CHARACTERISATION OF RESIDUAL STRESS AND INVESTIGATION OF ENVIRONMENTAL EFFECTS ON ATMOSPHERIC-INDUCED STRESS CORROSION CRACKING OF AUSTENITIC STAINLESS STEEL NUCLEAR WASTE CONTAINERS

A THESIS SUBMITTED TO THE UNIVERSITY OF MANCHESTER FOR THE DEGREE OF DOCTOR OF ENGINEERING IN THE FACULTY OF ENGINEERING AND PHYSICAL SCIENCES

2012

YIN JIN JANIN

SCHOOL OF MATERIALS
6.7.5.3 3D Shell with Static Heat Source ................................................................. 142
6.7.5.4 3D Shell with Moving Heat Source ............................................................. 142
6.7.5.5 3D with Static Heat Source ........................................................................ 143
6.7.5.6 3D with Moving Heat Source ..................................................................... 143
6.7.6 Step 5: Finite Element Model ........................................................................ 144
6.7.7 Step 6: Thermal Analysis ............................................................................... 144
6.7.7.1 Weld Heat Input Calculation ...................................................................... 144
6.7.7.2 Modelling Weld Heat Input ....................................................................... 146
6.7.7.3 Thermal Boundary Conditions .................................................................... 147
6.7.7.4 Thermal Stability ....................................................................................... 148
6.7.8 Step 7: Mechanical Analysis .......................................................................... 148
6.7.8.1 Mechanical Boundary Conditions .............................................................. 148
6.7.8.2 Mechanical Constitutive Behaviour of Austenitic Stainless Steels ............ 148
6.7.8.3 Results Evaluation ..................................................................................... 149
6.7.9 Step 8: Validation of Weld Residual Stress Calculation .................................. 149
6.8 Simulation of Welding the ILW Container Flange Using ABAQUS .................... 149
6.8.1 Objectives ...................................................................................................... 149
6.8.2 ABAQUS/CAE as Simulation Tool ................................................................. 149
6.8.3 2D Model with Static Heat Source .................................................................. 151
6.8.4 Results of 2D Analysis .................................................................................. 152
6.8.5 3D Model with Moving Heat Source ............................................................... 163
6.8.6 Results and Discussion of 3D Analysis .......................................................... 165
6.8.7 Comparison between 2D and 3D analysis ...................................................... 166
6.9 Discussion on the Discrepancy between Simulation and Measurements ............ 172
6.10 Concluding Remarks ....................................................................................... 177
References ............................................................................................................. 178
7 Discussion ........................................................................................................... 183
7.1 Hypothesis ......................................................................................................... 183
7.2 Residual Stress in Container ............................................................................ 184
7.3 Effect of Stress on AISCC Susceptibility of the Container Material .................. 187
7.4 Industrial Relevance ......................................................................................... 188
References ............................................................................................................. 192
8 Conclusions ....................................................................................................... 195
9 Recommendations for Further Research ............................................................ 196
Word count: 44,737
List of Tables

Table 1-1: Comparisons of government funding on research of energy and nuclear fission in different countries .................................................................19

Table 2-1: Susceptibility of 304L to AISCC with different salt contamination under varying temperatures. RH_{\text{range}} is the range of RH at which SCC was observed. RH_{\text{max}} is the RH at which SCC rate is at maximum. RH_{\text{sat}} is the RH at which the solution becomes saturated. ..............................34

Table 3-1: Tensile testing results on parent metal in both circumferential and longitudinal directions ........................................................................................................59

Table 3-2: Chemical analysis (%) of the parent specimen extracted from the container body ..........59

Table 4-1: Displacements and calculated stresses of the 4-point bend parent specimen labelled P2. ..........................................................................................................................65

Table 4-2 Preparation of salt solution with different loading densities .......................................66

Table 4-3: List of 4-point bend and control specimens ................................................................69

Table 4-4: List of specimens and their associated testing conditions ...........................................72

Table 4-5: List of specimens and their associated testing period .................................................73

Table 4-6: A summary of AISCC susceptibility of various specimens ...............................................82

Table 5-1: Types of stress .............................................................................................................90

Table 6-1: Thermal properties with varying temperatures ..........................................................155

Table 6-2: Solidus and liquidus temperatures, latent heat and coefficient of heat transfer ......155

Table 6-3: Mechanical properties .................................................................................................156

Table 6-4: Yield stress data ............................................................................................................157

Table 6-5: The welding parameter for both top and bottom welds of container flange section...157

Table 6-6: Temper colours that are likely to form on austenitic stainless steels as an approximate indication of temperature .................................................................157
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>A Cogent model to illustrate how a programme of 12 new nuclear power stations to deliver 16GW energy by 2025 might develop</td>
</tr>
<tr>
<td>1-2</td>
<td>Comparison of greenhouse gas emissions from various electricity generation sources</td>
</tr>
<tr>
<td>1-3</td>
<td>Block diagram of the steps of radioactive waste management at a centralised facility</td>
</tr>
<tr>
<td>1-4</td>
<td>Schematic of radioactive management, distinguishing pre-disposal and disposal</td>
</tr>
<tr>
<td>2-1</td>
<td>Components of SCC</td>
</tr>
<tr>
<td>2-2</td>
<td>Bare metal surface created on passivated metals. Pits and stress corrosion cracks may initiate from these local exposed sites</td>
</tr>
<tr>
<td>2-3</td>
<td>Hydroscopic growth of inorganic particles as RH increases. Particles transform from solid to aqueous phase at the deliquescence RH (DRH). As RH increases, the aqueous particle also increases in size</td>
</tr>
<tr>
<td>2-4</td>
<td>Variation of mass loss as a function of RH and exposure time for iron with 20 μg cm⁻² surface contamination by NaCl</td>
</tr>
<tr>
<td>2-5</td>
<td>Growth and evaporation of a mixed-salt particle at 17.5°C. The filled circle line represents the mass change with increasing RH and the open circle line represents the mass change with decreasing RH</td>
</tr>
<tr>
<td>2-6</td>
<td>Schematic presentation of moisture retention at the base of a particle on a metal surface</td>
</tr>
<tr>
<td>3-1</td>
<td>Schematic illustration of an ILW container</td>
</tr>
<tr>
<td>3-2</td>
<td>Weld preparation details for circumferential butt weld between drum body and base</td>
</tr>
<tr>
<td>3-3</td>
<td>Weld preparation details for circumferential butt weld between drum body and neck</td>
</tr>
<tr>
<td>3-4</td>
<td>Weld preparation welds for the two circumferential welds between 316L drum neck and 304L flange</td>
</tr>
<tr>
<td>3-5</td>
<td>As-received ILW container</td>
</tr>
<tr>
<td>3-6</td>
<td>Illustration showing locations from which specimens were prepared</td>
</tr>
<tr>
<td>3-7</td>
<td>Numbered marks indicate the locations at which hardness measurements were taken</td>
</tr>
<tr>
<td>3-8</td>
<td>Dashed boxes indicate the locations at which images were taken</td>
</tr>
<tr>
<td>3-9</td>
<td>Vickers hardness profile across the circumferential weld</td>
</tr>
<tr>
<td>3-10</td>
<td>A macroscopic image of the circumferential weld section from region D of the ILW container</td>
</tr>
<tr>
<td>3-11</td>
<td>Metallographic images of the drum neck sections labelled (1), (2) and (3) as in Figure 3-8 and Figure 3-10</td>
</tr>
<tr>
<td>3-12</td>
<td>Metallographic images of HAZ of the drum neck sections labelled (4), (5) and (6) as in Figure 3-8 and Figure 3-10</td>
</tr>
<tr>
<td>3-13</td>
<td>Metallographic images of the weld regions labelled (7), (8) and (9) as in Figure 3-8 and Figure 3-10</td>
</tr>
<tr>
<td>3-14</td>
<td>Metallographic images of the HAZ of the body sections labelled (10), (11) and (12) as in Figure 3-8 and Figure 3-10</td>
</tr>
</tbody>
</table>
Figure 4-1: A parent specimen fitted on a four-point bend jig .........................................................63
Figure 4-2: Illustration of a 2D stress-strain field ............................................................................64
Figure 4-3: Linear plot of displacement against calculated stress from Table 4-1 .......................65
Figure 4-4: Salt deposition matrix for four-point bend parent specimens labelled P1, P2 and P3 .67
Figure 4-5: Salt deposition matrix for four-point bend weld specimens labelled W1 and W2, and annealed parent specimen labelled P9, etched specimen labelled P12 ..............................67
Figure 4-6: Salt deposition matrix for small unstrained weld specimens (control specimen) labelled U1, U2, U3, U4, U5 and U6. Shaded region indicates weld ......................................................68
Figure 4-7: A control specimen .......................................................................................................68
Figure 4-8: Arrows indicate the corrosion attack on a four-point bend parent specimen ......... 75
Figure 4-9: A comparison between (a) sea salt and (b) magnesium chloride showing the areas covered by corrosion product ..........................................................................................76
Figure 4-10: Image showing pits and cracks surrounded by corrosion products. Figure 4-11 to Figure 4-14 show the chemical analysis at locations (1), (2), (3) and (4). ..........................78
Figure 4-11: EDX analysis at location (1) in Figure 4-10 .................................................................79
Figure 4-12: EDX analysis at location (2) in Figure 4-10 .................................................................79
Figure 4-13: EDX analysis at location (3) in Figure 4-10 .................................................................80
Figure 4-14: EDX analysis at location (4) in Figure 4-10 .................................................................80
Figure 4-15: Pits and cracks in Figure 4-10 are revealed after removal of corrosion products ... 81
Figure 4-16: Deliquescence relative humidity of sodium nitrate NaNO₃ as a function of temperature ........................................................................................................................................83
Figure 4-17: Deliquescence relative humidity as a function of temperature for mixed Na₃SO₄-NaNO₃ particles ..................................................................................................................84
Figure 5-1: Examples of residual stresses arise from misfits .........................................................89
Figure 5-2: Diffraction in a crystal lattice obeying Bragg's Law ......................................................94
Figure 5-3: Focussed geometry .......................................................................................................95
Figure 5-4: Defocused geometry ....................................................................................................96
Figure 5-5: Linear $d$ vs $\sin^2 \psi$ behaviour: an increasing slope indicates tensile stress while a decreasing slope indicates compressive stress .................................................................................97
Figure 5-6: Measurement positions (marks as 'X') on specimens with each position being 1cm apart ........................................................................................................................................98
Figure 5-7: (a) Instrument layout of SALSA (b) Hexapod with six hydraulic legs [Source: ILL] .... 103
Figure 5-8: A schematic illustration of an ILW container showing a shaded region from which a 90° arc was prepared ...........................................................................................................103
Figure 5-9: The direction of strain measurement ............................................................................104
Figure 5-10: Positions of measurements made in 304L flange region ........................................ 105
Figure 5-11: Positions of measurement adjacent to top and bottom welds ..................................106
Figure 5-12: Positions of measurements adjacent to top weld .....................................................107
Figure 5-13: Specimen set up for measurement of residual strains ...............................................108
Figure 5-14: Specimen set up for measurement of residual strains................................. 109
Figure 5-15: Specimen set up for strain measurement adjacent to welds.......................... 109
Figure 5-16: Specimen set up for strain measurement along drum wall and adjacent to welds...110
Figure 5-17: The unsuccessful attempt at positioning the specimen which caused a collision between the specimen and detector collimator................................................................. 111
Figure 5-18: The D-nought specimen mounted onto hexapod. The regions marked with "X" indicate positions at which residual strain measurements were made............................................. 111
Figure 5-19: Residual stress profile of a 15 x 15cm specimen containing a circumferential weld.112
Figure 5-20: Residual stress profile of a four-point bend weld specimen prepared from ILW container................................................................................................................................. 113
Figure 5-21: Residual stress profile on the external wall surface of a four-point bend parent specimen................................................................................................................................. 114
Figure 5-22: Residual stress profile on the internal wall surface of a four-point bend parent specimen................................................................................................................................. 114
Figure 5-23: Measured residual stress in 304L flange, 1.5mm from top surface ................. 116
Figure 5-24: Measured residual stress in 304L flange across mid thickness......................... 117
Figure 5-25: Measured residual stress in 304L flange, 1.5mm from bottom surface ......... 117
Figure 5-26: A diagram showing the measurement points adjacent to top weld. Label A, B and C indicate the columns along which measurements were taken...................................................... 118
Figure 5-27: Measured radial strains adjacent to top weld. A, B and C represent the columns along which readings were taken as seen in Figure 5-26 ........................................................................ 119
Figure 5-28: A simplified Figure 0-57 to show columns labelled D (1mm from internal drum surface) and E (1mm away from external drum surface) ............................................................. 120
Figure 5-29: Measured stress along column labelled D (1mm from internal drum surface) ......121
Figure 5-30: Measured stress along column labelled E (1mm from external drum surface) ....122
Figure 5-31: A simplified Figure 5-11 to show measurements taken in and around bottom weld. Note that column labelled F is along a vertical path beginning from 304L flange into bottom weld ................................................................. 122
Figure 5-32: A simplified Figure 5-11 to show measurements taken in bottom weld along a column labelled G. Note that column labelled G is along a diagonal path descending from top .......... 123
Figure 5-33: Measured stress along column labelled F ......................................................... 123
Figure 5-34: Measured strain along column labelled G.......................................................... 124
Figure 5-35: Residual stress in welding direction (i.e. hoop direction) .................................. 125
Figure 5-36: Stress profile across the thickness of a rolled sheet........................................ 126
Figure 5-37: The effect of overestimating and underestimating $d_0$ on the calculated residual strains in the radial direction, 1.5mm from the top surface of the flange.............................. 127
Figure 5-38: The effect of overestimating and underestimating $d_0$ on the calculated residual stresses in the radial direction, 1.5mm from the top surface of the flange......................... 128
Figure 6-1: Simplified phenomena during welding .............................................................. 135
Figure 6-2: Thermal analysis followed by mechanical analysis by simplifying the couplings...... 136
Figure 6-3: A time step in a staggered approach for thermal and mechanical analysis......... 136
Figure 6-4: A schematic diagram of the physical processes and interactions that occur during arc welding .......................................................... 137
Figure 6-5: Flow chart for deciding global FEM approaches for structural welds ............. 142
Figure 6-6: Flux heat input profile function, $f(t)$ .............................................................. 145
Figure 6-7: Prescribed temperature for a node associated with a weld ............................ 147
Abstract

The University of Manchester

Candidate name: Yin Jin Janin

Faculty: Engineering and Physical Sciences

Degree Title: Doctor of Engineering, EngD

Thesis Title: Characterisation of Residual Stress and Investigation of Environmental Effect on Atmospheric-Induced Stress Corrosion Cracking of Austenitic Steel Nuclear Waste Containers

Date: 05/03/2013

This research has investigated the conditions necessary for atmospheric-induced stress corrosion cracking to occur in material taken from an intermediate level nuclear waste storage container by means of experiments in a humidity chamber. It has also characterised the residual stresses associated with the container welds by modelling and measurement. Based on the work conducted in this research, the major findings can be summarised as follows:

- Deliquescence of salt particles is dependent on relative humidity but independent of the quantity of salt present.
- The time to initiate cracking may be sensitive to temperature, getting longer as the temperature decreases, but the timeframe of work as not long enough to establish this conclusively.
- AISCC can occur at a stress (residual or applied) of 400MPa (0.2% strain) or more if the other necessary conditions are present. While AISCC was not observed when no stress was present, the threshold of stress below which AISCC will definitely not occur has not been determined in this work.
Declaration

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

The author of this thesis (including any appendices and/or schedules to this thesis) owns any copyright in it (the “Copyright”)

1 and s/he has given The University of Manchester the right to use such Copyright for any administrative, promotional, educational and/or teaching purposes.

Copies of this thesis, either in full or in extracts, may be made only in accordance with the regulations of the John Rylands University Library of Manchester. Details of these regulations may be obtained from the Librarian. This page must form part of any such copies made.

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

Further information on the conditions under which disclosure, publication and exploitation of this thesis, the Copyright and any Intellectual Property Rights and/or Reproductions described in it may take place is available from the Head of School of Materials (or the Vice-President) and the Dean of the Faculty of Engineering and Physical Sciences, for the Faculty of Engineering and Physical Sciences.

---

1 This excludes material already printed in academic journals, for which the copyright belongs to said journal and publisher. Pages for which the author does not own the copyright are numbered differently from the rest of thesis.
Acknowledgements

I am heartily thankful to my both supervisors, Professor Stuart Lyon of The University of Manchester and Mr John Wintle of TWI Ltd., whose encouragement, supervision and support from the preliminary to the concluding level enabled me to develop an understanding of the subject. I would also like to thank Professor Andrew Sherry and the late Dr Guang Xu, both whom offered this opportunity in the beginning.

I am grateful to my colleagues at The University and TWI for letting me make use of the resources and equipment available as well as offering valuable advice and assistance, especially Dr Simon Smith, Dr Philippe Bastid and Mr Fouad Hantouti. It would not have been possible without their generous help and advice. I also wish to thank Dr Alexander Evans and Dr Thilo Pirling for all the assistance they offered during my time at ILL, Grenoble.

I wish to thank my husband, Lilian, who has always believed in me, and my parents, Mr Wai Woh Yee and Madam Bee Huan Yaw, sister, Yin Yii and brother, Jasper, who all have and continue to show great understanding and support over the past four years. I would like also to express my appreciation to my son, Savinien, who has been very considerate during the days of my writing-up.

This research was jointly supported by EPSRC and Core Research Programme of TWI.

Lastly, I offer my regards and blessings to all of those who supported me in any respect during the completion of the project.
1 Introduction

1.1 Nuclear Engineering Doctorate Programme

1.1.1 Background
This thesis reports a research project undertaken as part of an EPSRC Nuclear Engineering Doctorate Programme. As well as research, the Engineering Doctorate programme also contains academic study, technical and business courses related to nuclear technology, and professional development within an industrial environment. The programme is a collaboration project between the University of Manchester Materials Performance Centre and TWI Ltd.

The research project relates to the containers used for storing intermediate level waste (ILW) within the context of the UK nuclear industry and the potential for atmospheric induced stress corrosion cracking (AISCC). The thesis contains a resume of the industrial relevance of the research, a literature review of previous work on AISCC, and a description of experimental work and computational simulation carried out within this project. Conclusions are drawn on the conditions under which AISCC can occur and the effect of the manufacturing route of the containers, such as welding and surface treatments, that may influence the susceptibility to AISCC.

1.1.2 Academic Host: University of Manchester
The Dalton Nuclear Institute at the University of Manchester is a leading centre for nuclear research in the UK. The Materials Performance Centre (MPC) is a component part of the University School of Materials and linked to both the Dalton Nuclear Institute and the Corrosion Centre. MPC was established to undertake research into the performance of materials in the nuclear industry.

1.1.3 Industrial Host: TWI Ltd
TWI Ltd is a leading membership-based research and technology organisation (RTO). It has the mission to create value and enhance quality of life for its members and stakeholders through engineering, materials and joining technologies. TWI therefore has an expert knowledge and understanding of welding processes and advises industries on the engineering measures necessary to ensure the quality of welds and structural integrity in service environments.

This research has been supported by a TWI Core Research Project (CRP). This CRP draws heavily on knowledge in the Materials, Corrosion and Surfacing (MCS) and Structural Integrity Groups
(SITG). MCS provides the knowledge and resources in supporting the experimental programme whilst SITG offers experiences in modelling of weld and prediction of residual stresses.

1.1.4 Collaboration
The collaboration brings together the academic resources of the University of Manchester and TWI’s industrial orientation for serving the nuclear industry. TWI has provided the experimental facilities and advice on computational techniques for simulating welding process and predicting residual stresses. The University of Manchester has provided the academic rigor with a good understanding of the mechanisms of stress corrosion cracking linked to other on-going researches on AISCC.

1.1.5 Supervision and Timescale
Initially Professor Andrew Sherry and Dr Guang Xu were the academic and industrial supervisors respectively. In April 2008, following the illness and subsequent death of Dr Guang Xu, the supervision at TWI was passed to Dr Geoff Booth and again to John Wintle in October 2008. In April 2009, Professor Andrew Sherry moved position at the University of Manchester and Professor Stuart Lyon was appointed as main academic supervisor in his place.

The programme of studies and period of time spent at each place were agreed between The University of Manchester and TWI. This Engineering Doctorate started on 7th January 2008. The first year was spent at the University of Manchester on attending courses and making preparations for the research project. Relocation to Cambridge began in August 2008 while completing the courses in Manchester. An interruption of study took place from 15th July 2009 to 15th January 2010 due to maternity leave. As a result, the four-year programme of studies completed in June 2012.

1.2 Nuclear Energy and Waste Management Strategy in the UK

1.2.1 Supply and Demand
Nuclear energy currently supplies around 16% (10 to 12GW) of the UK’s electricity generation capacity according to a report by the UK Department of Energy and Climate Change (DECC) [1]. It also reported that from now until 2050, nuclear energy could supply up to 49% of the electricity demand. The need for security of supply and to reduce carbon footprint have driven a policy for nuclear energy.
A strategy for energy and climate change was announced by Government in 2009. This confirms the importance and role of nuclear energy and the demand for new build systems. Over the next 15 years, 14 of the 15 UK’s existing nuclear power plant reactors will cease operation. Life extension of these plants will not be sufficient to meet the energy demand in the future.

The blue area in Figure 1-1 [2] indicates the existing nuclear generation capacity which gradually declines. The green area indicates the 10 sites have been identified for new builds. If these should go ahead they could provide an additional 12 to 17 GW of capacity [3]; if 12 new reactors were completed by 2025, the total nuclear capacity will exceed the current capacity.

![Figure 1-1: A Cogent model to illustrate how a programme of 12 new nuclear power stations to deliver 16GW energy by 2025 might develop [2]](image)

The investment required for new build reactors is estimated to range between £40 billion and £64 billion, which is equivalent to between £2500 and £4000 per kW [4]. Initially three consortia expressed their interest in constructing new reactors but two have withdrawn. Only EDF is planning to build 4 EPRs with a capacity of 6.4GW at Sizewell and Hinkley Point.

Emissions of greenhouse gases from nuclear power mainly originate from the construction, decommissioning, waste management and the mining, processing and transportation of uranium. The actual power generation produces negligible amounts of carbon dioxide. According to the Department of Business Innovation and Skills (formerly Business Enterprise and Regulatory Reform) White Paper on Nuclear Power in 2008 [5], the whole life-cycle carbon dioxide emissions are between 7 and 22 gCO₂eq/kWh. This is in good agreement with figures (see Figure 1-2) published by IAEA based on the analysis of the existing reactors [6].
The future development of nuclear energy in the UK relies on three crucial factors [7]:

- The scale of deployment of nuclear energy that will in turn determine the decisions on waste management and new build design.
- The contribution of UK to the Non-Proliferation Treaty (NPT) commitment with the intent to establish a centre of excellence to coordinate all research and development programmes.
- The revival of UK nuclear energy expertise and manufacturing capacity in the global market.

1.2.2 UK Nuclear Research and Development Capability

In 2011 the House of Lords Science and Technology Committee published an extensive report on the nuclear R&D capabilities in the UK [8]. This report examines the commitment and role of the UK Government with regard to the source of energy to provide a secure, affordable and green electricity supply for the future. The findings concluded that there was a lack of commitment and support from the UK Government in maintaining and developing the nuclear R&D and capabilities and expertise in the UK.

Poor leadership and strategy at government level have resulted in a lack of coordination in nuclear R&D activities and a failure to recognise the strengths and potentials that are available and present in the UK. It has also weakened the role of the UK in the world nuclear industry. There is also a high degree of difference and discrepancy between the opinions of government officials, industry and nuclear agencies, academic experts as well as regulators and advisers.

This House of Lords report hopes to convince the UK Government to commit: firstly, to develop a long-term strategy for nuclear energy; secondly, to establish a roadmap for nuclear R&D and
thirdly, to set up an independent nuclear R&D board, consisting of representatives from government, academia and industry. Table 1-1 shows a summary of government-funded researches on energy and nuclear fission in chronological order. It is clear that the UK contributes least to such R&D.

Table 1-1: Comparisons of government funding on research of energy and nuclear fission in different countries [8]

<table>
<thead>
<tr>
<th>Country</th>
<th>Fission R&amp;D (€M)</th>
<th>Total energy R&amp;D (€M)</th>
<th>Percentage of Fission R&amp;D per total energy</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia</td>
<td>8.214</td>
<td>184.524</td>
<td>4.5%</td>
<td>2007</td>
</tr>
<tr>
<td>Belgium</td>
<td>39.442</td>
<td>97.184</td>
<td>40.6%</td>
<td>2007</td>
</tr>
<tr>
<td>Canada</td>
<td>140.444</td>
<td>531.408</td>
<td>26.4%</td>
<td>2009</td>
</tr>
<tr>
<td>Czech Republic</td>
<td>12.779</td>
<td>36.556</td>
<td>35.0%</td>
<td>2009</td>
</tr>
<tr>
<td>Finland</td>
<td>9.452</td>
<td>170.606</td>
<td>5.5%</td>
<td>2008</td>
</tr>
<tr>
<td>France</td>
<td>445.665</td>
<td>931.272</td>
<td>47.9%</td>
<td>2008</td>
</tr>
<tr>
<td>Germany</td>
<td>41.98</td>
<td>563.715</td>
<td>7.4%</td>
<td>2009</td>
</tr>
<tr>
<td>Italy</td>
<td>35.816</td>
<td>373.438</td>
<td>9.6%</td>
<td>2007</td>
</tr>
<tr>
<td>Japan</td>
<td>1835.532</td>
<td>2907.79</td>
<td>63.1%</td>
<td>2009</td>
</tr>
<tr>
<td>South Korea</td>
<td>131.998</td>
<td>323.456</td>
<td>40.8%</td>
<td>2007</td>
</tr>
<tr>
<td>Netherlands</td>
<td>9.58</td>
<td>138.905</td>
<td>6.9%</td>
<td>2006</td>
</tr>
<tr>
<td>Norway</td>
<td>9.163</td>
<td>127.781</td>
<td>7.2%</td>
<td>2009</td>
</tr>
<tr>
<td>Spain</td>
<td>4.083</td>
<td>89.818</td>
<td>4.5%</td>
<td>2009</td>
</tr>
<tr>
<td>Sweden</td>
<td>7.433</td>
<td>121.091</td>
<td>6.1%</td>
<td>2009</td>
</tr>
<tr>
<td>Switzerland</td>
<td>16.574</td>
<td>118.674</td>
<td>14.0%</td>
<td>2009</td>
</tr>
<tr>
<td>UK</td>
<td>4.493</td>
<td>292.992</td>
<td>1.5%</td>
<td>2009</td>
</tr>
<tr>
<td>USA</td>
<td>560.664</td>
<td>8466.969</td>
<td>6.6%</td>
<td>2009</td>
</tr>
</tbody>
</table>

However, over the past decade, several research initiatives have been started by both academic bodies, government funders (e.g. the UK research councils) and private industries to ensure the sustainability of nuclear research in the UK. This includes the ‘Keeping the EPSRC Nuclear Options Open’ (KNOO) Programme, the University Nuclear Technology Forum (UNTF) and the Decommissioning, Immobilisation and Management of Nuclear Waste for Disposal (DIAMOND) initiative.

