primary coolant of PWR, which are of great importance to mitigate the eventual IGSCC problem that may occur in the ‘dead space’ regions, where the oxygen level could be higher. The PGM-doped (Ru3MC and Pd3MC) and standard (304MC) alloys were in the sensitised condition in order to promote IGSCC susceptibility.

7.10.1 Effect of PGM additions on the open circuit potential of a sensitised type 304 SS (304MC)

The influence of PGMs on the open circuit potential (OCP) also called electrochemical corrosion potential (ECP) has been investigated under aerated, deaerated with nitrogen and hydrogenated conditions at 25°C and 70°C. These conditions evaluated the influence of PGM additions on the kinetics of the oxygen reduction reaction, water reduction, metal dissolution and hydrogen oxidation.

Under aerated conditions, the oxygen level in solution can be estimated at 8 ppm (2.5x10^{-4} mol/l). Assuming that the deaeration with nitrogen can only remove 90% of the oxygen level, thus the oxygen level would be around 0.8 ppm (2.5x10^{-5} mol/l) when nitrogen is purged in the solution. These oxygen contents are both well above that under PWR conditions but they simulate critical conditions which were interesting to investigate. It is critical to know the cathodic and anodic reactions involved in each environment to understand how PGM additions affect the electrochemical behaviour in a given environment. First of all, the OCP was measured for thirty minutes prior to each polarisation measurement. This was carried out in order to investigate the influence of PGM additions on the OCP of the standard alloy 304MC as well as the stability of the alloys in the environment. The OCP is based on the mixed potential theory, developed
by Wagner and Traud [64, 108]. At high temperature as found in light water reactors (LWRs), the concentration of dissolved oxygen largely influences the OCP values, with increases to levels of ~ 80-100 ppb resulting in the oxygen reduction, the cathodic reaction (~ -200 mV vs. SHE so ~ -441 mV vs. SCE) dominating over the water reduction(~ -600 mV vs. SHE so ~ -841 mV vs. SCE) [45, 155, 156]. This was confirmed by the experiments conducted in this study under aerated and deaerated (with nitrogen) conditions, which contained respectively about 8 ppm and less than 0.8 ppm dissolved oxygen (see Figure 100 and Figure 103 for instance).

The main investigation of this study was focussed on the influence of 1 wt% PGM (Ru and Pd) additions on the electrochemical behaviour of the standard alloy 304MC in the sensitised conditions. So the general comparison was mostly between 304MC, Pd3MC and Ru3MC. Pure Pt was also considered in order to understand better the effect of small PGM additions (1 wt%) compared to a pure noble metal (Pt) or a virgin (0 wt% PGM) alloy (304MC). The OCP response for all the alloys investigated in the present work, subjected to aerated conditions in the lithiated and borated solution at 25°C, demonstrated that 1 wt% Ru additions shifted the OCP of the standard alloy 304MC towards more positive values (+0.15). 1 wt% Pd additions had no obvious effect on the OCP of the standard alloy 304MC in aerated conditions during the OCP measurements, see Figure 98). This suggested that at ambient temperature in oxygenated solution of (1000 ppm B + 2 ppm Li), 1 wt% Ru catalysed the oxygen reduction reaction thus moving the potentials towards more positive values. By enhancing the exchange current density for the oxygen reduction reaction, Ru additions shifted the OCP of the standard alloy 304MC. This can be explained by the Evans diagram presented in Figure 101. The redox potential for the oxygen reduction reaction was calculated by using the Nernst equation (see Equation 24). It was estimated at about +0.509-+0.569V vs. SCE (see Equation 26) in a solution of (1000 ppm B + 2 ppm Li) under aerated conditions at
25°C. In addition to the effect on the OCP, Ru additions decreased the passive current and anodic dissolution rate.

Increasing the temperature from 25°C to 70°C affected the OCP response. Indeed both PGM-doped alloys (Ru3MC and Pd3MC) demonstrated more positive OCP values at 70°C than at 25°C. This suggested that anodic dissolution rates increased, as it is likely that \(O_2\) concentrations (the other significant contributing factor governing OCP values) would have decreased with increasing temperature.

Equation 28  
\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \]

E°=0 at 25°C for the hydrogen oxidation reaction

E=0-0.06x7=-0.42V vs SHE at pH=7

E=-0.66 V vs SCE at pH=7 and E=-0.71V vs. SCE at pH=8

Deaerating the solution with nitrogen decreased the OCP values at 25 °C; similar observations were recorded at 70 °C (between aerated and deaerated conditions with nitrogen). Indeed lowering the dissolved oxygen, reduces the limiting current for the oxygen reduction reaction, hence shifting the OCP towards more negative values.

In hydrogenated conditions, the hydrogen partial pressure was about 20 psi \((1.37 \times 10^5 \text{ Pa})\) so according to Henry’s law (see Equation 29), the hydrogen dissolved in the electrolyte was about 23 cc/kg at 25°C against about 20-30 cc/kg in PWR.

Equation 29  
\[ P = k.C \]

Where,

- \(P\) is the partial pressure of the gas
- \(k\) is the constant
- \(C\) is the concentration of the solute
At 25°C, the constant $k$ for hydrogen is equal to 0.85 psi/kg/cc (5860 Pa/kg/cc), so for a partial pressure of hydrogen equal to 20 psi ($1.37 \times 10^5$ Pa), the dissolved hydrogen is 23 cc/kg ($1.58 \times 10^5$ Pa) at 25°C.

Hydrogenated conditions showed that the OCP of the standard alloy 304MC was lower with PGM (Ru or Pd) additions. PGM additions catalysed the hydrogen oxidation reaction, which has a redox potential of about $-0.66/-0.71$ V vs. SCE at pH~7-8 according to the Nernst equation (see Equation 24). PGMs have a high exchange current density for the hydrogen oxidation reaction, therefore they tend to shift the OCP of stainless steels towards more negative values in the presence of sufficient hydrogen. This can be explained by the Evans diagram presented in Figure 37.

A similar study conducted by Andresen [108] in simulated BWR environment showed that 0.1 and 0.3 wt % Pt and Pd additions to engineering materials improved the catalytic efficiency of hydrogen and oxygen recombination in water containing oxygen, hydrogen and hydrogen peroxide at 288°C. The work demonstrated that even at relatively high oxygen and hydrogen peroxide levels, the potential was kept below the critical value for IGSCC ($-0.23$ V vs. SHE) with Pt and Pd additions. In addition, it was demonstrated that 0.3 wt % PGM additions had the same effect as pure Pt in terms of lowering the OCP under hydrogenated conditions. This full catalytic effect occurred for different dissolved hydrogen contents depending on the PGM additions. Indeed, palladium addition lowered the OCP to a constant value below the critical value for IGSCC at 40 ppb dissolved $H_2$, while only 28 ppb dissolved $H_2$ was required for pure Pt.

In this study, PWR chemistry was simulated and Ru (from 0.1 wt% to 1 wt%) additions under hydrogenated conditions at 25°C revealed catalytic efficiency for the hydrogen oxidation reaction. Also, it seemed that the catalytic effect of Ru1MC (0.1 wt%), Ru2MC (0.25 wt%) and Ru3MC (1 wt%) was relatively similar despite the different Ru
content. This suggested that there might be a range of Ru content to add to stainless steel to obtain a fully catalytic power. Moreover, the Ru doped alloys revealed an open circuit potential very similar to that of pure Pt under hydrogenated conditions at 25°C (see Figure 115). 1 wt% Pd additions were less efficient than 1 wt% Ru in terms of catalytic efficiency for the hydrogen oxidation reaction.

7.10.2 Effect of PGM on the electrochemical behaviour of the standard alloy 304MC in a solution of (1000 ppm B + 2 ppm Li)

Polarisation scans were conducted on the PGM-doped alloys (Ru3MC, Ru2MC, Ru1MC, Pd3MC) and the standard alloy (304MC) that were in the sensitised condition. The study investigated particularly the influence of PGM (Ru or Pd) additions on the electrochemical behaviour of the standard alloy 304MC in terms of kinetics and catalysis of the main electrochemical reactions (oxygen reduction, water reduction and hydrogen oxidation) in PWR environments. Therefore three environments were studied: borated and lithiated solution in aerated, deaerated with nitrogen and hydrogenated. The effect of temperature on the electrochemical behaviour of the PGM-doped and standard alloys was also investigated.

Both 1 wt% Ru and 1 wt% Pd additions seemed to improve the corrosion resistance in aerated and deaerated (with nitrogen) conditions, as they lowered the current density in the anodic region. Under aerated conditions at 25°C, the current density in the anodic region was about $1 \times 10^{-7}$, $5 \times 10^{-7}$ and $1 \times 10^{-6}$ A/cm$^2$, respectively for Ru3MC, Pd3MC and 304MC (see Figure 105). The influence of PGM additions on the anodic behaviour of stainless steels has already been demonstrated by Potgieter who studied the effect of PGMs on the anodic behaviour of stainless steels in sulphuric acid [2]. Indeed, Potgieter suggested that PGMs could lower the anodic dissolution current density, increase the passive range, as well as increasing the effectiveness of the cathode process by lowering
the hydrogen overvoltage on PGMs. It is important to point out that the environment investigated by Potgieter was more acidic. Therefore the alloys were in the active state. Increasing the temperature from 25°C to 70°C increased the current density in the anodic region. This can be explained by the influence of temperature on metal dissolution. Temperature is a parameter affected the corrosion rates; therefore, it is sensible to observe higher current density when the temperature increases. In this case, the oxygen level is lower with increasing temperature and metal dissolution is faster.

Under deaerated conditions with nitrogen, dissolved oxygen concentrations were very low comparing to those under aerated conditions. The electrochemical behaviour was different and revealed higher net current densities. This is due to the passivation that is more effective in the presence of oxygen.

The noble metal (Ru and Pd) additions appeared to enhance the exchange current density of the oxygen reduction process, thus leading to more positive open circuit potentials (see Figure 105, Figure 106, Figure 107 and Figure 108). This is well summarised in Figure 110. 1 wt% Ru seemed to be more efficient than 1 wt% Pd to catalyse the oxygen reduction, as the shift in OCP of the standard alloy 304MC was more significant with 1 wt% Ru additions than 1 wt% Pd additions (see Figure 105 and Figure 107). Indeed, 1wt% Ru increased the OCP of 304MC by +0.1 V under aerated conditions at 25°C while 1wt% Pd did not show any significant shift. In deaerated conditions with nitrogen, 1wt% Ru showed a shift of +0.15 V while 1 wt% Pd showed a shift of +0.1 V with respect to the OCP of the standard alloy 304MC. This was consistent with the work performed on the kinetics of oxygen reduction reaction on nano-sized Pd electrocatalyst in acid media, which revealed that Pd showed a poorly catalytic activity compared to Ru and Pt [157]. At 25°C, the effect of dissolved oxygen on the electrochemical corrosion potential was more pronounced, see Figure 110. At this temperature, the anodic current density was higher in deaerated environment.
compared to it under aerated conditions, as the cathodic current negligible (due to low oxygen levels).

Because 1 wt% Ru additions revealed a higher catalytic power for the oxygen reduction reaction compared to 1 wt% Pd, the influence of the Ru content was also investigated by conducting the experiments on alloys containing various Ru amounts (from 0.11 wt% to 1 wt%) of Ru. For each experiment, the three tested alloys were compared with the standard alloy for more understanding of the influence of the Ru level on the electrochemical response in PWR chemistry.

In aerated environment at 25°C, the different Ru additions showed a similar effect on the anodic behaviour of the standard alloy 304MC. Essentially, all (0.11 wt%, 0.25 wt% and 1 wt%) Ru additions lowered the current density in the anodic region under aerated conditions at 25°C, see Figure 112. Indeed Ru1MC (0.11 wt% Ru), Ru2MC (0.25 wt% Ru) and Ru3MC (1 wt% Ru) lower the anodic current density of the standard alloy 304MC by half a decade. They also reduced the anodic dissolution peak. The catalytic effect of the different Ru doped alloys for oxygen reduction was demonstrated under aerated conditions at 25°C as Ru1MC, Ru2MC and Ru3MC shifted the OCP of the standard alloy 304MC by +0.1 V (see Figure 112). By contrast, under deaerated conditions with nitrogen, only Ru3MC shifted the OCP of the standard alloy 304MC by +0.1 V (see Figure 113).

By contrast with the aerated and deaerated (with nitrogen) environments, in hydrogenated conditions, PGM (Ru and Pd) additions lowered the electrochemical corrosion potential and increased the anodic current density of the standard alloy 304MC in the following order: Ru3MC > Pd3MC > 304MC. The electrochemical reactions in this environment are different from those in aerated and deaerated (with
nitrogen) environments. The main anodic reactions to consider are now hydrogen oxidation and metal dissolution, and the main cathodic reaction is water reduction [108]. The potential at which hydrogen oxidation occurs has been calculated from the Nernst equation, (see Equation 24 and Equation 27). At and below E=-0.66 V vs. SCE, hydrogen gas produces protons and electrons as presented in Equation 27.

