The Effect of Cold Rolling on the Susceptibility of Austenitic Stainless Steel to Stress Corrosion Cracking in Primary Circuit Pressurised Water Reactor Environment

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# Contents

Contents ................................................................................................................................................. 2  
List of Figures .......................................................................................................................................... 5  
List of Tables .......................................................................................................................................... 13  
List of Abbreviations ............................................................................................................................. 14  
Abstract ................................................................................................................................................. 16  
Declaration .............................................................................................................................................. 17  
Copyright Statement ............................................................................................................................... 18  
Acknowledgements ................................................................................................................................. 19  
1 Introduction ......................................................................................................................................... 20  
2 Literature Review ................................................................................................................................. 22  
  2.1 Austenitic stainless steels .................................................................................................................. 22  
  2.2 Deformation of austenitic stainless steels ......................................................................................... 26  
  2.3 Light water reactors ......................................................................................................................... 39  
  2.4 Stress Corrosion Cracking ................................................................................................................ 41  
  2.5 SCC of austenitic stainless steels in LWR environments ............................................................... 42  
  2.6 Observations from laboratory testing .............................................................................................. 45  
  2.7 Deformation heterogeneity and SCC ............................................................................................. 59  
  2.8 Surface oxide characteristics .......................................................................................................... 63  
  2.9 Crack characteristics ...................................................................................................................... 66  
  2.10 Models of SCC ............................................................................................................................. 69  
  2.11 Discussion of mechanisms ............................................................................................................ 74  
  2.12 Summary and project objectives ................................................................................................. 76  
3 Experimental ...................................................................................................................................... 78  
  3.1 Introduction ................................................................................................................................... 78
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2</td>
<td>Material</td>
<td>78</td>
</tr>
<tr>
<td>3.3</td>
<td>Cold rolling procedure</td>
<td>79</td>
</tr>
<tr>
<td>3.4</td>
<td>Optical microscopy</td>
<td>79</td>
</tr>
<tr>
<td>3.5</td>
<td>Mechanical property determination</td>
<td>81</td>
</tr>
<tr>
<td>3.6</td>
<td>Scanning electron microscopy</td>
<td>83</td>
</tr>
<tr>
<td>3.7</td>
<td>Transmission electron microscopy</td>
<td>86</td>
</tr>
<tr>
<td>3.8</td>
<td>Digital image correlation</td>
<td>86</td>
</tr>
<tr>
<td>3.9</td>
<td>Stress corrosion cracking tests</td>
<td>89</td>
</tr>
<tr>
<td>3.10</td>
<td>EBSD analysis</td>
<td>92</td>
</tr>
<tr>
<td>3.11</td>
<td>Image analysis – line parameterisation</td>
<td>95</td>
</tr>
<tr>
<td>4</td>
<td>Material Characterisation</td>
<td>97</td>
</tr>
<tr>
<td>4.1</td>
<td>Introduction</td>
<td>97</td>
</tr>
<tr>
<td>4.2</td>
<td>Optical microscopy</td>
<td>97</td>
</tr>
<tr>
<td>4.3</td>
<td>Grain boundary character</td>
<td>100</td>
</tr>
<tr>
<td>4.4</td>
<td>Deformation Microstructure</td>
<td>101</td>
</tr>
<tr>
<td>4.5</td>
<td>Deformation at grain boundaries</td>
<td>103</td>
</tr>
<tr>
<td>4.6</td>
<td>Anisotropy of the deformation microstructure</td>
<td>105</td>
</tr>
<tr>
<td>4.7</td>
<td>Texture evolution</td>
<td>110</td>
</tr>
<tr>
<td>4.8</td>
<td>Discussion and summary</td>
<td>112</td>
</tr>
<tr>
<td>5</td>
<td>Mechanical Testing</td>
<td>114</td>
</tr>
<tr>
<td>5.1</td>
<td>Introduction</td>
<td>114</td>
</tr>
<tr>
<td>5.2</td>
<td>Mechanical Properties</td>
<td>114</td>
</tr>
<tr>
<td>5.3</td>
<td>Tensile tests</td>
<td>115</td>
</tr>
<tr>
<td>5.4</td>
<td>Digital image correlation</td>
<td>122</td>
</tr>
<tr>
<td>5.5</td>
<td>Discussion and summary</td>
<td>124</td>
</tr>
<tr>
<td>6</td>
<td>Slow Strain Rate Testing</td>
<td>126</td>
</tr>
<tr>
<td>6.1</td>
<td>Introduction</td>
<td>126</td>
</tr>
<tr>
<td>6.2</td>
<td>Susceptibility</td>
<td>126</td>
</tr>
<tr>
<td>6.3</td>
<td>Oxide appearance</td>
<td>128</td>
</tr>
</tbody>
</table>
List of Figures

Figure 2.1 a) Fe-C phase diagram [9], b) Fe-Cr-Ni phase diagram constructed at 400°C [10] ........................................................................................................................................................................................................................................ 23

Figure 2.2 Schaeffler diagram - prediction of the microstructure following quenching [13] ........................................................................................................................................................................................................................................ 24

Figure 2.3 Sensitisation: a) grain boundary chromium depletion [14], b) time-temperature curves [15] ........................................................................................................................................................................................................................................ 26

Figure 2.4 a) dissociation of a dislocation, b) wide stacking faults observed in 304 stainless steel [18] ........................................................................................................................................................................................................................................ 27

Figure 2.5 a) constriction of an extended screw dislocation to enable cross slip, in b) [16] ........................................................................................................................................................................................................................................ 28

Figure 2.6 The effect of alloying on SFE of austenitic stainless steels [21] ............... 29

Figure 2.7 Schematic of deformation twinning in FCC metals [17] ...................... 30

Figure 2.8 TEM image of a deformation twin 'bundle' in rolled brass [26].......... 30

Figure 2.9 TEM observation of α'-martensite nucleation at the intersection of two ε-martensite platelets [34] ........................................................................................................................................................................................................................................ 33

Figure 2.10 111 pole figures for 95 % cold rolled a) copper and b) 70:30 brass [44]..... 34

Figure 2.11 ODF displaying important texture fibres in rolled FCC metals [44] .......35

Figure 2.12 The effect of deformation shear band formation on work hardening in FCC alloys [28] ........................................................................................................................................................................................................................................ 36

Figure 2.13 The Bauschinger effect observed in copper: tension following compression (solid line) is seen to produce a decrease in the yield strength and permanent softening compared to reloading in compression (interrupted line) [52] .................. 37

Figure 2.14 The effect of a complex strain path change on plastic deformation in MP35N alloy [57] ........................................................................................................................................................................................................................................ 38
Figure 2.15 The use of austenitic stainless steels in PWR primary circuit (adapted from [61])........................................................................................................................................40

Figure 2.16 Schematic of the factors required for SCC .................................................................41

Figure 2.17 The stages of development of SCC with time [65] ...................................................42

Figure 2.18 Field experience of primary circuit SCC of austenitic stainless steels: a) association with contamination, b) association with cold work [5] ..............................44

Figure 2.19 Typical specimens: a) CT specimen, b) tensile specimen with cold worked hump [69]..................................................................................................................46

Figure 2.20 The effect of alloy Cr and Mo content on IGSCC crack growth rates during SSRT [71]........................................................................................................................................47

Figure 2.21 The influence of grain boundary chemistry on IGSCC susceptibility [71]. 49

Figure 2.22 The strain path effect on IGSCC and TGSCC [80].........................................................51

Figure 2.23 CT specimen orientations, for rolled plate L is equivalent to the rolling direction [81] ..............................................................................................................................51

Figure 2.24 IG crack propagation favoured in the RT plane, a) T-S orientation [82], b) T-L orientation [6] .....................................................................................................................................52

Figure 2.25 Effect of yield strength and martensite on CGR [62] ..................................................54

Figure 2.26 The effect of stress variables on CGR [87] .................................................................55

Figure 2.27 CGR vs. temperature for various levels of cold rolled grade 316 steel ....... 56

Figure 2.28 a) the temperature dependence on CGR of cold rolled 316 stainless steel oxygenated and hydrogenated water, b) the effect of dissolved hydrogen on CGR [82] ........................................................................................................................................58

Figure 2.29 IGSCC initiation during SSRT relative to the surface strain measured by image correlation [78] ................................................................................................................60

Figure 2.30 Initiation of intergranular voids at the intersection of shear bands [79] ...61
Figure 2.31 Surface oxide characteristics following 500 hours exposure to simulated PWR coolant [105] ................................................................. 64

Figure 2.32 Surface oxide thickness variation: a) with degree of cold work [88], b) alloy Cr content and c) coolant [H₂] [106] .............................................................................. 65

Figure 2.33 Schematic of a crack tip formed in a CERT specimen tested under simulated PWR conditions [105] ............................................................ 67

Figure 2.34 EFTEM maps showing elemental variation of O, Fe, Cr and Ni in the vicinity of an intergranular crack initiated during SSRT testing in simulated PWR conditions [78] .................................................................................................................. 67

Figure 2.35 TEM images of a crack tip in 20 % cold worked 316L tested in BWR HWC [112] .................................................................................. 68

Figure 2.36 The concept of the slip dissolution model [116] ................................................................. 70

Figure 2.37 Ford-Andresen model prediction of crack propagation rates in sensitised 304 [122] ........................................................................................................ 72

Figure 2.38 Schematic illustration of initiation and growth by selective internal oxidation [125] ........................................................................................................ 73

Figure 3.1 Schematic of how the original hot rolled plate a) was sectioned for cold rolling b) ......................................................................................................... 79

Figure 3.2 General mechanical test specimen geometry, dimensions are defined in Table 3.2 ........................................................................................................ 83

Figure 3.3 EBSD IPF colour key for FCC crystal structure ........................................................................ 85

Figure 3.4 The flat tensile specimen geometry used for DIC experiments ........................................ 87

Figure 3.5 SEM BSE image of the surface following gold remodelling ............................................. 88

Figure 3.6 a) local average misorientation (M_L), b) directional average misorientation (M_X and M_Y) calculation approach (adapted from Kamaya [149]) ....................................... 95

Figure 3.7 Illustration of the Radon transform for parameterisation of straight lines: a) an image, b) the transform of the image ........................................................................... 96
Figure 4.1 Delta ferrite content estimation: a) microstructure following NaOH etching, b) threshold image

Figure 4.2 Optical microscope images for the annealed material; a) oxalic etch and b) nitric etch.

Figure 4.3 Optical microscope images for the 20% cold rolled condition material, nitric etch.

Figure 4.4 a) EBSD map of grain boundary types in the annealed condition material (black: HAGB; green: LAGB; yellow: ATB), b) grain boundary character distribution by length fraction (LAGB < 10° ≤ HAGB)

Figure 4.5 SEM BSE/ECCI image of the annealed material, showing three grains.

Figure 4.6 SEM BSE/ECCI of the deformed microstructure showing clear planar deformation bands in the 20% cold rolled material.

Figure 4.7 TEM images of deformation twins within an austenite grain, specimen tilted along [110] zone axis.

Figure 4.8 EBSD maps produced from the RN plane of the 20% cold rolled material: a) IPF map, b) IQ map with boundaries satisfying Σ3 ± 5° orientation relationship delineated in yellow (IPF coloured with respect to ND, see Figure 3.3 for the IPF key)

Figure 4.9 SEM BSE/ECCI images showing the interaction of deformation bands with grain boundaries.

Figure 4.10 TEM images showing planar slip / deformation twin intersection with grain boundaries.

Figure 4.11 RN plane scan; a) EBSD IPF map, b) local average, c) x (rolling) direction average, and d) y (normal) direction average misorientation plots (IPF coloured with respect to ND, see Figure 3.3 for the IPF key).

Figure 4.12 Frequency distribution of the direction average misorientation along the rolling and normal plate directions.
Figure 4.13 Cumulative frequency distribution of the direction average misorientation along the rolling and normal plate directions.

Figure 4.14 Analysis of the deviation from the deformation twin trace and the rolling direction; a) rolling-transverse plane and b) rolling-normal plane.

Figure 4.15 ODFs for the annealed and 20% cold rolled conditions; top and bottom respectively.

Figure 5.1 Cross-section hardness for the cold rolled material.

Figure 5.2 True stress – strain curve for the annealed material in tension.

Figure 5.3 True stress – strain curves for the annealed material in tension and compression.

Figure 5.4 Strain hardening behaviour of the annealed material in tension and compression.

Figure 5.5 True stress – strain behaviour for compression to a strain of 0.22 followed by tension to a strain of 0.10.

Figure 5.6 True stress-strain curves for the cold rolled material in tension along three orientations.

Figure 5.7 Tensile strain hardening rate behaviour for the cold rolled material in three orientations.

Figure 5.8 True stress-strain in tension for the 20% rolled material and material compresses to an equivalent reduction.

Figure 5.9 True stress – strain in tension for the cold worked material at room temperature and 300 °C along the normal rolling direction.

Figure 5.10 a) and b); EBSD IPF and IQ maps following cold rolling, c) shear strain map from DIC for 5% tensile reloading along the normal rolling direction (IPF coloured with respect to ND, see Figure 3.3 for the IPF key).
Figure 6.1 SEM SE image showing the typical surface appearance of the SSRT specimens, the straining direction is horizontal, an IG crack is visible in the lower right of the image, arrows mark oxide cracks.

Figure 6.2 The surface of an IG crack, showing evidence for preferential oxidation of deformation bands.

Figure 6.3 A region with three intergranular cracks, the central and right cracks have extended to several grain boundaries.

Figure 6.4 A wide intergranular crack, showing secondary cracking.

Figure 6.5 Transgranular cracking, associated with deformation twin bands.

Figure 6.6 Crack 1 (left column – a), c) and e.) and crack 2 (right column – b), d) and f.) found on specimen SSRT3. Post-test SEM images a) and b), pre-test EBSD IPF c) and d), pre-test EBSD IQ e) and f). The straining direction is horizontal. IPF coloured with respect to ND, see Figure 3.3 for the IPF key.

Figure 6.7 Frequency distribution of the angle between the SSRT straining direction and the trace of each cracked HAGB.

Figure 6.8 Frequency distribution showing the interaction of cracked HAGB’s with deformation twin bands (DTB) and annealing twin boundaries (ATB).

Figure 6.9 Frequency distribution of the angle between SSRT straining direction and deformation twin band (DT) trace for DT’s intersecting cracked HAGB’s.

Figure 6.10 Failed HAGB’s associated with annealing twins in an adjacent grain. The pre-test scan EBSD IPF maps b) and d) correspond to the post-test SEM images a) and c) respectively. IPF coloured with respect to ND, see Figure 3.3 for the IPF key.

Figure 6.11 The resistance of an annealing twin boundary to SCC, a) EBSD IPF map – pre-test, b) SEM image as-tested- oxide cracks, c) and d) SEM image following oxide removal – d) corresponds to boxed region in c). IPF coloured with respect to ND, see Figure 3.3 for the IPF key.
Figure 6.12 One of two cracks formed on an annealing twin boundary, at a site of intersection with deformation bands, a) EBSD IPF map – pre-test, b) post-test SEM BSE image following oxide removal. IPF coloured with respect to ND, see Figure 3.3 for the IPF key.

Figure 6.13 Crack images from cross-section of SSRT 2: a) a tight IG crack, b) the tip of the deepest branch of the crack in a), c) a very large intergranular crack, from the necked region of the specimen.

Figure 7.1 Crack length versus time plots for three orientations of CT specimen tested simultaneously in simulated PWR conditions – DCPD data corrected following post-test fractography measurements.

Figure 7.2 A region of IGSCC, from the fracture surface of specimen 20JM.

Figure 7.3 Optical microscope images of the fracture surfaces of a) 20JM, b) 21JM and c) 23JM.

Figure 7.4 Specimen 21JM, (LS orientation – load along RD), crack tips marked.

Figure 7.5 EBSD a) IPF and b) IQ maps of the upper arm of cracking as shown in Figure 6.3. IPF coloured with respect to ND, see Figure 3.3 for the IPF key.

Figure 7.6 Crack tip from 21JM (LS orientation – load along RD). In part a) the IPF is coloured with respect to ND, see Figure 3.3 for the IPF key.

Figure 7.7 Heavily oxidised section of the crack in 21JM association with deformation banding. IPF coloured with respect to ND, see Figure 3.3 for the IPF key.

Figure 7.8 Cross-section observation of the crack leading to its tip in specimen 6ET (S-L orientation), a) BSE SEM image and b) EBSD map showing all boundaries with > 5° misorientation in black with the crack path highlighted in red.

Figure 7.9 Higher magnification view of region ‘A’ from Figure 7.8 highlighting a resistant grain boundary section between the arrows in a), which is a SEM BSE image and b) EBSD IPF map (IPF coloured with respect to ND, see Figure 3.3 for the IPF key).
Figure 7.10 Misorientation line profiles determined from EBSD data in the vicinity of the resistant grain boundary section illustrated in Figure 7.9 (IPF coloured with respect to ND, see Figure 3.3 for the IPF key) ................................................................. 162

Figure 7.11 SCC occurring transgranularly along suitably aligned deformation twin boundaries to join two sections of IGSCC, as a result of a resistant IG section: a) SEM BSE image and b) EBSD IPF map (IPF coloured with respect to ND, see Figure 3.3 for the IPF key) .............................................................................................................. 164

Figure 8.1 Representation of the variation in grain boundary energy with change in misorientation angle, with the suggestion of an energy threshold below which IGSCC is suppressed ................................................................. 169
List of Tables

Table 2.1 Composition limits for several wrought austenitic stainless steel grades (wt %) [11] ................................................................................................................................. 24

Table 2.2 Major texture components for rolled FCC metals [44] ........................................ 35

Table 3.1 Material composition ......................................................................................... 78

Table 3.2 Mechanical test specimen dimensions .................................................................. 82

Table 3.3 Water chemistry for SCC testing ........................................................................ 90

Table 4.1 Grain sizes determined for the annealed and cold rolled material conditions .................................................................................................................................................. 100

Table 5.1 Tensile and compression properties summary ....................................................... 116

Table 6.1 Slow strain rate test details, observations relate only to the area recorded by pre-test EBSD ........................................................................................................................................ 127

Table 7.1 Details of the CT specimens investigated .............................................................. 148

Table 7.2 The loading conditions during the various stages of CGR testing (20, 21 and 23JM) ........................................................................................................................................... 148
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM</td>
<td>American society for testing and materials</td>
</tr>
<tr>
<td>ATB</td>
<td>Annealing twin boundary</td>
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<tr>
<td>BCC</td>
<td>Body centred cubic</td>
</tr>
<tr>
<td>BSE</td>
<td>Backscattered electron</td>
</tr>
<tr>
<td>BWR</td>
<td>Boiling water reactor</td>
</tr>
<tr>
<td>CERT</td>
<td>Constant extension rate test</td>
</tr>
<tr>
<td>CGR</td>
<td>Crack growth rate</td>
</tr>
<tr>
<td>CT</td>
<td>Compact tension</td>
</tr>
<tr>
<td>DIC</td>
<td>Digital image correlation</td>
</tr>
<tr>
<td>DTB</td>
<td>Deformation twin boundary</td>
</tr>
<tr>
<td>EBSD</td>
<td>Electron backscatter diffraction</td>
</tr>
<tr>
<td>ECCI</td>
<td>Electron channelling contrast imaging</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive spectroscopy</td>
</tr>
<tr>
<td>FCC</td>
<td>Face centred cubic</td>
</tr>
<tr>
<td>FEG</td>
<td>Field emission gun</td>
</tr>
<tr>
<td>HAGB</td>
<td>High angle grain boundary</td>
</tr>
<tr>
<td>HELP</td>
<td>Hydrogen enhanced localised plasticity</td>
</tr>
<tr>
<td>HWC</td>
<td>Hydrogen water chemistry</td>
</tr>
<tr>
<td>IASCC</td>
<td>Irradiation assisted stress corrosion cracking</td>
</tr>
<tr>
<td>IG</td>
<td>Intergranular</td>
</tr>
<tr>
<td>K</td>
<td>Stress intensity factor</td>
</tr>
<tr>
<td>L</td>
<td>Longitudinal direction</td>
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<td>IGSCC</td>
<td>Intergranular stress corrosion cracking</td>
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<td>LAGB</td>
<td>Low angle grain boundary</td>
</tr>
<tr>
<td>LWR</td>
<td>Light water reactor</td>
</tr>
<tr>
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<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>--------------------------------------</td>
</tr>
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<td>N</td>
<td>Normal direction</td>
</tr>
<tr>
<td>ODF</td>
<td>Orientation distribution function</td>
</tr>
<tr>
<td>OIM</td>
<td>Orientation imaging microscopy</td>
</tr>
<tr>
<td>PWR</td>
<td>Pressurised water reactor</td>
</tr>
<tr>
<td>R</td>
<td>Rolling direction</td>
</tr>
<tr>
<td>S</td>
<td>Short direction</td>
</tr>
<tr>
<td>SCC</td>
<td>Stress corrosion cracking</td>
</tr>
<tr>
<td>SFE</td>
<td>Stacking fault energy</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard hydrogen electrode</td>
</tr>
<tr>
<td>SIO</td>
<td>Selective internal oxidation</td>
</tr>
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<td>SSR(T)</td>
<td>Slow strain rate (test)</td>
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<td>T</td>
<td>Transverse direction</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope / microscopy</td>
</tr>
<tr>
<td>TG</td>
<td>Transgranular</td>
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Abstract

“The effect of cold rolling on the susceptibility of austenitic stainless steel to stress corrosion cracking in primary circuit pressurised water reactor environment”

David Marc Wright

Doctorate of Engineering, The University of Manchester, 2012

The stress corrosion cracking (SCC) of components which are fabricated from austenitic stainless steel has been observed in the primary circuit of pressurised water reactors (PWR). In recent years it has become an increasing concern that cold work can induce susceptibility to SCC in these materials, even when exposed to good-quality flowing coolant. Laboratory studies which were launched in response to this observation have confirmed that SCC susceptibility is enhanced by cold work.

The intention of this study is therefore to investigate the link between the effects of cold work on the material and the susceptibility to SCC. The investigation has been conducted on a grade 304 austenitic stainless steel. Characterisation of the microstructure and mechanical properties has been carried out in the annealed condition, and following cold rolling to a reduction in thickness of 20%. The cold rolled material has then been subjected to SCC tests in simulated PWR primary circuit coolant. Two types of test were utilised: slow strain rate tests (SSRTs) were carried out in order to investigate the initiation of cracks from a smooth surface and constant load tests using pre-cracked specimens were used to investigate the crack propagation behaviour.

In both types of test the SCC produced was predominantly intergranular. The SSRTs revealed that the most susceptible grain boundaries separated grains which had dissimilar deformation microstructures (one grain deformed heavily by planar bands, the other more homogenously). It was also observed that initiation could occur on a grain boundary which is adjacent to an annealing twin. In both microstructural configurations the susceptibility is likely to be due to the deformation incompatibility across the failed boundary, possible indicating that shear at the boundary is important for the initiation of cracking.

The crack propagation behaviour of the rolled material was particularly anisotropic; regardless of the loading direction (specimens were manufactured to allow loading along the rolling, transverse and normal plate directions) cracking was observed to occur parallel to the rolling-transverse plane. The origin of this behaviour was explored in terms of preferential alignment of the deformation microstructure and the anisotropic mechanical properties of the rolled plate. Limited transgranular cracking was also observed, which occurred along oxidised deformation bands. The results overall indicate that heterogeneous deformation between different regions of the material, and preferential alignment of the deformation microstructure are important with respect to the SCC susceptibility of the rolled material.
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1 Introduction

Stress corrosion cracking (SCC) is an environmentally sensitive form of material degradation whereby affected materials, although usually ductile, will develop cracks more typical of a brittle failure. This type of damage can only occur through the combination of specific material, environmental and mechanical parameters. Furthermore, the initiation of a stress corrosion crack may only occur after several years, if not decades, of the exposure of a material to a specific environment. The necessary synergy between different parameters, coupled with existence of a variable initiation period has meant that the occurrence of SCC is extremely difficult, if not impossible, to predict. The result is that systems may be widely in-service before it is recognised that SCC presents a potential threat.

Within nuclear power generation SCC is a problem which has affected both boiling water reactors (BWRs) and pressurised water reactors (PWRs). Austenitic stainless steels and, less frequently, nickel based alloys have been observed to suffer from intergranular SCC (IGSCC) during BWR operation. Many of these problems were associated with sensitisation (grain boundary chromium depletion) of the material, and so the prevention of sensitisation and the implementation of 'hydrogen water chemistry' were able to significantly improve the situation [1]. In PWR service, primary side SCC (PWSCC) of nickel based alloy 600 components has been the main concern, with austenitic stainless steels generally performing well [2].

Intergranular stress corrosion cracking of austenitic stainless steel components has also been associated with a non-sensitised, cold worked microstructure in both BWR and PWR systems. The occurrence of cracking in such components has been often associated with out-of-specification conditions due to coolant impurities (Cl⁻, SO₄²⁻, O₂) which may concentrate in ‘dead leg’ or coolant stagnant areas of plant [3, 2]. However, accumulated field experience has suggested that IGSCC is possible in heavily cold worked austenitic stainless steel components in nominal flowing primary circuit PWR coolant [4, 5].
Laboratory testing has confirmed that cold work may induce SCC susceptibility in austenitic stainless steels in simulated PWR primary circuit conditions. Several interesting behaviours have been identified, for example, a dependence of the SCC susceptibility on the orientation of the test specimen with respect to the direction of prior cold work [6]. However, the origin of the increased susceptibility to SCC due to cold work is not well understood. This lack of understanding is compounded by the international demand for life extension of the current fleet of light water reactors, making it essential that degradation processes are better understood and therefore can be well managed into the future.