1.2.3 Nuclear Waste Management Practice

Radioactive wastes are generated from many operations. These include the reprocessing of spent fuel, plutonium production and uranium mining, as well as commercial, research and medical activities. Practices for waste management vary across the nuclear industry, but they share the common significance of treating the wastes as highly hazardous materials with a requirement to protect the environment.
The ideal way to manage radioactive waste management is to perform all operations at a centralised facility, see Figure 1-3 [9]. This is rarely the case as a facility of this size would require detailed and complex planning and operations. Most facilities, such as Sellafield, offer more than one method of waste management.

Another approach is to divide the waste into pre-disposal and disposal stages, where disposal is the final step in waste management. Pre-disposal includes decommissioning, pre-treatment, treatment, conditioning, immobilisation, storage and transport, as illustrated in Figure 1-4. The ultimate aim is to deposit all the nuclear waste in a permanent underground facility and work is now under way to establish a geographical deposit repository in the UK.

Figure 1-3: Block diagram of the steps of radioactive waste management at a centralised facility [9]
1.2.4 Intermediate Level Waste and Current Storage Options

According to the World Nuclear Association, radioactive waste is divided into three different levels, namely, high-level, intermediate-level and low-level waste. The High and Intermediate Level Waste (HLW and ILW) streams must be placed in containers which are stored or disposed under conditions where the wastes are isolated from the environment for 10s or 100s of millennia. Nuclear waste falls within the ILW category when the radioactive emission exceeds 4GBq/te of alpha and 12 GBq/te of gamma with thermal power below 2kW/m$^3$ without the need for cooling. The symbol Bq stands for Becquerel. It is the SI-derived unit of radioactivity with unit of s$^{-1}$. One Bq is defined as the activity of a quantity of radioactive material in which one nucleus decays per second.
Before further elaboration on ILW, it is essential to first understand the radioactivity of nuclear waste. When radioactive isotopes decay, they radiate particles. Three types of radiation are alpha, beta and gamma particles. A fourth type is neutron radiation, which only occurs in a nuclear reactor.

The penetrating power of alpha radiation (helium ions) is very low and can be stopped by a sheet of paper. Beta radiation (electrons) can penetrate into human body but an aluminium foil is sufficient to block its penetration. However, gamma radiation comprises electromagnetic waves with high penetrating power. Shielding of gamma radiation requires a few centimetres of lead or concrete.

There are approximately 45000 ILW containers stored at various locations in the UK, usually in ventilated buildings next to coastal areas. These containers contain wastes that consist of large quantities of radioactive material that requires shielding. Typical contents of an ILW container include reactor components, stripped fuel rods, used ion exchange resins and parts from reactor decommissioning and are encapsulated/immobilised by cement mortar.

The Letter of Compliance (LoC) procedure requires that ILW containers should maintain containment for up to 500 years with the first 150 years under surface storage. The current practice in the UK is to keep these ILW containers in an above ground ventilated storage warehouse. Maintaining the structural integrity of these containers during such a storage period is therefore crucial.

1.3 Atmospheric-Induced Stress Corrosion Cracking

The subject of research in this Engineering Doctorate is the Atmospheric Induced Stress Corrosion Cracking (AISCC) of austenitic stainless steels and welds. This is particularly important for the ILW storage containers, which are manufactured from 316L and 304L austenitic stainless steels and fabricated using Tungsten Inert Gas (TIG) welding. Despite being highly resistant to general uniform corrosion, susceptible microstructures of these materials and welds could, when subject to sufficient stress, suffer localised attack induced by the presence of aerosol salt particles on the surface at certain level of humidity and temperature.

In the UK, the current practice is that the containers are kept above ground in ventilated storage buildings, often close to coastal areas. These containers will eventually be transferred to a deep underground repository, but this may not occur for many years and the surface storage period
has now been extended to up to 150 years. Thus there is a need to maintain structural integrity of these ILW containers during this period to avoid cracking and loss of containment.

There are 4 types of environments to which these containers will be exposed. The inside surface of the containers will be exposed to the encapsulant material and nuclear waste. The exterior of the containers will undergo three different stages of exposure: first when they are kept in ventilated storage buildings, second when they are transferred to the repository (pre-backfill) and third, after backfill. Under all these environments, they may be prone to localised forms of corrosion and environmental cracking such as AISCC which is caused by airborne particles in the atmosphere.

During planned storage in ventilated sheds near coastal locations, the exterior of the container will be exposed to the prevailing atmospheric conditions. Contamination comes from dusts, salts etc, forming a thin layer of electrolyte when sufficient moisture is present. The electrolyte on the metal surface will be affected by temperature, local airflow, relative humidity as well as contamination such as soil and salt, and pollution. The concentration of electrolyte will vary with relative humidity as it becomes more diluted at high relative humidity and more saturated at low relative humidity.

Typically containers will be subjected to continuous depositions of airborne and atmospheric contamination. The particulates of salts from sea water such as MgCl$_2$ or CaCl$_2$ will adhere to metal surface and are very likely to become wetted at relative humidity > 30-35%. Dusts, soils and particles can induce a capillary effect and trap moisture and become potential sites for crevice corrosion. Cracking may initiate from crevices under the effect of high residual stresses, e.g. near welds.

The general assumption that stress corrosion cracking of austenitic stainless steels does not occur at temperatures below 60°C has now been found to be incorrect. Emerging researches in the past decade have reported the occurrence of AISCC particularly in investigations of the failure of public equipment such as swimming pools [10, 11, 12, 13]. In all the reports, AISCC appears to be the main cause of failure.

Fielder et al. [10, 11] and Faller et al. [12] examined the collapse of suspended swimming pool roofs in Uster, Switzerland, which caused twelve fatalities. Their investigation found that most of the collapses were associated with the failure of load bearing components caused by AISCC.
Ropes, fasteners, wires etc. were the sites of high stress concentrations and operated at a temperature of around 30°C and in a humid condensing atmosphere above the pool.

Other reported incidents of AISCC include beer kegs (manufactured from stainless steel) transported on a ship and architectural finishes on buildings, etc. [14, 15, 16]. The common findings in these cases are the presence of chloride and stress either residual (caused by fabrication process such as rolling, welding, forming etc) or applied in service. Moreover there was no requirement for the material to have undergone sensitisation before chloride exposure. It is believed that AISCC will eventually develop if the exposure time of the stagnant electrolyte remains sufficiently long.

1.4 Limitations of Current Understanding

Most of the previous research on AISCC of austenitic stainless steels has studied the effect of temperature and relative humidity (RH). The techniques employed involved:

- Either, U-bend specimens, which do not provide good quantified control over applied stress, resulting in an uneven stress distribution around the apex. This technique loads specimens to stresses well beyond their yield values [13, 17, 18].
- Or, four-point bend specimens tightened by hand and a spanner [19]. The applied load was not measured and there was no attempt to determine the actual stress present in the parent and weld materials.

Thus, there is a need for an investigation with improved control over stress distribution and a more detailed analysis of the effect of residual stress on the susceptibility to AISCC. With the advantage of quantifying the residual stress and applied stress, it may be possible to determine the stress threshold for AISCC in both parent and weld specimens. The temperature at which AISCC can occur is also of practical importance, but the time for cracking to occur at lower temperatures was limited by the time frame of this study.

1.5 Technical Objectives of the Research

The technical objectives of the research are:

- To determine by experiment the relative significance of the metallurgy (parent material and weld metal composition and microstructure), the environment (temperature and relative humidity), and the stresses (residual, magnitude) on AISCC of samples of a ILW container;
• To increase knowledge by measurement and modelling of the residual stresses in the container as a result of fabrication processes;

• To explore means of mitigating the risk of AISCC either by appropriate control of residual stress from fabrication process, microstructure and composition, or the environment.
References


2 Stress Corrosion Cracking and Atmospheric-Induced Stress Corrosion Cracking of Austenitic Stainless Steel: Literature Review

2.1 Overview

Stress Corrosion Cracking (SCC) is a general term used to describe failures in stressed components that occur by crack propagation under corrosive environments. The requirements for SCC to occur include the presence of (a) a tensile stress, (b) a corrosive environment, and (c) a susceptible material or microstructure as illustrated below.

SCC is a time-dependent environmentally assisted process that requires sufficient conditions of electrochemical potential, mechanical stress and susceptible material for it to occur. Its occurrence may be preceded by surface corrosion reactions and pitting. Crack growth results from the combined reaction between mechanical stress and corrosion.

Conventionally SCC occurs as a result of the exposure of a metal surface to a flowing or stagnant fluid (gas or liquid) containing corrosive species. Atmospheric induced stress corrosion cracking (AISCC) is a particular form of SCC. The corrosive environment is generated by a deliquesced salt on a metal surface that forms a layer of electrolyte in the absence of full immersion in aqueous solution.

Stress can be as a result of static or cyclic loads under service conditions and/or residual and thermally-induced stresses due to processing and fabrication. In general, stresses that cause SCC are tensile in nature, although controversy exists as to whether residual plastic strain in the microstructure is required or not. Work by Van Boven et al. [1] showed that both micro pitting and SCC were promoted by the presence of tensile residual stress from fabrication.
A commonly argued mechanism explains SCC as a rupture of the protective passive (oxide) film leading to the initiation of cracking at the ruptured sites which are more susceptible to localised corrosion attack. The level of tensile stress in the material generally determines the rate of crack propagation, thus the greater the stress the shorter the expected time to failure [2]. Crack growth tends to occur perpendicular to the principal stress direction although microstructural effects cause variations in this general trend.

### 2.2 Susceptibility of Stainless Steel ILW Containers

Austenitic stainless steels are used in many industries and engineering applications. The reasons for their selection often include cost, aesthetic value, durability and ease of maintenance. Under most conditions, stainless steels can provide excellent corrosion resistance. However when aggressive ions are present, such as chlorides, stainless steels are susceptible to localised corrosion.

The susceptibility of stainless steels to SCC decreases with reduction in stress. There is generally a threshold of stress below which SCC is unlikely to occur in a given length of time. However, this threshold of stress may not be a constant and may decrease slowly with increasing exposure time. The threshold is certainly affected by the amount of chloride present as well as the temperature. Thus, SCC may still develop if sufficient time is given even in conditions that are conventionally well below the threshold [3].

In the context of an ILW waste container manufactured from austenitic stainless steel, stresses arise from fabrication processes such as cold working and welding. During welding, part of the material is heated up to melting point forming a molten weld pool. It is then cooled rapidly to room temperature. Contraction resulting from cooling of the weld pool gives rise to localised stress around the weld.

No heat treatment is usually performed after welding of ILW containers. In addition to that, the cold working on metal sheets in the manufacturing process also contributes towards residual stresses. During manufacture, metal sheets are plastically deformed causing development of residual plastic strain together with an overall increase in stored energy (dislocation density) in the microstructure [4, 5].

A criterion for SCC to take place is to have an environment which provides the necessary driving force for corrosion. The breakdown of the protective passive film generally occurs when austenitic stainless steel is exposed to an aqueous environment containing halide or other aggressive
species. Process waters often show the presence of chlorides, usually in the form of NaCl, CaCl$_2$ and MgCl$_2$ and therefore stainless steel structures in the chemical sector are commonly at risk. Scientific literature reports that an increase in oxygen and chloride concentration of the environment raises the risk of SCC [5].

There is a common engineering assumption that SCC only occurs when the temperature is greater than 60°C. This may be because the initiation and propagation rate of SCC becomes much slower below this temperature. Susceptibility increases as the temperature rises above this threshold [6].

Emerging evidence over the past decade has shown this assumption is not valid. It has been demonstrated that given sufficient time SCC can occur at ambient temperatures [3, 7, 8, 9]. The evidence also indicates that an environment that promotes condensation of moisture and adsorption of water from an atmosphere by crystalline salts provides the necessary requirements for SCC to occur [7].

2.3 Mechanisms of SCC

Potential sites for initiation of stress corrosion cracking include pits, grain boundaries, slip steps, pre-existing surface defects and local mechanical damage which all generally form on a passive surface. Pits form on the metal surface but not all of them will progress into cracks. Cracks develop according to the following stages [10]: (1) Pit initiation, (2) Pit growth, (3) Transition from pit to crack, and (4) Crack growth.

SCC often initiates at corrosion pits which often, but not exclusively, are associated with surface breaking of non-metallic inclusions such as MnS. Pits behave as potential local micro anodes and, if there is sufficient local stress at a nucleated pit, it may grow into a primary crack. Such cracks eventually grow laterally into the specimen and perpendicular to the principal stress direction [6, 11, 12, 13].

Electrochemistry, pit geometry, local stress and strain level affect the transition from pitting to cracking. SCC can also initiate at a grain boundary if the local chemistry makes it susceptible for intergranular attack. A bare metal surface can be introduced via the sliding of slip planes (see Figure 2-2) upon application of stress thus rupturing the passive film on the surface, or by chemical attack which removes the protective oxide layer.

Cracks can also initiate as a result of selective dissolution at the metal matrix and oxide interface. Investigation of SCC crack tips in 316 stainless steels has shown the presence of chromium-rich
oxides at such an interface [14]. The presence of Cr₂O₃ has been noted but the material showed no sign of Cr depletion under the oxide layer. In stainless steels cracking is mostly induced by chloride and a strong influence of the mechanical factor is often required. For SCC to occur, these two criteria must be met [15]:

- A threshold stress or strain must be exceeded for SCC to initiate
- A threshold stress intensity factor, K_{SCC} must be exceeded for SCC propagation

However, it has been argued that these are only valid when considering SCC in high strength alloys or for crack arrest in strongly decreasing residual stress fields [16].

When SCC initiates from pre-existing surface defects or localised corrosion sites, the mechanism of growth changes, for example from pit widening to crack extension at the crack tip. There are two major classes of model that have been used to describe stress corrosion cracking: (a) dissolution models and (b) mechanical fracture models. Dissolution models include the film-rupture mechanism as well as active path corrosion processes (such as slip-dissolution and corrosion tunnelling). Mechanical fracture models include both ductile and brittle crack growth mechanisms. Hydrogen-enhanced localised plasticity (HELP) and adsorption-enhanced plasticity mechanisms both fall under ductile crack growth models. Brittle mechanical models include film-induced cleavage, tarnish rupture and hydrogen embrittlement. It is likely that more than one of these mechanisms may be active at different times during the crack lifetime.
2.4 Atmospheric-Induced Stress Corrosion Cracking (AISCC)

Most studies on conventional SCC are focussed on high-temperature environments, or at least above 60°C, with immersed exposure in a fluid [17, 18]. However, in an early article by Staehle [19] he notes a few important points, one of which states that SCC is not inherently a high-temperature process. For example, SCC can occur below 0°C in dry hydrogen and at 0°C in aqueous environments; and in other systems which require temperatures above 100 to 200°C. He also argues that a concentrated or aggressive environment is not necessary for SCC to occur.

Current understanding of AISCC is that it occurs when a hygroscopic salt or aerosol particle deposits on a metal surface and starts absorbing moisture from the surrounding atmosphere at a critical relative humidity. The absorption results in a thin layer of saturated salt solution on the metal surface. Localised attack such as pitting or crevice corrosion can then occur.

If sufficient stress, either residual or applied, is present in the component, cracks may initiate and grow in susceptible materials. At locations of high stress concentration, for example welds and structural discontinuities, the susceptible microstructures become vulnerable to cracking. Often cracking initiates in surface pits which may act as stress and environment concentrators.

The major differences between conventional SCC (CSCC) and AISCC are:

- Unlike CSCC, AISCC does not require full immersion or large quantities of corrosive media.
- AISCC is usually triggered by deliquescence of salts that have settled on the component surface, or by capillary action which draws moisture toward inert particles.
- AISCC is dependent on salt type hence making it dependent on RH and temperature.
- AISCC requires long exposure (initiation) times before cracking at ambient temperatures.
- AISCC occurs in atmospheres generally regarded as benign.

Atmospheres are not consistent: the level of relative humidity and contaminants in the air can vary significantly between urban and coastal areas.

2.5 AISCC in Public Facilities

In the failure investigation of the collapse of some public facilities such as swimming pools [3, 7, 8, 9], AISCC appeared to be the main cause. The collapse of a swimming pool roof in Uster, Switzerland which caused twelve fatalities was associated with the failure of load bearing components caused by AISCC. Ropes, fasteners, wires etc were the sites of high stress concentrations. The operating temperature was around 30°C.
This represents a classic example of corrosion induced by airborne corrosive species and has been reported elsewhere [20]. Corrosion did not occur on the steel surface immersed in the pool water but at locations away from the pool water. However, pool water was still the primary source of contamination in the form of an atomised spray. The design of the air circulation system of the swimming pool encouraged the deposition of dust and airborne particles onto the metal surface. The dust and particles were transported from the pool water to remote locations where water vapour condensed and formed crevices, resulting in dissolution of chemical species.

The corrosion behaviour of the alloy in a vapour phase is highly dependent on temperature and RH. Tests conducted in a vapour phase at 30°C showed the presence of open pits. When a similar test [21] was conducted at 50°C, no localised attack was observed. This was believed to be contributed by the higher rate of condensation at lower temperature. AISCC has also been observed in beer kegs (manufactured in stainless steel) transported on a ship, architectural finishes on buildings and at other swimming pools [22].

AISCC is also sometimes known as external SCC (ESCC) by some Japanese researchers [20, 23, 24].

### 2.6 Factors Affecting AISCC

Unlike immersed stress corrosion cracking, the tendency to AISCC varies with chloride type due to the varying deliquescence of different salts. Thus, the amount (concentration) of chloride and pH in liquid films vary according to the type of salt and the RH. Japanese researchers [25, 26] observed that AISCC was unlikely under sodium chloride but, if the RH was kept within a certain range (see Table 2-1), AISCC could occur under calcium, magnesium and zinc chloride. Deposits of synthetic seawater also behaved similarly to those of magnesium chloride and the susceptibility to cracking depended on the chloride type of the electrolyte, which itself was dependent on RH. When RH was high, too much water was absorbed and the electrolyte became too diluted to induce AISCC. At low RH, the ionic mobility in the surface electrolyte might be insufficient, thus the resistance was too high to establish a viable corrosion cell.

Other evidence for AISCC being dependent on salt type is described in the work by Prosek et al. [27]. Their U-bend specimens were deposited with chloride droplets of various compositions and left at temperatures between 20 to 50°C and 15% to 70% RH. Their work concluded that both 304L and 316L grades were susceptible to SCC when magnesium and calcium chlorides were present, at relatively low humidity with temperatures above 30°C. The SCC tendency increased with a rise in temperature and drop in RH. Calcium chloride was most aggressive; magnesium chloride was less aggressive than calcium chloride but still more than sodium chloride. Calcium
chloride was more aggressive than other salts as a more concentrated solution is formed upon deliquescence of this salt.

Table 2-1: Susceptibility of 304L to AISCC with different salt contamination under varying temperatures [25, 26]. RH\textsubscript{range} is the range of RH at which SCC was observed. RH\textsubscript{max} is the RH at which SCC rate is at maximum. RH\textsubscript{sat} is the RH at which the solution becomes saturated.

<table>
<thead>
<tr>
<th>Species</th>
<th>25°C</th>
<th>50°C</th>
<th>70°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RH\textsubscript{sat}</td>
<td>RH\textsubscript{max}</td>
<td>RH\textsubscript{range}</td>
</tr>
<tr>
<td>NaCl</td>
<td>75%</td>
<td>No SCC</td>
<td>No SCC</td>
</tr>
<tr>
<td>MgCl\textsubscript{2}</td>
<td>33%</td>
<td>30%</td>
<td>25-50%</td>
</tr>
<tr>
<td>Synthetic seawater</td>
<td>–</td>
<td>30%</td>
<td>30-50%</td>
</tr>
</tbody>
</table>

2.7 Storage Conditions of ILW Containers

In the UK, the current practice is that the containers are kept above ground in a ventilated storage building. The location is often close to coastal areas. These containers will eventually be transferred to a deep underground repository, but this may not occur for many years.

There are 4 types of environment to which these containers will be exposed. The interior of the containers will be subjected to corrosion resulting from encapsulant and waste. The exterior of the containers will undergo three different stages of exposure; first when they are kept in ventilated storage buildings, second when they are transferred to the repository (pre-backfill) and third, after backfill. Under all these environments they are prone to localised forms of corrosion and environmental cracking such as AISCC which is caused by airborne particles in the atmosphere. This literature review only considers the external environment (atmosphere) of the container. The internal corrosion issue will not be discussed.

During planned storage in ventilated sheds near coastal locations, the exterior of the container will be mainly exposed to prevailing atmospheric conditions. Contamination comes from dusts, salts etc, forming a thin layer of electrolyte when sufficient moisture is present. The condensation of electrolyte on the metal surface will be affected by temperature, local airflow, relative humidity as well as contamination such as soil and salt, and pollution. The concentration of electrolyte will vary with relative humidity as it becomes more dilute at high relative humidity and more saturated at low relative humidity.

ILW containers are subjected to continuous deposition of airborne and atmospheric contamination. Salt aerosol particulates from sea water such as MgCl\textsubscript{2} and CaCl\textsubscript{2} will adhere to metal surface and are very likely to become wetted at relative humidity greater than 30-35%.
Dusts, soils and particles can induce a capillary effect and also trap moisture at lower than anticipated RH, becoming potential sites for crevice corrosion.

The currently suggested control concept is to keep relative humidity well below 75%, i.e. below the deliquescence point of NaCl. However with the presence of other contaminants, whether this is a good approach remains to be discovered.

2.8 Salt Deliquescence

Substances such as salts that have a strong affinity for moisture (i.e. hygroscopic), will absorb moisture from the atmosphere if exposed to it, forming a liquid solution; this is the phenomenon of deliquescence. In order for this absorption to occur, the vapour pressure of water in the air must be greater than the vapour pressure of the saturated solution. When water is mixed with a non-volatile substance, the vapour pressure is proportional to the mole fraction of water in the solution according to Raoult’s Law [28]. However, because of the electrostatic attraction between ions, electrolyte solutions do not exactly follow Raoult’s Law particularly at high concentration.

At a given temperature the molecules and ions in the solution have the same kinetic energy. Essentially there are the same number of particles at the surfaces of both solution and pure water. But in a solution where only water particles can escape from solution, the vapour pressure is lower. At 25°C, a saturated salt solution of NaCl has a saturated RH (RH_{sat}) of 75.3% and MgCl₂ of 32.8%. This RH_{sat} is dependent on temperature. For example, at 20°C, magnesium nitrate has RH_{sat} of 54.4% ± 0.2. This value decreases to 53.5% ± 0.2 at 23°C and further to 52.3% ± 0.2 at 27°C. RH_{sat} is also known as critical relative humidity (RH_{crit}) or deliquescence relative humidity (DRH).

At or above this DRH, deliquescence will occur [29]. In other words, there is sufficient moisture in the air to wet the settled salts. At low RH, salt particles are solid, i.e. crystalline. As RH increases, the particles will remain solid until a DRH is achieved at which salt particles start to absorb moisture from atmosphere and become a droplet of saturated solution (i.e. aqueous phase) as illustrated in Figure 2-3.
It is believed that corrosion starts at the RH values corresponding to the deliquescence point. For example, for sodium chloride-contaminated samples at RH between 65% and 95%, corrosion increases with rising RH above around 75%. Below 75% RH, no corrosion would be expected to occur even after long exposure, while corrosion started at RH>75% exactly at deliquescence point as illustrated in Figure 2-4 (for corrosion of iron that was pre-contaminated with NaCl) [29].

### 2.9 Atmospheric Pollutants

Contamination on metal surfaces can come from aerosols or gases [31]. They can be in the form of dust, soil or inert particulates; basically anything that is airborne. Aerosols come in the form of suspended fine liquids or solid particles in a gaseous medium, in either pure or mixed forms. Typical examples of these include salt spray and dust. They consist of hygroscopic salts such as chlorides, sulphates and nitrates. The presence of chloride- and sulphate-enriched particles is very common in marine atmospheres.

As some storage sites are close to coastal areas, the composition of marine aerosol is of interest as well. According to Leck and Bigg [32], marine aerosols consist of sea-salt, non sea-salt sulphate particles and possibly organic particles from the ocean micro-layer. The early work by Blanchard and Woodcock [33], and O’Dowd and Smith [34] presented the production of aerosols by air bubbles. Gong et al. [35] later suggested that marine aerosols could also be a product of wave-breaking. When the wind speed exceeds 4m/s, the resulting wind stress generates ocean waves. As these waves break, thousands of small sea-salt particles are formed; they usually have a diameter greater than 10μm [36]. This wave-breaking action also introduces air bubbles into the surface water. These bubbles rise onto the ocean surface and burst producing several hundreds of
film drops and around ten jet drops per bubble. The wave activity increases with wind speed. Higher wind speed produces more air bubbles, thus generating more film and jet drops. As a result of updrafts, sea-salt particles are transported into the atmosphere where they are carried away by winds [34]. Because of the compositional character of these sea-salt particles, the hygroscopicity of seawater samples was always lower than that of pure chloride particles. Niedermieler *et al.* [37] suggest this was caused by the insoluble or less hygroscopic compounds in seawater particles.

These aerosols exhibit deliquescence and efflorescence in air, hence the corresponding RH at which these happen is known as the deliquescence relative humidity, DRH and efflorescence relative humidity, ERH. The transformation from solid to aqueous phase occurs when the RH reaches a value specific to the chemical composition of the aerosol. When the RH drops, the moisture evaporates and the aerosol crystallises again. A simple illustration of DRH and ERH was thoroughly explained by Tang and Munkelwitz [38].

Figure 2-5 demonstrates the behaviour of deliquescence and efflorescence of an aerosol mixture of salts. When RH reaches approximately 72% (lower than DRH, approximately 75.5%), the solid particle experiences an abrupt change in mass. As RH increases further, it progresses into the multiphase region BC with some undissolved salt in an electrolyte. At point C which is the DRH, it turns into a completely saturated solution.