The calculated redox potential (E=-0.66 V vs. SCE) is that corresponding to the OCP of Pt in hydrogenated environment, see Figure 115. In this environment, Pt behaved like a hydrogen electrode and its potential set the redox potential for hydrogen oxidation/proton reduction.

1wt% Ru additions seemed to be more effective than 1 wt% Pd to catalyse the hydrogen oxidation process. However, it has been demonstrated (see Figure 117) that 0.1 wt% Ru was enough to achieve a low potential under hydrogenated conditions. 0.1 wt% Ru doped 304 SS would be much cheaper than 1 wt% Ru doped 304 SS and the effect on the OCP would be identical. Consequently, these results have shown that the additions of small amounts of Ru can lower the potential of the standard alloy under hydrogenated conditions. In terms of keeping the OCP sufficiently low to avoid IGSCC, it is in practical terms better. The increase in anodic current density in the presence of PGM additions under hydrogenated conditions is explained by the electrons from the hydrogen anodic oxidation. Indeed, PGM additions seemed to catalyse the hydrogen oxidation, therefore there are more electrons produced and the anodic current increased.

Figure 118 displays the potentiodynamic scans of Pt, the doped and standard alloys in hydrogenated and deaerated conditions at 25°C. From the curves, the current due to hydrogen oxidation was calculated by subtracting the current density under deaerated conditions with nitrogen from that under hydrogenated conditions in the anodic region. According to Figure 118, Pt and Ru3MC revealed higher net current densities in the anodic region under hydrogenated conditions. Indeed, the anodic current densities were
about $2 \times 10^{-7} \text{A/cm}^2$ for Pt and Ru3MC under deaerated conditions with nitrogen while there were about $5 \times 10^{-5} \text{A/cm}^2$ and $9 \times 10^{-7} \text{A/cm}^2$ respectively for Pt and Ru3MC under hydrogenated conditions. Therefore the current densities for hydrogen oxidation were $4 \times 98.10^{-5} \text{A/cm}^2$ and $7 \times 10^{-7} \text{A/cm}^2$ respectively for Pt and Ru3MC. On the other hand, 304MC and Pd3MC revealed higher current density under deaerated conditions than under hydrogenated conditions in the anodic region. This suggests that there was probably some residual oxygen left while running the polarisation scans under deaerated conditions with nitrogen.

Figure 118 Polarisation scan in a solution of (1000 ppm B + 2 ppm Li) at 25°C, at pH~7-8: in hydrogenated conditions (solid lines) and deaerated condition with nitrogen (dashed lines): Ru3MC (blue), Pd3MC (green), 304MC (red), Pt (black)

The solution of (1000 ppm B + 2 ppm Li) simulates PWR chemistry. Nevertheless, it does not take into consideration the pressure, temperature and the irradiation effect that induces hardening due to neutron damage. So it is not possible to compare the potential values obtained in this study with that expected in PWR. However, the general effect of
the PGM additions in simulated PWR chemistry has been investigated in this work. The results showed the catalytic effect of PGM additions on the hydrogen oxidation reaction under hydrogenated conditions (23 cc/kg) and the catalytic power for oxygen reduction under aerated (8 ppm) and deaerated with nitrogen conditions. If the potential is the key parameter to control IGSCC susceptibility, PGM additions could be detrimental in the “dead space regions”, where higher level of oxygen may be present. The exact oxygen levels in the “dead space regions” are not known, but are expected to increase during shut downs and then go back to the same level as that in the bulk. By shifting the potential towards more positive values, PGM additions could alter the IGSCC resistance, if the hydrogen level is not sufficiently high, or the oxygen level is too high for the oxygen reduction to be catalysed by PGM additions. However, there are other parameters than the potential that contribute to the IGSCC susceptibility, therefore it cannot be said that PGM additions are definitely critical in terms of IGSCC where the oxygen level is too high. In order to explain the difference between 1 wt% Pd and 1 wt% Ru additions, more investigations should be carried out on the film formation of Ru3MC and Pd3MC. Indeed, studying the structure of the film and how Pd and Ru are incorporated in the film could elucidate on the film properties and the corrosion resistance. Also looking into the effect of different Pd concentrations on the electrochemical response could be helpful. Work has been performed by the University of Oxford to better understand the surface properties of Pd3MC and Ru3MC. The atom probes revealed that the palladium segregates with manganese, leading to a depletion of palladium in the matrix. This alters the nobility of Pd doped alloys. However, Ru seemed to be included in the film, which explains the better electrochemical performances of Ru doped alloys [158].

As was already investigated by Zhang et al [159], borate environment tends to suppress the IGSCC susceptibility of type 304 SS, and particularly the crack initiation stage. The
effect of boron on SCC and IGSCC of type 304 and 316 SS in high temperature water was also performed by Sharkawy et al [45]. They found that boron inhibits the crack propagation of type 304 and 316 SS.

7.11 Summary of the PGM effect in (1000 ppm B + 2ppm Li)
To summarise, the (1000 ppm B + 2 ppm Li) solution is of great interest in order to understand the electrochemical behaviour of sensitised standard and PGM -doped type 304 SS, in PWR chemistry. This work is novel as most of the research previously conducted on the PGM effect in light water reactors was performed under BWR conditions or on coated samples. In this study, aerated, deaerated with nitrogen and hydrogenated environments helped understand better the effect of oxygen and hydrogen, which are amongst the key parameters to mitigate or accelerate IGSCC in PWR. Under hydrogenated (23 cc/kg) conditions, PGM (Ru and Pd) lowered the OCP of the standard alloy 304MC by catalysing the hydrogen oxidation reaction. This study showed that using PGM additions, particularly Ru (0.11 wt%, 0.25 wt% or 1 wt%) additions, catalysed the hydrogen oxidation by enhancing the exchange current density for hydrogen oxidation. Deaeration with nitrogen removed significantly the oxygen present in the solution, making the potentials lower. Only sufficient hydrogen content made the PGM keep the potential low.
Chapter 1: Introduction

Chapter 2: Literature review

Chapter 3: Materials characterisation

Chapter 4: Crack initiation

Chapter 5: Fracture mechanics approach to stress corrosion crack propagation: fatigue precracking

Chapter 6: SCC propagation study

Chapter 7: Electrochemistry in borated and lithiated water

Chapter 8: Electrochemistry in IGSCC simulated environment

Chapter 9: Electrochemistry in high temperature water

Chapter 10: Discussion

Chapter 11: Conclusions

Chapter 12: Future work
8. Electrochemical experiments simulating IGSCC environment

8.1 Introduction
The aim of this study is to investigate the electrochemical behaviour of standard and PGM-doped type 304 SS in an environment enhancing IGSCC of sensitised stainless steel (potassium tetrathionate [152]) in order to elucidate the influence of PGM additions on the IGSCC resistance of a type 304 SS (304MC). This section is structured as follows: this introduction, the experimental procedure, the results, discussion and summary.

8.2 Experimental procedure

8.2.1 Materials tested
The tested materials were 304MC, Ru3MC, Pd3MC and pure Pt (see Chapter 3 for material compositions and microstructures). They were all in the sensitised condition (heat treated at 650°C for 24 hours under an argon atmosphere).

The electrode preparation was the same as that explained in Chapter 7. The electrode area was of 1cm². The samples were spot welded to a copper wire. A plastic tube 30cm long was then used to protect the copper wire and the samples were embedded in an epoxy resin. The exposed surfaces were polished in two perpendicular directions to a 1200 grade SiC finish, and cleaned with distilled water and acetone before the start of each electrochemical experiment.

The interface between the sample edges and the mounting material was masked using a commercial lacquer (Lacomite) to prevent the initiation of crevice corrosion while running the experiments.

Two electrodes of each material were prepared and all the experiments were repeated three times to verify the consistency of the results. The results section presents only one representative graph of the materials in each investigated environmental condition.
8.2.2 Preparation of the electrolyte

It was chosen to run the electrochemical experiments in 0.01 M $\text{K}_2\text{S}_2\text{O}_6$, at pH=1.5 as previous work has shown IG/IGSCC susceptibility of sensitised stainless steel in this environment.

The required mass to prepare 1 litre of solution is explained as follows:

$$m(\text{K}_2\text{S}_2\text{O}_6) = n(\text{K}_2\text{S}_2\text{O}_6) \times M(\text{K}_2\text{S}_2\text{O}_6) = 0.01 \times 302 = 3.02 \text{ g}.$$ 

The electrolyte was prepared in a one litre flask. The measured amount was placed in the flask prior to filling with deionised water up to the mark. The solution was stirred using a magnetic stirrer until the solution was homogeneous.

The pH of the solution was measured using a pH meter (pH meter Hanna instruments HI 8519N) and diluted sulphuric acid was added until the pH reached 1.5.

8.2.3 Temperature

All the experiments were run at 25 ± 1°C and the temperature was controlled using a water bath (Grant GD 100).

8.2.4 Scan rate

Two different scan rates were used: 0.5 mV s$^{-1}$ and 5 mV s$^{-1}$ in order to determine their impact on the electrochemical responses of the PGM-doped and standard alloys.

8.2.5 Atmosphere

The experiments were run in aerated and deaerated (with nitrogen) environments. The solution was purged with nitrogen for about one hour prior to the experiment.

8.2.6 Set up of the experiment

The set up of the experiments is similar to that used to run the electrochemical experiments in the solution of boric acid and lithium hydroxide (see Chapter 7). A three electrode cell was used with the platinum counter electrode, the sample under test and a saturated calomel electrode (SCE). A 500 ml cell made of glass was used and the
reference electrode was connected to the cell using a gel bridge. A capillary probe was placed close to the sample in order to overcome the IR drop problem.

8.3 Results

8.3.1 Open circuit potential (OCP) in aerated and deaerated (with nitrogen) conditions

The open circuit potential (OCP) of the PGM-doped and standard alloys was measured in 0.01 M K$_2$S$_4$O$_6$ at 25°C, pH = 1.5 in aerated and deaerated (with nitrogen) conditions for one hour. These measurements were conducted to investigate the alloy stability in potassium tetrathionate as well as the influence of PGM additions on the OCP of a sensitised type 304 SS (304MC). The results are presented in Figures 117-118.

Figure 119 Open circuit potential in a solution of 0.01 M K$_2$S$_4$O$_6$, pH=1.5 at 25°C in aerated environment: Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (solid black line)
From Figure 119, the OCP values varied for Ru3MC, Pd3MC and 304MC. Indeed, the measurements were carried out for one hour and after 800 s, 2100 s and 2500 s, the respective OCP values of Ru3MC, Pd3MC and 304MC shifted spontaneously towards the positive direction. The OCP values of Ru3MC, Pd3MC and 304MC were about -0.5 V vs. SCE at the start of the measurements, and then they respectively increased to about -0.1 V vs. SCE, -0.2 V vs. SCE and -0.25 V vs. SCE. By contrast, pure platinum maintained an OCP value at about +0.4 V vs. SCE throughout the duration of the measurements (one hour). It seemed that 1 wt% Ru additions encouraged earlier film formation as the surface of Ru3MC turned dark after 800 s, while 1 wt% Pd additions developed a film after 2100 s compared to 2500 s for the standard alloy 304MC. Following the abrupt change in OCP values, the OCP of the PGM-doped alloys seemed to keep increasing slightly while that of 304MC decreased again. According to the observations made while running the experiments, the surface of the PGM-doped and standard alloys became black when the shift of the OCP values occurred, indicating the film formation. Pure platinum remained shiny and did not form any film on the surface. These OCP measurements revealed that the PGM-doped and standard alloys were not stable in 0.01 M K2S2O6 as demonstrated by the change in OCP values. Besides, PGM additions promoted the film formation as noticed by an earlier change in OCP values with 1 wt% Ru and 1 wt% Pd.
From Figure 120, the OCP was stable for one hour for pure platinum, the PGM-doped and standard alloys. Indeed, pure Pt revealed an OCP of about +0.18 V vs. SCE, while Ru3MC, Pd3MC and 304MC revealed respectively OCP values of about -0.42 V vs. SCE, -0.45 V vs. SCE and -0.46 V vs. SCE. Under deaerated conditions with nitrogen, the OCP values remained constant by contrast with the observations under aerated conditions. This implied that oxygen is necessary for the change in OCP values. Under deaerated conditions with nitrogen, the surface of the PGM-doped and standard alloys did not seem to change colour, suggesting that there was no film formed on surface.
8.3.2 Potentiodynamic scan in aerated conditions

8.3.2.1 Potentiodynamic scan in aerated conditions at a scan rate of 0.5 mV.s\(^{-1}\)

The potentiodynamic scans of pure platinum, the PGM-doped and standard alloys were measured from -0.5 V below the OCP to +1 V above the OCP. The experiments were performed in aerated conditions at 25 °C at a scan rate of 0.5 mV.s\(^{-1}\). The objective was to investigate the electrochemical behaviour of 304MC in an environment simulating IGSCC as well as to investigate the influence of PGM additions on the IGSCC susceptibility of 304MC. The results are presented in Figure 121.