The intention of this work is therefore to investigate the role of the material condition which results from cold rolling on the resultant SCC behaviour. Specifically, the SCC susceptibility of a grade 304 austenitic stainless steel, following deformation to 20% by cold rolling has been investigated in conditions simulating the primary circuit of a PWR. The research project is divided into two main sections: the effect of cold rolling on the microstructure and mechanical properties of the material has been determined, comprising chapters 4 and 5; subsequently slow strain rate (SSR) and crack propagation tests have been undertaken on the cold rolled material in order to determine the SCC behaviour, as described in chapters 6 and 7 respectively. The possible links between the deformation characteristics of the alloy and the SCC susceptibility are then able to be discussed, forming chapter 8.

The work described in the dissertation has been undertaken in collaboration with a research programme at Serco, UK, the overall aim of which is to improve the understanding of the effects of heterogeneous deformation on the SCC susceptibility.
2 Literature Review

2.1 Austenitic stainless steels

2.1.1 Introduction

Stainless steels are a group of ferrous alloys which contain a minimum of 11 weight % (wt %) chromium (Cr). The addition of Cr allows the formation of a stable, adherent and self-healing surface oxide layer, resulting in a very low general corrosion rate in most environments [7]. The inclusion of other alloying additions will cause the stable crystal structure to vary. Therefore there are different classes of stainless steel: ferritic, austenitic and martensitic, which are distinguished from one another by their crystal structure. The ferrite (α) phase is body centred cubic (BCC), the austenite (γ) phase is face centred cubic (FCC) and the martensite (α’) phase has the body centred tetragonal (BCT) crystal structure. A fourth family of stainless steels are the duplex stainless steels, which are composed of a mixture of the ferrite and austenite phases [8]. This dissertation concerns the SCC of austenitic stainless steels. Therefore a description of the effects of alloying, and of the relevant effects of thermal and mechanical processing histories on the microstructures and properties of austenitic stainless steels will be given.

2.1.2 Composition and microstructure

The FCC austenite phase of iron (Fe) is not stable below a temperature of 725 °C, as can be observed from the Fe-carbon (C) phase diagram in Figure 2.1 a). Below this temperature the transformation of austenite (γ) to ferrite (α) is favoured energetically. In the basic stainless Fe-Cr alloy system, chromium addition does not suppress the transition of austenite to ferrite at lower temperatures, as may be seen from the Fe-Cr axis of the ternary Fe-Ni-Cr phase diagram in Figure 2.1 b). Further alloying is required to establish stability of the austenite phase to functional temperatures [8, 9].
Sufficiently increased austenite stability is achieved through the incorporation of nickel (Ni) into the basic Fe-Cr stainless steel alloy. The introduction of the region of γ phase stability with the addition of Ni may be observed from the Fe-Ni-Cr phase diagram. Based on these considerations, the basic composition of the austenitic stainless steel alloy is around 10 wt % Ni and 18 wt % Cr. However, a range of other elements may be present in smaller quantities in different alloys. The maximum allowable alloying content for a number of elements in several different grades of austenitic stainless steel, based on US and German nuclear specifications are shown in Table 2.1 [11]. Alloying additions are made to optimise certain properties, for example Mo is known to improve pitting corrosion resistance in chloride containing environments [12]. The grades 321 and 347 which are included in Table 2.1 are stabilised against sensitisation (described in section 2.1.3) by additions of Ti or Nb and Ta. Additionally, further alloying elements may improve the austenite stability (Mn, C, N, Cu), whilst others may stabilise the ferritic phase (Cr, Mo, Si, Nb) [8, 11, 13].

Figure 2.1 a) Fe-C phase diagram [9], b) Fe-Cr-Ni phase diagram constructed at 400°C [10]
### Table 2.1 Composition limits for several wrought austenitic stainless steel grades (wt %) [11]

<table>
<thead>
<tr>
<th>AISI #</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
<th>P</th>
<th>S</th>
<th>Mo</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>304</td>
<td>0.08</td>
<td>2.0</td>
<td>1.0</td>
<td>18-20</td>
<td>8-10.5</td>
<td>0.045</td>
<td>0.03</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>304L</td>
<td>0.03</td>
<td>2.0</td>
<td>1.0</td>
<td>18-20</td>
<td>8-12</td>
<td>0.045</td>
<td>0.03</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>316</td>
<td>0.08</td>
<td>2.0</td>
<td>1.0</td>
<td>16-18</td>
<td>10-14</td>
<td>0.045</td>
<td>0.03</td>
<td>2.0-3.0</td>
<td>-</td>
</tr>
<tr>
<td>316L</td>
<td>0.03</td>
<td>2.0</td>
<td>1.0</td>
<td>16-18</td>
<td>10-14</td>
<td>0.045</td>
<td>0.03</td>
<td>2.0-3.0</td>
<td>-</td>
</tr>
<tr>
<td>321</td>
<td>0.08</td>
<td>2.0</td>
<td>1.0</td>
<td>17-19</td>
<td>9-12</td>
<td>0.03</td>
<td>0.03</td>
<td>-</td>
<td>Ti</td>
</tr>
<tr>
<td>347</td>
<td>0.08</td>
<td>2.0</td>
<td>1.0</td>
<td>17-19</td>
<td>9-13</td>
<td>0.045</td>
<td>0.03</td>
<td>-</td>
<td>Nb+Ta</td>
</tr>
</tbody>
</table>

The alloying effect on the phase constitution of the material may be illustrated by the Schaeffler diagram, Figure 2.2, which groups together austenite stabilising elements (as ‘Ni equivalent’) and ferrite stabilising elements (as ‘Cr equivalent’) [13, 11]. Based on the proportions of austenite and ferrite stabilising elements present, the room temperature microstructure following rapid cooling from a temperature of around 1100 °C may be predicted. In addition to the equilibrium phases, room temperature austenitic stainless steel microstructures often contain small amounts of untransformed δ-ferrite phase, which is formed initially on solidification from the liquid phase (Figure 2.1 a) [8, 11].

![Figure 2.2 Schaeffler diagram - prediction of the microstructure following quenching [13]](image-url)
2.1.3 Sensitisation

Where rapid quenching is not carried out, or as a result of heating from processes such as welding, the precipitation of chromium rich metal carbides (M\textsubscript{23}C\textsubscript{6}) may occur [14]. Carbide precipitation occurs preferentially at the grain boundaries, enabled by chromium and carbon diffusion to the interface. As a result, the adjacent metal is likely to be depleted of chromium, as illustrated in Figure 2.3 a). Where significant carbide precipitation is able to occur, the metal may become sufficiently depleted in chromium to prevent the formation of a protective passive film, and is referred to as being sensitised. In the sensitised condition the grain boundary region may be vulnerable to severe intergranular corrosion or IGSCC, with the grain boundary region becoming anodic with respect to surrounding material [15, 11].

A temperature in the range of 350-800 °C will allow the precipitation of carbides. As the growth of the precipitates occurs by carbon and chromium diffusion to the grain boundary, the length of time at the elevated temperature determines the degree of sensitisation. The temperature and time dependency of carbide precipitation is illustrated in Figure 2.3 b) for the common austenitic stainless steels grades 304, 304L, 316 and 316 L. The composition of these alloys has been described in Table 2.1, it can be noted from this figure that the reduction of the carbon content of the alloy is an effective way in which to significantly prevent sensitisation [8, 15]. Also, as previously mentioned, stabilisation of the material by alloying with titanium (Ti) or tantalum (Ta) reduces sensitisation as these elements have a greater affinity for carbon than chromium does [11].
2.2 Deformation of austenitic stainless steels

2.2.1 Dislocation slip and stacking faults

The simplest model for deformation of a metal is by the shear of the crystal lattice by linear defects, dislocations, which move along certain crystallographic planes producing a displacement of the lattice. In an FCC metal shear of the crystal is energetically favoured on the close packed \(\{1\bar{1}1\}\) planes in a \(<1\bar{1}0>\) direction. Ideal crystallographic slip would occur by the movement of perfect dislocations, possessing a Burgers vector of the type \(\frac{1}{2}[110]\) as this would require that no interruption to the FCC crystal stacking sequence were made \([16, 17]\). However it is well established from experimental observation that perfect dislocations commonly dissociate into a pair of
partial dislocations in austenitic stainless steels (e.g. [18, 19]). Concerning dislocation slip, the most important dislocation dissociation reaction leads to the formation of Shockley partials, this reaction is described by Equation 2.1 and illustrated in Figure 2.4 a) [20, 16].

\[
\frac{a}{2} [1\bar{1}0] \rightarrow \frac{a}{6} [2\bar{1}1] + \frac{a}{6} [1\bar{2}1]
\]

*Equation 2.1*

The two partial dislocations combined constitute the same displacement as a perfect dislocation, hence the first partial dislocation interrupts the stacking order of the crystal and the second partial dislocation restores the stacking order. The area between the two partial dislocations is known as a stacking fault. The intrinsic stacking fault found between Shockley partials changes the usual ABCABCABC stacking of the \{111\} planes to ABCACABC, which is equivalent to 4 layers of hexagonal close packed (HCP) crystal stacking [16, 17]. An example of wide stacking faults observed in deformed 304 stainless steel by TEM are shown in Figure 2.4 b) [18].

![Figure 2.4 a) dissociation of a dislocation, b) wide stacking faults observed in 304 stainless steel [18]](image)

The partial dislocation spacing, \(d\), is given by Equation 2.2, where the other terms in this equation are the shear modulus (\(G\)), the Burger's vector (\(b\)) and the stacking fault energy (\(\gamma\)) [16]. The stacking fault energy (SFE) is inversely proportional to the width of the fault; the lower the SFE the wider the stacking fault and vice versa.
The most significant difference in the behaviour of an extended dislocation is the increased difficulty with which cross-slip can occur. An extended screw dislocation may cross-slip, but first the stacking fault must be removed through constrition, as illustrated in Figure 2.5 a). The un-extended section of dislocation may then move onto an intersecting slip plane and be free to slip, and eventually the whole dislocation may follow as illustrated in Figure 2.5 b) [16]. It is clear that the wider the stacking fault is, then the more difficult cross slip will be.

Pure metals will generally have a high SFE value, and alloying will normally cause this to be reduced. The typical compositions of austenitic stainless steels produce low to medium values of SFE. Figure 2.6 shows the collated values from 12 experimental studies into the SFE of austenitic stainless steels at ambient temperature [21]. The information is displayed in such a way that for the chart on the left the Cr content of
the alloy is roughly fixed in the range 13-16 wt %, and on the right the Ni content is roughly fixed at 17-19 wt %. The figure illustrates the variability of SFE between different austenitic stainless alloys. Generally however, an increased Cr content and/or reduced Ni content is seen to decrease the SFE. It can be seen that the stacking fault energy values presented in this figure occupy a range of approximately 15 - 45 mJm⁻².

The importance of the stacking fault width on the plasticity of FCC materials cannot be overstated. The dissociation of dislocations, by limiting the freedom to cross-slip enhances the concentration of shear into planar bands. Additionally, as the stacking fault energy is reduced different deformation modes become active, namely deformation twinning and strain induced martensite formation [22, 23].

2.2.2 Deformation twinning

Deformation (or mechanical) twinning may occur as a mode of deformation in lower SFE FCC alloys (< 25 mJm⁻²), including austenitic stainless steels [23]. Twinning causes an ordered shear displacement of the crystal, creating a volume of material which mirrors the parent grain orientation [17]. The twinning planes in FCC metals are {111} planes, with the shear displacement occurring along the <112> type direction [17, 24]. A schematic of FCC deformation twinning is shown in Figure 2.7. In most FCC metals which undergo deformation twinning, including austenitic stainless
steels, the onset of twinning is observed to occur following an appreciable amount of deformation by slip [25, 24].

Figure 2.7 Schematic of deformation twinning in FCC metals [17]

Experimentally, deformation twinning in FCC materials is frequently observed to occur on a number of closely spaced \{111\} planes; which leads to the formation of twin ‘bundles’, to use the terminology of Leffers and Bilde-Sørensen [26]. An example of a twin bundle is shown in Figure 2.8, essentially this is a composite structure of twin lamellae separated by regions of the parent grain matrix. A very high level of shear deformation is capable of being translated within the bundles of deformation twins.

Figure 2.8 TEM image of a deformation twin ‘bundle’ in rolled brass [26]
The mechanisms of deformation twin nucleation and growth have not been established beyond doubt, and it is likely several different mechanisms may be possible within the same alloy system dependent on the specific conditions. However, most experimental observations and the most likely proposed mechanisms for twin formation support the nucleation of the twins at some critical defect configuration, usually associated with several stacking faults [24]. The growth of FCC deformation twins most likely occurs by through the glide of twinning partials on adjacent \{111\} planes, although thickening may occur by incorporation of twin embryos from adjacent planes [24, 25, 27].

As the nucleation and growth of mechanical twins is linked to stacking faults, there is an increase in the propensity for deformation twinning as a deformation mechanism (in favour of further slip) as the SFE is reduced. Venables suggested that there exists a direct relationship between the SFE and stress necessary to nucleate deformation twinning [25]. However more recent work has suggested that the onset of twinning is linked to a critical dislocation density, and therefore the SFE has an indirect role in achieving this necessary dislocation content [28, 29, 30].

An important distinction to make is that between deformation twins and annealing twins. Although the orientation relationship across the twin boundary is the same for both types of twin, the conditions leading to the formation of each, and subsequently the structure of the twinned volume is very different.

As described above, a deformation twin is formed at high stress from a microstructure containing a high density of dislocations. The structure of the twin is highly dislocated, and has been observed to be made up of a large number of differently oriented cells [31]. Additionally mechanical twins tend to form with a lenticular shape, as this minimises the elastic strain energy introduced [24]. Contrasting annealing twins form in a low stress condition, for example during solidification or annealing. As a result the interface is not highly stressed and the twinned volume is no more defective than the parent grain [32]. For many purposes the annealing twin
can be considered to be no different to a regular grain; certainly the volume of material forming the annealing twin will deform according to the orientation of its own slip systems, and deformation twinning may occur within larger annealing twins!

2.2.3 Strain induced martensite

During straining of an austenitic stainless steel, the deformation triggered phase transformation of austenite to martensite is also possible. Two martensite phases are possible in austenitic stainless steels, these are HCP $\varepsilon$-martensite and BCC $\alpha'$-martensite [33, 34]. $\varepsilon$-martensite formation can be considered to be similar to deformation twining, as it also nucleates from specific stacking fault formations and produces a shear. Overlapping faults on adjacent {111} planes will produce mechanical twinning, whereas overlapping faults on every second {111} plane will produce $\varepsilon$-martensite [35, 36].

Early investigations into the formation of strain induced martensite observed that the $\alpha'$-martensite needles formed at the intersection of $\varepsilon$-martensite platelets, for example as shown in Figure 2.9. The $\varepsilon$-martensite shear bands were therefore regarded as an intermediary in transformation of austenite to $\alpha'$-martensite, and the full phase transformation explained by the process: $\gamma$-austenite (FCC) $\rightarrow$ $\varepsilon$-martensite (HCP) $\rightarrow$ $\alpha'$-martensite (BCC) [34, 37]. More recently however, $\alpha'$-martensite nucleation has also been observed at the intersection of deformation twins [38, 39]. $\alpha'$-martensite is therefore generally observed to form at the intersection of shear bands (deformation twinning or $\varepsilon$-martensite). The growth of $\alpha'$-martensite has been observed to occur by the coalescence of neighbouring embryos of the phase [19, 35, 40].
The volume fraction of martensite formed during a specific deformation process is sensitive to a number of additional parameters. As the SFE determines the formation of stacking faults and therefore shear band formation, a higher SFE will reduce the propensity for $\alpha'$-martensite formation. The effective SFE has been reported to decrease with applied stress or a reduction in temperature, thus making shear band formation more likely [24, 35, 27]. Secondly, as the FCC to BCC phase change is produced by a chemical driving force, alloying changes to stabilise the FCC phase with respect to the BCC phase will also reduce the amount of $\alpha'$-martensite formed [35, 13]. Additionally an increased temperature of deformation is observed to reduce the stability of the $\alpha'$-martensite phase [41, 42].

Furthermore, processing differences which affect the formation of shear bands will have an effect on the martensite transformation. Nakada found that less martensite was formed in cold rolling compared to an equivalent strain in uni-axial tension [38]. Microstructural observations found that it was common in the rolled case for only one shear system to be activated per grain, thus preventing band intersections and reducing the number of nucleation sites for the $\alpha'$-martensite phase.
2.2.4 FCC rolling texture

The development of rolling texture in FCC metals has been investigated extensively. It is now well known that the textural evolution in high SFE FCC alloys will differ from that in low SFE FCC alloys, which is a result of the differences in deformation behaviour at different values of the SFE \[43\]. A clear example of the different texture formed in high versus low SFE materials is given in Figure 2.10, the 111 pole figures for 95% cold rolled copper (SFE ~ 80 mJm\(^{-2}\)) and 70:30 brass (SFE ~ 25 mJm\(^{-2}\)) \[44\].

![Figure 2.10 111 pole figures for 95% cold rolled a) copper and b) 70:30 brass \[44\]](image)

The orientations of four of the most important texture components are given in Table 2.2. These orientations may be grouped along texture ‘fibres’, as illustrated in the orientation distribution function (ODF) displayed in Figure 2.11. The strength of the orientations about the fibres may be used to illustrate the differences in texture evolution for low and high SFE alloys; the α-fibre becomes much stronger in low SFE materials, whereas the β fibre is stronger in high SFE materials \[43, 45\]. The origin of the texture transition for lower SFE alloys was originally attributed directly to the presence of deformation twinning, as a ‘volume effect’, however it is now more widely accepted that the twin lamellae cause further shear to be localised on parallel slip planes, and that this results in the final ‘brassy’ texture \[44, 46\].
Table 2.2 Major texture components for rolled FCC metals [44]

<table>
<thead>
<tr>
<th>Component</th>
<th>(hkl)</th>
<th>&lt;uvw&gt;</th>
<th>(\phi_1)</th>
<th>(\Phi)</th>
<th>(\phi_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper, C</td>
<td>112</td>
<td>111</td>
<td>90</td>
<td>35</td>
<td>45</td>
</tr>
<tr>
<td>S</td>
<td>123</td>
<td>634</td>
<td>59</td>
<td>37</td>
<td>63</td>
</tr>
<tr>
<td>Goss, G</td>
<td>011</td>
<td>100</td>
<td>0</td>
<td>45</td>
<td>90</td>
</tr>
<tr>
<td>Brass, B</td>
<td>011</td>
<td>211</td>
<td>35</td>
<td>45</td>
<td>90</td>
</tr>
</tbody>
</table>

Figure 2.11 ODF displaying important texture fibres in rolled FCC metals [44]

The study of rolling texture specific to austenitic stainless steels has been investigated by a several authors [47, 48, 49]. The textural evolution in both 304 and 316 stainless steels is typical of the low SFE FCC rolling texture as discussed above. The potential significance of texture evolution to the study of SCC is through the introduction of anisotropy. As the properties of individual grains are dependent on the crystallographic direction, the bulk properties of a textured polycrystalline material are also directionally variable [49].
2.2.5 Work hardening behaviour

The low SFE FCC alloys, including austenitic stainless steels are capable of high levels of work hardening. This fact is illustrated by Figure 2.12, which shows the general form of work hardening behaviour observed for a number of low SFE FCC alloys by El-Danaf et al. in simple compression [50, 28, 29]. Microstructural observations at different levels of strain were used to correlate the first plateau in work hardening rate (stage B) to the initial formation of shear bands. This is explained by the fact that shear bands formed on one slip system resist dislocation motion on non-coplanar slip systems. This illustrates the microstructural dependency of work hardening, especially for systems where internal barriers to dislocation slip (such as shear bands) form.

![Figure 2.12 The effect of deformation shear band formation on work hardening in FCC alloys [28]](image)

2.2.6 Strain path effects

Changes in strain path are known to produce differences in the plastic behaviour of metals compared to continued deformation in the original strain condition [51]. Perhaps the most widely known illustration of this is the Bauschinger effect, where reversal of the strain direction produces a reduction in strength during the early stages of reverse flow, which may be followed by a period of low (or non) work hardening and possibly permanent softening [52]. The Bauschinger effect for copper
pre-strained to 0.08 in compression, then strained in tension is illustrated in Figure 2.13.

![Graph showing stress-strain relationship](image)

Figure 2.13 The Bauschinger effect observed in copper: tension following compression (solid line) is seen to produce a decrease in the yield strength and permanent softening compared to reloading in compression (interrupted line) [52]

The reduction in flow stress on load reversal may be explained by dislocation - obstacle interactions. During forward loading, dislocations pile-up at obstacles and the stress required for further slip increases. When the straining direction is reversed, dislocations are able to move away from the obstacle at a reduced applied stress [53]. Precipitation hardened alloys often produce a large Bauschinger effect, as the hard precipitates provide an effective barrier to dislocation shear [54, 55]. A study published by Karaman et al. has also observed a strong Bauschinger effect in a Hadfield steel when twinning is the primary deformation mechanism in forward loading, the yield stress in reverse loading is significantly reduced [56]. This effect is attributed to the back-stress acting on dislocation pile-ups at the boundary of the twin deformation bands.

Studies of more complex strain paths may further illustrate the complex deformation behaviour of low SFE FCC alloys. For example, in one study, samples produced from
MP35N alloy (35 % Ni – 35 % Co – 10 % Mo – 20 % Cr), were deformed in simple compression, shear only, and shear followed by simple compression [57]. A number of interesting points can be made from the findings of this investigation, which are illustrated in Figure 2.14. Under simple compression the work hardening rate is higher than in simple shear, due to slip and twinning being coplanar in the latter case, resulting in fewer slip-twin intersections. However a change in deformation mode to simple compression following shear produces very rapid hardening of the material, attaining a similar strength as at an equivalent strain following simple compression only. The activation of different slip systems during compression leads to the rapid rise in strength, as the planar deformation features formed in shear deformation are able to act as obstacles to deformation on the newly activated slip systems.

Figure 2.14 The effect of a complex strain path change on plastic deformation in MP35N alloy [57]
2.2.7 Summary

An overview of the deformation behaviour of low stacking fault energy FCC materials has been given, with relevance to the austenitic stainless steels. The origin of the SFE parameter and its role as the most important factor determining the deformation behaviour of FCC alloys has been explained. In particular the modes of deformation which lead to a localisation of strain have been highlighted, these being planar slip, deformation twinning and ε-martensite formation, which may be collectively referred to as shear bands. In general deformation will occur by dislocation activity for higher SFE materials or at a higher temperature of deformation then by deformation twinning and martensite transformation as the SFE or temperature is reduced. Additionally, the development of anisotropic material properties as a result of crystallographic texture evolution and the relationship between work hardening and the deformation microstructure have been considered.

The localisation of strain and the effects of latent hardening or softening achieved by a strain-path change are believed to significantly influence the SCC susceptibility of cold worked austenitic stainless steels in PWR primary circuit conditions. Later sections will therefore discuss the influence of these factors on the SCC behaviour in this system.

2.3 Light water reactors

The light water reactors (LWRs) are a group of reactor designs which use ordinary water as their coolant [58]. Their relative simplicity has led to widespread use, with more than three-quarters of the current worldwide fleet of reactors being accounted for by two types of LWR: the boiling water reactor (BWR) and the pressurised water reactor (PWR) [59]. In BWRs coolant is boiled directly within the reactor vessel and the steam is fed through pipes to the turbine. PWRs differ in that direct boiling is
prevented by pressurisation of the coolant. Instead heat is transferred to a separate, secondary coolant circuit where steam is generated [58, 2].

The PWR design can therefore be classified into two main sections: the primary and secondary circuits. The primary circuit contains the reactor core, and is operated under pressure (~ 155 bar) to prevent boiling of the coolant. Typically two, three of four coolant loops are connected to the reactor. Each coolant loop contains a steam generator, where the primary coolant transfers heat to the secondary coolant. The secondary circuit is not kept under pressure, the coolant is allowed to boil and the steam used to drive the turbines for power generation [60]. A schematic of the primary circuit is shown in Figure 2.15, with the use of austenitic stainless steels highlighted. It may be seen that the most significant use of austenitic stainless steels is for the piping and as cladding for the different vessels [61].

The temperature of the coolant within the primary circuit varies, with temperatures of 288 °C at the core inlet, 330 °C at the core outlet and 345 °C at the pressuriser [62, 60]. The chemistry of the primary coolant is carefully controlled; the main factors are
the application of hydrogen overpressure (~3000 ppb H₂), and the additions of lithium (~2.8 ppm as LiOH) and boron (~1000 ppm as H₃BO₃) to the coolant. Hydrogen is dissolved in the coolant to suppress the decomposition of water caused by radiolysis, and additionally has the effect of making the electrochemical conditions reducing. The lithium benefits corrosion prevention through control of the pH (~7.1 at temperature), and boron acts as a neutron moderator, helping to control the core reactivity [1, 62, 60].

2.4 Stress Corrosion Cracking

2.4.1 Introduction

Stress corrosion cracking (SCC) is an environmentally induced form of degradation, where under constant applied load an expectedly ductile component will fail by the initiation and propagation of cracking which has a brittle aspect. To occur, SCC requires the combination of specific material, environmental and mechanical parameters, as illustrated in Figure 2.16. With modification to one of the parameters, the deleterious synergy which exists may be removed, and SCC will not occur [63].

![Figure 2.16 Schematic of the factors required for SCC](image)
The major material parameters are the composition, the microstructure (dependent on heat treatments and deformation history), and the surface condition. Significant environmental parameters include the temperature, composition, electrode potential and flow conditions. Stress contributions may occur during service, may result from ‘fit-up’ or may be residual stresses in the material [11, 63]. Failure by SCC is classified into two stages, which are initiation and propagation. As illustrated in Figure 2.17, the duration of the initiation stage is many times that of the propagation stage. The transition to the propagation regime occurs when the initiation defect reaches a critical size, therefore in the propagation stage SCC may be detected by non-destructive methods [64, 63].