As RH further increases, the droplet keeps growing with the increased supply of moisture from condensation. The droplet grows because it needs to maintain the equilibrium with its
surrounding water vapour. Deliquescence occurs when the free energy of the crystal and that of the droplet are equal. In the solid crystalline state, the free energy is lower at low RH. In an aqueous phase, the free energy is lower at high RH [39].

When RH falls, the water content in the droplet also reduces and evaporation continues even after RH falls below DRH (point C). The droplet will expel all its water content and crystallise when the RH becomes sufficiently low. Along the line EC, the droplet has entered a metastable state at which a supersaturated solution is formed. This behaviour agreed with the observations of Rood et al. [40]. They concluded that, in both urban and suburban environments, meta-stable droplets exist more than half of the time when the ambient RH is between 45% and 75%.

As the temperature rises, the humidity also increases because the air can hold more water; hence the vapour pressure of a droplet at a given concentration will increase. A stable droplet is able to exist at a higher salt concentration as water continues to evaporate into the air. Thus, DRH decreases as temperature increases.

At low RH, the presence of absorbent particles such as carbon can increase the amount of water present on metal surfaces [41]. Inert, non-absorbent particles do not have a significant effect on corrosion but they can also serve as ideal sites for capillary condensation to occur [42]. Contaminant gases are often present in the form of nitrogen oxide, sulphur oxide, hydrogen sulphide, carbon dioxide or organic acid vapours. The concentration and composition of these gases will depend on the external atmosphere (site specific), and the control procedure within the waste store.
Sinclair [43] has classified airborne particulates according to their size. Fine particulates with diameters between 0.1 and 2.5\(\mu\)m are mainly products from combustion of fossil fuel (anthropogenic origin). They are generally more corrosive and more water-absorbent. Coarse particulates with diameters between 2.5 and 15\(\mu\)m are of mineralogical origin. They are usually less corrosive and carry lower amounts of water soluble species. They settle more rapidly due to gravity and are easily removed by an air filtration system.

Local crevice corrosion could occur beneath soil/dust deposits on metal surfaces as well [42]. Differential aeration induces an increase in corrosion rate when capillary effects draw moisture towards the base of the particle as illustrated in Figure 2-6. The surface tension of the retained moisture will determine the duration for which the moisture is trapped, thus affecting the corrosion rate.

![Figure 2-6: Schematic presentation of moisture retention at the base of a particle on a metal surface [42]](image-url)
References


3 Characterisation of Intermediate Level Waste Containers

3.1 Container Design

The design of UK intermediate level nuclear waste containers is shown in Figure 3-1. They are cylindrical drums fabricated from UNS S31603 (Type 316L) and UNS S30403 (Type 304L) stainless steels welded using the tungsten inert gas (TIG) process. The containers comprise a circular flat base (316L) of nominally 800mm diameter and 2.9mm wall thickness with a shallow up-stand edge that is welded to a cylindrical body nominally 2.3mm wall thickness made from a single cylindrical strake (316L). The upper end of the body is welded to a reducing diameter neck section (316L).

The body has a series of circumferential contours providing added strength against side impact. The top edge of the body is welded onto a flange (304L). The drum lid (316L) of 2.9mm wall thickness also with a welded flange (304L) is sealed onto the drum by bolted outer rings around the flange of the lid. A sintered stainless steel filter element is incorporated in the container lid vents. This container is made of thin-walled steel and is not aimed to provide any shielding against radiation.

Figure 3-1: Schematic illustration of an ILW container [1]
3.2 Container Fabrication

There are two circumferential welds on the container body (connecting neck, body and base) and two longitudinal welds (each on neck and body section respectively). During weld preparation for circumferential welds, the stainless steel sheets are clamped up for automated TIG welding with a maximum gap of 0.25mm without any edge preparation (see Figure 3-2 and Figure 3-3).

The container flange is fabricated by two circumferential welds (top internal and bottom external) as illustrated in Figure 3-4. No filler material was used in these two runs. Welding is achieved by fusion between two components.

The manufacture of these ILW containers follows the TWI [2] and British Nuclear Fuels Ltd (BNFL, now Sellafield Ltd.) standards [3, 4] for welding and materials. Wet particle impact cleaning or dry bead blasting is used to achieve a uniform and low-glare surface finish on drum and to remove contamination.
3.3 Rationale and overview of the testing programme

In this research an experimental programme was developed to investigate the effect of stress and environment on the susceptibility to AISCC of parent material and weld metal. The main elements of the programme are a series of AISCC experiments on specimens sectioned from parent material and welded areas and measurements of residual stress within these specimens and the drum as a whole. To support this work, the programme includes the characterisation of the parent metal and weld properties and microstructure of the container materials.

The following testing methods were used in this work:

- **Materials characterisation**
  - Mechanical properties: Tensile and hardness testing.
  - Chemical/materials properties: chemical and phase analysis.
  - Metallographic examination of parent material and weld metal

- **Residual stress profiling**
  - X-ray diffraction
  - Neutron diffraction

- **4-point bend AISCC tests using different salt solutions.**
  - Sodium chloride
  - Magnesium chloride
  - Synthetic seawater (ASTM D1141)

The AISCC tests are described in Chapter 4 while residual stress characterisation is in Chapter 5. The mechanical/chemical/metallographic characterisation techniques and results are described below.
3.4 Source of materials and specimen preparation

Materials for the testing programme were taken from an unused complete ILW container originally sourced from Sellafield Ltd. and supplied to TWI by the University of Manchester. Figure 3-5 shows the container as received by TWI. This container was manufactured by Deva Manufacturing Ltd according to the design and fabrication route described in the preceding section.

Figure 3-6 illustrates the locations on the container from which specimens were removed. These locations were chosen because the neck and body sections of the ILW container are of the same thickness (2.3mm) as are most parts of the container, making them more representative (note: only the base section is slightly thicker at 2.9mm). The 2.3mm thick materials are approximately 1.2m in height around a circumference of 2.51m. This equals to a total surface (one side) area of approximately 2.51m². Three parent and two weld specimens were taken from region C around the circumferential weld. Control specimens were prepared from region D.

![Figure 3-5: As-received ILW container](image)

3.5 Material properties characterisation procedures

3.5.1 Tensile and hardness testing

The characterisation of Tensile and hardness properties was undertaken according to the normal standards [5, 6]. A flat cross section sample each from regions E and F (see Figure 3-6) was polished to a 0.25μm finish. Hardness measurements were made using a Vickers hardness tester with a 0.5kg load and repeated with a 10kg load according to BS EN ISO 6507-1:2005 [5]. Readings were taken across the section of the weld as shown in Figure 3-7.
Tensile tests were carried out on four specimens of parent metal, two longitudinally orientated and two circumferentially orientated without flattening. The tests were carried out according to BS EN ISO 7500-1:2004 [6].

3.5.2 Chemical analysis
Elemental chemical analysis was conducted using the optical emission spectroscopy (OES). Specimens containing circumferential welds were mounted in conductive Bakelites and polished to a particle size of 0.25µm.

3.5.3 Metallographic sectioning
Metallographic examination was conducted on cross-sections of the parent materials and weld regions of the circumferential weld (see Figure 3-8) between the neck and body section (Region D).
of the container, the longitudinal weld in the container body and the flange weld. The sections were etched electrolytically in a mixture of 20% sulphuric acid + 80% distilled water (de-ionised water) and 0.1 mg/litre of ammonium thiocyanate. The voltage was 2V and the specimen was etched for no more than 10 seconds. This etchant attacks and reveals the ferrite phases in the specimen.

![Figure 3-8: Dashed boxes indicate the locations at which images were taken](image)

### 3.6 Materials properties results and discussion

#### 3.6.1 Hardness

Figure 3-9 shows the Vicker’s hardness profile across the circumferential weld between the cylindrical body and neck taken at Region D. The graph shows a drop in hardness to about 160 Hv as it enters the heat affected zone (HAZ) on the cylindrical body side of the weld, an increase up to approximately HV165 at the centre of the weld and a further decrease again as it re-enters the HAZ on the other side. It finally increases sharply to over 200 HV from the HAZ to the parent neck region.

The drop in hardness as it enters the HAZ is probably due to the larger grains produced by the welding heating/cooling cycle of the HAZ. The hardness increases from the HAZ into the recrystallisation zone of the weld where the grains are very small. The higher hardness values in the neck section of the container are likely to be caused by cold working required to form this profile.

#### 3.6.2 Metallographic sections and microstructures

A macroscopic image of the section of circumferential weld between the neck and body of the container is presented in Figure 3-10 below. To the left is the neck section (316L) and to the right is the body section (316L). More detailed images at a higher magnification were taken at the numbered positions shown on the image.
The metallographic images of the parent material taken on the outer, middle and inner regions of the section (Figure 3-10) are reproduced in Figure 3-11 and Figure 3-15. They show a cold-worked structure throughout with visible austenite grains. There are also dark particles/stringers consistent with inclusions. The density of these particles/stringers increases in the middle of the section. This could be caused by the segregation of alloying elements when the sheet was first produced.

![Vicker's hardness Distribution across Circumferential Weld of Region C](image)

*Figure 3-9: Vickers hardness profile across the circumferential weld.*

The weld metal consists of interdendritic network, which was later verified by X-ray diffraction to be ferrite (see Figure 3-13 and Figure 3-16), in an austenite matrix. It is known that the susceptibility of stainless steel to chloride stress corrosion cracking decreases with an increase in the amount of ferrite in the austenite matrix [7]. Ferrite has the tendency to block the propagation of chloride transgranular SCC (but not hydrogen embrittlement).

However, there are opposing opinions about the impact of ferrite on SCC in welds [8, 9, 10] where some opinions have suggested that ferrite has a negative effect on SCC. The work by Krishnan and Rao [8] showed that increasing ferrite content decreased SCC resistance in austenitic clad metals at room temperature. They found that the ferrite network was attacked and propagation progressed by the stress-assisted dissolution of ferrites. They also suggested that the resistance to SCC could be improved when the heat input of welding was lower.
Figure 3-10: A macroscopic image of the circumferential weld section from region D of the ILW container

The HAZ is relatively narrow, which is a few hundred microns wide (Figure 3-9 and Figure 3-11). This is because a low heat input TIG process was used. The HAZ microstructures have no significant features that would make this region more susceptible than the parent material or weld metal.
Figure 3-11: Metallographic images of the drum neck sections labelled (1), (2) and (3) as in Figure 3-8 and Figure 3-10
Figure 3-12: Metallographic images of HAZ of the drum neck sections labelled (4), (5) and (6) as in Figure 3-8 and Figure 3-10
Figure 3-13: Metallographic images of the weld regions labelled (7), (8) and (9) as in Figure 3-8 and Figure 3-10
Figure 3-14: Metallographic images of the HAZ of the body sections labelled (10), (11) and (12) as in Figure 3-8 and Figure 3-10
Figure 3-15: Metallographic images of the drum body sections labelled (13), (14) and (15) as in Figure 3-8 and Figure 3-10
3.6.3 Tensile properties

The results (Figure 3-17 and Figure 3-18) of tensile testing the parent metal show significantly higher yield stress (0.2% proof stress) in the longitudinal direction (approximately 400MPa) than in the circumferential direction (approximately 300MPa). Both these values are greater than the specified minimum yield stress of annealed 316L, which is close to 170MPa (ASTM A240/A240M-09b, ASTM A666-03). Further, the elongation was found to be greater in the circumferential direction than in the longitudinal direction.

The ultimate tensile stresses obtained from the four tensile specimens (616 to 651MPa, see Table 3-1) exhibited similar values to that of the manufacturer’s inspection certificate. There was no significant difference between the values obtained for the circumferential and longitudinal directions.

These results indicate the presence of significant cold-work during manufacturing of the containers including rolling of the sheet and fit-up for welding. The rolling also had an effect on the residual stress distribution and contributed to the elongated grains and the anisotropic properties observed. The anisotropy of tensile properties and elongation means that the ductility in the longitudinal direction would be expected to be less than that in the circumferential direction.
Figure 3-17: Stress strain curve of a parent specimen along longitudinal direction.

Figure 3-18: Stress strain curve of a parent specimen along circumferential direction.
Table 3-1: Tensile testing results on parent metal in both circumferential and longitudinal directions

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Description</th>
<th>Proof stress $\sigma_{0.2%}$</th>
<th>Ultimate tensile stress</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Load [kN]</td>
<td>Stress [MPa]</td>
<td>Load [kN]</td>
</tr>
<tr>
<td>1</td>
<td>Parent tensile in circumferential direction</td>
<td>9.16</td>
<td>324</td>
</tr>
<tr>
<td>2</td>
<td>Parent tensile in circumferential direction</td>
<td>8.64</td>
<td>299</td>
</tr>
<tr>
<td>3</td>
<td>Parent tensile in longitudinal direction</td>
<td>11.56</td>
<td>41</td>
</tr>
<tr>
<td>4</td>
<td>Parent tensile in longitudinal direction</td>
<td>11.44</td>
<td>403</td>
</tr>
</tbody>
</table>

3.6.4 Chemical and phase analysis

The results of chemical composition analysis are very close to that of the manufacturer’s conformance report and are presented in Table 3-2. (Note: The manufacturer’s conformance report is included in the same table for reference.)

Table 3-2: Chemical analysis (%) of the parent specimen extracted from the container body

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Al</th>
<th>As</th>
<th>B</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer conformance report No. 10732</td>
<td>0.02</td>
<td>0.58</td>
<td>1.1</td>
<td>0.03</td>
<td>0.001</td>
<td>17</td>
<td>2.09</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>TWI chemical analysis report No. S/08/163</td>
<td>0.024</td>
<td>0.55</td>
<td>1.08</td>
<td>0.03</td>
<td>&lt;0.002</td>
<td>17</td>
<td>2.00</td>
<td>11</td>
<td>0</td>
<td>0.01</td>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>BS EN 10088-1:2005</td>
<td>0.030 max</td>
<td>1.00 max</td>
<td>2.00 max</td>
<td>0.045 max</td>
<td>0.015 max</td>
<td>17</td>
<td>2.00 max</td>
<td>10</td>
<td>19</td>
<td>2.50</td>
<td>13</td>
<td>10</td>
</tr>
</tbody>
</table>

Figure 3-19 shows the X-ray diffraction peaks from the samples (marked as “YJ” and followed by numerical identification, see legend on the top right corner) taken from various weld locations on the container. These show the presence of austenite and ferrite phases. No diffraction peaks of other phases were detected.
Figure 3-19: Diffraction peaks of various samples from different locations on the ILW container body
References


4 AISCC Tests and Examination

4.1 Specimen Preparation

All AISCC tests were undertaken on specimens machined from the neck and upper body sections (regions C and D) of the 500L ILW container (see Figure 3-6). The specimens were in the form of slightly curved longitudinally orientated strips or bars with dimensions of 100mm long x 15 mm wide x 2.3mm deep (the full thickness of the container). Some specimens were wholly of parent metal whereas others contained the neck-to-body weld across their mid-length.

The sides and ends of the specimens were ground to the correct width and length but the top and bottom surfaces and weld areas were maintained in the as-received condition. One parent specimen was annealed at 1100°C for two hours and allowed to furnace cool for 24 hours to reduce residual stresses to a low level. Another parent specimen was etched using a mixture of 8% perchloric acid and 92% glacial acetic acid at 40-45V to remove a thin surface layer of 100microns. All the specimens were mechanically etched with an alphanumeric identification. They were cleaned in acetone then deionised water to remove all residues and debris from manufacturing and handling.

From this point onwards, all specimens were only handled using powder-free gloves. After cleaning with deionised water, they were kept in a desiccator for at least 24 hours to ensure thorough drying. Biaxial strain gauges were then attached on the bottom (inner) surface in line with the main axis.

4.2 External Loading of Specimens

The specimens to be externally loaded were placed in a jig with adjustable rollers to apply 4-point bending. (Other specimens were retained unloaded as control specimens.) The strain gauges were connected to a converter (‘strain box’) which allowed strain logging. The strain box (Spectra MS System by National Instruments Ltd.) converts the changed in electrical resistance in the strain gauges under loading into electrical signals from which micro-strain is derived and displayed by the logging software.
The jig was tightened by hand sufficiently to lock the specimen securely between the rollers. It was then further tightened to increase displacement of the specimen and the resulting biaxial strain and displacements were measured and recorded. The displacement at the mid-length was measured using a displacement gauge.

The stress induced by an imposed displacement was calculated from measured strains according to Equation 4-1. $E$ is the Young’s modulus, $\sigma_1$ is the longitudinal stress with respect to ILW container, $\sigma_2$ is the corresponding transverse stress, $\varepsilon_1$ is the corresponding longitudinal strain, $\varepsilon_2$ is the transverse strain and $\nu$ is the Poisson’s ratio.

$$\sigma_1 = \frac{E}{(1 - \nu^2)} (\varepsilon_1 + \nu \varepsilon_2)$$

Equation 4-1
Displacement was applied to a level of strain sufficient to raise the stress to the measured yield strength of the parent material i.e. around 400MPa (0.2% proof strain). An example of the data recorded is presented in Table 4-1.

The nominal stress is the measured proof stress of the parent metal. Both Young’s modulus and proof stress were obtained from the tensile testing (see Section 3.6.3) of a longitudinal sample extracted from the ILW container. The straining of these four point bend specimens was performed within the elastic region of stress curve and was kept as close to the proof stress as possible.
Table 4-1: Displacements and calculated stresses of the 4-point bend parent specimen labelled P2 (Note that $E = 194000$ MPa and Poisson’s ratio = 0.3, both values were obtained from tensile testing).

<table>
<thead>
<tr>
<th>Displacement, mm</th>
<th>Strain gauge reading, $\mu$e</th>
<th>Stress, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Longitudinal</td>
<td>Transverse</td>
</tr>
<tr>
<td>0.1270</td>
<td>213</td>
<td>67</td>
</tr>
<tr>
<td>0.2540</td>
<td>376</td>
<td>117</td>
</tr>
<tr>
<td>0.3810</td>
<td>529</td>
<td>164</td>
</tr>
<tr>
<td>0.5080</td>
<td>695</td>
<td>216</td>
</tr>
<tr>
<td>0.6350</td>
<td>868</td>
<td>270</td>
</tr>
<tr>
<td>0.7620</td>
<td>1036</td>
<td>323</td>
</tr>
<tr>
<td>0.8990</td>
<td>1205</td>
<td>377</td>
</tr>
<tr>
<td>1.0160</td>
<td>1366</td>
<td>429</td>
</tr>
<tr>
<td>1.1430</td>
<td>1535</td>
<td>485</td>
</tr>
<tr>
<td>1.2700</td>
<td>1696</td>
<td>539</td>
</tr>
<tr>
<td>1.2954</td>
<td>1725</td>
<td>549</td>
</tr>
</tbody>
</table>

Figure 4-3: Linear plot of displacement against calculated stress from Table 4-1

### 4.3 Application of the Surface Salt

Three levels of surface salt density (10, 30 and 100$\mu$gcm$^{-2}$) were chosen to investigate the relation between surface density and AISCC. Droplets of solution were placed by a pipette on the outer surface of the specimens in an array of positions on the parent metal and weld metal. After
application of salt solution, the specimens were dried in a desiccator for at least 24 hours so that the droplets evaporated, leaving the salt on the surface.

Three different types of salt were used in this investigation: sodium chloride, magnesium chloride and synthetic sea-salt. The droplet diameters (and hence the surface areas formed upon evaporation) were all consistent. The pipette dispensed droplets of 5±0.1μL and approximately 3±0.1mm in diameter. If the surface area of a droplet is defined as \( A \) and the amount of salt contained in a 5μL droplet is \( m \), then for a surface density of 100μgcm\(^{-2}\):

\[
100 \text{ μg cm}^{-2} = \frac{m}{A}
\]

A 5μL droplet with a diameter of 3mm will give surface area \( A \) of 0.070686cm\(^2\) and thus contain \( m = 7.0686\text{μg} \) of salt in the 5μL droplet. The amounts of salt for other deposition rates can be determined simply by the ratio. Finally, in order to calculate the quantity of salt added to the stock solution in order to achieve the required deposition rate, the chemical formula (and molecular weight) of the species added is required; for example, sodium chloride is NaCl (58.5 g mol\(^{-1}\)) while magnesium chloride is MgCl\(_2\).6H\(_2\)O (203.31 g mol\(^{-1}\)). The concentrations of solutions required to achieve the desired surface densities is tabulated in Table 4-2.

### Table 4-2 Preparation of salt solution with different loading densities

<table>
<thead>
<tr>
<th>Salt type</th>
<th>Amount of salt required per litre, g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Loading density</td>
</tr>
<tr>
<td></td>
<td>100μg/cm(^2)</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>1.4137</td>
</tr>
<tr>
<td>Magnesium chloride</td>
<td>3.0179</td>
</tr>
<tr>
<td>Synthetic sea salt</td>
<td>1.4137</td>
</tr>
</tbody>
</table>

The list of specimens is tabulated in Table 4-3. There were eight 4-point bend specimens in total: three of parent material, two of weld metal, one of annealed parent material and one of etched parent material.

Solution droplets were arranged as presented in Figure 4-4 and Figure 4-5 below:
4.4 Control Specimens

Six control specimens, as shown in Figure 4-6 and Figure 4-7 were prepared from region D (see Figure 3-6) with sodium chloride, magnesium chloride and synthetic seawater salt deposits. The specimens were placed in an environmental chamber but not loaded in 4-point bending so as to investigate the effect of residual stress alone.
Figure 4-6: Salt deposition matrix for small unstrained weld specimens (control specimen) labelled U1, U2, U3, U4, U5 and U6. Shaded region indicates weld.

Figure 4-7: A control specimen.
Table 4-3: List of 4-point bend and control specimens

<table>
<thead>
<tr>
<th>Material</th>
<th>Condition</th>
<th>Synthetic seawater†</th>
<th>Magnesium chloride</th>
<th>Sodium chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>100µg/cm²</td>
<td>30µg/cm²</td>
</tr>
<tr>
<td>Four-point bend specimens</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1</td>
<td>316L parent</td>
<td>As-received</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>P2</td>
<td>316L parent</td>
<td>As-received</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>P3</td>
<td>316L parent</td>
<td>As-received</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>W1*</td>
<td>316L weld</td>
<td>As-received</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>W2*</td>
<td>316L weld</td>
<td>As-received</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>P9</td>
<td>316L weld</td>
<td>Annealed</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>P12</td>
<td>316L weld</td>
<td>Etched</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Control specimens (unloaded)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U0</td>
<td>316L weld</td>
<td>Annealed</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>U1</td>
<td>316L weld</td>
<td>As-received</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>U2</td>
<td>316L weld</td>
<td>As-received</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>U3</td>
<td>316L weld</td>
<td>As-received</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>U4</td>
<td>316L weld</td>
<td>As-received</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>U5</td>
<td>316L weld</td>
<td>As-received</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>U6</td>
<td>316L weld</td>
<td>As-received</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

*Reapplied with magnesium chloride and synthetic seawater solutions only
† Diluted to 100µg/cm², 30µg/cm² and 10µg/cm²
4.5 Environmental Chamber Exposure

The environmental chamber used was a CTS -40/60 model manufactured by Climatic Testing Systems Inc. The chamber consists of a stainless steel interior, and a digital display on the door with a soft control panel. It allows testing under different levels of relative humidity and temperature. It can be programmed easily and any extra peripherals such as a logger can be readily attached to it for monitoring purposes. The chamber was visited on a daily basis whenever possible to ensure correct functioning and intermittent temperature checks were carried out with a calibrated thermometer.

The externally loaded and control specimens were kept at 40°C and 40%RH for the first nine months (March to December 2010). As there had been no cracking in this time, the decision was taken to raise the temperature to 80°C, with a corresponding reduction in RH to 27%. The DRH of magnesium chloride at 80°C is 26%. The same specimens remained in the chamber and some additional welded specimens were loaded with magnesium chloride and sea-salt droplets added. These conditions were maintained for a year until December 2011.

The decision to increase the temperature was taken because the observations of highly plastically strained U-bend specimens in previous experiments at The University of Manchester [1, 2] suggested that it might take too long before cracking would occur in the four point bending specimens loaded to yield. (It took five months before cracking occurred in the U-bend specimens tested in Manchester). It seemed reasonable enough to accelerate the exposure testing by increasing the temperature and decreasing the RH to still be above the DRH of magnesium chloride and sea-salt, which has a high proportion of magnesium chloride, hoping it would produce some visible cracks, even though the reduced RH would be below the DRH of sodium chloride where no cracking would be expected.

In December 2011, the temperature was decreased and RH increased to intermediate values between the first and second testing conditions. The third testing condition was at 60°C and 32%RH. This condition was maintained from December 2011 until the end of the experimental programme as indicated in Table 4-4 and Table 4-5.