![Potentiodynamic scan graph](image)

Figure 121 Potentiodynamic scan (0.5 mV.s\(^{-1}\)) in a solution of 0.01 M K\(_2\)S\(_4\)O\(_6\) at 25 °C and pH=1.5 in aerated environment: Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (solid black line)

The potentiodynamic scans of the PGM (Ru and Pd) doped and standard alloys in a solution of 0.01 M K\(_2\)S\(_4\)O\(_6\) in aerated environment are presented in Figure 121. According to Figure 121, pure platinum had a lower anodic current density than the other alloys (at least two orders of magnitude). Indeed, platinum revealed a current density in the anodic region of about 1x10\(^{-6}\) A/cm\(^2\) while the lowest current density
value was about \(1 \times 10^{-4}\) A/cm\(^2\) for the PGM-doped alloys (Ru3MC). The potential range in the anodic dissolution peak of the standard alloy 304MC was reduced with (PGM) additions and especially with 1 wt% Ru additions. Indeed, the potential range in the anodic region was significantly broad: from -0.5 to +0.05 V vs. SCE for 304MC; and from -0.5 to -0.1 V vs. SCE for Ru3MC and Pd3MC. This indicated that PGM additions affected anodically the standard alloy by lowering the current in the anodic region.

There were three decreases in the current density of the PGM-doped and standard alloys. This change in the corrosion potential is due to passivation, which is time-dependent as seen in the OCP measurements presented in Figure 117. According to Figure 119, Ru3MC, Pd3MC and 304MC displayed two OCP values; one before passivation and one after passivation. Indeed, the first OCP values were about -0.5 V vs. SCE and the second OCP values were -0.1, -0.1 and +0.05 V vs. SCE, respectively for Ru3MC, Pd3MC and 304MC. Under these environmental conditions, the main electrochemical reactions are complex as there is the oxygen reduction, proton reduction, hydrogen oxidation, metal dissolution but also diverse electrochemical reactions from the electrolyte (potassium tetrathionate). The redox potential for oxygen reduction in 0.01 M \(K_2S_4O_6\), at 25 °C and pH = 1.5 was calculated using the Nernst equation and estimated at 0.89 V vs. SCE (see Equation 30). The electrochemical reactions for hydrogen oxidation and water reduction are displayed in Equation 31 and Equation 32 and the reversible potential for hydrogen oxidation/proton reduction is presented in Equation 31.

**Equation 30 oxygen reduction:** \(O_2 + H_2O + 4e^- \rightarrow 4OH^-\) \(E = E^\circ - 0.06 \text{ pH}\)

Where \(E^\circ = 1.23\) V,

\(E = 1.23 - 0.06 \times 1.5 = 1.14\) V vs. SHE = 0.89 V vs. SCE at pH = 1.5
Equation 31: hydrogen oxidation: \( H_2 \rightarrow 2H^+ + 2e^- \quad E = E^\circ - 0.06pH \)

Where \( E^\circ = 0 \) V.

\[ E = 0 - 0.06 \times 1.5 = 0.09 \text{ V vs. SHE} = -0.331 \text{ V vs. SCE at pH} = 1.5 \]

Equation 32: proton reduction: \( 2H^+ + 2e^- \rightarrow H_2 \)

8.3.2.2 Potentiodynamic scan in aerated conditions at 5 mV.s\(^{-1}\)

The potentiodynamic scan of pure platinum, the PGM -doped and standard alloys were measured from -0.5 V below the OCP to + 1 V above the OCP. The experiment was performed in aerated conditions at 25°C at an increased scan rate of 5 mV.s\(^{-1}\). This second set of polarisation measurements was conducted in order to investigate the influence of the scan rate on the electrochemical response of the materials. The potentiodynamic scans are presented in Figure 122.

Figure 122 Potentiodynamic scan (5 mV.s\(^{-1}\)) in a solution of 0.01 M \( \text{K}_2\text{S}_2\text{O}_8 \) at 25°C and pH=1.5 in aerated environment: Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (solid black line)
From Figure 122, PGM additions significantly reduced maximum current density in the anodic region of the standard alloy 304MC. Indeed, the maximum current densities were $4 \times 10^{-2}$, $1 \times 10^{-2}$ respectively for 304MC and the PGM-doped alloys. The OCP values of the PGM-doped and standard alloys were about -0.5 V vs. SCE, while it was -0.3 V vs. SCE for pure platinum. So PGM (Ru and Pd) additions did not affect the OCP of the standard material but only the anodic behaviour and more especially the passivation. Under these conditions, the electrochemical reactions involved on the PGM-doped and standard alloys are obviously the same as those explained previously for Figure 121: oxygen reduction, proton reduction, hydrogen oxidation, metal dissolution and additionally electrochemical reactions of potassium tetrathionate (e.g. reduction to sulphide and oxidation to sulphate).

### 8.3.3 Potentiodynamic scan in deaerated conditions with nitrogen

#### 8.3.3.1 Potentiodynamic scan in deaerated conditions at 0.5 mV.s$^{-1}$

The potentiodynamic scan of pure Pt, the PGM (Ru and Pd) doped and standard alloys were measured from -0.5 V below the OCP to + 1 V above the OCP. The experiment was performed in deaerated conditions with nitrogen at 25°C at a scan rate of 0.5 mV.s$^{-1}$. The objective was to investigate the influence of the oxygen level on the electrochemical response of the materials as well as on the effect of PGM additions. The results are presented in Figure 123.
From Figure 123, the results showed that PGM additions lowered the potential range in the anodic dissolution peak of the standard alloy 304MC. The current density in the anodic dissolution peak was also reduced with 1 wt% PGM additions as the maximum current density was $3 \times 10^{-2}$, $1 \times 10^{-2}$ and $5 \times 10^{-3}$ A/cm$^2$, respectively for 304MC, Pd3MC and Ru3MC. So, 1 wt% Ru additions were more beneficial than 1 wt% Pd additions to lower the current density range. The anodic region of Ru3MC, Pd3MC and 304MC revealed a slight decrease in the current density around -0.3 V vs. SCE. This was also observed in Figure 121, which presented the potentiodynamic scans at 0.5 mV/s under aerated condition. From this graph, the trend was the same as that observed in Figure 119 in aerated conditions. This suggests that passivation is potential controlled and does not depend on the oxygen level. At more positive potentials than the anodic dissolution
peak, a “hump” was observed around +0.3 V vs. SCE for Ru3MC, Pd3MC and 304MC. This feature may be explained by the film electrochemistry, generating complex electrochemical reactions.

### 8.3.3.2 Potentiodynamic scan in deaerated conditions at 5 mV.s\(^{-1}\)

The potentiodynamic scan of pure Pt, the PGM-doped and standard alloys were measured from -0.5 V below the OCP to +1 V above the OCP. The experiment was performed in deaerated conditions with nitrogen at 25°C at an increased scan rate of 5 mV.s\(^{-1}\). The objective was to investigate the electrochemical response when a faster scan rate is applied, as well as the effect of PGM additions on the electrochemical behaviour of the standard alloy 304MC. The results are presented in Figure 124.

![Polarisation scan](image)

**Figure 124** Polarisation scan (5 mV.s\(^{-1}\)) in a solution of 0.01 M K\(_2\)SiO\(_6\) at 25°C, at pH=1.5, in deaerated environment with nitrogen: Ru3MC (solid blue line), Pd3MC (solid green line), 304MC (solid red line), Pt (solid black line)

From Figure 124, PGM additions reduced significantly the potential range in the anodic dissolution peak of the standard alloy 304MC. Indeed, Ru3MC and Pd3MC displayed
respectively a potential range from -0.5 to -0.3V vs. SCE and from -0.5 to -0.2V vs. SCE in the anodic dissolution peak, while 304MC showed a significantly wider potential range from -0.5 to +0.2 V vs. SCE. In addition, the maximum current density in the anodic dissolution region was also affected by 1wt% PGM additions. The OCP values of Ru3MC, Pd3MC and 304MC were about -0.5V vs. SCE. Pure platinum presented an OCP value at -0.4 V vs. SCE with a current density of about $1 \times 10^{-5}$ A/cm$^2$ in the anodic region, which was five orders of magnitude less than that of 304MC. Figure 122 displays graphs with a similar trend as that observed under aerated condition at the same scan rate (5 mV.s$^{-1}$). It confirms that passivation is potential controlled and does not depend on the oxygen concentration.

8.3.4 Surface characterisation in potassium tetrathionate

Optical micrographs of the alloy surfaces were taken after immersing the samples in 0.01 M $\text{K}_2\text{S}_4\text{O}_6$, at pH=1.5 and 25°C. The objective was to analyse the microstructure and assess the possible intergranular attack of the standard alloy and PGM-doped alloys in order to determine any beneficial or detrimental effect of PGM additions in terms of intergranular (IG) attack of the standard alloy 304MC. The results are presented in Figure 125.
Figure 125 Optical micrographs showing the surface of the alloys after immersion in 0.01 M K$_2$S$_4$O$_6$ at pH=1.5 and 25°C for 1 hour: (a): 304MC; (b): Pd3MC; (c): Ru3MC.

From Figure 125, intergranular attack was revealed on the surface of Pd3MC and 304MC. Ru3MC showed the sensitised microstructure but did not appear intergranularly attacked. However, 304MC seemed to display more severe intergranular...
corrosion as shown by the presence of ditches and deep corrosion attack at the grain boundaries. The film formed on surface of the alloys displayed dissimilarities in terms of colour. Indeed, 304MC revealed a dark film that covered the grinding marks, suggesting that it could be thicker than the film on the surfaces of Ru3MC and Pd3MC. While, Ru3MC and Pd3MC showed films that were variously blue, red and gold. These differences could be explained by either the composition of the film, its properties or its thickness. But more investigation on the film should be undertaken in order to understand better the observed differences.

8.4 Discussion

The polythionates (S$_x$O$_6^{2-}$) have been found to be important in redox transformations involving many sulphur compounds [94]. Potassium tetrathionate is a polythionate; hence it has important complex redox transformations and its electrochemistry remains unclear. The chemical and electrochemical reactions involved are quite difficult as sulphur may exist in a wide range of oxidation state.

The initiation of IGC and IGSCC by potassium tetrathionate or polythionic acids is well known [89, 160, 161]. Sulphur containing aqueous fluids are amongst the more corrosive environments experienced in the industry. Also the high lability of the sulphur species such as the polythionic acids and polysulphides contributes to the high corrosivity as they form unstable compounds. Besides, sulphur is thought to promote Cr depletion along the grain boundaries of sensitised stainless steels [80]. S.Ahmad et al [90] have investigated the stress corrosion cracking of type 304 SS in 1% tetrathionate solution at different pH values. It was shown that cracking was observed for pH between 3 and 5.3, while abundant metal dissolution due to vigorous reaction was revealed for pH between 1 and 2. This confirms the severe intergranular attack observed for 304MC after one hour immersion in 0.01 M K$_2$S$_4$O$_6$ pH=1.5, (see Figure 125).
Previous work on IGSCC in PWR, supposed that in PWR environment, sulphur could come from tube contamination by oil, sulphur dioxide in the atmosphere, deoxygenating agents or degradation of ion-exchange resins [91]. However, the solution of potassium tetrathionate has been chosen to conduct the electrochemical experiments as it is known to enhance IGC/IGSCC of sensitised stainless steels and the purpose was to investigate the influence of PGM additions on the susceptibility to IGC/IGSCC of sensitised 304MC. It is important to keep in mind that the solution of potassium tetrathionate has not been used to simulate PWR chemistry but only to investigate IGC/IGSCC resistance as it may be the problem of concern in the ‘dead space’ region of PWR, where oxygen may be trapped.

In this discussion the effect of the experimental parameters (oxygen level and scan rate) and the PGM additions on the electrochemical behaviour (OCP, anodic dissolution peak and anodic behaviour) of 304MC is discussed.

### 8.4.1 Effect of the experimental parameters on the electrochemical response

In 0.01 M $K_2S_4O_6$ at pH=1.5 and 25 °C, the scan rate and the atmospheric environment (deaerated with nitrogen and aerated) seemed to affect the electrochemical behaviours of the PGM -doped (Ru3MC and Pd3MC) and standard (304MC) alloys. Indeed by increasing the scan rate, an increase in the anodic current density was observed (see Figure 121 and Figure 122). The faster scan rate (5 mV/s) revealed fewer features than the slower scan rate (0.5 mV/s). Indeed, a decrease of the current in the anodic region around -0.3 V vs. SCE was observed only for the slow scan rate (0.5 mV/s). This can be explained by the fact that there is a time dependent effect for passivation and at fast scan rate, there is not sufficient time for passivation to occur. Hence, by lowering the scan rate, some features are visible while they disappear at higher scan rates.
In deaerated environment (saturated nitrogen electrolyte), the anodic current density of the PGM-doped and standard alloys was higher than that in aerated environment. This is sensible as passivation is promoted with oxygen.