Figure 2.17 The stages of development of SCC with time [65]

2.5 SCC of austenitic stainless steels in LWR environments

Austenitic stainless steels are widely used in LWRs. However, SCC of austenitic stainless steel components has been observed in both BWR and PWR systems, although generally the performance is considered to be better during primary circuit exposure as a result of the lower electrochemical potential [2]. Sensitisation of the metal was found to be the major factor leading to susceptibility in many instances of SCC in BWR plant operation. These problems were well mitigated by modified alloying and improved manufacturing processes, both aimed at the prevention of sensitisation. In addition to sensitisation, cold work has been observed to increase
the susceptibility of components to SCC under BWR conditions. Operation under ‘hydrogen water chemistry’ has also been found to reduce the occurrence of SCC in BWR plants [1, 2].

In the PWR primary circuit, the SCC of nickel base alloys has been more of a concern than that of austenitic stainless steels [2]. Despite this the SCC of austenitic stainless steel components has been observed to occur. Degradation in the primary circuit is often associated with occluded, or dead-leg, regions where the coolant flow may not be properly regulated. The build-up of water contaminants in these reduced flow regions, including chloride, sulphur and oxygen has been associated with an increased risk of cracking. Recent events have suggested that SCC is also possible in good quality flowing coolant, and that severe cold work in the material is an aggravating factor [3, 4].

A recent survey of field experience, conducted by The Electric Power Research Institute (EPRI) illustrates these points [5]. The survey includes 137 cases of SCC of austenitic stainless steel components in primary circuit operation. Two graphs have been reproduced from this survey, and make up Figure 2.18. As it may be seen from Figure 2.18 a), the majority (83 %) of these events occurred in components associated with occluded conditions, where the coolant was not free flowing. Around half of these cases were confirmed to be associated with contaminants and the vast majority of these out of specification cracks were transgranular (TG).

Contrastingly, all of the cracks found to have occurred in free flowing, non-contaminated regions were of an intergranular (IG) morphology (13 were IG, whilst 9 may have been IG with some TG), furthermore, none of these IG cracks were associated with material sensitisation. Regarding Figure 2.18 b) it can be seen that all of the cracks which occurred in components expected to be exposed to free flowing nominal composition coolant (for which there is data) were associated with high material hardness of 300 H, or greater [5].
These observations of in-service degradation may be used to define the problem for the current research. The emerging concern is that IGSCC susceptibility of stainless steels in good quality PWR primary coolant is enabled by cold work of the material. The field data available indicates that coolant contamination is not a necessary prerequisite for SCC, provided the material is sufficiently hardened. It is of key importance to understand the specific influence of prior deformation on SCC enhancement, so that the risk can be properly assessed and if necessary mitigating actions may be taken.
2.6 Observations from laboratory testing

2.6.1 Introduction

The derivation of understanding of the SCC process from instances of cracking observed in plant is limited by the lack of accurate information concerning the conditions prior to, and during cracking. The uncertainty covers all influences: the cold work on plant components is variable, and often components include a cold worked surface layer; operational stresses are similarly poorly quantified, and have multiple origins and frequently vary; environmental deviations may occur as a precursor to SCC, but leave no trace for subsequent analysis. Furthermore, transients in plant operation (for example during start-up and shut-down) are often not considered. For these reasons laboratory studies, where parameters and conditions can be better defined are required to ascertain the conditions required for cracking.

Laboratory studies are able to investigate the influence of a wide range of material, environmental and mechanical parameters on both the initiation and propagation behaviour of SCC. The majority of publications regarding the SCC of cold worked stainless steels in good quality primary conditions have been released in the past decade. As such the amount of information is relatively limited, and has not reached the same level of mechanistic involvement as, for example, the research into SCC of alloy 600 in PWR coolant which has been ongoing since the 1960’s.

Crack propagation studies are most commonly reported, and are typically conducted on pre-cracked compact tension (CT) specimens (Figure 2.19 a), where pre-cracking is usually achieved through high-cycle fatigue. As the fatigue pre-crack is transgranular, these tests usually incorporate a period of loading with a low frequency triangular waveform in order to transition the crack front to an intergranular path [66]. The study of ‘true’ SCC initiation, which is the formation of a crack at a smooth surface under a constant applied load is difficult due to the extended period of time which is required. Slow strain rate testing (SSRT) is often used for the study of cracking from a smooth surface as the dynamic strain condition greatly assists cracking.
However, it should be considered that due to the relatively short duration and aggressive loading nature of SSR testing, any results obtained may not be representative of the SCC behaviour observed at constant load, or indeed reflective of field behaviour. As described by Beavers and Koch, SSRT results can indicate both false negative and false positive susceptibility to SCC [67]. With respect to plant integrity, relying on SSRT results for the assurance of a lack of SCC susceptibility is a concern, as in fact SCC may occur on plant following a long and necessary incubation period which is not present in this type of test. For the study of IGSCC of cold worked austenitic stainless steels however, straining is reported to increase the amount of cracking [68]. SSRT may therefore be used to obtain an indication of SCC susceptibility over a reduced testing period, but observations should be considered in parallel to tests conducted at constant load.

For both propagation and initiation tests specimens may be manufactured from bulk cold worked material which is most often achieved by rolling, although other bulk cold working methods such as uni-axial loading have been used also. Slow strain rate tests may be performed on tensile specimens which have been pre-deformed by punching a ‘hump’ into the gauge section, as shown in Figure 2.19 b). A limited number of studies have limited cold work to a surface layer, in order to study initiation in a more plant realistic material condition [68].

Figure 2.19 Typical specimens: a) CT specimen, b) tensile specimen with cold worked hump [69]
2.6.2 Parametric effects

2.6.2.1 Alloying

The composition of any alloy is the largest contributor to its properties and attributes. As mentioned in section 2.1, stainless steels owe their excellent resistance to corrosion in the majority of environments to the formation of a self-healing, passive Cr rich surface oxide layer. The effect of variation to the Cr content of the alloy on the SCC susceptibility has therefore been the subject of several investigations [70, 71, 31]. For both crack initiation (SSRT) and crack propagation, a decrease in the SCC susceptibility has been observed with increasing Cr content in the alloy during testing in simulated PWR coolant [71, 70].

Figure 2.20, below, illustrates the correlation between Cr and Mo concentrations and the IGSCC crack growth rate determined from SSRT on specimens pre-deformed by the cold hump technique [71]. A direct correlation was observed between the IGSCC crack growth rate (CGR) and the Cr content of the alloy, with a significant decrease in the CGR observed at the higher level of alloying. The combined effect of Cr and Mo concentration on the CGR does not drastically change the correlation, suggesting that the significance of Mo is low. Based on this observation the resistance of type 316 steels to SCC should not be higher than type 304 steels.

Figure 2.20 The effect of alloy Cr and Mo content on IGSCC crack growth rates during SSRT [71]
The strong dependency of cracking on the chromium content of the alloy suggests that the ability of the material to maintain a passive chromium rich oxide layer is essential for SCC resistance. This is perhaps not surprising as the oxide layer reduces the dissolution kinetics of the metal significantly. Furthermore, thermodynamic calculations suggest that at the test temperature molybdenum dioxide is not a stable oxide, which explains why Mo concentration has little effect on the SCC susceptibility [71].

2.6.2.2 Sensitisation

The effect of sensitisation on the SCC resistance of austenitic stainless steels has widely been observed to be beneficial in low potential conditions [70, 72, 73, 74]. As a sensitised microstructure will usually include both the depletion of grain boundary chromium concentration and the formation of grain boundary M$_{23}$C$_{6}$ precipitates, it is necessary to consider the effect of these two factors separately. However, from the previous section it can be expected that the depletion of chromium at the grain boundary would have a detrimental effect, and therefore the benefit to IGSCC must originate with the precipitates.

SSRTs carried out on type 316 stainless steel specimens including a cold deformed hump showed significantly reduced susceptibility to IG cracking for the material in a pre-sensitised condition, compared to the same material without sensitisation [71]. These results are presented in Figure 2.21, where the degree of sensitisation is represented by measurement of the local grain boundary Cr + Mo concentration. Additionally data obtained in an oxygenated environment is shown, where it is noted that the relationship between IG cracking and the degree of sensitisation is reversed.
The beneficial effect of sensitisation prior to cold work in the reducing PWR primary environment has also been observed in crack propagation experiments [70, 72, 74, 73]. For example, Tice et al. have reported the complete prevention of IGSCC propagation in type 304 stainless steel where high crack growth rates can be sustained in equivalent non-sensitised cold worked specimens [73]. Yamada et al. found that grain boundary carbide coverage of around 60% was sufficient to fully reduce the SCC propagation rate [72].

Grain boundary carbide precipitation has also been observed to be beneficial to the PWSCC resistance of nickel based alloys [75, 76]. A number of hypotheses have been put forward to explain the beneficial effect of grain boundary carbides in these austenitic alloys based on modification to certain processes which may be involved in SCC. Grain boundary carbides have been observed to act as sites of intense dislocation emission, leading to the suggestion that a reduction in stress concentration may be produced by crack-tip blunting in the vicinity of a grain boundary precipitate [77]. A second possibility is that the carbides locally reduce the rate of grain boundary sliding, which may be an important process in IGSCC [70, 75, 76]. It is also possible that the carbides would react with any oxidising species as they travel along the crack, thereby preventing them from reaching the crack tip.
2.6.2.3 Strain path

Couvant et al. have investigated the effect of strain path variation on the initiation of SCC during SSRT, that is to say that the test strain has been performed along different directions with respect to the prior deformation process \cite{78, 79, 80}. The parameter $\beta$, which is defined by Equation 2.3 has been used to describe the strain path change during two stage deformation. In the equation, $\tilde{\varepsilon}_1$ is the strain tensor during pre-deformation and $\tilde{\varepsilon}_2$ is the strain tensor during the SSR test in simulated PWR coolant. In the case of re-straining along the same path, $\beta = 1$, and in the case of reverse loading (i.e. a Bauschinger test), $\beta = -1$. In the work conducted by Couvant et al., the material was pre-deformed by shear and specimens were manufactured with orientations to achieve $\beta$ values close to 1, -1 and 0.

$$\beta = \frac{\tilde{\varepsilon}_1 : \tilde{\varepsilon}_2}{\|\tilde{\varepsilon}_1\| \cdot \|\tilde{\varepsilon}_2\|}$$  \hspace{1cm} \text{Equation 2.3}

It was observed that the strain history had an effect on both the SCC mode and severity, Figure 2.22 \cite{79}. No IG cracking occurred during the pseudo-monotonic tests, but did occur for the pseudo-Bauschinger and cross ($\beta = 0$) tests. These results suggest that intergranular SCC is favoured with increasing strain path complexity, and also by a higher pre-strain. A continuation of this investigation utilised cruciform specimens, allowing the pre-strain and test-strain to be applied orthogonally \cite{78}. It was observed that IGSCC initiation may occur at constant load after a moderate (0.111) pre-strain, clearly indicating that an orthogonal strain path change strongly promotes IGSCC. TGSCC was observed increasingly toward higher test-strains.
Similar observations of varied SCC susceptibility with strain path have been made for crack propagation experiments [70, 6, 73]. An illustration of the six orientations in which CT specimens may be manufactured from a deformed plate is given in Figure 2.23, as defined by ASTM standard E399 [81]. In cold rolled material, the highest crack growth susceptibility has been reported for the S-L and S-T orientations, where the specimen is manufactured for crack growth parallel to the rolling (RT) plane. Conversely, very low susceptibility has been observed in equivalent materials for L-S and T-S orientation specimens, where the crack front is perpendicular to the rolling plane [6].
Further to this, the increased susceptibility to cracking of grain boundaries which are aligned with the rolling plane is evident in specimens which are manufactured in orientations other than S-L/S-T. The whole crack front has been observed to deviate toward the rolling plane by an angle of 60-70° for a T-S orientation CT specimen, whilst retaining a dominant IG morphology, as shown in Figure 2.24 a) [82, 70]. Specimens manufactured in the T-L/L-T orientations have been observed to undergo very little uniform SCC growth, instead producing localised advance parallel to the rolling plane, as shown in Figure 2.24 b) [6]. Despite this striking behaviour, very little investigation into the material origin of favoured propagation along the rolling plane has been conducted.

![Figure 2.24 IG crack propagation favoured in the RT plane, a) T-S orientation [82], b) T-L orientation [6]](image)

### 2.6.2.4 Character of cold work

It is important to consider the characteristics of deformation which are required to induce susceptibility of SCC of austenitic stainless steels, most obviously the level of deformation. However, from the previous section on strain-path effects, it is clear that the situation is not as simple as defining a threshold level of cold work below which SCC will not occur. For example Kaneshima et al. reported an apparent higher susceptibility to SCC by SSRT for specimens deformed by the cold hump method
compared to straining along the RD of rolled material [83]. If strength thresholds were to be determined from these two types of tests they would not be the same; the difference would be accounted for by the more complex strain history in the cold-hump specimens.

Nevertheless, in general an increase in the level of cold work also increases the IGSCC susceptibility (where most studies are in the range 0 - 30 % deformation). Tice et al. have observed a threshold for localised regions of SCC growth to occur following deformation equivalent to 10 % by rolling, with around 20 % cold reduction required for homogenous susceptibility in type 304 stainless steels. Increasing the cold work level to 30 % produces a further increase in CGR [6, 73, 74]. A comparison made for the same material cold rolled to 40 % and 60 % reduction found no significant increase in the CGR at the higher level of cold work, suggesting that saturation of the susceptibility increase due to deformation occurs around 30 – 40 % cold work [84].

Figure 2.25 illustrates measured IGSCC crack growth rates in hydrogenated water at 288 °C as a function of yield strength for several austenitic stainless steel and alloy 600 specimens [62]. As a yield stress value of 600 MPa is typical of material cold rolled to a level of 20 % reduction, the data illustrated is of a similar range as for the discussion in the previous paragraph [6]. Although scattered, the points also show a trend of increasing CGR with yield strength. The presence of strain induced martensite, which is formed preferentially during deformation at lower temperatures appears to have little effect on the observed CGR [62, 85, 86].
Regarding the initiation of SCC, a minimum hardness threshold of 240 H\textsubscript{v} has been reported for SSRT [4, 79]. A hardness value of 240 H\textsubscript{v} corresponds to a cold work level of 15 – 20 % by rolling, and therefore this is similar to the reported level of cold work required for limited crack growth [6]. No significant influence of strain induced martensite has also been reported in the study of initiation by SSRT [68].

2.6.2.5 Stress and strain

A tensile stress is fundamentally required for both the initiation and propagation of SCC. During crack propagation tests using CT specimens, the magnitude of the crack-tip stress field may be described by the fracture mechanics parameter K\textsubscript{i}, the stress intensity factor. Results generally indicate that the CGR increases as a function of the stress intensity factor, with crack growth at values of K\textsubscript{i} in the range 10 – 60 MPa\sqrt{m} reported [87, 88, 84]. Crack growth may not occur at a value of K\textsubscript{i} which is less than 10 MPa\sqrt{m} [84, 87, 89].

Dynamic loading has also been shown to lead to a significant increase in the susceptibility to SCC compared to ‘true SCC’ testing at constant load. This is reflected by the higher success rate of initiating cracks from smooth specimens during SSRT compared to constant load tests [68]. During CGR tests a dynamic strain condition
may be introduced by the periodic partial unloading of the specimen, producing a trapezoidal load waveform. The ratio of unloading, R, is calculated by the minimum load divided by the maximum load during the cycle. This has also been observed to increase the rate of crack growth, with a larger degree of unloading (lower R) producing the more significant effect [87, 66]. The effects $K_I$ and R on the crack growth rate are illustrated in Figure 2.26.

![Figure 2.26](image)

**Figure 2.26** The effect of stress variables on CGR [87]

### 2.6.2.6 Temperature

Stress corrosion crack propagation experiments are usually conducted within the temperature range 288 °C to 350 °C, roughly corresponding to the range of temperatures experienced within the primary circuit [62, 60]. Results have generally indicated that the crack growth rate increases with temperature [82, 66]. The temperature dependence of crack growth rate is illustrated in Figure 2.27, for 10 %, 15 % and 20 % cold rolled type 316 stainless steel [82]. As discussed previously, the CGR increases with the level of cold work. For all three levels of cold work it is seen that the CGR decreases above a certain temperature, which corresponds to approximately 330 °C for the 10 % and 15 % cold rolled material and 350 °C for the 20 % cold rolled material. This type of behaviour suggests that the rate controlling process in the temperature range 250 °C to 330–350 °C is replaced by a second process at higher temperatures.
As temperature dependent processes can be described by an Arrhenius relationship, researches have calculated values for the activation energy of the rate controlling process. The values of activation energy which have been calculated from the temperature dependence of crack growth rate observations are in the range 65 – 100 kJ/mol, with more evidence towards the higher end of this range [82, 66, 90, 91, 62, 92].

Arioka et al. have discussed the typical activation energies for a number of processes which may be relevant to the SCC of austenitic stainless steels in high temperature water [82]. It was reported that the bulk diffusion of substitutional elements in austenitic stainless steels typically has an activation energy of around 240 kJ/mol, the diffusion of ionic species in water has a much lower activation energy, around 30 kJ/mol and that the diffusion of hydrogen in austenitic stainless steels also has a lower activation energy, less than 50 kJ/mol. The activation energy of ~ 100 kJ/mol is therefore too high for a process controlled by ionic diffusion in the water or related to hydrogen. However, enhanced diffusion rates of substitutional atoms could occur through diffusion at the grain boundaries, from interactions with cold work induced defects or as a result of a higher vacancy concentration in the material introduced by corrosion [82].
2.6.2.7 Potential – H2 concentration

The electrochemical potential is maintained at a value around -0.8 V$_{\text{SHE}}$ in the PWR primary circuit by the application of hydrogen overpressure. By contrast the operating potential during normal BWR operation is around +0.2 V$_{\text{SHE}}$, although the use of BWR-hydrogen water chemistry reduces this to within the range -0.25 to -0.55 V$_{\text{SHE}}$ [62, 60]. Throughout this entire range of potential in service and in laboratory conditions cold work has been shown to increase susceptibility to SCC for austenitic stainless steels [2, 5, 82].

For equivalent test conditions, the CGRs observed on cold worked material in oxygenated water are higher than those observed in hydrogenated water [82, 93]. Figure 2.28 a) illustrates this for the IGSCC crack growth rate of 20 % cold rolled type 316 stainless steel. It is interesting that the same temperature dependence, as described in section 2.6.2.6, is followed in both the high and low potential test environments. This suggests that the same process is rate controlling across the range from oxygenated to hydrogenated water in cold worked materials.

For the low potential SCC of nickel base alloys significant studies indicate that an increase in the susceptibility of the material to cracking occurs near to the potential of the Ni/NiO stability transition [94, 95]. A limited number of studies have reported the effect of the hydrogen concentration on the SCC of cold worked stainless steels [82, 62, 73]. Unlike the situation for Ni base alloys, it appears that once low potential conditions are established there is little effect of increasing the hydrogen concentration on the CGR of stainless steels, as shown in Figure 2.28 b).
2.6.2.8 Summary parametric dependencies

The amount of published data concerning the influence of the many variable experimental parameters on the SCC susceptibility of cold worked austenitic stainless steels in simulated light water reactor conditions is limited, particularly in low potential conditions. However it has been possible to identify certain threshold conditions and behavioural trends from a survey of the SCC data. It should be noted that the observations reported have focussed mainly on instances of IGSCC, which have been identified as most relevant to the instances of in-plant cracking as described in section 2.5. Transgranular cracking has been observed however, especially during SSRT, and particularly favoured by higher strain rates and an absence of strain path change [80]. In particular the higher strain rates utilised for SSRT investigations can be considered as non-representative of plant conditions [67]. Transgranular cracking is however also nucleated at folds and scratches in the surface, and this may be relevant to plant components [4, 96].

Parameters associated with the material seem to have the most influence over the SCC behaviour, most obviously the increase in susceptibility with an increasing level of cold work. However there is also interrelation of some features, for example the threshold for susceptibility and the morphology of cracking depend on the strain path history [97, 78]. Further difficulty in understanding the role of cold work comes from...
the fact that deformation may modify both the corrosion properties and the mechanical properties of the material, thus potentially having an effect on SCC through either, or both of these channels. It is clear therefore that a better understanding of the contribution of cold work to the SCC susceptibility is required.

2.7 Deformation heterogeneity and SCC

2.7.1 Introduction

During the deformation of a polycrystalline material, the distribution of stress and strain is not homogenous. At the microstructural scale the main contributors to deformation heterogeneity are the interactions between neighbouring grains of different orientation, and the localisation of deformation into shear bands. Concerning intergranular failure, either of these sources of heterogeneity may be important precursors to the subsequent degradation of the grain boundary. Recent studies suggest that the accumulation of heterogeneous deformation adjacent to a grain boundary may contribute to the IGSCC susceptibility [98, 99].

2.7.2 Intergranular incompatibility

Variations in the elastic and plastic properties of different grains in a polycrystalline material, and indeed within different regions of individual grains, may produce local incompatibilities of both stress and strain. Such incompatibilities have been shown to be significant toward the initiation of SCC by Couvant et al. [78]. Figure 2.29 illustrates that the initiation of an intergranular crack during SSRT has occurred on the boundary separating regions of high and low strain, as determined from digital image correlation during the test.
The relative ease of deformation in different grains may be predicted from calculation of the Schmid or Taylor factors for a particular strain condition. Recent work has highlighted a possible correlation between intergranular cracking and the presence of grains which are predicted to be more resistant to slip [100, 101]. In addition to the grain orientation, at a local scale the deformation microstructure resulting from pre-deformation will influence the strain incompatibility between grains during subsequent deformation. As described in section 2.2, complex strain path changes lead to the activation of different deformation systems, potentially causing a rapid latent hardening effect in certain grains. Such an effect may increase the stresses between grains, and may contribute to the observed tendency for IG cracking following a stain path change (as described in section 2.6.2.3).

2.7.3 Shear localisation

The localisation of stain into micro-shear bands by concentrated planar dislocation slip, deformation twinning or ε-martensite formation (as described in section 2.2) represents another potentially significant form of deformation heterogeneity for IGSCC. Mechanically, the intersection of a band of concentrated shear with a grain boundary presents a significant chance of damage to the grain boundary [99]. Indeed, evidence of intergranular void formation at the intersection of slip bands with
a grain boundary has been observed during the SSRT of pre-deformed type 304L stainless steel, Figure 2.30 [79].

The effect of localised deformation bands on IGSCC initiation has been researched most extensively for irradiated materials; analogy can be made between shear localisation effects on irradiation assisted stress corrosion cracking (IASCC) of austenitic alloys in LWR environments and that of cold worked materials [102, 103]. During deformation following irradiation, dislocation slip clears irradiation-induced crystal defects, making the passage of subsequent dislocations easier. As a consequence of this process deformation becomes highly localised in defect free ‘clear bands’ [103]. Results have indicated that for SCC in high temperature water, the degree of strain localisation into clear bands correlates well with the propensity for IG cracking [102, 103]. The link between grain boundary – shear band intersections on IASCC is most likely due to localised grain boundary shearing, which causes rupture of the protective oxide [100, 98]

In addition to the mechanical aspect of localised damage on IGSCC initiation, there is also evidence that enhanced oxidation occurs along shear bands in high temperature water environments [78, 80, 31]. These observations have led Lozano-Perez et al. to
suggest that the oxidation of deformation bands (specifically deformation twins) at the crack tip could contribute additional stresses locally, which may subsequently cause deformation band shearing and assist the propagation of the crack [31].

2.7.4 Summary

Evidence for the contribution of heterogeneous and localised deformation on the increased susceptibility to IGSCC of cold worked austenitic stainless steels has been discussed. During deformation the incompatibility between different grains, which result largely from their orientations is known to result in intergranular residual stresses, and indeed these may contribute to damaging processes [104]. Figure 2.29 also indicates that the strain gradient across a grain boundary during testing may be significant to SCC initiation. Strain localisation in the form of intense shear bands is also a possible contributor to grain boundary cracking. In this case, the damaging effect is also likely to be sensitive to the ability of the grain boundary to transmit strain, and therefore the structure of the boundary [98].

Deformation heterogeneity is likely to contribute to mechanical stress gradients and modified corrosion resistance. As a result a variety of factors and processes which may contribute to SCC may be affected, and very little is known about specifically about this. The behaviour is further complicated by the interaction between deformation occurring during testing and the microstructural artefacts from prior cold work on a grain to grain basis, for example as a result of latent hardening or softening effects. It is likely that such a factor would explain the strain path sensitivity of SCC which is observed in cold worked stainless steels as described previously. It is clear that further work is required to understand the specific microstructural contributions to SCC which result from the deformed microstructure.
2.8 Surface oxide characteristics

The surface oxide formed in hydrogenated water have been reported by Terachi et al., and others [105, 88, 106, 107, 108]. Figure 2.31 shows the oxide formed cold worked section of an SSRT specimen fabricated from type 316 stainless steel, after 500 hours exposure to simulated PWR coolant [105]. As visible from part a) of the figure, the surface oxide consists of two layers. Adjacent to the metal is a fine grained chromium rich oxide layer (400 – 500 nm thick), which is covered by a much coarser grained iron rich oxide layer (particle size 1 – 2 µm). The Cr rich oxide layer has been characterised as being chromite spinel (FeCr$_2$O$_4$) and the outer layer is reported to be magnetite (Fe$_3$O$_4$). These oxides are calculated to be the most stable oxides in the iron-chromium-water and iron-water systems respectively [106].