When the temperature was increased in the second phase to 80°C, the logging of the strain gauges was discontinued as the gauges were affected by high temperature and gave false readings. As the use of strain gauges was no longer feasible at this temperature, it was logical to explore other means to investigate the effect of temperature changes on the load applied to the specimens. Annex F of API 579 [3] allows users to compensate the change in proof stress as a function of temperature.
According to API 579 equations, a proof stress of 400MPa at room temperature would decrease to 383.8MPa at 40°C, 364.8MPa at 60°C and 348.3MPa at 80°C.
Table 4-4: List of specimens and their associated testing conditions

<table>
<thead>
<tr>
<th>Specimen label</th>
<th>Material</th>
<th>Loading</th>
<th>Condition</th>
<th>2010</th>
<th>2011</th>
<th>2012</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mar</td>
<td>Apr</td>
<td>May</td>
</tr>
<tr>
<td>P1</td>
<td>316L</td>
<td>4-point bend</td>
<td>Parent</td>
<td>40°C, 40%RH</td>
<td>80°C, 27%RH</td>
<td></td>
</tr>
<tr>
<td>P2</td>
<td>316L</td>
<td>4-point bend</td>
<td>Parent</td>
<td>40°C, 40%RH</td>
<td>80°C, 27%RH</td>
<td></td>
</tr>
<tr>
<td>P3</td>
<td>316L</td>
<td>4-point bend</td>
<td>Parent</td>
<td>40°C, 40%RH</td>
<td>80°C, 27%RH</td>
<td></td>
</tr>
<tr>
<td>W1</td>
<td>316L</td>
<td>4-point bend</td>
<td>Weld</td>
<td>40°C, 40%RH</td>
<td>80°C, 27%RH</td>
<td>80°C, 27%RH</td>
</tr>
<tr>
<td>W2</td>
<td>316L</td>
<td>4-point bend</td>
<td>Weld</td>
<td>40°C, 40%RH</td>
<td>80°C, 27%RH</td>
<td>80°C, 27%RH</td>
</tr>
<tr>
<td>P9</td>
<td>316L</td>
<td>4-point bend</td>
<td>Annealed</td>
<td></td>
<td></td>
<td>80°C, 27%RH</td>
</tr>
<tr>
<td>P12</td>
<td>316L</td>
<td>4-point bend</td>
<td>Etched</td>
<td></td>
<td></td>
<td>80°C, 27%RH</td>
</tr>
<tr>
<td>U0</td>
<td>316L</td>
<td>Unloaded</td>
<td>Annealed</td>
<td>40°C, 40%RH</td>
<td>80°C, 27%RH</td>
<td>80°C, 27%RH</td>
</tr>
<tr>
<td>U1</td>
<td>316L</td>
<td>Unloaded</td>
<td>Weld</td>
<td>40°C, 40%RH</td>
<td>80°C, 27%RH</td>
<td>80°C, 27%RH</td>
</tr>
<tr>
<td>U2</td>
<td>316L</td>
<td>Unloaded</td>
<td>Weld</td>
<td>40°C, 40%RH</td>
<td>80°C, 26%RH</td>
<td>80°C, 26%RH</td>
</tr>
<tr>
<td>U3</td>
<td>316L</td>
<td>Unloaded</td>
<td>Weld</td>
<td>40°C, 40%RH</td>
<td>80°C, 26%RH</td>
<td>80°C, 26%RH</td>
</tr>
<tr>
<td>U4</td>
<td>316L</td>
<td>Unloaded</td>
<td>Weld</td>
<td>40°C, 40%RH</td>
<td>80°C, 26%RH</td>
<td>80°C, 26%RH</td>
</tr>
<tr>
<td>U5</td>
<td>316L</td>
<td>Unloaded</td>
<td>Weld</td>
<td>40°C, 40%RH</td>
<td>80°C, 26%RH</td>
<td>80°C, 26%RH</td>
</tr>
<tr>
<td>U6</td>
<td>316L</td>
<td>Unloaded</td>
<td>Weld</td>
<td>40°C, 40%RH</td>
<td>80°C, 26%RH</td>
<td>80°C, 26%RH</td>
</tr>
</tbody>
</table>
## Table 4-5: List of specimens and their associated testing period

<table>
<thead>
<tr>
<th>Specimen label</th>
<th>Material</th>
<th>Loading</th>
<th>Condition</th>
<th>Total exposure time (hrs) at 40°C and 40%RH</th>
<th>Total exposure time (hrs) at 80°C and 27%RH</th>
<th>Total exposure time (hrs) at 60°C and 32%RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>316L</td>
<td>4-point bend</td>
<td>Parent</td>
<td>6480</td>
<td>2880</td>
<td>NA</td>
</tr>
<tr>
<td>P2</td>
<td>316L</td>
<td>4-point bend</td>
<td>Parent</td>
<td>6480</td>
<td>2880</td>
<td>NA</td>
</tr>
<tr>
<td>P3</td>
<td>316L</td>
<td>4-point bend</td>
<td>Parent</td>
<td>6480</td>
<td>2880</td>
<td>NA</td>
</tr>
<tr>
<td>W1</td>
<td>316L</td>
<td>4-point bend</td>
<td>Weld</td>
<td>6480</td>
<td>6480</td>
<td>3600</td>
</tr>
<tr>
<td>W2</td>
<td>316L</td>
<td>4-point bend</td>
<td>Weld</td>
<td>6480</td>
<td>6480</td>
<td>3600</td>
</tr>
<tr>
<td>P9</td>
<td>316L</td>
<td>4-point bend</td>
<td>Annealed</td>
<td>NA</td>
<td>2160</td>
<td>3600</td>
</tr>
<tr>
<td>P12</td>
<td>316L</td>
<td>4-point bend</td>
<td>Etched</td>
<td>NA</td>
<td>2160</td>
<td>3600</td>
</tr>
<tr>
<td>U0</td>
<td>316L</td>
<td>Unloaded</td>
<td>Annealed</td>
<td>6480</td>
<td>6480</td>
<td>3600</td>
</tr>
<tr>
<td>U1</td>
<td>316L</td>
<td>Unloaded</td>
<td>Weld</td>
<td>6480</td>
<td>6480</td>
<td>3600</td>
</tr>
<tr>
<td>U2</td>
<td>316L</td>
<td>Unloaded</td>
<td>Weld</td>
<td>6480</td>
<td>6480</td>
<td>3600</td>
</tr>
<tr>
<td>U3</td>
<td>316L</td>
<td>Unloaded</td>
<td>Weld</td>
<td>6480</td>
<td>6480</td>
<td>3600</td>
</tr>
<tr>
<td>U4</td>
<td>316L</td>
<td>Unloaded</td>
<td>Weld</td>
<td>6480</td>
<td>6480</td>
<td>3600</td>
</tr>
<tr>
<td>U5</td>
<td>316L</td>
<td>Unloaded</td>
<td>Weld</td>
<td>6480</td>
<td>6480</td>
<td>3600</td>
</tr>
<tr>
<td>U6</td>
<td>316L</td>
<td>Unloaded</td>
<td>Weld</td>
<td>6480</td>
<td>6480</td>
<td>3600</td>
</tr>
</tbody>
</table>
4.6 Examination

The areas under the salt deposits on the specimens (see Sections 4.1, 4.2 and 4.3 for specimen preparation) were examined approximately twice a month using an optical microscope to determine if any corrosion, pits or cracks were present. Photographs were taken periodically and the digital images stored and compared with prior images. Changes between corresponding images were tracked. Further analysis was conducted using an Olympus LEXT OLS4000 3D confocal laser microscope for 3D scanning to determine the depth of the pits.

One parent metal specimen (labelled Parent 2) was removed from the chamber in February 2011 and examined by EBSD. Images were taken before and after the removal of corrosion products. Surface analyses with energy dispersive spectroscopy (EDX) were also conducted on a location deposited with sea-salt.

4.7 Results

4.7.1 General Observations

During the first nine months, the specimens underwent exposure at 40°C and 40% RH. Rust coloured corrosion products (discoloured region on specimens) were observed beneath precipitated salt crystals of magnesium chloride and sea-salt only (not sodium chloride). The presence of pits or cracks could not be confirmed, because the surfaces were masked by corrosion products and any pitting or cracking present was too small to be detected under the optical microscope available.

During the first phase of exposure at 40%RH and 40°C, the MgCl$_2$ droplets of 10 and 30μg/cm$^2$ surface density had less severe corrosion than those of 100μg/cm$^2$. The corrosion associated with the sea-salt droplets appeared more severe than that for the MgCl$_2$ as observed in Figure 4-9. The area covered by corrosion product in a sea-salt deposit was wider than that in magnesium chloride. Corrosion appeared in a random manner over the area within the perimeter of each droplet.

After increasing the temperature to 80°C and decreasing the relative humidity to 27% in the second phase, the corrosive discolouration of the metal surfaces spread beyond each droplet. After one month, pits up to 260μm across were observed on both weld and parent material specimens (externally loaded and control) under the magnesium chloride and sea-salt droplets (not sodium chloride) of all three surface densities. While the number of pits increased in
subsequent months, the pit sizes did not change appreciably over the remaining course of the experiment. Pit formation could occur at different times but was complete within one month.

Corrosion products were present in the pits. Some pits also appeared to have shiny surfaces. Cracks up to 100 µm long and 20 µm wide were observed in some of the pits on the externally loaded specimens but not in the pits on the control specimens. The number of cracks increased in subsequent months but it is not clear whether this was directly associated with the number of pits.

Table 4-6 shows a summary of the AISCC susceptibility for the different specimens.

In the third phase, the conditions were altered again to 60°C and 32%RH. The original specimens remained and new specimens were included. During the five months of experiments, there were no observable changes to the numbers and sizes of the pits and cracks in the original specimens. The new specimens became corroded with the exception of the specimen that was etched, where no corrosion was evident. This is believed to be because pickling removed the surface inclusions such as manganese sulphide (MnS). MnS inclusions are commonly the sites of localised attack where pits initiated. Thus the pitting tendency for the pickled surface should be reduced.

Figure 4-8: Arrows indicate the corrosion attack on a four-point bend parent specimen
Figure 4-9: A comparison between (a) sea salt and (b) magnesium chloride showing the areas covered by corrosion product.
4.7.2 Observation of Specific Pits and Cracks

As little was observed in the first phase, the same specimens were kept in the humidity chamber and proceeded into the second phase with an increase in temperature and a decrease in RH.

The electron backscatter diffraction technique (EBSD) was used to investigate the morphology of specific pits and cracks before and after the surface had been cleaned of corrosion products. The EBSD image in Figure 4-10 shows localised attacks induced by a synthetic sea-salt droplet on a parent material specimen labelled P2. This confirms the visual observation mentioned in the previous section that the size of the pits was approximately 260 microns across.

Figure 4-10 shows two suspected cracks as indicated by arrows. It also shows regions labelled (1), (2), (3) and (4) at which EDX has been conducted to analyse the chemical composition of the surface.

The results of EDX analysis are presented in Figure 4-11, Figure 4-12, Figure 4-13 and Figure 4-14. The qualitative EDX analysis of regions labelled (1) and (2), in Figure 4-10, presented in Figure 4-11 and Figure 4-12, respectively shows the peaks for oxygen and chlorine, which is a clear indication that it is a corrosion product. The EDX analysis of region labelled (3) (see Figure 4-13) shows peaks for Fe and Cr. The peak of O is much lower than in the two previous analyses. Only Na and Cl were detected in region labelled (4) (see Figure 4-14). Figure 4-15 confirms the presence from cracks from the droplet presented in Figure 4-10. There were visible cracks in at least three pits.
The observations at the end of the third stage exposures show no significant difference from the second phase. Corrosion was observed on weld specimens for both magnesium chloride and sea salt deposits. The pits on the control specimens inherited from the second phase did not seem to have advanced. The etched specimens did not pit. The annealed 316L specimen only showed light corrosion at locations deposited with synthetic seawater.
Figure 4-11: EDX analysis at location (1) in Figure 4-10

Figure 4-12: EDX analysis at location (2) in Figure 4-10
Figure 4-13: EDX analysis at location (3) in Figure 4-10

Figure 4-14: EDX analysis at location (4) in Figure 4-10
Figure 4-15: Pits and cracks in Figure 4-10 are revealed after removal of corrosion products
### Table 4-6: A summary of AISCC susceptibility of various specimens

<table>
<thead>
<tr>
<th></th>
<th>Parent (P1, P2 and P3)</th>
<th>Weld (W1 and W2)</th>
<th>U3, U4, U5 and U6</th>
<th>Annealed (P9)</th>
<th>Etched (P12)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Four-point bend</td>
<td>Four-point bend</td>
<td>Unloaded</td>
<td>Four-point bend</td>
<td>Four-point bend</td>
</tr>
<tr>
<td></td>
<td>NaCl</td>
<td>MgCl₂</td>
<td>Sea salt</td>
<td>NaCl</td>
<td>MgCl₂</td>
</tr>
<tr>
<td>100 30 10</td>
<td>100 30 10</td>
<td>100 30 10</td>
<td>100 30 10</td>
<td>100 30 10</td>
<td>100 30 10</td>
</tr>
<tr>
<td>40°C, 40%RH</td>
<td>○ ○ ○ ○</td>
<td>○ ○ ○ ○</td>
<td>○ ○ ○ ○</td>
<td>○ ○ ○ ○</td>
<td>○ ○ ○ ○</td>
</tr>
<tr>
<td>80°C, 27%RH</td>
<td>○ ○ ○ ★</td>
<td>★ ★ ★ ★</td>
<td>○ ○ ○ ★</td>
<td>★ ★ ★ ★</td>
<td>○ ○ ○ ★</td>
</tr>
<tr>
<td>60°C, 32%RH</td>
<td>-- -- -- --</td>
<td>-- -- -- --</td>
<td>-- -- -- --</td>
<td>-- -- -- --</td>
<td>-- -- -- --</td>
</tr>
</tbody>
</table>

- ○ no corrosion
- ★ corrosion and no pitting
- ▲ pitting and no cracking
- ● cracking
4.8 Discussion

The corrosion products under all salt droplets are the result of the deliquescence chlorides of sodium, magnesium or calcium (from sea salt) in the humid atmosphere of the chamber. Storage of the specimens in a desiccator prior to the test did not produce any corrosion. The DRH of these salts is approximately 30-35%RH at room temperature, 26-31%RH at 80°C and 31-34%RH at 60°C.

No corrosion was observed under any of the NaCl droplets which have a deliquescence threshold of about 75%RH. However, corrosion under synthetic seawater droplets was observed to occur in a random pattern probably due to the uneven precipitation of other salts present in the seawater mixture at the low RH (i.e. mainly sodium chloride but also calcium sulphate etc.). There is a suggestion by NDA to keep the RH of a storage building below 70%RH. But the aerosol particles present in the atmosphere are rarely composed of a single pure element but in a mixture of a few constituents such as salts of nitrates and sulphates.

The effect of other less soluble precipitates on AISCC susceptibility remains undetermined but the presence of other salts such as sodium nitrate (NaNO₃) in the salt mixture influences the DRH. Figure 4-16, taken from Tang and Munkelwitz [3], is presented to illustrate the literature data for NaNO₃ [3, 4, 5, 6]. The DRH is plotted as a function of temperature. It is clear that at room temperature of 25°C the DRH of sodium nitrate is approximately 74%.

![Figure 4-16: Deliquescence relative humidity of sodium nitrate NaNO₃ as a function of temperature [3]](image-url)
When NaNO₃ is mixed with Na₂SO₄, as illustrated in Figure 4-17, the DRH follows the temperature dependence behaviour of NaNO₃. Tang and Munkelwitz suggested that this is because NaNO₃ is more soluble than Na₂SO₄ in solution. They showed that the DRH of a salt mixture is lower than the minimum DRH of each component:

$$DRH_{salt_1, salt_2, ..., salt_n} < \min\{DRH_{salt_1}, DRH_{salt_2}, ..., DRH_{salt_n}\}$$

Equation 4-2

The DRH of the mixture does not have a unique value. It is a function of mixture composition and is commonly known as Mutual Deliquescence Relative Humidity (MDRH) or eutonic point. At MDRH the aqueous phase is saturated with respect to all components in the mixture, so it is the only RH at which an aqueous solution can coexist with a precipitate consisting of all the aerosol salts.

![Figure 4-17: Deliquescence relative humidity as a function of temperature for mixed Na₂SO₄-NaNO₃ particles [3]](image)

But one important factor to take into consideration is the behaviour of deliquescence and efflorescence of an aerosol mixture of salts [3]. A solid particle consisting of mixed salts (for example NaCl-NaSO₄-NaNO₃, see Figure 2-5) experiences an abrupt change in mass when RH changes. As the RH increases further, the particle transforms into a multiphase form with some undissolved salts in an electrolyte. It only turns into a completely saturated solution when DRH is reached. Both
deliquescence and efflorescence behaviours are independent of salt quantity. They always occur when the correct RH is met.

When RH falls, the water content in an electrolyte also drops. Evaporation continues even after RH falls below the DRH value. The droplet will only expel all its water content and crystallise when the RH becomes very low. Before the complete evaporation of water, the droplet undergoes a metastable state at which a supersaturated solution is formed. In both urban and suburban environments, meta-stable droplets exist more than half of the time when the ambient RH is between 45% and 75%. So only by decreasing RH to a very dry state, one can be certain all the moisture trapped within the salt mixture will be completely evaporated and only dry salts are left on the metal surface.

The corrosion attack observed on four-point bend parent specimens and control specimens after a month at 80°C and the lack of such observation on four-point bend weld specimens may have been attributed to the nine-month incubation period that the parent specimens and control specimens were subject to a test temperature of 40°C. It is therefore possible to suggest that long exposure time at a low temperature could have been an important factor in determining the susceptibility of the alloy to AISCC. As discussed previously in Section 3, the presence of ferrite in weld metal, which is approximately 10% [7], may have enhanced the resistance of weld specimens to AISCC [8].

4.9 Summary of Results

At 40°C, although corrosion products were evident on the surface of the samples, pitting was not visible under optical examination of the surfaces and it is believed that any pits present were masked by the corrosion products. No samples had cracked during the initial exposures thus, following the findings from Manchester suggesting that cracking at 40°C would have taken more than 3 years (i.e. beyond the time frame of this study), the temperature was increased to 80°C and the RH decreased to the deliquescence point of magnesium chloride in order to ensure that it was present as a saturated solution. This was intended to accelerate pitting and cracking. Cracking was observed after one month. The temperature was reduced to 60°C to investigate the AISCC susceptibility at this temperature.

So far none of the specimens has failed (as observed in U-bend specimens at Manchester). A possible reason for this could be the presence of residual stresses in the specimens. Residual stress measurement (see Section 5) shows that the residual stress at the metal surface was compressive. It could mean that any pit or crack opening would be obstructed by this compressive residual stress and any propagation would have been inhibited. However, this still requires further examination.
4.10 Implications of Results

The findings in this work are consistent with those of other work in that AISCC initiates only when the humidity is at or above the DRH value. AISCC occurs without the need of immersion in aqueous media but requires the presence of aggressive ions (even in very small quantity) and tensile stress, either as residual (induced by fabrication such as welding, rolling, forming etc) or applied. There is no requirement for the material to have undergone sensitisation before chloride exposure [9, 10].

The finding in this work that no corrosion occurs under sodium chloride droplets also agrees with the early work by Shoji et al. [11, 12]. When RH is too high, too much water is absorbed and the electrolyte became too diluted to induce AISCC. When RH is too low, the ionic mobility is insufficient to establish a corrosion cell. Table 2-1 in Section 2 summarizes the findings of Shoji et al. on AISCC susceptibility of 304L, which is more susceptible to than the 316L used in this study. Since most parts of the ILW containers are manufactured from 316L and the AISCC susceptibility of 304L has been well established, it was reasonable that this work focussed on the 316L stainless steel.

Although in this study, the results were obtained from samples of an ILW container, they are relevant to austenitic stainless steel plant of similar composition exposed to humid salt atmospheres. Such conditions can be found at coastal chemical plants and on offshore installations.
References


5 Residual Stresses

5.1 An Overview

Residual stresses may be described as any stresses that exist in a stationary component without the application of external load. Residual stresses arise from a number of factors, including production and processing, and may be localised or widely distributed within the material. The combined effect of residual (intrinsic) and applied (extrinsic) stresses may cause failure at applied stress levels that are much lower than anticipated from the materials properties.

As residual stresses are self-equilibrating (i.e. all tensile stresses must be balanced by compressive stresses within the material), it is very difficult to calculate them from forces, impulses or couples. They are often classified according to either their causes (e.g. thermal and mechanical stresses), their length scales (i.e. macro- or micro-stresses), or the methodology used to measure them. Regardless of their origins or classification, they can be considered to result from size misfits within the material [1, 2, 3]. Such misfits may span over long or short distance (see Figure 5-1 and Table 5-1). Stresses can be described by their characteristic length, \( l_0 \), which is the length over which the stresses equilibrate [2].

![Figure 5-1: Examples of residual stresses arise from misfits](image)

Long range or Type I stresses equilibrate over macroscopic dimension with \( l_{0,1} \) almost equivalent to the scale of the structures. In principle, Type I stresses can be calculated using finite element models where it is common practice to ignore microstructural effects and to consider the material
as an isotropic continuum. These types of stress generally arise from manufacturing or in-service loading and span structural distances.

Moving down the size range, micro-stresses can be present that are equilibrated over a small number of grains. An example of these is an interphase thermal stress in a composite material. They are also known Type II or intergranular stresses with \( l_{0,II} \) approximately equals to three to ten times the grain dimension. Type II exists almost in all polycrystalline materials because the elastic and thermal properties of differently oriented grains adjacent to each other are different.

Stresses can also vary across atomic level and usually balance within a grain. They are known as Type III. A typical example of Type III stresses is those that are caused by lattice imperfections such as point defects and dislocations.

<table>
<thead>
<tr>
<th>Types of stress</th>
<th>Level</th>
<th>Characteristic length</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>scale of structure</td>
<td>Macro</td>
</tr>
<tr>
<td>II</td>
<td>3 to 10 times of grain size</td>
<td>Micro</td>
</tr>
<tr>
<td>III</td>
<td>&lt; grain size</td>
<td>Atomic</td>
</tr>
</tbody>
</table>

### 5.2 Origins of Residual Stresses

A recently published handbook [4] outlines the processes and treatment that introduce residual stresses into components or structures but there was no clear categorisation for these processes and treatment. Withers and Bhadeshia [3] classified the origins of residual stress into four major categories. According to them, there are at least 4 mechanisms by which residual stress can be introduced into structures or components:

- **Through the interaction caused by misfit between parts within an assembly**: for example the stresses induced by mechanical jointing of parts together (e.g. by riveting) rest wholly within the component and are thus residual.

- **Through the generation of chemically induced misfit**: a typical example of this may be from surface treatments such as nitriding where the process causes volumetric expansion (formation of nitrides) at the metal surface.

- **Through the generation of thermally induced misfit**: commonly this occurs during and after welding, where components undergo a large thermal gradient as the distance from weld zone increases. The thermal expansion and contraction of component causes thermal stresses in the vicinity of welded joints.
Through the generation of plastically induced misfit: these are usually introduced by non-uniform plastic deformation for example after grinding [5] and shot-peening [5, 6]. These processes tend to result in significant compressive stresses at the surface of the component which are balanced by tensile stresses further within the bulk. Such stresses may be measured by layer removal, x-ray, neutron and synchrotron diffraction [7, 8, 9].

Type I macrostresses can be further sub-divided into stresses of long (Type $l_{\text{long}}$), medium (Type $l_{\text{med}}$) and short (Type $l_{\text{sh}}$) length scales [10]. The length scales of stresses are dependent on the interaction between misfit and the structure.

Surface measurement of residual stress is not really suitable to measure the macro stresses within a component as surface stress is often a poor presentation of the bulk component as a whole. Destructive techniques for near surface residual stress measurement are often considered non-destructive and sufficiently safe for large structures. For example, hole drilling and layer removal with X-ray diffraction methods do not seem to affect the structural integrity of a large pressure vessel with thick wall [3]. If there is sufficient understanding while inferring the overall condition of stress, the bulk measurement methods are sufficiently efficient to measure macro stresses as the characteristic length $l_o$ usually spans over long distance of a scale of the structure.

### 5.3 Importance of Residual Stress

Residual stress, not only affects the in service performance of a structure, it can also be pre-conditioned into a component to improve the service life. For example, the performance of a brittle material can be enhanced to a great extent by introducing residual stress. Thermally toughened glasses undergo rapid cooling from elevated temperatures to generate compressive stresses on the surface and tensile stresses within. Any surface flaws introduced on the surface would experience in-plane compression resulted from the surface compressive stress, which is around 100MPa. The interior of the glass undergoes a counterbalancing tensile stress. If a crack propagates into the interior which is under tension, it can grow rapidly and the glass might shatter in a mosaic manner.

### 5.4 Methods of Measurement of Residual Stresses

#### 5.4.1 Summary

Most residual stress measurement methods monitor the changes in distortion of components. It can be either when the residual stress is generated or afterwards. The methods are divided into destructive and non-destructive.
### 5.4.2 Curvature Measurements

Curvature measurements are useful to determine the stresses within coatings and layers [11]. When a substance is deposited on a sample surface, it may cause the substrate to bend by inducing stresses [12]. It is possible to calculate the stress variation from the changes in curvature. This curvature can be measured using strain gauges or profilometry. This method can also be used to determine stresses by incremental layer removal in composites and coated components [13, 14, 15, 16].

The Stoney Equation [9] is used to calculate the stress $\sigma$ from deflection $g$ of a thin beam of length $l$ with stiffness $E$, where $h$ is the current thickness.

$$\sigma = -\frac{4}{3}E \frac{h^2 \partial g}{l^2 \partial h}$$

Equation 5-1: The Stoney Equation

### 5.4.3 Hole Drilling

A sample containing residual stresses, when machined, will relax into a different shape. This enables data collection to back-calculate the residual stresses. This method usually involves drilling a hole at a designated location where commonly a rosette of strain gauges is attached to measure the changes in strain. The equation below is used to determine the residual stress:

$$\sigma = (\sigma_{\text{max}} + \sigma_{\text{min}})\tilde{A} + (\sigma_{\text{max}} - \sigma_{\text{min}})\tilde{B} \cos 2\beta$$

Equation 5-2

$\tilde{A}$ and $\tilde{B}$ are hole drilling constants. $\beta$ is defined as the angle from $x$-axis to the direction of maximum principal stress, $\sigma_{\text{max}}$.

The variation in stress with depth can be possibly reduced by increasingly deepening the hole but the reliability of measurement suffers when the depth is greater than the hole diameter [17]. The use of a three strain gauges rosette only allows a measurement in the two in-plane directions. If the residual stress is 50% greater than the yield stress, then the errors can arise as a result of localised yielding [18]. It is however cheap and accepted as non-destructive if the sample size is much larger (a few orders of magnitude greater) than the hole diameter, for example a pressure vessel.

### 5.4.4 Compliance Methods

The crack compliance method is also known as successive cracking method, slotting method and termed fracture mechanics based approach [19]. It involves introducing a small slot in a sample to observe the stress relaxation in the vicinity of the slot. By steadily increasing the depth of the slot,
the stress field normal to the slot can be resolved as a function of depth [20, 21]. Some researches [22, 23] showed that the crack compliance method is superior to other residual stress measurement methods because of the improved resolution of residual stress variation with depth; the specimen size is not limited to small components but the measurement on a large component is also possible; the ability to derive or measure stress intensity factor caused by the residual stresses; measurement of crack closure stresses; improved sensitivity compared to removal methods; and the ability to measure stresses in non-crystalline materials.

5.4.5 Non-destructive Methods and Bragg's Law

A given material with the same chemical formula can have different crystal structures and properties. In a crystalline material, the atoms are arranged in regular, repeated arrays (a lattice) where the planes of atoms are separated by a characteristic spacing of the order of 0.1 nm. Diffraction methods, such as X-ray and neutron diffraction, provide the advantage of measuring the lattice d-spacing according to Bragg's Law, which is the basis of X-ray and neutron diffraction. When a crystalline material with atoms arranged in a regular array is illuminated with radiation of a characteristic energy, the scattered radiation undergoes interference, either constructively or destructively, depending on the d-spacing and wavelength of incident beams. Bragg’s Law governs constructive interference, i.e. diffraction. When a constructive interference occurs, the scattered beams remain in phase since the path length of each beam equals to an integer multiple of the wavelength. The difference in the path length between two constructively interfered beams equals to $2d_{(hkl)} \sin \theta = n\lambda$ (this is also known as Bragg’s Law) as illustrated in Figure 5-2.