The effect of the experimental parameters on the electrochemical response of the PGM-doped and the standard alloys is summarised in Figure 126, which displays the electrochemical behaviour of Ru3MC under various experimental conditions (different scan rates and oxygen levels). The main variations observed are representative for Pd3MC and 304MC as well but not for pure platinum. Indeed, the latter did not show significant differences in terms of its electrochemistry in potassium tetrathionate. This is explained by the fact that the PGM-doped and standard alloys passivate in potassium tetrathionate while platinum does not.

Figure 126 Potentiodynamic scan of Ru3MC in 0.01 M K$_2$S$_4$O$_6$: Ru3MC in aerated environment at 0.5 mV.s$^{-1}$ (red solid line), Ru3MC in deaerated environment with nitrogen at 0.5 mV.s$^{-1}$ (red dashed line), Ru3MC in aerated environment at 5 mV.s$^{-1}$ (black solid line), Ru3MC in deaerated environment at 5 mV.s$^{-1}$ (black dashed line)
According to Figure 126, at a slow scan rate (0.5 mV/s), more features are observed. Indeed, the anodic dissolution peak revealed a slight decrease around -0.3 V vs. SCE at 0.5 mV/s while it was not observed when the scan rate used was ten times faster (5 mV/s). In addition, the OCP values were -0.5 V vs. SCE at 0.5 and 5 mV/s. However, the slower scan rate (0.5 mV/s) showed a second OCP value (about -0.3 V vs. SCE) under both aerated and deaerated conditions with nitrogen. The current density in the anodic region was higher at faster scan rate. Indeed, about two orders of magnitude under deaerated conditions and one order of magnitude under aerated conditions. Under these experimental conditions, the main cathodic reactions and anodic reactions were probably the oxygen reduction, proton reduction, hydrogen oxidation, metal dissolution and some electrochemical reactions from the solution of potassium tetrathionate. The complexity of these reactions was not investigated so only the calculation of the redox potentials for oxygen reduction, water reduction and hydrogen oxidation were calculated and displayed in Equation 30-Equation 32. In 0.01 M $\text{K}_2\text{S}_4\text{O}_6$, at pH = 1.5 and 25 °C, it would be more appropriate to use a slow scan rate (0.5 mV/s) as it gives much more detail on the OCP and passivation for instance, which are important to investigate the electrochemistry.

### 8.4.2 Effect of (PGM) on the open circuit potential of the standard alloy 304MC in the sensitised conditions

In aerated conditions, the open circuit potential of the PGM (Ru and Pd) doped and standard (304MC) alloys revealed a transition towards more positive values (see Figure 119). Indeed, this transition occurred after 800 s, 2100 s and 2500 s, respectively for Ru3MC, Pd3MC and 304MC. 1 wt% PGM additions seemed to promote the change in OCP of the standard alloy sooner. This influence was more pronounced with 1 wt% Ru than 1 wt% Pd. The shift in OCP observed was higher for Ru3MC than Pd3MC and 304MC. Indeed, after the OCP step, the OCP values were -0.1, -0.2 and -0.25 V vs.
SCE, respectively for Ru3MC, Pd3MC and 304MC in aerated conditions (see Figure 119). The OCP measurements showed that there is a time dependent effect for passivation. The OCP results showed that passivation occurred sooner with PGM additions, which is in agreement with the findings of Potgieter that showed self passivation of stainless steels in reduced acid media [128]. Platinum displayed a constant OCP value of +0.4 V vs. SCE in aerated conditions. As platinum is noble and did not show any significant OCP variations in 0.01 M K2S4O6 at pH = 1.5 and 25°C, the transitions observed for Ru3MC, Pd3MC and 304MC is explained by the formation of a passive film in potassium tetrathionate, which certainly vary with PGM additions in terms of composition and structure. In potassium tetrathionate, passivation of the PGM-doped alloys and standard alloy is potential controlled as in both aerated and deaerated conditions at the same scan rate, similar trend was obtained in the passive region.

In deaerated environment, the OCP remained relatively constant for one hour, which was the whole duration of the measurements (see Figure 120). The OCP were about -0.5 V vs. SCE for the PGM-doped and standard alloys and about 0.2 V vs. SCE pure platinum. 1 wt% PGM (Ru and Pd) additions did not seem to affect the OCP of the standard alloy 304MC in deaerated conditions with nitrogen. So, two points could be highlighted from these OCP measurements. First, oxygen seemed to be necessary for the OCP transition to happen and second, PGM additions did not influence the OCP measurements under deaerated conditions with nitrogen. However, the potentiodynamic scans at 0.5 mV/s showed three OCP values for the PGM-doped and standard alloys. Pure platinum seemed to reveal a lower OCP value in deaerated conditions than in aerated conditions (see Figure 119 and Figure 120). The OCP measured in the OCP measurements (see Figure 119 and Figure 120) were slightly different from those obtained in the potentiodynamic scans (see Figure 121-Figure 124) conducted under similar conditions. This is explained by the fact that the material surface is modified
when cathodically polarised, which changes slightly the OCP. Therefore the more relevant OCP values are those obtained during the OCP measurements and not those obtained during the potentiodynamic scans. Table 22 displays the different OCP values for each experiment. Indeed, under aerated conditions, the OCP values varied throughout the duration of the measurements (Figure 119) and two main values were noticed for Ru3MC, Pd3MC and 304MC. The first values (-0.5 V vs. SCE) was also determined in the potentiodynamic scans (see Table 22, Figure 121 and Figure 122). However, the second value was only observed at slow scan rate (0.5 mV/s) under aerated and deaerated conditions. The slight differences observed in the OCP values can be attributed to the effect of the scan rate.

Table 22 Table summarising the OCP values under different environmental conditions

<table>
<thead>
<tr>
<th>OCP measurement</th>
<th>OCP (V vs. SCE) Ru3MC</th>
<th>OCP (V vs. SCE) Pd3MC</th>
<th>OCP (V vs. SCE) 304MC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerated</td>
<td>-0.5</td>
<td>-0.5</td>
<td>-0.5</td>
</tr>
<tr>
<td>Deaerated</td>
<td>-0.42</td>
<td>-0.45</td>
<td>-0.46</td>
</tr>
<tr>
<td>Aerated potentiodynamic 0.5mV/s</td>
<td>-0.5</td>
<td>-0.5</td>
<td>-0.5</td>
</tr>
<tr>
<td>Deaerated potentiodynamic 0.5mV/s</td>
<td>-0.5</td>
<td>-0.5</td>
<td>-0.5</td>
</tr>
<tr>
<td>Aerated potentiodynamic 5mV/s</td>
<td>-0.5</td>
<td>-0.5</td>
<td>-0.5</td>
</tr>
<tr>
<td>Deaerated potentiodynamic 5mV/s</td>
<td>-0.5</td>
<td>-0.5</td>
<td>-0.5</td>
</tr>
<tr>
<td>OCP deaerated</td>
<td>-0.5</td>
<td>-0.5</td>
<td>-0.5</td>
</tr>
</tbody>
</table>

In these environmental conditions, the thermodynamically possible electrochemical reactions to consider while measuring the OCP were the hydrogen oxidation (see Equation 31), proton reduction and metal dissolution (see Equation 32). Moreover, electrochemical reactions involving potassium tetra thionate are also to take into account. These electrochemical reactions are complex and still not fully understood. In this study, the influence of PGM additions was the main purpose; therefore, there was
no investigation on the electrochemical reactions due to the presence of potassium tetrathionate. The points to notice were that passivation of 304MC, Pd3MC and Ru3MC is time-dependent and potential controlled.

Previous work demonstrated that for cracking to occur in potassium tetrathionate, oxygen was necessary [161]. From this, the film formed (see Figure 125) could be detrimental to the alloys in terms of intergranular stress corrosion cracking (IGSCC).

The OCP measured in aerated conditions (see Figure 119) revealed a transition before being stable around -0.1 V vs. SCE, which coincides with the important reduction of current observed in the polarisation scans around -0.1 V vs. SCE in aerated and deaerated conditions at 0.5 mV/s (see Figure 121 and Figure 123). At pH = 1.5, $S_4O_6^{2-}$ is reduced to $S$ at potential below 0.02V vs. SCE and $S$ is reduced to $HS^-$ at potential below -0.3 V vs. SCE. $S_4O_6^{2-}$ is also oxidised to $S_2O_6^{2-}$ at potential above 0.165V vs. SCE. So, -0.1 V and pH = 1.5 is the stability domain of sulphur [34].

8.4.3 Effect of (PGM) on the anodic dissolution current density of the standard alloy 304MC in the sensitised conditions

PGM additions seemed to influence the passivation of sensitised 304MC. The maximum current density in the anodic dissolution peak and the potential range of the anodic peak, were significantly lowered by 1 wt% Ru. The anodic dissolution peak is characteristic of the dissolution of the alloy in the environment; therefore, by lowering the size of the anodic dissolution peak, PGM additions have shown a beneficial effect in terms of metal dissolution in potassium tetrathionate. The anodic dissolution peaks were smaller under deaerated conditions with nitrogen as observed in Figure 126, indicating that the oxygen level could influence the metal dissolution. According to the micrographs obtained after immersing in 0.01 M $K_2S_4O_6$, intergranular corrosion (IGC) was much less pronounced with PGM additions. This observation was consistent with the
electrochemical results that revealed smaller anodic dissolution peaks for Ru3MC and Pd3MC.

The anodic region revealed more features at slow scan rate. Indeed, a slight decrease in the current was noticeable around -0.3 V vs. SCE. This is in agreement with the OCP step observed during the OCP measurements (see Figure 116). Indeed, the OCP of the PGM-doped and standard alloys vary with time, therefore it is sensible to observe a second OCP in the potentiodynamic scan at a potential of -0.3 V vs. SCE, which is in the potential range of the OCP step (-0.5 V to -0.1 V vs. SCE for Ru3MC). At higher scan rate (5mV/s), this was not observed as the whole potentiodynamic scan took 280 s to be run. According to the OCP measurements presented in Figure 116, it took 800 s, 1500 s and 2100 s respectively for Ru3MC, Pd3MC and 304MC to show a variation in the OCP. Therefore there was not sufficient time to observe a change in OCP or passivation at fast scan rate. This confirms that there is a time dependent process for passivation.

8.4.4 Effect of PGM additions on the potentiodynamic scan of the standard alloy 304MC

The polarisation curves obtained under aerated conditions in acidified tetrathionate (pH 1.5) with a slow scan rate of 0.5 mV/s showed features around -0.3 V vs. SCE and +0.3 V vs. SCE in addition to the anodic dissolution peaks. It was then concluded that both film formation and etching occurred as the result of electrochemical reactions in the tetrathionate solution at sufficiently low pH, and that the subsequent oxidation peak at ~ +0.3 V vs. SCE is a feature of the film electrochemistry, or the influence of the film/etch on the electrochemistry of the underlying metal. Numerous researchers have worked on potassium tetrathionate and tried to understand the complexity of potassium tetrathionate in terms of electrochemistry. Fang and Staehle [162] suggested possible reduction reactions as expressed in Equation 33-Equation 34:
Equation 33  \[ S_4O_6^{2-} + 12H^+ + 10e^- = 4S + 6H_2O \]

Equation 34  \[ S_4O_6^{2-} + 16H^+ + 18e^- = 4HS^- + 6H_2O \]

During the experiments, the characteristic odour of H2S was noticed as well as colloidal particles at the bottom of the electrochemical cell. These observations indicated that sulphur and H2S were produced during the experiments. The film is likely to be the result of the reaction of one of these reaction products with the metal electrode. Tetrathionate attacks chromium depleted (i.e. Fe-rich) regions of sensitised stainless steels. Indeed, in sensitised stainless steels the grain boundaries are depleted in chromium which makes them anodic with respect to the matrix and therefore susceptible to intergranular corrosion (IGC) and intergranular stress corrosion cracking (IGSCC) [23]. From optical micrographs (see Figure 125), it can be seen that there is substantial intergranular attack in the 304 SS. 1 wt% Ru additions appeared to exhibit a more beneficial effect than 1 wt% Pd to improve IGC/IGSCC. No such film formed on Pt and the polarisation curve for Pt in the same solution showed no reduction in the anodic current at \(-0.3\) V vs. SCE.

A study on polythionic oxidation kinetics and mechanism, revealed that tetrathionate oxidation with Fe\(^{3+}\) and molecular oxygen produces sulphate according to the reaction given by Equation 35 [94].

Equation 35  \[ S_4O_6^{2-} + 3Fe^{3+} + 2.75O_2 + 4.5H_2O \rightarrow 4SO_4^{2-} + 3Fe^{2+} + 9H^+ \]

Green [163] also found that upon increasing the pH, deposition of a film was less significant, although a change in appearance from black to red/blue to gold was noted. The peaks found at \(+0.3\) V vs. SCE may be associated with oxidation of these iron
sulphide scales, which has previously been shown to give rise mostly to Fe$_2$O$_3$ and elemental sulphur[164].