Energy dispersive spectroscopy (EDS) line profiles taken across the oxide film and into the base metal show the compositions of the major alloying elements and oxygen in part c) of the Figure 2.31. It is interesting to note that enrichment of nickel at the metal/oxide interface is observed, which is reported to occur to a depth of ~ 70 nm and to more than double the bulk concentration [105]. Regarding the formation of the oxide, it is believed that the inner oxide layer forms by inward diffusion of oxygen, whereas the outer oxide layer forms by the outward diffusion of metal ions. This is supported by the observation that the position of the inner/outer oxide interface corresponds to the original metal interface [106, 105, 78].
Several material and environmental variables may affect the formation of the surface oxide layers in high temperature water. These include, but are not limited to, the level of cold work, alloy chromium content and the hydrogen content of the water. Each of these factors may be influential toward the SCC susceptibility of the material. The effect of cold work on the oxide thickness is presented in Figure 2.32 a), and indicates that a slight increase in the oxide thickness occurs with increasing degree of cold work [88]. With decreasing chromium content in the alloy the thickness of both oxide layers increased, with a coarser particle size in both layers also observed [106].
A slight increase in the oxide film thickness is observed with increased hydrogen concentration in the water at 320 °C [106].

![Graph a) Average oxide film thickness (include outer and inner layer)](image)

![Graph b) Oxide film thickness (μm)](image)

![Graph c) Oxide film thickness (μm)](image)

Figure 2.32 Surface oxide thickness variation: a) with degree of cold work [88], b) alloy Cr content and c) coolant [H₂] [106]

Increasing cold work level, decreasing chromium alloy content and increased hydrogen in the environment therefore appear to result in a less protective oxide and higher general corrosion rate. Both increased cold work and decreased chromium alloy levels have been shown to lead to a rise in the susceptibility to SCC of the alloy, correlating with these observations. The effect of hydrogen concentration on SCC is less well defined. The contribution of higher dissolved hydrogen levels on the oxide film formation is possibly related to an increased solubility of iron ions or increased rate of cation diffusion through the chromium rich oxide layer [106]. Additionally a
number of mechanisms by which hydrogen may cause embrittlement of the material have been postulated, and the most likely of these are summarised in Section 2.10.3. The apparent lack of correlation between SCC and the hydrogen concentration may suggest that these processes, nor a possible influence of hydrogen on the oxide film formation are controlling with respect to the SCC mechanism, or that the environment in the crack is not sensitive to the bulk coolant hydrogen composition.

2.9 Crack characteristics

High resolution characterisation of the material and oxide structures at the crack tip provides an opportunity to gain information on the local environment and processes involved in stress corrosion cracking. Physically, intergranular stress corrosion cracks formed in cold worked austenitic stainless steels in low potential water tend to be very narrow, tapering to a width at the crack tip in the range of a few nanometres [79, 109].

The crack oxide structure reported for cold worked (non-sensitised) stainless steels in low potential coolant (hydrogenated BWR (BWR-HWC) and simulated PWR) conditions are reported to consist of a chromium-rich spinel oxide layer formed adjacent to the metal which extends to the grain boundary ahead of the open crack tip, and a central iron-rich oxide within the opened crack [110, 109, 105, 111, 31, 112]. The oxide structures formed within stress corrosion cracks are therefore believed to have the same character as the surface oxides reported in the previous section. The conditions within a propagating crack are therefore expected to be similar to within the bulk coolant. A schematic of these features, derived from observation of cracks produced during SSRT in simulated PWR coolant is provided in Figure 2.33.
As illustrated in Figure 2.33, the enrichment of metallic nickel along the grain boundary ahead of the crack tip has been observed for cracks formed in PWR by several authors [105, 31, 111, 78, 82] and BWR-HWC [112]. This feature is also clearly shown in the compositional energy-filtered TEM (EFTEM) maps in Figure 2.34 [78].
The extent of this feature has been reported to be highly sensitive to the chromium content of the alloy, with a typical length of 20 nm reported in a type 304 stainless steel (18.3 weight % Cr) compared to a length of 100 nm in a laboratory material with 15 weight % Cr but otherwise similar composition [31]. It is most likely that the rejection of nickel into the metal occurs as the chromium rich oxide forms along the leading grain boundary. This feature is therefore not likely to be directly related to the SCC mechanism.

The observations of Bruemmer [112, 110] on crack propagation specimens in BWR-HWC suggest that very high local stress conditions exist ahead of the crack tip, as illustrated in Figure 2.35. Deformation induced planar faults are seen parallel to the grain boundary in one grain ahead of the crack tip, it is possible that such features contribute to the fracture of the protective oxide ahead of the crack tip, and would lead to propagation of the crack according to a slip-dissolution type mechanism (which is discussed in the following section).

![TEM Brightfield and <111> relrod darkfield left grain](image)

Figure 2.35 TEM images of a crack tip in 20 % cold worked 316L tested in BWR HWC [112]
2.10 Models of SCC

A number of general models for SCC have been developed to attempt to explain the observations of SCC in a variety of systems. The features of three of these models, which may be relevant to SCC in LWR conditions are outlined in the following section. The models are slip dissolution, internal oxidation and hydrogen embrittlement. A successful model would predict the parametric dependencies and microstructural observations of SCC cracks which have been discussed in previous sections; therefore to summarise the applicability of each of the models will be considered.

2.10.1 Slip dissolution model

The original concept of a periodic film-rupture mode of crack propagation of stress corrosion was proposed by Logan in the early 1950's, and attention has returned to this type of mechanism at various times in the period since [113]. Crack advance as described by the slip dissolution model occurs through repetition of the cycle of oxide fracture, dissolution and re-passivation at the crack tip [114, 115]. The fracture of the oxide is assumed to be caused by localised strain in the metal ahead of the crack tip, whereas the protective oxide on the crack flank is not damaged. The slip dissolution mechanism is illustrated schematically in Figure 2.36. Immediately following the film rupture event localised dissolution of the newly exposed metal at the crack tip produces an increase in the anodic current. As the metal re-passivates the current gradually decreases, and the rate of crack advance slows until sufficient stress is accumulated to fracture the oxide and allow the cycle to be repeated.
The concept of the slip-dissolution model has been developed into an empirically based predictive model, which has been successful in the prediction of crack growth rates in LWR applications by Ford and Andresen [116, 117]. The key points of the Ford-Andresen approach are outlined in the following. Under a slip dissolution process of crack growth, the crack propagation rate depends on the increase in crack length following each film rupture event, and the time following repassivation for the film fracture to re-occur. The increase in the crack length may be related to the anodic charge density \( (Q_f) \) which passes due to the dissolution process. The rate of oxide rupture is related to the crack tip strain rate, \( \dot{\varepsilon}_c \), and the oxide fracture strain, \( \varepsilon_f \). Based on Farady’s law of electrolysis, the crack propagation rate, \( \bar{V}_t \), can therefore be predicted by the following equation [118].

\[
\bar{V}_t = \frac{M}{p z F} \frac{Q_f}{\varepsilon_f} \dot{\varepsilon}_c
\]

Equation 2.4
The additional terms in this equation are: $M$ and $\rho$ – respectively, the atomic weight and density of the metal, $z$ - the charge of the metal cation and $F$ – the Faraday constant. The rate of film reformation is incorporated next, assuming power law behaviour for the repassivation current transient, given in general form by [115]:

$$i = i_0 \cdot \left(\frac{t}{t_0}\right)^{-n}$$ \hspace{1cm} \text{Equation 2.5}

Where $-n$ is the slope of the repassivation current transient. Combination of the two equations leads to the full expression of the Ford-Andresen slip dissolution model [115]:

$$\hat{V}_t = \frac{M}{\rho z F} \frac{i_0 \cdot t_0^n}{(1-n) \varepsilon_f^n} \left(\varepsilon_{ct}\right)^n$$ \hspace{1cm} \text{Equation 2.6}

The additional terms are: $i_0$ – the current density of the exposed metal and $t_0$ – the time taken for repassivation to occur. It is common for the authors to simplify the model to the following form [117]:

$$\hat{V}_t = A \cdot \left(\varepsilon_{ct}\right)^n$$ \hspace{1cm} \text{Equation 2.7}

Where the parameter ‘$A$’ is typically observed to be a function of ‘$n$’ [117]. The crack tip strain rate parameter is based on empirical relationships derived from creep relaxation experiments and expressed at a function the stress intensity factor, $K$ [117]. Therefore, in this form model predictions are essentially empirically based, and not fundamentally predictive of the processes involved in the propagation stress corrosion.

These simplifications have been the source of criticism of the Ford-Andresen derivation of the slip-dissolution mechanism [119], and recent attempts have been made to improve the true predictive capacity of the model, particularly through the incorporation of a more fundamentally derived crack tip strain rate term [120]. Nevertheless, the model has been able to predict the EAC behaviour of stainless steels.
and nickel based alloys in LWR conditions, as shown for example in Figure 2.37. The data assembled in this figure covers a range of water chemistry and loading conditions, and includes annealed and sensitised materials. The Ford-Andresen formulation does not account for crack initiation however [121].

![Figure 2.37 Ford-Andresen model prediction of crack propagation rates in sensitised 304](image)

**Figure 2.37** Ford-Andresen model prediction of crack propagation rates in sensitised 304 [122]

### 2.10.2 Internal oxidation model

Selective internal oxidation (SIO) as a mechanism for SCC was originally suggested to explain intergranular primary circuit SCC of nickel based alloy 600 by Scott and Le Calvar [123]. The concept of the SIO model states that embrittlement of the metal occurs by inward oxygen diffusion. By definition, oxidation of the major element should not be favoured but instead oxidation of the minor alloying elements will occur; for nickel base alloys in primary circuit conditions chromium in particular is oxidised, leading to the formation of internal Cr₂O₃ [124]. Alternatively it is possible that the adsorption of oxygen onto grain boundary surfaces or the formation of gas bubbles may also cause embrittlement [121]. Embrittlement is expected to be deeper
at the grain boundaries due to the ease of diffusion (relative to a grain surface), thus SIO is applicable to IGSCC.

Crack initiation is expected to occur following the embrittlement of a grain boundary to a critical depth. Here, the stress is sufficient to fracture the oxide, thus initiating the crack. Crack propagation then occurs in a similar manner; the diffusion of oxygen from the open crack tip into the grain boundary ahead causes embrittlement, leading to incremental crack advance. The process of SCC initiation and propagation by the internal oxidation mechanism is illustrated in Figure 2.38 [124, 125].

Figure 2.38 Schematic illustration of initiation and growth by selective internal oxidation [125]

2.10.3 Hydrogen embrittlement mechanisms

Observations of cracking have been linked to the ingress of hydrogen into the material in a range of alloys. The origin of hydrogen embrittlement has been postulated to be due to several mechanisms, these are [64]:

- Decohesion: hydrogen ahead of the crack tip weakens the bond strength, enabling separation of the atoms at a reduced applied stress and with very little plasticity.
- Deformation: hydrogen may interact with dislocations or obstacles to reduce the stress necessary for slip, forming the basis of the hydrogen enhanced localised plasticity (HELP) model. Highly localised plasticity may result in cleavage-like failure.
- Adsorption: surface adsorption of hydrogen may reduce the surface energy of the metal, allowing crack growth at a lower stress.
- Pressure: molecular hydrogen formation in existing voids or micro-cracks may produce an internal stress which reduces the necessary external stress for cracking.
- Vacancy model: hydrogen may stabilise lattice vacancies, leading to a higher vacancy content in the metal. This may enhance diffusion creep or lead to a stronger HELP effect. Additionally the condensation of vacancies may create voids.

2.11 Discussion of mechanisms

None of the models described appear to be suitable to the prediction of all of the observed experimental dependencies and SCC characteristics. The slip dissolution model is a strong candidate, and has been successfully applied to the prediction of crack growth rates for austenitic alloys in LWR environments [122]. However certain parametric dependencies are not well described, for example the model would not predict the beneficial effect of carbide precipitation at the grain boundaries which has been observed in low potential coolant. On the other hand, the beneficial effect of sensitisation may fit into the SIO framework as the oxidation of the precipitate would prevent further ingress of oxygen along the boundary, and could lead to crack blunting.

The major criticism of the internal oxidation model is that the observed intergranular oxidation rates in austenitic alloys cannot be explained by the diffusion of oxygen at the grain boundaries alone [126, 124]. Several solutions to this problem have been suggested. Firstly, it is possible that the application of a stress, or the stress associated with oxidation might increase the rate diffusion [127]. Secondly, porosity has been observed in the oxide which would provide a path for unhindered movement of oxygen to the crack tip [124]. Alternatively it has been proposed that vacancies are injected into the metal during oxidation, which pair with ions to increase the solid state diffusion rates [127, 128].
Limited evidence of hydrogen induced cracking has been reported in cold worked austenitic stainless steels tested in PWR primary coolant [68]. However, a hydrogen controlled mechanism of SCC lacks support for a number of reasons. Andresen has reported that the permeation of hydrogen into the steel is controlled by the coolant hydrogen fugacity, but that there is no correlation to the crack propagation rate; in fact an inverse correlation was generally observed [85]. Additionally the possibility of hydrogen embrittlement of austenitic materials at temperatures in excess of 100-150 °C is in contention [1].

The lack of a satisfactory model for SCC is underpinned by poor understanding of the fundamental processes involved in cracking, and the effect which cold work has on these. For example, the nature and role of interactions between corrosion processes and the deformed microstructure, and the increased diffusion rates induced in regions of high stress and strain are not well known [129].

The possibility that vacancy diffusion to the crack tip under applied stress precedes crack growth has been suggested by Arioka et al. [82]. This hypothesis was made by virtue of the similar dependence of IGSCC and IG creep crack growth rate on cold work, and the observation of similar compositional gradients at creep induced voids to those which have been observed at IGSCC crack tips. Similarities between creep and SCC behaviour could also be attributed to grain boundary sliding. Furthermore, there is evidence that deformation at the grain boundary is linked to the SCC susceptibility of cold worked and irradiated austenitic stainless steels and nickel base alloys in PWR environment, suggesting that grain boundary deformation may be a generic requirement for SCC susceptibility in austenitic alloys [71, 76, 130, 98].
2.12 Summary and project objectives

Cold work has been shown through laboratory testing to induce susceptibility to SCC of austenitic stainless steels in an environment which is representative of normal primary circuit PWR conditions. It seems highly likely therefore that the in-service SCC of a number of PWR plant components which are fabricated from austenitic stainless steels are directly linked to prior deformation of the material. Clearly the degradation of any plant component raises immediate safety concerns and the loss of productivity. There is a clear requirement to understand the phenomenon of SCC to enable the problem to be managed proactively. Currently however, the fundamental processes which are involved in the SCC of austenitic stainless steels in PWR coolant are not clearly understood.

The deformation of austenitic stainless steels is inherently heterogeneous. There is some evidence to suggest that microstructural heterogeneity is strongly linked to SCC initiation, for example: enhanced oxidation has been observed along deformation bands [31]; crack initiation has been observed between grains where a strain mismatch has been observed [78]; the intersection of micro-shear bands with a grain boundary is seen to form cracks [79]. Additionally there is evidence that macroscopic strain heterogeneity also influences the SCC behaviour, as evidenced by the observation of preferred crack propagation parallel to the rolling plane [70, 6].

The aims of this project are therefore to improve the understanding of the link between microstructural heterogeneity induced by cold rolling on the SCC behaviour in simulated PWR primary circuit coolant. It is noted that cold rolling doesn't necessarily represent well the cold work occurring on plant components, which tends to be more complex (for example due to bending) and which is often localised to the surface as a result of finishing operations. However, cold rolling does provide a route for deformation which is easily repeatable, induces a relatively homogenous strain and allows subsequent deformation to be performed with a well-defined direction to the rolling process, allowing 'strain-path' effects to be considered.
This work has been undertaken as part of wider project aimed at establishing the effects of deformation heterogeneity on SCC susceptibility at The University of Manchester (UoM) and Serco.
3 Experimental

3.1 Introduction

The focus of the project is to improve understanding of why cold work, and in particular the heterogeneous microstructure resulting from cold work, confers increased susceptibility to SCC of austenitic stainless steel in simulated PWR primary circuit conditions. The two streams of this work have been firstly to investigate the effects of cold work on the material, and secondly to assess the effect of cold work on the SCC susceptibility of the material. Both slow strain rate tests and crack propagation tests have been performed in simulated PWR environment in order to study the behaviour of both the initiation and propagation stages of SCC. This chapter provides a description of the experimental procedures and methods of analysis which have been used.

3.2 Material

The material under investigation is a type 304 austenitic stainless steel. The composition of the alloy is given in Table 3.1. The material was received in the form of a 30 mm thick plate which had been manufactured by hot rolling. The plate was subsequently annealed by thermal treatment at 1050 °C for one hour, followed by water quenching.

<table>
<thead>
<tr>
<th>Element</th>
<th>Cr</th>
<th>Ni</th>
<th>C</th>
<th>Mn</th>
<th>Mo</th>
<th>Si</th>
<th>S</th>
<th>P</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight %</td>
<td>18.42</td>
<td>9.75</td>
<td>0.056</td>
<td>1.52</td>
<td>0.01</td>
<td>0.52</td>
<td>0.001</td>
<td>0.025</td>
<td>Bal.</td>
</tr>
</tbody>
</table>
3.3 Cold rolling procedure

Following annealing the material was deformed by rolling at ambient temperature to a reduction of 20% thickness. Pieces of material were cut from the original plate, as indicated by the dotted line in Figure 3.1 a), with a thickness of 40 mm. Each section of material was then turned so that cold rolling was performed along the transverse direction of the original plate, as illustrated in part b) of the figure. The 20% reduction in thickness was achieved by four rolling passes, each producing a reduction of 2 mm.

The cross-sectional dimension of each of the cold rolled pieces of material was approximately 32 mm by 32 mm. This indicates that a component of the reduction in thickness had been accommodated by strain along the transverse direction, which amounted to approximately a 7% increase in width. The extension along the rolling direction was therefore approximately 16.5%.

Figure 3.1 Schematic of how the original hot rolled plate a) was sectioned for cold rolling b)

3.4 Optical microscopy

The basic microstructure of the material has been investigated using light microscopy. Plane sections were produced which were perpendicular to each of the three primary plate directions for both the annealed and cold rolled material.
conditions. The surface of each specimen was then prepared by grinding and polishing as described below.

3.4.1 Mechanical grinding and polishing

Specimens were mechanically ground with silicon carbide (SiC) paper (grades P240 through to P2500) to ensure a flat surface which is free from any large scratches. Subsequently two stages of polishing, using diamond suspensions with particle sizes of 6 µm and 1 µm respectively were conducted. Between each stage specimens were washed and dried thoroughly.

3.4.2 Microstructural etches

To reveal features of interest within the microstructure for observation, a number of different etchants have been used. These are:

- 10 % oxalic acid: grain structure including annealing twin boundaries
- 60 % nitric acid: grain structure without annealing twin boundaries
- 40 % sodium hydroxide: darkens ferrite phase

Each etch was conducted in accordance to the procedures described within ASTM E407 – Standard Practice for Microetching Metals and Alloys [131].

3.4.3 Grain size estimation

The average grain size for the material was estimated according to the linear intercept procedure outlined in ASTM E112 – Standard Test Methods for Determining Average Grain Size [132]. Micrographs taken of specimens which had been etched using nitric acid were used for the grain size estimation, so that annealing twin boundaries would not be included in the count.
3.4.4 Delta ferrite phase fraction estimation

Following the sodium hydroxide etch, delta ferrite is darkened relative to the austenite matrix. Simple image analysis may be performed on micrographs taken of the material following this etch, so as to estimate the fraction of the second phase in the material. This analysis was carried out using the freely available ImageJ software, which allows pixel value statistics to be easily obtained [133].

3.5 Mechanical property determination

3.5.1 Hardness measurement

Flat sections were prepared according to the process described above for general metallography. The hardness of the annealed material was measured across the plate thickness along a number of lines which were spread across the width of the plate at 5 mm intervals. Measurements were taken every 2 mm along each of the lines, using with a load of 30 kg. For the cold worked material, the cross sectional (i.e. in the transverse – normal plane) hardness variation was also mapped using a Fischerscope HM2000 hardness tester with programmable specimen stage. The area covered by the scan was 28 mm by 26 mm, with a measurement made every 2 mm.

3.5.2 Tensile testing

The behaviour of the material during tensile straining was assessed, both in the annealed and cold rolled conditions. Due to the restrictions from the plate dimensions, particularly for the cold rolled material sections, under-sized tensile specimens were designed according to the guidelines for specimen design outlined in ASTM E8 – Standard Test Methods for Tension Testing of Metallic Materials [134]. Three specimen geometries were used, the key dimensions of which are summarised in Table 3.2 with Figure 3.2 as a guide to these details. The three specimen designs
are referred to as M6, M5 and M10 in reference to the metric thread designation of each.

3.5.2.1 Annealed material

Both tension and compression-tension tests were carried out on the annealed material at room temperature. M6 type specimens were used for tensile testing, and M10 type specimens were used for compression-tension tests. In all cases straining was conducted at a rate of 0.05 %/s, with extension along the transverse direction of the as-received plate.

3.5.2.2 Cold rolled material

Tensile specimens were manufactured to allow testing along the rolling, transverse and normal directions of the cold rolled material. Tests along all three specimen orientations were conducted at ambient temperature. Further tests were conducted at a temperature of 300 °C for the normal orientation only. All specimens were strained at a rate of 0.05 %/s. The specimens were manufactured according to the M5 geometry outlined in Table 3.2.

<table>
<thead>
<tr>
<th>Specimen reference</th>
<th>Dimensions (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M6</td>
</tr>
<tr>
<td>Thread diameter (M)</td>
<td>6.0</td>
</tr>
<tr>
<td>Gauge diameter (D)</td>
<td>3.5</td>
</tr>
<tr>
<td>Specimen length (L)</td>
<td>38.9</td>
</tr>
<tr>
<td>Minimum parallel length (L_p)</td>
<td>17.5</td>
</tr>
<tr>
<td>Shoulder radius (R)</td>
<td>3.5</td>
</tr>
</tbody>
</table>
3.6 Scanning electron microscopy

Scanning electron microscopy (SEM) has been performed for three reasons. These are: standard surface/topographical imaging, microstructural imaging at the surface of polished specimens using electron channelling contrast (ECCI), and for electron backscattered diffraction (EBSD) measurements. The principal instrument which has been used is a FEI Quanta 200 field emission gun (FEG) microscope.

3.6.1 Colloidal silica polishing

For EBSD and microstructural imaging in the SEM an additional polishing step is required to remove the damaged surface layer introduced by mechanical grinding and polishing. In this case, further polishing using a colloidal silica suspension with typical particle sizes 0.04 – 0.06 µm for 30 minutes is adequate.

3.6.2 Electron channelling contrast imaging

ECCI is possible due to the dependence of the intensity of back-scattered electrons (BSEs) on the angle between the incident electron beam and the crystal orientation at the specimen surface [135]. As a result the technique may be used to qualitatively investigate the microstructures formed by deformation as a result of the associated crystallographic orientation changes (for example [136, 137]). Specimens for ECCI were prepared by grinding and polishing, and finished with colloidal silica polishing as
described above. The microscope was typically operated at a moderate accelerating voltage, 8-15 keV. A standard pole-piece mounted BSE detector was used for imaging, with tilting of the sample within a range of ~ 10° to provide optimum contrast from specific regions.

3.6.3 Electron backscattered diffraction

EBSD allows the local orientation of the crystalline lattice to be determined by the indexing of Kikuchi diffraction patterns [135]. By recoding the crystal orientation at many points as the electron beam is translated across the specimen surface in a regular pattern, it is possible to represent the microstructure in terms of the variation in crystal orientation; resulting in the use of the additional term orientation imaging microscopy (OIM) [138]. Specimens for EBSD were prepared as for ECCI. Data collection was performed using the FEI Quanta 200 FEG microscope in conjunction with an EDAX Hikari EBSD detector.

3.6.3.1 Texture

The texture of the material in the annealed and cold worked conditions has been measured. The scan step size of 100 µm was used with the aim of sampling approximately one point per grain. An area large enough to allow the sampling of 7000 – 8000 grains was sampled in both conditions. This was achieved by performing a number of individual scans on adjacent areas of the specimen surface, the specimen being translated by a stage shift between each scan. The combined area of the multiple scans was 12 mm × 6 mm. The texture data has been interpreted with the EDAX OIM™ Analysis software [138].

3.6.3.2 Microstructure

EBSD ‘maps’ of a higher resolution have been produced from polished specimens to enable quantification of aspects of the microstructure. For the annealed material a step size of 2 µm was used during data collection, which is suitable for assessment of
the general microstructure and the grain boundary character distribution. For the cold rolled material, a 0.25 µm step size was used during specimen mapping. This scan resolution was deemed suitable with respect to capturing sufficient detail from the microstructure without producing unmanageable equipment demands. Analysis has been performed with the EDAX OIM™ Analysis software and bespoke routines developed in the Python programming language [139, 138]. The details of the bespoke analyses are described in section 3.10.

Where EBSD data has been represented in the form of an inverse pole figure (IPF) map, the colour key in Figure 3.3 has been used to represent the crystal direction with respect to the plate rolling normal direction (ND) in all cases, irrespective of the surface which the EBSD scan was conducted on.

![Figure 3.3 EBSD IPF colour key for FCC crystal structure](image)

EBSD data has also been represented by the image quality (IQ) parameter, which is a measure of the quality of the diffraction pattern obtained to determine the orientation at each point [138]. The IQ parameter may be used as a qualitative indication of the strain history in a particular region of the material; as the material is deformed the pattern from the diffracting region becomes more diffuse, and the IQ parameter is decreased [140].