The diffraction method for residual stress measurement measures the angles at which the maximum diffracted intensity takes place at a set of lattices when a crystalline sample is irradiated with a set of rays. Using these angles and Bragg’s Law (see Equation 5-3), it is possible to calculate the $d$-spacing. The incident beam diffracts the incoming beams of a given wavelength $\lambda$ from the planes that fulfil Bragg's Law within an interaction depth that depends on the energy of the X-rays (usually a surface layer of about 10-20μm).
Figure 5-2: Diffraction in a crystal lattice obeying Bragg’s Law

\[ 2d_{(hkl)} \sin \theta = n\lambda \]

Equation 5-3

\(d_{(hkl)}\) = d-spacing of a set of lattices with Miller’s indices \(\{hkl\}\)

\(\theta\) = Bragg’s angle

\(\lambda\) = wavelength of incident beam, Å

\(n\) = integer, usually omitted

For monochromatic radiation (i.e. of known wavelength), the diffraction angle can be measured and the d-spacing calculated.

5.4.6 X-ray Diffraction by \(\sin^2\psi\) Method

In X-ray diffraction, the \(\sin^2\psi\) method can be used to measure residual stresses in materials. This method does not require a strain-free specimen when considering biaxial cases. The d-spacing is measured given that the angle of incidence and of reflection of the radiation is the same (known as focussed geometry) as illustrated in Figure 5-3. These planes are parallel to the sample’s free surface and they are unstressed but not unstrained.
The residual stresses close to the inner and outer surfaces of the parent and weld metal specimen can thus be easily measured using X-ray diffraction. For stresses in bulk volume, neutron diffraction is a better method (see Section 5.4.7).

When a crystal is subjected to X-ray beams, the beams are reflected not only from the surface atoms of the crystal but also from the atoms below the surface to the depth of up to 20μm in this case. Therefore X-ray diffraction offers the advantage of measuring near surface residual stresses (or strains) but is unable to probe further into bulk volume.

When the sample is tilted through an angle $\psi$, the lattice planes are no longer parallel to the free surface. The $d$-spacing measured is affected by the strain in the sample. This is known as a defocused geometry, see Figure 5-4. Tilting the sample through an angle $\psi$ allows the measurement of normal and shear strains, under a given range of $\psi$ from $X^\circ$ to $Y^\circ$. The specimens can also be rotated through an angle $\Phi$ to determine the principal strains in the orthogonal direction.

The $\sin^2 \psi$ method assumes that the specimen has met equilibrium requirements, i.e. stress normal to an unrestrained surface must always equal be zero. Since laboratory X-rays can only has limited penetration depth, one can normally assume that the specimen is in an in-plane biaxial field where $\sigma_{33} = 0$. 

![Diffraction vector, normal to sample surface](image)
Hauk et al. [24] proposed a method that implies for a biaxial stress state, at some angle $\psi$, the $d$-spacing will be equal to $d_0$. $d_0$ is then determined as the value of $d$ at $\psi$ when $\Phi = 0^\circ$.

$$\frac{d_{\Phi\psi} - d_0}{d_0} = \frac{1 + \nu}{E} \sigma_{\Phi} \sin^2 \psi$$

Equation 5-4

Where:

$d_{\Phi\psi}$ = calculated $d$-spacing when the specimen is tilted to angle of $\psi$ and rotated to $\Phi$

$d_0$ = unstressed $d$-spacing

$E$ = Young’s modulus

$\nu$ = Poisson’s ratio

$\sigma_{\Phi}$ = calculated stress in the direction.

For a biaxial stress analysis, Equation 5-4 predicts linear behaviour of $d_{\Phi\psi}$ vs $\sin^2 \psi$. Experimental readings are used to obtain the least squares line. For a given material with known $E$, $\nu$ and $d_0$, the stress $\sigma_{\Phi}$ is derived from the slope of the least squares line as illustrated in Figure 5-5. An increasing slope indicates tensile behaviour and a decreasing slope indicates compressive behaviour.
The equipment used to carry out residual stress measurement was the Proto i-XRD, which is a small portable residual stress diffractometer. The X-ray anode tube used was manganese which has a wavelength of 0.21031nm, operating at a 20kV voltage and a current of 4mA (80W). The most appropriate diffraction peak for measuring strain in an austenitic stainless steel corresponds to the (311) plane (151° 2θ, with a Mn tube) since this includes information on all principal directions of a FCC lattice.

Residual stress measurements were performed on the small samples and two longitudinal 4-point bend specimens from an ILW container. The sample surfaces were left in the as-received state, i.e. no grinding and polishing was performed since this would change the conditions of the surface.

Measurements were made transverse to the weld on the external surface. At each position, the measurements were taken at 2 angles; first when \( \Phi = 0^\circ \) and secondly when \( \Phi = 90^\circ \) (\( \Phi \) is the angle of rotation of the sample about its surface normal). The stress measured at \( \Phi = 0^\circ \) is transverse to the weld and the stress measured at \( \Phi = 90^\circ \) is longitudinal to the weld.

The residual stresses on both external (i.e. top in the four-point bend specimen) and internal (i.e. bottom in the four-point bend specimen) surfaces were measured as illustrated in Figure 5-6.
It is important to note that in a three-dimensional context, the longitudinal direction corresponds to the axial direction and the transverse direction corresponds to the hoop direction with respect to the ILW container.

The results of measurement are presented in Section 5.5.

![Measurement positions in a four point bend parent specimen](image)

(a) Positions of measurement in a four point bend parent specimen

![Measurement positions in a four point bend weld specimen with shaded region represents circumferential weld](image)

(b) Positions of measurement in a four point bend weld specimen with shaded region represents circumferential weld

![Measurement positions in a 15 x 15 cm weld specimen](image)

(c) Positions of measurement in a 15 x 15 cm weld specimen

*Figure 5-6: Measurement positions (marks as ‘X’) on specimens with each position being 1cm apart*

### 5.4.7 Neutrons

A neutron is a particle that does not carry any electrical charge and is slightly heavier than a proton (mass of a neutron is $1.675 \times 10^{-24}$ grams). It can be emitted as a free particle. Free neutrons have the tendency to transform into protons by emitting an electron and a neutrino, thus exhibiting radioactivity. The half-life of a free neutron is approximately 13 minutes. The
absence of an electrical charge allows neutrons to approach an atomic nucleus without being repelled by the positive charge of the nucleus. The frequency of collision between neutrons and atoms within a target material is relatively low because the nucleus of an atom is extremely small, creating sufficient space between atoms for free moving neutrons to pass through without collision. The penetration depth is approximately 5cm in steel and 30cm in aluminium.

Neutrons are not usually found in the free state outside the nucleus of an atom but they can be emitted from nuclei using the following methods:

- Bombardment of a suitable target material with charged particles from an accelerator
- Irradiation of a material with gamma rays
- Nuclear fission

The initial velocity of neutrons depends on the method used for their generation. Neutrons travel in a straight line and cannot be accelerated or have their direction of travel changed significantly either by electrical or magnetic fields. However, their average velocity can be altered by allowing them to pass through a material such that they become in thermal equilibrium (a process known as “moderation”). Effective moderators for neutrons consist of relatively light elements such as a heavy water, paraffin or wax and graphite. Neutrons that have passed through a moderator are known as thermal neutrons and have a characteristic velocity comparable to a hydrogen molecule at the same temperature. At room temperature their velocity is around $2200\text{ms}^{-1}$ with a kinetic energy of 0.0253eV and a wavelength of 0.18nm. This wavelength is close to that of the crystallographic spacing in materials and, hence, neutrons are diffracted effectively by materials.

5.4.8 Interactions between Neutrons and Atoms

When a free-moving neutron collides with the nucleus of an atom, there are a number of reactions that could happen:

- Diffraction of the neutron to a new trajectory (scattering)
- Displacement of the struck atom to an adjacent site
- Ejection of one or more neutrons from a nucleus
- Capture of the neutron by the nucleus to form a heavier atom
- Capture of the neutron, followed by fission of the nucleus to form lighter atoms

The probability that an incident neutron interacts with a nucleus is proportional to the geometrical cross-section of an atom and its nucleus, and is a unit of area “barn” (b). It is equal to
the product of the nuclear geometric cross sectional area, the number of nuclei per unit volume, the number of neutrons entering a specimen per unit area (fluence) and the number passing through a unit area.

5.4.9 Neutron Diffraction

5.4.9.1 Basic Principles

The main advantages of neutron diffraction for strain measurement are:

- Increased penetration which allows measurement to be made within the bulk of a sample
- The ability to measure three-dimensional stress fields which allows a comparison with finite element models

The volume of material sampled by a particular diffractometer is defined by the intersection of the incident beam and the scattered beam within the sample. The incident beam of neutrons bombarded onto a specimen, diffracted then picked by the detector is defined by the beam entry or exit slit sizes (which are usually determined by horizontal and vertical apertures). This sampled volume is also known as gauge volume.

The detector scans through \( \Phi_{hkl} = 2\theta_{hkl} \) (where \( \theta_{hkl} \) is the Bragg’s angle for the \( \{hkl\} \) reflection) to determine the peak-count angle. This peak-count angle corresponds to the average \( d \)-spacing of those grains correctly oriented for diffraction in the gauge volume. A fitting routine using the least-squares minimisation is then applied to calculate the angle and angular width of the peak.

The average lattice strain, \( \varepsilon \), is given by

\[
\varepsilon = \frac{d_{hkl} - d_0}{d_0} = \frac{\theta_{hkl} - \theta_0}{\tan \theta_0}
\]

Equation 5-5

Where \( d_0 \) or \( \theta_0 \) is the strain-free lattice spacing or diffraction angle of a corresponding stress-free (e.g. an annealed) sample [25]. The direction in which the strain \( \varepsilon_{hkl} \) is measured is that of the scattering vector, \( Q \).

In order to determine the strains in all the desired directions, the sample should be rotated about the centre of the gauge volume so that each diffraction direction lies along \( Q \). This is often difficult to achieve in practice as it requires careful alignment, centring of the sample, flexibility of the collimators and a sufficient working space.
Strain measurements in three perpendicular directions are required in determining the stresses in these directions. These three directions are generally selected as the principal axes [26].

5.4.9.2 Analysis of Lattice Strain Data and Calculation of Stresses
Stress (\(\sigma\)) and strain (\(\varepsilon\)) are tensor quantities which are related by the elastic stiffness tensor \(C\) and the elastic compliance tensor \(S\):

\[
\sigma_{ij} = \sum_{kl} C_{ijkl} \varepsilon_{kl}, \text{ and } \varepsilon_{ij} = \sum_{kl} S_{ijkl} \sigma_{kl}
\]

Equation 5-6

There are 3 x3 components in \(\sigma\), 6 of which are independent, while \(\varepsilon\) and \(S\) both have 3 x 3 x 3 x 3 components, 36 of which are independent [27]. This causes complexity and difficulty when it comes to the conversion of measured strain components to a stress, requiring the measurement of strain in many directions before the stress at a point can be determined. However, for most isotropic engineering materials, \(C\) may be reduced to two independent elastic components: Young’s modulus, \(E\), and Poisson’s ratio, \(v\). This allows the relationship between stress and strain to be expressed in a simplified manner using generalised Hooke’s Law equations:

\[
\sigma_{ij} = \frac{E}{(1 + \nu)} \left[ \varepsilon_{ij} + \frac{\nu}{(1 - 2\nu)} (\varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33}) \right]
\]

Equation 5-7

The notations \(i, j = 1,2,3\) indicate the components relative to the selected axes.

The calculation of tri-axial stress requires the knowledge of \(d_0\). But \(d_0\) is affected by the metallurgical changes in the specimen, it needs to be determined at different regions such as parent metal and fusion zone separately to say the least. Reference samples containing these region are needed to determine the respectively \(d_0\) of each region. There are several methods of which the reference samples could be prepared. The ideal method would be to cut out small reference samples of a specimen in form of combs using electrical discharge machining [28]. But this was not an available option during the course of this project, thus it was reasonable to prepare the reference stress by the simple method of annealing a small cut-out specimen at 1100°C then cooling it in a furnace. More detailed description is included in Section 5.4.11.

The difference between the stresses in two directions can be expressed by Equation 5-8:

\[
\begin{align*}
\sigma_1 - \sigma_2 &= \frac{E}{1 + \nu} \left[ \varepsilon_1 + \frac{\nu}{1 - 2\nu} (\varepsilon_1 + \varepsilon_2 + \varepsilon_3) \right] - \frac{E}{1 + \nu} \left[ \varepsilon_2 + \frac{\nu}{1 - 2\nu} (\varepsilon_1 + \varepsilon_2 + \varepsilon_3) \right] \\
&= \frac{E}{1 + \nu} [\varepsilon_1 - \varepsilon_2]
\end{align*}
\]

Equation 5-8
Inserting Equation 5-5 into Equation 5-8 gives

\[
\sigma_1 - \sigma_2 = \frac{E}{1 + v} \left[ \frac{d_1 - d_0}{d_0} - \frac{d_2 - d_0}{d_0} \right] = \frac{E}{1 + v} \left[ \frac{d_1 - d_2}{d_0} \right]
\]

Equation 5-9

From Equation 5-9 above, \( d_0 \) is eliminated from the numerator. Variations of \( d_0 \) in the denominator are not critical, \( d_1 \) or \( d_2 \) can be used as first approximation, making it unnecessary to have the value of \( d_0 \) when considering stress differences.

This is different when absolutes stress values in the three principal directions are required. In this case, reference samples must be prepared. This is critical as significant variations of \( d_0 \) can occur across parent metal and fusion zone.

To determine the absolute stress values, it can be assumed that specimens are in force balance conditions. This means that \( d_0 \) does not change along the line on which strains are measured, thus the stresses normal to a cross sectional area, \( A \), of a specimen equals to zero, see Equation 5-10 below:

\[
\int_A \sigma_i dA = 0
\]

Equation 5-10

Assuming a plane stress condition (i.e. \( \sigma_3 = 0 \)) in the specimen will allow the calculation of \( d_0 \) [26] according to the equation below:

\[
d_0 = \frac{1 - v}{1 + v} d_1 + \frac{v}{1 + v} (d_1 + d_2)
\]

Equation 5-11

The stresses \( \sigma_1 \) and \( \sigma_2 \) can then be determined using the biaxial equation as below:

\[
\sigma_{1,2} = \frac{E}{1 - \nu^2} \left[ \varepsilon_{1,2} + \nu \varepsilon_{2,1} \right]
\]

Equation 5-12

5.4.10 SALSA

The measurement of residual stress by neutron diffraction was conducted at Institut Laue-Langevin (ILL), Grenoble, France. The ILL contains a high neutron flux research reactor with a number of neutron beam lines attached. The neutron diffraction instrument used in this research is known as SALSA which stands for Strain Analyser for Large and Small scale engineering Applications.
In most strain measurement experiments, the movement of a specimen about the neutron beam is somewhat limited by traditional X, Y, Z translators. SALSA incorporates a hexapod design which is driven by six hydraulic legs, allowing more freedom in movement and manoeuvring of specimen. The hexapod is able to sustain a specimen up to 900kg and still gives excellent spatial positioning of the order of a few microns. The incident beam is bombarded onto a specimen and the diffracted beam is collected by a detector. The general layout of SALSA is illustrated in Figure 5-7. A more in-depth description of SALSA can be found elsewhere [29, 30].

![Figure 5-7: (a) Instrument layout of SALSA (b) Hexapod with six hydraulic legs [Source: ILL]](image)

5.4.11 Specimen Preparation and Measurement
As mentioned previously, the drum flange section is an area of interest since it is the primary lifting feature that will determine the overall integrity of the ILW containers during transfer. A quarter of the flange (as illustrated in Figure 5-8) was prepared from the ILW container.

![Figure 5-8: A schematic illustration of an ILW container showing a shaded region from which a 90° arc was prepared](image)
Ideally the strains should be measured in three principal directions: hoop, axial and radial as shown in Figure 5-9. Blue represents measurement in radial direction, red in hoop direction and green in axial direction. The measurements were made at those positions marked with “X” in Figure 5-10, which shows the locations in the 304L flange region. There are three measurement paths across the flange region, each consisting of 10 measurement positions. The first measurement path is 1.5mm from top surface of the flange. The second measurement path runs across the mid-section of the flange, 7.5mm away from the top surface. Similar to the first, the third measurement path is 1.5mm from the bottom surface.

![Figure 5-9: The direction of strain measurement](image)

The first measurement position on all three paths began at 1.5mm away from the flange edge and measurements were repeated at intervals of 3mm for the subsequent nine positions. The last position extended as far as 28.5mm into the flange. A blue dot represents the measurement in the radial direction, red in hoop direction and green in axial direction. The yellow point on the top left of flange is the reference point with respect to the locations of measurement.

Figure 5-11 shows the locations of measurements taken surrounding the top and bottom weld regions. Two columns of 6 measurements were made in the thin 316L wall, with strains measured in all three principal directions. Four positions in and adjacent to the bottom weld were identified and measured for residual strain. In a number of other positions measurements were only made in one direction. This is because either the travel path for the neutrons was too long to give any significant readings (thus required a very long time before sufficient data could be collected) or the positioning of the specimen underwent an offset and was shifted during the experiment,
invalidating the data. The reference point as indicated by a yellow dot laid on the top surface of the flange.

Figure 5-10: Positions of measurements made in 304L flange region
Figure 5-12 shows the positions adjacent to the top weld where strains in axial direction were measured. Again, the yellow dot indicates the reference point. Starting from right to left, there are three columns each of which consists of 7 measurements. The first column is situated 1mm from the reference point, 3mm for the second column and 5mm for the third. Along the columns, the measurement positions are 1mm apart. The positioning of the specimen is presented in Figure 5-13, Figure 5-14, Figure 5-15 and Figure 5-16.

Several attempts to continue such measurements in the hoop and radial direction were compromised by the specimen geometry and the limited working space between specimens and collimators. This caused one of the collimators to crash into the specimen (see Figure 5-17).
A strain-free or $d_0$ sample was prepared by annealing a thin specimen sectioned from the flange. This specimen was prepared carefully to include the 304L flange; the 316L drum wall and both the top and bottom welds in order to include lattice variation caused by compositional differences. It was then subjected to heat treatment at 1100°C and furnace-cooled. This 3mm wide specimen was mounted onto the hexapod and residual strains were measured.
Figure 5-13: Specimen set up for measurement of residual strains
Figure 5-14: Specimen set up for measurement of residual strains

Figure 5-15: Specimen set up for strain measurement adjacent to welds
Figure 5-16: Specimen set up for strain measurement along drum wall and adjacent to welds
Figure 5-17: The unsuccessful attempt at positioning the specimen which caused a collision between the specimen and detector collimator.

Figure 5-18: The D-nought specimen mounted onto hexapod. The regions marked with "X" indicate positions at which residual strain measurements were made.
5.5 Results and Discussion

5.5.1 X-ray Diffraction

The distribution of residual stresses in a longitudinal specimen measured by the X-ray diffraction technique is presented in Figure 5-19 below. As the penetrating depth of an X-ray beam is only up to 20μm, any stresses measured and presented below are near surface. The stresses within a body of material balance each other.

Both longitudinal (i.e. axial) and transverse (i.e. hoop) residual stresses around the weld metal exhibit similar behaviour with maximum stress values of approximately 400MPa and 300MPa respectively. Both peaks are approximately 15mm to the right of the weld. The residual stress became compressive when the distance from weld goes beyond 15mm. The transverse residual stress stayed fairly tensile even at 25mm to the right of the weld, whereas the longitudinal residual stress becomes compressive beyond 20mm to the right of the weld.

Figure 5-20 represents the residual stress behaviour of a four-point bend weld specimen which was prepared from the ILW container. The stress profile is different from that of Figure 5-19. In Figure 5-20, only the longitudinal stress exhibits a tensile peak value of approximately 110MPa in parent metal, at 10mm to the right of the weld. Then it decreases sharply to a compressive stress.
of -500MPa. The transverse residual stress remains fairly compressive across the parent metals and the weld with a peak compressive value of -550MPa.

Figure 5-20: Residual stress profile of a four-point bend weld specimen prepared from ILW container

Figure 5-21 illustrates the stress distribution on the external wall surface of the 4 point bend parent specimen. The measured stresses are all compressive in nature. The axial stress ranges between -120 and -100MPa whereas the hoop stress is more positive, varying from -80 to -20MPa.

In Figure 5-22, the measurements on the internal wall surface of the same specimen are in compression, similar to that of the external surface. The longitudinal (axial) stress fits in a narrow band between -120 and -90MPa. The transverse (hoop) stress spreads between -70 and -35MPa. The compressive stress profiles on both external and internal surfaces exhibit the characteristics of a typical rolled sheet. The compressive surface stresses are balanced by the tensile stresses within the material.
The residual stress profiles in Figure 5-19 and Figure 5-20 do not exhibit a similar behaviour. In these cases, only a few of the measurements of longitudinal and transverse stresses were close,
suggesting only a limited degree of equal biaxial stress. Figure 5-21, on the other hand, represents a very good equal-biaxial stress distribution in parent material. The residual stress profile in Figure 5-19 and Figure 5-20 suggests that: (a) the discontinuity introduced by welding was the main cause of the inconsistent stress distribution, and thus the difference in magnitude of both the longitudinal and transverse stresses; (b) the degree of cold work could vary even when the drum has undergone the same manufacturing and fabrication process; and (c) relaxation occurs to a significant level and is dependent upon specimen size as the larger specimen exhibits higher values of stress (Figure 5-19) than the smaller four-point bend specimen (Figure 5-20).

The net surface residual compressive stresses probably arise from a combination of the manufacturing process (rolling) and glass bead blasting which is used as a finishing process for the containers.

5.5.2 Neutron Diffraction

5.5.2.1 304L Flange

The near surface residual stresses measured in the 304L flange are overall compressive.

The measured residual stresses in the flange, along a path 1.5mm from the top surface are presented in Figure 5-23. The radial stress is relatively consistent (i.e. ranging between -350 and -200MPa) compared to the hoop and axial stresses. Hoop stresses show a steady decrease as the distance draws closer to the internal radius of the flange. The axial stress shows a gradual drop from below -50MPa to approximately -240MPa. This decreasing behaviour in hoop and axial directions is unclear but it is possible that the internal corner of the flange may have been removed after the welding operation and this may have an effect on the stress field around this corner. It is, however, only speculative judging from the geometry of the weld preparation illustrated in Figure 3-4. (see Section 3.2).

Figure 5-24 illustrates the measured residual stress across the mid thickness of the 304L flange. All the three stresses begin with fairly consistent values until the distance reaches before 15mm. They all decrease but with different magnitudes. The measured stress in hoop direction sees the greatest drop, reaching a minimum of -550MPa whereas the minimum of both radial and axial stresses is -400MPa and -280MPa respectively. All three components increase again when they approach the weld zone. The observed behaviour matches the typical stress distribution of a weld structure.
The residual stresses along the bottom surface are presented in Figure 5-25. The hoop stress exhibits similar behaviour of that of Figure 5-24. It falls very gradually and reaches a minimum value of -425MPa before rising gain to -200MPa. There is no significant fluctuation in the radial stress, with the associated values varying between -290MPa and -340MPa. The measured stress in axial direction shows a gradual fall from -125MPa to below -200MPa but the last reading was slightly higher with a value of approximately -140MPa.

Figure 5-23: Measured residual stress in 304L flange, 1.5mm from top surface
Figure 5-24: Measured residual stress in 304L flange across mid thickness

Figure 5-25: Measured residual stress in 304L flange, 1.5mm from bottom surface
5.5.2.2 Adjacent to the Top Weld as in Figure 5-12

Figure 5-26 is labelled with A, B and C to indicate the columns along which the strain in the radial direction was measured. As observed from Figure 5-27, the strains exhibit to an increasing positive region as the distance is closer to top weld.

The blue diamonds are measurements taken along column labelled A. The readings fluctuate around -200με, except the second reading which is just above -400με, the third reading is about -100με.

The red squares represent measurements made along column labelled B. They show a series of less negative values and are either close to or above -100με.

The green triangles indicate the measurements taken along column labelled C which is closest to, if not, at the boundary of the weld. They are all in tension and exhibit a profile far less regular than that of columns labelled A and B, with values between 200 and 600με.

Figure 5-26: A diagram showing the measurement points adjacent to top weld. Label A, B and C indicate the columns along which measurements were taken.
5.5.2.3  \textit{316L Drum Wall as in Figure 5-11}

Figure 5-28 shows a simplified version of Figure 5-11 to highlight the measurement paths along the container thin wall. Column labelled D is 1mm from internal surface of the container whilst column labelled E is 1mm from external surface of the container.

Figure 5-29 shows the stress measured along column labelled D. The blue diamonds are stress measured in radial direction. These values are in compression and remain fairly small along the measurement path, ranging between -60 and -35MPa. Interestingly, the stresses in both axial and hoop directions exhibit very similar pattern. They are both tensile and do not differ too greatly. This stress profile along column D is a typical that of a thin sheet with low radial stresses but greater hoop and axial stresses.

Figure 5-30 shows the stress measured along column labelled E. All three stresses display identical profile. The measured stresses in hoop and axial direction are of very similar values. The radial stress is only less than 50MPa lower.

Figure 5-31 and Figure 5-32 are simplified to illustrate the measurement positions in and adjacent to bottom weld. Figure 5-31 shows a vertical column labelled F which consists of three
measurements in all three principal directions. In Figure 5-32, an inclined column labelled G consists of three positions in the bottom weld at which residual strains were measured.

Figure 5-28: A simplified Figure 5-11 to show columns labelled D (1mm from internal drum surface) and E (1mm away from external drum surface)

The residual stresses presented in Figure 5-33 are those measured along column labelled F. The first set of the readings are taken adjacent to the weld. Their values are greater than the rest. The second set may possibly be around the edge of the weld. These values are lower than that of the
first set. The third set only shows a very slightly increase. Stresses measured in radial direction are all compressive whereas those in hoop and axial direction are either close to neutral or tensile.