8.5 Summary

1 wt% Ru and 1 wt% Pd additions stabilise passivation of type 304 SS in potassium tetrathionate. Passivation has a time dependent effect and is potential controlled. In terms of intergranular attack, PGM additions seemed to be beneficial to the standard alloy 304MC in the sensitised conditions although they did show some susceptibility.
Chapter 1: Introduction

Chapter 2: Literature review

Chapter 3: Materials characterisation

Chapter 4: Crack initiation

Chapter 5: Fracture mechanics approach to stress corrosion crack propagation: fatigue precracking

Chapter 6: SCC propagation study

Chapter 7: Electrochemistry in borated and lithiated water

Chapter 8: Electrochemistry in IGSCC simulated environment

Chapter 9: Electrochemistry in high temperature water

Chapter 10: Discussion

Chapter 11: Conclusions

Chapter 12: Future work
Chapter 9  Electrochemistry in high temperature water

9 Electrochemistry in high temperature water

9.1 Introduction
The aim of this study was to investigate the effect of PGM additions on the electrochemical behaviour of a sensitised standard type 304 SS (304MC) in PWR environment (high temperature, high pressure, lithiated and borated water). The same solution as that presented in Chapter 7 was used in this study. The experiments were run in an autoclave under deaerated and hydrogenated conditions. This section is structured as follows: this introduction, the experimental procedure, the results, discussion and summary.

9.2 Experimental procedure

9.2.1 Material tested
In this work, four materials were investigated. The investigation has been conducted on 304MC, Pd3MC (1 wt% Pd), Ru3MC (1 wt% Ru) and pure platinum, also used as a counter electrode. All the materials were in the sensitised condition (heat treated at 650°C for 24 hours under an Ar atmosphere) except platinum. The material compositions and microstructures are presented in Chapter 3.

9.2.2 Sample preparation
The samples made of 304MC, Pd3MC and Ru3MC were 1cm$^3$ cubes and platinum was a rectangle of dimensions 1 x 3 mm. The alloys were ground down in two perpendicular directions to a 1200 SCi surface finish on all the faces. Then, they were cleaned with deionised water and acetone prior to being spot welded to a nichrome wire, which was insulated with PTFE tube. The whole sample was exposed while running the electrochemical measurements.
9.2.3 Operating conditions

9.2.3.1 Autoclave
The measurements were run in a static autoclave (Cormet testing systems). The autoclave was made of stainless steel type 316. The maximum operating temperature was 350°C and the maximum operating pressure was 220 bar (22 MPa).

9.2.3.2 Temperature
In this study, the operating temperature was 260°C. This temperature is below that of the real PWR conditions (about 300°C) because the experiments were run according to the temperature used in the autoclave experiments presented in Chapter 4. If there was more availability to use the autoclave, the experiments would have also been run at 300°C (PWR operating temperature) and 360°C (operating temperature in crack initiation study presented in Chapter 4). The temperature was computer controlled. A ramp rate of 100 °C/hour was used to increase the temperature up to the set temperature. It was monitored to visualise when it was stable and ready to start each experiment.

9.2.3.3 Pressure
The corresponding pressure was 48 bar (4.8 MPa) at 260°C.

9.2.3.4 Chemistry
The solution used was the same one used in the experimental work described in Chapter 7. It was made of (1000 ppm B + 2 ppm Li), pH~7-8 at 25°C.

9.2.3.5 Atmosphere
The autoclave was under deaerated conditions with nitrogen or hydrogenated conditions. Under deaerated conditions, nitrogen was purged for forty minutes prior to starting the experiments, which was considered adequate given the small volume of solution (0.3 litres). Deaeration was conducted by first sealing the autoclave, bubbling nitrogen to the bottom and venting it from the top, closing taps and warming the autoclave to 260°C. In the test carried out in hydrogenated water, the vessel was sealed
and the solution was purged with a 5% H$_2$-N$_2$ mixture at a pressure corresponding to the Henry’s law to obtain the wanted H$_2$ concentration (1 cc/kg in this work).

### 9.2.3.6 Electrochemical measurements

The scan rate used was 1 mV/s. The electrochemical cell included two samples (working electrodes), a counter electrode made of Pt and a Pd-Pt hydrogen reference electrode. The measurements were also carried out on platinum by using the two samples as a counter electrode (Ru3MC and Pd3MC or Ru3MC and 304MC) after the polarisation on these samples had been carried out. The cell consisted of the working electrode (the sample investigated), the counter electrode (a Pt electrode) and the reference electrode (a hydrogen electrode consisting of a palladium wire of 25 mm long and 1 mm in diameter mildly cathodically polarised below the H$_2$ reversible potential using a Pt wire coiled around it as a counter electrode). This type of reference electrode is known as a quasi reversible hydrogen electrode (QRHE) and it has been shown that its potential differs from the reversible hydrogen electrode by less than 30 mV [165]. This reference electrode is suitable to conduct electrochemical experiments at high temperature/high pressure as its components (palladium, hydrogen gas and hydrogen ions) are stable in the autoclave environments, in addition they do not contaminate the environment being used. The samples were connected to an EG&G Versastat potentiostat to perform the electrochemical measurements.

In order to compare the potential measured to the standard hydrogen electrode (SHE), accurate measure of the pH at the operating temperature is required. Indeed the potential of the QRHE can be converted to the scale of SHE by using Equation 36 [166]. The pH was not measured in this study.

\[
\text{Equation 36} \quad E = -2.303 \frac{RT}{2F} \log f_{\text{H}_2,T} - 2.303 \frac{RT}{F} \text{pH}_T
\]
Where,

- $E$ is the potential measured with the reference electrode (QRHE)
- $T$ is the operating temperature
- $pH_T$ is the thermodynamic pH at the operating temperature
- $R$ is the gas constant
- $F$ is the faraday’s constant
- $f_{H2}$ is the hydrogen fugacity

For each set of experiments, the reference electrode was calibrated in order to apply the right current to the reference electrode and generate hydrogen on the Pd. The calibration was performed by polarising the reference electrode with a current ranging from -60 µA to +60 µA and recording the corresponding cell potential. By plotting the polarisation curves and extrapolating the Tafel’s slopes it was possible to estimate the exchange current and choose a suitable polarisation current (this was usually about 7 µA).

Once the temperature was stable and the reference electrode was calibrated, the electrochemical measurements (OCP + potentiodynamic measurements) were performed on each working electrode one at a time.

First, the OCP was measured until it was stable and then a potentiodynamic measurement was run from -0.3 V below the OCP to +2 V above the OCP.

### 9.3 Results

#### 9.3.1 Calibration of the reference electrode

The reference electrode was accurately calibrated prior to each test once the temperature reached a steady state. A representative calibration graph is presented in Figure 127.

The graph shows the cathodic and anodic parts as well as the calibration point (green triangle) at 260°C.
9.3.2 Open circuit potential (OCP) and potentiodynamic measurements

9.3.2.1 In deaerated conditions with nitrogen at 260°C

Under deaerated conditions with nitrogen, two different sets of experiments were carried out in order to investigate the reproducibility of the results. The first set contained Ru3MC, Pd3MC, the counter electrode (platinum) and the reference electrode. The second set was composed of Ru3MC, 304MC, the counter electrode and the reference electrode. The results showing the polarisation measurements are presented in Figure 128-Figure 132.

While running the first set of experiments, the potential of the materials present inside the autoclave was monitored in order to investigate the evolution of the potential while polarising one particular material (see Figure 129).
Figure 128 Polarisation measurements under deaerated conditions with nitrogen at 260°C: Pd3MC (green line), Ru3MC (blue line), Pt (black line)

Figure 129 Potential measurements under deaerated conditions with nitrogen at 260°C: Pd3MC (green line), Ru3MC (blue line), Pt (black line), autoclave body (red line)
From Figure 128, it was observed that Pt displayed an OCP of about +150 mV vs. RE while Ru3MC and Pd3MC revealed similar OCP values (-100 mV vs. RE). The electrochemical response of the PGM-doped alloys was very similar, although Pd3MC showed a greater current density in the anodic region between 0 and 1000 mV. The anodic dissolution peaks of both Pd3MC and Ru3MC were revealed around 0 V vs. RE, and the maximum current density in the anodic dissolution peak of Ru3MC and Pd3MC was respectively $1 \times 10^{-5}$ and $3 \times 10^{-5}$ A/cm$^2$. The second peaks were revealed at around 300 mV vs. RE and the third peaks were shown around 700 mV vs. RE. The latter could be the onset of the transpassive region. Pt seemed to have a lower current density in the anodic region, which is sensible as it is inert. However, from 1000 mV vs. RE, an increase in the current density was observed due to oxygen evolution. Indeed, above 1000 mV vs. RE, the three materials presented very similar electrochemical behaviour, this was probably the ohmic resistance. This is due to the resistance of the solution when high potentials are applied. The electrochemical reactions involved in this environment were probably water reduction, oxygen evolution and metal dissolution.

In Figure 129, the potential against time was presented. The objective of these measurements was to detect any interference between the different materials while measuring the potential of a given material. Indeed, if there is any interference, the measured potential could not be exact. After 2000 s, Ru3MC was polarised cathodically so its potential decreased (-200 mV) and that of Pt increased (+1000 mV) as it was used as the counter electrode. The potential of Pd3MC decreased (a few mV) slightly but this is not significant for interference. The potential of the autoclave body remained constant revealing no interference between Ru3MC and the autoclave body. While polarising anodically Ru3MC, its potential increased (+2000 mV) and that of
pure platinum decreased (-750 mV) as it was the counter electrode. Similarly, when Pd3MC was polarised cathodically after 5000s, its potential decreased (-300 mV) and that of Pt increased (+1000 mV). Around 1200 s, platinum was polarised anodically so its potential increased (+2000 mV) and those of Pd3MC and Ru3MC decreased (respectively -500 and -700 mV) as they were coupled and used as the counter electrode. After 1300 s, none of the materials were polarised so their potentials stabilised.

Figure 130 Potential measurements from 260°C to room temperature under deaerated conditions with nitrogen: Pd3MC (green line), Ru3MC (blue line), Pt (black line), autoclave body (red line)

The potential was monitored while the temperature was gradually decreasing from 260°C to room temperature. The objective was to determine the influence of the temperature on the potential. There were three main stages observed: first, the general trend showed that the potential was relatively constant (0 mV) until 9000 s for the autoclave body, Pd3MC and Ru3MC and 1200 s for platinum; then, the potentials increased (+500 mV) between 9000 s and 16000 s, then they kept increasing at a slower
rate from 16000s to 25000s up to 700mV vs. RE. So decreasing the temperature revealed higher potentials.

From Figure 131, it was observed that pure platinum displayed a more noble OCP (about 150 mV vs. RE) than Ru3MC and 304MC, which respectively revealed OCP values of about 0 V vs. RE. This observation was also made at room temperature (see Chapter 7). The OCP of Pt was repeatable as the same value was measured previously (see Figure 128) under similar environmental conditions. The current density in the anodic region of Ru3MC revealed two peaks: one at 0 V vs. RE and the other one at about +300 mV vs. RE. The first one corresponded to the anodic dissolution peak. The second peak was not observed for 304MC, so it is certainly from PGM enrichment in the film. Around 700 mV vs. RE, an increase in potential was observed for 304MC and...
Ru3MC; it was probably the onset of the transpassive region. In terms of current density in the anodic region, 304MC and Ru3MC showed a maximum value ($2 \times 10^{-5}$ A/cm$^2$) in the anodic dissolution peak at around +0 V vs. RE. 1 wt% Ru additions did not seem to affect significantly the electrochemical behaviour of sensitised 304MC as the cathodic region, anodic dissolution peak and anodic region displayed very similar behaviours.

Figure 132 Polarisation measurements under deaerated conditions with nitrogen at 260°C: 304MC (red line), Ru3MC (blue line), Pd3MC (green line)

Figure 132 showed the electrochemical response of 304MC, Ru3MC and Pd3MC for a better comparison of the electrochemical responses in deaerated conditions with nitrogen at 260°C. In the cathodic region, the electrochemical response of the PGM-doped and standard alloys was similar in terms of reaction rates. In the anodic regions, Pd3MC and Ru3MC revealed similar behaviour however Pd3MC had a greater current density (twice higher). 304MC did not reveal the same peaks as Pd3MC and Ru3MC around +300 mV vs. RE. The three alloys showed a clear increase in the current density...
from 700 mV vs. RE, corresponding to the transpassive region. According to Figure 132, 1 wt% PGM additions lowered the anodic dissolution peak of 304MC.

9.3.2.2 In hydrogenated conditions at 260°C

Under these conditions, the experiments were conducted three times in order to investigate the repeatability of the results. In each set of experiments two alloys (Ru3MC and 304MC or Ru3MC and Pd3MC) and Pt were investigated. The following sections only show one representative graph of the materials in each environmental condition investigated.

Figure 133 Polarisation measurements under hydrogenated conditions at 260°C: Pt (black line), Ru3MC (blue line), 304MC (red line)

From Figure 133, the OCP of the standard alloy 304MC and the doped alloy Ru3MC were identical (-50 mV vs. RE). On the other hand, Pt was more noble as it revealed an OCP of about +50 mV vs. RE. The OCP values suggested that 1 wt% Ru additions did not affect the OCP of the standard alloy 304MC. The cathodic and anodic behaviours of
the standard and doped alloys were very similar as the cathodic regions overlapped, which indicated similar reaction rates for the anodic and cathodic electrochemical reactions involved in this environment.