Where different grain boundary types have been distinguished based on a misorientation criterion, the following definitions have been applied (where \( \theta \) is the rotation angle):
• If $5^\circ \leq \theta < 10^\circ$, the points are separated by a low angle grain boundary (LAGB);
• If $10^\circ \leq \theta$, the points are separated by a high angle grain boundary (HAGB);
• Unless, the rotation calculated is $\pm 5^\circ$ of a $60^\circ$ rotation about a $<111>$ type axis, in which case the points are separated by a twin boundary.

3.7 Transmission electron microscopy

Transmission electron microscopy (TEM) has been performed in order to observe certain aspects of the microstructure. Conventional 3 mm circular TEM foils were prepared according to the following procedure. Thin slices of the material were made using a Struers Accutom 5 Precision cut-off machine, with an ultrafine abrasive alumina cut-off wheel. The slices were ground down to a thickness of ~200 μm using SiC paper (P600-P1200), then punched into 3 mm discs. Further grinding, using P2500 SiC paper was then carried out. Twin-jet electropolishing was performed on the discs using an acetic acid:perchloric acid (92:8 v/v %) solution at 42 V. Investigations were performed using a FEI Tecnai F30 FEG instrument, operating at 300 keV.

3.8 Digital image correlation

Digital image correlation (DIC) allows the strain at the surface of a specimen to be mapped, by computation of the displacement of surface features occurring between images taken at different stages of deformation [141]. The length-scale at which the strain is calculated therefore depends on the magnification of the images used, and requires that the images contain features of a suitable size. Recently, Di Gioacchino et al. have developed a method to conduct DIC at the microstructural scale, with imaging performed in the SEM [142]. In this approach, a dense and random population of gold particles are created on the specimen surface, which when imaged
in SEM-BSE mode provide a high contrast speckle pattern which is suitable for DIC. With 50-100 gold particles per $\mu$m$^2$ and a typical particle size of 50-150 nm, sub-micron resolution DIC may be achieved.

In order to observe the influence of existing deformation features on the evolution of strain following a path change, DIC experiments have been conducted on the material following 20% cold rolling. Small flat tensile specimens were machined to allow straining along the cold rolled plate normal direction, with the specimen geometry illustrated in Figure 3.4. The specimen surface was polished to a colloidal silica finish as described previously, to allow EBSD scans to be conducted on a region of the gauge section of the specimen. From these EBSD scans a region of interest was identified for the investigation by DIC.

Images for DIC were obtained according to the method described by Di Gioacchino et al. as introduced above; full explanation of the experimental procedures and apparatus are described within this reference [142]. In summary, a continuous layer of gold nano-particles, approximately 50 nm thick, is sputtered onto the specimen surface. The gold layer is then ‘remodelled’ to form isolated gold particle clusters by heating to 280 °C in an environment containing water vapour for one hour (the agglomeration of the gold particles is likely to be driven by the reduction of the total gold particle surface area and gold-substrate surface area). Kinetically the process is assisted by capillary condensation of the solvent, which has been predicted to create attractive forces between nano-particles [143].
A typical SEM BSE image of the specimen surface following gold remodelling is shown in Figure 3.5. SEM BSE images were taken of the region of interest in the rolled condition and following tension to 1% and 5% elongation, where straining was performed at a rate of 20 µms⁻¹.

![SEM BSE image of the surface following gold remodelling](image)

Figure 3.5 SEM BSE image of the surface following gold remodelling

A review of the numerical treatment involved in two-dimensional image correlation has been provided by Pan et al., and can be referred to for further detail [144]. To undertake the image correlation, each image is subdivided into square subsets. The position of each subset, rather than the position of an individual pixel, is tracked at subsequent deformation stages. This is because the group of pixel values can be more reliably tracked than a single pixel value, as there may be several identical pixels within a small area.

At the centre of each subset is the point to be tracked. One complication to DIC is that in addition to a translation of each subset due to deformation, there is also a change in shape of the subset, thus it is necessary to apply a 'shape function' to the analysis. A number of algorithms have been developed for both the cross correlation and the shape functions correction, and these are summarised in the review by Pan et al. [144].
The image correlation analysis was carried out using the DaVis imaging software from LaVision GmbH [145]. The subset size used in the analysis allowed the calculation of approximately 30 displacement vectors per \( \mu \text{m}^2 \). Here the results are represented in terms of the maximum in-plane shear strain component, which is defined by Equation 3.1, where \( \varepsilon_{xx} \) is the strain along the loading direction, \( \varepsilon_{yy} \) is the strain along the normal in-plane direction and \( \varepsilon_{xy} \) is the in-plane shear.

\[
\varepsilon_{xy}^{(\text{max})} = \sqrt{\left(\frac{\varepsilon_{xx}-\varepsilon_{yy}}{2}\right)^2 + \varepsilon_{xy}^2}
\]  

Equation 3.1

Digital image correlation experimental work and data analysis were conducted in collaboration with Fabio Di Gioacchino, PhD candidate at The University of Manchester.

3.9 Stress corrosion cracking tests

SCC investigations have been performed on the material in the 20 % cold rolled condition. Slow strain rate tests have been conducted on miniature round tensile specimens in order to study the initiation of cracks from a smooth surface. Additionally, the SCC propagation behaviour of the material from a pre-existing sharp crack has been investigated through the use of high-cycle fatigue pre-cracked CT specimens. All SCC tests were conducted at the laboratories of Serco Technical Consulting Services, near Warrington, England.

3.9.1 Environment

The water chemistry specification is given in Table 3.3; tests were conducted in hydrogenated water containing 2 ppm Li (as LiOH), additionally anionic impurities were monitored to ensure a concentration below the levels indicated throughout the tests. The electrochemical potential of each specimen was monitored by an external
reference electrode, and maintained at a value of around -800 mV versus standard hydrogen electrode (SHE). The test temperature was 300 °C during the SSRT tests, and 288 °C during the crack growth tests.

![Table 3.3 Water chemistry for SCC testing](image)

<table>
<thead>
<tr>
<th>LiOH ppm</th>
<th>H₂ cc/kg H₂O</th>
<th>SO₄²⁻ ppb</th>
<th>Cl⁻ ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>33</td>
<td>&lt; 5</td>
<td>&lt; 5</td>
</tr>
</tbody>
</table>

3.9.2 Slow strain rate tests

3.9.2.1 Specimen details

The slow strain rate tests were conducted on under-sized tensile specimens of the M5 geometry described in Table 3.2 and Figure 3.2. Specimens were manufactured from the cold rolled material to allow straining along the normal direction. Each specimen was ground longitudinally using p2500 silicon carbide paper to minimise any small circumferential scratches which may have been present from the machining process.

3.9.2.2 Pre-test EBSD data collection

For each specimen prior to testing, a flat area was created along the entire length of the specimen gauge section, which measured approximately 1 mm in width. To achieve this, material was gently removed from the specimen using p2500 silicon carbide abrasive paper. Subsequently the flat area was polished using diamond suspension and colloidal silica as described previously for EBSD specimen preparation. Throughout all stages care was taken to ensure that an even amount of material was removed along the entire length of the specimen to prevent the introduction of a notched region which may cause premature necking of the specimen during straining. Microstructural data was subsequently collected from the polished region of each specimen by EBSD, scans were located towards the centre of the gauge length.
3.9.2.3 Test procedure

Prior to testing each specimen was cleaned with acetone in an ultrasonic bath, before loading into the autoclave. Tests were conducted under constant cross-head displacement rate. The nominal strain rate applied was $1.0 \times 10^{-7} \text{s}^{-1}$ for 100 hours to approach the yield strength of the specimen. Subsequently the nominal strain rate was reduced to $1.0 \times 10^{-8} \text{ms}^{-1}$ for the remainder of the test.

3.9.3 Crack growth testing

3.9.3.1 Specimen details

Crack propagation tests were conducted on ASTM standard 12.5 mm (0.5 T) compact tension (CT) specimens. Specimens have been tested in three orientations with respect to the cold rolling process; these are the S-L, L-S and L-T orientation as designated by ASTM standard E399, as previously illustrated in Figure 2.23 [81]. Specimens are pre-cracked by high-cycle fatigue in air to obtain a sharp crack.

3.9.3.2 Test procedure

Experiments were conducted according to the standard approach for crack growth testing which has been developed at Serco, which has been described by Tice et al. and Nouraei et al. [73, 74]. Prior to loading in the autoclave, specimens were cleaned in acetone in an ultrasonic bath. The tests progress through several stages of triangular and trapezoidal wave-form loading, of decreasing severity prior to the application of constant load; this process is designed to transition the transgranular fatigue pre-crack to an intergranular path. The details of the various loading stages are summarised with the test results. Throughout testing the crack length was monitored by reversing DCPD operating at 6 A. Following testing each specimen was sectioned into two halves. One half of the specimen was opened using high-cycle fatigue in air to allow investigation of the fracture surface.
3.10 EBSD analysis

In addition to the use of TSL-EDAX OIM analysis software for EBSD data analysis, bespoke routines have been developed with the use of the Python Programming Language [139, 138]. The following provides the basis for performing calculations from orientation data and describes the microstructural analyses performed in the current study. Extensive EBSD mapping of the cold worked material has been conducted. Scans at a resolution (step size) of 0.25 µm were conducted on the rolling-transverse (RT) plane and the rolling-normal (RN) planes. The scan step size was chosen as suitable to identify many of the larger bundles of deformation twins formed whilst allowing a significant number of grains to be covered. In total 20 scans measuring 450 µm × 450 µm were conducted in each of the two planes. Analysis routines have been developed, programmed in the Python language [139] to investigate two parameters; the directionality of the point-to-point misorientation within deformed grains and the trace angle of deformation twins intersecting the sample surface.

3.10.1 Orientation calculations with quaternions

At each point in the EBSD scan, the orientation of the sampled crystal volume is described with respect to the specimen reference frame. The orientation as determined by the commercial EDAX OIM EBSD software is returned as three Euler angles, $\phi_1$, $\Phi$, $\phi_2$, which are defined according to the convention of Bunge to be rotations about the specimen $z$, $x$, and again $z$ axes. Performed in sequence these three rotation will bring the specimen reference frame into coincidence with the crystal reference frame [138]. The product of three rotation matrices, composed from the Euler rotations and given by $(R(\phi_1, z), R(\Phi, x), R(\phi_2, z))$, may be used to calculate a rotation. Alternatively it is possible to represent a rotation in the form of a unit quaternion, $\mathbf{q}$. The quaternion form of a rotation may be expressed in terms of a rotation of angle $\omega$ about an axis $\mathbf{r}$, as given in Equation 3.2.
The quaternion description of rotations has been used due to several advantages over the use of rotation matrices. As described by Salamin, quaternions are more efficient for computation; the composition of each rotation requires that 16 multiplications and 12 additions be performed where quaternions are used, in comparison to 27 multiplications and 18 additions where matrices are used, furthermore each quaternion requires the storage of four numerical values whereas each matrix requires nine values are stored \[ [146] \]. Where large EBSD data sets are used, containing potentially hundreds-of-thousands of individual data points, any reduction in computational and storage demand becomes a significant advantage. An additional advantage of the use of quaternions relates to the ease with which orthogonality, which may be lost due to accumulated computational errors, can be restored \([146]\).

Much of the microstructural investigation using EBSD data is based on the calculation of the rotation between different data points; for example the definition of a grain boundary will be typically be linked to a rotation angle between adjacent points which exceeds some critical value, commonly 10 or 15° \([147]\]. Taking a pair of orientations which are produced by two rotations \(q_A\) and \(q_B\) with respect to the sample reference frame, the single rotation which is equivalent to rotation \(q_A\) followed by rotation \(q_B\) is defined by the quaternion product given by Equation 3.3 \([148]\).

\[
q = q_B q_A = \left( \begin{array}{c} q_0^B q_0^A - \bar{q}_A^B \cdot \bar{q}_A^A \\ q_0^B \bar{q}_A^A + \bar{q}_B^A q_0^A + \bar{q}_B^B \times \bar{q}_A^A \end{array} \right) \quad \text{Equation 3.3}
\]

In a similar manner, the rotation between two orientations, which is commonly referred to as the misorientation in EBSD metallurgy studies, is given by the quaternion product of the inverse (or conjugate) of the first rotation, \(q_A^{-1}\) and the
second rotation $q_B$. The conjugate of the quaternion is given by Equation 3.4, and the calculation of the misorientation, $\Delta q$, given by Equation 3.5. Note that the misorientation calculated from this second equation is given in the reference frame of the first orientation [148]. It is therefore possible to determine the rotation between the two points as a misorientation angle about a crystallographic axis.

$$q^{-1} = \begin{pmatrix} q_0 \\ -\bar{q} \end{pmatrix}$$ \hspace{1cm} \text{Equation 3.4}

$$\Delta q = q_B q^{-1}_A = \begin{pmatrix} q_0 \\ \bar{q} \end{pmatrix} = \begin{pmatrix} \cos \left( \frac{\omega}{2} \right) \\ \sin \left( \frac{\omega}{2} \right) \end{pmatrix}$$ \hspace{1cm} \text{Equation 3.5}

3.10.2 Crystallographic misorientation analysis

During deformation, crystal rotation is caused by the multiplication and movement of dislocations. It is possible to assess the lattice rotation from EBSD misorientation analysis; frequently a parameter known as the kernel average misorientation (KAM) is used. This KAM parameter is calculated for each point by the average value of misorientation with all the surrounding point. In the current investigation it is of interest whether misorientation values vary with analysis direction; i.e. is the point-to-point misorientation value along a certain axis higher than along another axis.

Figure 3.6 and Equations 3.6 – 3.8, which are adapted from publication by Kamaya [149], describes the calculation method. For the point $P_0$, the directional average misorientation parameters $M_X$ and $M_Y$ are calculated respectively as the mean value of the adjacent points horizontally and vertically. The local average misorientation, $M_L$, is the mean value of all four adjacent points. The value of misorientation has been shown to be sensitive to the step size used for the analysis, and therefore should be kept constant for an accurate comparison. Additionally, the use of a larger step size will typically result in a larger misorientation value, thereby reducing the significance of measurement error [149].
3 Experimental

Figure 3.6 a) local average misorientation (M_L), b) directional average misorientation (M_X and M_Y) calculation approach (adapted from Kamaya [149])

\[ M_L(P_0) = \frac{1}{4} \{ \beta (P_0, P_1) + \beta (P_0, P_2) + \beta (P_0, P_3) + \beta (P_0, P_4) \} \]  
\[ \text{Equation 3.6} \]

\[ M_X(P_0) = \frac{1}{2} \{ \beta (P_0, P_{X1}) + \beta (P_0, P_{X2}) \} \]  
\[ \text{Equation 3.7} \]

\[ M_Y(P_0) = \frac{1}{2} \{ \beta (P_0, P_{Y1}) + \beta (P_0, P_{Y2}) \} \]  
\[ \text{Equation 3.8} \]

3.11 Image analysis – line parameterisation

The Radon transform, a function described by the equation below can be used to detect and parameterise a straight line in an image in terms of its angle of inclination (\(\theta\)) and perpendicular distance (\(r\)) from the origin.

\[ R(r, \theta) = \iint f(x, y) \delta(r - x \cos \theta - y \sin \theta) \, dx \, dy \]  
\[ \text{Equation 3.9} \]
The function $f$ transfers points in the image domain, $(x,y)$, to the parameter domain $(r,\theta)$. An ideal straight line in the image domain $(x,y)$ correlates to a point maxima in the $(r,\theta)$ domain, from which the line parameters are obtained; $\theta$ being the inclination of the line and $r$ being the perpendicular distance of the line from the image centre [150]. The final term in the equation is the Dirac delta function, $\delta$. Figure 3.7 illustrates the parameterisation of an image containing three lines, from the transform it is possible to determine that the three lines are at $-45^\circ$, $-30^\circ$ and $80^\circ$ to the horizontal.

![Figure 3.7 Illustration of the Radon transform for parameterisation of straight lines: a) an image, b) the transform of the image](image)

The Radon transform has been previously used to study the alignment of dislocation boundaries in deformed aluminium [151] and has been used in the current work to study the alignment of the deformation twin traces in boundary maps produced from EBSD data.
4 Material Characterisation

4.1 Introduction

The first stage of the investigation was to characterise the material in the as-received annealed condition, and subsequently in the 20 % cold rolled condition. The aim of the work was to obtain a representative understanding of how the material deforms, to allow this to be later correlated to the SCC susceptibility. Effort has been made to characterise the deformation heterogeneity at the microstructural scale, as this is anticipated to be influential to the occurrence of IG failure [99, 78, 98]. Additionally, evidence for the directionality of the deformed microstructure has been investigated in response to observations that the SCC crack growth behaviour of cold rolled austenitic stainless steels is often anisotropic [6, 70]. Furthermore, the characteristics of the grain boundaries within the material have been investigated.

4.2 Optical microscopy

Optical microscopy has been used for the determination of the basic microstructure, both in the annealed and 20 % cold rolled material conditions.

4.2.1 Phases

The content of residual ferrite in the material is estimated from image analysis following electrolytic etching with sodium hydroxide (NaOH) to be less than 0.5 %. Elongation of the second phase with the plate hot rolling direction was noticeable in some of the larger grains, but generally was not discernible. A typical area from the annealed material is shown in Figure 4.1 to illustrate the typical ferrite distribution. Both the original and contrast-threshold images are shown, the hot rolling direction is in the image vertical direction. Therefore, the material in the annealed condition is
composed of austenite, with negligible second phase content. The effect of the small amount of ferrite on the properties of the alloy is expected to be very minor.

4.2.2 Grain structure

Areas of typical grain structure for the annealed material are shown in the micrographs included in Figure 4.2. The oxalic acid etch used in part a) reveals grain boundaries and annealing twin boundaries; it may be noted that the vast majority of grains contain at least one annealing twin. With nitric acid etching only the grain boundaries are revealed, as in part b) of the figure. It was common for the grain size distribution to be somewhat bimodal, with groups of smaller grains (50-100 µm diameter) separating larger grains (250-500 µm diameter).

A similar image illustrates the grain structure following cold rolling in Figure 4.3 a). For comparison with the annealed microstructure the images are from the same plane of the material. As expected, the grains appear less equiaxed with elongation toward the rolling direction. Deformation bands may also be seen in a number of grains, as shown in part b) of Figure 4.3.
4.2.3 Grain size estimation

The basic grain dimensions have been measured for the material in the annealed condition and following 20\% reduction by cold rolling, by the linear intercept method [132]. The results are presented in Table 4.1. The mean grain diameter calculated for the annealed material is 133 µm, a similar value of 137 µm is obtained for the cold rolled material. The annealed grain shape is close to being equiaxed, despite some plane to plane variations in the dimensions. Following cold rolling the grains are elongated toward the rolling direction, with the largest aspect ratio seen in the rolling-normal (RN) plane.
Table 4.1 Grain sizes determined for the annealed and cold rolled material conditions

<table>
<thead>
<tr>
<th>Plane Direction</th>
<th>RT plane</th>
<th>RN plane</th>
<th>TN plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT Plane</td>
<td>R 144</td>
<td>R 123</td>
<td>T 130</td>
</tr>
<tr>
<td>RN Plane</td>
<td>T 142</td>
<td>N 123</td>
<td>N 135</td>
</tr>
<tr>
<td>TN Plane</td>
<td>T 143</td>
<td>N 123</td>
<td>N 133</td>
</tr>
<tr>
<td>Grain size (µm)</td>
<td>1.01 : 1.00</td>
<td>1.00 : 1.00</td>
<td>1.00 : 1.04</td>
</tr>
<tr>
<td>Annealed condition</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cold rolled condition</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>168 1.26 : 1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>133 1.53 : 1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>158 1.39 : 1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.3 Grain boundary character

In a variety of materials and environments, it has been reported that high angle grain boundaries (HAGBs) are less resistant to intergranular corrosion or IGSCC than low angle grain boundaries (LAGBs), where the misorientation angle is typically defined as being less than 10 or 15° [152]. Furthermore, annealing twin boundaries (ATBs) have been reported to be extremely resistant to degradation [153, 154]. Therefore, the grain boundary character distribution of the annealed condition material has been investigated through the use of EBSD. A typical area of the microstructure with HAGBs, LAGBs and ATBs delineated by black, green and yellow lines respectively is shown in Figure 4.4. The relative proportion of these three types of boundary, by length fraction is illustrated in the chart (based on an area of material ~ 12 mm² and a scan step size of 2 µm). The vast majority of grain boundaries have a misorientation angle exceeding the used threshold of 10°, in fact LAGBs account for only 0.04% of the total. The material contains a very high number of annealing twins, resulting in the total length of ATB exceeding the total length of HAGB. The ATB fraction of the total boundary length is 53.1%. 

4 Material Characterisation
4.4 Deformation Microstructure

Initial investigation of the deformation microstructure was carried out in the SEM operating in back-scattered mode, using electron channelling contrast imaging (ECCI). As a number of recent publications have described [137, 155, 136], the technique is capable of producing microstructural images with a relatively high spatial resolution, therefore providing a convenient supplement to TEM. As the ECCI images in Figure 4.5 and Figure 4.6 respectively show, the annealed material has no significant sub-grain scale structure whereas following cold rolling the microstructure is characterised by a high density of planar deformation bands. Large area ECCI investigation found that regular planar deformation features were present in 65-75 % of the grains, although the technique is not able to discriminate between the various forms of deformation band which may form in austenitic stainless steels.

Subsequent analytical TEM investigation produced similar observations of a high density of planar deformation features within the austenite grains, as illustrated in Figure 4.7. Selected area diffraction investigation confirmed the presence of deformation twinning (an example of which is included in the appendix), although it is possible that ε-martensite bands were also present. No α’-martensite was confirmed during the TEM investigations of the 20 % cold rolled material.
Figure 4.5 SEM BSE/ECCI image of the annealed material, showing three grains.

Figure 4.6 SEM BSE/ECCI of the deformed microstructure showing clear planar deformation bands in the 20% cold rolled material.

Figure 4.7 TEM images of deformation twins within an austenite grain, specimen tilted along [110] zone axis.
Characterisation of the cold rolled material by EBSD also revealed a dense population of planar deformation bands in a large number of grains. The EBSD IPF and IQ maps for a section of the RN plane of the 20 % cold rolled material are shown in Figure 4.8 parts a) and b), respectively. Clearly from the IPF map, deformation bands have formed which have a very different orientation from the parent grain. The IQ map is overlaid with boundaries which delineate points determined to satisfy the coherent twinning orientation relationship (within a range of 5°). Comparison of the two images demonstrates that the deformation bands (green) are in most cases in the Σ3 orientation with the parent grain (magenta). This tends to suggest that the deformation bands are large bundles of deformation twin lamellae.

![Figure 4.8 EBSD maps produced from the RN plane of the 20 % cold rolled material: a) IPF map, b) IQ map with boundaries satisfying Σ3 ± 5° orientation relationship delineated in yellow (IPF coloured with respect to ND, see Figure 3.3 for the IPF key)](image)

4.5 Deformation at grain boundaries

For the study of IGSCC any modification of the grain boundary structure which occurs at the grain boundary due to deformation may be significantly important. Due to the strong tendency for the deformation by localised shear bands, the arising intersections between the bands and grain boundaries will represent sites of high strain at the grain boundaries. Damage to the structure of the grain boundary, such as the creation of holes could also occur.
The images in Figure 4.9 and Figure 4.10 are complimentary ECCI and TEM images respectively, of deformation twins interacting with grain boundaries. In part a) of each figure a grain which has undergone significant deformation, including extensive localisation into bands, is adjacent to a grain which has undergone much less deformation. The incompatibility between the behaviour of the bulk grains necessitates high local strain in a volume of material adjacent to the grain boundary. This is seen in both images as the region of brighter contrast adjacent to the grain boundary in the upper grain of Figure 4.9 and as the high density of tangled dislocations adjacent to the boundary in Figure 4.10. Image b) of each two figures shows a slightly different situation, where both grains have deformed planarly, although to different degrees. Both the ECCI image and the TEM image show that the grain boundary itself is stepped, and this may be associated with the intersection of deformation bands. However it is seen that the strain is accommodated at the boundary, and no voids or holes were observed during the high resolution TEM observations.

Figure 4.9 SEM BSE/ECCI images showing the interaction of deformation bands with grain boundaries.
4.6 Anisotropy of the deformation microstructure

Processes which plastically deform a material such as rolling are directional. As a result, the microstructure of the deformed material will be in some way directional, and consequently the properties of the formed component may be anisotropic. As deformation is the factor inducing SCC susceptibility, the possibility of the preferential alignment of plasticity artefacts being the origin of the anisotropic SCC behaviour has been explored.

4.6.1 Point-to-point misorientation

Grain rotations which occur as a result of dislocation multiplication and movement during deformation are quantifiable by EBSD analysis. Areas of high misorientation necessarily contain a large number of stored dislocations to induce the curvature in the lattice [156]. A number of recent investigations into SCC have used the KAM approach (as described in section 3.10.2) to explore the link, if any, between susceptibility and the local misorientation. In the current work this has been extended to include the directional misorientation analysis which is also described in section 3.10.2.
The EBSD data from the RN plane has been analysed. The analysis used a step size of 2 \(\mu m\), coarsened from the scan data step size of 0.25 \(\mu m\). Only point-to-point misorientation values of 5° or lower were included in the analysis, higher values were considered to represent grain boundaries. For illustration, Figure 4.11 shows the IPF map from one EBSD scan area, and the corresponding local average misorientation, averaged x-direction and averaged y-direction misorientation plots. The area is typical of all regions in that the highest values of misorientation (\(\theta > 2^\circ\)) occur adjacent to grain and annealing twin boundaries. The majority of points within a grain are surrounded by points with a low (\(\theta < 1^\circ\)) deviation from their own orientation.