Figure 5-34 illustrates the measured residual stress along column labelled G, which descends approximately from the weld toe adjacent to bulk 304L flange to the other weld toe adjacent to the 316L thin wall. The general profile of the stress field shows an ascending slope. All three set of readings are within the bottom weld. The first set of measurements consists of the lowest values and all three principal stresses are in compression: hoop stress of -40MPa, radial stress of -140MPa and axial stress of -175MPa. The second set sees a shift in both hoop and axial stresses to more positive values. Hoop stress is just above neutral and axial stress reads 40MPa. The third set, which is adjacent to the lower weld toe of bottom weld, consists of hoop and axial stresses at the same value (i.e. 25MPa) and the radial stress remains in compression.
Figure 5-30: Measured stress along column labelled E (1mm from external drum surface)

Figure 5-31: A simplified Figure 5-11 to show measurements taken in and around bottom weld. Note that column labelled F is along a vertical path beginning from 304L flange into bottom weld.
Figure 5-32: A simplified Figure 5-11 to show measurements taken in bottom weld along a column labelled G. Note that column labelled G is along a diagonal path descending from top.

Figure 5-33: Measured stress along column labelled F.
5.6 Discussion
When the two sections (flange and cylinder) were joined together by TIG welding, the thermal cycle caused huge temperature gradients in the welds and in the surrounding regions. The residual stresses arise as a result of these heating and cooling cycles.

The overall stress profile measured by neutron diffraction demonstrates that the bulk flange is in compression overall but there is some indication of the effect of welding on its stress properties. The hoop stresses at the distance furthest from the weld regions show a gradual declining slope before they reach a minimum and return to a less compressive level. This phenomenon is similar to the stress distribution of a simple welded plate. The residual stress measured in the flange (refer to Figure 5-24 and Figure 5-25) resembles closely the compressive region highlighted in a red box as illustrated in Figure 5-35. The region is followed by lowest compressive stresses which usually appear as a minimum value, and the stress becomes less compressive as it moves further from the weld region.
Hoop stresses contract circumferentially. The tensile stresses exist within a narrow band close to the welds. The hoop and axial stresses in first set of reading of column labelled F are in tension and they are adjacent to the bottom weld. There are also a few other measurements which give tensile values but they are fairly low.

The more interesting finding is that all the stresses measured along column labelled E (which is situated close to the bottom weld, see Figure 5-30) are in tension. These values are the highest measured in the whole volume. Moreover the hoop and axial stresses (first and second sets are around 360MPa) in particular approach the level of 0.2% proof stresses (i.e. approximately 400MPa in axial direction and 310MPa in hoop direction) obtained from tensile testing. Furthermore, the residual stress measured by XRD in the hoop direction along the circumferential weld connecting neck and body sections of the container also shows a value of approximately 400MPa.

This may potentially be an issue of concern as the container wall (2.3mm) is very thin compared to the bulk flange. It is also the case that the flange will be the lifting feature during the transport to a permanent repository. When an ILW container is filled, it can weigh up to 2000kg and the mass may be another contributing factor in promoting the susceptibility of this particular region to AISCC.
Another appreciable finding is that the hoop and axial stresses measured within the container wall are all in tension. This corresponds well to the results measured by XRD in which the residual stresses near both external and internal surfaces are compressive. In a rolled structure, the near surface compressive stresses are balanced by the tensile stresses within the bulk volume as illustrated in Figure 5-36.

The values of $G_5$ can have a significant impact on the calculation of stress. As seen from Equation 5-5 and Equation 5-7, a change in $d_0$ will affect the calculated $\epsilon$ and thus subsequently the values of $\sigma$. A simple way of investigating this is to apply the underestimated and overestimated values of $d_0$ into the two equations mentioned previously. Figure 5-37 shows the changes in the measured radial strains along a path 1.5mm away from the top surface of the flange. Assuming that all other properties remain unchanged and only the radial $d_0$ undergoes changes of ±0.05%, an overestimate in $d_0$ (red lines) gives more negative values of strains and more compressive stresses, as demonstrated in Figure 5-38. When $d_0$ is overestimated (green lines), both strains and stresses shift upwards to more positive direction.
The effect of overestimating and underestimating $d_0$ on the calculated residual strains in the radial direction 1.5mm from the top surface of the flange.

Figure 5-37: The effect of overestimating and underestimating $d_0$ on the calculated residual strains in the radial direction, 1.5mm from the top surface of the flange.
The effect of overestimating and underestimating $d_0$ on the calculated residual stresses in the radial direction 1.5mm from the top surface of the flange

Figure 5-38: The effect of overestimating and underestimating $d_0$ on the calculated residual stresses in the radial direction, 1.5mm from the top surface of the flange
References


6 Computer-based Simulation of Welding of an ILW Container

6.1 Introduction to Welding Simulation

Welding is the primary method used to join component parts of ILW containers. The heating and cooling cycle during the welding process produces uneven thermal expansion and contraction of the weld and the adjacent parent material, while differential cooling of the weld metal from the melt can cause distortion and the generation of residual stresses. Tensile stresses generated in and around the weld area must be counter-balanced by compressive stresses in the adjacent parent material such that the sum of the stresses in all volumes of the material equals to zero.

Factors that affect the post-weld properties and residual stresses of a welded structure include [1]:

- Materials properties, metallurgy and composition of parent metal and weld metal
- Restraint or constraint of the welded material (i.e. those parts that need to expand or contract are prevented from doing so by the surrounding volume of metal or the structure)
- Design of structure
- Weld fit-up and manufacturing accuracy
- Welding parameters such as heat input, welding sequences and pre-heat temperature

Verhaeghe [1] conducted an extensive literature review of the formulae for predicting distortion during welding. His review incorporated simplifications based on either theoretical or empirical information and was, therefore, limited to analytical models only. Analytical formulae can to some extent be a relatively rapid method of evaluating the distortion and residual stress in a weld. However, the associated accuracy is limited and the formulae only are only valid for a few situations. Thus, it is often the case that a numerical simulation is preferred.

In the 1970s, Hibbit and Marcal [2], and Ueda et al. [3] presented their work on the numerical simulation of the thermal and mechanical behaviour of materials during welding. The availability and development of commercial software such as ABAQUS, SYSWELD and ANSYS have encouraged the use of finite element (FE) methods to simulate welding processes. The recent finite volume (FV) method has also been used to perform computational modelling of weld phenomena [4]. In the work of Taylor et al. [4], they demonstrated with software called PHYSICA that the FV method could be used to perform computational fluid dynamics (CFD) analysis of the fluid dynamics of the weld pool as well as the thermal-elastic-plastic deformation during the welding process.
Modelling is the process of preparing computational software with an underlying deliverable of an input file. The process of preparing a model involves some simplification of problems and requires assumptions. Mackerley [5, 6] compiled over a thousand of references to FE modelling work published up to 2002 with a very brief description of the topics related to FE modelling of welding processes. However, a more thorough review, conducted by Lindgren [7, 8, 9] in three parts includes fusion welding simulations, 1D to 3D simulations and the effect of multi-pass welding.

TIG welding is a fusion process in which metal parts are heated by an electric arc from a tungsten electrode under an inert gas shield until they melt together. The use of filler material is not always necessary. TIG welding is a low heat input welding process and is used in applications where a greater control to produce a fine grained consistent high quality weld is required. Welding creates complicated interactions of temperature history, stress and strain. The metallurgy and materials properties evolve according to the changes in microstructure during cooling which in turn are dependent on the cooling rate and deformation histories as illustrated in Figure 6-1 below. The possible couplings include:

- #1a: Thermal expansion which is dependent on microstructure
- #1b: Volumetric changes as a result of phase changes
- #2a: Plastic behaviour which is dependent on microstructure
- #2b: Elastic behaviour which is dependent on microstructure
- #3a: Heat conductivity and heat capacity
- #3b: Latent heats caused by phase changes
- #4a: Deformation changes thermal boundary condition
- #4b: Heat caused by plastic strain rate
- #4c: Heat caused by thermal strain rate
- #4d: Heat caused by elastic strain rate
- #5: Temperature dependent microstructural changes
- #6: Deformation dependent microstructural changes

Most of the dependencies listed above may be approximated or ignored in the analysis [10]. It is thus possible to simplify a FE model of a weld to a two-step analysis as illustrated in Figure 6-2. The first step is a thermal analysis to determine the temperature distribution as a function of
time. The second step is a structural analysis to estimate the differential thermal expansion and contraction from the temperature distribution and the associated residual strain and stress when the weld has cooled to a uniform ambient temperature.

In short, the modelling of a welding process involves the calculation of the heat fluxes into and out of a specified surface or volume with prediction of associated temperatures during the heating and cooling phases. The thermal displacements are the sum of thermal expansion/contraction and volume changes caused by phase transformations. (Unlike ferritic materials, the austenitic materials considered in this work do not undergo phase transformations during cooling). The thermal and structural properties of the parent and weld materials affecting the behaviour are very often highly temperature dependent.

The deformation changes during thermal analysis when the fixtures alter the thermal boundary conditions (coupling #4a). The thermal and mechanical analyses can then be conducted in a simultaneous or staggered fashion. In the staggered approach [11, 12] thermal dilation is the driving force, each time step begins by solving for the temperatures, $T^{n+1}$, for time $t^{n+1}$ and thereby using the geometry $x^n$. This geometry updates accordingly in the subsequent mechanical analysis for this time step as shown in Figure 6-3.

![Figure 6-1: Simplified phenomena during welding](image)
There is another method able to solve temperatures and displacements simultaneously. This is known as the coupled approach and has not been widely recommended because it involves an asymmetric system of coupled nonlinear equations that do not solve easily [13, 14, 15, 16]. Besides that the staggered approach offers the advantage that both thermal and mechanical analysis can be performed using a single software suite.

Figure 6-2: Thermal analysis followed by mechanical analysis by simplifying the couplings

Figure 6-3: A time step in a staggered approach for thermal and mechanical analysis
6.2 The Physics of Welding Processes

The complex physical processes that occur in arc welding and that determine the development of residual stresses are illustrated in Figure 6-4. From a thermodynamic perspective, the thermal processes can be examined from three different positions namely within the weld pool, at the surface of the weld pool and the surrounding material. Within the weld pool, there is conductive and convective heat transfer. Heat loss occurs through convection, radiation and evaporation at the surface of weld pool. Heat also conducts away to the surrounding material.

R6 is a procedure titled Assessment of the Integrity of Structures Containing Defects [17]. It was first developed by British Electricity Generation Limited (BEGL) in 1976 to assess the integrity of structures containing flaws in all loading conditions. R6 defines a basic route to establish the integrity of a component containing crack-like defects which are either as a result of fabrication process such as welding or from in-service conditions.

This includes a step-by-step procedure with advice on the associated input and alternative approaches. It also contains compendia of solutions for load limit, stress intensity factor, residual stress (particularly of welding) as well as constraint parameter. Whenever an approach is suggested, this document includes validation techniques and worked example to illustrate the application of procedures.

The R6 assessment procedure breaks down the physical interactions into four processes:
6.3 The Electromagnetic Processes

In the electromagnetic processes, the welding arc acts as the heat source with the heat generation rate quantified by the arc power. Arc power is the product of arc voltage, $V$, and the welding current, $I$ if it is a direct current; or the time-averaged sum of this product if alternating or pulsed current is used. Most of the energy generated by the welding arc is transferred to the weld pool from the plasma via thermal conduction and radiation. Some heat is still lost to the surroundings as well as via thermal conduction to the tungsten electrode used in TIG welding. The proportion of the arc power transferred to the work piece is defined as the welding efficiency.

The electromagnetic processes also influence the transport of heat. A Lorentz force will result under a divergent electric current in the welding arc. The plasma jet will induce a downward pressure (which is often referred as arc pressure) on the surface of the weld pool. The free surface of the weld pool may distort under the effect of both these forces.

6.4 Mass Transport and Fluid Flow Processes

The heat transport during welding and the fusion profile are also affected by convection in the weld pool. Convection flow patterns are generally determined by:

- Gradients of surface tension on the weld pool surface
- The electromagnetic force resulted from the divergence of the current in the weld pool
- The buoyancy forces caused by the density change of the molten metal with varying temperature

Surface tension effects, that arise as a result of the temperature gradient with the molten metal immediately under the arc being hotter than the liquid along the edge of the weld pool, may cause the surface tension at the edge of the pool to be much higher than directly under the arc. This can result in flat and shallow fusion profiles.

Surface tension, in an arc welding process, is a function of temperature and composition and can be affected by the preferential evaporation of some elements present. The electromagnetic force in the weld pool encourages the superheated liquid to flow downward towards the bottom of the
weld pool. As a higher welding current increases the electromagnetic force, the use of high welding currents will result in a greater weld penetration. The buoyancy forces have an opposite effect to that of the electromagnetic force by their tendency to spread the melt towards the edge of the weld pool.

### 6.5 Metallurgical Processes

The solidification of weld pool is not only determined by cooling rates but also the convective flow patterns, the compositional gradient as well as the welding speed. Alloys usually solidify over a range of temperatures. Unlike ferritic steels, austenitic stainless steels very rarely experience solid-state phase transformations upon cooling.

### 6.6 Mechanical Processes

The welding residual stresses are often estimated from a mechanical analysis which is dependent on the accuracy of the thermal analysis. The complication involved in the physical processes during welding make it necessary to simplify some assumptions. Thus, it is normal to make an assumption that the arc is an idealised heat source, eliminating the need to compute complicated scenarios of heat, electromagnetic and mass transport, providing adequate prediction of residual stresses acting on the structure. However, the model will then encounter difficulty in predicting the weld profiles accurately. It is mostly overcome by a metallurgical examination and measurement of an actual specimen, if available, then incorporation of the measured dimensions into the model.

### 6.7 Finite Element Modelling Procedure

#### 6.7.1 Objectives

This procedure identifies the important steps in order to estimate and calculate the residual stress in a weld by means of a finite element method. At each step the key decisions for modelling and the input parameters are identified and defined.

#### 6.7.2 Step 1: Define Analysis Objectives

This first step defines the reasons behind the need for a residual stress simulation, how the results will be used and the degree of confidence and conservatism in them. In the context of this project, it is the structural integrity of the ILW container and the comparison to the residual stress measurement by neutron diffraction that are the weld simulation objectives. The key objectives are:
• To characterize residual stress
• To establish a FE model to predict the residual stress profile at locations of interest, which is the flange of the ILW container
• To validate the FE model using the measurement obtained by X-ray and neutron diffraction
• To assess the sensitivity of predicted residual stresses to analysis input parameters

In an engineering component residual stresses can range over length scales from nanometers to several meters. Residual stresses originate from misfits between parts and the magnitude is determined by the interaction between the misfit and the restraint of the surrounding material.

6.7.3 Step 2: Collect Input Data
The second step is to identify and compile basic information before proceeding with the analysis. The ideal information requirements include fabrication procedure, design drawings, weld geometry, weld procedure, basic materials data, plant survey data, etched macrograph, welding efficiency, thermal and mechanical properties. Fabrication procedure provides a record of the method of fabrication which may be useful in assessing long range mechanical effects. The weld procedure will include information such as groove profile, welding processes, weld heat input, weld pass sequence, preheat and so forth. In short it should tell how the weld should have been prepared and made.

It is worth mentioning that the thermal and mechanical properties should be defined from room temperature to well above the melting point of the materials to improve the accuracy of the analysis. A thermal analysis requires input of thermal conductivity, \( k \), specific heat capacity, \( c_p \), and density, \( \rho \). Constant density at room temperature is commonly assumed in small and simple weld simulations.

Mechanical properties input required to perform a mechanical analysis cover tensile properties, elastic modulus, \( E \), Poisson’s ratio, \( \nu \), and the coefficient of thermal expansion, \( \alpha \). A finite value of elastic modulus is assigned from temperatures ranging from room temperature until above melting temperature to reduce the possibility of convergence problems. It is not uncommon to use 1% of the room temperature elastic modulus at high temperatures as some sensitivity studies conducted by Frazer-Nash showed that the prediction residual stresses calculated from linear interpolation between 400°C and melting point were within ±5% of those calculated from temperature-dependent data [18].
Poisson’s ratio value at room temperature is usually employed in FE models because of the lack of reliable temperature dependent data available at the present. The coefficient of thermal expansion is an important property in the simulation of welding. It is highly temperature dependent and varies according to material classes.

6.7.4 Step 3: Resource Requirements
The welding simulation requires intensive calculations, knowledge of physical and metallurgical processes involved in welding and an understanding of residual stress development. The software should be able to implement a simple modelling approach such as the prescribed temperature method or a more complicated approach such as the volumetric heat flux approach (see Step 6, Section 6.7.7).

The FE code needs to be capable of handling temperature dependent properties and calculate heat conduction and losses via convection and radiation. A weld simulation requires a large number of elements around the critical features such as weld and its adjacent vicinity.

6.7.5 Step 4: Weld Modelling Approach

6.7.5.1 Overview
After defining the objectives of the simulation and the residual stresses of interest, given the resources available, the approach for welding simulation is decided from the five modelling options below. They are listed in order of increasing complexity and accuracy:

- 2D cross section with static heat source
- 3D shell with static heat source
- 3D shell with moving heat source
- 3D with static heat source
- 3D with moving heat source

A good guideline on deciding the type of approach suitable for a particular welding simulation, according to R6 is shown in Figure 6-5.
6.7.5.2 2D Cross Section with Static Heat Source

This approach utilises plain strain or axisymmetric cross section models of a welded joint. An equivalent heat flux is applied to the weld metal as a function of time that assumes the entire length of weld metal is heated simultaneously at the same rate. It does not incorporate the features associated with a moving heat source. The heat source may be considered to be static.

The run time of this approach is relatively short. It gives reasonable predictions of short range (Type I) stress variations in both normal and transverse directions. The disadvantage of this approach is its inability to predict any variation of stresses along the length of the weld.

6.7.5.3 3D Shell with Static Heat Source

This method usually comes with a block-dumped equivalent static heat source. It is a simple option to model long range stress variation in the longitudinal direction, medium range stress variations in the normal direction as well as short range stress variations in the transverse direction.

6.7.5.4 3D Shell with Moving Heat Source

This is a combination of a moving heat source representation with a simple 3D shell computed model. It predicts stress variations of short range in the longitudinal direction.
6.7.5.5 3D with Static Heat Source

This practice involves a 3D brick element with block-dumped equivalent static heat source that allows the prediction of short range stress variations for all stress components in the transverse and normal directions and long range stress variation in the longitudinal direction.

6.7.5.6 3D with Moving Heat Source

A 3D brick element model with moving heat source represents the most realistic form of weld simulation. It predicts short range stress variations for all stress components, in all directions. It is, however, the most complicated simulation that requires a long analysis time and often requires high performance hardware.

The use of 2D cross section models for welding simulations is a widely applied method especially when it involves thick section components with multiple of weld passes. The main advantage is that it allows a high degree of mesh refinement to evaluate the critical stresses in or adjacent to the weld with the assumption that heat flow and displacement in the travelling direction of the weld heat source is zero.

3D models are often used for a more detailed analysis in all three principal directions to analyse the variation of stress along the welding direction. It usually requires longer time for model construction, computing and analysis.

The options to employ arc welding heat can be in the form of either an equivalent static or a moving heat source. An equivalent static heat source is a function of 2D space and time. This method idealises a zero heat flux on the direction of welding, assuming an applied heat input at a given time \( t \). This heat input will peak until it is sufficient to increase the temperature at the designated weld zone to above melting temperature and also with an area large enough to represent the weld bead.

The moving heat source model follows the rule that the density of the arc welding distributed on the surface of the weld obeys the Gaussian distribution approximately. A moving Gaussian distribution of heat flux is applied to the surface of the component, assuming heat input is effectively distributed throughout the volume of the component. Another improved method is to apply a more realistic Gaussian function where the spatial volumetric heat input, \( q_v \), reduces when it moves away from the torch position. The heat source radii, position in weldment and weld pool length must be defined.
6.7.6 Step 5: Finite Element Model

Most FE software provides various types of elements for meshing. They are in the form of either linear, quadratic, hybrid or reduced integration elements. Triangular and tetrahedral elements offer the least accuracy compared to other types but still offer some advantages over standard linear elements. Tetrahedral elements are geometrically versatile and are commonly used in many automatic meshing algorithms. Triangular elements are robust for large deformation problems and contact analysis. They can produce accurate results but only with extremely fine meshes thus making them not the most efficient elements time-wise and resource-wise.

A high degree of mesh refinement is usually used to model the large thermal gradients in the weld and HAZ. Weld macrographs are used to estimate the weld geometry and cross section. The models described in this work utilize a simplified approach without introducing an addition of weld material as this is the actual practice when the ILW containers are fabricated. The model is constructed according to the final weld geometry then heat input is applied to it.

6.7.7 Step 6: Thermal Analysis

6.7.7.1 Weld Heat Input Calculation

In arc welding, of a given welding speed, $v$, welding current, $I$ and welding voltage, $V$, the arc energy per unit length of weld, $q$, is defined as

$$q = \frac{VI}{v}$$

Equation 6-1: Welding arc energy

The unit of $q$ is often expressed in kJ/mm and $v$ in mm/second. According to Smith and Blunt [19], most simplified finite element analyses only simulate the heat flow caused by conduction: the true heating and cooling within the molten zone is poorly simulated. According to them, thermal conductivity has the greatest impact on convective heat loss in the weld pool. Thermal conductivity is defined as a property of the ability of a material to conduct heat.

The reference heat energy level is assumed to be associated with the ambient temperature, $T_a$. The arc energy, $q$, is the electrical energy used by the welding process per mm of weld length. Each welding process has an associated welding efficiency, $\eta$, which defines the fraction of the electrical energy absorbed by the weldment. The $\eta$ of TIG welding is usually assumed to be 0.65 but could be either increased or decreased in a simulation to achieve the desired heat input coverage [19].
Finite element analysis assumes the function of temperature follows a polynomial form across any element. To ensure heat flow between elements, the nodes shared by adjacent elements should be at the same temperature at a given time. In the welding procedure of the ILW containers, there is no preheating. So the heat input comes directly from the product of arc welding energy and welding efficiency.

The fraction of energy received or input by the model is in the form of either surface or volumetric flux into the area, $A_f$. This flux lasts for a time, $\tau$, the assumed period during which the weld pool passes through the model. For a welding speed, $v$, and a weld pool length, $L$, time $\tau$ is given by

$$\tau = \frac{L}{v}$$

*Equation 6-2: Duration ($\tau$) of heat flux as a function of weld pool length and welding speed*

The heat flux is assumed to rise to a peak and then fall to zero during a time period, $\tau$. A flux $K \cdot f(t)$ was assumed when $f(t)$ is shown in Figure 6-6. Assume that a 2D transverse slice to the welding direction, the energy received is defined as: $\eta q d$; where $d$ is the slice thickness. If there is preheat prior to welding, the heat energy $\eta q d$ is therefore given by

$$\eta q d = \rho c (T_p - T_c) A_n d + \int_{t}^{t+\tau} K \cdot f(t) \cdot dA_f \cdot dt$$

*Equation 6-3: Total energy input*

![Figure 6-6: Flux heat input profile function, $f(t)$ (19)](image)

Integration of Equation 6-2 and Equation 6-3 gives

$$K = \frac{2v[\eta q - \rho c(T_p - T_a)A_n]}{L \cdot A_f}$$

*Equation 6-4*
Where: $\rho$ is the material density, $c$ is the specific heat capacity, $T_p$ is the preheat temperature; $T_a$ is the ambient temperature, $A_n$ is the area of the deposited metal and $A_f$ is the area of the final weld.

The heat input is therefore defined by the welding variables above. In the case where there is no weld preheating (as in the welding of ILW containers), so $T_p = T_a$, which ultimately simplifies the equation above into:

$$K = \frac{2\nu \eta q}{L \cdot A_f}$$

Equation 6-5

The weld pool length, $L$, can be derived by assuming a closed form solution for heat flow during welding. An empirical version has been developed by Leggatt [20] to account for the temperature-dependent materials properties and finite boundaries.

$$L = \frac{1.9 \eta q v}{2\pi \cdot k(T_a) \cdot T_m}$$

Equation 6-6: Weld pool length as a function of temperature-dependent properties and finite boundaries

$T_m$ is the melting temperature and $k(T_a)$ is the thermal conductivity at room temperature. Substituting $L$ into Equation 6-2 will give $w$ and $w/3$ as illustrated in Figure 6-6.

### 6.7.7.2 Modelling Weld Heat Input

There are three approaches to modelling the heat input from welding. They are described below in the order of increasing complexity and accuracy.

**Static heat source with prescribed temperature:** This is the simplest method for modelling a weld heat input by defining and holding a fixed temperature above $T_m$ for a period of $\Delta t$ (usually in units of seconds) as illustrated in Figure 6-7. Too long a hold time introduces errors in the predicted temperature transients and gradients and inaccuracy in the size of the plastically deformed zone surrounding the weld zone and thus the residual stress field. Any assumption of $\Delta t$ made must be reasonable to represent a simple TIG weld, for example $\Delta t=1$ would be unrealistic.
Static heat source with volumetric flux: This is an improved method from the prescribed temperature technique. Having defined the welding arc energy input and welding efficiency, the weld pool length can be calculated, giving the estimated value \( \tau \). If at a given value of \( \tau \), the temperature within the weld zone does not exceed the melting point or the weld zone spreads too far, then \( \eta \) is altered accordingly until a reasonable heating profile is achieved. In a 2D model, this technique is considered as thermal analysis of a slice of the weld component. In a 3D model, it is often deemed as the whole weld undergoes increase in temperature and decrease at the same time.

Moving heat source with volumetric flux: This method is usually employed in a 3D welding simulation where the heat source is allowed to travel along a predefined path. All the welding parameters are calculated. In ABAQUS, a user-subroutine is required to generate a moving heat source for any welding simulation.

6.7.7.3 Thermal Boundary Conditions

The thermal boundary conditions affect the welding simulation especially when there is preheat and more than one weld pass is involved. Since there is no preheat in the fabrication of ILW containers and only one weld pass, the surface boundary conditions are convective and radiation heat transfer.
Convection is transfer of heat from one point to another or from a surface by the movement of a fluid such as air. Radiation heat loss occurs when heat radiating from a surface is greater than the heat radiation entering the surface. Heat radiation is generated when an object with temperature greater than absolute zero emits thermal radiation, which is an electromagnetic radiation produced by thermal motion of charged particles in matter.

Convective and radiative heat transfer boundary conditions are applied to all the surfaces of the model including weld surface unless they are insulated. All insulated surfaces are treated as adiabatic which means no heat transfer should occur.

### 6.7.7.4 Thermal Stability

In most simulation work, there is a recommendation for the minimum time step size that will generate stable thermal solutions. This time step size is related to heat flow parameters and mesh size. The mesh refinement is therefore determined by the materials of the model. A simple thermal heat source has shown to predict the correct level of temperature in the weld pool region [17].