**Equation 37** \( 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \)

**Equation 38** \( E = E^\circ - 0.06 \text{pH} \)

\( E^\circ = 0 \text{ V at 25°C for the water reduction/hydrogen oxidation} \)

\( E = 0 - 0.06 \times 7 = -0.42 \text{ V vs. SHE at pH=7} \)

\( E^1 = 0 - 0.06 \times 8 = -0.48 \text{ V vs. SHE at pH=8} \)

In the anodic region, the anodic dissolution peaks of the PGM and standard alloys was revealed at 0 V vs. RE with a maximum current density of about \( 2 \times 10^{-5} \text{ A/cm}^2 \). From \( \sim +700 \text{ mV vs. RE} \), the current density increased significantly, revealing the transpassive region. Around 1200 mV vs. RE, the potentials increased significantly, probably due to the ohmic resistance. Platinum had a similar cathodic behaviour as 304MC and Ru3MC in terms of kinetics. However the anodic behaviour was very different due to hydrogen oxidation.

---

\(^1\) Potential is expected to be different at 260°C
From Figure 134, the OCP values of Ru3MC and Pd3MC were identical (-50 mV vs. RE), suggesting that 1 wt% Ru and 1 wt% Pd had similar effect on the OCP of the standard alloy 304MC. However, pure platinum revealed an OCP of about 0 mV vs. RE. It was slightly less (-50 mV) than that observed under similar conditions (see Figure 133), but still in the experimental error so it can be said that the results are reproducible. In terms of cathodic electrochemical behaviour, the PGM -doped alloys and Pt were similar, as the cathodic region revealed similar kinetics or reaction rates according to the slope observed in the cathodic region. In the anodic region, only Pd3MC and Ru3MC behaved similarly, with an anodic dissolution peak observed at 0 mV vs. RE and a maximum dissolution current density of about 2x10^{-5} A/cm^2. These values were consistent with Figure 133, which displayed the electrochemical behaviour of Ru3MC as well under hydrogenated conditions. In Figure 134, it was evident that 1 wt% Pd and
1 wt% Ru had exactly the same effect on the electrochemical behaviour of 304MC as both their electrochemical anodic and cathodic behaviours were similar.

For more clarity, the electrochemical behaviour of the PGM-doped and standard alloys in hydrogenated conditions were plotted on one graph and presented in Figure 135. From this graph, PGM additions did not influence the electrochemical behaviour of 304MC under 1 cc/kg hydrogen in a solution of (1000 ppm B + 2 ppm Li) at 260°C.

![Figure 135 Polarisation measurements under hydrogenated conditions at 260°C: Ru3MC (blue line), Pd3MC (green line), 304MC (red line)](image-url)

Figure 135 Polarisation measurements under hydrogenated conditions at 260°C: Ru3MC (blue line), Pd3MC (green line), 304MC (red line)
9.4 Discussions

9.4.1 Effect of PGM on the electrochemical response in deaerated conditions in high temperature PWR water chemistry

From the results section, it was seen that at 260°C under high pressure (4.8 MPa) and deaerated conditions with nitrogen, PGM additions had an effect on the electrochemical behaviour of the standard material 304MC in PWR chemistry (1000 ppm B + 2 ppm Li). Indeed, the main points to discuss are the OCP values, the anodic dissolution peak and general electrochemical behaviour of the standard and PGM-doped alloys. The OCP showed that 1 wt% PGM additions did not affect the OCP of 304MC as Pd3MC, Ru3MC and 304MC displayed similar OCP values: about 0 mV vs. RE. In terms of anodic dissolution peak, 1 wt% Ru additions were beneficial as the maximum current density in the anodic dissolution peak was reduced by half (1x10\(^{-5}\) A/cm\(^2\) against 2x10\(^{-5}\) A/cm\(^2\) for 304MC), see Figure 132. In deaerated conditions with nitrogen, a peak was observed for Pd3MC and Ru3MC around 300 mV vs. RE. It is probably the oxidation of dissolved hydrogen in the alloys as more hydrogen is absorbed in the alloys containing PGM. This is explained by the high exchange current density that PGMs have for the proton reduction/hydrogen oxidation reactions. Around 800 mV vs. RE the increase in potential corresponds to the transpassive region, which is the dissolution of the passive film according to Equation 39 [167].

\[
\text{Equation 39} \quad \text{Cr}^{3+} \rightarrow \text{Cr}^{6+} + 3e^-
\]

Above 1200mV vs. RE, the potentials were not of interest as the ohmic resistance was probably too high, which revealed a significant increase in potential.

The potential measurements revealed that under deaerated conditions with nitrogen, the autoclave body had a stable potential. The potential of the autoclave body was very close to that of 304MC, indeed the autoclave body was made of type 316 SS, which is
similar to type 304 SS in terms of material composition. The potential variations of the PGM -doped and standard materials were not significant further to polarising as the materials had similar potentials prior and further to polarising (see Figure 129). This indicates that no surface enrichment of the PGM occurred during polarisation. PGM additions did not seem to influence significantly the reaction rates of the cathodic reaction as the kinetics observed for the PGM -doped and alloys were the same. In the “dead space” regions of PWRs, where oxygen may be trapped and therefore the oxygen level may be above that in the bulk, 1 wt% Ru additions would lower the anodic dissolution peak, therefore reducing general corrosion. In terms of intergranular stress corrosion cracking (IGSCC) susceptibility, the oxygen level raises the potential of non catalytic surfaces (unless H₂ is in amount significantly greater than the stoichiometric amount (e.g. molar ratio H₂O>2), and increases the IGSCC susceptibility. Therefore it is better to keep low potential [20]. The results can only show that PGM additions do not affect the electrochemical behaviour of 304MC under deaerated conditions containing a residual oxygen level.

9.4.2 Effect of PGM on the electrochemical response in hydrogenated conditions in high temperature PWR water chemistry

Under hydrogenated conditions using 1 cc/kg H₂O, the behaviour of the PGM-doped (Pd3MC) and standard (304MC) alloys was relatively similar. Under hydrogenated conditions, the anodic reaction to consider was metal dissolution and the cathodic reaction was water reduction (see Equation 37). The OCP values of Pd3MC, Ru3MC and 304MC were about -50 mV vs. RE. So, these results demonstrated that 1 wt% PGM (ruthenium and palladium) additions did not influence the cathodic or anodic electrochemical reactions at equilibrium in 1000 ppm B + 2 ppm Li at 260°C under hydrogenated conditions (1 cc/kg). The OCP of the PGM -doped and standard alloys was lowered by 50 mV under hydrogenated conditions (1 cc/kg) compared to the
deaerated conditions with nitrogen. This is explained by the fact that the electrochemical reactions rates are different in these two environments. Moreover, the addition of hydrogen shifts the OCP towards more negative values, as the reversibility of the hydrogen oxidation/evolution reaction is improved.

For Pd3MC, Ru3MC and 304MC, there were two peaks observed in the anodic region. The first peak occurred at 0 V vs. RE and was probably the anodic dissolution peak of the alloys. This peak was of course not observed on platinum, which is inert. The second peak observed was the transpassive region and it happened at about 800 mV vs. RE. By comparing to the deaerated conditions with nitrogen, in hydrogenated conditions, PGM additions did not shift the anodic current density towards more positive values (~1x10^{-5} A/cm^2) at 300 mV vs. RE (see Figure 132 and Figure 135). PGM additions catalyse the hydrogen oxidation reaction, present with hydrogen but not nitrogen. One important point to highlight is that the hydrogenated conditions (1 cc/kg) used were not representative of PWR conditions, which contain between 20 and 30 cc/kg of hydrogen [20]. Only the influence of PGM on the electrochemical behaviour of 304MC under low hydrogen level can be discussed. It was shown that low hydrogen level such as 1 cc/kg do not influence the kinetics of the main reactions (water reduction and metal dissolution) as similar electrochemical behaviour was obtained for the PGM-doped and standard alloys. This is in agreement with the experiments performed under BWR conditions that showed that the OCP was lowered towards more negative values using PGM additions only if there was a molar ratio H:O>2 [13] [168].

9.5 Summary
Under deaerated conditions with nitrogen, 1 wt% Ru additions seemed to lower the anodic dissolution peak of the standard alloy 304MC while 1 wt% Pd additions seemed to increase it. The OCP, which is a key parameter to assess the IGSCC susceptibility of stainless steel in PWR, was investigated in both deaerated conditions with nitrogen and
hydrogenated conditions (1cc/kg). Under deaerated and hydrogenated conditions, 1 wt%
Ru and 1 wt% Pd did not influence the OCP of the standard alloy 304MC.
Chapter 1: Introduction

Chapter 2: Literature review

Chapter 3: Materials characterisation

Chapter 4: Crack initiation

Chapter 5: Fracture mechanics approach to stress corrosion crack propagation: fatigue precracking

Chapter 6: SCC propagation study

Chapter 7: Electrochemistry in borated and lithiated water

Chapter 8: Electrochemistry in IGSCC simulated environment

Chapter 9: Electrochemistry in high temperature water

**Chapter 10: Discussion**

Chapter 11: Conclusions

Chapter 12: Future work
10. Discussion

10.1 Introduction

The influence of platinum group metals (PGMs) on the open circuit potential (OCP) and intergranular stress corrosion cracking (IGSCC) susceptibility of sensitised type 304 SS (304MC) has been investigated. The influence of PGM additions on the OCP measurements, polarisation scans, crack initiation in the autoclave and crack propagation under constant extension has been investigated in pressurised water reactor (PWR) chemistry (1000 ppm B + 2 ppm Li) and simulated IGSCC (potassium tetrathionate) environments. These experiments have been conducted in order to obtain a clear understanding of the potential beneficial effect of PGM additions, and particularly ruthenium and palladium, on the stainless steel IGSCC susceptibility in PWRs [20]. This section discusses the results presented in the previous chapters (Chapter 3-Chapter 9) and explains the relationship between the different results in order to elucidate the influence of PGM additions on the IGSCC susceptibility of sensitised stainless steel type 304 (304MC) in PWR application. Previous work has shown that platinum group metals have revealed both adverse and beneficial effects in terms of corrosion resistance (pitting and general corrosion) in different media such as sulphuric acid and hydrochloric acid [106, 128]. For example, the positive effect of PGM additions to titanium or stainless steel in sulphuric acid was explained by a mechanism called “cathodic modification”, where PGM enhance hydrogen evolution due to their high exchange current density for this reaction. Consequently, PGM additions promote self passivation of the alloy in sulphuric acid, which lowers the corrosion rate [2, 117]. This is explained by the fact that the kinetics of the cathodic reaction (proton reduction) and the anodic reaction (metal dissolution) intersect is in the passive region of the alloys (see Chapter 2 section 2.5.4). In most boiling water reactors (BWRs), small additions of PGM were effective in lowering the OCP below the critical
value (-230 mV vs. SHE) above which IGSCC may occur [13]. The alloys investigated in this study contained various amounts of PGM (ruthenium or palladium) additions between 0.11 and 1 wt%. The materials investigated in more detail were those with 1 wt% PGM (Pd3MC and Ru3MC) as well as the standard alloy 304MC. Particular attention was focused on the sensitised state, which makes the alloy more susceptible to IGSCC. The following section is divided into four parts which discuss the influence of PGM additions on the four aims of this study:

- The material properties of type 304 SS
- The cathodic and anodic kinetics in PWR chemistry
- The cracking resistance in PWRs
- The cracking resistance in potassium tetrathionate solution which promotes IGSCC susceptibility

10.2 PGM effect on the material properties of type 304 SS
Tensile properties, hardness, microstructure and grain size have been investigated for the standard and PGM-doped alloys. PGM additions to the alloys did not result in any notable differences in the austenitic microstructure. The grain size was not significantly different with PGM additions as Pd3MC, Ru3MC and 304MC revealed respectively an average grain size of about 47, 54 and 55 µm. In the sensitised samples, the time required to etch the grain boundaries was longer for the PGM-doped alloys. This was attributed to the fact that PGM can enhance self passivation in acids and therefore in oxalic acid, which was used to etch the alloys; the PGM-doped materials were more resistant to the etching process. An alternative etchant is a solution of 4% picral plus hydrochloric acid [142]. In PWRs, self passivation of the PGM-doped alloys present many advantages as it will improve the general corrosion resistance. However, the passive state promotes localised corrosion such as pitting. SCC may initiates from pits, nevertheless the cracking mode of concern in PWRs is intergranular, therefore, it is
unlikely to initiate from pits. The tensile properties have been measured at 300°C as the operating temperature in PWRs is between 300 and 315°C. At 300°C, Ru3MC [53] showed higher yield stress (173 MPa) and maximum stress (428 MPa) than 304MC, which revealed a yield stress of 147 MPa and a maximum stress of about 393 MPa. More importantly, Ru3MC was more ductile as its nominal strain at failure was 35% against 30% for 304MC. By contrast, Pd3MC had poorer tensile properties as its yield stress and tensile strength were respectively 166 MPa and 363 MPa. Kim and Niedrach evaluated the effects of PGM additions on processing and claim that noble metal additions have no adverse effect on tensile yield stress, ultimate tensile strength and elongation to failure [105]. In titanium alloys containing PGMs (grades 7, 11, 27, 29…), the yield stress and ultimate tensile strength are the same as the titanium alloys that are not composed of PGMs (i.e: grades 1 and 2) [112]. Titanium has a body-centered cubic (bcc) structure while type 304 SS has a face-centered cubic (fcc) structure so this could explain why PGM additions influenced slightly the maximum stress in type 304 SS while no variations were noticed in titanium alloys. In summary, the material characterisation of the alloys presented similarities but also differences that may influence the IGSCC resistance under PWR conditions and on the mechanical performance.