The scan x-axis corresponds to the rolling direction, the y-axis to the normal direction; hence the parameters \(M_x\) and \(M_y\) correspond to misorientation along the rolling and normal direction, respectively. From inspection of parts c) and d) it is possible to see that there are spatial variations in the distribution of local misorientation value between the rolling direction (c) and the normal direction (d). Predominantly, the highest misorientation values are observed adjacent to boundaries which are near perpendicular to the analysis direction. This trend is not entirely surprising, although suggests that the crystal rotation in the near grain boundary region occurs along an axis close to the grain boundary trace. In order to quantify any differences between the parameters \(M_x\) and \(M_y\) the frequency distribution and cumulative frequency distribution of the calculated misorientation values, for the entire set of EBSD data, are plotted in Figure 4.12 and Figure 4.13 respectively.
The frequency distributions of the directional average misorientation parameter along the rolling and normal directions are similar. There is a slight tendency for misorientation values calculated along the normal direction to skewed toward higher values. Based on this trend, and the discussion of Figure 4.11 in the preceding paragraph, it is possible to suggest that the crystal rotation adjacent to grain boundaries which are close to horizontal in the scan is slightly more intense. The implication is that boundaries which are aligned more closely with the rolling plane are associated with a region of higher dislocation content.
4.6.2 Deformation twin lamellae trace orientation

The second aspect of the deformation induced microstructure which has been investigated for any preferred alignment with respect to the cold working process is the orientation of the surface traces of deformation twins, as identified from the EBSD. Twinning in FCC materials is described by a 60° rotation of the lattice about a
<111> crystallographic axis, and so the boundaries of the twinned volume may be identified from the orientation data [24]. An example of this has previously been shown in Figure 4.8. The analysis quantified the angle made between the most prominent deformation twin trace in a grain, and the rolling direction for the bulk cold rolled material. Data from both the RT plane and the RN plane was used, with the trace angle for more than 150 grains with confirmed deformation twinning analysed in each plane. The analysis utilised of the Radon Transform, as described in Section 3.11. For each grain which was investigated, an image was produced showing only the deformation twin boundaries, which was then used in the analysis.

In the literature, a previous study of the orientation of deformation twin lamellae in cold rolled copper has been reported by Leffers and Van Houtte [157]. This study involved manual measurement of the traces of the twin lamellae observed by TEM. Comparatively, approaching this study with EBSD combined with the Radon Transform for image analysis presents a number of advantages. Most significantly, the angular error of the measured trace is significantly reduced by the use of the Radon Transform algorithm. Secondly the entire data analysis process can be automated, again removing user error and additionally making the process more time efficient. Compared to a TEM study, the number of grains which can be sampled is vastly increased allowing better statistics to be collected, and as a final advantage is experimentally is much simpler. The main disadvantage of the current analysis is that for each grain the statistics on only the dominant deformation twinning system are extracted, where in some cases two twinning systems may have been activated within a single grain. This is not an inherent weakness in the approach however, and could be remedied by distinguishing between the two twinning systems and performing the alignment analysis separately on twin boundary maps for the two systems.

The result of this analysis, showing the frequency of grains against the angular deviation of the twin lamellae from the rolling direction is shown in Figure 4.14. A clear trend in the twin lamellae trace alignment is observed in both planes. For the
RT plane, there is a tendency for the traces of the twin lamellae to be oriented towards a high deviation from the rolling direction. In the RN plane the relationship is reversed; the twin lamellae are aligned more closely with the rolling direction.

![Graphs showing deviation of twin lamellae orientations](image)

**Figure 4.14** Analysis of the deviation from the deformation twin trace and the rolling direction; a) rolling-transverse plane and b) rolling-normal plane.

The orientation distributions are in general agreement with those measured by Leffers and Van Houtte through TEM investigations on brass rolled to 40% reduction [157]. Although the number of grains investigated was fewer in this previous study, the third plane (the TN plane) was also investigated. It was found that the trace orientation of the twin lamellae tended to be towards the transverse direction. The plane of the deformation twin lamellae is therefore likely to be found to be close to the macroscopic RT plane.

### 4.7 Texture evolution

The orientation distribution functions (ODFs) shown in Figure 4.15 fully describe the texture measured in the annealed and cold rolled condition materials. There are no strongly favoured orientation components in the annealed material. Following cold
rolling the emerging texture components are in agreement with the well established FCC rolling texture [44]. The observation of orientation clustering along both the $\alpha$-fibre and the $\beta$-fibre is in agreement with other studies of the rolling texture evolution in austenitic stainless steels at relatively low levels of reduction (less than 50%) [47, 48, 40].

Figure 4.15 ODFs for the annealed and 20% cold rolled conditions; top and bottom respectively.
4.8 Discussion and summary

The austenitic stainless steel under investigation has been characterised in the annealed condition as being almost entirely a single phase material. The grain boundaries are almost entirely high angle (misorientation $>10^\circ$). It is also noted that the material contains a high density of annealing twins, with most grains containing at least one coherent twin boundary.

Following cold rolling to a reduction in thickness of 20% the formation of extensive deformation bands is observed in the majority of grains. Crystallographic orientation analysis of these deformation bands suggests that they are predominantly deformation twins, although other deformation structures are possibly also present. A recent investigation identified strain induced martensite formation during the deformation of a grade 304 stainless steel at cryogenic temperatures, but not during room temperature deformation through neutron diffraction [158]. Additionally the activation of deformation twinning has been observed to occur at a strain of around 0.08 in low-moderate SFE FCC alloys, including austenitic stainless steels during ambient temperature deformation, with the occurrence of strain induced martensite formation at much higher strains [28, 29, 38]. Therefore the observation of deformation twinning in the current 20% cold rolled material is in agreement with the literature.

High resolution investigation of the intersection of deformation bands with grain boundaries found no evidence of void formation. The local stain was accommodated by a 'bloom' of dislocations in the opposite grain, or in some cases it appeared that the grain boundary had sheared.

A small variation in the crystallographic misorientation when measured along the normal direction compared to the rolling direction was observed. The lattice rotation within the grain interior was typically low, with the higher values of misorientation occurring adjacent to the grain boundaries. This is typical of KAM-type distributions in deformed materials, and results from the additional crystal rotation which is
needed to maintain geometric compatibility between two differently deforming grains [149]. Physically a larger crystal rotation is accommodated by the storage of a higher density of dislocations, termed geometrically necessary dislocations (GNDs) [156, 159]. It is possible that a higher density of stored dislocations in the volume of material adjacent to the grain boundary would enhance SCC susceptibility, for example by allowing faster diffusion or oxidation to occur, and this may indeed explain to some extent the increased susceptibility to IGSCC with increasing degree of cold work in the current material-environment system. However, as the distribution of misorientation calculated along the plate normal and rolling directions is very similar, this is in itself unlikely to explain the anisotropy of susceptibility which has been observed for SCC in cold rolled materials [70, 6].

The alignment of the trace which deformation bands made with the RT and RN plane has been quantified. This analysis was performed from EBSD, where it is possible to identify the deformation bands from the parent-twin orientation relationship. It was found that the deformation twin bands had a tendency to be aligned towards the rolling (RT) plane, which is in agreement with a previous study of twin lamellae alignment in rolled brass [157]. Twin deformation bands have previously been identified as possibly playing an important role in the decreased resistance of the cold worked material to SCC [31]. It is therefore possible that the alignment of the deformation twin bands in the material could contribute to the anisotropy of the SCC response of the material by some modification of either the mechanical or corrosion properties. This is to be explored in subsequent chapters.
5 Mechanical Testing

5.1 Introduction

The mechanical properties of the material have been investigated. Foremost, the hardness and yield strength of the cold rolled material has been determined to allow comparison with the threshold values for SCC reported in the literature. Various uniaxial extension tests incorporating different strain histories have been conducted on the as-received and cold rolled materials in order to determine the effect of the deformation history on the mechanical behaviour. These tests have been undertaken in order to explore the potential significance of mechanical property anisotropy on the directional variation of SCC susceptibility. Finally, digital image correlation has been used to directly observe the interaction between the pre-existing deformation microstructure from rolling and the evolution of strain during tensile loading.

5.2 Mechanical Properties

5.2.1 Hardness

The mean hardness of the annealed material is 133 H$_v$, with a slight variation in the value across the thickness of the plate producing a standard deviation of 7.9. For the rolled material a two-dimensional hardness scan was performed on the cross-section (TN plane), which is presented in Figure 5.1. Cold rolling increased the mean hardness to 315 H$_v$, however the values are scattered across a much wider range of 236 – 410 H$_v$. A strong variation in the measured value is observed over the normal direction of the plate; the hardest points (350 – 410 H$_v$) are observed near to the rolled surfaces, while the values measured are reduced towards the centre.
5.3 Tensile tests

A summary of the mechanical properties of the material, as determined from uniaxial straining is given in Table 5.1. Given are the Young’s Modulus, the yield strength (as 0.2% proof stress) and the ultimate tensile strength. At room temperature the tensile and compressive behaviour of the annealed material has been investigated. Additionally the tensile behaviour of the 20% cold rolled material has been recorded along the rolling, transverse and normal directions of the plate. Finally at room temperature, the tensile behaviour following compression to a true strain of 0.22 (equivalent to 20% reduction by rolling) has been measured. The final series of tests were conducted at 300 °C to gain accurate information on the mechanical properties at the temperature of SCC testing. These tests were also conducted on the rolled material with straining along the normal orientation; the same configuration also used for SCC slow strain rate testing.
Table 5.1 Tensile and compression properties summary

<table>
<thead>
<tr>
<th></th>
<th>Modulus (GPa)</th>
<th>Yield (MPa)</th>
<th>UTS (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Annealed material</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Tension</td>
<td>196</td>
<td>217</td>
<td>562</td>
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<tr>
<td>Compression</td>
<td>207</td>
<td>211</td>
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<td><strong>Cold rolled material</strong></td>
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<tr>
<td>Rolling</td>
<td>187</td>
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<tr>
<td>Normal</td>
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<td>462</td>
<td>646</td>
</tr>
<tr>
<td>Normal (300 °C)</td>
<td>143</td>
<td>359</td>
<td>491</td>
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<tr>
<td><strong>Following 20 % simple compression</strong></td>
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</tr>
<tr>
<td>Tension</td>
<td>150-160 (^{2})</td>
<td>~ 300 (^{2})</td>
<td>- (^{1})</td>
</tr>
</tbody>
</table>

5.3.1 Annealed material

The complete stress-strain curve for the annealed material in tension is shown in Figure 5.2. The same curve is compared with the behaviour of the annealed material in compression up to a true strain of 0.2 in Figure 5.3. The Young’s Modulus and yield behaviour match well for the forward and reverse loading directions. However, at a strain around 0.07 the two curves begin to diverge, as an increase in the hardening rate is observed in compression. This is presented more clearly in Figure 5.4, where the strain hardening rate behaviour is plotted. After initially decreasing, the strain hardening rate in compression does begin to increase after a strain of approximately 0.07. In tension this behaviour was not observed; the strain hardening rate decreases steadily.

The behavioural difference suggests that differences in the deformation modes are present between tension and compression. The increase in strain hardening rate

\(^{1}\)Test interrupted before UTS.
\(^{2}\)The linear elastic region of the curve was difficult to determine, as yielding commenced at a very low stress.
observed in compression is consistent with the observations of the behaviour of a range of low SFE FCC alloys made by El-Danaf [29] and Asgari [28]. These authors were able to correlate the onset of deformation twinning to the increase in hardening rate. The mechanical behaviour would suggest therefore that extensive deformation twinning takes place during simple compression, but does not during tensile extension.

![Figure 5.2 True stress – strain curve for the annealed material in tension](image)

**Figure 5.2 True stress – strain curve for the annealed material in tension**

![Figure 5.3 True stress – strain curves for the annealed material in tension and compression](image)

**Figure 5.3 True stress – strain curves for the annealed material in tension and compression**
5.3.2 Compression-tension behaviour

The tension behaviour of the material following compression to a true strain of 0.22 (20 % reduction in height) is presented in Figure 5.5. The observed behaviour; gradual yielding and a reduction in the flow stress is consistent with the Bauschinger effect, which has been discussed in section 2.2.6. The effect is an indication that directional back-stresses are created during compression, which then assist dislocation movement along the same slip systems in the reverse direction during the reversed loading direction [53].
Figure 5.5 True stress – strain behaviour for compression to a strain of 0.22 followed by tension to a strain of 0.10

5.3.3 Cold rolled material

5.3.3.1 Directional anisotropy of the rolled plate

The most striking characteristic of the tensile behaviour of the cold rolled material is the significantly reduced flow stress along the normal direction relative to the rolling and transverse directions. The yield stress measured along the transverse direction is 708 MPa, which corresponds to 1.5 times the yield stress determined along the normal direction (462 MPa). Additionally, from inspection of both Figure 5.6 and Figure 5.7, the amount of strain hardening immediately following yield is higher for the specimen tested along the normal rolling direction, suggesting that dislocation flow is easier at low stresses but this effect is quickly exhausted. The stiffness of the material has been reduced compared to the annealed condition in all orientations.
5.3.3.2 Comparison to the Bauschinger effect

The reduced yield strength and permanent softening of the material along the normal direction is reminiscent the Bauschinger effect shown in Figure 5.5. Therefore, in Figure 5.8 the tensile behaviour along the normal rolling direction is compared to the tensile behaviour following compression; both rolling and compression were conducted to 20 % reduction. The yield behaviour following compression is more
gradual than following rolling. However, following this initial transient phase the stress-strain behaviour observed becomes similar for the two situations, reaching a similar flow stress and hardening rate. The origin of the reduced yield strength in tension along the normal rolling direction is likely to be similar to the origin of the Bauschinger effect. In the compression-tension case the second stage of loading is a direct reversal of the first stage, and therefore the majority of the forward direction slip systems would be expected to be reused in the reverse direction. As rolling-tension does not correspond to a direct reversal of the strain direction, not all slip systems would be so easily reactivated; this perhaps explains the less gradual yield behaviour.

Figure 5.8 True stress-strain in tension for the 20% rolled material and material compresses to an equivalent reduction

5.3.3.3 Room temperature versus 300 °C

Finally the effect of temperature on the tensile stress-strain behaviour of the rolled material has been investigated. Straining was conducted at 300 °C along the rolling normal direction as this is the configuration used for SSR testing (chapter 6). The stress-strain curves at room temperature and at 300 °C are presented in Figure 5.9. The increase in temperature has decreased the yield strength by approximately 100 MPa and has also caused a reduction in the modulus from 180 to 140 GPa. The
5 Mechanical Testing

The elongation of the specimen is also reduced to around half of that obtained at room temperature.

![Graph showing true stress-strain relationship at room temperature and 300°C](image)

**Figure 5.9** True stress–strain in tension for the cold worked material at room temperature and 300 °C along the normal rolling direction

5.4 Digital image correlation

SEM based DIC has been used to quantify strain evolution during tensile loading in the material previously deformed by rolling. The purpose of this experiment was to observe the influence of pre-existing microstructural features on the magnitude and location of strain developed during tension. Firstly EBSD was used to identify a region where a grain containing significant planar deformation features is adjacent to a grain where less localised deformation had occurred. The microstructure of the region is shown in the EBSD IPF and IQ images in Figure 5.10 a) and b) respectively. A number of the deformation bands in the upper grain which are visible from the IQ map have been indexed as having a twin orientation relationship to the parent grain.

The specimen was subjected to a macroscopic tensile strain of 5% along the normal rolling direction. The distribution of maximum shear strain as a result of the tensile deformation is shown in Figure 5.10 c). Representation of the deformation as the in-
plane shear is appropriate to represent deformation occurring by crystallographic shear, additionally the lack of out-of-plane information (which is not collected by DIC) does not detract from the accuracy of the calculation \cite{142}. The strain distribution is heterogeneous, as particularly in the upper grain deformation has occurred on well defined, localised bands. The shear in the lower grain is more diffuse. Often the highest shear is linked to the impingement of deformation bands from the upper grain.

By comparison to the rolled microstructure, in the upper grain it is evident that deformation has occurred on the same slip system which was active during rolling. The local shear strain along these bands nears a value of 0.30, which is six times the macroscopic strain. By comparison the maximum shear strain during 7% tensile reloading along the normal rolling direction (IPF coloured with respect to ND, see Figure 3.3 for the IPF key)
elongation of an annealed stainless steel approaches a value of 0.20, as reported by Di Gioacchino et al. using the same method as reported here [142]. This provides evidence that shear is able to occur on previously operational slip systems at a much reduced applied stress, despite the strain path change not being a direct reversal when straining along the normal direction following rolling.

5.5 Discussion and summary

It is established that cold work leads to the reduced SCC resistance of austenitic stainless steels in conditions which are representative of good quality primary circuit PWR coolant. Hardness thresholds associated with SCC initiation of 240-250 H, and for propagation of 310-320 H, have been reported in the literature [4, 78]. Based on the mean hardness value measured for the 20 % cold rolled material (316 H, ) it would be expected that the material would be susceptible to cracking. Similarly a yield strength of 600 MPa has been reported to be necessary to produce sustained susceptibility [62, 6]. Assuming that the reported mechanical data is obtained from tensile straining along the rolling or transverse plate directions (which is likely due to the ease of specimen extraction versus the normal direction), then the cold rolled material also exceeds the threshold for susceptibility.

The tension behaviour of the annealed material differed from the compression behaviour in the sense that more work hardening occurred in compression. The increase in work hardening rate which occurs at a strain of ~ 0.08 is similar to previous studies which have correlated this behaviour to the onset of deformation twinning [28, 29].

Following cold rolling the tensile properties of the material are strongly anisotropic, with a yield stress of 462 MPa recorded when testing along the normal direction compared to values of 631 MPa and 708 MPa when testing along the transverse and rolling directions respectively (Figure 5.6). The measured texture in the rolled
material (section 4.7) is relatively weak, and therefore is not sufficient to explain the mechanical anisotropy observed for the cold rolled material.

Comparison of the tensile behaviour along the normal direction following rolling to the tensile behaviour following compression demonstrated that the behaviour in the two cases is quite similar (Figure 5.8). This is interpreted as an indication that yield in the second stage of deformation is assisted by stresses at the microscale, according to the generally accepted origin of the Bauschinger effect [53, 52, 56]. High resolution DIC has been used to provide evidence in support of this hypothesis, as the intense localisation of shear was observed in tension along slip planes which had previously been active during rolling.

As an additional remark from the DIC, it is possible to see that the intense shear in the upper grain causes deformation in the lower grain. The shear bands form an angle of ~90° to the grain boundary, and appear to active multiple slip systems in the lower grain, resulting in more diffuse shear. The ability of a grain boundary to transfer localised shear between grains has been identified as potentially significant for IGSCC resistance [100]. Where slip transfer is inadequate, high local stresses may develop and deformation of the grain boundary may be greater, both of which may play a role in intergranular failure [99].

Finally, the highest susceptibility of rolled material to SCC has been reported to be when loading is applied along the normal rolling direction. This corresponds to the lowest strength direction of the plate, as discussed above. Therefore where crack propagation tests have been conducted with CT specimens of different orientations in series loading, as for example by Tice et al., the higher SCC growth rates could be attributed to the additional plastic deformation which would occur in the specimen loaded along the normal direction [6]. However this does not explain the observations that the crack will deviate toward a preferential plane for crack growth irrespective of the loading direction, as reported by Arioka et al. [70].
6 Slow Strain Rate Testing

6.1 Introduction

Tensile slow strain rate tests (SSRT) have been performed on material cold rolled to 20 % thickness reduction, with straining along the normal direction. Prior to the SSRT, each specimen had been prepared to include a flat, highly polished section suitable for EBSD measurement and microstructural observations to be made. Following the SCC test, the same region of each specimen has been re-investigated to allow correlation of the known pre-test microstructure with any evidence of SCC. The aim of this approach was to identify the microstructural and deformation induced characteristics resulting in the highest probability of SCC initiation.

6.2 Susceptibility

Slow strain rate testing proved to successfully produce stress corrosion cracking in all specimens. The surface condition was found to strongly influence the local susceptibility to cracking. Typically the frequency and length crack formation was reduced within the polished section of the specimen. Outside of the region polished to a finish suitable for EBSD measurements to be undertaken, the specimen had been ground longitudinally to a finish of grade P2500 silicon carbide paper. Any severe circumferential grooves resulting from specimen manufacture, and the associated possibility of cracks developing at such geometric features were thus removed. The general surface condition therefore influences the processes involved in crack initiation, with increased polishing inhibiting crack initiation. The following discussion does not concern any cracks which formed on the unpolished areas.

Within the polished area of each specimen intergranular (IG) cracking was observed during post-test examination. In the first two tests, with durations of 918 and 764
hours, significant and extended intergranular cracks were observed. Additionally, limited transgranular cracking was observed for these first two tests. Only two IG cracks were identified in the third test and a single IG crack in the fourth test.

In Table 6.1 key details of each of the tests are summarised, with comments relating to the area of each specimen which had been previously by recorded using EBSD. None of the specimens were strained to failure, as the intention was to observe the locations of the first cracks to form. However the durations of the first two tests were significantly high as to allow the initiated cracks to grow to a length of several grain boundaries. The duration, and accordingly the specimen elongation of the final two tests were shorter. The intergranular cracks observed in these specimens were limited to a single grain boundary and considered to accurately represent initiation sites.

Table 6.1 Slow strain rate test details, observations relate only to the area recorded by pre-test EBSD

<table>
<thead>
<tr>
<th>Test</th>
<th>Comments</th>
<th>Max load (kN)</th>
<th>Elongation (%)</th>
<th>Duration (h)</th>
<th>EBSD Area (mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Significant intergranular initiation, some extending to crack growth. Instances of transgranular cracking. Most IG cracks 1-3 grain boundaries long, width &lt; 5 µm.</td>
<td>3.03</td>
<td>3.56</td>
<td>918</td>
<td>0.90</td>
</tr>
<tr>
<td>2</td>
<td>Significant intergranular cracking, many extending to crack growth. Instances of transgranular cracking. Largest IG cracks follow 10+ grain boundaries and &gt; 15 µm wide. The largest cracks were unsurprisingly found within the tensile necked region.</td>
<td>2.87</td>
<td>2.92</td>
<td>764</td>
<td>3.75</td>
</tr>
<tr>
<td>3</td>
<td>Two intergranular cracks, limited to the initiation stage.</td>
<td>3.25</td>
<td>2.05</td>
<td>478</td>
<td>5.25</td>
</tr>
<tr>
<td>4</td>
<td>One intergranular crack, limited to the initiation stage.</td>
<td>2.97</td>
<td>1.67</td>
<td>350</td>
<td>3.78</td>
</tr>
</tbody>
</table>
6.3 Oxide appearance

6.3.1 Surface oxide

Following extraction of each of the specimens from the test autoclave the surface was imaged in the SEM. The appearance of the surface of each specimen is typical of the two-layer oxide structure which forms on stainless steels during exposure to simulated PWR environment. In the secondary electron SEM image shown in Figure 6.1 an outer oxide layer of separate particles, commonly 0.5-2 µm in diameter (although occasionally as large as 5 µm) is seen on top of the inner oxide layer which covers the metal. Given the similarities with the surface oxide structures reported in the literature, for example by Terachi et al. [105], it is reasonable to assume that the outer oxide particles are Fe-rich and the inner oxide layer is Cr-rich.

![Image showing typical surface appearance of SSRT specimens](image)

Figure 6.1 SEM SE image showing the typical surface appearance of the SSRT specimens, the straining direction is horizontal, an IG crack is visible in the lower right of the image, arrows mark oxide cracks

An intergranular crack can be seen on the right side of the image. The inner oxide layer shows frequent narrow cracks, which are perpendicular to the horizontal loading direction, four of which are indicated by the arrows in the image. These cracks were commonly observed on all specimens, and were found not to penetrate into the underlying metal. They are likely to result from stress build-up in the brittle oxide layer as the alloy underneath deformed during the test. Similar cracking in the
inner oxide layer has previously been reported by Terachi et al., who also noted that these cracks would not necessarily be associated with a grain boundary in the underlying metal [105].

6.3.2 Oxidation of deformation bands

Previous studies have concluded that there are no differences in the types of oxide forming on the specimen surface and within stress corrosion cracks [105], additionally the formation of Cr-rich oxide along deformation bands of the same type as that of the Cr-rich oxide formed on the specimen surface has been reported [31]. It is generally accepted that in PWR conditions the Cr-rich oxide forms through ingress of oxygen into the metal, whilst Fe-ions are rejected into solution and re-precipitate to form the outer Fe-rich oxide.