### 6.7.8 Step 7: Mechanical Analysis

#### 6.7.8.1 Mechanical Boundary Conditions

The primary function of mechanical boundary condition is to reproduce the actual or potential restraint applied to the model. It can be in the form of external restraint such as pressure, or a restrained condition imposed by the rest of the component for example when only a section of a vessel is modelled, the edges of the section would have to meet the boundary conditions as if in the case of a whole vessel simulation.

#### 6.7.8.2 Mechanical Constitutive Behaviour of Austenitic Stainless Steels

The properties of the constituent materials of the weld at room temperature will have significant effects on the final predicted residual stress. For example an $x$ percent change in yield properties will cause an $x$ percent change in the predicted residual stress. The materials properties are defined from room temperature up to above melting point such to improve the accuracy of the predicted result. The FE simulation requires tensile properties to be defined over a range of predicted transient temperatures. The materials properties used in this work are taken from Leggatt and Olden [21] and Mochizuki et al. [22]. They are the standard material data and welding parameters for most FEM at TWI.
6.7.8.3  Results Evaluation
The key outputs from stress simulation include plastic strain, displacement and residual stress. The predicted result should be examined and assessed against similar models or if available measurement. Contour plots of longitudinal, transverse and normal stress are compared with measurements if available. It may be necessary to volumetrically average the FE results to make a reasonable comparison at locations of interest.

6.7.9  Step 8: Validation of Weld Residual Stress Calculation
Commercial requirements often demand that new joining technologies must be introduced in an efficient and safe way. Many parameters can be altered to minimise the residual stresses and distortion. Finite element modelling can provide significant direction at optimising welding processes. The predicted results from a weld analysis should be validated by comparing them with measured readings. Neutron diffraction offers the advantage of providing three-dimensional information to compare with the predicted strain or stress of a FE model.

6.8  Simulation of Welding the ILW Container Flange Using ABAQUS

6.8.1  Objectives
The main purpose of constructing a weld simulation model in this research was to calculate the residual stresses associated with the welds of the container. The first model was a 2D model with a static heat source as it is least complicated to achieve and requires least time and resources. This 2D model is an axisymmetric representation of the cross-section of the ILW container flange and was used to gain a basic understanding of the temperature and stress fields that could be used for validating more complex analyses.

The second phrase in simulation was the construction of a 3D moving heat source model. This was expected to be more accurate than the 2D simulation. The residual stresses predicted from the 3D model could be compared with residual stress measurements obtained from neutron diffraction.

6.8.2  ABAQUS/CAE as Simulation Tool
The simulation software used to construct a FE model for this work is ABAQUS/CAE. This is mainly because the host company TWI has extensive experience in using this software and is able to offer adequate guidance and assistance to complete a reliable model. ABAQUS/CAE allows simulation to be constructed in blocks called modules which stage different phases in building a model. There are nine modules: PART, PROPERTY, ASSEMBLY, STEP, INTERACTION, LOAD, MESH, JOB and VISUALISATION.
The first module is PART and its function is to create the geometry and regions for sections, if necessary. Part geometry can also be imported from other systems such as CAD and ACIS. The sketch can be further partitioned to assist better meshing.

The second module PROPERTY defines the materials properties either as a whole or per additional region. When there are several parts that carry different properties, each part must refer to a section property, for instance, in a weld of dissimilar materials.

The ASSEMBLY module assists in positioning the parts to present actual configuration. For example, a model of a car frame would consist of several different items (i.e. parts) and they all require to be assembled in a specific order.

The STEP module defines the analysis time steps and output requests. It is a tool to prescribe the simulation history, making the results dependent on the order of events. The output can be preselected to include desired variables for a given analysis as well as the output results times.

The fifth module is INTERACTION that defines and manages the mechanical and thermal interactions between regions of a model or between a model and its surroundings. A typical thermal interaction is surface heat loss. Friction between two contacting surfaces is a type of mechanical interaction.

The LOAD module is the stage at which loads and BCs are applied to regions or defined sets, and subsequently assigning them to STEPs in the analysis history. Thermal loads are either distributed (as in a large surface area subjected to heating) or concentrated heat flux (as in a welding torch). Mechanical loads can be in the form of concentrated forces, moments, pressure loading or body forces such as gravity and rotational forces. BCs can be either prescribed temperatures (such as preheat in welding) or prescribed translations or rotations for mechanical conditions (such as a beam with one end fixed onto a wall).

MESH splits assembly into meshable regions with different types of element and density. In other words, MESH discretises geometry by introducing nodes and elements.

Any analysis submitted needs to be created as a job in the JOB module. It is at this stage that an input file containing all the necessary information is generated. An input file consists of data lines that define the bulk information for example, element type, element numbers, materials properties, BCs, so on and so forth. Upon submission, the job can be monitored and managed.
The VISUALISATION module, as the name implies, examines the results of the simulation. An undeformed shape can be compared against a deformed one. Results can be plotted according to specific contour or path. X-Y plots can be generated to compare revolution of result against time.

### 6.8.3 2D Model with Static Heat Source

As it has been discussed in the previous chapter, the drum flange weld is one of the most significant features in deciding the structural integrity of ILW containers as it is required for lifting the containers. Thus this FE work has concentrated on investigating the residual stress around this region. It has been suggested that a simplified model will suffice when most interest is in the maximum value of the residual stress [23].

The geometry and the dimensions of the drum flange section were taken from measurements made on the supplied container. The weld geometry has been simplified to reduce the potential complexity in sketching. The finished part is a simplified 2D axisymmetric deformable continuous solid as presented in Figure 6-9 and Figure 6-10.

The materials properties for thermal and mechanical analysis are temperature dependent. In an effort to improve the numerical simulation and consistency with experimental validation, this work has employed a standard set of material data for austenitic stainless steels [24]. This work has used this set of material data as the input for all simulations (see Table 6-1, Table 6-2, Table 6-3 and Table 6-4).

The first simulation in this research began by prescribing a linear increase in the temperature of the whole weld volume and holding at the maximum temperature for specified period of time before reducing it. This prescribed temperature model was later discarded as the calculated total heat input did not correspond to the heat input to the weld as determined from the welding parameters. A second simulation prescribed the heat generation within the weld volume as a function of time. This was used as the input into a transient heat transfer and elastic-plastic stress analysis.

The heat input for a weld, as mentioned in 6.7.7.1, is defined as welding arc energy per unit length of a weld pass (see Table 6-5). The associated heat flux $K \cdot f(t)$, weld pool length $L$, and the time over which heat flux will last $\tau$ were subsequently calculated. The values of $K \cdot f(t)$ and $\tau$ were input as tabulated amplitudes for volumetric heat flux.
The model consists of 15023 elements. The elements are 4-node linear axisymmetric heat transfer quadrilateral type (DCAX4) for thermal analysis and 4-node bilinear axisymmetric quadrilateral type (CAX4R) for stress analysis [25]. In this simulation, the absolute zero temperature is set to -273K and Stefan-Boltzmann black body radiation constant is $5.67 \times 10^{-14} \text{Js}^{-1}\text{mm}^{-2}\text{K}^{-4}$. All dimensions are in mm and temperatures are in Kelvin.

The welding efficiency ($\eta$) of TIG is often taken as 0.65 but can be adjusted in practice to achieve the desired weld profile. According to the welding procedure of the as-received ILW container, the top weld was the first run then followed by the bottom weld. There was no filler material used. The edges were prepared and fused together by a TIG torch. There was no preheating prior to welding.

The principal stress directions are designated by X, Y and Z. X represents radial direction, Y represents axial direction and Z is hoop direction as illustrated in Figure 6-8 below.

![Figure 6-8: Markers showing XYZ as principal stress directions](image)

### 6.8.4 Results of 2D Analysis

The accuracy of the thermal analyses may be determined from two parameters: (1) the coverage of melting temperature within the designated weld pool, and (2) the heat tint [19].

The coverage of melting temperature within the designated weld pool simply means that the distribution of $T_m$ at time $\tau$ should be no less than the area of which the weld pool lies. According to the equations in Section 6.7.7.1, welding efficiency has an impact on the heat flux and weld pool length.
The 2D simulation for the top weld (which was run no.1) began with weld efficiency $\eta=0.60$ and the temperature distribution at time $t$ shows that this was insufficient to cover the whole weld area. Hence, $\eta=0.65$ and 0.70 were used to improve thermal analysis model. An increase in weld efficiency showed a better coverage of $T_m$ as demonstrated in Figure 6-11. The bottom weld (which was run no.2) showed the same agreement that $\eta$ of at least 0.65 gave better coverage.

This alone was not sufficient to determine the accuracy of the thermal model. The next step was to revisit the physical feature of the as-received container to investigate if there were other welding characters which could support the above finding. According to Smith and Blunt [19], a direct comparison of heat tint could also be helpful; guidance published by the British Stainless Steel Association, temper colours that form on stainless steels after heat treatment can be a good indication of temperature reached (see Table 6-6). A specimen extracted from the drum flange section of an ILW container shows the band of dark blue heat tint around the top weld. This heat tint was approximately 4mm wide and corresponds to a temperature of 600°C or over.

A temperature history profile at a distance of 4mm away from the weld toe was plotted to verify this assumption (see Figure 6-13). At this node, the maximum temperature achieved with $\eta=0.60$ was 592°C whilst with $\eta=0.65$ and 0.70, the temperatures reached as high as 626°C and 658°C respectively. So only a welding efficiency of at least 0.65 could achieve a temperature above 600°C at this point.

The predicted strain and stress profiles from the 2D simulation 1.5mm from top surface of the flange section are presented in Figure 6-14 and Figure 6-15. Please note that the “distance” is the dimension from the flange edge, with the edge being at 0mm. Values are plotted as micro-strain ($\mu$ε).

In Figure 6-14, both radial and axial strains begin at approximately the same value, i.e. around 250$\mu$ε before splitting when the distance from the flange increases beyond 10mm. Radial strain shows a shallow peak around 15mm from flange edge giving an approximate value of 480$\mu$ε, whilst axial strain decreases and falls below -500$\mu$ε. The hoop strain stays relatively consistent at the level of 800$\mu$ε before it exceeds a distance of 15mm. Beyond this it increases sharply to above 1300$\mu$ε when approaching distance of 25mm.

The stress profile predicted from the 2D model as in Figure 6-15 sees an increase in hoop stress from -180MPa (from 15mm onwards) to just below 300MPa at distance of 24mm and further. Axial stresses remain low, close to a neutral state. Radial stress shares the same profile as that of
axial but increases when distance reaches 10mm, and peaks at 90MPa (at 23mm) before decreasing.

Figure 6-16 and Figure 6-17 show the predicted stress and strain across the midsection of the flange. In Figure 6-16, the strains in the radial and axial direction begin as an almost consistent profile at around 400με before dividing when the distance reaches beyond 10mm. The radial strain drops gradually to less than -500με. The axial strain undergoes a very gradual increase to 500με but falls below zero to almost -400με. The hoop strain shares a similar profile as that of the top measurement path. It remains at -1250με when the distance is smaller than 15mm then increases sharply to above 1500με.

The predicted stresses in Figure 6-17 represent a very similar profile to that of Figure 6-15. Axial and radial stresses both start at zero and as the distance proceeds further to almost 10mm, they separate, giving difference in magnitude with axial stress being slightly more tensile and radial compressive. Both reach a minimum with the radial stress at approximately -60MPa when distance is around 22.5mm and the axial stress slightly more compressive. They also increase again with radial stress remaining compressive whilst axial stress returns to the tensile region. The hoop stress is consistent with a value of around -250MPa until the distance from the flange edge stretches beyond 17mm and it rises sharply to above 300MPa at the end of the path.

Figure 6-18 shows the predicted strain in the flange along a path 1.5mm from its bottom surface. The curves closely resemble those of the top surface (see Figure 6-14). Radial strain begins as a rather flat profile of 400με then increases when the distance exceeds 10mm. It rises slowly and reaches a peak of 60με around 18mm before decreases to below -500με. The axial strain falls below -500με and reaches a minimum of approximately -750με at 25mm and increases again with a sharp rise when the distance is close to 30mm.

Figure 6-19 represents the prediction of residual stress in flange along the same path as in Figure 6-18. This stress prediction shares the similarity observed in Figure 6-15. It sees a hike in hoop stress from -200MPa (from approximately 17mm onwards) to above 300MPa at distance of 25mm and further. Axial stress remains at very low, close to neutral state and only suffers a small dip at distance of 25mm with less than -50MPa of stress. Radial stress shares the same profile as that of axial but increases when distance reaches 10mm, and peaks at 100MPa (at around 23mm) before decreasing.
Table 6-1: Thermal properties with varying temperatures [22]

<table>
<thead>
<tr>
<th>Temperature</th>
<th>°C</th>
<th>20</th>
<th>100</th>
<th>200</th>
<th>400</th>
<th>600</th>
<th>1000</th>
<th>1500</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity</td>
<td>kJ/mm/s/°C</td>
<td>1.46x10^-5</td>
<td>1.56x10^-5</td>
<td>1.70x10^-5</td>
<td>1.97x10^-5</td>
<td>2.24x10^-5</td>
<td>2.76x10^-5</td>
<td>3.43x10^-5</td>
<td>4.12x10^-5</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>kg/mm^3</td>
<td>3.78x10^-6</td>
<td>7.86x10^-6</td>
<td>7.86x10^-6</td>
<td>7.86x10^-6</td>
<td>7.86x10^-6</td>
<td>7.86x10^-6</td>
<td>7.86x10^-6</td>
<td>7.86x10^-6</td>
</tr>
<tr>
<td>Specific heat</td>
<td>kJ/kg·°C</td>
<td>0.452</td>
<td>0.493</td>
<td>0.523</td>
<td>0.553</td>
<td>0.578</td>
<td>0.62</td>
<td>0.678</td>
<td>0.737</td>
</tr>
</tbody>
</table>

Table 6-2: Solidus and liquidus temperatures, latent heat and coefficient of heat transfer [21]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solidus temperature</td>
<td>°C</td>
</tr>
<tr>
<td>Liquidus temperature</td>
<td>°C</td>
</tr>
<tr>
<td>Latent heat</td>
<td>kJ/kg</td>
</tr>
<tr>
<td>Coefficient of heat transfer</td>
<td>kJ/mm/s/°C</td>
</tr>
</tbody>
</table>
Figure 6-10: A close-up sketch of 2D drum flange model

Table 6-3: Mechanical properties [22]

<table>
<thead>
<tr>
<th>Temperature</th>
<th>°C</th>
<th>20</th>
<th>100</th>
<th>300</th>
<th>600</th>
<th>800</th>
<th>1000</th>
<th>1050</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young's modulus</td>
<td>GPa</td>
<td>199</td>
<td>194</td>
<td>190</td>
<td>152</td>
<td>97</td>
<td>48</td>
<td>10†</td>
<td>10†</td>
</tr>
<tr>
<td>Poisson's ratio</td>
<td></td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Coefficient of linear expansion</td>
<td>°C⁻¹</td>
<td>1.52x10⁻⁵</td>
<td>1.58x10⁻⁵</td>
<td>1.72x10⁻⁵</td>
<td>1.86x10⁻⁵</td>
<td>1.94x10⁻⁵</td>
<td>2.00x10⁻⁵</td>
<td>2.01x10⁻⁵</td>
<td>2.36x10⁻⁵</td>
</tr>
</tbody>
</table>

† These values are adjusted to get better convergence and have no effect on final result as long as they are lower than those at room temperature, the predicted behavior can be considered realistic.
Table 6-4: Yield stress data [21]

<table>
<thead>
<tr>
<th>Temperature</th>
<th>°C</th>
<th>20</th>
<th>250</th>
<th>500</th>
<th>750</th>
<th>900</th>
<th>1000</th>
<th>1100</th>
<th>1200</th>
<th>1300</th>
<th>1500</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2% proof stress</td>
<td>MPa</td>
<td>296</td>
<td>215</td>
<td>175</td>
<td>137</td>
<td>90</td>
<td>62</td>
<td>34</td>
<td>17</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>1% proof stress</td>
<td>MPa</td>
<td>338</td>
<td>255</td>
<td>214</td>
<td>169</td>
<td>99</td>
<td>63</td>
<td>35</td>
<td>18</td>
<td>9</td>
<td>5</td>
</tr>
<tr>
<td>10% proof stress</td>
<td>MPa</td>
<td>480</td>
<td>375</td>
<td>344</td>
<td>232</td>
<td>109</td>
<td>64</td>
<td>36</td>
<td>19</td>
<td>10</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 6-5: The welding parameter for both top and bottom welds of container flange section

<table>
<thead>
<tr>
<th></th>
<th>Welding speed, ( v ) (mm/min)</th>
<th>Welding current, ( I ) (A)</th>
<th>Welding voltage, ( V ) (V)</th>
<th>Calculated arc energy, ( q ) (kJ/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top weld</td>
<td>170-210</td>
<td>150-210</td>
<td>12*</td>
<td>0.6821</td>
</tr>
<tr>
<td>Bottom weld</td>
<td>165-205</td>
<td>220-260</td>
<td>12*</td>
<td>0.9341</td>
</tr>
</tbody>
</table>

* Not specific in fabrication documents but 12V is the standard voltage used in TIG welding

Table 6-6: Temper colours that are likely to form on austenitic stainless steels as an approximate indication of temperature [Source: BSSA]

<table>
<thead>
<tr>
<th>Temper colour formed</th>
<th>Approximate temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pale yellow</td>
<td>290</td>
</tr>
<tr>
<td>Straw yellow</td>
<td>340</td>
</tr>
<tr>
<td>Dark yellow</td>
<td>370</td>
</tr>
<tr>
<td>Brown</td>
<td>390</td>
</tr>
<tr>
<td>Purple brown</td>
<td>420</td>
</tr>
<tr>
<td>Dark purple</td>
<td>450</td>
</tr>
<tr>
<td>Blue</td>
<td>540</td>
</tr>
<tr>
<td>Dark Blue</td>
<td>600</td>
</tr>
</tbody>
</table>
Figure 6-11: The effect of welding efficiency on top weld; $\eta=0.60$ (top), $\eta=0.65$ (middle) and $\eta=0.70$ (bottom)
Figure 6-12: The effect of welding efficiency on bottom weld; $\eta=0.60$ (top), $\eta=0.65$ (middle) and $\eta=0.70$ (bottom)
Figure 6-13: Temperature history of a node approximately 4mm away from the toe of top weld with different weld efficiencies

Figure 6-14: Prediction of residual strain in flange, 1.5mm from the top surface in 2D stress analysis
Figure 6-15: Prediction of residual stress in flange, 1.5mm from top surface in 2D stress analysis

Figure 6-16: Prediction of residual strain in flange across mid thickness in 2D stress analysis
Figure 6-17: Prediction of residual stress in flange across mid thickness in 2D stress analysis

Figure 6-18: Prediction of residual strain in flange, 1.5mm from the bottom surface in 2D stress analysis
6.8.5 3D Model with Moving Heat Source

The second phase in simulation is to extend 2D simulation to 3D. The 3D model (as shown in Figure 6-20) is a quarter arc of the container flange section with symmetrical boundary conditions applied at both ends of the arch. It was constructed with 69300 linear elements. Energy was applied using a volumetric moving heat course via the use of user-subroutine.
All welding parameters and materials properties were the same as those used in 2D simulation. An ellipsoidal shape was used for the heat source in the welding direction. The heat source distribution was assumed to be Gaussian in all directions (depth and circumferential). Welding efficiency was assumed to be 0.65 as derived from the 2D model above.

The heat input for 3D analysis is defined separately in a user-subroutine. This heat input value varies over two regions: ahead of the arc centre where z>0 and behind the arc centre. As illustrated in Figure 6-21 the model is defined for an arc (i.e. the heat source) starting at a given origin at time $t=0$ and moving along the positive z-axis (which is also the circumference defined in user-subroutine). This is then included as one of the real variables in the script for user-subroutine. A typical heat distribution at heat source is often displayed as a plot of heat input at the model surface as presented in Figure 6-22.

Again, similar to the approach employed for 2D simulation, temperature histories from thermal analyses were applied to the model in the mechanical analysis. The boundary condition remained symmetrical and restrained until welding was completed. Then they were removed to study the effect of relaxation and to provide closer comparison to the specimen prepared for neutron diffraction measurement.

Figure 6-21: Geometry of a double ellipsoid heat source [7]
6.8.6 Results and Discussion of 3D Analysis

Figure 6-23 to Figure 6-31 represent the comparison between plots of predicted and measured stresses in the flange. There is a general lack of agreement between prediction and measurement results. Figure 6-23 illustrates the difference between the predicted and measured radial stress. The difference in magnitude is up to 300MPa.

In Figure 6-24, the simulated result exhibits a region of tensile residual stress that is too large in comparison to the values measured by neutron diffraction. This implies that the heat input used in this analysis is too great thus causing a wide area of high temperature and subsequent strains resulted from it. The measured hoop stress shows a constant decrease (which is consistent with weld residual stress behavior, as described in Section 5, without the expected increase as the distance draws closer to the weld. This may suggest that the cut-out corner at the internal circumferencel could have been performed after welding was completed and such an operation may have altered the stress field in the adjacent region.

Figure 6-25 demonstrates that the predicted axial stresses in all analysis (2D and 3D) are very similar but they do not match the measured results. The model suggests all axial stresses are very low and close to 0 whereas the measurements show an increase in compressive stress as the distance draws closer to the weld area. The actual cause beyond this is not clear but judging from the appearance of the flange that it has undergone surface treatment and the machining of bolted holes may have some unknown impact on it.
The residual radial stress profiles across mid thickness of the flange, as seen in Figure 6-26, although share more similar patterns but the difference of magnitude between them is too large. The simulated results, again, predicted relatively low compressive stresses whilst the measurements demonstrate that the radial stress is overall quite compressive with a minimum of -400MPa.

Figure 6-27 is the only plot that displays some agreement between predictions and measurements up to distance of approximately 13.5mm. The measured hoop stress displays the characteristic dip in magnitude before increasing again. In the case of predicted stress, the rise in magnitude occurs much further away from the weld. Again, it potentially suggests that an incorrect heat input has been used.

The comparison of residual axial stress in the flange across its mid thickness is presented in Figure 6-28. The stress obtained from analysis share a similar pattern with that obtained via neutron diffraction but the lack of agreement is put down to the difference in magnitude. Whilst the simulation predicts relatively low compressive axial stresses, the measurements exhibit more compressive values throughout with value as low as -210MPa.

Figure 6-29 presents the residual radial stress along the bottom surface of the flange. Like the predicted stress behaviour previously observed, the simulated stresses are in tension whereas the measured stress is in compression. The difference of value is up to 400MPa.

In Figure 6-30, the measured residual hoop stress in the flange, along the path 1.5mm from bottom surface, shares the similar profile as the measured hoop stresses previously discussed. It exhibits a characteristic fall to a value below -400MPa before increasing again as it approaches the bottom weld region. The computed stresses share the same profiles that that in Figure 6-27 and still suggest that issue with heat input that may have caused an overly wide region of high temperature.

The predicted residual axial stress, as seen in Figure 6-31, begins with neutral values then fluctuates as the distance becomes nearer to the weld region. The measured stress is compressive overall and remains quite consistent between -150 and -200MPa.

### 6.8.7 Comparison between 2D and 3D analysis

Axisymmetric model is typically used to simulate circumferential welds of thin-walled structures such as pipes. 2D analysis employs plane strain conditions [7], which means the weld is divided
into a series of thin slices perpendicular to the welding direction. And these slices are assumed not to have any interaction with the others adjacent to them. The limitation of 2D analysis of this kind includes assuming that longitudinal heat flow and longitudinal displacements are zero.

While the longitudinal heat flow may not be of very great magnitude [26], the longitudinal interaction in the stress may be significant. During welding, a component may have undergone some small longitudinal displacement prior to the arrival of the heat source at a given location. And it is then followed by larger displacement after the heat source has passed. Using 2D analysis also implies that the whole plane is fixed rigidly in the longitudinal direction and net longitudinal residual stress after cooling does not counterbalance each other and hence its value is not zero.

In the 2D model, the full length of the weld is effectively heated at the same time and the welding speed is often assumed to be infinite making the 2D model inadequate to model the hoop behaviour, see Figure 6-32 and Figure 6-33. The 2D axisymmetric model in this work regards that the whole circumference at a high temperature at the same time, although only for a short period.

Three dimensional simulations are based solid models in which all components of stress are included. The 3D analysis in this work employs the same materials properties as in 2D analysis. The comparison between 2D and 3D models show some degree of good agreement with very small difference in magnitude.
Figure 6-23: Plot of predicted and measured radial stress in flange, 1.5mm from top surface

Figure 6-24: Plot of predicted and measured hoop stress in flange, 1.5mm from top surface
Residual axial stress in flange, 1.5mm from top surface

Residual radial stress in flange across mid thickness

Figure 6-25: Plot of predicted and measured residual axial stress in flange, 1.5mm from top surface

Figure 6-26: Plot of predicted and measured residual radial stress in flange across mid thickness
Residual hoop stress in flange across mid thickness

Figure 6-27: Plot of predicted and measured hoop stress in flange across mid thickness

Residual axial stress in flange across mid thickness

Figure 6-28: Plot of predicted and measured residual axial stress in flange across mid thickness
Figure 6-29: Plot of predicted and measured residual radial stress in flange, 1.5mm from bottom surface

Figure 6-30: Plot of predicted and measured residual hoop stress in flange, 1.5mm from bottom surface
6.9 Discussion on the Discrepancy between Simulation and Measurements

The complexity (and thus the predicted strains and stresses) of the simulation is related to several factors concerned with:

- Heat loading (including heat loss from convection and radiation)
- Mechanical loading (including support conditions at contacts and fixtures)
- Material modelling (including phase changes, coupling effect and fluid behaviour)
- Geometric modelling (including the dimensions of model, description of motion)
- Meshing (including size and type)

This means any simplification or modification associated with these factors may potentially reduce the predictive capability of a finite element analysis.

Therefore it is possible to pinpoint the differences between experimental and numerical results to several factors:

- The numerical model used the predefined standard set of parameters (material properties) and do not always represent the best accuracy especially at high temperature, especially at temperatures close to and above fusion temperature.
• The heat input derived from the welding certificate of ILW container. Whilst the document provides the parameters used in the welding process, it is unlikely to be constant during a given run. The real heat input for each run would have to be dynamically adjusted during welding. This requires dynamic recording of heat input parameters during welding in real time which was not done or available [27].