10.3 PGM additions influence on the anodic and cathodic kinetics in PWR chemistry
The solution used to carry out the electrochemical measurements was specifically chosen as it simulates PWR chemistry, which contains boron (as boric acid) to control neutron flux and lithium hydroxide to control the pH [20]. PGM additions to the environment used in BWRs lower the electrochemical corrosion potential and this technique is known as noble metal chemical addition (NMCA). In acids such as sulphuric acid, PGMs cathodically modify stainless steels. This results in self passivation and promotes pitting resistance. By contrast to other studies, polarisation
measurements in PWR chemistry have been conducted in this study. The purpose was to investigate the kinetics in PWRs.

The simulated solution was used at room temperature, 70°C and 260°C and under aerated, deaerated with nitrogen and hydrogenated conditions in order to assess the influence of PGM additions at different temperatures as well as to investigate their influence on the kinetics of the main electrochemical reactions involved in PWR environment: oxygen reduction, hydrogen oxidation, water reduction and metal dissolution.

In aerated environment, PGM additions lowered the anodic dissolution rate as observed by the smaller anodic dissolution peak of the PGM modified alloys compared to that of the standard alloy; therefore they improved the metal dissolution resistance. Moreover passivation was promoted. The anodic current densities of Ru3MC, Pd3MC and 304MC were respectively about $1 \times 10^{-7}$, $5 \times 10^{-7}$ and $1 \times 10^{-6}$ A/cm$^2$ under aerated conditions at 25°C. This suggests that there is a surface enrichment that prevents further metal dissolution. However, in PWR environments metal oxidation has a minor role as evidenced in the present work by the low passive current density. In aerated conditions at 25°C, PGMs act also cathodically as they shifted the electrochemical corrosion potential towards more positive values, indicating a higher exchange current density for the oxygen reduction reaction. These findings are consistent with literature data as noble metals catalyse the oxygen reduction reaction by enhancing higher exchange current density of this reaction [105]. The shift in OCP was of the order $+0.015$ V for 1 wt% Ru additions at 25°C under aerated conditions. Increasing the temperature shifted the OCP towards more positive values. This observation was consistent with the fact that the kinetics of the electrochemical reactions (oxygen reduction and metal dissolution) differ as temperature increases. Specifically, rates for metal dissolution increase with temperature while dissolved oxygen concentration decreases with increasing
temperature. At 70°C, PGM-doped alloys maintained a more positive OCP than 304MC as an increase by +0.15 and +0.05 V was respectively observed for Ru3MC and Pd3MC.

So, under excess oxygen conditions, PGM-doped alloys have a more positive corrosion potential, therefore they could increase the risk of IGSCC susceptibility, which is believed to be related to an increase in potential [65]. However, the results from the autoclave tests under oxygenated conditions (see Chapter 4), revealed that PGM-doped alloys were more resistant to crack initiation than the standard alloy 304MC. The reader is reminded that dissolved oxygen concentrations used in this work were much higher than those expected in PWRs, even in dead space regions.

Deaeration with nitrogen shifted the OCP of the PGM-doped and standard alloys towards more negative values when compared to the aerated conditions as the oxygen concentration was negligible. However, the PGM-doped alloys maintained a more positive potential than 304MC. Indeed, Ru3MC, Pd3MC and 304MC revealed OCP values of approximately -0.5, -0.6 and -0.7 V vs. SCE, respectively at 25°C under deaerated conditions with nitrogen.

In order to investigate PWR environmental conditions in more detail, electrochemical experiments including OCP measurements and polarisation measurements from -0.5 V below the OCP to +2 V above the OCP, were carried out at 260°C. These experiments were conducted under deaerated conditions by purging nitrogen in the autoclave one hour prior to start the experiment. The results showed that PGM additions did not influence the OCP in deaerated environments with nitrogen as the OCP of Ru3MC, Pd3MC and 304MC was about 0 V vs. SHE. In contrast to trials performed at room
temperature and 70°C, experiments under these conditions suggested that PGM additions did not influence the behaviour of the standard alloy 304MC. Obviously, the kinetics and electrochemical reactions involved during high temperature work are expected to be different from those at room temperature and 70°C. Indeed, PGM additions catalyse the oxygen reduction reaction and/or the hydrogen oxidation reaction depending on the ratio H:O. This has already been demonstrated previously on PGM-coated samples [13].

Some research work has already demonstrated the importance of the OCP and the oxygen level in terms of IGSCC susceptibility in light water reactors such as BWRs and PWRs [12, 18]. In PWR, the chemistry is different as there is sufficient hydrogen (about 30 cc/kg) to prevent IGSCC. Nevertheless, the ‘dead space’ region may suffer from IGSCC if the oxygen level rises locally. The threshold oxygen level or potential that may initiate IGSCC is not known and is currently being investigated. It is for this reason that it is of great interest to understand how PGMs influence the potential under different oxygen levels. The limited access to the apparatus did not allow the investigation of the influence of PGMs in many different oxygenated conditions. If only the OCP is considered under conditions of excess oxygen, the study presented in Chapter 7 demonstrates that PGM additions could be detrimental to sensitised type 304 SS in terms of IGSCC susceptibility under excess oxygen conditions.

Under hydrogenated conditions, PGM additions influence the anodic process as they appear to catalyse the anodic hydrogen oxidation reaction for which they have a high exchange current density. Under excess hydrogen conditions, the OCP measurements have demonstrated a beneficial effect of PGM additions, especially Ru modifications as the OCP of the standard alloy 304MC was significantly lowered. Indeed, 0.1, 0.25 and 1 wt% Ru shifted the OCP of 304MC towards more negative values, towards the redox
potential for hydrogen oxidation/water reduction. Indeed, under hydrogenated conditions (23 cc/kg), according to the Nernst equation, the electrochemical reactions involved were the hydrogen oxidation ($H_2 \rightarrow 2H^+ + 2e^-$), metal dissolution and water reduction ($2H_2O + 2e^- \rightarrow H_2 + 2OH^-$). PGM additions, and in particular Ru additions have led to lower potentials (~0.66 V vs. SCE) and catalyse the hydrogen oxidation reaction, by enhancing high exchange current density for this reaction, therefore lowering the OCP of the standard alloy 304MC. This observation was consistent with previous studies that showed the catalytic effect of PGMs in the presence of hydrogen [22, 133]. The OCP of Ru1MC (0.11 wt% Ru), Ru2MC (0.25 wt% Ru) and Ru3MC (1 wt% Ru) was the same as that of pure platinum, which behaved like a hydrogen electrode. In contrast to work under aerated conditions, trial performed using hydrogenated media (23 cc/kg) at 25°C produced very different results. The anodic current density profile was shifted towards more positive values; however this is a consequence of the hydrogen oxidation anodic reaction, rather than anodic metal dissolution. Indeed, 304MC revealed anodic current density of about $1x10^{-7}$ A/cm$^2$ while Ru1MC, Ru2MC and Ru3MC revealed respectively anodic current density values of about $2x10^{-6}$, $1x10^{-6}$ and $1x10^{-5}$ A/cm$^2$ respectively at the onset of the anodic region.

OCP measurements and polarisation measurements in the range -0.5 V below the OCP to +2 V above the OCP, were carried out under hydrogenated conditions (1 cc/kg) at 260°C. The results showed that PGM additions did not influence the OCP in the given hydrogenated environment as the OCP of Ru3MC, Pd3MC and 304MC were similar and of the order ~50 mV vs. SHE. Pd and Ru additions do not have an effect on the OCP of type 304 SS under hydrogenated environment containing a low level of hydrogen.
A tentative conclusion from these results is that Pd and Ru additions do not have an effect on the OCP of type 304 SS under hydrogenated environments containing a low level of hydrogen. Furthermore, both aerated and hydrogenated environments revealed that depending on the oxygen level, PGMs could either catalyse the oxygen reduction reaction or the hydrogen oxidation reaction. The former leads to more positive OCP value while the latter results in more negative OCP value.

10.4 The influence of PGMs on the cracking resistance in PWR chemistry

Crack initiation susceptibility was investigated in autoclaves using different solutions including PWR chemistry (see Chapter 4). In order to promote crack initiation, U-bend samples were tested on autoclave so that several samples could be investigated under identical conditions simultaneously during a single trial. Under hydrogenated conditions (30 cc/kg), at 260°C or 360°C, for 500 and 800 hours, cracking was not initiated in any of the sensitised PGM-doped or standard alloys. After increasing the time of exposure (up to 1060 hours), temperature (360°C), and adding impurities such as 750 ppb SO$_4^{2-}$, 1000 ppb Cl$^-$, cracking was still not initiated in PWR model solutions containing 3.5 ppm Li under hydrogenated conditions (50 cc/kg at the start of the experiment; see Chapter 4 test A6). However, in an oxygenated environment containing about 40 ppm O$_2$ at the start of the experiment (see Chapter 4 test A7), and the ionic species 82.5 ppb SO$_4^{2-}$, and 531 ppb Cl$^-$, cracking was initiated on sensitised 304MC within 1460 hours at 360°C. Specifically, cracking was observed in the region of the U-bend sample which was under high tensile stress (the bent part) and was about 900 µm long. On the other hand, Pd3MC and Ru3MC, which were also investigated in this environment, did not undergo crack initiation processes. These observations suggests that crack initiation of sensitised stainless type 304 SS under PWR conditions is relatively difficult. This observation is consistent with some work performed by Tice that demonstrated the
difficulty of initiating cracking, even on cold worked materials under cyclic loading [20]. Increasing the temperature, time of exposure or corrosive nature of the environment enhanced crack initiation on 304MC but not on the PGM-doped alloys, which implied that 1 wt% Ru or 1 wt% Pd enhance resistance to crack initiation. This behaviour can be the consequence of the formation of a film formed on the surface, or alternatively as a result of better corrosion resistance promoted by the PGM surface enrichment. According to the cracking results in PWR environment (see Chapter 4) and the electrochemical behaviour in a solution of (1000 ppm B + 2 ppm Li) at room temperature, 70°C and 260°C, PGM additions decrease the OCP of the standard alloy 304MC towards more negative value in the presence of sufficient hydrogen (23 cc/kg for instance). They also promote IGSCC resistance under severe conditions containing sulphate and chloride, which are known to promote IGSCC susceptibility or pitting. Furthermore, pitting can initiate when there is a passive film. In the presence of a surface defect, the breakdown of the passive film may occur, which results in metal dissolution and the accumulation of metal cations and electromigration of anions such as chloride. Sulphur can also promote hydrogen embrittlement. In addition, it is a strong cathodic reactant, which can therefore increase the corrosion rate of the main anodic reaction which is often metal dissolution [70, 72]. The evidence thus suggests that the OCP may not be the only parameter controlling IGSCC resistance of sensitised type 304 SS in PWR environment.