The surface of each specimen was observed to be covered in dense oxide. However, other surfaces which would have had a shorter duration of exposure to the environment, such as crack flanks, showed preferential oxidation in certain areas. One example of this is shown in Figure 6.2. It is clear that the outer oxide particles are located preferentially along deformation bands; suggesting that Fe is able to rapidly diffuse along the deformation band and locally contribute to the oxide formed at the surface. This has previously been suggested by Lozano-Perez et al., who also demonstrated that oxidation and diffusion rates would be significantly increased along stressed deformation bands [31].
6.4  Surface crack morphology

6.4.1  Intergranular cracks

The majority of cracks observed were intergranular, as clearly shown in Figure 6.3. The shortest IG cracks observed were around 20 µm in length, ranging to several hundreds of microns. Within larger intergranular cracks secondary cracking was often observed, most likely occurring along deformation bands. An example of this is shown in Figure 6.4.
6.4.2 Transgranular cracks

A number of instances of short transgranular cracking have been observed. Comparison with the pre-test EBSD data has confirmed that these are always associated with deformation twin bands resulting from cold rolling. Instances of cracks having formed on deformation twin boundaries were observed only in the longer duration tests. As it has already been noted, the oxidation of deformation twin bands has been reported several times and so embrittlement leading to cracking is unsurprising. Compared to the intergranular cracks observed, the transgranular cracks are shallow and were not observed to easily propagate to a significant size.
6.5 Interpretation of crack initiation

6.5.1 Longer cracks

For the specimens from SSRT1 and SSRT2 the vast majority of intergranular cracks extend along several grain boundaries, with a number of cracks from SSRT2 following a network of boundaries with a total length in excess of 500 µm. Clearly the identification of a particular grain boundary segment or junction to designate as the initiation site for such cracks is not straightforward. Certain assumptions could be made, for example the widest section of the crack could be considered to be the most likely to have been the first section to crack, however there is no guarantee that such an assumption would be correct. Therefore with regard to identifying the most susceptible grain boundaries to SCC, cracks comprising two or more fully cracked grain boundaries are limited in their suitability.

Some useful observations are possible from these longer cracks however. The high frequency of long cracks formation suggests that once a crack has formed and extended to a full grain boundary, and the process shifts from one of SCC initiation toward propagation, the majority of grain boundaries are capable of cracking. The raised stress intensity and increased access of the environment to the alloy which are caused by the initial crack formation are likely to make the adjacent grain boundaries more likely to crack. It is fairly common for the longer cracks to have arrested where the crack follows from the susceptible boundary to an annealing twin boundary. This observation is not surprising given the widely reported 'special' characteristics of coherent twin boundaries of their resistance to various forms of intergranular corrosion and stress corrosion cracking [152, 160, 161].

6.5.2 Short cracks

Cracks which are limited to a single grain boundary or grain boundary junction will be considered to represent initiation sites. Across all specimens a total of 63
intergranular cracks were observed to have occurred within the area for which microstructural data had been collected. These particular cracks have been analysed.

6.6 Microstructure at points of crack initiation

6.6.1 The most susceptible boundaries

As summarised in Table 6.1, only 2 cracks were found to have initiated within the EBSD scanned region of the specimen during the third SSRT. Shown in Figure 6.6 are the SEM images, EBSD inverse pole figure (IPF) maps and EBSD image quality (IQ) maps for crack 1 (parts a), c) and e) respectively) and crack 2 (parts b), d) and f) respectively) from SSRT3. Both of the cracks are fully intergranular along high-angle grain boundaries, with crack 1 located on a single complete grain boundary and crack 2 following four short sections of grain boundary with a common large grain of the right half of the images.

The largest amount of EBSD mapping had been conducted on this specimen prior to the test, with an area of 5.25 mm²; corresponding to approximately 750 grains. Both of these cracks can therefore be considered to have occurred at a position of highly susceptible microstructure. Furthermore, the only crack observed in SSRT4 had a very similar microstructure. The EBSD data collected prior to SSRT4 was of an area of 3.78 mm², corresponding to around 550 grains.

It is immediately striking that the deformed microstructure, introduced by cold rolling, is significantly different in the grains either side of the cracked grain boundary. This is most easily seen from the EBSD pattern quality maps, Figure 6.6 e) and f) for cracks 1 and 2 respectively. In both cases the grain(s) to the left of the cracked boundary display dense planar deformation features and the grain to the right does not. In both cases the planar deformation features are indexed as deformation twins from the EBSD data.
In the figure the straining direction is horizontal. It is clearly seen that the failed grain boundaries are almost perpendicular to the loading direction, as would be expected. Additionally the deformation twins which intersect the failed boundaries also form a high angle to the direction of loading. A final observation from the Figure is that the widest part of crack 2 is adjacent to an annealing twin boundary.

6.6.2 Analysis

Across all of the specimens 63 short, isolated intergranular cracks were found. These have been categorised based on their location and the local microstructure. 61 of the cracks had initiated on high-angle grain boundaries (HAGB’s), where the misorientation across the grain boundary is defined as $10^\circ$ or greater. The remaining 2 cracks were located on annealing twin boundaries, both of which were adjacent to grains where heavy deformation banding had occurred.

The angle formed between each cracked high-angle grain boundary and the direction of load applied to the specimen has been recorded (to the nearest degree), and is presented in Figure 6.7. There is a strong tendency for the grain boundaries where crack initiation has occurred to form a high angle to the straining direction. As the straining direction corresponds to the rolling-normal direction of the plate, the failed grain boundaries lie close to the rolling plane.
Figure 6.6 Crack 1 (left column – a), c) and e),) and crack 2 (right column – b), d) and f),) found on specimen SSRT3. Post-test SEM images a) and b), pre-test EBSD IPF c) and d), pre-test EBSD IQ e) and f). The straining direction is horizontal. IPF coloured with respect to ND, see Figure 3.3 for the IPF key.
The cracked grain boundary in 41 of the 61 HAGB cracks observed is directly intersected by deformation twin bands. Of the remaining 20 HAGB cracks, 14 have occurred adjacent to an annealing twin boundary. Only the remaining 6 cracks were observed to be not intersected by deformation twin bands or an annealing twin boundary. Of the grain boundaries intersected by deformation twin bands, 14 were also intersected by an annealing twin boundary. This information is presented in Figure 6.8.
For the failed grain boundaries which are intersected by deformation twin bands, the angle which the surface trace of the deformation twin bands make with the straining direction has also been recorded (again to the nearest degree); Figure 6.9. Here, the surface traces of 85% of the deformation twin bands seen to interact with grain boundaries which are sites of crack initiation form an angle of 60-90° to the direction of strain. Within this range the mean deformation twin inclination is 75.3°, with a standard deviation of 7.5°.

![Figure 6.9 Frequency distribution of the angle between SSRT straining direction and deformation twin band (DT) trace for DT’s intersecting cracked HAGB’s.](image)

The most susceptible grain boundaries based on this analysis are orientated at a high angle to the direction of loading and interact with deformation bands which are introduced during cold rolling. A second microstructural configuration which leads to an increased probability of SCC initiation has also been identified; these are high-angle grain boundaries which are adjacent to an annealing twin boundary.
6.6.3 Annealing twins and crack initiation

6.6.3.1 Effect on adjacent grain boundaries

As almost 50\% of the short initiated cracks were in proximity of an annealing twin, further investigation of the role of annealing twin boundaries on the initiation of cracking is necessary. Two examples of HAGB cracks which are associated with an annealing twin in an adjacent grain are shown below in Figure 6.10. The pre-test EBSD inverse pole figure map in part b) corresponds to the cracked area in a). Similarly the EBSD IPF map d) corresponds to the same area shown in c). The annealing twin involved with the first crack is relatively narrow, around 15 \(\mu m\). The widest part of the first crack is aligned with the annealing twin, suggesting that this section of the grain boundary is where the crack would have initiated.

It is possible to propose an explanation for why such a microstructure would lead to crack initiation. The parent grain volume and the annealing twin volume have very different orientations and therefore would be expected to deform differently. As deformation proceeds the strength and coherency of the annealing twin boundary will resist shearing, and so it follows that adjacent ‘non-special’ boundaries will be deformed instead.

The differences in deformation occurring in the material either side of the annealing twin boundary is further illustrated in parts c) and d) for the second crack. On the crack interface slip steps are clearly visible for the volume above the annealing twin boundary, while there are no similar features below the twin boundary (note also the elongated oxide particles associated with the slip steps in contrast to the globular oxide particle on the lower half of the interface).
6.6.3.2 Resistance to cracking of annealing twin boundaries

The development of cracks on annealing twin boundaries was extremely uncommon, considering the density of annealing twins in the material. Evidence which demonstrates the resistance of annealing twin boundaries to cracking was in fact observed. An example of this is shown in Figure 6.11, where the same region of the material is represented by the pre-test EBSD IPF image in part a), the as-tested SEM image in part b) and the SEM image following oxide removal in part c). Indicated on the EBSD IPF are two boundaries of interest, one a HAGB and the other an annealing twin boundary. In part b) of the figure two cracks are visible, corresponding to each of these boundaries.
Following removal of the surface oxide layer it is clear that the crack has penetrated the metal significantly at the HAGB, as seen in part c). Very shallow cracking or oxidation of the metal at the annealing twin boundary is visible in part d) of the figure, which is an enlargement of the boxed region in c). It is worth noting that a small amount of metal will have been removed from the specimen surface with the oxide, and so the cracking of the annealing twin boundary may have been slightly more extensive. However the susceptibility of the HAGB is clearly much more significant. Under the fairly severe conditions of SSR testing, the variation in the strain between different grains most likely leads to the fracture of the surface oxide which covers any type of boundary. Thus the underlying metal is exposed to the environment, however, the structure of the interface strongly influences whether embrittlement and subsequent cracking of the grain boundary occurs.

![Figure 6.11](image)

Figure 6.11 The resistance of an annealing twin boundary to SCC, a) EBSD IPF map – pre-test, b) SEM image as-tested- oxide cracks, c) and d) SEM image following oxide removal – d) corresponds to boxed region in c). IPF coloured with respect to ND, see Figure 3.3 for the IPF key.
Confirmed SCC which actually penetrated the metal along the interface of an annealing twin was only confirmed in two cases. In both of these cases the location of SCC was associated with significant planar deformation; most likely deformation twinning based on the indexed EBSD orientation relationships. Figure 6.12 illustrates the position of one such crack from the SSR1 specimen. The pre-test EBSD IPF map is shown in part a) and the post-test specimen surface examined by SEM in following the removal of the surface oxide in part b). As no other cracks were found to correlate to annealing twin boundaries, this is an indication that the intersection of deformation bands with another boundary is extremely damaging.

![Figure 6.12 One of two cracks formed on an annealing twin boundary, at a site of intersection with deformation bands, a) EBSD IPF map - pre-test, b) post-test SEM BSE image following oxide removal. IPF coloured with respect to ND, see Figure 3.3 for the IPF key](image)

### 6.7 Section investigation

In addition to surface observations, the specimens from SSRT2 and SSRT4 have been sectioned parallel to the loading direction to allow investigation of the depth and path taken by cracks. By SEM investigation any feature with a depth < 2 µm was difficult to distinguish as a crack from other causes of surface roughness. All features in excess of this depth appeared to be intergranular. This suggests that transgranular cracks observed from the surface do not penetrate more than a few microns into the alloy.
Two cracks from SSRT2 are shown in Figure 6.13; part b) is a higher magnification image of the dominant tip of crack a). This crack is typical of many observed in this specimen, having reached a significant depth (150 µm) whilst remaining narrow (< 4 µm) in a region of low uniform macroscopic strain. The second crack, part c) occurred in the necked region of the SSRT specimen. At the surface the width of this crack is 70 µm and the tip is located at a depth is 320 µm from the surface. This crack is intergranular except for a small region which shows evidence of ductile failure, likely to be the result of a resilient ‘crack bridge’ which then failed under the increased strain as the specimen underwent necking. It is pertinent to note that this macroscopic localisation of strain is most likely attributed to the reduction in cross sectional area due to the development of such deep cracks, and consequently the higher strain in the area would drive further cracking. Despite the increased strain rate in this area the crack tip has remained intergranular and relatively sharp.
As for the surface observations, there is again evidence in Figure 6.13 that the cracking is favoured along grain boundaries with differing deformation microstructures. In part b) the channelling contrast effect possible in the SEM has been used to observe the regular planar deformation features in the lower grain. A similar observation can be made for part c); below the intergranular branch to the right, the grain below appears much more homogenous than the grain above, although not all grains show a clear sub-structure as-imaged here.
6.8 Discussion and summary

Slow strain rate testing of the 20% cold rolled material has successfully produced SCC initiation from an un-notched surface. The shortest test, with a duration of 350 hours and uniform extension of 1.67 % was sufficient to produce a susceptible grain boundary condition. In this test only one crack was found within the pre-polished and EBSD scanned area. However IGSCC was observed to be more frequent where the specimen surface was in the ground condition, and so a reduced exposure duration and extension would be required for IGSCC initiation. Therefore, even though the alloy is significantly cold worked in the bulk, any additional cold work which is limited to the surface layer is important to the SCC resistance. Removal of some of the damaged surface layer by polishing contributed to an increase in SCC resistance compared to the surface in the fully ground condition.

Where initiated cracks were observed on the boundary between two grains (rather than at a triple point, for example) the entire boundary was typically observed to have failed, suggesting that once the crack is initiated it rapidly extends to the entire boundary, as shown for example in Figure 6.11.

Crack initiation was preferred on grain boundaries forming a high surface trace angle with the tensile direction, as 60 % of the initiated cracks fell in the range of 70- 90° to the loading direction. During tensile loading it is predicted that the highest grain boundary normal stresses will occur on grain boundaries which form a high angle with the loading direction [162]. The normal stresses may drive crack initiation, however it is clear that the deformation microstructure introduced by cold rolling is also influential.

Figure 6.6 illustrates two of the three cracks which were found in the EBSD scanned regions of the SSRT\textsubscript{3} and SSRT\textsubscript{4}. Combined, EBSD mapping had been performed over a surface area of 9.03 mm\textsuperscript{2} - corresponding to approximately 1300 grains for these two specimens. These three cracks are therefore regarded as being located at sites of extremely susceptible microstructure. Based on analysis of all of the short cracks
formed, it has been found that these two illustrated cracks do illustrate well the general conditions for cracking. Regarding the deformation microstructure, it has been observed that initiation is favoured where:

- Deformation bands have occurred in one grain
- The trace of the deformation bands form a high angle to the loading direction

The alignment of the deformation twins with the rolling plane is much stronger where the boundaries are cracked than was found to be characteristic of the bulk material (Figure 4.14), suggesting that a low angle between the shear bands and grain boundary enhances crack initiation. Previous studies have found a correlation between IGSCC in PWR coolant and grain boundary deformation [163, 164]. Based on this it is possible to offer a possible explanation for the current observation, as from a geometric consideration transmission of shear across the grain boundary is less likely when the deformation bands are aligned closely with the boundary, as a suitable slip system is less likely to be found. Shear of the grain boundary is therefore more likely, which in turn may contribute to the increased susceptibility.

A separate class of susceptible microstructure was linked to the role of annealing twins adjacent to HAGBs. Where crack initiation was not associated to deformation twin impingement, it was almost always linked to an annealing twin. However annealing twin boundaries were themselves resistant to SCC.

The oxidation of deformation bands has been observed, and has in extreme cases enabled transgranular crack initiation. The rapid oxidation of deformation twins has been reported by Lozano-Perez in simulated PWR water, and it was proposed that SCC could be linked to this preferential oxidation [31]. Based on the twin alignment, a larger intersection of the twins is likely with the boundary, possibly causing more rapid and extensive oxidation.

The observations suggest that the microstructure resulting from cold work is important to the locations of crack initiation. Strain heterogeneity between grains
provided the most susceptible microstructure; the presence of planar deformation bands on one side of the boundary favoured initiation. Both mechanical effects, from the reactivation of prior slip bands (as discussed in the previous chapter), or the enhanced oxidation rates due to deformation bands may be influential.
7 Crack Propagation Testing

7.1 Introduction

The propagation behaviour of SCC in simulated primary circuit PWR conditions was investigated through tests on compact tension (CT) specimens, produced from the material in the 20% cold rolled condition. Previous investigations of crack propagation have suggested that the rate of crack propagation may depend on the orientation of the specimen with respect to the direction of the previous deformation process, although there has been very little investigation into the origin of this behaviour [70, 6]. In order to investigate this phenomenon, three different orientations of CT specimen were utilised. Subsequent analysis of the SCC path has been performed with the objective of improving understanding the SCC behaviour in terms of the cold worked microstructure.

7.2 Susceptibility

7.2.1 Specimen and test details

The SCC propagation characteristics of four CT specimens are to be discussed; the details of these four specimens are summarised in Table 7.1. Each specimen is fabricated following 20% reduction in plate thickness by cold rolling. Specimens 20JM, 21JM and 23JM were tested simultaneously, and were loaded in series in the autoclave. Analysis is also presented for specimen 6ET, which was tested separately in a similar arrangement with another two specimens which are not discussed here. The initial load was applied to produce a stress intensity factor of 30-32 MPa√m. The test temperature during crack propagation experiments was 288°C. The crack propagation tests include various stages with different loading conditions. Initially partial unloading with a triangular wave form is used, before transitioning to a
trapezoidal wave, during which the frequency of unloading is gradually decreased. This approach is used as standard during crack propagation testing at Serco as it has been observed that partial unloading during the early test stages favours the transition of the fatigue pre-crack front (which is invariably transgranular) to an intergranular path [66, 6, 73].

Table 7.2 details the loading conditions in the five stages of the test including specimens 20JM, 21JM and 23JM. The conditions in the test of specimen 6ET were very similar. The ratio of unloading, R (the minimum load divided by the maximum load during the cycle), is held at a value of 0.7 throughout. Crack advance occurring during the early stages of the test, particularly stage one may be better described as corrosion fatigue. The final stage of the test is conducted under constant load, and therefore crack advance during this stage is due to SCC.

<table>
<thead>
<tr>
<th>Specimen number</th>
<th>CT orientation</th>
<th>Crack plane</th>
<th>Growth direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>20JM</td>
<td>S-L</td>
<td>RT</td>
<td>R</td>
</tr>
<tr>
<td>21JM</td>
<td>L-S</td>
<td>NT</td>
<td>N</td>
</tr>
<tr>
<td>23JM</td>
<td>L-T</td>
<td>NT</td>
<td>T</td>
</tr>
<tr>
<td>6ET</td>
<td>S-L</td>
<td>RT</td>
<td>R</td>
</tr>
</tbody>
</table>

Table 7.2 The loading conditions during the various stages of CGR testing (20, 21 and 23JM)

<table>
<thead>
<tr>
<th>Stage</th>
<th>Loading conditions</th>
<th>Duration (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Triangular wave: R = 0.7 at 0.01 Hz</td>
<td>23</td>
</tr>
<tr>
<td>2</td>
<td>Triangular wave: R = 0.7 at 0.001 Hz</td>
<td>141</td>
</tr>
<tr>
<td>3</td>
<td>Trapezoidal wave: R = 0.7 at 500 s rise and fall, 1000 s hold</td>
<td>195.5</td>
</tr>
<tr>
<td>4</td>
<td>Trapezoidal wave: R = 0.7 at 500 s rise and fall, 9000 s hold</td>
<td>358</td>
</tr>
<tr>
<td>5</td>
<td>Constant</td>
<td>782.5</td>
</tr>
</tbody>
</table>

1500
7.2.2 Propagation susceptibility

In Figure 7.1 the crack length versus time is illustrated for three CT specimens which were tested simultaneously. This chart is produced from crack length monitoring during the test by reversing direct current potential drop (DCPD). The three specimens were manufactured from the 20% cold rolled material to produce crack growth along the three plate directions corresponding to the rolling, transverse and normal directions. The orientation of these specimens as defined by the ASTM standard E399 are given in Table 6.2 (refer also to the illustration in Figure 2.23) [81]. It is also useful to consider the orientation of the specimens in terms of the plane and direction of cracking with respect to the cold rolling process, hence this has also been included in Table 7.1. Note that specimens 21JM and 23JM are both manufactured with the crack plane parallel to the NT plane of the material, but the growth direction is along the normal direction for 21JM and along the transverse direction for 23JM.

Figure 7.1 Crack length versus time plots for three orientations of CT specimen tested simultaneously in simulated PWR conditions – DCPD data corrected following post-test fractography measurements

---

3 CT specimen orientations are provided using the ‘LTS’ nomenclature which is generalised for various forming processes, however as the material currently under investigation has been formed by rolling it is intuitive to use ‘RTN’ nomenclature as defined in Figure 3.1.
The crack growth behaviour indicated by the DCPD curves indicates that a similar rate of advance for all three specimen orientations during the first two stages of the test (triangular wave loading) was produced. During stage 3 of the test, which includes a short hold period between loading and unloading, a difference in behaviour between the specimen 20 JM and the specimens 21JM and 23JM begins to show; a slight increase in crack growth rate is observed for the former specimen which is not seen for the two latter specimens. Subsequently, throughout the second stage of trapezoidal loading (500 s rise and fall, 9000 s hold period) and the final stage of constant load the crack growth rates for specimens 21JM (L-S) and 23JM (L-T) remain fairly constant. The rate determined for these two specimens remains in the range $0.5 \times 10^{-10} \text{ ms}^{-1}$. On the other hand specimen 20JM (S-L) shows an increase in the crack growth rate following the change to trapezoidal loading, a clear indication of SCC, which becomes particularly evident midway through stage four of the test. During the constant load stage of the test the crack propagation rate in specimen 20JM (S-L) occurs at a fairly constant rate of $\sim 3.4 \times 10^{-10} \text{ ms}^{-1}$. A more detailed description of the crack growth data for these specimens, and for other materials tested at Serco has recently been provided by Nouraei et al. [74].

The enhanced SCC crack growth rate of specimen 20 JM (S-L) with respect to the other two specimens is in agreement with the observations of previous investigations, where it has been reported that a higher SCC susceptibility is found where propagation occurs along the rolling plane [73].

7.3 Fracture surface observations

Following the conclusion of the test, each specimen was sectioned into two halves parallel to the thickness of the specimen. One half of each specimen was then opened by high-cycle fatigue in air to allow examination of the fracture surface in order to obtain further information about the crack growth behaviour.
7 Crack Propagation Testing

7.3.1 SCC morphology

Observation of the fracture surface in each specimen revealed that SCC had occurred in a predominantly IG manner. A region of the IGSCC area from specimen 20JM is shown in Figure 7.2. SCC propagation is typically observed to be IG in cold worked austenitic stainless steels tested in simulated normal primary circuit conditions, and so this morphology is expected [62].

![Figure 7.2 A region of IGSCC, from the fracture surface of specimen 20JM](image)

7.3.2 Susceptibility

Observed at lower magnification, differences in the SCC susceptibility of the three specimen orientations become apparent. Shown in Figure 7.3 are images of the fracture surfaces of the specimens 20JM (S-L orientation), 21JM (L-S orientation) and 23JM (L-T orientation). Each image is labelled to indicate the position of the machined notch and the front of the fatigue pre-crack, in addition to the extent of environmental crack advance during the transitional (partial unloading) and constant load stages of the test. In the figure the crack advance during the different periods of the test has been distinguished simply from the differences in the appearance of the fracture surface. The classical transgranular appearance of the high cycle fatigue section gives way to a mixed transgranular and intergranular topography in the
partial unloading stages. The crack advancement during constant load is almost exclusively intergranular and incorporates some non-cracked sections. The extent of the crack front advance during the period of transitional loading is fairly constant across the width of each specimen, at a length of 150-200 µm. By contrast, the region of SCC is seen to vary between the three orientations of specimen; fairly uniform propagation is seen across the width of specimen 20JM, whereas very little SCC is visible for specimen 21JM. Compared to 21JM the SCC advance appears more extensive in specimen 23JM, although tends to be focussed in certain areas which are separated by non-corroded material.

Figure 7.3 Optical microscope images of the fracture surfaces of a) 20JM, b) 21JM and c) 23JM
These observations of general SCC advance parallel to the notch surface demonstrate the expected influence of specimen orientation on CGR; the material is more susceptible to SCC growth parallel to the RT plane. However the behaviour of the two specimens 21JM and 23JM, which are both manufactured to produce cracking in the TN plane is much more interesting than it appears. In both specimens significant IG cracking has occurred near-parallel to the RT plane, perpendicular to the image plane in both cases. The significance of the out of plane cracking can be seen for specimen 23JM in image c) of Figure 7.3 where the crack is indicated by the large arrow. The penetration of this crack is ~ 2.5 mm from the pre-crack front, therefore being more extensive than the depth of cracking in 21JM, which is generally considered to be the most susceptible orientation [6]. The crack growth in specimen 21JM (L-S) occurred parallel to the pre-crack front and out of the image plane, so the extent of the cracking is not visible in Figure 7.3. As a result specimens were prepared to investigate the cross-section.

7.4 Cross-section observations

7.4.1 L-S orientation specimen

The polished cross section of specimen 21JM is shown in Figure 7.4, clearly illustrating that IGSCC has occurred almost perpendicular to the intended direction of crack propagation. The growth direction of the upper arm of the crack is almost parallel to the loading direction (RD); under these conditions mode II loading would dominate. The lower arm of the crack has grown overall at an angle of ~ 60° to the pre-crack, which is similar to the behaviour reported by Arioka whilst testing T-S orientation specimens [70]. In Figure 7.4 each of the black arrows mark a grain boundary triple point where some crack advance from the main crack has occurred. Frequent branching of this nature is not observed in the equivalent image of specimen 20JM, which is included in the appendix. The branching is likely to be due to the favourable alignment of these boundaries to the direction of applied load, however the
propagation is never significant and boundaries which are closely aligned to the RT plane provide an inherently more susceptible path for propagation.

EBSD IPF and IQ maps corresponding to the upper arm of the crack are shown in Figure 7.5. The two white boxes outline areas which have been chosen for further discussion in the following. As propagation has occurred from the nearest grain boundary to the end of the fatigue pre-crack, it is unwise to suggest that the path taken represents a set of grain boundaries which are extremely susceptible; if the pre-crack had extended through another few grains propagation would most likely still have occurred in a similar fashion. Whereas crack is expected to occur at the points of highest susceptibility, the stress concentration associated with a propagating crack will increase the range of boundaries along which degradation may occur [100].
Figure 7.4 Specimen 21JM, (LS orientation – load along RD), crack tips marked
Figure 7.5 EBSD a) IPF and b) IQ maps of the upper arm of cracking as shown in Figure 6.3. IPF coloured with respect to ND, see Figure 3.3 for the IPF key.
The tip of the dominant crack, which is labelled in Figure 7.5 within the region marked ‘A’, is shown at higher magnification in Figure 7.6. Images a) and b) are the EBSD IPF and IQ maps respectively, which show that the two grains deformed incompatibly during rolling. The lower grain has undergone dense deformation bands / twin formation, whilst the upper grain shows gradual orientation rotation, and some regions of higher misorientation associated with the transfer of localised shear from the deformation bands in the other grain. Images c), d) and e) show, at increasing magnification SEM BSE images of the failed grain boundary.