• There was no record of the thermal history during welding, making it impossible to match node locations with points of interest on the flange. Besides, since the simulation has been simplified to reduce complexity, the calculated weld fusion zone profile has not been matched with the actual weld fusion zone profile [27].

• In order to save analysis time, only a quarter section of the flange was modelled. In actual practice, the temperature differences between the regions above and below the weld occur as a result of convection (also known as chimney effect) as it is assumed that the container was welded in a vertical position. Chimney effect may potentially give different thermal-mechanical histories from each section of the flange [27].

• At high temperature, the combined isotropic-kinematic strain hardening model is more applicable than the elastic-plastic isotropic strain hardening model since isotropic straining has the tendency to overestimate residual stresses [28, 29, 30].

During welding, the metal along the welding path melts and solidifies as the heat source moves forward. A common solution in most simulation software including ABAQUS and employed in this work is to calculate an effective specific heat based on the local slope of the enthalpy. This is then introduced into an algorithm which is then used to compile the final mechanical properties.

The simulation of weld heat input has always been a concern in FEM. The quantity of energy input into the material and the associated heat distribution in time and space cannot be easily determined even with sufficient information from process parameters and welding velocity. Information such as welding energy and size of weld pool provide some clues for how the heat input could be modelled but could not guarantee good agreement between simulation and experimental measurements [31]. In this work, only welding parameters are available. The other inputs such as temperature-dependent materials properties could only be taken from literature. The weld pool size is calculated based on the averaged values of welding parameters. The lack of agreement between calculation and measurement as suggested by Lindgren could not only be put down to the mentioned issues but also inability to employ any more sophisticated material models than a simple elastic-plastic model as used in this work. It is seldom worthwhile to
introduce models with more parameters and complexity when there is a lack of experimental data.

The thermal history influences the mechanical behaviour to a significant degree not only because temperature is directly responsible for the thermal expansion which gives strains and then stresses, but also temperature has an effect on the mechanical properties such as Young’s modulus or the yield strength [32, 33]. On the other hand, the effect of mechanical properties on thermal properties is negligible as argued by Asserin et al. [34]. The heat generated by mechanical non-linearities (such as plasticity) is very low compared to the heat input of welding.

An issue related to latent heat has been noted by a few researchers [35, 36, 37]. Their simulation gives a higher release of latent heat in the upper part of the $T_{\text{solidus}}$ to $T_{\text{liquidus}}$ interval. The common assumption in most simulations and also in this work is that the distribution of latent heat is even during the melting and solidification stages. However in the actual welding process, heat in the weld pool is not only conducted but also convected as a result of fluid flow.

Moreover, with the latent heat effect, the thermal-physical properties of 304L stainless steel exhibit a sudden change at melting temperature. This directly affects the thermal conductivity and diffusivity, both of which are usually essential constants and disturbs the thermal history of the welding process. In addition, expansion coefficients and specific heat also experience changes at melting point. The sudden increase promotes residual strain during the heating phase. In the subsequent cooling phase, the drop in heat causes the residual stress in the HAZ [38].

The thermal-mechanical properties of 304L and 316L stainless steel are limited in the range of their usual operating temperatures. Most literature data including those used in this work has been improved to allow better convergence in simulation but it does not necessarily represent the real properties in practice. Above a third of the melting temperature, most metals would suffer from creep, impacting their mechanical behaviour to a very significant degree and thus causing great difficulty in estimating their values near melting temperature. Stainless steel is not an exception in this case [39].

Over-simplification of the model may have contributed to the discrepancy discussed. The geometry used in this work only considers the final geometry of the component which includes the less complicated weld dimensions and dismisses the other feature such as the presence of unfused land between the 304L flange and 316L container wall and the edge preparation prior to welding.
With regard to mechanism of heat deposition, work by Berglund [40] also suggests that including initial prior welding geometry in the simulation will result in better prediction of residual deformations. The final geometry can be achieved by block dumping approach in which a weld bead is deposited simultaneously along its length in the welding direction [17].

Lindgren [31] also notes that the modelling of a steel component especially one that has undergone thermal cycles (such as welding) introduces additional problems. The properties are not only temperature-dependent but they are also dependent on the associated temperature history. The latter is as a result of the interaction between microstructure and material properties. Both thermal dilatation and yield strength are functions of temperature history.

The calculation of thermal dilatation is complicated [38, 41]. It requires a thermal analysis and a subsequent programming of a weld simulator (such as the Gleeble machine) with incorporation of computed thermal history and finally measurement of the expansion of the specimen as it undergoes the thermal cycle. Winker et al. also agree that measuring yield stress as a function of temperature and temperature history, in the same approach as thermal dilatation will cause too much difficulty. Therefore it was decided that literature material data would be sufficient.

It is arguable that computing material properties from microstructure evolution will pose some inherent issues. Not only that it challenges the experimental evidence (such as transformation diagrams) but also it has been difficult to formulate a theory applicable for arbitrarily thermal histories. Most formulation of material properties by microstructure is only possible when assumed simplifications are taken into account. Lindgren [31] suggested that this simplification could be achieved by assigning each phase with properties as a function of temperature then combining by mixture rules to calculate the bulk properties but this method remains invalid for yield stress. In practice, it is often impossible to conduct uniaxial tensile testing for all the combinations of thermal histories.

The d-spacing (or diffraction angle) is determined by the lattice structure and parameter, both of which are in turn determined by chemical composition, microstructure and grain structure. This impacts the weld zone significantly since the composition, microstructure and grain structure undergo changes from that of base metal to a complicated build in the weld region. The welds in the flange are a typical structure consisting of columnar and epitaxial grains with inter-dendritic network of ferrite. Thus, even in a strain/stress-free weld zone, the diffraction angles (also the d-spacing) of the parent metal and of the weld are expected to be different. This implies the need to
measure a stress-free reference weld under identical measurement conditions as that in the case of the parent metal [42].

But this also implies that any residual stress measured by neutron diffraction is extremely sensitive to this stress-free reference, $d_0$. Moreover, the lattice spacing itself can be affected by the grain structure and compositional elements in the metal, which also means that it is highly sensitive to grain orientation thus it is affected by anisotropic properties.

Figure 6-32: 2D analysis model at the step of applying heat input to top weld; the left image represents the axisymmetric model as a slice of the container flange the left image represents a swept model (from 0 to 90°)

Figure 6-33: 2D analysis model at the step of applying heat input to bottom weld; the left image represents the axisymmetric model as a slice of the container flange the left image represents a swept model (from 0 to 90°)
6.10 Concluding Remarks

Still, 2D simulation should not be omitted in any future work as it is still able to provide information about residual stresses and allow a finer mesh for weld and adjacent regions. It is also a simple model if the aim is to investigate the effect of different welding parameters on residual stresses. 3D models remain popular as a tool to investigate long-range stresses.

Simulations can be improved by estimating plasticity and computing the materials properties according to fabrication history [43, 44]. The use of finer or adaptive meshing to give smaller elements after the welding finishes, with smaller time steps may be helpful in improving the realism of models. Comparisons with mock-ups constructed with same materials of similar dimension and welding parameters could possibly pinpoint the difference or overlooked issues during simulation.

The approach in this work does not consider the precise mechanism of heat deposition, which differs according to the type of welding process and the use or lack of filler material. It also does not take into account the heat convection generated by the molten metal flow in the weld pool. A number of analyses which addressed this issue reported a better accuracy in their results [45, 46]. Combining thermal-mechanical models with fluid flow models, as demonstrated by Amberg and Winkler [47, 48], seem to improve the predictive capability of FE models.

The material properties used in this work is based on a standard in-house data provided by TWI. It is likely that some of the data notably yield properties may not correspond sufficiently close to the actual properties of the ILW container although it has been suggested by Smith and Blunt [19] that yield strength does not have a significant impact on the final simulated results. Perhaps improvement could be achieved if future work is able to characterise the actual materials properties of these containers over a wide range of temperatures.

Choi and Mazumder [49] performed a stress analysis based on a GMAW-welded 304L stainless steel plate and found that increasing the welding speed will result in an equivalent increase in residual stresses. They argue that cooling rate could the major factor in deciding the residual stress behaviour. According to them, the associated cooling rate is related to the welding speed; therefore a high welding speed may lead to a fast cooling rate, giving rise to high residual stresses.
References


7 Discussion

7.1 Hypothesis

The hypothesis that this work has tested is that the austenitic stainless steels used in the manufacture of ILW containers in the UK are susceptible to AISCC under certain combinations of conditions; as well as to examine those conditions under which AISCC will never occur and conditions where AISCC might only occur after a very long time has elapsed.

Recent research [1, 2, 3, 4, 5, 6, 7, 8] has demonstrated some of the requirements for AISCC. For austenitic stainless steels the required conditions for AISCC are deposits of an electrolyte (commonly from marine sources and, hence, predominantly sea-salt) on the container surface and the presence of the correct combination of humidity, temperature and mechanical stress. While progress has been made in understanding relative humidity and temperature effects, the minimum level of stress required for initiation of cracking is not well understood.

Previous AISCC testing, generally using U-bend specimens [9], did not accurately characterise the stress and strain in the surface of the specimens, except to understand that the material had undergone significant plastic deformation in the formation of the “U” bend. In addition, the magnitude of residual stresses associated with welds and other manufacturing processes in a typical ILW container has not previously been studied in depth. A key aim of this research, therefore, has been to investigate the relationship between the stress required for AISCC to occur and the residual stress associated with the welds of a typical container.

The work has involved characterisation of the properties of the container material, the measurement and calculation of the residual stresses in the region of the flange weld. A major component of the work has been a series of AISCC tests over a period of more than twenty four months on specimens charged with deposits of different salts at various levels of temperature, relative humidity (RH) and stress. The methodology and results of this work are given in Sections 3 to 6.

This discussion puts the results in a perspective with respect to their accuracy and limitations of the techniques employed. It draws together the experimental AISCC test results within the context of residual stresses in an actual container. The industrial relevance of the results in terms of the conditions required for the avoidance or delay of AISCC is discussed.

The practical importance of this work to the nuclear industry is to define conditions under which the risk of AISCC of ILW containers in storage can be minimised. The knowledge gained can be
used to modify the environmental conditions in existing stores or to implement a monitoring and/or inspection scheme appropriate to the risk. The work may help to optimise the design of new storage buildings and will provide a benchmark for the reduction in residual stress by modifying the welding and other manufacturing procedures.

There are currently over twenty thousand ILW containers in storage in the UK and many more containers will be needed as the current generation of Magnox reactors and chemical processing sites are decommissioned. Containers are currently located in “interim stores”, which are large ventilated warehouses and are to be used until a final underground repository is built. Under the current estimate, containers may be in interim storage for up to 150 years and possibly a further 350 years in underground storage prior to a permanent backfill in the repository. Thus the absolute integrity of the ILW containers is essential for at least this timescale. If the results of this work have contributed to the safety of the containers in storage in reducing the risk of AISCC then this research will have been worthwhile.

### 7.2 Residual Stress in Container

The residual stress associated with the flange weld of the container has been investigated using a combination of measurement and computational techniques. Measurements of residual stress near the surface were made using X-ray diffraction while measurements throughout the volume of the flange were made using neutron diffraction. Finite element analyses simulating the thermal cycle of the welding process were conducted to predict residual stresses in the flange region.

With a penetrating depth of 20μm, the X-ray diffraction method only measured near surface stresses on both internal and internal wall surfaces of a four-point bend specimen (prepared from the as-received ILW container). The compressive stress behaviour observed on all these surfaces agrees with that of a rolled sheet in which the outer surfaces are in compression and these compressive stresses are balanced by the tensile stresses within the bulk material. This was further verified by the presence of tensile residual stresses measured in the axial and hoop direction within the bulk volume of the 316L wall using neutron diffraction.

The degree of sophistication in finite element computational models of the welding process is often determined by (1) heat loading (heat loss from convection and radiation), (2) mechanical loading (boundary conditions, support constraints etc), (3) material modelling (phase transformation, coupling effect and fluid behaviour), (4) geometric modelling (model dimension, welding direction etc) and (5) meshing (size and type) [10].
This means any simplification or modification associated with these parameters may potentially reduce the predictive capability of a finite element analysis (FEA). Most of these parameters are either obtained from predefined data or are affected by the physics of the welding process. Therefore, the agreement between computational stress analysis and measurement or lack of it could be explained accordingly to this establishment.

Most computational calculations employ a standard set of inputs especially in the case of material properties. However, the accuracy of these data still requires more investigation as research [11] has shown that the material properties at temperatures as high as the fusion point undergo significant changes.

An example is the issue associated with latent heat. The literature [12, 13, 14] shares a common finding that there is a higher release of latent heat in the upper part of the $T_{\text{solidus}}$ to $T_{\text{liquidus}}$ interval. In most simulations as well as in the FEA in this work it is assumed that the distribution of latent heat remains uniform during the melting and solidification stage. But this differs from the actual welding process in which the weld pool experiences not only conductive heat loss but also convective heat loss caused by the fluid behaviour within the molten zone.

Subsequently the latent heat effect causes a significant change in the thermal-physical properties of a 304L stainless steel when the temperature reaches the melting point. As a result it alters the thermal conductivity and diffusivity and thus changes the thermal history of a welding process. Besides this, there is a sudden increase in expansion coefficient and specific heat. This promotes residual strains during the heating phase. In the subsequent cooling phase, the drop in heat causes residual stresses [15]. Furthermore, at temperatures above about one-third of the melting point, most metals including 304L and 316L stainless steels experience creep. This has an effect on the mechanical behaviour and modelling or measurement of such processes measurements is not always feasible [16].

The heat input used in this work was calculated according to the welding parameters provided by the supplier. These parameters do not remain constant throughout the welding process. The quantity of energy input into the material and the associated heat distribution in time and space cannot be easily determined even with sufficient information from process parameters and welding velocity. To achieve sufficient accuracy in a welding simulation, it would require dynamic real-time recording of heat input parameters during welding. This is not always feasible and thus the real time data are not available for this research [17].
Welding arc energy and weld pool length may be a good indicator on how the heat input could be modelled but could not guarantee good agreement between simulation and experimental measurements [17]. The lack of information from the manufacturer implies that other inputs such as temperature-dependent materials properties could only be taken from literature.

The weld pool size is calculated based on the averaged values of welding parameters. Lindgren [17] also suggested that the inability of either human or machine contribute to some extend the delay to establish more sophisticated material models. This work employed a simple elastic-plastic isotropic strain hardening analysis. With the lack of reliable experimental data, particularly thermal history, the introduction of more complicated models may not necessarily provide better accuracy as many additional assumptions would have to be established.

As there was no information regarding the thermal history of the welding process used to manufacture ILW containers, it represents a significant difficulty to validate the simulated nodal temperatures. The validation of thermal analysis was then dependent on less accurate comparisons such as the colour of the heat tint [18] produced than recorded temperatures. Besides, since the simulation has been simplified to reduce complexity, the calculated weld fusion zone profile has not been closely matched with the actual weld fusion zone profile [11].

The thermal history affects the mechanical properties not only due to the fact that temperature is directly responsible to the thermal expansion which gives strains and then stresses, but also temperature has an effect on the mechanical properties such as Young’s modulus or the yield strength [19, 20, 21].

The flange section was modelled as a single quarter section but with boundary conditions to imitate axisymmetric conditions as in a case of a whole intact flange. This offers the advantage of time and resources. However, temperature differences can occur between the regions above and below the weld. This is known as the chimney effect which is a form of convective heat loss. The impact of this phenomenon is arguable and not quantifiable in the current work. Some researchers [11, 22] believe it may potentially give different thermal-mechanical histories from each section of the flange as the convective heat loss has a tendency to pull the shielding gases away from the weld zone. Others [18] think its effect is negligible and does not affect the thermal-mechanical histories to an appreciable level.
At higher temperatures, a combined isotropic-kinematic strain hardening model is more applicable than the elastic-plastic isotropic strain hardening model since isotropic straining has the tendency to overestimate residual stresses [23, 24, 25].

This work only considered the final geometry of the component which includes the less complicated weld dimensions and dismissed other features such as the edge preparation prior to welding between the 304L flange and the 316L container wall. Berglund’s work [26] suggests that incorporating the initial detailed material geometry prior to welding into the simulation may provide better predictive accuracy. The final geometry of the weld bead can more easily be accomplished using a block dumping approach in which material elements representing the weld bead are deposited as the heat source is moving along its length in the welding direction [27].

Consideration of the detailed material microstructures may improve the realism of a simulation but this is only possible when assumed simplifications are taken into account. Lindgren has shown that simplification could be achieved by assigning each phase with properties as a function of temperature then combining by mixture rules to calculate the bulk properties but this method remains invalid for yield stress [17].

It is also possible that the failure to include plastic strain annealing in the welding simulations in this work could have contributed to the lack of agreement between measured strains and predictions [28]. The inclusion of this capability would have removed the plastic strain history when the temperature rises above the specified melting point. Without this, the plastic strains developed during molten phase of the material are retained throughout the analysis and are included into the strain and therefore stress calculation.

7.3 Effect of Stress on AISCC Susceptibility of the Container Material

AISCC tests were carried out on as-received specimens loaded in four-point bending to a surface stress of 400MPa and on the as-received control specimens without external load. One test specimen was annealed and loaded under four-point bending to a surface stress of approximately 170MPa; i.e. close to, but not exceeding the elastic yield limit. Cracking was observed under sea salt and magnesium chloride deposits on the specimens loaded to 400MPa at 80°C and 27%RH, but no cracking was observed in either the control specimens or in the annealed specimen loaded to 170MPa under the same environmental conditions for the same time.

The state of residual stress in specimens will be different and probably less than that in the container itself since the small pieces that have been extracted from the container no longer have
the longitudinal and hoop constraints. Calculations and X-ray diffraction measurements indicate that the surface stress adjacent to the circumferential weld is significantly less than that in the whole uncut container.

The measurements and computations of residual stress in the container indicate that tensile stress values above 400MPa (0.2% proof stress) are present in the vicinity of the welds. Some uncertainty over the exact value remains because the model contained simplifications and the measurements were subjected to some experimental error. Further work to improve the accuracy is recommended.

Cracking was detected in the as-received parent and weld specimens loaded to a stress of 400MPa. The unloaded control specimens only showed evidence of pitting under the same environmental and salt conditions. Therefore, with the level of residual stress well above 400MPa, the as-fabricated containers are at risk of AISCC if the required environmental and salt conditions are present.

Observations of a fully annealed specimen loaded to a stress of 170MPa found no cracking after exposure at 80°C for 6 months. Evidence of corrosion was observed beneath the magnesium chloride and sea salt deposits but there was no indication of cracking. In comparison with the specimens of as-received material loaded to a stress of 400MPa, which cracked within one month, the difference in behaviour can only be attributed to the lower level of stress and/or the return of the material to its original unworked state.

7.4 Industrial Relevance

One of the major concerns for the safety of ILW containers is their structural integrity during surface storage in a repository building for 150 years prior to disposal by burial and backfill. Recent studies and experience of failures have shown that AISCC can occur from airborne salt particles under ambient environmental conditions. The results of this work provide an insight for the avoidance of AISCC of ILW containers through understanding the effects of the container manufacturing process and the design and environmental management of storage buildings.

The logical prevention method is to avoid particles settling on the container surface before and during the storage period. A simple washing process to rinse off the residues of dust and aerosol particulates from the outer surface of an ILW container would minimise any contamination caused by either an airborne mechanism or manual handling. Subsequent storage should be
equipped with effective ventilation and a filter system to prevent any entry of particulates into the storage space.

From the results of the AISCC experiments (Section 4) it is sufficiently conclusive to argue that the risk of cracking is greatly reduced by controlling the relative humidity within the repository at a level below the DRH of a single salt or the MDRH of a mixture of salts at the relevant temperature.

As the temperature rises, the humidity also increases because the air can hold more water; hence the vapour pressure of a droplet at a given concentration will increase. A stable droplet is able to exist at a higher salt concentration as water continues to evaporate into the air. Thus, DRH decreases as temperature increases.

At low RH, the presence of absorbent particles such as carbon can increase the amount of water present on metal surfaces [29, 30]. Inert, non-absorbent particles do not have a significant effect on corrosion but they can also serve as ideal sites for capillary condensation [30] to occur.

One important factor to take into consideration is the deliquescence and efflorescence of an aerosol mixture of salts [29, 31], which is of significance as the main contaminant is expected to be derived from sea-salt. A mixture of salts (for example NaCl-MgSO4-MgCl2) experiences abrupt changes in mass as a function of RH. As the RH increases, the particle mixture transforms into a multiphase with some undissolved salts (i.e. those where the RH is below their deliquescence point) in an electrolyte consisting of those species for which the RH is above their deliquescence points. Importantly, both deliquescence and efflorescence behaviours are independent of salt quantity. They will always occur when the correct RH is met.

When the RH decreases, the water content in the electrolyte also drops; however, evaporation is likely to continue even after the RH falls below the DRH value until a final equilibrium is reached. Thus, the droplet will only expel all its water content and crystallise when the RH becomes very low. Before the complete evaporation of water, the droplet undergoes a metastable state at which a supersaturated solution is formed. In both urban and suburban environments, metastable droplets exist for more than half of the time when the ambient RH is between 45% and 75%. So only by decreasing RH to a very dry state can one be certain all the moisture trapped within the salt mixture will be completely evaporated and only dry salts are left on the metal surface (where the corrosion risk is minimal).
Reducing the residual and other stress in the container welds to as low a level as possible will also reduce the risk of cracking significantly. Lowering the temperature of the container surfaces by cooling would significantly slow the onset of AISCC if other conditions for its occurrence were present.

As observed in this work with the experiments on sodium chloride deposits, the relative humidity (RH) in the repository atmosphere needs to be lower than the MDRH of the salts to ensure that AISCC will not occur. As airborne particles may consist of a mixture of different salts, the relative humidity must be below the DRH of the salt with the lowest value (26% for magnesium chloride at 80oC or 33% at 40oC). In practice the margin between the relative humidity and the DRH needs to be sufficient to allow for possible measuring errors and variations within the repository space.

There is a suggestion from the NDA to keep the RH of the repository atmosphere below 70% (i.e. below the deliquescence RH for NaCl). This work has shown that this suggestion is no longer advisable. While the suggestion may provide some protection against AISCC from sodium chloride with a DRH of around 75%, the DRH of other salts such as magnesium and calcium chloride (e.g. 31% at 40oC for both), which are commonly found in sea salt at coastal locations, are well below 70%. Another opinion, opposed to that above, is to keep the RH higher, which will result in a diluted salt solution on the metal surface and consequently, a reduced risk of cracking.

This work has suggested that the time to initiate AISCC is sensitive to temperature. In Section 4 it is reported that no cracking was observed at 40oC within 9 months, but cracking occurred at 80oC within one month. Other research (University of Manchester) has found cracking at 40oC but only after a year in U bend specimens under high stress with a large amount of plastic strain. Lowering the repository temperature to less than 40oC would therefore be beneficial and delay any on-set of AISCC given that the storage period of ILW containers may be a few hundred years.

Lowering the surface density of the salt deposit does not guarantee that cracking will not occur but may influence the probability. With low surface density, fewer salt crystals are present on the metal surface, thus reducing the potential sites for corrosion to initiate. As the quantity of salt on the surface increases there are more potential sites for corrosion attack. The probability of cracking in a given time is also likely to depend on the temperature, relative humidity, cold work, stress, the material micro-structure and the electrochemical potential of the salt-material combination. So far there is no unified model to determine the probability of crack initiation in a given time and set of these parameters.
The pickled specimen with the outer surface layer removed showed no sign of corrosion, pitting or cracking under any of the salt deposits after exposure at 80°C and 400MPa stress for six months. Only precipitates of the salt crystals were evident on the metal surface, which retained its bright shiny appearance. The understanding of this observation is that the pickling process has removed initial surface defects and strengthened the passive oxide film that protects the metal surface.

In order to use stress as a controlling factor, the welds of the containers would need to be stress relieved. Alternatively, the containers could be pickled in acid for a short period of time to build up an oxide film. Annealing and pickling may be beneficial to minimise the risk of AISCC in austenitic stainless steel, however it is unclear how practical these procedures would be for ILW containers.

The relative humidity and temperature within the storage facility should be adequately controlled, monitored and recorded. If there is a possibility that the conditions for AISCC could exist, then inspection of sample containers to detect AISCC may be required at intervals. The inspection period could relate to the time for initiation and on the basis of this work could be at least one year. Alternatively, given the difficulty and hazards of inspecting containers, it may be possible to install loaded surveillance specimens with salt deposits as a monitoring measure.
References


8 Conclusions
This research has investigated the conditions necessary for AISCC to occur in the material taken from an ILW container by means of experiments in a humidity chamber. It has also characterised the residual stresses associated with the container welds by modelling and measurement. Based on the work conducted in this research, it is concluded that:

- For AISCC to occur a combination of a relevant salt deposit on a susceptible material a sufficient tensile stress and humid atmosphere is required.
- Deliquescence of salt particles is dependent on relative humidity but independent of the quantity of salt present.
- The time to initiate cracking may be sensitive to temperature, getting longer as the temperature decreases, but the timeframe of work was not long enough to establish this conclusively.
- AISCC can occur at a stress (residual or applied) of 400MPa (0.2% strain) or more if the other necessary conditions are present. While AISCC was not observed when no stress was present, the threshold of stress below which AISCC will definitely not occur has not been determined in this work.
- The maximum residual stress associated with the welds of the ILW container supplied determined by modelling and measurement is in excess of the measured 0.2% proof stress of the material of 400MPa in the longitudinal direction.
- The environment within the repository storage building must be controlled to ensure that salt particles in the atmosphere, the relative humidity and temperature remain at a level as low as reasonably practicable to reduce the risk of AISCC.
- Post weld heat treatment (PWHT) of the container welds to reduce the residual stress below the threshold required for cracking might also be an option to reduce the risk of AISCC. This may not be a practical proposition since the threshold stress is not currently known, PWHT may not relax the residual stress completely, PWHT would be expensive and could involve practical difficulties once the container has been filled with waste.
9 Recommendations for Further Research

The recommendation for future work circles around the AISCC experiment, the residual stress measurement and the stress simulation. On the experimental front, further work could concentrate on testing large specimens. Longer exposure time periods should be allowed especially when experimenting at low temperatures. Other materials such as duplex stainless steel could be subjected to the same environment for comparison. Residual stress measurements should be made on a whole container if possible, or at least an intact full circumferential specimen which is more representative of an ILW container than a quarter of a flange. Measurements could be extended into other regions of interest such as the circumferential weld around the container base. Stress simulation could focused on improving the realism of the weld model, particularly taking into account the fabrication history and its associated effect on the materials properties.