10.5 The influence of PGMs on the cracking resistance in potassium tetrathionate

10.5.1 Fatigue precrack

Crack propagation was performed using circumferential cracked bar (CCB) specimens, which were fatigue pre-cracked under rotation using a rotating bend rig. This technique was used by Ibrahim et al. [96-98] who demonstrated its advantages. Importantly, they
showed that the CCB samples under fatigue rotation could generate circumferential and uniform precracks. One of the key advantages of this technique is obviously the uniform stress intensity factor $K_I$ that makes the crack propagation study much easier. In the present, preliminary study on fatigue precracking only a type 304 SS (see Chapter 5) alloy has been investigated and no trials were run using PGM-doped alloys. The findings were consistent with the literature [96-98] in terms of uniformity of the fatigue precrack and reproducibility of the technique. Monitoring the fatigue precrack was performed using a direct current potential drop (DCPD) method, which involved applying a constant current and measuring the corresponding potential drop while the precrack was growing under fatigue rotation. The results did not reveal accurate resistance variation. Sixteen CCB samples were investigated under different conditions (load, number of cycles). It was possible to determine the relationship between the resistance variation and the fatigue precrack length (including the notch). According to the results in Chapter 5 (see Figure 75), the DCPD method was not accurate enough to determine with precision the fatigue precrack length when considering the resistance variation. Specifically, the voltmeter and ammeter did not provide sufficient precision and the precrack length variation was too small to be detected with accuracy. The thermal effect and the large number of experimental errors induced during the measurements made this technique not appropriate to investigate precarck length as a function of the resistance variation. The DCPD technique has already been used and it was shown that for high currents, the results were not very precise. The process appears to be more appropriate for detection of long cracks (bigger than a grain size) [101]. However, the results in this study revealed that the resistance variation was not easy to measure for small cracks (~50-200 µm), which are between one and four grains size. Above 1 mm, the applied stress intensity factor is too high; therefore the stress conditions applied were too severe as well as enhancing the risk of failure. For the stress
corrosion crack propagation study, the samples were fatigue pre-cracked under a load of 17 kg for 3000 cycles, as these conditions generated fatigue precrack length of the order 2.2 mm to 2.5 mm. This range of precrack lengths was of interest in order to control more efficiently the stress corrosion crack propagation in potassium tetrathionate (see Chapter 6) further to fatigue precracking. The main issue encountered with the fatigue precrack study concerned the diversity of the specimens used. The fatigue properties of the alloys investigated were different, therefore under similar fatigue conditions, the precracks obtained were different and consequently the initial stress conditions for the IGSCC study (see Chapter 6) were not identical. This made the comparative study for the influence of PGM additions on the crack propagation in potassium tetrathionate difficult. The stress corrosion cracking study was performed on fatigue pre-cracked CCB samples (Ru1MC, Ru2MC, Ru3MC, Ru3HC, Pd2MC, Pd3MC, Pd3HC and 304MC). It is important to remind the reader that the fatigue pre-cracking study has only been carried out on 304MC, therefore the fatigue behaviour of the PGM-doped alloys has not been investigated. This is due to the limited number of samples available for this study.

10.5.2 SCC study
PGM-doped and standard alloys were investigated in an aqueous solution of 0.01M K₂S₄O₆ at pH=1.5 and 25°C. This medium has been used by many researchers and demonstrated to enhance IGSCC in sensitised stainless steels [71, 91, 104]. The purpose of the crack propagation study was to investigate the influence of PGM additions on the IGSCC resistance in an environment promoting IGSCC as it is the cracking mode of interest in PWRs. Further to fatigue pre-cracking and constant extension in potassium tetrathionate (see Chapter 6), the fracture surfaces were analysed and revealed four regions: the notch, the fatigue pre-crack, IGSCC and the final ligament.
This is consistent with the results found previously by other workers that revealed four regions after fatigue precracking and SCC experiments [145, 150]. The mode of cracking in potassium tetrathionate is known to be intergranular[69], therefore the results presented in Chapter 6 are consistent with previous work. Additions of ruthenium in medium carbon samples revealed that increasing the Ru content from 0.26 wt% to 1.01 wt% improved the IGSCC resistance as an increase in time to failure was observed (Ru2MC failed after 15 hours for an initial $K_I$ of 18.8 MPa√m while Ru3MC failed after 24 hours for the same initial $K_I$).

In addition to the PGM level, the carbon content was also investigated. It was shown that high carbon PGM-doped alloys Ru3HC (C=0.96 wt%) and Pd3HC (C=0.75 wt%), failed after 11 hours under an initial $K_I$ ~10 MPa√m. These findings revealed that the IGSCC susceptibility increased significantly with the carbon content. Indeed, sensitisation is more important when the carbon level increases, hence the high carbon doped alloys were more sensitised than the medium carbon doped alloys, which made them more susceptible to IGC and IGSCC [24]. In the tested solution, the carbon level was detrimental as it accelerated the SCC propagation growth rate. This confirms the choice of the carbon level used for structural materials. Nevertheless the influence of PGMs on high carbon 304 SS was not investigated as 304MC has a medium carbon content (0.056 wt%).

The alloy 304MC can only be sensibly compared to Pd3MC as they were both under similar initial stress conditions ($K_I$~15.4 and 16.2 MPa√m). The results of this work reveal that 1 wt% Pd did not improve the IGSCC of the standard alloy in 0.01 M $K_2S_4O_6$, at pH=1.5 and 25°C. However, only one specimen made of 304MC was investigated and the delta ferrite level was higher than that of the PGM-doped alloys (see Table 7). Therefore this 304MC sample was probably more resistant to cracking.
due to residual delta ferrite. Indeed, delta ferrite improves crack propagation resistance as the cracks are stopped by it.

The electrochemical trials conducted using aqueous potassium tetrathionate media revealed that 1 wt% Pd decreased the metal dissolution rate as the anodic dissolution peak was reduced in aerated conditions at 25°C. The anodic dissolution peak does not assess the IGSCC susceptibility but it gives an indication on the kinetics of the metal dissolution in the environment. Micrographs of the surface were recorded further to immersion in 0.01 M K$_2$S$_4$O$_6$, at pH=1.5 and 25°C, and they revealed significantly more IGSCC in 304MC than Pd3MC and Ru3MC. It was expected that Ru doped alloys, especially Ru3MC (1.01 wt%) would improve the IGSCC of 304MC in 0.01 M K$_2$S$_4$O$_6$, at pH=1.5 and 25°C, as the electrochemical results showed that the rate of anodic dissolution was significantly lowered.

With reference to the crack depth measurements, medium carbon Pd doped alloys revealed a maximum crack depth of 300 µm, while Ru doped alloys only showed grain dropouts. These results confirmed that Ru additions would be more beneficial to 304MC in 0.01 M K$_2$S$_4$O$_6$, at pH=1.5 and 25°C, in terms of IGSCC resistance. The beneficial influence of Ru as compared to Pd could be rationalised in terms of the mechanism by which PGM are incorporated in the alloy. Previous work has already shown that Pd forms small island nuclei while Ru is incorporated into the oxide on surface [132]. In addition, atom probe work has been undertaken by the University of Oxford on a type 304 SS containing Pd (Pd3MC) that was exposed to the autoclave under oxygenated conditions. It was shown that the poor resistance to IGSCC could be due to nano-precipitation of PdMn at grain boundaries resulting in local palladium depletion, which negates the electrochemical benefits of the alloying element [169].

The crack propagation study revealed that the PGM-doped alloys were susceptible to IGSCC in potassium tetrathionate.
Electrochemical measurements revealed that the PGM-doped and standard alloys passivate in potassium tetrathionate. Passivation is promoted by PGMs and more effectively with ruthenium additions than palladium additions. The results showed that passivation has a time dependent effect as by increasing the scan rate (from 0.5 mV/s to 5 mV/s) passivation was not observed. In addition, passivation is potential controlled as in both aerated and deaerated conditions, similar trend were observed under the same scan rate. The mechanism of IGSCC involved in potassium tetrathionate is thought to be hydrogen embrittlement and more specifically hydrogen induced cracking (HIC) [92].

The work presented in this study simulates IGSCC and investigates the influence of PGM additions on the IGSCC of type 304 SS. Therefore the influence on the main kinetics driving the OCP was investigated as well as the intergranular attack, which enhances IGSCC. The limitations of this study concern the cracking mechanism involved as well as the effect of the environmental parameters such as the temperature, neutron irradiation and pressure that affect the material properties and microstructure. So it is important to bear in mind that the SCC study in potassium tetrathionate does not represent PWRs.
Chapter 1: Introduction

Chapter 2: Literature review

Chapter 3: Materials characterisation

Chapter 4: Crack initiation

Chapter 5: Fracture mechanics approach to stress corrosion crack propagation: fatigue precracking

Chapter 6: SCC propagation study

Chapter 7: Electrochemistry in borated and lithiated water

Chapter 8: Electrochemistry in IGSCC simulated environment

Chapter 9: Electrochemistry in high temperature water

Chapter 10: Discussion

Chapter 11: Conclusions

Chapter 12: Future work
11. Conclusions

From this study, the following conclusions can be drawn.

• The main goals of the PhD study were relatively well met. Indeed, the influence of PGMs on the material properties, kinetics in PWR environment and crack initiation could be established quite well. However, the effect of PGMs on crack propagation could not be elucidated.

• Electrochemical studies in model solutions to simulate PWR chemistry showed that PGM additions, and in particular 1 wt% Ru catalyse the oxygen reduction reaction or the hydrogen oxidation reaction, depending on the oxygen/hydrogen levels. This catalytic process influences the open circuit potential of the standard alloy 304MC by shifting it towards more positive values in the case of the catalysis of the oxygen reduction reaction and towards more negative values in the case of the catalysis of the hydrogen oxidation reaction.

• Within the range studied, small concentrations such as 0.11 wt% Ru catalyse the hydrogen oxidation reaction.

• 1 wt% Ru additions are more beneficial than 1 wt% Pd additions to mitigate anodic dissolution of sensitised type 304 SS in simulated solution for PWR chemistry containing boric acid and lithium hydroxide under oxygenated conditions at temperatures between 25°C and 260°C.

• Standard and PGM-doped alloys are resistant to IGSCC initiation in high temperature water under hydrogenated conditions.

• 1 wt% Pd and Ru additions mitigate IGSCC initiation in high temperature water (360°C) even under oxygenated conditions containing sulphate and chloride.

• The DCPD method did not provide successful results in terms of determining the precrack length with accuracy.
Conclusions

- Fatigue rotation under rotating bend rig followed by constant extension in 0.01 M $\text{K}_2\text{S}_4\text{O}_6$ is not well appropriate to investigate IGSCC resistance of materials that have different fatigue behaviour.

- IGSCC propagation in 0.01 M $\text{K}_2\text{S}_4\text{O}_6$ revealed susceptibility to IGSCC in the standard and 1 wt% PGM (Pd and Ru) doped-alloys.

- 1 wt% PGM additions self passivate type 304 SS in 0.01 M $\text{K}_2\text{S}_4\text{O}_6$. 
Chapter 1: Introduction

Chapter 2: Literature review

Chapter 3: Materials characterisation

Chapter 4: Crack initiation

Chapter 5: Fracture mechanics approach to stress corrosion crack propagation: fatigue precracking

Chapter 6: SCC propagation study

Chapter 7: Electrochemistry in borated and lithiated water

Chapter 8: Electrochemistry in IGSCC simulated environment

Chapter 9: Electrochemistry in high temperature water

Chapter 10: Discussion

Chapter 11: Conclusions

Chapter 12: Future work
12. Future work

Following from the above conclusions, future work should be conducted in order to amplify the present study findings and develop a better understanding of the complex physiochemical processes through which PGMs may influence the IGSCC resistance of type 304 SS in PWR conditions. For example, characterisation of the as-formed film in PWR chemistry and potassium tetrathionate using X-ray photoelectron spectroscopy would be a useful and relatively straightforward approach. Analysis could be performed after running autoclave experiments in oxygenated water containing impurities such as sulphate and chloride, in addition to samples collected after immersion in potassium tetrathionate. The former would lead to better analysis of the oxide and potentially allow for the experimentalist to relate the film properties to the cracking behaviour of 304MC; the latter would be relevant to better understand the mechanism involved and detect the eventual PGM surface enrichment. Issues such as whether or not Pd and Ru are present in the film and their oxidation state could be investigated. Focused ion beam (FIB) studies on the crack tip of the U-bend sample 304MC that failed in the autoclave may also provide useful information such as the cracking mode and the oxide present at the crack tip. Electrochemistry at high temperature in mixed hydrogenated and oxygenated conditions should be carried out in order to investigate the influence of PGMs on the kinetics controlling the OCP of standard type 304 SS. Electrochemistry in chloride containing environments will provide more information on the pitting behaviour of standard and PGM-doped alloys. Notably pits can be initiation sites for SCC so it is of great importance to assess the susceptibility of the materials to pitting. Crack initiation investigation can be performed using cyclic loading to initiate cracking more easily and evaluate the resistance of the materials of interest. IGSCC propagation could be performed by using slow strain rate tensile test, which importantly do not require precracking and therefore would be more
appropriate for a comparative study. The crack propagation experiments should be conducted with type 304 SS containing less delta ferrite than that of 304MC.

Crack propagation investigation in PWR chemistry containing sulphate and chloride is also to consider as it is more representative of the real environment of interest. Impurities such as chloride and sulphate would accelerate the cracking process. In terms of IGSCC mechanism, it would be more appropriate than potassium tetrathionate.
References


39. H.E. Hanninen, *Stress corrosion cracking*


49. O. Raquet, et al., *SCC of cold worked austenitic stainless steels in PWR conditions*. Advances in Materials Science, 2007. 7(1).

50. *MSc course/ Module 0, Localised corrosion 2002-2004*. Manchester.


122. G. Chaudron, *US Euratome programme, project 293, Euras reports 1749 and 1804*.


137. www.gordonengland.co.uk/hardness/vickers.htm.


144. H.Nathorst, Stress corrosion cracking of stainless steel. 1943.
159. S.Zhang. Inhibition effect of the borate ion on intergranular stress corrosion cracking of sensitised type 304 stainless steel. in NACE international. 1998.
165. V.Marichev, Corrosion, 1996. 52(1).
166. Internal palladium- hydrogen reference electrode operating manual, ed. C.t. systems, P.O. BOX 35, 00411, Helsinki, Finland.