It is evident that the boundary is ‘kinked’ due to the deformation in the grains, although it cannot be said whether this occurred during cold rolling or subsequently during SCC propagation. However, the features on either side of the cracked boundary are clearly matching, as image e) is annotated to highlight. On the upper side of the grain boundary positions a – e are highlighted which geometrically correspond to positions a’ – e’ on the lower face of the boundary. This provides evidence that the grain boundary has opened in mode II, with the magnitude of displacement of ~ 1 μm. As the load is applied along the rolling direction it is unsurprising that shearing of the grain boundary would take place in this specimen.
Further attention may also be drawn to the section marked ‘B’ in Figure 7.5, which is shown at higher magnification in Figure 7.7. This section is positioned between two grains which are heavily deformed by planar slip and deformation twinning (as confirmed from the EBSD data). Unlike most of the crack which tends to be narrow
with smooth faces, significant oxidation of the grain boundary and of a transgranular path parallel to the grain boundary has occurred (although it is possible that the broad appearance of the crack is due to the section plane forming a small angle with the crack plane). A second interesting observation from this area is that an isolated crack has occurred on the left of the image adjacent to an annealing twin in the grain on the left of the image. This is similar to the observations from the SSRT specimens which suggested that annealing twins can be associated with high stresses on adjacent grain boundaries, however.

![Image of heavily oxidised section of the crack in 21JM association with deformation banding. IPF coloured with respect to ND, see Figure 3.3 for the IPF key.]

Figure 7.7 Heavily oxidised section of the crack in 21JM association with deformation banding. IPF coloured with respect to ND, see Figure 3.3 for the IPF key.
7.4.2 S-L orientation specimens

For the S-L orientation specimens crack propagation was achieved along the expected path; that is to say that mode I crack opening dominated, as seen for example in the cross-section of specimen 21 JM in the appendix. Although the general behaviour is IGSCC occurring approximately perpendicular to the loading direction, certain deviations from this behaviour were observed. The discussion of atypical behaviour is useful to generate a fuller description of the microstructural influences upon susceptibility. The final ~ 250 µm of SCC leading up to the crack tip in CT specimen 6ET (S-L) is useful for this purpose, and is shown in Figure 7.8. Image a) in the figure is an SEM BSE image and image b) is an EBSD grain boundary map, showing all boundaries with a misorientation angle greater than 5°. The two boxed regions, A and B in will be discussed further.

![Image of SEM BSE image and EBSD map](image_url)

Figure 7.8 Cross-section observation of the crack leading to its tip in specimen 6ET (S-L orientation), a) BSE SEM image and b) EBSD map showing all boundaries with > 5° misorientation in black with the crack path highlighted in red

In the region labelled ‘A’ in Figure 7.8 the IG crack has grown between a heavily twinned grain and an untwinned grain, which is typical of the most susceptible
boundaries observed in the SSRT experiments described in section 6. A higher magnification SEM BSE image and the corresponding EBSD IPF of this area are shown in Figure 7.9. Attention has been brought to this section due to the fact that a short section, ~ 15 µm in length has remained resistant to IGSCC. The entire grain boundary is a HAGB, and the heavy planar deformation continues throughout the lower grain adjacent to the intact section. However, the deformation in the upper grain on the left where the crack terminates and in the intact region is clearly different, with significant crystal orientation change associated with the deformation banding in the lower grain.

![Figure 7.9](image)

Figure 7.9 Higher magnification view of region ‘A’ from Figure 7.8 highlighting a resistant grain boundary section between the arrows in a), which is a SEM BSE image and b) EBSD IPF map (IPF coloured with respect to ND, see Figure 3.3 for the IPF key)

7.4.2.1 Intergranular resistance

Further analysis of this region is presented in Figure 7.10. The lattice misorientation in the upper grain along two lines parallel to the deformation features in the lower grain, and a third line which is parallel and close to the grain boundary is presented in Figure 7.10. The numerical analysis confirms the observation that localised crystal rotation in the upper grain has occurred as a result of the localised deformation in the lower grain. Considering the misorientation profile along line 3, a rotation of ~ 15° separates the parent grain (green colour) from the two locally deformed regions
This degree of misorientation is therefore enough to constitute consideration of the rotated region as a separate grain. Misorientation line profile 1 indicates a similar misorientation (~15°) on moving from the white to green volume. However line profile 2 indicates a much more gradual change in crystal orientation associated with the boundary where cracking has occurred.

It is therefore possible that the high local misorientation which results from the transmission of shear across the boundary indicates a beneficial condition with regard to the SCC resistance of the boundary. Several mechanisms would possibly contribute to this effect. The deformation in the upper grain may have caused blunting of the crack, alternatively the activation of dislocation sources in the upper grain suggests that the strain transfer between grains is locally more effective, resulting in less damage / fewer residual dislocations in the grain boundary plane, after the hypothesis of Bieler et al. [99]. Finally, the crack driving force may be a
locally reduced by the incompatibility stress between the two grains. Further investigations of the slip transfer behaviour and the impact which this has on the susceptibility of the grain boundary to SCC would be required to test these hypotheses.

7.4.2.2 Transgranular crack propagation

In the region marked 'B' in Figure 7.8 the crack deviates from an IG path, passing through a grain before the typical IG crack path is restored. A higher magnification SEM and EBSD IPF map of this region are given in Figure 7.11 parts a) and b) respectively. Investigation of the misorientation angle between the different grains in the region is able to offer a possible explanation this behaviour. The crack is propagating from left to right, along the boundary below the red coloured grain which is visible in part b) as it enters the area of the image. Intersecting this susceptible grain boundary are an annealing twin boundary and secondly an LAGB (defined as having misorientation less than 10°), both indicated by arrows in the figure. Both of these boundaries have proven to be resistant to SCC; the crack instead continues to the next section of IGSCC by travelling along the deformation twin boundaries in the largest central grain shown in the images (EBSD indicates that the bands satisfy the twin orientation relationship with the parent matrix). The resistance of coherent (annealing) twin boundaries and LAGBs has been reported in a number of alloy and environment systems with respect to IG corrosion and IGSCC resistance [152, 160, 161]. These observations are therefore in agreement with the current behaviour.
Failure along the deformation bands may have occurred as continuous propagation between the IG sections, or may have involved the formation of a resistant ligament which subsequently failed. Resistant ligaments have been observed to be associated with resilient grain boundaries in ductile materials, and have been observed to fail in a ductile manner as the load is increased by the continued advance of the crack front [161]. Clearly though, the presence of favourably aligned deformation twins in the ligament region has provided a path for low energy fracture.

It has been determined for the bulk rolled material that the deformation bands are typically aligned towards the RT plane as illustrated in Figure 4.14. The deformation bands along which transgranular cracking has progressed area aligned at \( \sim 18^\circ \) to the rolling direction, thus are typical. The favourable alignment of the deformation twin boundaries with the crack propagation direction would favour the transition to
transgranular cracking. Although TGSCC is rare (particularly as the material contains very few LAGBs), the removal of resistant ligaments due to cracking along deformation bands would assist higher susceptibility in the S-L orientation specimens.

7.5 Discussion and Summary

Crack propagation has been successfully produced in the 20 % cold rolled material, using CT specimens. Significant variation in the propagation behaviour was observed for the different orientations, although all were found to be highly susceptible to IGSCC. Propagation was the most uniform across the width of the specimen in the S-L orientation, and occurred parallel to the pre-crack as would be expected. However, the L-S and L-T orientation specimens produced cracking perpendicular to the pre-crack, despite the unfavourable loading conditions for this direction of crack propagation. The overall result is that in all specimens crack growth was favoured along grain boundaries which were aligned towards the RT plane of the material. In the literature it has been reported that the RT plane is the most susceptible to crack propagation, and so the current results are in agreement although the behaviour observed here is perhaps more severe than in other reported materials [6, 70].

The most penetrative crack was observed in the L-T orientation specimen however. The crack growth monitoring by DCPD did not describe this behaviour well, nor did it for specimen 21JM. It has been described in previous investigations that potential-drop methods are inadequate where the advance of the crack front is not uniform [6, 165]. Certainly additional care is required when assessing the susceptibility of the different orientations to propagation.

Regarding the microstructure of the susceptible boundaries, many of the observations are similar to those made for the SSRT specimens. Cracking occurred along HAGBs whilst LAGBs and ATBs were resilient and susceptibility appears to be favoured by
incompatible deformation in adjacent grains. There is also evidence that ATBs may negatively influence adjacent HAGBs, as observed for initiation in SSRT. It has been noted however that the path of the crack is largely due to the location of the pre-crack, and that a wider range of boundaries would be expected to be susceptible to propagation than are to initiation due to the concentration of stress at the crack tip.

The resilient grain boundary section illustrated in Figure 7.9 and Figure 7.10 illustrates that the conditions required for grain boundary susceptibility due to deformation are complex. The high misorientation adjacent to the grain boundary appears to be associated with the prevention of further propagation, whereas the cracked grain boundary is associated with significantly lower misorientation values. It is possible to propose several explanations for the apparent beneficial effect associated with the high misorientation: first, the deformation in the upper grain may have caused blunting of the crack; second, the activation of dislocation sources in the upper grain suggests that the strain transfer is locally more effective, resulting in less damage / fewer residual dislocations in the grain boundary plane, as suggested by Bieler et al. [99]; or third, a local reduction in the incompatibility stress between the two grains is produced.
8 Discussion

8.1 Introduction

The objective of this work has been to improve the understanding of the role which cold work plays in reducing the resistance of austenitic stainless steels to SCC in hydrogenated high temperature water. From the literature survey it was clear that the specific microstructural conditions which correlate to a high SCC susceptibility are not known, although heterogeneous strain at the microstructural scale is likely to be important. Therefore, the aim of the work was to characterise the effect of cold rolling on material condition, and to subsequently correlate this to the observations of SCC susceptibility. Each of the result sections (material characterisation, mechanical characterisation, SSRT testing and CGR testing) have featured a self-contained discussion. Now the complete findings will be discussed, with respect to the project aim.

8.2 SCC test methodology and interpretation

In this study the role of the cold worked microstructure on the susceptibility to stress corrosion cracking has been investigated by slow strain rate testing. Whether observations made by SSRT can be considered faithful to instances of SCC in plant is an issue without consensus. This is the case because the loading conditions experienced in SSRT do not represent the conditions which any plant components are exposed to. Additionally the relatively short duration of the test, and constant crack opening may prevent the development of certain surface or solution condition which is produced at constant load. Fundamentally, the concern is that the mechanism of SCC produced by SSRT may differ from causing cracking at in constant load.
SSRT tests were necessitated in the current study as attempts to initiate SCC at constant load using blunt notch CT specimens (with notch radii of 1.5 mm and 3.0 mm) were unsuccessful. Previously, other constant load tests conducted by Serco using C-ring specimens and proving ring loading had also failed to initiate cracking in simulated primary circuit coolant. It is clear therefore that the increased stresses and/or the dynamic strain condition produced by SSRT stimulate cracking.

Two important questions which remain unanswered are: does SSRT change the cracking behaviour from constant load testing?; and are cracks formed during SSRT representative of cracks occurring in plant? There is very little information available concerning the deformation microstructures in the locality of SCC produced at constant load, or from stress corrosion cracks extracted from plant components. Ultimately it is this information would be able to assess the validity of the observations made by SSRT in the present study.

8.3 Microstructure and susceptibility

8.3.1 Grain boundary character

It has been determined that the material contains a high number of annealing twins, the total boundary fraction (by length) of ATBs actually slightly exceeds the fraction of HAGBs (misorientation > 10°), additionally the content of LAGBs in the material was very low (Figure 4.4). In both the SSRT and crack growth observations, every crack was formed on a HAGB (with the exception of two small cracks, < 20 µm in length which had formed at the intersection of deformation bands with an annealing twin boundary), indicating that the susceptibility of the ATBs to cracking is exceptionally low. Indeed direct evidence of the resistance to cracking of ATBs has been observed in both the SSRT (Figure 6.11) and CGR tests (Figure 7.11).
The resistance of ATBs to IGSCC or intergranular corrosion has been observed in several combinations of material and environment conditions [152, 166]. LAGB’s are also often observed to provide improved resistance to IGSCC [152, 166]. The origin of the resistance of ATBs and LAGBs to degradation is believed to be due to their low energy structure, which is a consequence of the grain boundary structure. Figure 8.1 illustrates the predicted variation in the grain boundary energy with misorientation. It is clearly seen that at the misorientation criteria matching that of an ATB (Σ₃) boundary the energy of the interface decreases significantly. A low energy is also seen for LAGBs. In the figure it is proposed that there may exist some grain boundary energy threshold below which resistance to cracking is achieved; both ATBs and LAGBs are illustrated to be below such a threshold.

![Figure 8.1 Representation of the variation in grain boundary energy with change in misorientation angle, with the suggestion of an energy threshold below which IGSCC is suppressed](image)

8.3.2 Local misorientation

The kernel averaged misorientation analysis, based on EBSD orientation measurements can be used as a measure of the spatial heterogeneity of deformation. Indeed, several recent SCC investigations have made correlations between cracking and areas of high KAM (for example [167, 168, 169]). Typically the highest values of KAM are observed adjacent to grain boundaries, rather than at the grain interior
This was the case for the 20 % cold rolled material (Figure 4.11), and is explained by the activation of additional slip systems adjacent to the grain boundary in order to retain geometric compatibility between the deforming grains.

Due to the anisotropic SCC propagation behaviour in the 20 % cold rolled material it was of interest as to whether the local misorientation values were higher near to the more susceptible boundaries (boundaries which were close to the RT plane) than it was adjacent to the least susceptible boundaries (which are close to the TN plane). The misorientation distributions were found to be very similar in both directions, indicating that the local misorientation was unlikely to be an explanation for the anisotropic crack growth behaviour.

Further observations have indicated that high values of misorientation may actually be beneficial to the SCC resistance, as discussed for Figure 7.9 and Figure 7.10. This may be accounted for by the fact that the transmission of shear between grains prevents damage to the grain boundary, may reduce local stresses and allows compatibility between the grains to be retained.

### 8.3.3 SSRT – susceptible microstructures

The SCC behaviour of the cold rolled alloy indicates that there is a strong link between the deformation microstructure which is induced by rolling and the susceptibility during SSRT. The key observation which supports this statement is that cracking was clearly favoured at HAGBs separating grains with differing deformation microstructures.

A second microstructural configuration was observed which also led to the initiation of IGSCC, this was the case of HAGBs adjacent to annealing twin boundaries.
8.4 Grain boundary deformation and IGSCC

The above observations can possibly be explained by considering the contribution of grain boundary deformation to IGSCC. Previous studies of the SCC of austenitic alloys in simulated LWR environments have identified a strong correlation between grain boundaries which are susceptible to deformation and those which fail by SCC. For example Alexandreanu et al., using Ni base alloys showed that boundaries which deform during straining in argon would subsequently almost certainly fail during further straining in PWR conditions [163, 130]. Conversely, boundaries which were observed not to deform in the inert environment were significantly less likely to undergo SCC.

In the case of IASCC of austenitic stainless steels a similar behaviour may also be responsible for cracking. Strain in irradiated materials tends to localise into defect free bands, known as ‘clear bands’. The intersection of these clear bands with the grain boundary provides an obvious site for critical damage to occur. Recently Was et al. discussed the role of localised strain in the clear bands on intergranular IASCC [164]. Clear band intersections with the grain boundary can result in two main effects: the first situation is the local formation of a ‘wedge-type’ crack, or small voids; alternatively, the interaction between the clear band and the grain boundary may result in dislocations which are active in the grain boundary plane, producing grain boundary sliding. It is believed that the second situation is more likely to induce susceptibility to IGSCC, as although the local wedge-crack formation is damaging it is observed that these cracks fail to propagate [164].

Based on these observations it is possible that grain boundary deformation is a generic precursor to IGSCC of austenitic materials in PWR conditions. The observations of the most susceptible microstructures in the current study may be rationalised by the contribution of grain boundary deformation. Additionally the beneficial effect of grain boundary sensitisation on SCC in cold worked stainless steel has been linked to the reduction of grain boundary sliding [70].
8.4.1 HAGBs separating grains with different deformation structures

The most susceptible grain boundaries to initiation during SSRT were observed where one grain showed evidence of extensive and localised planar deformation, whilst the other grain showed much less evidence of deformation. At the macroscopic scale, cracking at the boundary between a highly deformed grain and a much less deformed grain could be explained in terms of the strain mismatch, which may contribute to boundary stresses. This is similar to previous observations made by Couvant et al., as shown in Figure 2.29 [78].

This possible explanation can be extended by considering microstructurally how strain is transmitted between two grains, and this would affect susceptibility to intergranular failure. It is possible to suggest that effective transmission of strain between grains reduces the ‘damage’ to the boundary, for example by reducing the number of dislocations accumulated in the boundary [99, 171]. This hypothesis fits with the above discussion of IASCC, and indeed correlations have been observed linking the lack of clear band continuity across a boundary to a higher susceptibility to cracking [100].

The efficacy of slip transmission at a grain boundary depends largely on the orientation of the grains and the structure of the boundary [99]. The degree of coplanarity between the slip systems in operation on either side of the boundary is also important, with fewer residual dislocations remaining in the grain boundary as the coplanarity increases [171, 99].

In the bulk cold rolled material it was determined that the orientation of the deformation bands with respect to the rolling direction was not random, and that there tended to be alignment of the bands with the RT plane. When the same analysis was repeated on the deformation bands associated with the boundaries which failed during SSRT the alignment was strengthened further, with 85% of the failed boundaries associated with deformation bands forming an angle of 60–90° to the RT plane. As the IG cracks tended to initiate on boundaries which were close to
the RT plane, the angle formed between the deformation bands and the grain boundary was typically low. It is possible that this arrangement would enhance grain boundary deformation as:

- There is difficulty in activating a dislocation source in the adjacent grain (lack of coplanarity)
- The shear direction in the banded grain is near the boundary plane

8.4.2 HAGBs adjacent to annealing twin boundaries

The second type of microstructural configuration found to be susceptible to initiation were HAGBs lying adjacent to an annealing twin boundary. In this configuration high shear stresses on the grain boundary and an increased chance of grain boundary deformation are also likely, as follows. The ATBs separate two volumes of material which have a different orientation and may therefore be deforming incompatibly. The twin boundary would not be expected to deform as a HAGB would to accommodate the strain mismatch, and so additional shear could occur on the adjacent HAGB.

8.5 Transgranular SCC

So far the discussion has focussed on the possible role of the heterogeneous deformation microstructure to SCC in terms of possible mechanical effects. However, clear evidence of the accelerated oxidation of deformation bands has been observed in the cold rolled material. It is possible therefore that the oxidation of deformation bands would also contribute to increased IGSCC, for example by contributing additional stresses to the crack tip region as suggested by Lozano-Perez et al. [31]. However the TG cracks which were initiated during SSRT did not propagate, and are therefore less significant than the IG cracks from an engineering perspective.
8.6 Anisotropy of crack growth behaviour

Regardless of the direction of loading during CGR testing, it was observed that crack propagation occurred parallel to the RT plane. Several factors can be proposed to potentially explain this behaviour.

8.6.1 Deformation microstructure alignment

As discussed above, the alignment of the deformation bands produced during rolling possibly results in more damage to the boundaries which are aligned with the RT plane, due to increased deformation in the boundary plane.

8.6.2 Internal stress

The yield strength of the material in tension along the normal direction of the plate is reduced by about a third compared to testing along the other orthogonal directions of the plate. This behaviour is attributed to the creation of local back-stresses at the pile-ups of dislocations at features such as grain boundaries, which assist plastic flow along the same slip systems but in the reversed direction when the strain path is changed [53]. It was observed that the slip systems which had been active during rolling could be reactivated during tension, and that the shear strains during re-loading were very high. It is possible that localised plasticity can occur on reactivated slip systems irrespective of the direction of applied load, and the variation of this with direction could contribute to the anisotropy of crack growth susceptibility.

8.6.3 Path effect

Strong evidence of the susceptibility of deformation twin bands to oxidation embrittlement, and subsequent cracking has been observed in both the SSRT specimens and the CT crack growth specimens. As illustrated in Figure 7.11 the favourable alignment of the deformation twin lamellae, combined with their susceptibility to cracking may contribute to the enhanced crack growth rates in the S-
L orientation specimen, by providing a transgranular path where a section of grain boundary is encountered which provides a higher resistance to cracking. This effect is observed to be rare.
9 Conclusions

The aim of the project was to establish a better understanding of the effect of cold work on the decreased resistance to SCC of an austenitic stainless steel alloy. The research conducted has quantified relevant aspects of the effect of cold rolling on the microstructure and mechanical properties of the material, which have then been discussed with respect to the observed SCC initiation and propagation behaviours.

Cold rolling was found to introduce a highly heterogeneous deformation structure. This has been characterised at the grain scale to reveal that the deformation bands are preferentially orientated with respect to cold rolling process, tending to be aligned toward the RT plane. It was found however that the distribution of local crystallographic misorientation within the material did not vary particularly with direction, although was always higher at the grain boundaries. The mechanical properties of the material were strongly anisotropic, and this is attributed to the back-stresses which develop during cold rolling. The strength of the rolled material is the lowest when tension is applied along the normal direction, consistent with the reactivation of previous slip systems in the reverse direction.

The initiation of SCC was observed to be linked to the heterogeneous deformation microstructure. Commonly crack initiation occurred along the grain boundaries separating grains with dissimilar deformation sub-structures. It has also been observed that failure is most likely when the grain boundary is closely aligned with the orientation of the deformation bands. It is possible that this structure produces shear along the grain boundary, which could be essential for cracking. Conversely, when the deformation bands formed a large angle with the grain boundary intense ‘blooms’ of strain transmission into the adjacent grain were observed. Potentially this could be beneficial in reducing cracking susceptibility. Crack initiation was also observed on high angle grain boundaries which were adjacent to an annealing twin boundary. This microstructure is also expected to produce a high shear strain on the grain boundary.
In the crack propagation tests, the RT plane was found to be favoured for cracking irrespective of the loading direction or the orientation of the pre-crack. This indicates the mode of crack opening is unimportant, and that SCC is perhaps assisted by internal stresses.
Based on the work described in this dissertation, a number of avenues for further work can be proposed. Relatively few specimens have been observed in this study, and so a general suggestion would be to increase the number of specimens tested, in order to strengthen any observations made.

The findings appear to support the suggestion that deformation due to the formation of microscale shear bands is important to SCC. In order to test this hypothesis, experiments could be conducted which vary this particular material parameter. For example, the use of different alloys with varied SFE would change the tendency for the formation of planar deformation bands. The occurrence of deformation band formation is also linked to other parameters such as the grain size; therefore this could also be varied.

The second aspect of strain localisation which has been determined to be potentially important is the orientation of the deformation bands. In order to validate this theory different pre-deformation routes which introduce a varied amount of structure alignment could be used. The starting texture of the material could also be used to control the deformation systems, and therefore orientations.

The effect of varying microstructure on the oxidation and failure of grain boundaries would be a useful. For example, focussed ion beam milling could be utilised to extract micro-pillars containing boundaries separating different grains with different deformation structures. In-situ deformation experiments could be conducted to assess the failure behaviour of the grain boundaries following exposure to hydrogenated water. The purpose of such experiments would be to gather more fundamental information on the effect which deformation bands have on grain boundary strength.
10 Recommendations for Further Work

Related to the above suggestion, an investigation of different grain boundary types, in terms of their efficacy of slip transmission and the susceptibility to SCC could be carried out. This would probe whether the ability of a grain boundary to transmit local shear as has been suggested in previous studies is important.

The role of the environment, simulated primary circuit coolant, has not been explicitly considered in this study despite the fact that without exposure to the environment intergranular cracking would not be expected to occur. Therefore, further experiments which probe the influence of the environment, particularly the hydrogen concentration and the temperature are required. These investigations could focus on the role of the environment on the deformation behaviour of the alloy in isolation, in addition to their effect on the SCC susceptibility. Such experiments would probe the role of environment-deformation interactions, such as those postulated in the HELP or corrosion enhanced plasticity model to be evaluated.

A factor limiting the majority of studies into SCC is that observations of what is a three-dimensional process are made on a planar section. Inevitably the information is limited and assumptions have to be made. Three-dimensional analysis techniques have been applied to some studies of SCC, but inherently the methods used are either limited in the volume of material which can be analysed or are capable of insufficient resolution to be of much use to the study of small defects such as incipient stress corrosion cracks. Nevertheless, such studies are a valuable accompaniment to the plane observations.
11 Appendix

11.1 Selected area diffraction

An example of deformation twinning in the 20 % cold rolled material, confirmed by selected area diffraction.

(a) Selected area diffraction pattern from grain tilted along [110] zone axis, (b) indexed diffraction pattern also shown reflections used for dark field images shown in c and d; (c) dark field image of austenite matrix; (d) dark field image of deformation twins.

11.2 Crack propagation specimens

Additional images of the crack propagation specimens, 20JM in the S-L orientation and 23JM in the L-T orientation.
Specimen 20JM – S-L orientation CT specimen, 20 % cold rolled
Specimen 23JLM – L-T orientation CT specimen, 20 % cold rolled
12 References


